Project No. <u>G-41-623 (Cont. of G-41-628)</u> Project Director: <u>Dr. U. Landman</u> Sponsor: <u>Department of Energy, Oak Ridge (</u> Type Agreement: <u>Contract DE-AS05-77ER05489; N</u> Award Period: From <u>1/1/83</u> To <u>12/31/83</u> Sponsor Amount: Total Estimated: <u>\$ 149,250*</u>	ATION DATA SHEET X ORIGINAL REVISION NO. XXXXX/GIT DATE 1/13/83 SchoolXXX Physics Operations Mod. #A005
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	Funded: \$ 149,250
Cost Sharing Amount: \$ 29,942	Cost Sharing No: G-41-312
Title: The Structure and Reactivity of Hetero	ogeneous Surfaces and Study of the Geometry
of Surface Complexes	
ADMINISTRATIVE DATA OCA Cont	
1) Sponsor Technical Contact:	2) Sponsor Admin/Contractual Matters:
Dr. T. A. Kitchens & B. C. Frazer	Mr. Walker K. Love, Contr. Officer
U. S. Dept. of Energy	Contract Mgmt. Branch/Proc. Contr. Div.
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Office of Basic Energy Sciences	Oak Ridge Operations
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Washington, D. C. 20545	Oak Ridge, TN 37830
	Phone: (615) 576-7564
Defense Priority Rating: None	Military Security Classification: None (or) Company/Industrial Proprietary:
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See Attached <u>Government</u> Supplemental Info	ormation Sheet for Additional Requirements.
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Equipment: Title vests with GIT, if acquired by u	s and listed in Appendix "A"
COMMENTS:	
Mod A005 adds \$149,250 as a continuation of	f G-41-628. New project number is because
of separate financial reporting requirement	ent.
	0151A15101/1873
* Total contract value (including previous	project numbers) is \$694,306 S JAN1003
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22	Date 9/6/84
Project No. <u>6-41-623</u>	SchoolXXX Physics
Includes Subproject No.(s)	
Project Director(s) DT. U. Lanoman	SIRX / GIT
Source Department of Frenzy Oak Ridge Operations	
sponsor_Department of Energy Oak Ridge Operations	
Title The Structure and Reactivity of Heterogeneo	us Surfaces and Study of the
Geometry of Surface Complexes	······································
Effective Completion Date: 12/31/83	(Performance) 12/31/83 (Reports)
Grant/Contract Closeout Actions Remaining:	
X None -Project Continued under	G-41-653
Final Invoice or Final Fiscal Report	
Closing Documents	
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THE STRUCTURE AND REACTIVITY OF HETEROGENEOUS SURFACES AND STUDY OF THE GEOMETRY OF SURFACE COMPLEXES

Progress Report

THE STRUCTURE AND REACTIVITY OF HETEROGENEOUS SURFACES AND STUDY OF THE GEOMETRY OF SURFACE COMPLEXES

Progress Report

Uzi Landman

School of Physics Georgia Institute of Technology Atlanta, Ga. 30332

January 1, 1983 - December 31, 1983

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT NO. DE-AS05-77ER05489

APPENDIX "E"

ATTACHMENT 5 Page 1

DOE Form RA-427 (10/80)

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U.S. DEPARTMENT OF ENERGY

OMB NO. 038-R0190

UNIVERSITY CONTRACTOR, GRANTEE AND COOPERATIVE AGREEMENT RECOMMENDATIONS FOR ANNOUNCEMENT AND DISTRIBUTION OF DOCUMENTS

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. (DOE Report No. DOE/ER/04589-1	3. Title	THE STRUCTURE AND REACTIVITY OF
2. (DE-AS05-77ER05489		THE GEOMETRY OF SURFACE COMPLEXES.
	Type of Document ("X" one)	•	
1	2 a. Scientific and technical report		
1	b. Conference paper:		
	Date of conference	-	
	Exact location of conference	_	
	Sponsoring organization		
	_ c. Other (Specify planning, educational, impact, market, so	cial, econ	omic, thesis, trenslations, journal article manuscript, etc./
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	School of Physics, Georgia Institute	of Teo	chnology
•	Signature		Date August 10, 1983
	FOR DOE OR	OTHER	AUTHORIZED
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 $\square\,$ a. DOE patent clearance has been granted by responsible DOE patent group.

D b. Report has been sent to responsible DOE patent group for clearance.

The statements of progress, manuscripts and presentations described in this report represent the principal results obtained during 1983 through the support of the Department of Energy under Contract No. DE-AS05-77ER05489. Since the beginning of this project, our group has been involved in theoretical studies of surface phenomena and processes, aimed toward increasing our understanding of fundamental processes which govern the properties of material surfaces. Our studies cover a wide spectrum of surface phenomena: surface reactivity, surface crystallography, electronic and vibrational structure, dynamical processes, phase transformations and phase change, the properties of interfaces and investigations of material processing and novel materials preparation techniques. In these investigations we develop and employ analytical and novel numerical, simulation, methods for the study of complex surface phenomena. Our recent surface molecular dynamics studies and simulations of laser annealing phenomena opened new avenues for the investigation of the microscopic dynamics and evolution of equilibrium and non-equilibrium processes at surfaces and interfaces.

In addition to the scientific merits, the project serves educational purposes through the training of graduate and postdoctoral students, collaborative work with scientists in government laboratories and abroad and via invited and contributed presentations in national and international meetings and the publication of research and review articles. The work of our group has been presented this year in 4 major conferences (3 talks at the March APS Meeting in Los Angeles, the 43rd Conference on Physical Electronics, Santa Fe, a Gordon Conference and the Europhysics School on "Chemisorption and Surface Reactions", Asperäsgarden, Sweden). In addition invited lectures have been delivered at universities and research laboratories in the U.S. and abroad.

I-1

In the following accounts the main accomplishments of our efforts, during the present period, are described under several categories, reflecting the breadth of our program. It is intended, that through the coordination of these studies we would achieve a coherent program enabling the theoretical investigations of fundamental processes underlying complex surface phenomena of coupled basic and technological interests.

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A. MOLECULAR DYNAMICS STUDIES

Main Achievements

A.1 Laser Annealing

1. Development of a molecular dynamics program for the simulation of laser annealing experiments. The unique features of our method are: The twodimensional periodic boundary conditions imposed on the system allow for dynamical evolution of the areal density; the incident beam, on the free side of the system is characterized by a realistic time profile of a short laser pulse. The coupling of the beam energy to the lattice modes is simulated via a time-stepwise scaling of particle velocities for the duration of the pulse using a realistic absorption profile; heat conduction to the underlying substrate is simulated according to $\hat{Q}(t) = A_{\kappa}(T) \left[\frac{dT(t)}{dz} \right]$ where $\kappa(T(t))$ is a temperature dependent heat conductivity taken from experimental data.

2. Development of analysis and graphic routines for the laser annealing experiments, in particular spatial profiles of pertinent physical quantities such as temperature profiles, potential energy, spatial distribution of orderparameters (orientational and translational), particle density, and diffusion profiles evaluated via velocity correlation functions.

3. Using these newly developed programs we performed studies of laser annealing systems. These investigations represent the first theoretical studies of the dynamics of laser annealing processes on the atomic scale. Besides the scientific findings, we demonstrated the unique value of molecular dynamics in studies of material processes of unusual nature. We have observed a diffuse interface, preceding the solidification front. This three-dimensional interface is characterized by "liquid layering" in planes normal to the direction of solidification front propagation. Physical properties of the interface

(e.g., transport coefficients) differ from those of the solid of the melt. This structured interface plays an important role in the solidification dynamics and affects impurity segregation and transport. At the rates of crystallization which we have studied (\sim 5-10 m/sec) such an interface was always dynamically formed. It will be of great interest to investigate systems with larger rates of crystallization, thus attempting to investigate the formation of amorphous crystals. We conjecture that the degree of perfection (in the sense of good crystals) obtained via laser annealing is related to the dynamics of formation of the "liquid-layered" interface. It is conceivable that the amorphotization occurs when the rate of heat transport away from the crystallization front exceeds the rate of atomic transport processes which are responsible for the evolution of the diffuse interface. In addition, we have observed in our studies constitutional undercooling and are now investigating the materials factors and experimental conditions which control segregation, solute trapping and cellular structure formation.

Our results for a system in which a heavy, strong binding impurity is initially randomly distributed in the sample are summarized in the enclosed Physical Review Letters article (<u>49</u>, 790 (1982)).

The L-J potential parameters for the above system where such that if A denotes the host and B the impurity $\sigma_{BB/\sigma_{AA}} = 1.07$, $\varepsilon_{BB/\varepsilon_{AA}} = 1.387$ and $M_{B'M_{A}} = 2.098$. In order to investigate the effects due to the mass and potential of interaction strength we have extended our calculation to the case $\sigma_{BB}/\sigma_{AA} = 1$, $\varepsilon_{BB}/\varepsilon_{AA} = 0.5$ and $M_{B'M_{A}} = 0.5$, i.e. a light weakly binding impurity with same atomic size as the host (i.e. $\sigma_{B}=\sigma_{A}$).

In Fig. 1 we show the impurity concentrations before (1a) and after (1b) the annealing experiment. As seen from this figure and comparing to the results in Fig 1d(i) and 1d(f) in the PRL article, in the case of the light weakly binding impurity the final impurity distribution shows a depletion in the

surface region since many of the impurities diffused to the solid-vacuum interface and evaporated.

The time developments of the density distribution in the system containing the light impurity (given at the selected indicated times) are given in Fig. 2 and should be compared to those for the heavy impurity case, given in Fig. 3. The comparison of the density profiles at roughly the same times into the annealing experiment shows that melting propagated further into the solid for the light impurity system. However, the velocity of recrystallization is roughly the same in the two systems. Comparison of the plots of the solid-melt interface position versus time for the light impurity (Fig. 4) with that for the heavy impurity case (Fig. 1d (v) in the PRL article) shows that in the former case the slowing down phenomena due to constitutional cooling resulting from an accumulation of the impurity at the solidification front which we observed in the heavy-impurity case, is now absent. This is due to the increased mobility and the tendency of the light weakly binding impurities to migrate to the surface.

We are currently investigating the effect of the exposed crystal face on the dynamics of the annealing process. Theoretical calculations using the Cluster Variation Method by J. Cahn and R. Kikuchi indicate less tendency for "liquid layering" at the fcc (110) solid-liquid equilibrium interface while verifying our observations with regard to the (100) interface. Based on the above and certain arguments originating with roughning theories we anticipate a difference in the annealing mechanism for the (110) surface. If indeed the layering is reduced at this interface (for energetic or kinetic reasons) it may be possible to obtain a disordered or amorphous annealed surface.

We have now transferred and implemented our annealing codes to the CRAY computer. While we find a significant improvement in the ability to perform large-scale calculations on the CRAY as compared to the Georgia Tech CDC-Cyber, we would like to emphasize the need for a larger CRAY-time allocation.

Molecular Dynamics of a Laser-Annealing Experiment

Charles L. Cleveland, Uzi Landman, and R. N. Barnett School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30345

(Received 12 July 1982)

A study of a laser-annealing system using a new molecular dynamics method modified to faithfully simulate typical experimental conditions is presented. Following melting, the recrystallization interface is layer structured in the melt. Rapid recrystallization, impurity segregation and constitutional undercooling, and the dynamics of the processes are demonstrated.

PACS numbers: 61.50.Cj, 64.75.+g, 66.70.+f, 68.45.-v

The processing of materials (semiconductors or metals) by using laser or electron beams, generically called "laser annealing,"^{1,2} provides novel techniques of crystal growth, damage recovery, and preparation of alloys of nonthermodynamic compositions. Aside from the varied important potential technological applications, the physical processes occurring in materials subject to intense radiation and the underlying mechanisms of ultrahigh-speed crystallization under conditions which could be far from equilibrium present an enormous theoretical challenge. The theoretical issues involve³ (a) the nature of the coupling of radiation (photons, particles) to solids, (b) thermodynamics, in particular nonequilibrium and stability analysis (metastability, morphological stability⁴), (c) rapid solidification kinetics, and (d) dynamics. All theoretical efforts to date are based³ on continuum phenomenological treatments of particle diffusion and heat flow (moving boundary problem), which while providing useful insight do not allow understanding of the dynamics and the atomic-scale processes which govern the kinetics. In this note we present the first theoretical investigation which addresses, and reveals, certain of the atomistic processes which underlie fast solidification phenomena under "laser-annealing" conditions. Additionally, we demonstrate the unique value of molecular dynamics (MD) simulation analysis in studies of material processes of unusual nature.

Prior to the presentation of results we outline certain of the pertinent features of the simulation. (i) The simulated system consists of a slab with thirty atomic planes (fifty atoms per plane, initial average layer spacing ~2.7 Å) forming an fcc crystal with the (100) face exposed. One side of the slab (starting at z = 0) interacts with a static extension of the crystal and the other side is free in the z direction. Two-dimensional periodic boundary conditions are imposed on the planes with the \vec{a} and \vec{b} vectors defining the basis of the MD cell treated as dynamical variables,⁵ thus allowing variations in both areal density and thickness. (ii) The incident beam, on the free side of the system, has a triangular intensityversus-time profile, 1.6 psec in duration and carrying a total energy of 6.3×10^{-5} J/cm². The coupling of the beam energy to the lattice modes is simulated via a time-stepwise scaling of particle velocities for the duration of the pulse using an absorption profile given by exp $[0.02z/(1 \text{ \AA})]$, where z in angstroms increases going out of the solid. (iii) The initial system consists of two species, 90 at.% of species α with species β substituted randomly, interacting via 6-12 Lennard-Jones potentials

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right],$$

with $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2$ and $\epsilon_{\alpha\beta} = (\epsilon_{\alpha\alpha}\epsilon_{\beta\beta})^{1/2}$. We choose $\sigma_{\beta\beta}/\sigma_{\alpha\alpha} = 1.07$, $\epsilon_{\beta\beta}/\epsilon_{\alpha\alpha} = 1.387$, and mass ratio m_{θ}/m_{α} = 2.098 [corresponding to argon (α) and krypton (β) parameters; σ_{Ar} = 3.4 Å]. Reduced units are used: temperature $T^* = k_B T / \epsilon_{\alpha\alpha}$ and reduced length = $L/\sigma_{\alpha\alpha}$. The system is initially equilibrated at $T^* = 0.4$ (the melting temperature of pure bulk α is $T_{m,\alpha}^* = 0.7$). The integration time step is $\Delta t = 0.0075 t_{\alpha}$, where $t_{\alpha} = 2.16$ psec for Ar. (iv) Heat conduction to the underlying substrate reservoir is simulated by scaling velocities in the bottom two layers according to $\dot{Q}(t) = A\kappa(T(t)) dT(t)/dz$, where A is the planar area and $\kappa(T(t))$ is a temperature-dependent heat conductivity taken from solid-Ar experimental data.⁶ The gradient dT(t)/dz is temporally determined by a linear extrapolation of the system temperature profile to a point in the substrate, distant from the bottom of the slab by 31.56 $\sigma_{\alpha\alpha}$ = 107.5 Å (different substrate material or temperature will yield different gradients).

To facilitate the presentation of results we define for any property g_i which depends on the phase-space point (\vec{r}_i, \vec{v}_i) of atom *i* located at z_i , a local density (per unit length) of that property at z by

$$\hat{\rho}_{e}(z) = (2\pi)^{-1/2} \sigma^{-1} \sum_{i} g_{i} \exp[-(z - z_{i})^{2}/2\sigma^{2}],$$

with $\sigma = 0.126$ of the average layer spacing. For particle number density (per length) profile (g_i = 1), $\hat{\rho}_n(z) \equiv \rho(z)$. In the following we present the per-particle property local densities $\rho_g(z) \equiv \hat{\rho}_g(z)/\rho(z)$. For the kinetic energy, KE, and potential energy, PE, $g_i = \frac{1}{2}m_i v_i^2$ and $\frac{1}{2}\sum_j V(|\vec{\mathbf{r}}_i - \vec{\mathbf{r}}|)$, respectively. The kinetic temperature is given by two-thirds of the KE. An additional quantity of interest is the planar orientational order parameter⁷ O_4 for which

$$g_i = W_i^{-1} \sum_{j \in \operatorname{nn}(i)} W_{ij} \exp(i4\theta_{ij}),$$

where $W_i = \sum_{j = nn(i)} W_{ij}$, $W_{ij} = \exp(z_j - z_i)^2 / 2\sigma_0^2$,

 $\sigma_0 \simeq 0.5$ layer spacing, and nn(i) denotes nearest neighbors to atom *i*. θ_{ij} is the angle that the "bond" between atoms *i* and *j* makes with the *x* axis. The absolute value of O_4 attains a value close to unity on a (100) face of an fcc layer, and is close to zero for a liquid.

In Figs. 1(a) and 1(b) the particle density, KE, PE, and $|O_4|$ vs z are shown for the initial system and immediately at the end of the 1.6-psec heat pulse. The minima in the PE profile occur at the location of atomic planes. It is seen [Fig. 1(b)] that while the kinetic energy is increased because of the pulse, disordering has just started to occur since not enough time has elapsed yet for thermal energy to be converted to potential energy. The initial random impurity distribution is shown in Fig. 1(d)(i). In Fig. 1(c) time-aver-



FIG. 1. (a)-(c): Profiles of number density (ρ), KE, PE, and $|O_4|$ vs $z^{*} = z/7.89\sigma_{\alpha\alpha}$ for the initial system, at the termination of the pulse, and for an isolated equilibrium system, respectively. (d)(i), (d)(f), and (d)(eq): Impurity density profiles for the initial, final, and equilibrated systems, respectively. (d)(v): Position, z^* , of the recrystalization interface vs time (in picoseconds). A straight-line fit yields a solidification velocity of 11 m/sec. Detailed analysis indicated that a region characterized by $|O_4| < 0.4$ lacks planar long- and short-range order. This criterion was adopted in the construction of Fig. (d)(v).

aged results are shown for a thermally isolated system ($\kappa = 0$), which has been subjected to an identical heat pulse and let develop for a very long time. In this case, an equilibrated system with solid-liquid coexistence has been produced (equilibrium temperature corresponds to KE of 0.96). Note the sharp drop in O_4 at about $z^*=1$ indicating loss of intralayer order while permanent layering in the particle density profile is evident beyond that point into the liquid. The time-averaged impurity distribution in the equilibrated system [Fig. 1(c)] shown in Fig. 1(d)(eq)reveals a feature which indicates a tendency of the impurity to avoid the interface. (This region is characterized by transport coefficients of a liquid.) The corresponding stabilization in these regions is indicated in the PE profile [Fig. 1(c)] by arrows.

Next we turn in Fig. 2 to a sequence of profiles for a heat-conducting system taken at selected time steps during the evolution of the system after the termination of the pulse. Figure 2(a) describes the system at the final stages of melting.

As seen in Fig. 2(b) recrystallization started while the kinetic temperature of the melt, T_{liquid} , was still above the solid-liquid coexistence temperature, T_{π} ; see Fig. 1(c). The ρ and $|O_4|$ profiles at 73 psec show clear evidence of a layered melted region, also seen in the PE profile. The moving recrystallization front is characterized by a structured three-dimensional interface, anisotropic in density and properties. The anisotropic structured nature of the interface may play an important role in the recrystallization kinetics and in phenomena such as solute trapping. Once T_{liquid} has dropped to T_m , the velocity of crystallization accelerates. Later, however, at 203 psec [Fig. 2(c)] the velocity of crystallization decreases sharply [Fig. 1(d)(v)] and interface layering temporarily becomes less evident. These changes are associated with an increase in impurity concentration at the interface resulting from the previous expulsion of the impurity into the liquid (and perhaps a tendency for cellular ordering). T_{liquid} subsequently falls below T_m (a manifestation of constitutional supercooling),



FIG. 2. (a)-(d): Profiles of number density (ρ), KE, PE, and $|O_4|$ vs z^* at time steps 25 (end of melting), 73, 203, and 333 psec, respectively.

the velocity of crystallization recovers, and layering is reestablished [see Fig. 2(d) at 333 psec]. At the end of the process (~500 psec) the total number density profile is identical to that in Fig. 1(a), and the impurity profile is shown in Fig. 1(d)(f). A certain amount of impurity segregation to the free surface is evident.

In this study we demonstrated the use of MD in an investigation of a complex nonequilibrium material process. Of interest is the "liquid layering" which, as we observed, precedes the solidification front, preparing the liquid for formation of perfect crystalline planes, and significantly affects impurity segregation and transport (see also Wood, Ref. 3), while in turn being affected by interfacial conditions that it, in part, brings about. MD studies can be instrumental in analyzing the dynamic interrelationship between the structure and properties of the interface and the solidification process. Investigations continue in our laboratory on the relationship between the time scale of interface processes (such as layering) and the nature of the resulting solid (crystalline versus amorphous) under various solidification rates, the effect of crystal face, crystallization on amorphous substrates, the role of "liquid layering" in solute trapping or expulsion, and the dependence on host and impurity interaction

potentials and mass ratios.

This work was supported by U. S. Department of Energy Contract No. EG-S-05-5489.

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Fig.1

N/e

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TIME [t*]

Fig. 4

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A.2 Solid-Liquid Interface at Equilibrium

A modification of the laser-annealing program (see A.1) in which heat conduction to the substrate was not allowed, permitted us to investigate the properties of a solid-melt coexistence (at equilibrium) system. The system was composed of two components (10% of impurities) interacting via Lennard-Jones potentials corresponding to Ar as host and Kr as an impurity. Studies of the equilibrium properties revealed: (a) a structured interface. (b) Features in the impurity particle distribution which indicate a tendency to avoid the interface. We are currently developing an analytical method based on Percus-Yevick and perturbation theory for the study of the properties of equilibrium solid-liquid interfaces of binary systems.

The density of particle profiles for the combined system, ρ_{A+B} and for the impurity ρ_B are shown in Fig. 1 (left and right columns, respectively). along with the corresponding kinetic energies (KE), potential energies (PE) and order parameters (|ANG 4|). Comparison of the ρ_{A+B} and |ANG 4| plots demonstrates the liquid layering phenomena. Furthermore, the impurity clustering effects in the liquid is evident in ρ_B .

In addition we have calculated diffusion constant profiles for this system. These have been calculated via the time integral of the velocity autocorrelation functions for the total system D^A) and for the impurity alone (D^B) and are given in Fig. 2.

$$Di_{\perp} = \int_{0}^{\Delta t} dt (V_{iz}(t) V_{iz}(0))$$

$$Di_{\parallel} = \frac{1}{2} \int_{0}^{\Delta t} dt (V_{ix}(t) V_{ix}(0) + V_{iy}(t) V_{iy}(0))$$

where z is normal to the (100) plane and x and y are parallel to the plane.

We observe that the diffusion constant profiles change continuously from a value of zero in the solid part of the system to a typical liquid value. $(D = 5.37 \times 10^{-4} \text{ cm}^2/\text{sec.})$ The region in between, whose width is about 21 Å, corresponds to the three-dimensional, diffuse, liquid-layered interface. Comparison of D₁₁ and D₁ does not indicate a pronounced anisotropy of the diffusion constant in this region. The above provides the first detailed characterization of transport properties for the equilibrium solid-liquid interface. We intend to perform similar equilibrium studies for the (110) surface-liquid interface in order to ascertain the crystal structure effect on the equilibrium properties.





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A.3 SURFACE DIFFUSION: clusters and single particles

Diffusion processes on or in the vicinity of surfaces are of importance in many surface controlled, or driven, physical and chemical phenomena. Such phenomena include crystal growth, surface phase transformations, annealing and recovery of damage, faceting, surface and interfacial (grain-boundary) segregation and chemical processes, heterogeneously catalyzed by surfaces.

While several experimental techniques provide valuable information about surface diffusion (such as Field Emission Spectroscopy (flicker noise), photoemission monitoring as the light beam traverses across the surface, changes in contact potential and scanning Auger methods) the most direct observations are provided via Field Ion Microscopy (FIM) techniques (See Review by G. Ehrlich and Kaj Stolt, Ann. Rev. Phys. Chem. <u>31</u>, 603 (1980)). FIM provides information on the atomic scale concerning the local structure of the system and configurations of the diffusing species which when analyzed properly provide information about the kinetics and energetics of surface diffusion processes. Of particular interest to us are observations of metal adatom clusters diffusing on metal surfaces since such systems are of great interest for a fundamental understanding of diffusion mechanism and in studies of many materials processes (See above mentioned review, and Review by Uzi Landman, Israel J. of Chem. <u>22</u>, 339 (1982), Section V and references therein).

The main objectives of our molecular dynamics studies of surface diffusion are to investigate the dynamics and energy pathways of surface diffusion, and to determine the structural, potential, species and temperature dependencies of the elementary diffusion events and their influence on diffusion rates. We have chosen to comparatively study self-diffusion and hetero-diffusion on these surfaces in order to elucidate the structural and potential factors governing the microscopic diffusion mechanisms.

Employing Lennard-Jones pair-potentials we have studied dimer and single particle self-diffusion on the above surfaces and that of Pb dimers and single particles on (100) and (110) Cu surfaces.

Among our observations we note:

- a) A dependence of the diffusion mechanism and rate on crystallographic surface orientation. On the (100) two-dimensional diffusion is observed for both dimer and single particle cases, with dimer rotations being a most frequent occurrance. On the (110) "onedimensional", channelled migration occurs. At higher temperatures cross-channel diffusion sets in both for the single particle and dimer case. The in-channel dimers are relatively immobile up to their dissociation limit.
- b) We observe two temperature regimes for single particle diffusion. While regular migration occurs at low temperatures, at higher temperatures particle exchange with the substrate becomes an important contributing mechanism. The particle exchange occurs for selfdiffusion (Cu on Cu) at lower temperatures than for the Pb particle diffusion on Cu. Contributing to the probability of particle exchange are the potential parameters (well-depth and atomic radii) of the substrate, and those between the diffusants and the substrate. The thermal stability of the substrate plays an important role in both particle exchange and trapping.

At intermediate temperatures regular diffusion and particle exchange are competing mechanism leading to a non-linear relationship in a plot of log D versus T^{-1} . (D is the diffusion constant which we determine via the velocity autocorrelation function or the positional variance of the diffusing species.)

c) We have discovered a most interesting dynamical effect in the diffusion of Pb dimers on the Cu surfaces. We found that for Pb dimers on Cu (110) the mode of dimer vibrations which couples first to the substrate modes is a dimer rotational mode. This mode serves as a doorway to the jump event. Upon getting populated it couples to another mode (of non-rotational character) which serves as the migrational channel. It is found that the amount of energy which gets transferred from the substrate to the rotational mode of the dimer exceeds in most cases the static potential barrier for diffusion. Consequently, upon coupling to the migrational mode the hopping particle is rather energetic, resulting in multiple hops (non-nearest neighbor jumps).

To demonstrate this phenomena we show in Figs. |a - |c| a sequence of Pb dimer molecular dynamics trajectories, on a dynamic Cu (110) surface (Equilibrium lattice positions denoted by X's). In these figures the time step is $\Delta t^* = 0.0075 t_{Cu}^*$ where $t_{Cu}^* = 2.3 \times 10^{-13}$ sec. In these trajectories one observes both multiple-site and temporally correlated return (round-trip) jump events. A plot of the Pb-Pb bond length vs. time is shown in Fig. 2. A discontinuous rise or decrease in bond length corresponds to a hop event. The angle, ϕ , between the dimer axis and the x direction (parallel to the channels in the (110) surface is shown in Fig. 3, while the time development of the angle between the dimer axis and the normal to the surface (110 direction) is shown in Fig. 4 demonstrating that the dimer is remaining parallel to the surface. The potential in the Pb-Pb bond is shown in Fig. 5. energy

Next we concentrate on the dynamics of the system prior to the hop-event which occurred around $t^* = 250$. Shown in Fig. 6 is the time evolution of the inplane angle ϕ exhibiting an envelope with maximum amplitude at $t^* = 232$. (The large amplitudes at t & 250 are directly related to the hop event). The period of the amplitude oscillations of φ is of the order of 1 X 10^{-13} sec. The rotational (kinetic) energy of the dimer is shown in Fig. 7, again maximizing at t * \approx 230 as is the kinetic energy and potential energy of the bond stretch shown in Fig. 8, and Fig. 9, respectively. Furthermore in Fig. 10 we show the quantity $V_{1x} V_{2x}$ where V_{ix} (i = 1,2) is the component of the velocity of dimer particle i in the x direction. It is seen that in the time interval around $t^* = 230, V_{1x} V_{2x} < 0$ while closer to the jump event $V_{1x} V_{2x} > 0$. The negative value of $V_{1x}^{}$ $V_{2x}^{}$ indicates motions of particle 1 and 2 in opposite directions (rotations) while $V_{1x}V_{2x} > 0$ indicates a mode in which both particles are moving in the same direction. This demonstrates that around t \sim 230 a rotational mode was excited. This excitation then got converted to energize another mode which served as the migrational mode. Inspection of the total energies and their comparison to the static diffusion barriers for these systems shows that the amount of energy transferred to the rotational (nonmigrational) mode, which served as a precursor to the jump event exceeds the barrier.

Finally the velocity -velocity time correlations functions for a particle of the dimer, decomposed into the 3 cartesian components are shown in Figs. (11a) - (11c). It is seen that the velocity-velocity correlation for the y component damps out fast and is rather erratic indicating strong coupling of the diffusant motion to the substrate in that direction (in plane normal to the channel axis). The x and z components exhibit oscillatory character with a larger period in the x-direction indicating less coupling (damping) for motion in that direction.

These sample results demonstrate the power of our molecular dynamics studies in investigations of microscopic details of diffusion processes. Studies are now in progress of hetero and self diffusion on the low-index planes of an fcc material (Cu) at different temperatures. Additionally, analytical models based on multi-state random walk theory which we have developed in the past and stochastic dynamics (generalized Langevin equation) are being developed particularly towards a description of the doorway rotational mode mechanism of the dimer diffusion mechanism.

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B. <u>SURFACE DEFECTS, INTERIONIC INTERACTIONS AND SURFACE SEGREGATION</u> Main Achievements

B.1 Ionic Interactions Near Simple Metal Surfaces

We have presented a model for semi-infinite simple metals which does not require crystalline order or a single species, and thus is applicable to problems of defect energetics near the surface and random-alloy surfaces as well as ideal metal surfaces. The formulation is based on the use of ionic pseudopotentials and linear-response theory. An expression for the total energy was obtained which depends explicitly on ionic species and position. This expression is decomposed into a density-dependent term and single-ion and ionic pair-interaction potential terms. The single-ion potentials oscillate about a constant bulk value, with the magnitude of the oscillation decreasing rapidly away from the surface. The interaction between pairs of ions near the surface was shown to be a noncentral force interaction which differs significantly from the central-force bulk pair potential. The effect of quantum interference in the response of the semi-infinite electron gas to the ions is seen in both the single-ion and the pair-interaction potentials. Results are presented for the simple metals sodium, potassium, and rubidium.

Single-ion and pair-interaction potentials near simple metal surfaces

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We present a model for semi-infinite simple metals which does not require crystalline order or a single species, and thus is applicable to problems of defect energetics near the surface and randomalloy surfaces as well as ideal metal surfaces. The formulation is based on the use of ionic psuedopotentials and linear-response theory. An expression for the total energy is obtained which depends explicitly on ionic species and position. This expression is decomposed into a density-dependent term and single-ion and ionic pair-interaction potential terms. The single-ion potentials oscillate about a constant bulk value, with the magnitude of the oscillation decreasing rapidly away from the surface. The interaction between pairs of ions near the surface is shown to be a noncentral force interaction which differs significantly from the central-force bulk pair potential. The effect of quantum interference in the response of the semi-infinite electron gas to the ions is seen in both the single-ion and tube pair-interaction potentials. Results are presented for the simple metals sodium, potassium, and rubidium.

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I. INTRODUCTION

Fundamental investigations of certain physical properties of solid materials such as crystallographic structure, dynamics, and defect energetics (formation and migration) require detailed knowledge of, and the ability to calculate, the total energy or total-energy differences for various configurations. The total energy of metals, simple metals in particular, contains contributions of different origins, e.g., terms in the electronic energy which are density dependent (independent of the location of atoms) and terms which depend on the spatial arrangement of the atoms.¹ It is important to recognize that the dominant factors underlying various physical properties may relate to terms in the total energy which are of different origins. Thus, for example, the determination of crystallographic structure requires a minimization of the total energy including the contribution which is only density dependent² while the dominant contributions in studies of vibrations of bulk metals come from those terms which depend on the interatomic position vectors.^{1,3} Determination of the surface atomic arrangement (relaxation and reconstruction) may require, in addition, terms which depend on the positions of individual atoms relative to ideal (truncated bulk) crystal planes.4

Essential to the construction of theoretical treatments of the properties of perfect bulk crystals is the translational invariance of the lattice. The lack of translational symmetry causes major difficulties in the exploration of properties of imperfect crystals, and theoretical formulations which can provide quantitative estimates of structure, energetics, and dynamics of real (imperfect) materials, while most desirable, are less abundant. Material surfaces in the ideal case possess two-dimensional translational symmetry along the surface plane but lack translational symmetry along the surface properties are complex and require new formulations or adaptations of bulk methods with major modifications. Among the formalisms which have greatly enhanced our understanding of surfaces are density-functional-based techniques,^{5,6} methods which employ real-space or mixed representations (recursion techniques,⁷ Green's functions^{δ}), and surface band-structure computations⁹ (slab and supercell techniques).

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While significant progress in the theory of the electronic structure of ideal metallic surfaces and with ordered arrays of adsorbates has been achieved, calculations which employ minimization of the total energy yielding surface structural information,4,10-12 calculations of force constants for use in surface vibrational studies, and evaluation of interaction potentials for use in molecular-dynamics and Monte Carlo simulations are in their infancy.^{13,14} The introduction of single or randomly arranged defects to the surface region compounds the complexity since the lack of translational invariance is exhibited by both components of the system. Thus traditional band-structure calculations are not applicable and application of the densityfunctional method becomes difficult, involving approximate perturbative (most often first-order¹⁵) treatments, or it may entail a reduction in the dimensionality through t averaging over the ionic potentials in layers.

The purpose of this article is to develop a theoretical method for simple (sp bonded) metals which retains the three-dimensional character of the system, maintains the essential features of the electronic structure, and allows (a) systematic investigations of ionic potentials (effective pair potentials and single-ion potentials in the surface region), (b) studies of surface structure (relaxation and reconstruction), (c) analysis of the energetics of single and randomly distributed defects, and (d) studies of surface segregation phenomena¹⁶ in alloys (layer concentration profiles) via minimization of the surface free energy. An application of the formulation developed here to the prediction of the : relaxed surface structure of the low-index faces of Na and Al, yielding good quantitative agreement with available experimental results, has been reported.¹⁷ A detailed description of the surface relaxation calculation and a discussion of the results are given in the second paper of this series.^{18a} Impurity and vacancy formation energies and i surface segregation in alloys have been reported^{18b} by us |

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and will be treated in forthcoming publications.

To enable us to perform the studies listed above we need first to obtain an expression for the total energy of a semi-infinite metal which depends explicitly on the atomic species and their positions. Pseudopotentials, often in conjunction with linear-response theory, have been instrumental in investigations of bulk metal systems.¹ In particular, the application of local model pseudopotentials has yielded effective interaction potentials which have been well tested in studies of vibrations,¹⁹⁻²² elastic properties and vacancy formation energy and volume,²²⁻²⁶ and in molecular-dynamics simulations.²⁷⁻²⁹

In Sec. II of this paper we present the general formulation and obtain an expression for the total energy of a semi-infinite simple metal. This total-energy expression is most general in that it does not require crystalline order or a single species. The formulation employs local model pseudopotentials embedded in a semi-infinite interacting electron gas. The response of the electron gas to an embedded ion is obtained through the solution of a single one-dimensional integral equation and involves the use of a linear-response model applicable to the semi-infinte system. A decomposition of the total energy into (a) a density-dependent term, (b) terms which depend on the coordinates of a single ion, and (c) terms which depend jointly on the coordinates of pairs of ions is accomplished. In Sec. III we apply the theory to the calculation of single-ion and pair-interaction potentials in the surface region of simple metals. We find that near the surface the single-ion potentials oscillate about the (constant) bulk values and that the pair-interaction potentials are anisotropic and differ significantly from the bulk interaction.

II. TOTAL ENERGY OF SEMI-INFINITE SIMPLE METALS

A. Total-energy expressions

The metal surface system which we wish to study is conveniently represented by a semi-infinite interacting electron gas in the presence of a neutralizing positive background (jellium model), to which we add the appropriate ionic potentials. The Hamiltonian for the electrons is written as

$$H = H^0 + \sum_i w_i . \tag{1}$$

 H^0 is the many-body Hamiltonian of the interacting electron-jellium system,

$$H^0 = T + V_{ee} + V_+$$
, (2)

where T and V_{ee} are the electron kinetic energy and electron-electron interaction operators, respectively, and $V_{+}(\vec{r})$ is the potential due to the positive background. The potentials associated with individual ions, w_i , are given by

$$w_{i}(\vec{r}) = V_{p}(\beta_{i}; | \vec{r} - \vec{r}_{i} |) - N^{-1}Z(\beta_{i})V_{+}(\vec{r}), \qquad (3)$$

where $V_p(\beta_i; |\vec{r} - \vec{r}_i|)$ and $Z(\beta_i)$ are the bare ionic pseudopotential and valence charge, respectively, of the ion of species β_i located at position \vec{r}_i , and $N = \sum_i Z(\beta_i)$. The second term in the right-hand side (rhs) of Eq. (1) sub-

tracts the potential due to the jellium background and adds the potential due to an arrangement of ions represented by local model pseudopotentials.

In this study we employ pseudopotentials of the simplified Heine-Abarenkov form,

$$V_{p}(\beta;r) = \begin{cases} -Z(\beta)e^{2}/r, \ r \ge r_{c}(\beta) \\ -Z(\beta)u_{c}(\beta)e^{2}/r_{c}(\beta), \ r < r_{c}(\beta) \end{cases}$$
(4a)
(4b)

where the core radius and level parameters, $r_c(\beta)$ and $u_c(\beta)$, are chosen to fit bulk properties (lattice constant and bulk modulus²⁵) of the pure species β .

The ground-state energy E_0 and electron density $\rho^0(\vec{r})$ of the jellium system described by H^0 [Eq. (2)] is given in a seminal study by Lang and Kohn.³⁰ With the use of the coupling-constant integration method and assuming linear response, the total energy E_T of the semi-infinite metal is given by

$$E_{T} = E^{0} + \sum_{i} \int d^{3}r \,\rho^{0}(\vec{r}) w_{i}(\vec{r}) + \frac{1}{2} \sum_{i,j} \int d^{3}r \,\rho_{i}(\vec{r}) w_{j}(\vec{r}) + E_{M} , \qquad (5)$$

where $\rho_i(\vec{r})$ is the electron density induced by the potential $w_i(\vec{r})$, and E_M is the Madelung energy of the ionic system. The second term in Eq. (5) is a first-order correction due to the replacement of the positive background by discrete ions, and the third term is second order in w_i , usually called the band-structure (BS) energy E_{BS} .

B. Screening

The major task in obtaining the total energy, Eq. (5), for an arbitrary arrangement of ions is to obtain a selfconsistent solution for the induced, or screening, electron density $\rho_i(\vec{r})$. We use linear-response theory, yielding a pair of coupled integral equations,

$$\rho_i(\vec{r}) = \int d^3 r' \alpha_0(\vec{r},\vec{r}\,') [w_i(\vec{r}\,') + \phi_i(\vec{r}\,')] , \qquad (6a)$$

$$\phi_i(\vec{r}) = \int d^3 r' g(\vec{r}, \vec{r}\,') v_C(\mid \vec{r} - \vec{r}\,'\mid) \rho_i(\vec{r}\,') , \qquad (6b)$$

where $\alpha_0(\vec{r}, \vec{r}')$ is the random-phase-approximation (RPA) response function (polarizability). $\phi_i(\vec{r})$ is the effective potential due to the electron density $\rho_i(\vec{r})$, which includes exchange and correlation effects via the function $g(\vec{r}, \vec{r}')=1-G(\vec{r}, \vec{r}')$, and $v_C(\vec{r})=e^2/r$ is the Coulomb interaction. $G(\vec{r}, \vec{r}')$ is a local-field correction, related to the electron pair correlation function of the jellium system, which takes into account short-range correlations arising from both Coulomb and exchange effects.³¹

Translational invariance parallel to the surface requires that

$$\alpha_0(\vec{r},\vec{r}') = \alpha_0(|\vec{R}-\vec{R}'|;z,z')$$

and

$$g(\vec{r}, \vec{r}') = g(|\vec{R} - \vec{R}'|; z, z'),$$

with $\vec{r} = (\vec{R}, z)$ (here and in the following, upper-case letters denote two-dimensional vector, parallel to the surface). An evaluation of the response function requires knowledge of the single-particle wave functions and energy eigenvalues of the interacting electron-jellium system. These are of the form

$$\Psi_{\vec{K},\kappa}(\vec{r}) = \Omega^{-1/2} e^{i \vec{K} \cdot \vec{R}} \psi_{\kappa}(z) , \qquad (7)$$
$$E(\vec{K},\kappa) = \hbar^2 K^2 / 2m + \epsilon_{\kappa} , \qquad (7)$$

respectively, where $\Omega = N\Omega_0$ is the volume of the semiinfinite metal (Ω_0 is the volume per electron). The response function (retarded polarizability) is given in a mixed representation by

$$\alpha_{0}(Q;z,z') = 2\Omega^{-2/3} \sum_{\kappa,\kappa'} \mathscr{L}(Q;\kappa,\kappa')\psi_{\kappa}^{*}(z)\psi_{\kappa'}(z) \times \psi_{\kappa'}^{*}(z')\psi_{\kappa}(z') , \qquad (8a)$$

$$\mathcal{L}(Q;\kappa,\kappa') = \Omega^{-2/3} \sum_{\vec{k}} \frac{f(\vec{k}-\vec{Q}/2,\kappa)-f(\vec{k}+\vec{Q}/2,\kappa')}{E(\vec{k}-\vec{Q}/2,\kappa)-E(\vec{k}+\vec{Q}/2,\kappa')},$$

where $f(\mathbf{\bar{K}},\kappa)$ is the Fermi-Dirac distribution function, and $\mathcal{L}(Q;\kappa,\kappa')$ is the two-dimensional RPA response function.³²

To obtain the response function, Eq. (8a), we must either numerically evaluate the single-particle wave functions, $\psi_r(z)$, or use an approximate analytical form. Our choice is to use the wave functions of a noninteracting electron gas confined to the half-space (z > 0) by an infinite barrier.³²⁻³⁵ This choice is dictated primarily by analytical convenience. Other choices are possible³⁶; for instance, one could solve for the single-particle wave functions resulting from the potential due to the Lang-Kohn electron density plus the positive background. However, the increased complexity of such choices results in formulations which are impractical or impossible to use in a systematic study which retains the three-dimensional character of the system. Lert and Weare³² have used the infinite barrier response model to calculate the electron density at the Na(100) surface and report that comparison of their results with the self-consistent nonlinear results of Appelbaum and Hamann³⁷ indicates the joint validity of the linear approximation and the infinite barrier response model. The overconfinement of the electrons outside the jellium surface in this model might contribute to the surface energy. However, we are interested primarily in total-energy differences resulting from a rearrangement of the ions or a change in species of some ions, and contributions due to overconfinement are expected to be of less significance due to cancellation. In addition, the success of this response model in predicting the relaxed surface structure of simple metals^{17,18a} lends some a posteriori validation to the approximation.

The basis-set wave functions and energies associated with the infinite barrier response model are given by

$$\psi_{\kappa}(z) = \sin(\kappa z) \Theta(z) , \qquad (9a)$$

$$\epsilon_{\kappa} = \frac{\hbar^2}{2m} \kappa^2 , \qquad (9b)$$

where Θ is the Heaviside unit step function. The surface barrier is located at z=0 and the jellium edge position, determined by charge neutrality, is $z_0 = 3\pi/8k_{\Gamma}$ (Ref. 38); the layers of an unrelaxed crystal will be located at $z_n = z_0 + (n - \frac{1}{2})D$, where n = 1 for the surface layer and D is the layer spacing. Substituting Eqs. (9) into Eq. (8a) gives the infinite barrier model response function

$$\alpha_{0}(Q;z,z') = 2\Omega^{-2/3} \sum_{\kappa,\kappa'} \mathscr{L}(Q;\kappa,\kappa') \sin(\kappa z) \sin(\kappa z') \times \sin(\kappa' z') \Theta(z) \Theta(z') . \quad (10)$$

The analytical convenience of this response model is due to the vanishing of $\alpha_0(Q;z,z')$ if either $z \le 0$ or $z' \le 0$, or both; thus it is possible to symmetrize the problem by reflecting across the z=0 plane. We define symmetrized quantities $\rho_{is}(\vec{r})$, $w_{is}(\vec{r})$, and $\phi_{is}(\vec{r})$, and their threedimensional Fourier transforms, by

$$\rho_{is}(\vec{r}) = \rho_i(R, |z|), \qquad (11a)$$

$$\rho_{is}(\vec{\mathbf{q}}) = \int d^3 r \, e^{i \, \vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} \rho_{is}(\vec{\mathbf{r}}) \,, \qquad (11b)$$

etc. Using these definitions, we obtain from Eq. (6a), after some manipulation, an equation in reciprocal space for the induced electron density in the symmetrized system (see Appendix A),

$$\rho_{is}(\vec{q}) = \alpha_0(q) [w_{is}(\vec{q}) + \phi_{is}(\vec{q})] -\pi^{-1} \int d\kappa \, \mathscr{L}(Q; \kappa + q_z/2, \kappa - q_z/2) \times [w_{is}(Q, 2\kappa) + \phi_{is}(Q, 2\kappa)].$$
(12)

Here $\alpha_0(q)$ is the three-dimensional Fourier transform of the polarizability of an infinite electron gas as given by Lindhard,³⁹

$$\alpha_0(q) = \pi^{-1} \int d\kappa \, \mathscr{L}(Q; \kappa + q_z/2, \kappa - q_z/2) \,. \tag{13}$$

Integrating Eq. (12) over q_z results in a useful sum rule,

$$\int dq_z \rho_{is}(\vec{q}) = 0 , \qquad (14)$$

expressing the fact that the induced density is zero at z=0.

The equation for the self-consistent effective potential, Eq. (6b), takes, in the symmetrized system, the form

$$\phi_{is}(\vec{q}) = \int d^{3}r \, e^{i\,\vec{q}\cdot\vec{r}} \int d^{3}r'g(|\vec{R}-\vec{R}'|;z,z')$$

$$\times v_{C}(|\vec{r}-\vec{r}'|)\rho_{is}(\vec{r}')$$

$$\times [1-\Theta(z)\Theta(-z')$$

$$-\Theta(-z)\Theta(z')]. \quad (15)$$

In order to simplify Eq. (15), and to allow the solution of the coupled integral Eqs. (12) and (15) to be reduced to the solution of a single one-dimensional integral equation, we will assume that $g(|\vec{R}-\vec{R}'|;z,z')$ can be adequately approximated by

$$g(|\vec{\mathbf{R}}-\vec{\mathbf{R}}'|;z,z')=1-G(|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|)$$

where $G(|\vec{r} - \vec{r}'|)$ is the local-field correction evaluated for the bulk electron density. This approximation may be justified for several reasons: (a) It introduces only second-order errors, (b) $G(\vec{r},\vec{r}')$ does not depend sensitively on the local density, and (c) experience with other systems indicates that anisotropic or inhomogeneous corrections in condensed systems are usually small.^{40,44}

Employing the above form of $g(\vec{r}, \vec{r}')$, Eq. (15) becomes (see Appendix B)

$$\phi_{is}(\vec{q}) = g(q)v_{\mathcal{C}}(q)\rho_{is}(\vec{q}) + v_{\mathcal{C}}(q)\sigma_i(Q) + X_i(\vec{q}) , \quad (16)$$

where g(q) is the Fourier transform of g(r) evaluated for the bulk electron density. We use the analytical fit

$$g(q) = 1 - A \left[1 - \exp(-Bq^2/k_f^2) \right]$$

given by Singwi et al.³¹ $v_C(q) = 4\pi e^2/q^2$ is the Fouriertransformed Coulomb potential. $v_C(q)\sigma_i(Q)$ and $X_i(\vec{q})$ are functions which subtract the interaction of the induced electron density with its image in the symmetrized system. The Coulomb interaction between the induced electron density and its image is cancelled by

$$\sigma_i(Q) = -(Q/2\pi) \int dq_z [\rho_{is}(\vec{q})/q^2] , \qquad (17)$$

which can be regarded as a fictitious surface electron density, and

$$X_{i}(\vec{q}) = -\int d^{3}r \, e^{i \, \vec{q} \cdot \vec{r}} \int d^{3}r' [g(|\vec{r} - \vec{r}'|) - 1]$$

$$\times v_{C}(|\vec{r} - \vec{r}'|) \rho_{is}(\vec{r}')$$

$$\times [\Theta(z)\Theta(-z')$$

$$+ \Theta(-z)\Theta(z')] \qquad (18)$$

subtracts the exchange-correlation potential due to the image electron density. Since the local-field correlation function G(r)=1-g(r) is short ranged, and since the induced electron density $\rho_{is}(\vec{r}')$ vanishes as $z \rightarrow 0$, $X_i(\vec{q})$ can be neglected. A posteriori validation of this approximation is provided by the observation that the sum rule, Eq. (14) (which was derived with no approximation), is satisfied by our numerical results when $X_i(\vec{q})$ is neglected.

The coupled integral equations, Eq. (12) and Eqs. (16)-(18), can be decoupled by setting

$$\rho_{ii}(\vec{q}) = \alpha_0(q) [w_{ii}(\vec{q}) + v_C(q)\sigma_i(Q)]/\epsilon(q) + [u_i(\vec{q}) + u_\sigma(\vec{q})\sigma_i(Q)]/[g(q)v_C(q)], \quad (19)$$

where

$$\boldsymbol{\epsilon}(q) = 1 - \boldsymbol{g}(q) \boldsymbol{v}_{\boldsymbol{C}}(q) \boldsymbol{\alpha}_{0}(q) \tag{20}$$

is the (bulk) electron dielectric function, and $u_i(\vec{q})$ and $u_\sigma(\vec{q})$ are to be determined. Combining Eqs. (12), (16), and (19), and requiring that the coefficients of $\sigma_i(Q)$ cancel, results in a single one-dimensional integral equation for $u_i(\vec{q})$,

$$u_{i}(\vec{q}) = -[g(q)v_{C}(q)/\epsilon(q)]\pi^{-1}$$

$$\times \int d\kappa \, \mathscr{L}(Q;\kappa + q_{z}/2,\kappa - q_{z}/2)$$

$$\times [u_{i}(\vec{q}') + w_{is}(\vec{q}')/\epsilon(q')], \qquad (21)$$

where $\vec{q}' = (\vec{Q}, 2\kappa)$, and in a similar equation for $u_{\sigma}(\vec{q})$ in which $w_{is}(\vec{q}')$ is replaced by $v_{C}(q')$ in the integral. These

equations are solved numerically by successive iteration. Since $\sigma_i(Q)$ is independent of q_z , substituting Eq. (19) into Eq. (17) yields immediately an expression for $\sigma_i(Q)$ in terms of $u_i(\vec{q})$ and $u_{\sigma}(\vec{q})$.

Note that in Eq. (19) the first term on the rhs describes the bulk response to the potential $[w_{is}(\vec{q}) + v_C(q)\sigma_i(Q)]$. It is apparent that $u_i(\vec{q})$ and $u_{\sigma}(\vec{q})$ in the second term contain the effects of quantum interference associated with the semi-infinite bounded electron gas. These quantum interference effects become small, as does $\sigma_i(Q \neq 0)$ (the nonvanishing contributions to the fictitious surface electron density due to w_i), as the ion position \vec{r}_i moves further from the surface, and bulk screening is obtained for ions far from the surface. The semiclassical limit $(\hbar \rightarrow 0 \text{ with } \hbar k_f = \text{const})$ amounts to neglect of these quantum interference terms.³³ However, in this limit the position of the jellium edge is at $z_0 = 0$ and, therefore, there is no response beyond the jellium edge.

C. Total-energy decomposition

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The total energy, Eq. (5), can be decomposed into a term $U^{(0)}(\Omega_0)$ which depends only on the average electron density of the semi-infinite metal, terms $U^{(1)}(\Omega_0;\beta_i,z_i)$ which depend on the species and the positions of individual ions relative to the surface, and terms $U^{(2)}(\Omega_0;\beta_i,\vec{r_i};\beta_j,\vec{r_j})$ which depend on the species and the coordinates of pairs of ions; thus the total-energy expression becomes

$$E_{T} = U^{(0)}(\Omega_{0}) + \sum_{i} U^{(1)}(\Omega_{0};\beta_{i},z_{i}) + \frac{1}{2} \sum_{i,j} U^{(2)}(\Omega_{0};\beta_{i},\vec{r}_{i};\beta_{j},\vec{r}_{j}) .$$
(22)

The purpose of this section is to show that this decomposition is possible and to derive the expressions for the single-ion and pair-interaction potentials, $U^{(1)}$ and $U^{(2)}$. It should be noted that this decomposition is not particularly useful in performing most calculations since it is usually simpler to take advantage of the geometry specific to the problem and do the calculation in reciprocal space. However, we can gain some insight into how ionic interactions differ at the surface and in the bulk, and the decomposition may be useful in, for instance, molecular-dynamics and Monte Carlo simulations.

We begin by separating $w_i(\vec{r})$ and $\rho_i(\vec{r})$ into ionic pseudopotential, \tilde{w}_i and $\tilde{\rho}_i$, and positive background, V_P and ρ_+ , parts:

$$w_i(\vec{\mathbf{r}}) = Z_i[\tilde{w}_i(\vec{\mathbf{r}}) - (\Omega_0/\Omega)V_+(\vec{\mathbf{r}})]$$
(23a)

and

$$\rho_i(\vec{r}) = Z_i[\tilde{\rho}_i(\vec{r}) - (\Omega_0/\Omega)P_+(\vec{r})], \qquad (23b)$$

where for notational convenience we have defined

 $\widetilde{w}_{i}(\vec{r}) = Z_{i}^{-1} V_{p}(\beta_{i}; |\vec{r} - \vec{r}_{i}|)$

[see Eqs. (3) and (4)] and $Z_i = Z(\beta_i)$. In defining the Fourier transforms of the symmetrized quantities $\tilde{w}_{is}(\vec{r})$ and $\tilde{\rho}_{is}(\vec{r})$ we shift the ions to the origin in the x - y plane,

$$\widetilde{w}_{ij}(\vec{q}) = \int d^2 R \ e^{i \vec{Q} \cdot (\vec{R} - \vec{R}_i)} \int dz \cos(q_z z) \widetilde{w}_{ij}(\vec{r}) , \qquad (24)$$

etc. The reciprocal-space representations of the potentials $\widetilde{w}_{is}(\vec{q})$ and $V_{+s}(\vec{q})$ are given by (see Appendix C)

$$\widetilde{w}_{is}(\vec{q}) = 2Z_i^{-1} V_p(\beta_i;q) \cos(q_z z_i) + v_c(q) e^{-Q z_i} , \qquad (25)$$

where $V_p(\beta_i;q)$ is the Fourier transform of $V_p(\beta_i;r)$, and

$$V_{+s}(\vec{q}) = (2\pi)^2 \Omega_0^{-2/3} \delta(\vec{Q}) v_{+s}(q_z) , \qquad (26a)$$

where

$$v_{+s}(q_z) = -2\Omega_0^{-1/3} v_C(q_z) [\pi \delta(q_z) - \sin(q_z z_0)/q_z] .$$
(26b)

The induced electron densities $\tilde{\rho}_{is}(\vec{q})$ and $\rho_{+s}(q_z)$ are obtained as before using $\tilde{w}_{is}(\vec{q})$ or $v_{+s}(q_z)$ with $\vec{Q}=0$, respectively, in place of $w_{is}(\vec{q})$ in Eq. (12). Finally, we de-

fine $\tilde{\sigma}_i(Q)$ by using $\tilde{\rho}_{is}(\vec{q})$ in place of $\rho_{is}(\vec{q})$ in Eq. (17). With this definition, $\sigma_i(Q)$ is given by

$$\sigma_i(Q) = Z_i[\tilde{\sigma}_i(Q) + (2\pi)^2 \Omega^{-2/3} \delta(\overline{Q})].$$
⁽²⁷⁾

It can be shown [see Eq. (B7)] that $\lim_{Q\to 0} \tilde{\sigma}_i(Q) = -1$, in agreement with our numerical results.

The total energy, Eq. (5), expressed in terms of the reciprocal-space functions $w_{is}(\vec{q})$ and $\rho_{is}(\vec{q})$, is

$$E_{T} = E_{0} + \sum_{i} \int d^{3}r \,\rho^{0}(\vec{r}) w_{i}(\vec{r}) + \frac{1}{4} \sum_{i,j} (2\pi)^{-3} \int d^{3}q \,\rho_{is}(\vec{q}) w_{js}(\vec{q}) + E_{M} \,.$$
(28)

The factor of $\frac{1}{4}$ instead of $\frac{1}{2}$ in the third term (the bandstructure energy) is due to the symmetrization of the system (in effect we have two noninteracting semi-infinite systems). Substitution of Eqs. (23)-(26) into Eq. (28) yields, after some algebra,

$$E_{T} = E_{0} - \int d^{3}r \rho^{0}(\vec{r}) V_{+}(\vec{r}) + \frac{1}{4} (\Omega / \Omega_{0}^{2})^{2/3} (2\pi)^{-1} \int dq_{z} \rho_{+s}(q_{z}) v_{+s}(q_{z}) + \sum_{i} Z_{i} \int d^{3}r \rho^{0}(\vec{r}) \widetilde{w}_{i}(\vec{r})$$

$$- \frac{1}{4} \Omega_{0}^{-2/3} \sum_{i} Z_{i} (2\pi)^{-1} \int dq_{z} [\widetilde{\rho}_{is}(0,q_{z}) v_{+s}(q_{z}) + \rho_{+s}(q_{z}) \widetilde{w}_{is}(0,q_{z})]$$

$$+ \frac{1}{4} \sum_{i} Z_{i}^{2} (2\pi)^{-3} \int d^{3}q \, \widetilde{\rho}_{is}(\vec{q}) \widetilde{w}_{is}(\vec{q}) + \frac{1}{4} \sum_{i,j} Z_{i} Z_{j} (2\pi)^{-3} \int d^{3}q \, \widetilde{\rho}_{is}(\vec{q}) \widetilde{w}_{is}(\vec{q}) + \frac{1}{4} \sum_{i,j} Z_{i} Z_{j} (2\pi)^{-3} \int d^{3}q \, \widetilde{\rho}_{is}(\vec{q}) \widetilde{w}_{js}(\vec{q}) e^{i \vec{Q} \cdot (\vec{R}_{i} - \vec{R}_{j})} + E_{M} , \qquad (29)$$

where the primed sum $\sum_{i,j}^{\prime}$ omits the i = j terms.

The only terms in Eq. (29) which depend on the coordinates of more than one ion are the last two terms. Thus we define the pair-interaction potential $U^{(2)}$ to be

$$U^{(2)}(\Omega_0;\beta_i,\vec{r}_i;\beta_j,\vec{r}_j) = Z_i Z_j / |\vec{r}_i - \vec{r}_j| + \frac{1}{4} Z_i Z_j (2\pi)^{-3} \int d^3 q [\tilde{\rho}_{is}(\vec{q}) \tilde{w}_{js}(\vec{q}) + \tilde{\rho}_{js}(\vec{q}) \tilde{w}_{is}(\vec{q})] e^{i \vec{Q} \cdot (\vec{R}_i - \vec{R}_j)}.$$
(30)

Since the two-dimensional (2D) vector \vec{R}_i does not appear in the definition of $\tilde{w}_{is}(\vec{q})$ or $\tilde{\rho}_{is}(\vec{q})$, it is evident that the pair-interaction potential depends on $|\vec{R}_i - \vec{R}_j|$, the magnitude of the distance between two ions parallel to the surface. However, this pair-interaction potential depends on the z coordinates of the two ions separately rather than just on $|z_i - z_j|$, i.e.,

$$U^{(2)}(\Omega_0;\beta_i,\vec{r}_i;\beta_j,\vec{r}_j) = U^{(2)}(\Omega_0; |\vec{R}_i - \vec{R}_j|;\beta_i,z_i;\beta_j,z_j).$$

For this reason $U^{(2)}$ is not a pair-potential in the usual sense but can be regarded as a three-body potential, where the third body is the electron-jellium system described by H^0 , Eq. (2).

The single-ion potential is contained in the fourth, fifth, and sixth terms on the rhs of Eq. (29) since these terms depend on the z coordinate of a single ion,

$$U^{(1)}(\Omega_{0};\beta_{i}z_{i}) = Z_{i} \int d^{3}r \,\rho^{0}(\vec{r})\widetilde{w}_{i}(\vec{r}) - \frac{1}{4}\Omega_{0}^{-2/3}Z_{i}(2\pi)^{-1} \int dq_{z} [\widetilde{\rho}_{is}(0,q_{z})v_{+s}(q_{z}) + \rho_{+s}(q_{z})\widetilde{w}_{is}(0,q_{z})] \\ + \frac{1}{4}Z_{i}^{2}(2\pi)^{-3} \int d^{3}q \,\widetilde{\rho}_{is}(\vec{q})\widetilde{w}_{is}(\vec{q}) .$$
(31)

The physical origins of the three terms on the rhs of Eq. (31) are, respectively, (i) the interaction of the bare ion with the unperturbed electron density, (ii) the interaction of the ion and the (subtracted) positive background density through their screening electron densities, and (iii) the interaction of the ion with its own screening electron density. The terms (i) and (ii) taken separately are divergent since the system is semi-infinite, but the sum of the two is finite.

In order to evaluate Eq. (31) the direct interaction of the ion with the positive background is added to the first term and subtracted from the second. The expression for this ion-positive background interaction energy is

$$-\int d^{3}r P^{J}(\vec{r}) Z_{i} \widetilde{w}_{i}(\vec{r}) = -\frac{1}{2} \Omega^{-2/3} Z_{i}(2\pi)^{-1} \int dq_{z} [\rho_{is}^{I}(q_{z}) v_{+s}(q_{z})] = -\frac{1}{2} \Omega^{-2/3} Z_{i}(2\pi)^{-1} \int dq_{z} [\rho_{s}^{J}(q_{z}) \widetilde{w}_{is}(0,q_{z})], \quad (32)$$

where $P^{J}(\vec{r}) = \Omega_{0}^{-1} \Theta(z - z_{0})$ is the positive background (jellium) density, with symmetrized Fourier transform

and

TABLE I. Parameters used in the calculations: $r_s = (3\Omega_0/4\pi)^{1/3}$ is the electron density parameter, r_e
nd u_c are the pseudopotential core radius and depth (Ref. 25) [see Eq. (4)], and A and B are the param-
ers in the local-field correction $G(q)$ Ref. 30 [see Eq. (6)].

Metal				A	B
Na	3.931a0	2.076a0	0.3079	0.9942	0.2631
К	4.862a0	3.033a0	0.5723	1.0119	0.2406
Rь	5.197a ₀	3.551a0	0.7273	1.0161	0.2337

$Z_i \rho_{is}^I(\vec{q}) = v_C(q)^{-1} 2 V_p(\beta_i;q) \cos(q_z z_i)$

e

is the positive density which gives rise to the ionic pseudopotential [see Eq. (C5)]. With the use of Eq. (32) as discussed above, the expression for the single-ion potential becomes

$$U^{(1)}(\Omega_0;\beta_i,z_i) = E_S + E_H + E_{BS}^0, \qquad (33)$$

where

$$E_{S} = \frac{1}{4} Z_{i}^{2} (2\pi)^{-3} \int d^{3}q \, \widetilde{\rho}_{is}(\vec{q}) \widetilde{w}_{is}(\vec{q}) , \qquad (34a)$$

$$E_{H} = Z_{i} \int d^{3}r [\rho^{0}(\vec{r}) - P^{J}(\vec{r})] \widetilde{w}_{is}(\vec{r}) , \qquad (34b)$$

and

$$E_{BS}^{0} = \frac{1}{4} \Omega_{0}^{-2/3} Z_{i}(2\pi)^{-1} \\ \times \int dq_{z} \{ [\rho_{is}^{I}(0,q_{z}) - \tilde{\rho}_{is}(0,q_{z})] v_{+s}(q_{z}) \\ + [\rho_{s}^{J}(q_{z}) - \rho_{+s}(q_{z})] \tilde{w}_{is}(0,q_{z}) \} .$$
(34c)

We remind the reader that $\tilde{\rho}_{is}$ and ρ_{+s} are induced electron densities corresponding to the potentials \tilde{w}_{is} and v_{+s} , respectively [Eqs. (25) and (26)], which are in turn the potentials due to the densities ρ_{is}^{l} and ρ_{s}^{J} which represent the ions and positive background, respectively. Having described in this section the physical model and derived the expressions needed for the evaluation of the total energy and its decomposition into density, single-ion, and pair-interaction potentials, we turn now to a discussion of results for the single-ion and pair-interaction potentials.

III. RESULTS AND DISCUSSION

In this section the theory developed in Sec. II is employed in a systematic study of the single-ion and ion pair-interaction potentials in the simple metals Na, K, and Rb. The values of the bulk electron density parameter r_s , the pseudopotential core radius and depth [Eq. (4)] r_c and u_c ,²⁵ and the parameters A and B in the analytical fit to the local-field (exchange-correlation) correction G(q) (Ref. 31) which were used in the calculations are given in Table I.

In general, the practice of determining model pseudopotential parameters is guided by the adequacy of the fit between calculated and measured material properties. When treating metal surfaces, and possible structural relaxations, it is essential to use a model which yields the correct bulk lattice constant and reproduces the elastic properties of the bulk. In addition, if the model is to be applied to alloys (heats of formation, surface segregation, etc.) it is of utmost importance that the model also yield the correct total energy, and thus the cohesive energy, of the bulk pure species. The pseudopotential parameters, r_c and u_c , which we employ were determined by Popovic *et al.*²⁵ to reproduce the experimental values of the bulk modulus and equilibrium lattice constant. These authors used the pseudopotentials, and the local-field correction of Singwi *et al.*³¹, in calculations of vacancy formation energies and volumes for the alkali metals and Al, obtaining results in good agreement with experimental values. We have calculated the cohesive energy of Na, K, and Rb using the pseudopotentials and find that the calculated and experimental values agree to within less than 0.3% in each case (experimental values are summarized in Ref. 20). To our knowledge these pseudopotentials have not been used in lattice-dynamics calculations; nevertheless, the bulk pairpotentials which we obtain are similar (in terms of loca-



FIG. 1. Electron densities $\Omega_0 \rho^0(z)$ for Na, K, and Rb. The Lang-Kohn (Ref. 30) densities are shown as solid curves and the dashed curves are the infinite barrier noninteracting electron density. The truncated bulk density is also shown as a solid line, and the (100) and (110) layer positions are indicated by arrows.





tion, depth, and curvature—see dashed curves in Figs. 3-7) to the M1 model pair potentials of Dagens *et al.*, ⁴⁰ which do yield rather satisfactory agreement with experimental dispersion curves.

The Lang-Kohn³⁰ surface electron density $\rho^0(z)$ for the three metals is shown in Fig. 1. These densities were obtained by Lagrange interpolation between the densities at the r_s values given in Ref. 30. The positions of the (100) and (110) crystalline layers, also shown in Fig. 1, are given by

$$z_l = z_0 + (l - \frac{1}{2})D , \qquad (35)$$

where $z_0 = 3\pi/8k_F$ is the position of the jellium edge, and

 $D = (2k_F)^{-1}(6\pi^2)^{1/3}$ for the (100) layers and $D = (\sqrt{2k_F})^{-1}(6\pi^2)^{1/3}$ for the (110) layers [the Fermi momentum k_F is related to r_s by $k_F = (9\pi/4)^{1/3}/r_s$]. The Lang-Kohn electron density enters the calculation through the first-order correction to the total energy and contributes to the E_H term in the single-ion potential, Eq. (34b). The surface electron density of the infinite barrier model³⁸ is also shown in Fig. 1. We have found that the use of this infinite barrier electron density in place of the Lang-Kohn density yields values of E_H which are in close quantitative agreement with the results obtained using the Lang-Kohn density, particularly for large z. We use the infinite barrier density to extend $\rho^0(z)$ to values of z larger than those provided in the tables of Ref. 18(a).

In performing the numerical integration over Q and q_z to obtain the results presented in this section we have used a grid of points in Q,q_z with spacing $\Delta Q = \Delta q_z = 0.04k_F$, and have truncated the integrals when convergence is obtained (in most cases a maximum of $q = 12k_F$ is sufficient). The derivatives of the potentials $U^{(1)}(z)$ and $U^{(2)}(R;z_1,z_2)$ which are presented in the tables were obtained numerically in each case by evaluating the quantities at points $z,z \pm 0.01D$ and $R,R \pm 0.01D$, where D is the (100) or (110) layer spacing. The units of energy and of length used in the tables are e^2k_F and k_F^{-1} , respectively, to facilitate comparison of the results for the different metals.

The single-ion-potential results are summarized in Tables II, III, and IV for Na, K, and Rb, respectively. The general behavior of $U^{(1)}$ as a function of ion position

TABLE II. Single-ion potential for Na, $U^{(1)}(z) = E_s + E_H + E_{bs}^0$ and derivatives, evaluated at the (100) and (110) layer positions $z = z_0 + (l - \frac{1}{2})D$; *D* is the layer spacing. The units of energy and length are, respectively, e^{2k_F} and k_F^{-1} , where $k_F = (9\pi/4)^{1/3}/r_s$ and r_s is given in Table I.

	1	• 2	3	4	5
			(100) layer		
E,	—0.273 9	-0.2697	-0.2660	0.2648	0.2643
E_H	0.0328	0.0356	0.0369	0.0359	0.0358
E ⁰ _{br}	0.0085	0.0002	0.0000	-0.0005	0.0009
U ⁽¹⁾	-0.2326	0.2338	-0.2290	0.2294	-0.2276
∂E, /∂z	-0.0107	0.0039	0.0008	0.0004	0.0002
$\partial E_H / \partial z$	0.0316	0.0039	-0.0004	0.0002	0.000
∂E ⁰ /∂z	-0.0304	0.0006	0.0026	-0.0015	0.0003
∂ U ⁽¹⁾ /∂z	-0.0095	-0.0006	0.0031	0.0009	-0.0000
$\partial^2 E_s / \partial z^2$	0.032	-0.003	-0.000	-0.000	0.000
$\frac{\partial^2 E_H}{\partial z^2}$	0.006	0.010	-0.002	0.000	0.000
$2E_{ba}^{0}/\partial z^{2}$	-0.010	0.007	-0.001	0.003	0.003
$\partial^2 U^{(1)} / \partial z^2$	-0.027	0.013	-0.003	0.003	-0.002
		(110)	layer		
E,	-0.2760	0.2668	-0.2648	-0.2642	
E _H	0.0428	0.0365	0.0360	0.0355	
E _{br}	-0.0013	-0.0015	-0.0009	-0.0002	
U ⁽¹⁾	0.2346	-0.2317	-0.2297	-0.2289	
∂E, ∕∂z	0.0008	0.0014	0.0003	0.0001	
∂E _H ∕∂z	0.0119	0.0016	0.0002	0.0000	
∂ <i>E</i> ‰ ∕∂z	-0.0128	0.0005	-0.0013	-0.0014	
∂ <i>U</i> (1)/∂z	0.0017	0.0035	-0.0008	-0.0013	
$\partial^2 E_s / \partial z^2$	0.017	-0.001	0.000	-0.000	
$\partial^2 E_H / \partial z^2$	0.059	0.003	-0.000	0.001	
$\partial E_{b1}^0 / \partial z^2$	0.051	0.005	0.003	0.000	
$\partial U^{(1)}/\partial z^2$	0.009	0.001	0.003	0.001	

	1	2	3	4	5
· · · · ·			(100) layer		
Ε,	0.2674	-0.2633	-0.2596	-0.2585	-0.2580
E _H	0.0222	0.0167	0.0185	0.0174	0.0176
E ba	0.0059	0.0001	-0.0001	-0.0005	0.0007
$U^{(i)}$	-0.2393	-0.2465	-0.2413	-0.2417	-0.2398
$\partial E_{r}/\partial z$	-0.0119	0.0039	0.0008	0.0004	0.0002
$\partial E_H / \partial z$	0.0134	-0.0034	-0.0003	0.0004	-0.0004
∂ <i>E</i> ⁰ /∂z	-0.0190	0.0001	0.0022	-0.0013	0.0002
∂ <i>U</i> ⁽¹⁾ /∂z	0.0175	0.0006	0.0027	-0.0005	0.0001
$\partial^2 E_z / \partial z^2$	0.034	-0.003	0.000	0 .000	0.000
$\partial^2 E_H / \partial z^2$	0.018	0.012	-0.003	0.001	0.000
$\partial^2 E_{ba}^0 / \partial z^2$	-0.019	0.007	0.000	0.002	-0.003
$\partial^2 U^{(1)}/\partial z^2$	0.032	0.002	-0.003	0.003	-0.001
		(110)	layer		
Ε.	- 0.2 698	-0.2604	-0.2585	-0.2579	
E _H	0.0277	0.0179	0.0175	0.0174	
E ba	-0.0020	-0.0013	-0.0006	0.0000	
$U^{(1)}$	-0.244 1	-0.2438	0.2417	-0.2404	
∂ <i>E</i> , ∕∂z	-0.0015	0.0013	0.0003	0.0001	
∂E _H /∂z	0.0066	0.0020	0.0005	0.0000	
$\partial E_{h}^{0}/\partial z$	-0.0128	0.0002	-0.0011	-0.0012	
∂ <i>U</i> ⁽¹⁾ /∂z	0.0077	0.0036	-0.0003	-0.0011	
$\partial^2 E_s / \partial z^2$	0. 019	-0.001	-0 .000	- 0 .000	
$\partial^2 E_H / \partial z^2$	-0.049	-0.002	0.000	0.000	
$\partial^2 E_{ba}^0 / \partial z^2$	0.047	0.004	0.003	0.000	
∂ <i>U</i> ⁽¹⁾ /∂z²	0.018	0.001	0.003	0.000	

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	1	2	3	4	5
			(100) layer		
E,	-0.2677	-0.2633	-0.2597	-0.2586	-0.2581
E _H	0.0203	0.0113	0.0128	0.0118	0.0120
- E ⁰ _{bs}	0.0046	-0.0002	-0.0000	0.0005	0.0004
U ⁽¹⁾	-0.2427	-0.2523	-0.2469	-0.2473	- 0.2456
∂E, ∕∂z	-0.0111	0.0039	0.0008	0.0004	0.0002
ӘЕ н/Әz	0.0060	-0.0032	0.0005	0.0004	-0.0000
∂ <i>E</i> ₀ /∂z	-0.0144	0.0006	0.0015	-0.0009	-0.0000
∂ <i>U</i> ⁽¹⁾ /∂z	-0.0196	0.0013	0.0019	-0.0000	0.0000
$\partial^2 E_s / \partial z^2$	0.034	-0.003	-0.001	0.000	0.000
$\partial^2 E_H / \partial z^2$	0.005	0.012	-0.002	0.000	0.000
$\partial^2 E_{ba}^0 / \partial z^2$	-0.007	0.006	-0.000	0.002	0.000
$\partial^2 U^{(1)} / \partial z^2$	0.032	0.003	-0.003	0.002	0.000
			(110) layer		
E,	-0.2701	-0.2605	-0.2586	-0.2580	
E_{H}	0.0229	0.0124	0.0119	0.0119	
E _{be}	-0.0015	-0.0009	-0.0005	-0.0000	
U ⁽¹⁾	-0.2487	-0.2490	-0.2472	-0.2461	
∂ <i>E</i> ,/∂z	-0.0007	0.0013	0.0003	0.0001	
$\partial E_H / \partial z$	0.0023	0.0017	0.0004	0.0001	
$\partial E_{ba}^{0}/\partial z$	-0.0112	0.0003	-0.0007	-0.0008	
∂ <i>U</i> ^(ī) /∂z	-0.0095	0.0033	0.0001	-0.0006	
$\partial^2 E_s / \partial z^2$	0.019	-0.001	-0.000	0.000	
$\partial^2 E_H / \partial z^2$	-0.032	-0.003	-0.000	0.000	
$\partial^2 E_{bs}^{\overline{0}} / \partial z^2$	0.031	0.003	0.002	0.000	
$\partial^2 U^{(1)} / \partial_z^2$	0.017	-0.001	0.002	0.000	



FIG. 3. Pair-interaction potentials, $U^{(2)}(R;z_1,z_2)$, for ions in the same (100) layer, plotted vs the interionic distance $r = (R^2 + (z_1 - z_2)^2)^{1/2}$ as R is varied and z_1, z_2 are constants. The z coordinates of the ions correspond to layer positions, $z_1 = z_0 + (l_1 - \frac{1}{2})D$, $z_2 = z_0 + (l_2 - \frac{1}{2})D$; the values of l_1, l_2 are indicated in the upper right-hand corner of each graph. The units of energy and length are 10^{-3} Ry and a_0 (Bohr radius), respectively.

z is shown graphically in Fig. 2, which was drawn from the values of $U^{(1)}(z)$ and its derivatives at the (100) and (110) layer positions for K.

The largest contribution to the single-ion potential $U^{(1)}$. Eq. (33), is the interaction of the ion with its own screening electron density E_{1} . The second largest contribution is E_H , which comes from the first-order energy and corresponds to the direct interaction of the ionic pseudopotential with the difference, $\rho^{0}(z) - \Omega_{0}^{-1}\Theta(z-z_{0})$, between the Lang-Kohn electron density and a truncated bulk density. Both E_s and E_H oscillate about a constant bulk value as z increases, and the magnitude of the oscillations decreases as the distance from the surface increases. The third contribution, $E_{\rm BS}$, is much smaller in magnitude and oscillates about a bulk value of zero, but the magnitude of the oscillation decreases more slowly as z increases. It is the oscillations in $U^{(1)}$ rather than the magnitude which are important in determining surface structure, since these oscillations give rise to forces on the ions normal to the surface plane. Differences in the magnitude of $U^{(1)}$ for different ionic species (evaluated for the same Ω_0) are important in determining impurity formation energies and surface concentration profiles in alloys, but this is the subject of a planned future publication and will not be discussed here.

The derivative of the single-ion potential, $\partial U^{(1)}/\partial z$, is negative for ions in the surface layer of both the (100) and (110) surfaces of each of the metals considered, corresponding to a force on the ions toward the bulk. There is a large amount of cancellation between the derivatives of the three terms E_s , E_H , and E_{BS}^0 near the surface. E_H and E_{BS}^0 are related in that E_H is a direct interaction while E_{BS}^0 is an interaction mediated by the screening electron densities, and the forces arising from these two interactions tend to cancel in the surface layer. The cancellation is almost complete for the higher electron density metal, Na. The single-ion forces on ions deeper than about the third (100) layer or second (110) layer are primarily due to oscillations in E_{BS}^0 , which are in turn due to quantum interference effects in the solution for the screening electron densities.

The results of calculations of the pair-interaction potential $U^{(2)}(R,z_1,z_2)$ are summarized in Figs. 3–7 and Tables V-VIII. These interaction potentials are not two-body central-force potentials in the surface region since they depend on the z coordinates of the two ions separately. However, $U^{(2)}$ does depend on the magnitude of the ionic separation parallel to the surface, R, and we can get some feeling for how $U^{(2)}$ differs from the bulk interaction by plotting $U^{(2)}(R,z_1,z_2)$ vs $r = [R^2 + (z_1 - z_2)^2]^{1/2}$ as R is varied while keeping z_1 and z_2 fixed. This is done in Figs. 3-7, where z_1 and z_2 are layer positions for (100) or (110) layers. The bulk pair potential is shown as the dashed curve in each figure. For ions near the surface the minimum in the pair-interaction potential may be significantly deeper or shallower than the bulk pair-potential minimum and may be shifted to larger or smaller interionic distance r depending on the z coordinates of the two



FIG. 5. Pair-interaction potentials for ions in next-nearest-neighbor (100) layers. See the caption for Fig. 3.





FIG. 7. Pair-interaction potentiais for ions in adjacent (110) layers. See the caption for Fig. 3.

TABLE V. First derivative of the pair-interaction potential with respect to z_1 , $\partial U^{(2)}(R; z_1, z_2)/\partial z_1$, for K ions in the same layer, $z_1 = z_2 = z_0 + (l_1 - \frac{1}{2})D$, evaluated for second- and third- nearest-neighbors (nn) ions in the first five (100) layers, and for first-, second-, and third- nearest-neighbor ions in the first four (110) layers. The units of energy and length are, respectively, e^{2k_F} and k_F^{-1} .

	1	2	3	4	5	Bulk
			(100) layer 1	$l_1 = l_2$		
Second nn	0.001 36	-0.00013	0.000 04	0.000 01	0.000 01	0.0
Third nn	-0.000 13	-0.000 02	0.000 00	0.000 02	0.000 01	0.0
•			(110) layer 1	$l_1 = l_2$		
First nn	-0.000 21	-0.000 01	0.000 01	0.000 01		0.0
Second nn	0.000 21	0.000 01	0.000 01	10 000.0		0.0
Third nn	0.000 09	0.000 03	0.000 02	0.000 01		0.0

ions. In addition, the magnitude of the Friedel oscillations in the interaction potential as r increases may be either increased or decreased. It has been shown by Lau and Kohn⁴² that the oscillatory part of the interaction between point ions adsorbed on a substrate with a spherical Fermi surface is proportional to $\cos(2k_F R)/R^5$, in contrast to the R^{-3} dependence in the bulk. We have not attempted such an asymptotic analysis, and the inclusion of quantum interference effects may alter this behavior. However, as the distance of the two ions from the surface increases, the bulk behavior must result. The interaction between ions in the same layer $(z_1 = z_2)$ is essentially bulklike for ions deeper than the third (100) layer, but the effect of the surface on the interaction between ions in different layers extends further, i.e., the interaction between ions in the third and fourth or third and fifth (100) layers still shows marked differences from the bulk interaction. The differences between $U^{(2)}$ and the bulk pair potential are fairly uniform for the three metals, although there is a trend toward larger differences in the higher electron density (smaller r_s) metal Na.

In order to examine the dependence of the pairinteraction potential on the z coordinates of the two ions we have calculated the first and second derivatives $\partial U^{(2)}/\partial z_1$, $\partial U^{(2)}/\partial z_2$, $\partial^2 U^{(2)}/\partial R \partial z_{1,2}$, $\partial^2 U^{(2)}/\partial^2 z_{1,2}$, and $\partial^2 U^{(2)}/\partial z_1 \partial z_2$ for ions at lattice sites in the (100) and (110) layers, and compare these to the derivatives of the bulk pair potential in Tables V-VIII (for K only). The units of energy and length used in these tables are again e^2k_F and k_F^{-1} , respectively.

The fact that the pair-interaction potential is not a central-force interaction is first clearly illustrated in Table V, which gives $\partial U^{(2)}/\partial z_1 = \partial U^{(2)}/\partial z_2$ for ions in the same layer $(z_1 = z_2)$. While in the bulk this derivative is zero, for ions in a layer near the surface it is not zero and for nearest and next-nearest neighbors it is about an order of magnitude smaller than the force due to the single-ion potential. This amounts to an additional force normal to the surface on each ion in the layer since the potential energy due to interaction between ions in the layer can be decreased by moving the entire layer. Table VI gives the derivatives $\partial U^{(2)}/\partial z_1$ and $\partial U^{(2)}/\partial z_2$ for ions in different contrast lavers. In to the bulk where $\partial U^{(2)}/\partial z_1 = -\partial U^{(2)}/\partial z_2$, in the surface region the derivatives with respect to z_1 and z_2 are not equal in magnitude and may not be opposite in sign [e.g., second nearest neighbors in (100) layers 1 and 3].

Table VII and VIII give the second derivatives of $U^{(2)}$ with respect to various combinations of z_1 , z_2 , and R. Again we see that the derivatives of the pair-interaction potential for ions in the surface region are significantly different from the derivatives of the central-force bulk

TABLE VI. First derivatives of the pair-interaction potential for K ions, $U^{(2)}(R;z_1,z_2)$, with respect to z_1 and z_2 , evaluated for ions in different layers, $z_1 = z_0 + (l_1 - \frac{1}{2})D$ and $z_2 = z_0 + (l_2 - \frac{1}{2})D$, for first nearest neighbors (nn) in (100) layers and first and second nearest neighbors in (110) layers. The units of energy and length are, respectively, e^{2k_F} and k_F^{-1} .

		(1,2)	(2,3)	(3,4)	(4,5)	Buik
- <u></u>			(100) layers (l ₁ , l	2)	
First nn	∂ <i>U</i> ⁽²⁾ /∂₁	0.005 86	0.005 13	0.005 09	0.005 20	0.00513
	$\partial U^{(2)}/\partial z_2$	-0.003 59	-0.005 33	-0.005 09	-0.005 10	0.005 13
-	•		(110) layers (l ₁ ,l	2)	
First nn	$\partial U^{(2)}/\partial z_{\perp}$	0.007 07	0.007 33	0.007 32		0.007 26
	$\partial U^{(2)}/\partial z_2$	0.007 44	-0.007 06	-0.007 12		-0.00726
Second nn	$\partial U^{(2)}/\partial z_1$	-0.00073	0.000 51	0.00049		0.000 51
	$\partial U^{(2)}/\partial z_2$	0.00012	0.00058	0.00060		-0.00051
			(100) layers (l_1, l_2)	2)	
Second nn	$\partial U^{(2)}/\partial z_1$	0.000 81	-0.000 66	-0.000 77		-0.00073
	$\partial U^{(2)}/\partial z_2$	-0.000 70	0.001 32	0.000 50		0.00073

TABLE VII. Second derivatives of the pair-interaction potential $U^{(2)}(R;z_1,z_2)$ for K ions in the same layer, $z_1 = z_2 = z_0 + (l - \frac{1}{2})D$, evaluated for second nearest neighbors (nn) in (100) layers and for first and second nearest neighbors in (110) layers. The units of energy and length are, respectively, e^2k_F and k_F^{-1} .

		1	2	3	4	5	Bulk		
		(100) layer $l_1 = l_2$							
Second nn	$\partial^2 U^{(2)} / \partial R \partial z_1$	0.002 11	- 0.000 02	-0.00001	0.000 00	0.00001	0.0		
	$\partial^2 U^{(2)} / \partial z_1^2$	0.002 15	0.000 13	0.00021	0.000 19	0.000 21	0.000 19		
	$\partial^2 U^{(2)} / \partial z_1 \partial z_2$	0.003 62	-0.000 18	-0.000 21	-0.00017	-0.000 20	-0.000 19		
				(110) lay	er $l_1 = l_2$				
First nn	$\partial^2 U^{(2)} / \partial R \partial z_1$	0.001 16	0.000 01	-0.000 01	0.000 01		0.0		
	$\partial^2 U^{(2)} / \partial z_1^2$	-0.001 30	-0.002 63	-0.002 62	-0.002 61		-0.002 63		
	$\partial^2 U^{(2)} / \partial z_1 \partial z_2$	0.005 30	0.002 75	0.002 65	0.002 61		0.002 63		
Second nn	$\partial^2 U^{(2)} / \partial R \partial z_1$	0.00047	0.000 05	0.000 00	0.000 00		0.0		
.•	$\partial^2 U^{(2)}/\partial z_1^2$	0.001 02	0.00021	0.00019	0.000 19		0.00019		
	$\partial^2 U^{(2)} / \partial z_1 \partial z_2$	0.001 12	-0.00012	-0.000 17	-0.000 19	-	-0.000 19		

pair potential, and may have the opposite sign.

The results presented in Tables V-VIII support the conclusions stated earlier in the discussion of the figures that (a) the pair-interaction potential in the surface region is significantly different from the bulk central-force pair potential, (b) the effect of the surface on the interaction between ions in different layers (different z coordinates) extends further than the effect on the interaction between pairs of ions both of which are deeper than about the fourth (100) or third (110) layer positions is essentially bulk like. The major differences of $U^{(2)}$ from the bulk pair potential are due to quantum interference effects in the solutions for the screening electron density, the terms $u_1(\vec{q})$ and $u_{\sigma}(\vec{q})$ in Eq. (19). If these quantum interference of the screening set equal to zero only the interaction is the interaction interaction interaction between interference effects in the screening set equal to zero only the interaction is a screening set equal to zero only the interaction is a screening set equal to zero only the interaction is in the interaction is a screening set equal to zero only the interaction is in the interaction is extended as the interaction interference is a screening set equal to zero only the interaction is in the interaction is in the interaction is in the interaction is in the interaction interference is interference is in the interaction interference is interference is in the interaction interference is interference is interference is interference is in the interaction is interference is interference is interference is in the interaction is is interference

between pairs of ions very close to the surface [the (100) surface layer] deviate from the bulk interaction.⁴³ In the semiclassical limit (mentioned in Sec. II B) the quantum interference terms do not occur, but the position of the jellium edge is $z_0=0$, so the effect of the surface on the pair-interaction potential in the semiclassical response model might extend somewhat further. However, the semiclassical response model restricts the choice of ionic pseudopotential since there is no response of the electron gas for $z \leq 0$, and therefore the positive charge density which gives rise to the ionic pseudopotential must not extend past the jellium edge (see Appendix C).

The single-ion and pair-interaction potentials derived in Sec. IIC and discussed in this section are, in principle, sufficient to treat problems involving surface relaxation, defect energies, and surface segregation in alloys. Howev-

TABLE VIII. Second derivatives of the pair-interaction potential $U^2(R;z_1,z_2)$, for K ions in adjacent layers, $z_1 = z_0 + (l_1 - \frac{1}{2})D$ and $z_2 = z_0 + (l_2 - \frac{1}{2})D$ with $l_2 = l_1 + 1$, evaluated for first nearest neighbors (nn) in (100) layers and for first and second nearest neighbors in (110) layers. The units of energy and length are, respectively, e^{2k_F} and k_F^{-1} .

		(1,2)	(2,3)	(3,4)	(4,5)	Bulk
			(1	00) layers (l ₁ ,l	·2)	
First nn	$\partial^2 U^{(2)} / \partial R \partial z_1$	-0.01706	-0.01618	-0.015 30	-0.016 38	-0.01629
	$\partial^2 U^{(2)} / \partial R \partial z_2$	0.015 51	0.016 54	0.016 22	0.016 34	0.016 29
	$\partial^2 U^{(2)} / \partial z_1^2$	0.008 86	0.009 02	0.008 80	0.008 92	0.008 88
	$\partial^2 U^{(2)} / \partial z_1 \partial z_2$	-0.010 22	-0.008 69	-0.008 93	0.008 92	0.008 88
	$\partial^2 U^{(2)}/\partial z_2^2$	0.008 85	0.009 18	0.008 68	0.009 00	0.008 88
			(1	10) layers (1,,1	2)	
First nn	$\partial^2 U^{(2)} / \partial R \partial z_1$	-0.016 39	-0.01641	-0.01635		-0.0162
	$\partial^2 U^{(2)} / \partial R \partial z_2$	0.01594	0.01612	0.016 23		0.0162
	$\partial^2 U^{(2)} / \partial z_1^2$	0.02013	0.020 37 ·	0.020 44		0.0204
	$\partial^2 U^{(2)} / \partial z_1 \partial z_2$	-0.02069	-0.020 54	-0.02048		-0.0204
	$\partial^2 U^{(2)} / \partial z_2^2$	0.01829	0.02001	0.020 43		0.0204
Second nn	$\partial^2 U^{(2)} / \partial R \partial z_1$	-0.003 97	-0.004 06	-0.004 05		-0.003 9
	$\partial^2 U^{(2)} / \partial R \partial z_2$	0.003 87	0.003 86	0.003 94		0.003 9
	$\partial^2 U^{(2)} / \partial z_1^2$	0.004 19	0.004 14	0.004 17		0.004 [
	$\partial^2 U^{(2)} / \partial z_1 z_2$	-0.00420	-0.004 23	-0.004 22		-0.004 1
	$\partial^2 U^{(2)} / \partial z_2^2$	0.003 14	0.003 86	0.004 13		0.004 1

er, due to the long-range nature of the pair interactions and the fact that in the surface region they are not twobody central-force potentials, a real-space approach to such problems is cumbersome. Calculations using a reciprocal-space approach to minimize the total energy and determine the relaxed surface structure are reported elsewhere, ^{17,18(a)} and surface segregation and defect energetics will be treated in planned future publications.

The model as developed here is not directly applicable to surface vibrations because the use of the jellium system as a starting point and the infinite barrier response model specifies the location and orientation of the surface plane with respect to the coordinate system; thus the dynamical matrix obtained from this model would not satisfy the condition of rotational invariance. It is clear, however, that two-body central-force potentials are not sufficient to describe the interionic interactions in the surface region and that the interaction of the ions with the inhomogeneous electron gas, which is the origin of the single-ion potentials, must be included. It may be possible to impose rotational invariance and obtain and approximate dynamical matrix.⁴⁴ The single-ion and pair-interaction potentials can be used in Monte Carlo or molecular-dynamics solutions. Monte Carlo studies on liquid-metal surfaces⁴⁵ have shown that the inclusion of a single-ion potential leads to stable density oscillations at the surface.

In summary, we have developed a formulation based on the use of ionic pseudopotentials and linear-response theory which is applicable to problems involving minimization of the surface energy of a simple metal with respect to ionic species and/or position. The formulation maintains the full three-dimensional nature of the system and does not require crystalline order; thus it is possible to treat defects near the surface and random alloys as well as ideal surfaces. We have decomposed the total-energy expression into a density-dependent term and real-space single-ion and pair-interaction potentials. An examination of these potentials shows that both the single-ion potentials and the non-central-force nature of the pairinteraction potentials are important in surface structure and energetics and in surface lattice virbations of simple metals.

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APPENDIX A

SIL

In this appendix Eq. (12) for the Fourier transform of the symmetrized screening electron density is derived. Substituting Eq. (6a) into Eq. (11b) and using the fact that $\alpha_0(|\vec{R}-\vec{R}'|;z,z')$ vanishes for negative z' gives

$$\boldsymbol{\rho_{is}}(\vec{\mathbf{q}}) = 2 \int d^2 R \ e^{i \vec{\mathbf{Q}} \cdot \vec{\mathbf{R}}} \int_0^\infty dz \cos(q_z z) \int d^2 R' \int_0^\infty dz' \alpha_0 (|\vec{\mathbf{R}} - \vec{\mathbf{R}}'|; z, z') [w_i(\vec{\mathbf{r}}') + \phi_i(\vec{\mathbf{r}}')] . \tag{A1}$$

When the integrals over \vec{R} and \vec{R} ' are performed we obtain

$$\rho_{is}(\vec{q}) = 2 \int_0^{\infty} dz' [w_i(Q,z') + \phi_i(Q,z')] \int_0^{\infty} dz \cos(q_z z) \alpha_0(Q;z,z') .$$
(A2)

The integral over z in Eq. (A2) is evaluated using Eq. (10) for $\alpha_0(Q;z,z')$ and the integral representation of the Dirac δ function

$$\pi\delta(k)=1+\int_0^\infty dz\,\cos(kz)\;.$$

The result is

$$\int_{0}^{\infty} dz \cos(q_{z}z) a_{0}(Q;z,z') = \frac{1}{\pi} \int d\kappa \sin(\kappa z') \int d\kappa' \sin(\kappa' z') \mathscr{L}(Q;\kappa,\kappa') \\ \times [\delta(q_{z}+\kappa-\kappa')+\delta(q_{z}-\kappa+\kappa')-\delta(q_{z}+\kappa+\kappa')-\delta(q_{z}-\kappa-\kappa')].$$
(A3)

From the definition of the two-dimensional RPA response function, Eq. (8b), it is clear that $\mathcal{L}(Q;\kappa,\kappa')$ is invariant to transformations which interchange k and k' or change the sign of κ,κ' , or both:

These symmetry properties are used together with the fact that κ and κ' are to be integrated over both positive and negative values to obtain

$$\int_0^\infty dz \cos(q_z z) \alpha_0(Q; z, z') = \pi^{-1} \int d\kappa \, \mathscr{L}(Q; \kappa + q_z/2, \kappa - q_z/2) [\cos(q_z z') - \cos(2\kappa z')] \,. \tag{A4}$$

We now substitute Eq. (A4) back into Eq. (A2) and evaluate the integral over z'. The result is Eq. (12) of the text:

$$\rho_{is}(\vec{q}) = \alpha_0(q) [w_{is}(\vec{q}) + \phi_{is}(\vec{q})] - \pi^{-1} \int d\kappa \, \mathscr{L}(Q; \kappa + q_z/2, \kappa - q_z/2) [w_{is}(Q, 2\kappa) + \phi_{is}(Q, 2\kappa)] , \qquad (A5)$$

where

$$\alpha_0(q) = \pi^{-1} \int d\kappa \, \mathcal{L}(Q; \kappa + q_z/2, \kappa - q_z/2)$$

is the RPA response function for an infinite system.

APPENDIX B

In this appendix we derive Eq. (16) for the Fourier transform of the self-consistent effective potential due to the screening electron density in the symmetrized system. From Eq. (6b) and the definition of the symmetrized system we have

$$\phi_{ij}(\vec{r}) = \int d^3 r' g(\vec{r}, \vec{r}') v_{\mathcal{C}}(|\vec{r} - \vec{r}'|) \rho_{ij}(\vec{r}') [1 - \Theta(z)\Theta(-z') - \Theta(-z)\Theta(z')], \qquad (B1)$$

where $g(\vec{r}, \vec{r}') = 1 - G(\vec{r}, \vec{r}')$ and $G(\vec{r}, \vec{r}')$ is the local-field correction discussed in the text. The Fourier transform of Eq. (B1) is

$$\begin{aligned} \phi_{is}(\vec{q}) &= v_C(q)\rho_{is}(\vec{q}) - \int d^3r \, e^{i\vec{q}\cdot\vec{r}} \int d^3r' G(\vec{r},\vec{r}\,') v_C(|\vec{r}-\vec{r}\,'|)\rho_{is}(\vec{r}\,') \\ &- \int d^3r \, e^{i\vec{q}\cdot\vec{r}} \int d^3r' v_C(|\vec{r}-\vec{r}\,'|)\rho_{is}(\vec{r}\,')[\Theta(z)\Theta(-z')+\Theta(-z)\Theta(z')] \\ &+ \int d^3r \, e^{i\vec{q}\cdot\vec{r}} \int d^3r' G(\vec{r},\vec{r}\,') v_C(|\vec{r}-\vec{r}\,'|)\rho_{is}(\vec{r}\,')[\Theta(z)\Theta(-z')+\Theta(-z)\Theta(z')] \,. \end{aligned}$$
(B2)

Owing to translational invariance in the x-y plane, $G(\vec{r}, \vec{r}') = G(|\vec{R} - \vec{R}'|; z, z')$; thus the remaining integrals over \vec{R} and \vec{R}' in Eq. (B2) result in two-dimensional Fourier transforms of the functions G, v_C , and ρ_{is} . If, as discussed in the text, we make the assumption that $G(\vec{r}, \vec{r}') = G(|\vec{r} - \vec{r}'|)$ the second term in the rhs of Eq. (B2) becomes

$$-\int d^{3}r \, e^{i\vec{q}\cdot\vec{r}} \int d^{3}r'G(|\vec{r}-\vec{r}'|)v_{C}(|\vec{r}-\vec{r}'|)\rho_{ii}(\vec{r}') = -G(q)v_{C}(q)\rho_{ii}(\vec{q}).$$
(B3)

To evaluate the third term on the rhs of Eq. (B2) we use the identity

$$v_{C}(r) = \frac{e^{2}}{r} = \frac{e^{2}}{2\pi} \int \frac{d^{2}K}{K} \exp(-i\vec{K}\cdot\vec{R}-K\mid z\mid)$$

and substitute the inverse Fourier transform of $\rho_{is}(\vec{k})$ for $\rho_{is}(\vec{r}')$ to get

$$-\int d^{3}r \, e^{i\,\vec{q}\cdot\vec{r}} \int d^{3}r' v_{\mathcal{C}}(|\vec{r}-\vec{r}'|) \rho_{is}(\vec{r}')[\Theta(z)\Theta(-z')+\Theta(-z)\Theta(z')] \\ = -\frac{2\pi e^{2}}{Q} \int dk_{z} \rho_{is}(Q,k_{z}) \int dz \, e^{iq_{z}z} \int dz' e^{-ik_{z}z'} [\Theta(z)\Theta(-z')+\Theta(-z)\Theta(z')] e^{-Q|z-z'|} \\ = -\frac{2\pi e^{2}}{Q} \int dk_{z} \rho_{is}(Q,k_{z}) \left[\int_{0}^{\infty} dz \, e^{(iq_{z}-Q)z} \int_{-\infty}^{0} dz' \exp[(-ik_{z}+Q)z'] + \int_{-\infty}^{0} dz \, e^{(iq_{z}+Q)z} \int_{0}^{\infty} dz' \exp[(-ik_{z}-Q)z'] \right] \\ = -\frac{2\pi e^{2}}{Q} \int dk_{z} \rho_{is}(Q,k_{z}) \frac{-k_{z}q_{z}+Q^{2}}{(k_{z}^{2}+Q^{2})(q_{z}^{2}+Q^{2})} .$$
(B4)

Since $\rho_{is}(Q, k_z)$ is an even function of k_z ,

$$\int dk_z \rho_{is}(Q,k_z) \frac{k_z}{k_z^2 + Q^2} = 0$$

and

$$-\frac{2\pi e^{2}}{Q}\int dk_{z}\rho_{is}(Q,k_{z})\frac{-k_{z}q_{z}+Q^{2}}{(k_{z}^{2}+Q^{2})(q_{z}^{2}+Q^{2})}$$

$$=-\frac{4\pi e^{2}}{q^{2}}\frac{1}{2\pi}\int dk_{z}\rho_{is}(Q,k_{z})\frac{Q}{Q^{2}+k_{z}^{2}}$$

$$=v_{C}(q)\sigma_{i}(Q), \qquad (B5)$$

where $v_C(q) = 4\pi e^2/q^2$ and

$$\sigma_l(Q) = -\frac{Q}{2\pi} \int dq_z \frac{\rho_{ls}(\vec{q})}{q^2} . \tag{B6}$$

It is also evident that

$$\lim_{Q \to 0} \sigma_t(Q) = \lim_{Q \to 0} \frac{Q}{2\pi} \int dq_z \frac{\rho_{is}(\vec{q})}{q^2}$$
$$= -\frac{1}{2} \rho_{is}(\vec{q} = \vec{0}) . \tag{B7}$$

 $\rho_{ii}(\vec{q}=\vec{0})$ is the integrated screening electron density induced by the potential $w_{ii}(\vec{r})$ and is equal to the amount

of positive charge (in units of the electron charge e) which gives rise to the potential, i.e., $\rho_{is}(\vec{q}=\vec{0})=0$, since $w_i(\vec{r})$ is a neutral perturbation due to the replacement of part of the jellium positive background by the ionic pseudopotential.

The last term in Eq. (B2) is

$$X_{i}(\vec{q}) = \int d^{3}r \ e^{i \vec{q} \cdot \vec{r}} \int d^{3}r' G(\vec{r}, \vec{r}') v_{C}(|\vec{r} - \vec{r}'|) \rho_{is}(\vec{r}') \times [\Theta(z)\Theta(-z') + \Theta(-z)\Theta(z')] .$$
(B8)

We do not attempt to evaluate this term here. It is not possible to reduce $X_i(\vec{q})$ to a form similar to $v_C(q)\sigma_i(Q)$, i.e., the Coulomb potential multiplying some function which is independent of q_z . Thus this term prevents the reduction of the problem of solving for $\rho_i(\vec{r})$ to the solution of a single-integral equation. However, $X_i(\vec{q})$ is negligible because, as discussed in the text, $G(\vec{r}, \vec{r'})$ is very short ranged and because $\rho_{is}(\vec{r})$ vanishes at z = 0.

APPENDIX C

In this appendix we derive Eqs. (25) and (26) which give the Fourier transforms of the symmetrized potentials $\widetilde{w}_{is}(\vec{r})$ and $V_{+s}(\vec{r})$. The definition of $\widetilde{w}_{is}(\vec{r})$ can be written as

$$\widetilde{w}_{is}(\vec{r}) = Z(\beta_i)^{-1} [V_p(\beta_i; |\vec{r} - (\vec{R}_i, z_i)|)\Theta(z) + V_p(\beta_i; |\vec{r} - (\vec{R}_i, -z_i)|)\Theta(-z)],$$
(C1)

where $\vec{r}_i = (\vec{R}_i, z_i)$ is the ion position, $Z(\beta_i)$ is the charge in units of e, β_i designates species, and $V_p(\beta_i; r)$ is the local-model pseudopotential for ionic species β_i . For notational convenience in the following we will omit the specification of ionic species. From Eq. (24) we have

$$\widetilde{w}_{is}(\vec{q}) = 2Z^{-1} \int_0^{L+z_0} dz \cos(q_z z) \int d^2 R \ e^{i \vec{Q} \cdot \vec{R}} \ V_p([R^2 + (z - z_i)^2]^{1/2}) , \qquad (C2)$$

where $L = \Omega^{1/3}$ is the thickness of the semi-infinite metal (the limit $L \to \infty$ will be taken) and z_0 is the distance of the jellium edge from the z = 0 plane. Substitution of the inverse Fourier transform of $V_p(k)$ for $V_p(r)$ yields

$$\widetilde{w}_{is}(\vec{q}) = \frac{Z^{-1}}{2\pi} \int dk_z e^{ik_z z_i} V_p(Q, k_z) \int_0^{L+z_0} dz \, e^{-ik_z z} 2\cos(q_z z) \,. \tag{C3}$$

The integral over z in Eq. (C3) is

$$2\int_{0}^{L+z_{0}} dz \exp[-ik_{z}(z-z_{i})]\cos(q_{z}z) = \frac{i}{k_{z}+q_{z}} \left[\exp[-ik_{z}(L+z_{0}-z_{i})]\exp[-iq_{z}(L+z_{0})] - e^{ik_{z}z_{i}}\right] + \frac{i}{k_{z}-q_{z}} \left[\exp[-ik_{z}(L+z_{0}-z_{i})]\exp[iq_{z}(L+z_{0})] - e^{ik_{z}z_{i}}\right].$$
(C4)

We will now express the ionic pseudopotential as

$$V_{p}(q) = -\frac{4\pi e^{2}}{q^{2}} Z \rho^{I}(q) , \qquad (C5)$$

where $Ze\rho^{I}(q)$ is the Fourier transform of a spherically symmetric positive charge density which gives rise to the local pseudopotential. An obvious restriction is that $\rho^{I}(|\vec{r}-\vec{r_{i}}|)=0$ for $z-z_{i}<0$; or, in the case of the simplified Heine-Abarenkov potential which we use, $r_{c} \leq z_{i}$, where r_{c} is the core radius [see Eq. (4)].

Equations (C4) and (C5) are substituted into Eq. (C3) to obtain

$$\widetilde{w}_{is}(\vec{q}) = \frac{1}{2\pi} \int dk_{z} \left[-4\pi e^{2} \rho^{I}(Q, k_{z}) \right] \frac{1}{2Q} \left[\frac{1}{k_{z} - iQ} - \frac{1}{k_{z} + iQ} \right] \\ \times \left[\frac{1}{k_{z} + q_{z}} \left\{ \exp\left[-ik_{z}(L + z_{0} - z_{i}) \right] \exp\left[-iq_{z}(L + z_{0}) \right] - e^{ik_{z}z_{i}} \right\} \\ + \frac{1}{k_{z} - q_{z}} \left\{ \exp\left[-ik_{z}(L + z_{0} - z_{i}) \right] \exp\left[iq_{z}(L + z_{0}) \right] - e^{ik_{z}z_{i}} \right\} \right].$$
(C6)

The integral over k_z in Eq. (C6) is done by contour integration, using contours which avoid the poles on the real axis at $k_z = \pm q_z$ and which close around either the upper or lower half-planes as required by the exponents. The result of this integration is

$$\widetilde{w}_{is}(\vec{q}) = \frac{4\pi e^2}{q^2} \rho^{I}(q) 2\cos(q_z z_i) + \frac{4\pi e^2}{q^2} \rho^{I}(Q, iQ) e^{-Q z_i} + \lim_{L \to \infty} \frac{4\pi e^2}{q^2} \rho^{I}(Q, -iQ) \left[\frac{q_z}{Q} \sin[q_z(L+z_0)] - \cos[q_z(L+z_0)] \right] \exp[-Q(L+z_0-z_i)] .$$
(C7)

Now $\rho^{I}(q) = \rho^{I}[Q^{2} + q_{z}^{2})^{1/2}]$, and thus $\rho^{I}(Q, \pm iQ) = \rho^{I}(q = 0)$ (a more rigorous proof of this identity is possible but will not be given here), and $\rho^{I}(q = 0) = 1$ since the ionic charge Ze is factored out of the definition, Eq. (C5).

In the limit $L \to \infty$ the last term in Eq. (C7) vanishes for $Q \neq 0$ due to the exponent. For Q = 0 the only contributions to an integral over q_z involving this term as part of the integrand are at $q_z = 0$ and at any poles due to other terms in the integrand. To evaluate such integrals, which occur in the single-ion potentials, it is useful to note the physical significance of the second and third terms of the rhs of Eq. (C7). In writing Eq. (C2) we have assumed an infinite periodic system with period $2(L + z_0)$ in the z direction, which is symmetric about both z = 0 and $z = L + z_0$. The second term on the rhs of Eq. (C7) represents the potential due to a two-dimensional density at z = 0 which cancels the interaction between the negative and positive z parts of the periodic system, and the third term does the same at $z = L + z_0$, so that $\tilde{w}_{is}(\vec{r}) = \tilde{w}_i(\vec{r})$ for $0 \le z \le L + z_0$. Thus, while these terms may contribute to the $(Q = 0, q_z)$ integrals involved in the single-ion potentials, their contribution is independent of the ionic posi-

tion and is in fact canceled by similar terms arising from the subtraction of the positive background potential.

The positive background potential $V_{+}(\vec{r})$ is given by

$$V_{+}(\vec{r}) = i \int d^{3}r' \Omega_{0}^{-1} \Theta(z'-z_{0}) e^{2} / |\vec{r}-\vec{r}'| , \qquad (C8)$$

where Ω_0 is the volume per electron in the bulk of the semi-infinite system. The symmetrized Fourier transform can be obtained from the expression on the rhs of Eq. (C7)

by replacing $\rho^{pp}(q)$ with Ω_0^{-1} [the Fourier transform of $\Omega_0^{-1}\delta(\vec{r})$ and integrating over the space occupied by the positive background density. The result of this operation is

$$V_{+s}(\vec{q}) = (2\pi)^2 \Omega_0^{-2/3} \delta(\vec{Q}) v_{+s}(q_z) , \qquad (C9)$$

where $v_{+s}(q_z)$ is given by

$$v_{+s}(q_z) = -\frac{4\pi e^2}{q_z^2} \Omega_0^{-1/3} [2\pi \delta(q_z) - 2\sin(q_z z_0)/q_z] + \lim_{L \to \infty} \frac{4\pi e^2}{q_z^2} \Omega_0^{-1/3} L \left[1 - \left[\frac{q_z}{Q} \sin[q_z (L + z_0)] - \cos[q_z (L + z_0)] \right] \right].$$
(C1)

The part of Eq. (C10) which depends on the system size L does not contribute to the single-ion potentials [see the discussion following Eq. (C7)].

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SINGLE-ION AND PAIR-INTERACTION POTENTIALS NEAR ...

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B. <u>SURFACE DEFECTS, INTERIONIC INTERACTIONS AND SURFACE SEGREGATION</u> Main Achievements

B.1 Ionic Interactions Near Simple Metal Surfaces

We have presented a model for semi-infinite simple metals which does not require crystalline order or a single species, and thus is applicable to problems of defect energetics near the surface and random-alloy surfaces as well as ideal metal surfaces. The formulation is based on the use of ionic pseudopotentials and linear-response theory. An expression for the total energy was obtained which depends explicitly on ionic species and position. This expression is decomposed into a density-dependent term and single-ion and ionic pair-interaction potential terms. The single-ion potentials oscillate about a constant bulk value, with the magnitude of the oscillation decreasing rapidly away from the surface. The interaction between pairs of ions near the surface was shown to be a noncentral force interaction which differs significantly from the central-force bulk pair potential. The effect of quantum interference in the response of the semi-infinite electron gas to the ions is seen in both the single-ion and the pair-interaction potentials. Results are presented for the simple metals sodium, potassium, and rubidium.

B.2 Surface Structure Studies

Relaxation at simple metal surfaces was studied via minimization of the total energy of a semi-infinite crystal. The expression for the total energy depends explicitly on the ionic positions, and is based on the use of pseudopotential theory and linear response. Electron screening is treated selfconsistently including exchange and correlation effects. From a systematic investigation of the energetics underlying metal surface relaxation, for the low-index surfaces of Na(bcc) and $A\ell(fcc)$ we concluded that to achieve quantitative surface structural predictions requires the use of the full total energy expression for the semi-infinite solid. Such an expression must maintain the three-dimensional nature of the system and account properly for the inhomogeneous surface electron density and the self-consistent response of the electron system to the ionic positions (screening). Multilayer relaxation was shown by us to be essential for quantitative structural predictions and the origins of the phenomena are discussed in detail demonstrating the relative effects of electrostatic terms and band-structure contributions. The results exhibit damped oscillatory multilayer relaxations (the relaxation being particularly pronounced for the open faces) with a period equal to the bulk layer stacking period and agree well with available structural determinations obtained via the analysis of experimental data.

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It should be noted that this work motivated a number of experimental groups to investigate in great detail multilayer relaxation in several metal surface systems. In particular we mention the A&(110) work (at Aarhus, Denmark headed by Professor D. L. Adams and that of the ORNL group (Drs. H. L. Davis, J. Noonan, and Professor F. Jona) which yielded results in agreement with our theoretical predictions.

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Most recently we have embarked upon investigations of the structure of high-index surfaces. Oscillatory multilayer relaxation of both interlayer spacing and registry at certain high index metal surfaces were predicted by us via minimization of a simple model for the total energy of a semi-infinite crystal. Results for the (210) and (211) surfaces of bcc and fcc simple metals indicate that the relaxation parallel to the surface plane moves the surface layers toward more symmetrical configurations with respect to adjacent layers. In this context it is of interest to note that the multi-layer registry shifts ((1x1)-reconstruction predicted by our model have recently been observed via a LEED analysis of data from F&(211), by F. Jona, P. Marcus and their collaborators.

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B-3

Multilayer lattice relaxation at metal surfaces

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Relaxation at simple metal surfaces is studied via minimizaton of the total energy of a semiinfinite crystal. Systematic analysis of the contributions to the total energy demonstrates the importance of a proper, three-dimensional treatment of electronic response. Multilayer relaxation is shown to be essential for quantitative predictions. Results for the low-index faces of Na and for Al(110) are presented. Good agreement with detailed low-energy electron diffraction data for oscillatory multilayer relaxation in Al(110) is obtained.

Metal surface structural information is essential for the understanding and elucidation of a large number of surface phenomena. Consequently, major efforts have been devoted in recent years to the development of surface structure experimental probes and their analysis. Progress in the formulation and implementation of theories of structurally predictive capability has been limited, hindered by the complexity of the problem. Such theories, however, are of great importance since they can provide structural input parameters to be employed in the analysis of data and reveal the nature of the forces (and their relative contributions) which govern the atomic arrangement and in particular structural modifications (relaxation and reconstruction) which are expected (and indeed observed) at the surface region of materials. These observations have led to the recent formulation¹ of a simple electrostatic model which predicted, semiquantitatively, multilayer surface relaxation in both fcc and bcc materials dependent upon surface crystallographic orientation and other material parameters. The existence of multilayer relaxation phenomena has since been verified by several careful examinations of low-energy electron diffraction (LEED) for several systems [e.g., Al(110,² Cu(110),^{2,3} V(100),⁴ $Re(0\overline{1}01)$ (Ref. 4)]. In this Rapid Communication we report the first results of calculations based on total energy minimization which provide quantitative estimates of metal surface structural parameters, elucidate the nature of forces governing the structure, multilayer relaxation in particular, and improve upon previous theories in several ways. We illustrate the theory by applying it to the low-index surfaces of Na and to Al(110) and obtain good agreement with recent experimental data.

The total energy E_T is expressed as the sum of the ground-state electron gas energy E_0 , the Madelung

electrostatic energy E_M of point ions in the presence of a semi-infinite negative neutralizing background, the interaction of point ions with the surface dipole layer E_{DL} , and of the Hartree and band-structure contributions, E_H and E_{BS} , respectively:

$$E_T\{\lambda_n\} = E_0 + E_M\{\lambda_n\} + E_{DL}\{\lambda_n\} + E_H\{\lambda_n\} + E_{BS}\{\lambda_n\} \quad .$$
(1)

In our calculation we retain the explicit dependence of the total energy on the crystalline structure. In particular the last four terms depend on layer positions, $z_n^{\lambda} = (n - \frac{1}{2} + \lambda_n)d$, n = 1, 2, ..., where d is the layer spacing in the bulk and $\lambda_n d$ is the deviation from the truncated bulk location of layer n. E_M and E_{BS} depend in addition on intralayer structure and on interlayer registry [$\Delta \vec{R}$ will denote the shift in origin of the two-dimensional (2D) lattice between adjacent layers, and is characteristic to the exposed face]. The total energy is minimized with respect to λ_n , $n = 1, 2, ..., N_s$.

In the evaluation of the Hartree and band-structure energies we use the local form of the Heine-Abarenkov model pseudopotential,

$$V_{P}(R,z) = \begin{cases} ZV_{C}(R,z), \quad R^{2} + z^{2} > r_{c}^{2} \\ -Ze^{2}u_{c}/r_{c}, \quad R^{2} + z^{2} \le r_{c}^{2} \end{cases}$$
(2)

where

$$V_C(R,z) = -e^2(R^2 + z^2)^{-1/2}$$

Z is the valence, and u_c and r_c are the pseudopotential parameters (chosen⁵ to fit the bulk compressibility and lattice parameter and used to determine vacancy formation energies). [For Na ($r_s = 3.931a_0$), $r_c = 2.076a_0$ and $u_c = 0.3079$; for Al ($r_s = 2.064a_0$), $r_c = 1.388a_0$ and $u_c = 0.3894$.]

The dipole-layer energy is given by

$$E_{\mathrm{DL}}\{\lambda_n\} = Z \sum_n \int d^2 R \int dz \left[\rho^e(z) - \rho^+(z)\right] V_C(R, z - z_n^{\lambda}) , \qquad (3)$$

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where \vec{R} is a 2D vector in the surface plane. The Hartree contribution,

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$$E_{\mathrm{H}}[\lambda_{n}] = \sum_{n} \int d^{2}R \int dz \, \rho^{e}(z) \left[V_{P}(R, z - z_{n}^{\lambda}) - ZV_{c}(R, z - z_{n}^{\lambda}) \right] \quad , \tag{4}$$

constitutes together with E_{DL} the first-order correction to the electron-jellium system (E_0) due to the replacement of the positive background by the ionic pseudopotentials. In Eqs. (3) and (4) the background density is denoted by $\rho^+(z) = (3/4\pi r_s^3)\theta(z)$, where $\theta(z)$ is the Heaviside step function, and the ground-state electron density in the presence of $\rho^+(z)$ is $\rho^e(z)$. In our calculations, we employ the Lang and Kohn⁶ electron density.

In the most primitive model (the PITB model) the system consists of point ions in the presence of a truncated bulk electron density, $E_T \{\lambda_n\}$ $= E_0 + E_M \{\lambda_n\}$. The addition of the dipole-layer and Hartree contributions (the DLH model) significantly improves the physical picture and predictive value by including a more realistic description of the inhomogeneous surface conduction-electron density and its first-order interaction energy with the ions.

However, the DLH model of surface relaxation (sometimes termed the "frozen profile model") which has been used previously to predict multilayer relaxation¹ does not include the response of the electrons to the presence of the ions. Attempts to further improve on this model have all been limited to single-layer relaxation⁷⁻⁹ and in certian of these an approximate one-dimensional potential has been used.⁹ As is demonstrated by our results and their comparison to experimental data both multilayer relaxation and the full three-dimensional nature of the ionic system must be included in a proper and quantitative treatment of surface relaxation.

The band-structure energy (second order in the pseudopotentials) can be written as

$$E_{\rm BS}\{\lambda_n\} = \frac{1}{2} \sum_{\vec{G}} \sum_{n,m} \left[\exp(i\vec{G} \cdot \Delta \vec{R}) \right]^{n-m} \int dz \, \rho_n^{\lambda}(G;z) \, W_m^{\lambda}(G;z) \quad , \tag{5}$$

where \vec{G} is the 2D reciprocal lattice vector, and $W_m^{\lambda}(G;z)$ is the 2D Fourier transform of

$$W_{m}^{\lambda}(R,z) = V_{P}(R,z-z_{m}^{\lambda}) - \frac{1}{N_{A}} \int d^{2}R' \int_{(m-1)d}^{md} dz' \rho^{+}(z') V_{C}(|\vec{R}-\vec{R}'|,z-z')$$
(6)

 $(N_A$ is the number of ions in a layer). The induced (screening) electron density is linearly related to W_n^{λ} through

$$\rho_{n}^{\lambda}(G;z) = \int dz' \alpha_{0}(G;z,z') \left[W_{n}^{\lambda}(G;z') + \phi_{n}^{\lambda}(G;z') \right] , \qquad (7a)$$

$$\phi_{\pi}^{\lambda}(G;z) = \int dz' g(G;z,z') V_{C}(G;z-z') \rho_{\pi}^{\lambda}(G;z') , \qquad (7b)$$

where α_0 is the random-phase approximation polarizability and correlation and exchange are included via the local field correction g. The solution of Eqs. (7) is facilitated by using the infinite barrier response model,^{10,11} and by the ansatz g(G;z,z')= g(G;|z-z'|) (Ref. 12).

Including only the $\vec{G} = 0$ contribution to E_{BS} [Eq. (5)] is equivalent to a one-dimensional treatment of the electron response obtained by averaging the ionic potential over the layers (we denote this 1D electron response model of E_T by DLHBS0, to contrast with the model, denoted by DLHBS, in which the complete E_{BS} is included).

Results for the surface structures of the low-index faces of Na and of A1(110) obtained via minimization of the total energies corresponding to the various models and those obtained by other theories, as well as values obtained from experimental analyses, are summarized in Table I. Percent changes, $\Delta_{n,n+1}$, of the interlayer distance between layers n and n + 1from the bulk value, for differing numbers N_s of layers allowed to relax, are given. Inspection of the results shows that relaxation is more pronounced for the open faces, and that multilayer relaxation is essential in all the models and systems considered. Note, for example, the change in sign in Δ_{12} obtained via DLHBS0 for Na(100) and Na(111) when allowing for multilayer relaxation. [Although for $N_s = 6$ the relaxations did not yet converge for Na(111), calculations with $N_s = 9$ in the PITB and DLH models did not significantly change the values of Δ_{12} through Δ_{34} .] We find damped oscillatory relaxations with a period equal to the stacking period [three for Na(111) and two for the other surfaces]. Comparison of the results of the DLH and PITB models illustrates that the interaction of the ions with the inhomogeneous surface electron density tends to decrease relaxations, resulting from a reduced deviation of the first layer from its position relative to the bulk. The importance of the full inclusion of the bandstructure contribution is vividly illustrated by comparing the results of the DLHBS and DLHBS0 models. Agreement with detailed experimental results² for Al(110) is dramatically improved by using the complete band structure (DLHBS) and allowing multilayer relaxation. These results also demonstrate

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TABLE I. Surface relaxations for the low-index faces of Na and for Al(110) expressed in percent changes $\Delta_{n,n+1}$ of the interlayer distance between layers n and n + 1 from the bulk value. N_s is the number of layers allowed to relax. The larger value of N_s is the one for which convergence is obtained. Negative values of $\Delta_{n,n+1}$ indicate contraction of the interlayer spacing. Results for the various models (see text) are shown in order of increasing complexity. Note the effect of the multilayer relaxations and their oscillatory character.

Model			Na(10	00)			Na(110)				
	N,	. 4	12	Δ ₂₃	Δ_{34}		N _s	. 4	12	Δ ₂₃	Δ_{34}
PITB	1	-	-7.0 10.8	4.0	-1.2		1	(().69).72	0.03	-0
DLH	1 9	-	-1.3 -1.9	0.7	-0.4		1 9	(0.29 0.15	0.12	0.01
DLHBS0	1 4	-	1.2 -0.4	1.2	0.4		1 3		1.0).09	0.25	0.82
DLHBS	1 4	-	-3.6 -2.7	0.7	-1.0		1 3	-(-().08).16	0.08	0.01
Expt.								≓ (Rei	= 0 (. 13)		
R ef. 8	1	-	-2				1	().0		
Ref. 9	1	+	• 1				1	-:	5.0		
		Na((11)						AI(110)		
Model	N _s	Δ_{12}	Δ ₂₃	Δ_{34}	Δ_{45}	Δ ₅₆	Δ_{67}	N _s	Δ ₁₂	Δ ₂₃	Δ ₃₄
PITB	1 9	-34 -67	-10	53	-40	6.	18	1 9	$-11 \\ -26$	16	-8
DLH	1 9	-13 +3	-35	27	0	-15	11	1 9	-4 -12	8	-4
DLH BS 0	1 6	-10 4	-32	24	0	-12	10	1 6	-5 -14	9	-2
DLHBS	1 6	-20 -8	-29	23	-2	-11	8	1 6	-14 -10	4	-3
Expt.									-8.4 ±0.8 (R	4.9 ± 1.0 ef. 2)	-1.6 ±1.1
Ref. 8 Ref. 9	1	-12.5						Could not find minimum			

that the multilayer relaxation phenomena predicted by the simple electrostatic models¹ (PITB and DLH) do occur when electron response is included properly, and is necessary for quantitative theoretical structural predictions. These observations resolve questions raised by several authors related to this issue.^{8,9} Finally, we note the magnitude¹⁴ and sequence of predicted relaxations for Na(111) which would pro-

vide an interesting challenge for experimental endeavor.

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MULTILAYER LATTICE RELAXATION AT METAL SURFACES:

A TOTAL ENERGY MINIMIZATION*

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Abstract

Relaxation at simple metal surfaces is studied via minimization of the total energy of a semi-infinite crystal. The expression for the total energy depends explicitly on the ionic positions, and is based on the use of pseudopotential theory and linear response. Electron screening is treated selfconsistently including exchange and correlation effects. From a systematic investigation of the energetics underlying metal surface relaxation, for the low-index surfaces of Na(bcc) and Al(fcc) it is concluded that to achieve quantitative surface structural predictions requires the use of the full total energy expression for the semi-infinite solid. Such an expression must maintain the three-dimensional nature of the system and account properly for the inhomogeneous surface electron density and the self-consistent response of the electron system to the ionic positions (screening). Multilayer relaxation is shown to be essential for quantitative structural predictions and the origins of the phenomena are discussed in detail demonstrating the relative effects of electrostatic terms and band-structure contributions. The results exhibit damped oscillatory multilayer relaxations (the relaxation being particularly pronounced for the open faces) with a period equal to the bulk layer stacking period and agree well with available structural determinations obtained via the analysis of experimental data.

Introduction

Knowledge of the surface crystallographic structure of metals, i.e. the location of atoms at the surface and in the near-surface region, is of fundamental importance for investigation and elucidation of various metal surface properties and surface phenomena. This problem is of particular interest since the surface structure of metals is expected, and indeed is observed¹⁻⁵. to deviate (both relaxation and reconstruction) from the truncated bulk atomic arrangement due to changes in atomic coordination and electron distribution in the surface region. Consequently, major efforts have been devoted in recent years to the development of experimental probes and associated theoretical analysis and data reduction methods for the determination of the structures of clean surfaces and in the presence of adsorbed species (e.g., LEED^{1a,b}, ion scattering^{1c}, Surface Extended Absorption fine structure^{6,7}, SEXAFS, Glancing angle x-ray scattering⁸, Stimulated Desorption Ion Angular Distributions SDIAD⁹ to name a few). However, the interpretation of these experiments involves analysis models which in addition to the structural variables contain a host of non-structural parameters (inner-potential, energy-dependent projectile mean-free-path, scattering phase-shifts, dynamical response functions, vibrational mean-square amplitudes, vibrational correlations, etc.). The optimization of the fit between the data and the corresponding analysis model requires variation of both the structural and nonstructural parameters (which may be interrelated). In addition the analysis is often complex and time consuming due to the wide range of possible values for the structural parameters, often hindering an exhaustive search except for certain simple systems. Thus, it is both timely and important to develop surface structure theories of predictive capability to guide data analysis.
Moreover, such theories (and their interplay with experiments) provide a fundamental understanding of the microscopic origins of the structure.

The development of such structure predictive theories, however, is hindered by difficulties in carrying out a self-consistent energy minimization for the coupled system of ions and conduction electrons. Semi-empirical methods, based on lattice static calculations with pair potentials derived semiempirically or using bulk pseudopotential pairwise interactions, are known often to yield results which contradict experiments, and their inadequacy has been discussed elsewhere.¹⁰ These observations have led recently¹⁰ to the development of a simple electrostatic model in which structural minimization of the total energy of a semi-infinite metal predicted, semiquantitatively, multilayer surface relaxation in both fcc and bcc materials, dependent upon surface crystallographic orientation and other material parameters. The existence of multilayer relaxation phenomena has since been verified by several careful examinations of low energy electron diffraction (LEED) and ion scattering experiments for several systems (e.g., A1(110)², $Cu(110)^3$, $V(100)^4$, $Re(0\overline{101})^5$). Nevertheless, the electrostatic model¹⁰ while containing certain essential ingredients (i.e., contributions to the force on ions in the surface layers due to the delocalized, inhomogeneous, valence electron distribution and due to the electrostatic interaction between ions) did not allow for self-consistency of the combined electrons-ions system. It is therefore a "frozen profile" model in which the electronic response to variations in ionic positions is not included. The objective of the present study is to alleviate this problem by formulating and implementing a theory which allows for a self-consistent structure determination¹². In the course of development of the theory we also provide a systematic and critical analysis

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of the various contributions to the energetics of surface relaxation. The theoretical model is described in Section II and draws upon, when necessary, the detailed discussion of the electron response model given in the preceeding paper¹³ (which will be referred to as Paper I). The relaxation algorithm is described in Section III. Analysis of various models and sample results for the low-index faces of fcc and bcc materials (Al and Na) and comparisons to other studies and to experimental results are discussed in Section IV.

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II. Theoretical Model

A prerequisite for a self-consistent energy minimization structure determination scheme is an expression for the total energy of the system which depends explicitly on the ionic positions. In this study we consider surface normal relaxation, i.e., changes in layer spacings (no reconstruction, i.e., lateral, intraplane structural modifications are considered). Thus the position vector of the i-th ion in layer n is given by

$$\vec{r}_{n,i} \equiv (\vec{R}_i + \Delta \vec{R}_n, z_n^{\lambda})$$
 (1a)

where

$$z_n^{\lambda} = z_0 + (n - \frac{1}{2} + \lambda_n)d$$
, $n = 1, 2, ...$ (1b)

 \vec{R}_1 is a 2D vector in surface plane $(\vec{R}_1 = \ell_1 \vec{a}_1 + m_1 \vec{a}_2, \text{ where } \vec{a}_1 \text{ and } \vec{a}_2 \text{ are}$ the primitive translation vector of the 2D mesh), and $\Delta \vec{R}_n$ specifies the origin of the 2D mesh of layer n,

$$\Delta \vec{R}_{n} = \mod_{n}(n) \Delta \vec{R}$$
 (1c)

where n_R is the repeat period of the layer stacking sequence and $\Delta \vec{R}$ is the registry shift between adjacent layers (see Table I). The bulk layer spacing is denoted by d and $\lambda_n d$ is the deviation of the z-coordinate of the n-th layer from its truncated bulk position (the superscript λ on z_n^{λ} serves to emphasize this dependence on λ_n). The constant z_o specifies the position of the "jellium edge" (our choice of $z_o = 3\pi/8k_F$, where $\hbar k_F$ is the Fermi momentum is dictated by notational convenience in discussing the electron response, see also Paper I).

We begin by writing the Hamiltonian for the conduction electrons in the presence of the ions as

$$E_{T}(\lambda_{1},\lambda_{2},\ldots) = E^{\circ}/N_{A} + \int d^{2}R \int dz \rho^{\circ}(z) \sum_{n>0} w_{n}^{\lambda}(R,z) + \frac{1}{2} \int d^{2}R \int dz \sum_{n>0} \rho_{n}^{\lambda}(R,z) \sum_{m>0} \sum_{j} w_{m}^{\lambda}(|\vec{R}-\vec{R}_{j}+\Delta\vec{R}_{n-m}|,z) + \frac{1}{2} \sum_{n>0} \sum_{m>0} \sum_{j} [-z^{2}V_{c}(|\vec{R}_{j}-\Delta\vec{R}_{n-m}|, z_{n}^{\lambda}-z_{m}^{\lambda})], \qquad (6)$$

where $\rho_n^{\lambda}(\mathbf{R}, \mathbf{z})$ is the induced (screening) electron density due to the potential $w_n^{\lambda}(\mathbf{R}, \mathbf{z})$. The last term in Eq. (6) is the Coulomb interaction energy between the ions (the primed sum over j omits the term with $\vec{\mathbf{R}}_j = 0$ when n = m). The induced electron density, ρ_n^{λ} , is taken to be linearly related to the potential w_n^{λ} , as expressed by the coupled integral equations

$$\rho_{n}^{\lambda}(R,z) = \int d^{2}R' \int dz' \alpha_{0}(|\vec{R} - \vec{R}'|;z,z') [w_{n}^{\lambda}(R',z') + \phi_{n}^{\lambda}(R',z')],$$

$$\phi_{n}^{\lambda}(R,z) = \int d^{2}R' \int dz' g(|\vec{R} - \vec{R}'|;z,z') \rho_{n}^{\lambda}(R',z') V_{c}(|\vec{R} - \vec{R}'|,z-z'). \quad (7)$$

In our calculation we use the infinite-barrier response model developed in Paper I, i.e., α_0 is the RPA response function for electrons confined to the half space $z \ge 0$. Exchange and correlation contributions are included through the function g (see Paper I, Section II.B).

Using the expression for w_n^{λ} given in Eq. (3), we rewrite the total energy as,

$$E_{T}(\lambda_{1},\lambda_{2}, \ldots) = [E^{0}/N_{A} - A_{o}\int dz \rho^{0}(z) \int dz' \rho^{+}(z') \int d^{2}R V_{c}(R,z-z')] + \sum_{n>0} \left\{ \frac{1}{2} \sum_{m>0} \sum_{j}' [-Z^{2} V_{c}(|\vec{R}_{j} - \Delta \vec{R}_{n-m}|, z_{n}^{\lambda} - z_{m}^{\lambda})] + \int dz \rho^{+}(z) \int d^{2}R ZV_{c}(R, z-z_{n}^{\lambda}) \right\} + \sum_{n>0} \int dz [\rho^{0}(z) - \rho^{+}(z)] \int d^{2}R ZV_{c}(R, z-z_{n}^{\lambda})$$

$$+ \sum_{n>0} \int dz \rho^{0}(z) \int d^{2}R \left[V_{p}(R, z-z_{n}^{\lambda}) - ZV_{c}(R, z-z_{n}^{\lambda}) \right]$$

$$+ \frac{1}{2} \sum_{n>0} \sum_{m>0} \sum_{j} \int d^{2}R \int dz \rho_{n}^{\lambda}(R, z) w_{m}^{\lambda}(|\vec{R}-\vec{R}_{j}+\Delta\vec{R}_{n-m}|, z)$$

$$= E_{0}^{*} + E_{M}^{\{\lambda\}} + E_{DL}^{\{\lambda\}} + E_{H}^{\{\lambda\}} + E_{BS}^{\{\lambda\}}.$$
(8)

The term denoted as E' in the above equation, which does not depend on ionic positions, consists of the ground state energy of the jellium system¹⁴, from which the electrostatic energy of the interaction of the ground state electron density, ρ^{o} , with the positive background, ρ^{+} , has been subtracted. The second term, $\boldsymbol{E}_{M}\{\boldsymbol{\lambda}\},$ is the Madelung energy, i.e., the electrostatic energy of positive point-ions in the presence of a neutralizing negative background. The third term, $E_{DL}^{(\lambda)}$, is the interaction of point-ions with the difference, $\rho^{o}(z) - \rho^{+}(z)$, between the jellium ground state electron density and the steptruncated uniform bulk density. This term will be called the "dipole layer" The fourth term, $E_{\mu}\{\lambda\}$, is the Hartree contribution, i.e., the energy. difference between the interactions of the jellium electron density, ρ° , with ionic pseudo-potentials, V_p , and with point ions. The combined contributions from E_{DL} and E_{H} constitute the first-order correction to the total energy due to the replacement of the positive background by a lattice of ions represented by pseudo-potentials. The second order correction to the total energy, $E_{BS}^{\{\lambda\}}$ is the last term in Eq. (8), and is referred to as the bandstructure energy. Note that while E_{DL} and E_{H} depend only on the positions of individual layers with no dependence on intralayer structure, E_{M} and E_{BS} depend on the relative positions of layers and their registry and on intralayer

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structure. In the band-structure energy, $E_{BS}^{}$, these dependencies are due to the interaction of the induced electron density associated with the pseudopotential at a given lattice site with the pseudo-potentials located at other sites. In addition $E_{BS}^{}$ contains contributions from the electron density associated with a given site interacting with the ionic pseudopotential located at that site. Due to the symmetry breaking in the surface normal direction, in the surface region these on-site interactions depend on the z-coordinate of the site, and approach a constant value away from the surface. In addition the inter-site contributions to $E_{BS}^{}$ depend separately on the z-coordinates of the ion-pairs. Thus, unlike in the bulk, $E_{M}^{} + E_{BS}^{}$ cannot be written as a sum over pair-potentials depending only on the relative positions of pairs of ions (see Paper I).

To find the equilibrium configuration the total energy, $E_T(\lambda_1, \lambda_2, ...)$, is minimized with respect to the layer relaxation parameters $\{\lambda_n\}$. We assume that in the relaxed configuration bulk arrangement is maintained beyond a certain number of layers, n_s (i.e., $\lambda_n = 0$ for $n > n_s$). The number of layers allowed to relax, n_s , is determined via investigation of convergence of the results vs. n_s . The minimization conditions are:

$$F(l) = 0$$
 for $l = 1, 2, ..., n$, (9a)

and

$$\sum_{m=1}^{n} \Phi(\ell, m) \delta \lambda_{m} > 0 \quad \text{for } \ell = 1, 2, \dots, n_{s}$$
(9b)

where $\{\delta\lambda_m\}$ are small but otherwise arbitrary and the force F(l) is obtained from $E_T(\lambda_1, \lambda_2, \dots)$ via

$$F(\ell) = -\frac{\partial E_{T}}{\partial \lambda_{\ell}} \equiv F_{M}(\ell) + F_{DL}(\ell) + F_{H}(\ell) + F_{BS}(\ell) , \qquad (9c)$$

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and

$$\Phi(\ell, \mathbf{m}) = \frac{\partial^2 \mathbf{E}_{\mathrm{T}}}{\partial \lambda_{\ell} \partial \lambda_{\mathrm{m}}} \equiv \phi_{\mathrm{M}}(\ell, \mathbf{m}) + \Phi_{\mathrm{DL}}(\ell, \mathbf{m}) + \Phi_{\mathrm{H}}(\ell, \mathbf{m}) + \Phi_{\mathrm{BS}}(\ell, \mathbf{m}) , \quad (9d)$$

where the subscripts on the F's and Φ 's specify the contributions obtained from the corresponding terms in the total energy expression, Eq. (8).

Prior to a discussion of the relaxation algorithm we discuss in the following the evaluation of the various terms in Eq. (8) and Eqs. (9). Those readers who are not interested in such details should skip to Sections III and IV.

(a) <u>Madelung Energy</u>, E

Using the identities

$$(R^{2} + z^{2})^{-1/2} = \frac{1}{2\pi} \int d^{2}K \frac{e^{-K|z|}}{K} e^{i\vec{K}\cdot\vec{R}}$$
(10)

where \vec{K} is a 2D reciprocal space vector, and

$$\sum_{i} e^{i\vec{K}\cdot\vec{R}_{i}} = \frac{(2\pi)^{2}}{A_{o}} \sum_{\vec{G}} \delta(\vec{K}-\vec{G})$$
(11)

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where \mathbf{A}_{o} is the 2D unit cell area and $\vec{\mathbf{G}}$ is a 2D reciprocal lattice vector;

$$\vec{G} = \ell \vec{b}_1 + \vec{mb}_2$$

where \vec{b}_1 and \vec{b}_2 are the primitive translation vectors of the 2D reciprocal mesh, the Madelung energy, E_M , can be written as

$$E_{M} = (Ze)^{2} \frac{2\pi}{A_{o}} \sum_{\vec{G}}^{\prime} \frac{1}{2} \sum_{n,m>0}^{\prime} [e^{i\vec{G}\cdot\Delta\vec{R}}]^{n-m} \frac{e^{-G\left|z_{n}^{\lambda}-z_{m}^{\lambda}\right|}}{G}$$

$$+ (Ze)^{2} \frac{1}{2\pi} \int d^{2}K \frac{(2\pi)^{2}}{A_{o}} \delta(\vec{K}) \sum_{\substack{n,m>0\\n,m>0}} \left\{ \frac{e^{-K\left|z_{n}^{\lambda}-z_{m}^{\lambda}\right|}}{K} - \frac{2}{d} \int_{z_{m}}^{z_{m}} dz' \frac{e}{K} \right\}$$

$$- (Z_e)^2 \frac{1}{2\pi} \int d^2 \kappa \frac{1}{2} \sum_{n>0} \kappa^{-1} , \qquad (12)$$

where the prime on the sum over \vec{G} omits $\vec{G} = \vec{0}$. Using Eq. (12) in the definitions (9c) and (9d) we obtain (for details see Reference 10)

$$F_{M}(\ell) = (Ze)^{2} \frac{2\pi}{A_{o}} d\left\{-2\lambda_{\ell} + \sum_{n=1}^{n} (1-\delta_{\ell,n}) \sum_{\vec{G}} [e^{i\vec{G}\cdot\Delta\vec{R}}]^{\ell-n} \operatorname{sign}(\ell-n) e^{-Gd|\ell+\lambda_{\ell}-n-\lambda_{n}|} - \sum_{\vec{G}} e^{Gd(\ell+\lambda_{\ell}-n_{s})} [1-e^{-n_{R}Gd}]^{-1} \sum_{m=1}^{n} [e^{i\vec{G}\cdot\Delta\vec{R}}]^{\ell-m-n_{s}} e^{-Gdm}\right\}$$
(13)

and

$$\Phi_{M}(\ell,m) = (Ze)^{2} \frac{2\pi}{A_{o}} \left\{ \left[\delta_{\ell,m}^{-1} \right] \sum_{\vec{G}}^{\prime} \left[e^{i\vec{G}\cdot\Delta\vec{R}} \right]^{\ell-m} Gde^{-Gd\left|\ell+\lambda}\ell^{-m-\lambda}_{m} \right| \right. \\ \left. + \delta_{\ell,m} \left[2 + \sum_{\vec{G}}^{\prime} Gde^{Gd\left(\ell+\lambda}\ell^{-n}s\right)} \left[1 - e^{n}R^{Gd} \right]^{-1} \sum_{m=1}^{n} \left[e^{i\vec{G}\cdot\Delta\vec{R}} \right]^{\ell-n}s^{-m} e^{-Gdm} \right. \\ \left. + \sum_{\vec{G}}^{\prime} \sum_{n=1}^{n} \left[1 - \delta_{n,\ell}^{\prime} \right] \left[e^{i\vec{G}\cdot\Delta\vec{R}} \right]^{\ell-n} Gde^{-Gd\left|\ell+\lambda}\ell^{-n-\lambda}n \right| \right] \right\} .$$
(14)

(b) <u>Dipole Layer Energy, E</u>DL

Substituting the expression for E_{DL} (third term in Eq. (8)) in the definitions (9c) and (9d) we obtain

$$F_{DL}(\ell) = 2\pi Z e^2 d \int dz \left[\rho^{\circ}(z) - \rho^{+}(z)\right] \operatorname{sign}(z - z_{\ell}^{\lambda}), \qquad (15)$$

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and

$$\Phi_{\rm DL}(\ell,m) = 4\pi Z e^2 d^2 \delta_{\ell,m} \left[\rho^{\rm o}(z_{\ell}^{\lambda}) - \rho^{+}(z_{\ell}^{\lambda})\right].$$
(16)

where $\rho^{o}(z)$ is taken from the calculations of Lang and Kohn¹⁴ (three point Lagrange interpolation is used to obtain ρ^{o} for the appropriate value of r_{s})

and the integration is performed numerically.

(c) <u>Hartree Energy</u>, E_H

Substituting Eqs. (4) and (5) for V_c and V_p in the fourth term in Eq. (8) and performing the d^2R integration yields

$$E_{\rm H} = -2\pi Z e^2 \sum_{n>0}^{z_{\rm h}^{\rm h} r_{\rm c}} \int_{z_{\rm h}^{\rm h} r_{\rm c}} dz \ \rho^{\rm o}(z) \left\{ \frac{u_{\rm c}}{2r_{\rm c}} \left[r_{\rm c}^2 - (z - z_{\rm h}^{\lambda})^2 \right] - r_{\rm c}^{\rm h} |z - z_{\rm h}^{\lambda}| \right\}, \quad (17)$$

which when used in Eqs. (9c) and (9d) yields

$$F_{\rm H}(\ell) = 2\pi Z e^2 d \int_{z_{\ell}^{\lambda} - r_{\rm c}}^{z_{\ell}^{\lambda} + r_{\rm c}} dz \ \rho^{\rm o}(z) \left\{ \frac{u_{\rm c}}{r_{\rm c}} (z - z_{\ell}^{\lambda}) - \operatorname{sign}(z - z_{\ell}^{\lambda}) \right\} , \qquad (18)$$

$$\Phi_{\rm H}(\ell,m) = -2\pi Z e^2 d^2 \delta_{\ell,m} \left\{ 2\rho^{\rm o}(z_{\ell}^{\lambda}) + (u_{\rm c}-1) \left[\rho^{\rm o}(z_{\ell}^{\lambda}+r_{\rm c}) + \rho^{\rm o}(z_{\ell}^{\lambda}-r_{\rm c})\right] - \frac{u_{\rm c}}{r_{\rm c}} \frac{z_{\ell}^{\lambda}+r_{\rm c}}{z_{\ell}^{\lambda}-r_{\rm c}} dz \rho^{\rm o}(z) \right\}.$$
(19)

(d) <u>Band-structure Energy</u>, E_{BS}

Evaluation of the band-structure energy requires a self-consistent solution for the induced electron density, ρ_n^{λ} (see Eqs. (7)). In the response model developed in Paper I

$$\rho_n^{\lambda}(\mathbf{r}, \mathbf{z}) = 0 \quad \text{for} \quad \mathbf{z} < 0 \quad , \tag{20}$$

thus we can specify symmetrized quantities

$$w_{ns}^{\lambda}(\mathbf{R},z) = w_{n}^{\lambda}(\mathbf{R},|z|) \text{ and } \rho_{ns}^{\lambda}(\mathbf{R},z) = \rho_{n}^{\lambda}(\mathbf{R},|z|)$$
 (21)

and their 3D Fourier transforms $w_{ns}^{\lambda}(Q,q_z)$, $\rho_{ns}^{\lambda}(Q,q_z)$ where $\vec{q} = (\vec{Q},q_z)$ is a 3D reciprocal space vector, and \vec{Q} is a 2D vector in the surface plane. $\rho_{ns}^{\lambda}(Q,q_z)$ is obtained as a function of q_z for specified Q, n, and λ_n as the solution of a single one-dimensional integral equation , as discussed in detail in Paper I. This symmetrization allows us to evaluate E_{BS} entirely in reciprocal space. We obtain

$$\mathbf{E}_{\mathrm{BS}} = \frac{1}{4A_{\mathrm{o}}} \sum_{\mathrm{n},\mathrm{m}>0} \sum_{\vec{G}} \left[e^{i\vec{G}\cdot\Delta\vec{R}} \right]^{\mathrm{n}-\mathrm{m}} \frac{1}{2\pi} \int \mathrm{d}q_{\mathrm{z}} \rho_{\mathrm{ns}}^{\lambda}(G,q_{\mathrm{z}}) w_{\mathrm{ms}}^{\lambda}(G,q_{\mathrm{z}}) \cdot (22)$$

Since the sums over layers converge slowly as |n-m| increases, we define an unrelaxed sublattice potential

$$W_{ms}(G,q_z) = \sum_{n(m)}^{\infty} w_{ns}(G,q_z), m = 1, 2, ..., n_R$$
 (23a)

and the corresponding induced electron density

$$P_{ms}(G,q_z) = \sum_{n(m)}^{\infty} \rho_{ns}(G,q_z) , m = 1, 2, ..., n_R$$
(23b)

where $\sum_{n(m)}^{\infty}$ means summation over the sequence n = m, $m+n_R$, $m+2n_R$, ..., where n_R is the layer stacking sequence period. We denote $w_{ns}^{\lambda}(G,q_z)$ and $\rho_{ns}^{\lambda}(G,q_z)$ with $\lambda_n = 0$ by $w_{ns}(G,q_z)$ and $\rho_{ns}(G,q_z)$, respectively in Eqs. (23). We also define layer difference quantities

$$\Delta w_{ns}^{\lambda}(G,q_z) = w_{ns}^{\lambda}(G,q_z) - w_{ns}^{\lambda}(G,q_z) , \qquad (24a)$$

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and

$$\Delta \rho_{\rm ns}^{\lambda}(G,q_z) = \rho_{\rm ns}^{\lambda}(G,q_z) - \rho_{\rm ns}(G,q_z) . \qquad (24b)$$

Since $w_{ns}(G,q_z)$ does not involve the variable λ_n , $W_{ms}(G,q_z)$ can be evaluated analytically, and $P_{ms}(G,q_z)$ and $\Delta \rho_{ns}^{\lambda}$ are obtained from $W_{ms}(G,q_z)$ and Δw_{ns}^{λ} in the same manner that ρ_{ns}^{λ} is obtained from w_{ns}^{λ} , by solving the integral equation. The expressions for $w_{ns}^{\lambda}(G,q_z)$ and $W_{ms}(G,q_z)$ are derived in Appendix A. Finally, using the above definitions in Eq. (22) we write the band-structure energy as:

$$E_{BS} = E_{BS}^{(0)} + \sum_{n=1}^{n} \Delta E_{BS}^{(1)}(n,\lambda_n) + \frac{1}{2} \sum_{n,m=1}^{n} \Delta E_{BS}^{(2)}(n,\lambda_n;m,\lambda_m) , \quad (25)$$

where

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$$E_{BS}^{(0)} = \frac{1}{4A_{o}} \sum_{\vec{G}} \sum_{n,m=1}^{n_{R}} [e^{i\vec{G}\cdot\Delta\vec{R}}]^{n-m} \frac{1}{2\pi} \int dq_{z} W_{ms}(G,q_{z}) P_{ns}(G,q_{z}) , (26a)$$

$$\Delta E_{BS}^{(1)}(n,\lambda_{n}) = \frac{1}{4A_{o}} \sum_{\vec{G}} \sum_{m=1}^{n} \left[e^{i\vec{G}\cdot\Delta\vec{R}} \right]^{n-m} \frac{1}{2\pi} \int dq_{z} \left[W_{ms}(G,q_{z}) \Delta \rho_{ns}^{\lambda}(G,q_{z}) + \Delta w_{ns}^{\lambda}(G,q_{z}) P_{ms}(G,q_{z}) \right], \quad (26b)$$

$$\Delta E_{BS}^{(2)}(n,\lambda_{n};m,\lambda_{m}) = \frac{1}{4A_{o}} \sum_{\vec{G}} [e^{i\vec{G}\cdot\Delta\vec{R}}]^{n-m} \frac{1}{2\pi} \int dq_{z} [\Delta w_{ms}^{\lambda}(G,q_{z}) \Delta \rho_{ns}^{\lambda}(G,q_{z}) + \Delta w_{ns}^{\lambda}(G,q_{z}) \Delta \rho_{ms}^{\lambda}(G,q_{z})]. \qquad (26c)$$

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Using Eqs. (25) and (26) in Eqs. (9c) and (9d) we obtain

$$F_{BS}(\ell) = \frac{-\partial}{\partial \lambda_{\ell}} \Delta E_{BS}^{(1)}(\ell,\lambda_{\ell}) - \sum_{n=1}^{n_{s}} [1 - \delta_{n,\ell}] \frac{\partial}{\partial \lambda_{\ell}} \Delta E_{BS}^{(2)}(\ell,\lambda_{\ell};n,\lambda_{n}) - \frac{1}{2} \frac{\partial}{\partial \lambda_{\ell}} \Delta E_{BS}^{(2)}(\ell,\lambda_{\ell};\ell,\lambda_{\ell}), \quad (27)$$

and

$$\Phi_{BS}(\ell,m) = \delta_{\ell m} \left\{ \frac{\partial^{2}}{\partial \lambda_{\ell}^{2}} \Delta E_{BS}^{(1)}(\ell,\lambda_{\ell}) + \frac{1}{2} \frac{\partial^{2}}{\partial \lambda_{\ell}^{2}} \Delta E_{BS}^{(2)}(\ell,\lambda_{\ell};\ell,\lambda_{\ell}) \right\} + [1-\delta_{\ell m}] \frac{\partial^{2}}{\partial \lambda_{\ell} \partial \lambda_{m}} \Delta E_{BS}^{(2)}(\ell,\lambda_{\ell};m,\lambda_{m})$$

$$(28)$$

Note that $\Delta E_{BS}^{(2)}(\ell,\lambda_{\ell};\ell,\lambda_{\ell})$ is actually a function of only one variable, namely λ_{ℓ} .

The derivatives of $\Delta E_{BS}^{(1)}$ and $\Delta E_{BS}^{(2)}$ are obtained numerically as follows: (i) Evaluate these functions for judiciously chosen values of the λ 's, (ii) fit with cubic or bicubic spline functions,

- (iii) obtain F_{BS} and Φ_{BS} by taking derivatives of the spline functions,
- (iv) relax the layers (by the algorithm described in Section III),
- (v) calculate the energies for additional values of λ 's around the relaxed positions obtained in step (iv) (as necessary to obtain an accurate spline fit near the λ 's determined in (iv)),

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(vi) repeat steps (ii) - (v) until convergence is obtained.

III. Relaxation Algorithm

The conditions for total energy minimization, with respect to the structural parameters (layer spacings for the case of normal relaxation), are given in Eqs. (9). We define the force vector $\mathbf{g}^{T}(\Lambda) \equiv (\mathbf{F}(1), \ldots, \mathbf{F}(n_{s}))$ and the relaxation parameter vector $\Lambda^{T} \equiv (\lambda_{1}, \ldots, \lambda_{n_{s}})$. The matrix elements of the energy second-derivative matrix, $\Phi(\Lambda)$, are given as $(\Phi(\Lambda))_{\ell_{m}} = \Phi(\ell, m)$, where $\Phi(\ell, m)$ is defined in Eq. (9d). The relaxation algorithm consists of the following steps:

(i) Evaluate $\mathcal{F}(\Lambda_i)$ and $\phi(\Lambda_i)$ for a given value of Λ_i .

(ii) Find the direction of steepest descent in the relaxation parameter space according to

$$\chi_{i} = \overset{\Phi^{-1}}{\sim} (\overset{\Lambda}{\sim}_{i}) \mathcal{F}(\overset{\Lambda}{\sim}_{i}) . \qquad (29)$$

(iii) Minimize the total energy with respect to displacements in the relaxation parameter space along the vector $\bigwedge_i + s\zeta \Upsilon_i$, where the scalar $\zeta > 0$ is found from the requirement

$$\chi_{i}^{T} \xi(\Lambda_{i} + s\zeta \chi_{i}) \approx 0$$
 (30)

and $s = sign [\chi_i^T \mathcal{F}(\Lambda_i)]$. This insures that the extremum is a minimum. (iv) Increment Λ_i according to $\Lambda_{i+1} = \Lambda_i + s\zeta \chi_i$, and repeat (i) through (iii) until $\chi_i = Q$, in Eq. (29).

IV. Models and Results

A. Models

In order to investigate systematically the energetics of surface relaxation and to facilitate comparison with other studies we distinguish several models which will be introduced in order of increasing complexity and realism.

a) In the most primitive model the system consists of point ions in the presence of uniform truncated bulk electron density. This model will be referred to as the <u>PITB</u> model. The total energy (see Eq. 8) of this model is given by

$$E_{T}^{PITB}\{\lambda\} = E_{O}' + E_{M}\{\lambda\} \quad . \tag{31}$$

b) Replacing the uniform truncated bulk electron density by the ground state electron density of the jellium system, $\rho^{O}(z)$, yields the <u>DL</u> model in which the total energy given in Eq. (31) is supplemented by the dipole-layer contribution, E_{pl} ,

$$E_{T}^{DL}\{\lambda\} = E_{O}' + E_{M}\{\lambda\} + E_{DL}\{\lambda\} .$$
 (32)

• c) Adding the Hartree energy, $E_{H}^{}$, to E_{T}^{DL} (Eq. 32) constitutes the <u>DLH</u> model,

$$E_{T}^{DLH} \{\lambda\} = E_{O}' + E_{M} \{\lambda\} + E_{DL} \{\lambda\} + E_{H} \{\lambda\}$$
 (33)

In this model the total energy is computed to first-order in the ionic pseudopotentials. This model is the electrostatic model investigated previously,¹⁰ sometimes referred to as the "frozen profile" model, since it does not include the response of the electrons to the presence of the ions. d) The next level of approximation is to include the $\vec{G} = 0$ contribution to the band-structure energy, E_{BS} (see Eq. 22). This is equivalent to a onedimensional treatment of the electron response obtained by averaging the ionic potentials over the layers. We include results for this <u>DLHBSO</u> model since this reduction in the dimensionality of the electron response has been employed in several previous studies.^{16,17} The total energy of this model is given by

$$E_{T}^{\text{DLHBSO}}\{\lambda\} = E_{T}^{\text{DLH}}\{\lambda\} + E_{\text{BS},\vec{G}=0}^{\text{C}}\{\lambda\} .$$
(34)

e) Finally, the model in which all contributions to second-order in the ionic pseudo-potentials are included is the <u>DLHBS</u> model. The total energy of this model is given by Eq. (8). This model retains the full three-dimensional nature of the system.

B. Results

Prior to a discussion of our results, we specify in Table I the material input parameters used in the calculations along with face-dependent crystallographic information. The parameters of the simplified Heine-Abarenkov pseudopotentials (Eq. 5) were taken after reference 15, where they have been chosen to fit the material lattice parameter and bulk modulus. We have verified that with this choice of pseudo-potential parameters the cohesive energy agrees to within 0.3% with experimental values. In addition they have been used¹⁵ in calculations of vacancy formation energies and volumes, yielding results in good agreement with experiments. Results for interlayer distance relaxation, $\Delta_{\ell,\ell+1} = (\lambda_{\ell+1} - \lambda_{\ell}) \times 100\%$, expressed in percent change of the interlayer distance from the bulk layer spacing value, d, for the low index faces of Na(bcc) and Al(fcc) as obtained via the various models are given in Tables II - IV. Negative and positive values of $\Delta_{\ell,\ell+1}$ correspond respectively to

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interlayer distance contraction and expansion. To demonstrate the effect of the number, n, of layers which are allowed to relax on the equilibrium structure we include results for several n values. In Tables II and III the results corresponding to the larger n value are those for which convergence with respect to increasing n_s has been obtained, with the exception of the results for Na(111) which are given in detail in Table IV. Results of previous calculations^{10,11,16,18,19} and those obtained via the analysis of experimental data are included in Tables II and III. In comparing to previous calculations it should be noted that with the exception of the electrostatic model,¹⁰ all others have considered single layer relaxation only. Also the inclusion of multilayer relaxation in the analysis of experimental data is a recent development. 2^{-6} From the inspection of the results in Tables II and III we note the tendency for larger relaxations at the more open faces (fcc(110) and bcc(111)). The necessity of allowing multilayer relaxation in each system and for all the theoretical models considered is clearly demonstrated. The multilayer relaxation results exhibit damped oscillatory relaxations, the period of the oscillations is equal to the period of the layer stacking sequence, np (see Table I).

The principal origin of the multilayer oscillatory relaxation lies in the 3D crystallinity of the system; i.e., in the intralayer structure and the registry shift between layers, and in the relation between intralayer structure and interlayer spacing. Thus the less open surfaces show smaller relaxations because the ions are more densely packed within the layer, i.e., the resulting potential has less variation both parallel and perpendicular to the surface plane since the layers are neutrally charged (ions plus negative background slab), and because the layer spacing is larger. These

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effects of crystallinity appear in the Madelung and bandstructure contributions: the Madelung force between adjacent unrelaxed (100) and (110) layers ($n_R = 2$) is attractive while the force between next nearest neighbor layers is repulsive, for (111) surfaces ($n_R = 3$) the interlayer forces oscillate with a period of 3 layers. The Madelung contribution is larger; the bandstructure terms reduce (screen) the Madelung interactions, but since the electron response is affected by the presence of the surface, this screening is complicated and gives rise to forces which are not simply related to the interlayer distances.

The dipole layer and Hartree energy terms also give rise to oscillatory forces on the layers. However, these forces come from single-ion potentials, i.e., potentials which depend on the position of an individual ion with respect to the bulk through the interaction with the jellium electron and positive background densities $\rho^{\circ}(z)$ and $\rho^{+}(z)$ (see also the discussion of single-ion potentials in Paper I). These forces, F_{DL} and F_{H} , are significant only for the topmost layer and, although they do oscillate due to the Friedel oscillations in $\rho^{\circ}(z)$, they approach zero rapidly as the z coordinate of the layer increases. The principle effect of the dipole layer and Hartree contributions is to limit the displacement of the first layer with respect to the bulk.

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To show the effect of incrementing n_s we choose the system of Na(111) which of all the systems studied exhibits the largest relaxations. We first note that in this system, even with $n_s = 9$, the layer spacings in the bottom of the surface region have not converged to the bulk value. However, increasing n_s from 6 to 9 does not substantially change the first three $(n_R = 3)$ layer spacings. We conclude that if n_s is a multiple of n_R , then the first $n_s - n_R$ layer spacings so obtained are reasonably close to the equilibrium values even though n_s is not large enough to obtain convergence of the deeper layer spacings to the bulk value. For this reason, and because

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the inclusion of the bandstructure energy is relatively costly in computer time, we have limited n_s to 6 in the DLHBSO and DLHBS model calculations for this, Na(111), system. In addition, it is improbable that analysis of experimental data will be able to accurately determine the layer spacings of such deep layers.

Also included in Table IV are results for the DL model, which are not included in Tables II and III. Note that the results of the DL model, which is an electrostatic model describing a system of point ions embedded in the Lang-Kohn electron density $\rho^{o}(z)$, qualitatively resemble the PITB model results, while the DLH model results are qualitatively closer to the results of the DLHBS model. Thus it is evident that a model in which the ions are treated as point ions is a poor approximation, and that the second-order (bandstructure, E_{BS}) effects are small compared to the first-order (Hartree, E_{H}) effects. Nevertheless, as will be discussed below, it is necessary to include the full 3D electron response properly in order to enable quantitative surface structure predictions to be made.

We turn now to a discussion of the results summarized in Tables II and III. Comparison of the results obtained via the PITB and DLH models shows that the inclusion of the dipole-layer and Hartree energies reduces overall the magnitude of relaxation. This reduction results from the interaction of the ions with the inhomogeneous surface electron density, which tends to fix the position of the first layer with respect to the bulk. In one case, Al(111), the inclusion of the Hartree term results in an outward displacement of the first layer and an expansion of the first interlayer spacing. In all other cases the Hartree force on the (unrelaxed) first layer is toward the bulk, thus does not oppose the Madelung force until the first layer is displaced inward.

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In this context we emphasize the cooperative nature of the multilayer relaxation, i.e., comparing results (Tables II - IV) obtained with increasing numbers, n_s , of layers participating in the relaxation, it is observed that the near-surface spacings change in response to the movement of added deeper layers. Comparison of the results obtained through the use of the electrostatic type of models (PITB and DLH) with those obtained via models which include electron screening (DLHBSO and DLHBS) demonstrates that the multilayer relaxation phenomena predicted by the simple electrostatic models does indeed occur when electron response is included. This observation resolves questions raised by several authors relating to multilayer relaxation.¹⁶,18

While certain qualitative features are revealed by the electrostatic model, from the comparison of the results obtained via the various models with values extracted from experimental data we conclude that <u>quantitative</u> structural predictions require a minimization of the complete total energy expression (Eq. 8) which retains the full 3D nature of the system, i.e., the DLHBS model. In particular, employment of the 1D electron response, DLHBSO, model, does not yield adequate results.

Further support to our conclusions regarding the importance of multilayer relaxation at metal surfaces is provided in Table V by the relaxation energies calculated using the DLHBS model for single (in parenthesis) and multilayer relaxation. The results demonstrate that the magnitude of the energy gained by relaxation is increased dramatically upon allowing for multilayer relaxation. In summary, we have derived an expression for the total energy of a semi-infinite simple metal which depends explicitly on the ionic positions. Using an efficient relaxation algorithm and the different models described in Section IVA, we have systematically studied the energetics underlying metal surface relaxation. From these studies we conclude that quantitative surface structural predictions require the use of the full total energy expression which maintains the 3D nature of the system and accounts properly for the inhomogeneous surface electron density and the response of the electronic system

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to the ionic positions (screening). Furthermore, the vital role of multilayer relaxation in achieving structural predictions in good agreement with experiment is clearly demonstrated by our results.

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Appendix A

4

In this appendix we derive expressions for $w_{ns}^{\lambda}(G,q_z)$ and $W_{ms}(G,q_z)$. The potential $w_n^{\lambda}(R,z)$ can be expressed in the form

$$w_n^{\lambda}(\mathbf{R}, \mathbf{z}) = \int d^2 \mathbf{R}' \int d\mathbf{z}' p_n^{\lambda}(\mathbf{R}', \mathbf{z}') V_c(|\vec{\mathbf{R}} - \vec{\mathbf{R}}'|, \mathbf{z} - \mathbf{z}')$$
(A1)

where e $p_n^{\lambda}(R,z)$ is some charge density (a local model pseudopotential can always be expressed in this form). From the definition of the symmetrized potential,

$$w_{ns}^{\lambda}(G,q_{z}) = \int d^{2}R \int dz \ p_{n}^{\lambda}(R,z) \left\{ \lim_{L \to \infty} \int dz' \cos(q_{z}z') \int d^{2}R' e^{i\vec{G}\cdot\vec{R}} v_{c}(|\vec{R}-\vec{R}'|,z'-z) \right\}$$
(A2)

We substitute

$$V_{c}(R,z) = \frac{1}{(2\pi)^{3}} \int dz \ e^{-ik_{z}z} \int d^{2}R \ e^{-i\vec{k}\cdot\vec{R}} \left[-4\pi e^{2}/(\kappa^{2}+k_{z}^{2})\right]$$

into Eq. (A2) to obtain

$$w_{ns}^{\lambda}(G,q_{z}) = \int d^{2}R \ e^{i\vec{G}\cdot\vec{R}} \int dz \ p_{n}^{\lambda}(R,z) \left\{ \lim_{L \to \infty} I(L,z;G,q_{z}) \right\} , \quad (A3)$$

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where

$$I(L,z;G,q_{z}) = \frac{1}{2\pi} \int dk_{z} \frac{-4\pi e^{2}}{2G} \left[\frac{1}{k_{z}-iG} - \frac{1}{k_{z}+iG} \right]$$

$$x \left\{ \frac{1}{k_{z}+q_{z}} \begin{bmatrix} e^{-ik_{z}(L-z)} & e^{-iq_{z}L} & e^{ik_{z}z} \end{bmatrix} + \frac{1}{k_{z}-q_{z}} \begin{bmatrix} e^{ik_{z}(L-z)} & e^{iq_{z}L} & e^{ik_{z}z} \end{bmatrix} \right\}$$

$$(A4)$$

The integral over k_z in Eq. (A4) is done by contour integration to give

$$I(L,z;G,q_z) = -\frac{4\pi e^2}{G^2 + q_z^2} \{2\cos(q_z z) - e^{-Gz}\} + \frac{4\pi e^2}{G^2 + q_z^2} \{(q_z/G) \sin(q_z L) - \cos(q_z L)\} e^{-G(L-z)}$$
(A5)

The second term in Eq. (A5) clearly vanishes in the limit L→∞ for all G \neq 0; with G = 0 this term is independent of z (and of R) and the density $p_n^{\lambda}(R,z)$ integrated over all space is zero. Thus there is no contribution to w_{ns}^{λ} from this second term of Eq. (A5) and Eq. (A3) becomes

$$w_{ns}^{\lambda}(G,q_z) = -\frac{4\pi e^2}{G^2 + q_z^2} \int dz \int d^2 R \ e^{i\vec{G}\cdot\vec{R}} p_n^{\lambda}(R,z) \ [2\cos(q_z z) - e^{-Gz}] \ . \tag{A6}$$

The density $p_n^{\lambda}(R,z)$ is given by

$$p_n^{\lambda}(\mathbf{R},z) = p(\mathbf{R},z-z_n^{\lambda}) - (N_A \Omega_o)^{-1} \left[\theta(z-z_o-(n-1)d) - \theta(z-z_o-nd)\right] \quad (A7)$$

where p(R,z) is the density which gives rise to the ionic pseudopotential V_p , so that $V_p(G,q_z) = [-4\pi e^2/(G^2+q_z^2)] p(G,q_z)$. The 3D Fourier transform of the pseudopotential used in our calculations, Eq. (5), is

$$V_{p}(G,q_{z}) = [-4\pi Ze^{2}/(G^{2}+q_{z}^{2})][(1-u_{c}) \cos([G^{2}+q_{z}^{2}]^{1/2}r_{c})$$
(A8)
+ $u_{c} \sin([G^{2}+q_{z}^{2}]^{1/2}r_{c})/([G^{2}+q_{z}^{2}]^{1/2}r_{c}).$

Substituting Eq. (A7) into Eq. (A6) yields finally the expression for $w_{ns}^{\lambda}(G,q_z)$, $w_{ns}^{\lambda}(G,q_z) = V_p(G,q_z) 2\cos(q_z z_n^{\lambda}) + (1-\delta_{\overrightarrow{G},\overrightarrow{0}}) [4\pi Ze^2/(G^2+q_z^2)] e^{-Gz_n^{\lambda}}$ (A9) $+ \delta_{\overrightarrow{G},\overrightarrow{0}}(4\pi Ze^2/q_z^2) 2\cos(q_z [z_0+(n-\frac{1}{2})d]) \sin(q_z d/2)/(q_z d/2)$. From the definition of $W_{ms}(G,q_z)$ and Eq. (A9) we have

$$W_{ms}(G,q_{z}) = \lim_{N \to \infty} \left\{ [V_{p}(G,q_{z}) + \delta_{\vec{G},\vec{0}}(4\pi Ze^{2}/q_{z}^{2}) \sin(q_{z}d/2)/(q_{z}d/2)] \\ \times 2 \sum_{\ell=1}^{N} \cos(q_{z}[z_{0} + (2\ell n_{R} + 2m - 3)d/2]) \\ + (1 - \delta_{\vec{G},\vec{0}}) [4\pi Ze^{2}/(G^{2}+q_{z}^{2})] 2 \sum_{\ell=1}^{N} e^{-G[z_{0} + (\ell_{R}+m-3/2)d]} \right\}.$$
(A10)

The sums over ℓ in Eq.(A10) can be done. We use the identity

$$\lim_{N \to \infty} \frac{\sin(Nq_z n_R^d)}{\sin(q_z n_R^d/2)} = \sum_{g_z} \frac{2\pi}{n_R^d} \delta(q_z - g_z) \cos(g_z n_R^d/2)$$
(A11)

where $g_z = m(2\pi/n_R^d)$, $m = 0, \pm 1, \pm 2, \ldots$, giving finally the expression for $W_{ms}(G,q_z)$,

$$W_{ms}(G,q_{z}) = [V_{p}(G,q_{z}) + \delta_{\vec{G},\vec{0}} (4\pi Ze^{2}/q_{z}^{2}) \sin(q_{z}d/2)/(q_{z}d/2)]$$

$$x \left\{ \cos(q_{z}[z_{o}+(2m-n_{R}-1)d/2]) \frac{2\pi}{n_{R}d} \sum_{g_{z}} \delta(q_{z}-g_{z}) \cos(g_{z}n_{R}d/2) - \sin(q_{z}[z_{o}+(2m-n_{R}-1)d/2]) [\sin(q_{z}n_{R}d/2)]^{-1} \right\}$$

$$+ (1 - \delta_{\vec{G},\vec{0}}) \frac{4\pi Ze^{2}}{g^{2}+q_{z}^{2}} e^{-G[z_{o}+(2m-1)d/2]}/[1 - e^{-Gn_{R}d}]. \quad (A12)$$

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Table I

Input parameters: r_s is the electron density parameter, Z is the valence, r_c and u_c are the pseudopotential core radius and level parameters, a is the lattice constant; A_o and d are the 2D unit cell area and bulk interlayer distance; \vec{b}_1 and \vec{b}_2 are the 2D reciprocal lattice primitive translation vectors; n_R is the repeat period of the layer stacking sequence, and $\Delta \vec{R}$ is the shift in the origin of the 2D lattice of adjacent layers.

metal	surface	A	d.	₿ 1	₿ ₂	n R	۵Ř
Al - fcc		·		· ·			
r _s = 2.064a _o	(001)	$\frac{a^2}{2}$	<u>a</u> 2	$\frac{2\pi}{a}$ (110)	$\frac{2\pi}{a}$ (110)	2	$\frac{a}{2}$ (100)
Z = 3					,		
$r_{c} = 1.388a_{o}$	(110)	$\frac{a^2}{\sqrt{2}}$	$\frac{a}{2\sqrt{2}}$	$\frac{2\pi}{a}$ (001)	$\frac{2\pi}{a}$ (110)	2	$\frac{a}{4}$ (112)
$u_{c} = .3894$							
$a = (16\pi Z/3)^{1/3} r_s$	(111)	$\frac{\sqrt{3a^2}}{4}$	<u>a</u> √3	$\frac{4\pi}{3a}$ (121)	$\frac{4\pi}{3a}$ (112)	3	$\frac{a}{6}$ (211)
Na - bcc				•			
r = 3.931a _o	(001)	a ²	<u>a</u> 2	$\frac{2\pi}{a}$ (100)	$\frac{2\pi}{a}$ (010)	2	<u>a</u> (110)
$\mathbf{Z} = 1$					• · · · •		
$r_{c} = 2.076a_{o}$	(110)	$\frac{a^2}{\sqrt{2}}$	<u>a</u> √2	$\frac{\pi}{a}$ (110)	$\frac{2\pi}{a}$ (110)	2	<u>a</u> (001)
$u_{c} = .3079$							
$a = (8\pi Z/3)^{1/3} r_{s}$	(111)	$\sqrt{3a}^2$	 2√3	$\frac{2\pi}{a}$ (121)	$\frac{2\pi}{a}$ (112)	3	a/3 (211)

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Table II

Summary of the surface relaxation results for the low index surfaces of Na obtained using the PITB, DLH, DLHBSO, and DLHBS models (see text); available experimental results and the results of other calculations are given in the columns labeled Exp. and Other, respectively. The results are presented as the percent change from the bulk value, $\Delta_{\ell,\ell+1}$, of the spacing between the layers numbered ℓ and $\ell + 1$. Negative (positive) values of $\Delta_{\ell,\ell+1}$ indicate contraction (expansion) of the layer spacing. n_s is the number of layers which were allowed to relax (the results of other calculations, in the last column, are all for single layer relaxation).

mo	del:	PITB	DLH	DLHBSO	DLHBS	EXP	Other
n s	<u></u>						
1	Δ ₁₂	- 7.0	-1.4	1.2	-3.6		$\Delta_{12} = -2$
4	Δ ₁₂	-10.8	-1.9	4	-2.7		(ref. 18)
	Δ ₂₃	4.0	0.7	1.2	0.7	•	$\Delta_{12} = +1$
	∆ ₃₄	-1.2	3	0.4	-1.0		(ref. 16)
	∆ ₄₅	0.2	0.1	0.4	.8	· .	
ns				[Na(110)]		
1	Δ ₁₂	7	3	1.0	1	×	$\Delta_{12} = 0$
3	Δ ₁₂	7	2	0.1	2	$\Delta_{12} = 0$	(ref. 18)
	[∆] 23	0.0	1	0.2	0.1	(ref. 21)	$\Delta_{12} = -5$
	[∆] 34	0	0	0.8	0.0		(ref. 16)
n s				[Na(111)]		
1	Δ ₁₂	-34	-13	-10	-20		$\Delta_{12} = -12.5$
6	Δ ₁₂	-63	2	4	-8		(ref. 16)
	[∆] 23	-10	-32	-32	-29		
	∆ ₃₄	46 、	25	24	23		
	۵ ₄₅	-30	-1	0	-2		
	۵ 56	5	-11	-12	-11		
	Δ ₆₇	3	6	10	8		

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тa	υ	Te	Ŧ	т	Τ.

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Summary of the surface relaxation results for the low index surfaces of Al. See the caption of Table II.

mod	lel:	PITB	DLH	DLHBSO	DLHBS	Exp	Other
n s				[A&()	100)]		
1	^Δ 12	-2.1	0.3	1.0	7		$\Delta_{12} = -7.5$
3	Δ ₁₂	-2.4	0.4	1.0	0.0	$\Delta_{12} = 0$	(ref. 16)
	[∆] 23	0.3	0.0	0.7	0	(ref. la)	$\Delta_{12} = -4.6$
	∆ ₃₄	0	0	1	0		(ref. 11)
ns			-	[A&(]	110)]		
1	Δ ₁₂	-11	-4	-5	-14	· .	Δ ₁₂ < -15
4	Δ ₁₂	-26	-12	-14	-10	$\Delta_{12}^{=-8.4+.8},$	(ref. 16)
	[∆] 23	15	8	9	4	[∆] 23 ^{=4.9<u>+</u>1.,}	$\Delta_{12} = 2.0$
	[∆] 34	-7	-4	-2	-3	$\Delta_{34}^{=-1.6+1.1},$	(ref. 19)
	۵ ₄₅	2	1	2	0	(ref. 2)	$\Delta_{12} = -16$
		_ .	_ 				(ref. 11)
n s				[Al(]	111)]		
1	۵ ₁₂	4	0.8	1.9	1.8	Δ ₁₂ =.9 <u>+</u> .5	$\Delta_{12} = 1$
3	Δ ₁₂	4	0.9	0.7	1.6	(ref. 20)	(ref. 16)
	[∆] 23	0.0	1	1	0.1	Δ ₁₂ =2.5	$\Delta_{12} = -1.6$
	∆ ₃₄	0	0.0	0.1	0.0	(ref. la)	(ref. 11)

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Table IV

The effect of incrementing the number of layers allowed to relax, n_s , on the interlayer spacings for Na(111). See also the caption of Table II.

mode	21:	PITB	DL	DLH	DLHBSO	DLHBS
n s	_		[Na(11	1)]		
1	Δ ₁₂	-34	-42	-13	-10	-20
2	Δ ₁₂	-56	-57	-9	5	-10
	∆ 23	15	10	-2	-5	-10
3	Δ ₁₂	-49	-45	0	1	8
	[∆] 23	-6	- 32	-24	-27	-26
	∆ ₃₄	15	30	13	20	17
4	Δ ₁₂	-56	-58	-3	1	-10
	[∆] 23	-14	-42	-26	-29	-25
	[∆] 34	40	65	23	25	22
	[∆] 45	-17	-23	-7	5	-7
6	Δ12	-63	-63	2	4	8
	Δ ₂₃	-10	-42	-32	-32	-29
	[∆] 34	46	73	25	24	23
	[∆] 45	- 30	-33	-1	0	-2
	[∆] 56	5	-5	-11	-12	-11
	[∆] 67	3	10	. 6	.10	8
9	Δ ₁₂	-67	-69	3		
	[∆] 23	-10	-43	-35		
	[∆] 34	53	84	27		
	[∆] 45	-40	-46	-0		
	[∆] 56	6	-7	-15		
	Δ ₆₇	18	34	12		
	Δ ₇₈	-18	-23	-1		
	Δ ₈₉	6	4	-5		
	Δ 91 0	0	2	3		

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Table V

Change in surface energy, $\Delta E_{SR} (R_y/2D$ unit cell), resulting from surface relaxation in the DLHBS model. The value in parenthesis is the result for single layer relaxation.

(100)	Na (110)	(111)	(100)	Al (110)	(111)
-2.7x10 ⁻⁴	-1.3×10^{-6}	-3.7×10^{-3}	-3.4×10^{-4}	-3.4×10^{-2}	-3.2×10^{-3}
(-2.2x10 ⁻⁴)	(-1.6×10 ⁻⁷)	(-2.5 \times 10^{-3})	(-6.8×10 ⁻⁵)	(-2.6×10 ⁻²)	(-3.1 \times 10^{-3})

Multilayer Relaxation of Interlayer Registry and Spacing at High-Index Metal Surfaces

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Abstract

Oscillatory multilayer relaxation of both interlayer spacing and registry at certain high index metal surfaces is predicted via minimization of a simple model for the total energy of a semi-infinite crystal. Results for the (210) and (211) surfaces of bcc and fcc simple metals indicate that the relaxation parallel to the surface plane moves the surface layers toward more symmetrical configurations with respect to adjacent layers.

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Theoretical predictions 1, 2, 3 and recent analysis of LEED data 4 have revealed damped oscillatory relaxations of the interlayer distances for the low index surfaces of several materials. While quantitative agreement (see results for Al (110) in reference 1,2) between the theoretical predictions based on minimization of total energy of the semi-infinite crystal required the inclusion of a realistic treatment of the electronic response to variations in the atomic positions, the qualitative features of the multi-layer relaxation phenomena were described already at the level of a "frozen profile" model³ (see also ref. 1,2) where band-structure contributions to the total energy are neglected. Motivated by these results and by the interest which they have created we embarked upon investigations of the structure of more open (higher index) surfaces of fcc and bcc simple metals. The major prediction resulting from our studies is that these less symmetrical surfaces undergo multilayer oscillatory interlayer registry relaxation (which may be termed (1X1) reconstruction) in addition to multilayer oscillatory relaxation of interlayer spacings. These results are obtained via minimization of the total energy expression which depends explicitly upon the atomic positions, with three-dimensional relaxations (with no change of the 2D unit cell) allowed. Following a brief description of the physical model we present results for the (211) and (210) surfaces of Na (bcc) and Al (fcc).

To facilitate our discussion we specify the position of the ith ion in layer 1 by

$$\vec{r}_{1,\ell} = \vec{R}_1 + \ell \Delta \vec{R} + \alpha_{1,\ell} \vec{A}_1 + \alpha_{2,\ell} \vec{A}_2 + [z_0 + (\ell - \frac{1}{2} + \lambda_{\ell})d]\hat{z}, \quad (1)$$

$$\ell = 1, 2, ...$$

-1-

where the capital letters are 2D vectors in the surface (x-y) plane, and \hat{z} . is a unit vector perpendicular to the surface plane and directed into the semi-infinite crystal; \vec{R}_i describes the 2D lattice of a layer, $\vec{R}_i = i_1 \vec{A}_1$ + $i_2 \vec{A}_2$ where i_1 and i_2 are integers, \vec{A}_1 and \vec{A}_2 are the 2D primitive translation vectors, $\Delta \vec{R}$ is the shift in origin (registry shift) between the 2D lattices of adjacent layers, and d is the bulk layer spacing. The quantities \vec{A}_1 , \vec{A}_2 , d, and $\Delta \vec{R}$ are given in Table I for fcc and bcc (211) and (210) surfaces.⁵ The difference between the equilibrium and truncated bulk location of the ions in layer ℓ is given by

$$\vec{\Delta r}_{\ell} = \alpha_{1,\ell} \vec{A}_{1} + \alpha_{2,\ell} \vec{A}_{2} + \lambda_{\ell} d\hat{z} .$$

To find the equilibrium configuration of the semi-infinite metal is is necessary to minimize the total energy with respect to $\alpha_{1,\ell}^{\alpha}$, $\alpha_{2,\ell}^{\alpha}$, and λ_{ℓ}^{α} for all $\ell > 0$. We assume that $\Delta \dot{r}_{\ell} = \vec{0}$ for $\ell > N_s$ and use the method of steepest descent² to minimize the total energy in this configuration space.

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To obtain the results discussed in this paper we have used two models for the total energy of the system, both models neglect the response of the conduction electrons to changes in ionic positions and thus are electrostatic, or "frozen profile", models.^{3,1,2} The simplest model is the <u>PITB model</u> in which the ions are represented by point positive charges and the conduction electron density is simply a truncated uniform bulk density, i.e., $\rho^{e}(z) = \rho^{+}(z) \equiv (3/4\pi r_{s}^{3}) \theta(z-z_{o})$ where r_{s} is the electron density parameter. The total energy in the PITB model is

$$E_{T}^{PITB}(\{\alpha_{1\ell}\},\{\alpha_{2\ell}\},\{\lambda_{\ell}\}) = E_{o}^{TB} + E_{M}(\{\alpha_{1\ell}\},\{\alpha_{2\ell}\},\{\lambda_{\ell}\})$$
(2)

-2-

where E_0^{TB} is the energy of the conduction electrons in the presence of a neutralizing positive background density $\rho^+(z)$, and E_M is the Madelung energy, i.e., the electrostatic energy of point ions in the presence of a neutralizing negative background ($\rho^+(z)$).

In the second model, the <u>DLH model</u>, the conduction electron density, $\rho^{e}(z)$, is taken to be the Lang-Kohn⁶ "jellium" system ground state density, and the interaction of the ions with this electron density is obtained using the local form of the Heine-Abarenkov model pseudopotential (pseudopotential parameters are given in ref. 1). The total energy in the DLH model is

$$E_{T}^{DLH}(\{\alpha_{1\ell}\},\{\alpha_{2\ell}\},\{\lambda_{\ell}\}) = E_{o}^{LK} + E_{DL}(\{\lambda_{\ell}\}) + E_{H}(\{\lambda_{\ell}\}) + E_{M}(\{\alpha_{1\ell}\},\{\alpha_{2\ell}\},\{\lambda_{\ell}\})$$
(3)

where E_o^{LK} is the jellium system electronic ground state energy, E_{DL} is the interaction of point ions with the "surface dipole layer", i.e., with $(\rho^e(z) - \rho^+(z))$, and E_H is the Hartree energy which together with E_{DL} constitutes the first-order correction to the jellium system energy, E_o^{LK} , due to replacing the positive background with the ionic pseudopotentials.^{1,2}

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Results obtained from the DLH model relaxation-(1x1) reconstruction calculations for the (211) and (210) surfaces of Na and AL are presented in Tables II and III, respectively. These results were obtained with the number of layers in the surface region, N_s, equal to the layer stacking sequence period, N_R. We find that, as in the relaxation results for low index surfaces, ¹⁻³ multi-layer oscillatory shifts in the ionic positions occur. Since calculations performed with several values of N_s < N_R have shown a dependence of the relaxed configuration on N_s, a multi-layer calculation is necessary to get reliable results. In general, the inter-layer registry relaxation brings the near surface layers into a more symmetric position with respect to adjacent layers. Although the relaxation-reconstruction parameters $\alpha_{1\ell}$, $\alpha_{2\ell}$, and λ_{ℓ} have not in all cases converged to zero near the bottom of the surface region $(\ell = N_s)$, the near surface layer results are not significantly affected when N_s is decreased by one or two layers.

In the PITB model the relaxed configuration is independent of material properties (density, ion valence Z, and pseudopotential parameters), and depends only on the crystal structure (fcc or bcc). Results obtained from the PITB model are not presented due to space limitations. In general, the relaxation in this model is much larger than the DLH model results but the qualitative nature of the relaxed configuration is the same. Thus it is shown that, as in the case of normal relaxation of low index surfaces, 1-3 the Madelung energy term is primarily responsible for establishing the trends. The principal combined effect of the dipole-layer and Hartree terms is to reduce the magnitude of the (inward) displacement of the surface layer. Thus, through coupling between layers and between the surface normal and parallel displacements, all components of $\Delta \hat{r}_{k}$ for each layer are reduced by the inclusion of the dipole-layer and Hartree terms.

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A further improvement of the model will consist of the inclusion of electron response contributions. However, in our previous systematic study of normal relaxations of low index surfaces^{1,2} we found that the neglect of electron response did not significantly effect the principal relaxation trends. Indeed, after the completion of the work reported here, we have been kindly provided with the results of a LEED analysis of the Fe (211) surface in which similar relaxation-reconstruction trends were found.⁷

We gratefully acknowledge H. L. Davis for suggesting the investigation of the open surfaces.

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Table Captions

- Table I. Surface structure parameters: \vec{A}_1 and \vec{A}_2 are the 2D primitive translation vectors, d is the distance between adjacent layers, $\Delta \vec{R}$ is the registry shift between consecutive layers, a is the cubic cell edge length, and N_R is the layer stacking sequence period.
- Table II. Relaxation/reconstruction results of the DLH model for Na (211) and (210) surfaces. The change in position of ions in layer ℓ is given by $\delta \vec{r}_{\ell} = \alpha_{1,\ell} \vec{A}_{1} + \alpha_{2,\ell} \vec{A}_{2} + \lambda_{\ell} d\hat{z}$. The quantities $\Delta \alpha_{1,\ell}$, $\Delta \alpha_{2,\ell}$, and $\Delta \lambda_{\ell}$ give the relative shift in the positions of ions in adjacent layers, defined by $\Delta \alpha_{1,\ell} = [\alpha_{1,\ell+1} - \alpha_{1,\ell}] \times 100\%$, etc. In each case the number of layers included in the surface region and allowed to relax is equal to the layer stacking sequence period, i.e., $N_s = N_R$.
- Table III. Relaxation/reconstruction results of the DLH model for AL (211) and (210) surfaces. See the caption for Table II.

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	bcc (211)	fcc (211)
1	√2 a x̂	$\frac{1}{\sqrt{2}}$ a $\hat{\mathbf{x}}$
2	$-\frac{1}{2}\sqrt{3} a \hat{y}$	- √3 a ŷ
1	a/√6	a/2√6
Ŕ	$\frac{1}{2}\vec{A}_1 + \frac{2}{3}\vec{A}_2$	$\frac{1}{2}\vec{A}_1 + \frac{1}{3}\vec{A}_2$
R	6	6
	bcc (210)	fcc (210)
, A1	a x̂	a x
• •	- √5 a ŷ	$-\frac{1}{2} = \hat{x} - \frac{1}{2} \sqrt{5} = \hat{y}$
d	a/2√5	a/2√5
۵Ř	$\frac{1}{2} \vec{A}_1 + \frac{7}{10} \vec{A}_2$	$\frac{7}{10} \vec{A}_1 + \frac{2}{5} \vec{A}_2$
N _R	10	10

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TABLE I

layer(l)	^α 1,ℓ	^α 2, l	λ _e	^{Δα} 1, ε ^(%)	Δα _{2, ℓ} (%)	۵۶ ککر (%)
			Na (1	211)		
1	0	.009	.115	0	-10.8	-21.1
2	0	100	096	0	11.9	16.0
3	0	.019	.064	0	-5.6	-11.1
4	0	037	047	0	4.6	7.6
5	0	.009	.029	0	-2.2	-4.5
6	0	013	016	0	1.3	1.6
			Na (3	210)		
1	0	.011	.513	0	-4.0	-41.1
2	0	029	.102	0	.7	-65.4
3	0	022	552	0	4.1	88.3
4	0	.019	.331	0	-2.1	-31.2
5	0	003	.019	0	3	-29,9
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TABLE II

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layer(£)	^α 1,٤	°2,1	λe	Δα _{1,ℓ} (%)	Δα2, ε (%)	Δλ _ℓ (%)
			AL	(211)		
1.	0	017	.449	0	4.0	-57.7
2	0	.023	128	0	-3.1	-15.6
3	0	009	284	0	1.0	51.4
4	0	.001	.230	0	0.9	-28.2
5	0	.010	052	0	-1.5	-1.4
6	0	004	065	0	.4	6.5
			Al	(210)		- <u> </u>
w						
L	.021	.042	.232	5	-1.0	-27.7
2	.016	.032	045	-2.0	-4.0	-10.2
3	004	008	147	0.7	1.5	25.9
ł	.003	.006	.112	2	4	-12.8
5	.001	.002	016	4	8	-2.4
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TABLE III

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B.3 <u>Surface Segregation</u>

Surface segregation in simple metal random binary alloys was studied via an electronic theory based on local ionic psuedopotentials and a linear electron response model appropriate for semi-infinite systems. Segregation of the larger species ions to the surface layer and (in most cases) a non-monotonic layer concentration profile are predicted. The segregation of the larger species ions to the surface layer is driven by single-particle terms (Hartree energy terms) in the total energy expansion. These single-particle energy terms are independent of coordination number and relative positions of the ions but depend on the position of the surface layer relative to the inhomogenious zeroth-order electron density at the metal surface, thus giving rise to crystal face specificity. The concentration in deeper layers is determined primarily by effective interionic interactions. The electronic theory was compared with a nearest-neighbor pair-bond model, and it is concluded that the pair-bond model is not applicable to surface segregation in simple metal alloys. The alloys considered in this work are composed of the alkali metals K, Rb, and Cs. Concentration profiles as functions of temperature are presented for the (100) and (110) surfaces.

In current studies the theory is extended to bon-homovalent alloys (A&-Ca, A&-Mg and A&-Li) of technological interest. In addition local ordering and effects due to elastic lattice distortions are investigated using analytical and molecular dynamics methods. -

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Surface segretation in simple metal alloys:

an electronic theory

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ABSTRACT

Surface segregation in simple metal random binary alloys is studied via an electronic theory based on local ionic psuedopotentials and a linear electron response model appropriate for semi-infinite systems. Segregation of the larger species ions to the surface layer and (in most cases) a nonmonotonic layer concentration profile are predicted. The segregation of the larger species ions to the surface layer is driven by single-particle terms (Hartree energy terms) in the total energy expansion. These singleparticle energy terms are independent of coordination number and relative positions of the ions but depend on the position of the surface layer relative to the inhomogenious zeroth-order electron density at the metal surface, thus giving rise to crystal face specificity. The concentration in deeper layers is determined primarily by effective interionic interactions. The electronic theory is compared with a nearest-neighbor pair-bond model, and it is concluded that the pair-bond model is not applicable to surface segregation in simple metal alloys. The alloys considered in this paper are composed of the alkali metals K, Rb, and Cs. Concentration profiles as functions of temperature are presented for the (100) and (110) surfaces.

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I. Introduction

Surface segregation is the enrichment of the concentration one component at the surface of an alloy. This phenomena is of great interest since the surface composition affects a number of properties such as oxidation and corrosion, catalysis, chemisorption, wear, and electrical and mechanical properties of thin films. Recent experiments, employing modern surface science techniques such as Auger electron spectroscopy,¹ ultraviolet photoelectron spectroscopy,² x-ray photoemission spectroscopy³, low energy ion scattering,⁴ and atom-probe field-ion microscopy⁵ have provided a wealth of detailed information on surface segregation systems. These studies present evidence for a dependence of the surface composition on bulk composition, surface crystallography, and temperature. In some cases multilayer segregation and a non-monotonic concentration profile⁵ (i.e. oscillations in the composition as **a** function of depth) are indicated.

The possibility of surface segregation was predicted first by Gibbs⁶ using thermodynamic arguments where the reduction of the surface energy serves as the driving force. More recent theories are of the pair-bond type⁷ in which surface bond breaking provides the driving force, and some theories include strain energy due to a mismatch in the atomic sizes⁸ in which case minimization of the bulk strain energy provides an additional driving force. Recently there have also been several efforts to develop electronic theories of surface segregation in transition-metal alloys based on the tight-binding approximation⁹. A different approach is that of Muscat¹⁰ in which a cluster of muffin-tin potentials is embedded at the surface or bulk of a free-electron gas; it was found in this study that the presence of the surface potential, rather than the number, positions, or species of neighboring atoms, plays the dominant role in surface segregation.

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Theoretical treatment of alloy systems using band-structure or density functional methods, sometimes in conjunction with the coherent potential approximation and its variants, have in general been employed for calculation of the electronic densities of states of nonperiodic solids.¹¹ The application of these methods to calculations of formation energies of bulk alloys is quite difficult.¹² Furthermore the use of these methods in studies of surface properties of metal alloy systems is prohibitively complex, particulary for disordered systems. Thus it is desirable to construct a theoretical formulation which would allow systematic studies of surface properties and the physical origins of segregation in such systems. In the case of simple metal (sp bonded) alloys, pseudo-potential theory in conjunction with linear response, or second-order perturbation theory, has been applied with notable success in calculations of bulk alloy formation energies (heats of mixing):¹³

The purpose of this paper is to present an electronic theory of surface segregation in simple, i.e. sp bonded, metals. Our theory is based on the use of local ionic psuedopotentials and a linear response model appropriate for a semi-infinite metal.¹⁴ The formalism is given in section II, and in section III we present and discuss the results (layer composition v.s. temperature for different bulk compositions) and compare the predictions of our theory with those of a simple pair-bound type theory. We find that the dominant factors which determine the composition of the surface layer are "single-particle" terms, i.e. terms in the total energy expansion which depend on the position and species of an individual atom with respect to the inhomogenous electron gas density in the surface region. In this respect our results are similar to those of Muscat¹³ mentioned above. However, the composition of succeeding layers is determined primarily by interionic

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interactions, and in some cases we find a non-monotonic concentration profile. The larger species always segregates to the surface layer, segregation is greater for (100) than for (110) surfaces, and depends on temperature and bulk composition. The present study is limited to homovalent alloys consisting of the alkali metals K, Rb, and Cs. Work now in progress will deal with more technologically important (and more difficult to treat theoretically) simple metal alloys such as Al-Li, Al-Mg, etc. In addition, we do not consider effects due to elastic strain and/or surface relaxation. These issues as well as local ordering effects will be discussed elsewhere.

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II A. General formulation

Consider a semi-infinite solid solution composed of A and B atoms. The average concentration of species A is \bar{x} , and the concentration in the nth crystalline layer parallel to the surface is $x_n = \bar{x} + \Delta x_n$. The total (ground state) energy of the system will depend on layer concentrations, $E_T = E_T(\bar{x}, \{\Delta x_n\})$. The heat of mixing is defined to be the difference between the total energy of the solid solution and that of a mechanical mixture of the pure species, ¹⁵

$$H_{m}(\bar{x}, \{\Delta x_{n}\}) = E_{T}(\bar{x}, \{\Delta x_{n}\}) - \bar{x} E_{T}(\bar{x} = 1) - (1 - \bar{x}) E_{T}(\bar{x} = 0).$$
(1)

The free energy of mixing can be approximated by

$$\mathbf{F}_{\mathbf{m}}(\mathbf{T},\bar{\mathbf{x}},\{\Delta\mathbf{x}_{n}\}) = \mathbf{H}_{\mathbf{m}}(\bar{\mathbf{x}},\{\Delta\mathbf{x}_{n}\}) - \mathbf{TS}_{\mathbf{m}}(\bar{\mathbf{x}},\{\Delta\mathbf{x}_{n}\})$$
(2a)

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where T is the temperature, and

$$S_{m}(\bar{x},\{\Delta x_{n}\}) = -k_{B} \sum_{n} \left[(\bar{x}+\Delta x_{n})\ln(\bar{x}+\Delta x_{n}) + (1-\bar{x}-\Delta x_{n})\ln(1-\bar{x}-\Delta x_{n}) \right]$$
(2b)

is the ideal entropy of mixing of the solid solution. In writing Eqs. (2) we have neglected any excess vibrational energy and entropy and we have assumed that the arrangement of species A and B within a given layer is completely random.

The equilibrium concentration profile is found by minimizing the free energy with respect to layer concentrations, subject to the constraint that the average concentration, \bar{x} , does not change. We define a surface region consisting of N_s layers, and require the concentration to be uniform outside this region, i.e.

$$\mathbf{x}_{n} = \bar{\mathbf{x}} + \Delta \mathbf{x}_{n} \text{ for } 1 \leq n \leq N_{s}, \qquad (4a)$$

$$\mathbf{x}_{n} = \bar{\mathbf{x}} + \Delta \mathbf{x}_{b} \text{ for } \mathbf{N}_{s} + 1 \leq n \leq \mathbf{N}_{L}$$
(4b)

where $N_{\rm L}$ is the total number of layers (the limit $N_{\rm L} \rightarrow \infty$ will be taken). The constraint is

$$\Delta x_{b} = - (N_{L} - N_{s})^{-1} \sum_{n=1}^{N_{s}} \Delta x_{n}$$
 (5)

The N $_{\rm S}$ coupled differential equations which determine the equilibrium configuration (layer concentration profile) are

$$\frac{\partial F_{m}}{\partial \Delta x_{n}} - (N_{L} - N_{s})^{-1} \frac{\partial F_{m}}{\partial \Delta x_{b}} = 0, \ 1 \le n \le N_{s}$$
 (6)

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II B. Psuedopotential-linear response formulation

The calculation of the surface concentration profile from Eq. (6) requires an expression for the total energy which depends explicitly on the atomic species and their concentration in the surface region layers and in the bulk. We have previously obtained an expression for the total energy of a semiinfinite simple metal using local model ionic psuedopotentials and linear response theory.¹⁴ In this section we will outline the theory presented in ref. 14 and apply it to the surface segregation problem.

The semi-infinite metal is represented by an interacting electron gas in the presence of a truncated neutralizing positive background (jellium model), to which we add a term which replaces the jellium positive background by a lattice of discrete ions. The electronic Hamiltonian is written as

$$H = H^{o} + \sum_{i} w_{i}$$
(7)

where H° is the many-body Hamiltonian of the electron-jellium system; the ground state energy, E° , and electron density, $\rho^{\circ}(\vec{r})$, of the semi-infinite electron-jellium system are given in the seminal study by Lang and Kohn.¹⁶ The potentials associated with individual ions, $w_i(\vec{r})$, are given by

$$w_{i}(\vec{r}) = V_{p}(\beta_{i}; | \vec{r} - \vec{r}_{i}|) - N^{-1} Z(\beta_{i}) V_{i}(\vec{r})$$
 (8)

where β_i is the species of the ion at position \vec{r}_i , $V_p(\beta,r)$ and $Z(\beta)$ are the bare ionic psuedopotential and valence charge, respectively, of the ion of species β , $N = \Sigma_i Z(\beta_i)$ is the total number of conduction electrons, and $V_+(\vec{r})$ is the potential due to the neutralizing positive background charge. Thus, $w_i(\vec{r})$ is a neutral perturbation which results from replacing a part of the positive background with an individual ion at site \vec{r}_i .

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Using the coupling constant integration method and assuming linear response, the total energy of the semi-infinite metal is given by 14

$$E_{T} = E^{o} + \sum_{i} \int d^{3}r \rho^{o}(\vec{r}) w_{i}(\vec{r})$$
$$+ \frac{1}{2} \sum_{i,j} \int d^{3}r \rho_{i}(\vec{r}) w_{j}(\vec{r}) + E_{M}$$
(9)

where $\rho_{i}(\vec{r})$ is the screening electron density induced by the potential $w_{i}(\vec{r})$, and E_{M} is the Madelung energy of the ions. The major task in evaluating E_{T} for an arbitrary arrangement of ions of different species is to obtain a self-consistent solution for the screening electron densities, $\rho_{i}(\vec{r})$. Linear response theory yields¹⁴ a pair of coupled integral equations

$$\phi_{i}(\vec{r}) = \int d^{3}r' \alpha_{o}(\vec{r},\vec{r}') [w_{i}(\vec{r}') + \phi_{i}(\vec{r}')], \qquad (10a)$$

$$\phi_{i}(\vec{r}) = \int d^{3}r' [1 - G(\vec{r}, \vec{r}')] \rho_{i}(\vec{r}') e^{2} / |\vec{r} - \vec{r}'| \qquad (10b)$$

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where $\alpha_{0}(\vec{r},\vec{r}')$ is the RPA response function and $\phi_{1}(\vec{r})$ is the self-consistent effective potential due to $\rho_{1}(\vec{r})$, which includes exchange-correlation effects through the local field correction G (\vec{r},\vec{r}') .^{17,14} In our calculations we use the infinite barrier response model developed in ref.14, i.e. α_{0} is the RPA response function for a free electron gas confined to the half-space $z \geq 0$ and the local field correction G (\vec{r},\vec{r}') is approximated by G $(|\vec{r}-\vec{r}'|)$. The details of this response model are dicussed in ref 14. This response model has also been used to predict the relaxed structure of the low index surfaces of Al and Na¹⁸, yielding good agreement with available experimental results including multilayer relaxation in Al(110).

For notational convenience the layer positions are given by

$$z_n = z_0 + (n - \frac{1}{2})d, \quad n = 1, 2, \dots$$
 (11)

where $z_0 = 3\pi/8k_F$, $\hbar k_F$ is the Fermi momentum, and d is the interlayer spacing. In this response model $\rho_n(\vec{r}) = 0$ for $z \leq 0$, thus we are able to define symmetrized quantities

$$\mathbf{w}_{is}(\vec{r}) = \mathbf{w}_{i}(\mathbf{R}, |\mathbf{z}|)$$
(12a)

and

$$\rho_{is}(\vec{r}) = \rho_{i}(R, |z|)$$
(12b)

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where $\vec{r} = (\vec{R}, z)$, \vec{R} is a 2D vector in the surface plane. Using these symmetrized, quantities, we are able to evaluate the second-order (bandstructure) energy term entirely in reciprocal space. Thus, the third term in Eq. (9) becomes

$$E_{BS} = \frac{1}{4} \sum_{i,j}^{-3} \int d^{3}q \ e^{i\vec{Q} \cdot (\vec{R}_{i} - \vec{R}_{j})} \rho_{is}(\vec{q}) w_{js}(\vec{q})$$
(13)

where $\rho_{is}(\vec{q})$ and $w_{is}(\vec{q})$ are the 3D Fourier transforms of $\rho_{is}(\vec{r})$ and $w_{is}(\vec{r})$, and $\vec{q} = (\vec{Q}, q_z)$ is a 3D reciprocal space vector. The screening electron density, $\rho_{is}(\vec{q})$ is obtained as a function of q_z for a given $|\vec{Q}|$, layer, and atomic species by solving a single one-dimensional integral equation, as discussed in ref. 14.

We will now use Eqs. (9) and (13) in the surface segregation problem. The theory described in the following is similar to that developed by Inglesfield¹⁹ for application to disorded alloys, except that we will allow for variations in concentration in the z direction. For the purpose of the present study we consider only homovalent alloys, Z(A) = Z(B)=Z, and assume that the ion positions are lattice sites of a truncated bulk crystal (no lattice relaxation at the surface and no distortion around impurity ions), thus E_m , the madelung energy, is independent of $\{\Delta x_n\}$. However, we do not assume Vegarad's law, i.e. we minimize the total energy of a homogenous bulk random alloy with respect to density to determine the lattice constant and (bulk) total energy for a particular concentration \overline{x} .

It is convenient to define average and difference potentials for layers,

$$\overline{w}_{n}(\vec{r}) = \overline{x} V_{p}(A, (R^{2} - z_{n}^{2})^{\frac{1}{2}}) + (1 - \overline{x}) V_{p}(B, (R^{2} - z_{n}^{2})^{\frac{1}{2}})$$

$$\cdot - N^{-1}Z V_{+}(z)$$
(14)

and

$$\Delta w_{n}(\vec{r}) = V_{p}(A, (R^{2}-z_{n}^{2})^{\frac{1}{2}}) - V_{p}(B, (R^{2}-z_{n}^{2})^{\frac{1}{2}}).$$
(15)

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where z_n (Eq. 11) is the z coordinate of the nth layer. Symmetrized reciprocal space potentials $\overline{w}_{ns}(\vec{q})$, $\Delta w_{ns}(\vec{q})$, and their corresponding screening electron densities $\overline{\rho}_{ns}(\vec{q})$ and $\Delta \rho_{ns}(\vec{q})$ are defined in analogy to Eqs. (12) (with $\vec{R}_i = \vec{0}$).

Using the definitions given above, the second term on the rhs of Eq. (9) (the first order, or "Hartree" energy) is

$$\sum_{i} \int d^{3}r \rho^{o}(\vec{r}) w_{i}(\vec{r}) = \sum_{n} \left[\overline{E}_{H}(n) + \Delta x_{n} \Delta E_{H}(n) \right] \sum_{i(n)} (1)$$
(16)

where

$$\overline{E}_{H}(n) = \int d^{3}r\rho^{o}(z) \ \overline{w}_{n}(\vec{r}), \qquad (17)$$

$$\Delta E_{\rm H}(n) = \int d^3 r \rho^{\rm o}(z) \Delta w_{\rm n}(\vec{r}), \qquad (18)$$

and where i(n) specifies a lattice site in layer n.

The third term on the rhs of Eq. (9), i.e. the bandstructure energy, Eq. (13), depends on the distribution of the atomic species within the layers as well as on the layer concentrations. Every site in a given layer is equivalent, i.e. each site in the layer sees on the average the same distribution of A and B species around it regardless of whether that site is occupied by an A or B atom. Thus the bandstructure energy can be written

$$E_{bs} = \frac{1}{4} \frac{1}{(2\pi)} 3 \int d^{3}q \sum_{n,m} \left[\overline{\rho}_{ns}(\vec{q}) + \Delta x_{n} \Delta \rho_{ns}(\vec{q})\right]$$

$$x \left[\overline{w}_{ns}(\vec{q}) + \Delta x_{m} \Delta w_{ms}(\vec{q})\right] \sum_{i(n),j(m)}^{i} e^{i\vec{Q}\cdot(\vec{R}_{i(n)} - \vec{R}_{j(m)})}$$

$$+ \frac{1}{4} \frac{1}{(2\pi)} 3 \int d^{3}q \sum_{n} \{(\overline{x} + \Delta x_{n}) [\overline{\rho}_{ns}(\vec{q}) + (1-\overline{x}) \Delta \rho_{ns}(\vec{q})]$$

$$x \left[\overline{w}_{ns}(\vec{q}) + (1-\overline{x}) \Delta w_{ns}(\vec{q})\right]$$

$$+ (1-\overline{x} - \Delta x_{n}) [\overline{\rho}_{ns}(\vec{q}) - \overline{x} \Delta \rho_{ns}(\vec{q})] \qquad (19)$$

$$x \left[\overline{w}_{ns}(\vec{q}) - \overline{x} \Delta w_{ns}(\vec{q})\right] \sum_{i(n)}^{i} (1).$$

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The primed sum omits the j(m) = i(n) terms, and the second integral in Eq. (19) results from the fact that the potential at a given site, and thus the "self interaction energy" $\int d^3r \rho_i(\vec{r}) w_i(\vec{r})$, cannot be expressed in terms of the averaged quantities for a layer.

For a Bravais lattice,

$$\sum_{i(n),j(m)} e^{i\vec{Q}\cdot(\vec{R}_{i(n)}-\vec{R}_{j(m)})} = N_{A} \sum_{\vec{G}} \frac{(2\pi)^{2}}{A_{O}} \delta(\vec{Q}-\vec{G}) (s \rightarrow)^{n-m}$$
(20)

where $N_A = \Sigma$ (1) is the number of ions in a layer, A_0 is the area per surface atom, \vec{G} is a two dimensional reciprocal lattice vector, and $s_{\vec{G}} = e^{i\vec{G}\cdot\Delta\vec{R}}$ where $\Delta\vec{R}$ is the registry shift between adjacent layers. Using Eq. (20) and rearranging terms in Eq. (19), the bandstructure energy can be written as

$$N_{A}^{-1} E_{bs} = \frac{1}{4A_{o}} \sum_{n,m} \frac{1}{2\pi} \sum_{\vec{c}} \int dq_{z} (s_{\vec{c}})^{n-m} \{ \overline{\rho}_{ns}(\vec{c},q_{z}) \overline{w}_{ms}(\vec{c},q_{z}) + \Delta x_{n} \Delta \rho_{ns}(\vec{c},q_{z}) \overline{w}_{ms}(\vec{c},q_{z}) + \Delta x_{m} \overline{\rho}_{ns}(\vec{c},q_{z}) \Delta w_{ms}(\vec{c},q_{z}) + \Delta x_{m} \Delta x_{m} \Delta \rho_{ns}(\vec{c},q_{z}) \Delta w_{ms}(\vec{c},q_{z}) + \Delta x_{n} \Delta x_{m} \Delta \rho_{ns}(\vec{c},q_{z}) \Delta w_{ms}(\vec{c},q_{z}) \} + \frac{1}{4} \sum_{n} (2\pi)^{-3} \int d^{3}q (\overline{x} + \Delta x_{n}) (1-\overline{x} - \Delta x_{n}) \Delta \rho_{ns}(\vec{q}) \Delta w_{ns}(\vec{q}).$$
(21)

Substituting Eqs. (16-18) and Eq. (21) into the total energy expression yields

$$N_{A}^{-1} E_{T} = N_{A}^{-1} \overline{E}_{T} + \sum_{n} f_{n} \Delta x_{n} + \frac{1}{2} \sum_{n,m} \phi_{nm} \Delta x_{n} \Delta x_{m}$$
(22)

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where the terms on the rhs are defined and discussed below: (a) \overline{E}_{T} is the total energy of a uniform ($\Delta x_{n} \equiv 0$) semi-infinite solid solution of concentration \overline{x} , given by

$$N_{A}^{-1} \overline{E}_{T} = N_{A}^{-1} E^{\circ} + \sum_{n} \overline{E}_{H}(n)$$

$$+ \frac{1}{4} \sum_{n,m} (2\pi A_{o})^{-1} \sum_{\vec{G}} \int dq_{z} \overline{\rho}_{ns}(\vec{G}, q_{z}) \overline{w}_{ms}(\vec{G}, q_{z})$$

+
$$\frac{1}{4} \sum_{n} (2\pi)^{-3} \int d^{3}q \,\overline{x}(1-\overline{x}) \,\Delta \rho_{ns}(\vec{q}) \Delta w_{ns}(\vec{q}).$$
 (23)

(b) f is the change in the total energy of the uniform solid solution resulting from replacing an atom of species B in the n-th layer with an atom of species A. It can be regarded as an "impurity" formation energy and is given by

$$\mathbf{f}_{n} = \Delta \mathbf{E}_{\mathrm{H}}(n) + \Delta \mathbf{E}_{\mathrm{bs}}'(n) + (1 - 2\overline{\mathbf{x}}) \Delta \mathbf{E}_{\mathrm{s}}(n)$$
(24)

where

$$\Delta E_{bs}'(n) = \frac{1}{4} \sum_{m} (2\pi A_{o})^{-1} \sum_{\vec{G}} (s_{\vec{G}})^{n-m} \int dq_{z} [\Delta \rho_{ns}(\vec{G}, q_{z}) \overline{w}_{ms}(\vec{G}, q_{z}) + \overline{\rho}_{ns}(\vec{G}, q_{z}) \Delta w_{ms}(\vec{G}, q_{z})]$$
(25)

and

$$\Delta E_{s}(n) = \frac{1}{4} (2\pi)^{-3} \int d^{3}q \Delta \rho_{ns}(\vec{q}) \Delta w_{ns}(\vec{q}). \qquad (26)$$

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The second term, $\Delta E_{bs}'(n)$, depends explicitely on the average concentration \overline{x} (through the definitions of \overline{w} and \overline{v} , see Eq. (13)), while $\Delta E_{H}(n)$ and $\Delta E_{s}(n)$ depend on \overline{x} only through the density parameter r_{s} which determines $\rho^{o}(z)$ and the lattice parameter and which is obtained by minimizing \overline{E}_{T} with respect to density for a given \overline{x} . These two terms, $\Delta E_{H}(n)$ and $\Delta E_{s}(n)$, depend on the z coordinate of the layer but are otherwise independent of crystal structure. For sufficiently deep layers (large n) f_{n} is independent of layer number and is equal to the bulk value, f_{bulk} , which can be calculated for an infinite solid solution. Since in the bulk case the calculation can be done entirely in reciprocal space and there are no sums over layers, this serves as a check on the accuracy of the calculations.

(c) $\phi_{nm}^{}$ serves to couple the concentrations in layers n and m, and is given by

$$\phi_{nm} = \frac{1}{4} (2\pi A_0)^{-1} \sum_{\vec{G}} (s_{\vec{G}})^{n-m} \int dq_z [\Delta \rho_{ns}(\vec{G}, q_z) \Delta w_{ms}(\vec{G}, q_z) + \Delta \rho_{ms}(\vec{G}, q_z) \Delta w_{ns}(\vec{G}, q_z)] - 2 \delta_{n,m} \Delta E_s(n)$$

$$(27)$$

where $\Delta E_s(n)$ is defined in Eq. (26). The only dependence of ϕ_{nm} on \overline{x} is through the density parameter r_s . ϕ_{nm} becomes negligably small for large |n-m|, and for sufficiently deep layers ϕ_{nm} is equal to the bulk value, $\phi_{bulk}(|n-m|)$, which also can serve as a check on the accuracy of the calculation.

We now return to the minimization of the free energy, or equivalently the free energy of mixing given by Eq. (2), with respect to layer concentration to find the surface concentration profile. Substituting Eqs. (1-3) and Eq. (22) into Eq. (6) yields a set of non-linear coupled algebraic equations for the Δx_n ,

$$0 = \sum_{m=1}^{N} \phi_{nm} \Delta x_{m} + (f_{n} - f_{bulk})$$
$$+ k_{B} T \ln \left[(\overline{x} + \Delta x_{n}) (1 - \overline{x}) / \overline{x} (1 - \overline{x} - \Delta x_{n}) \right], \qquad (28)$$

$$1 \leq n \leq N_{e}$$
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In writing Eq. (28) we have taken the limit of an infinite number of layers, $N_L \rightarrow \infty$, so that Δx_{ij} (see Eqs. (5)) is negligable in the entropy term, $N_L / (N_L - N_S) = 1$, and N_S is large enough so that $f_n = f_{bulk}$ for $n > N_S$. (N_s must also be large enough so that $\Delta x_n = \Delta x_b$ for $n > N_s$, see Eqs. (4) and (5)). The free energy of segregation, i.e. the difference between the free energy of the equilibrium configuration and that of the uniform solid solution, is

$$\Delta F_{seg} = F_{m}(\overline{x}, \{\Delta x_{n}\}) - F_{m}(\overline{x}, \{\Delta x_{n} \equiv 0\})$$

$$= \sum_{n=1}^{N} \Delta x_{n} \{-(f_{n} - f_{bulk}) + \frac{1}{2} \sum_{m=1}^{N} \Delta x_{m} \phi_{nm}\}$$

$$+ k_{B} T \sum_{n=1}^{N} \{(\overline{x} + \Delta x_{n}) \ln (\overline{x} + \Delta x_{n}) - \overline{x} \ln (\overline{x})$$

$$+ (1 - \overline{x} - \Delta x_{n}) \ln (1 - \overline{x} - \Delta x_{n}) - (1 - \overline{x}) \ln (1 - \overline{x})\}$$
(29)

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II C. Pair-bond model

Before presenting our results in Section III we will discuss briefly a simple version of the pair-bond enthalpy formulation and contrast it with our psuedopotential-linear response formulation. In the pair-bond model the cohesive energy of the alloy is written as a sum over bonds,

$$E_{c} = \frac{1}{2} \sum_{i,j}^{\prime} \varepsilon_{ij}.$$
 (30)

The cohesive energy is related to the total energy, E_{T} , by

$$E_{c}(\overline{x}, \{\Delta x_{n}\}) = E_{T}(\overline{x}, \{\Delta x_{n}\}) + N [\overline{x} E_{I}^{A} + (1-\overline{x}) E_{I}^{B}]$$
(31)

where E_{I}^{A} and E_{I}^{B} are the ionization energies of the A and E atoms. The heat of mixing is thus

$$H_{m} = E_{c}(\overline{x}, \{\Delta x_{n}\}) - \overline{x} E_{c}(\overline{x} = 1) - (1-\overline{x}) E_{c}(\overline{x} = 0).$$
(32)

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For a bulk alloy, assuming nearest neighbor interactions only, the cohesive energy is given by

$$\frac{1}{N} E_{c}(\overline{x}) = \frac{C}{2} [\overline{x}^{2} \varepsilon_{AA} + (1-\overline{x})^{2} \varepsilon_{BB} + 2\overline{x}(1-\overline{x}) \varepsilon_{AB}].$$
(33)

where C is the coordination number. If ε_{AA} and ε_{BB} do not depend on \overline{x} then they can be obtained from the pure species cohesive energy (experimental, or from Eq. (31) using a calculated E_{T}),

$$\varepsilon_{AA} = \frac{2}{C} E_{c} (\overline{x} = 1), \varepsilon_{BB} = \frac{2}{C} E_{c} (\overline{x} = 0).$$
 (34)

The interspecies bond strength is written as

$$\epsilon_{AB} = \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) + \epsilon$$
 (35)

For an ideal solution $\varepsilon = 0$, but if the heat of mixing is known (again either an experimental or calculated bulk value), then

$$\varepsilon (\overline{\mathbf{x}}) = [\mathrm{NC} \ \overline{\mathbf{x}}(1-\overline{\mathbf{x}})]^{-1} H_{\mathrm{m}}(\overline{\mathbf{x}}).$$
 (36)

The surface segregation problem can be cast in the form of Eq. (28). We define the layer coordination number C_{nm} to be the number of nearest neighbors that an ion in layer n has in layer m (or vice versa). The formation energies are

$$\mathbf{f}_{\mathbf{n}} = \sum_{m=1}^{\infty} C_{\mathbf{n}m} [(1-2\overline{\mathbf{x}}) \ \epsilon + \frac{1}{2} \ (\epsilon_{AA} - \epsilon_{BB})], \qquad (37)$$

and the layer coupling matrix elements are

$$\phi_{nm} = -2 C_{nm} \varepsilon$$
 (38)

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For a Bravais lattice $C_{nm} = C (|n-m|)$; the only non-zero C for bcc (100) layers is C(1) = 4, and for bcc (110) layers the non-zero C's are C (0) = 4 and C (1) = 2. Thus, for bcc (100) and (110) surfaces only the surface layer has a formation energy different from the bulk, and there is no coupling beyond adjacent layers. In addition, the same-layer coupling term for (100) layers is zero. The pair-bond model can be extended to include interactions beyond nearest neighbors and to allow for different bond strengths near the surface, but it is difficult to uniquely determine the additional parameters. In any case the pair-bond model cannot account for terms which arise from the direct and indirect interaction of a single ion with the inhomogenous electron gas (see ref. ¹⁴).

III. Results and Discussion

In this section the theory developed in section II is applied to the simple metal alloys $Rb_{\overline{x}}K_{1-\overline{x}}$, $Cs_{\overline{x}}K_{1-\overline{x}}$, and $Cs_{\overline{x}}Rb_{1-\overline{x}}$. The choice of ionic psuedopotentials and properties of the bulk alloys are discussed in section III A. In section III B we discuss the various contributions to the formation energy, f_n , and differences, $f_n - f_{bulk}$, using the $Cs_{\overline{x}}K_{1-\overline{x}}$ system as an example. We also discuss the layer coupling matrix elements, ϕ_{nm} , and differences between bulk and surface terms. The results of surface segregation calculations, in the form of layer concentration, x_n , versus temperature curves, are presented.

III A. Bulk properties

In general, the choice of a model psuedopotential is guided by the adequacy of the fit between certain calculated and measured material properties. When treating metal surfaces it is essential that the model yields the correct bulk lattice constant at zero pressure and reproduces, as well as possible with a limited number of parameters, the elastic properties of the bulk metal. In addition, if the model is applied to alloys, it is of utmost importance that the model also yield the correct total energy, and thus the correct cohesive energy, of the pure species.

The simplified Heine-Abarenkov²⁰ model psuedopotential has been used by a number of authors ¹³ to calculate properties (heat of mixing, phase diagrams, etc) of Alkali metal alloys. We will use this form,

$$V_{p}(\beta,r) = -Z(\beta) e^{2}/r, \quad r \ge r_{c}(\beta)$$

$$= -Z(\beta) e^{2} u_{c}(\beta)/r_{c}(\beta), \quad r \le r_{c}(\beta),$$
(39)

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where $Z(\beta)$ is the charge of the ion of species β in units of the electron

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charge, e $(Z(\beta) = 1$ for the allkali metals), and $r_c(\beta)$ and $u_c(\beta)$ are the core radius and depth parameters. These parameters, r_c and u_c , are chosen to reproduce the lattice constant and bulk modulus of the pure species²¹ and are given in Table I. The model psuedopotentials were used in ref. ²¹ to calculate vacancy formation energy and volume, and yielded results in good agreement with experiment. We have verified that these potentials give the correct lattice constant by minimizing the total energy of the pure species with respect to the electron density parameter, r_s ; the resulting values of r_s and total energy per atom, $N^{-1}E_T$, are also given in table I. The calculated total energy values agree with experiment²² (see Eq.(31)) to within a fraction of 1% in each case. We have also verified that that these psuedopotentials predict a bcc structure by comparing the total energies with those obtained by assuming fcc and hcp structures.

The results of minimizing the total energy of the random alloy systems with respect to r_s are summarized in table II where we give results for concentrations \overline{x} = .1, .5, and .9 (these are the bulk concentrations used in the surface segregation calculations). The deviations from Vegard's law for volumes, $r_{x}(\bar{x}) = [\bar{x} r_{x}^{3}(1) + (1-\bar{x})r_{x}^{3}(0)]^{1/3}$, are small and negative. The calculated values of the heat of mixing are all positive, due to the structureindependent contributions²³; the bandstructure contribution can be positive or negative and are about an order of magnitude smaller than the structure independent contribution in each case. The quantity $N^{-1} H_m/\overline{x}(1-\overline{x})$ shown in table II is proportional to the alloy potential, ε , of the pair-bond model (see Eq. (36)). This quantity is zero for an ideal solution and is constant for a regular solution pair-bond model. The qualitative behavior of $H_m(x)$ is in argreement with other calculations^{24,25} and with liquid alloy experimental results²⁶ regarding the assymmetry of $H_m(\overline{x})$ about $\overline{x} = 0.5$. In particular, $H_m(\overline{x})/\overline{x}(1-\overline{x})$ is approximately a linear function of \overline{x} , except for the Cs-K system, and $H_{m}(\overline{x})/\overline{x}(1-\overline{x})$ increases with increasing concentration of the larger species. Yokokawa and Kleppa²⁶ have obtained approximate values of H_m for the solid solutions

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Rb. 7^{K} .3, Cs. 5^{K} .5, and Cs. 5^{Rb} .5 by extrapolation from their liquid metal experimental results, and these values are compared to the results of several calculations²⁴ in Table I of ref. 25. The calculated values reported there are all much greater than the experimental values, as are ours. We get values of H_m which are about 2, 3.5, and 11 times the extrapolated experimental values for Rb. 7^{k} .3, Cs. 5^{k} .5, and Cs. 5^{Rb} .5 respectively. However, our values are generally lower than the other reported calculated values. The discrepancy between calculated and experimental values may be due to the assumption that the heat and entropy of mixing are independent of temperature which is made in ref. 25 in extracting the solid solution H_m from liquid alloy measurements as well as in the calculations. The "disordering" temperature, T_D(\overline{x}), below which the free energy of a mechanical mixture (clustered, or segregated) of the pure species is lower than that of the <u>random</u> solid solution of concentration \overline{x} is given by

$$T_{D}(\bar{x}) = H_{m}(\bar{x}, \{\Delta x_{n}=0\}) / S_{m}(\bar{x}, \{\Delta x_{n}=0\}).$$
(40)

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Values of $T_{D}(\bar{x})$ for alloys studied in this paper are also given in Table II. The assumption that the alloy is a random solid solution is invalid near and below $T=T_{D}(\bar{x})$. A correct treatment of the bulk heat of mixing and of surface segregation would require the inclusion of short range order in both the energy and entropy terms,²⁷ which has only been accomplished in the context of simple pair-bond models²⁸ limited to nearest neighbor bonds. Available phase diagrams²⁹ indicate that each of the alloy systems considered here (with the possible exceptions of K-Cs³⁰) form continous solid solutions near room temperature, but information regarding the presence and degree of short range order is not available. Our results for $Rb_{x}K_{1-x}$ and $Cs_{x}Rb_{1-x}$ are consistent with these experimental phase diagrams. The results for $Cs \underset{x}{K}_{1-x}$ are not necessarily inconsistent with experiment since we have assumed a totally random solid solution, the inclusion of short range order would certainly lower the predicted clustering (i.e. segregating) temperature.

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III E. Formation energies and layer coupling matrix.

In this section we discuss the formation energies, f_n (Eq.24), and layer coupling matrix, ϕ_{nm} (Eq.27). Table III lists the numerical values of the bulk formation energies, f_{bulk}, for the alloy systems which are treated in this paper, along with the contributions ΔE_{H} , ΔE_{s} , and $\Delta E'_{bs}$ (Eqs. 18,25, and 26 respectively). The Hartree (first order in the ionic psuedopotentials) contribution, $\Delta E_{_{_{\rm H}}}$, is by far the largest in magnitude, and is larger in the Cs-K alloys where the difference in ionic size (psuedopotential core radius, or pure species volume/ion) is larger than in either the Rb-K or Cs-Rb alloys. Also note that ΔE_{μ} is positive and decreases as the concentration of the larger species increases. f is defined to be the change in energy of the $A_{x}B_{1-x}$ alloy when one of the smaller B ions is replaced by a larger A ion. Thus we see that more energy is required to substitute a large ion in an alloy consisting primarily of smaller ions than vice versa. This is what one would expect based on elastic strain arguments, however the mechanism involved is different here since the Hartree energy is independent of structure (relative positions of ions). The "self interaction difference", ΔE_s , is also structure independent and is relatively insensitive to concentration (when expressed in units of $e^2 k_F$). The last contribution, ΔE_{bs} , is essentially a sum over effective ionic interactions. This term may be either positive or negative and decreases (or becomes more negative) as the concentration of the larger species increases.

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The formation energy difference, $f_n - f_{bulk}$, is the driving force which gives rise to surface segregation. The dependence of this quantity on layer number and on alloy composition is illustrated in Table IV, using the Cs-K (100) alloy surfaces as an example. The formation energy difference is always negative for the first layer, indicating that the larger species will segregate

-23-

to the surface. The principal contribution to this first layer energy difference is again the Hartree energy term and results from the fact that the "zeroth order" electron density, $\rho^{0}(z)$, is smaller at the position of the first layer. In the second layer the Hartree and second-order (bandstructure) contributions tend to cancel, and past the second layer all contributions are essentially zero, so that only the first layer has a significant formation energy difference. This is similar to the simple nearest neighbor pair-bond model in which $f_n - f_{bulk} = 0$ for n > 1 at low index surfaces. However, we emphasize again that the mechanisms involved are not the same. In our psuedopotential - linear response model the surface layer formation energy difference is determined almost entirely by the Hartree energy contribution which is independent of coordination number and depends only on $r_{_{
m S}}$ and on the position of the layer with respect to the zeroth order electron density, $\rho^{c}(z)$. In Table V we give the first layer formation energy differences for all the alloy systems considered. Note that the magnitudes for the (110) surfaces are smaller than those for the (100) surfaces. This is due to the fact that the (110) layer spacing, d, is larger and thus the z coordinate of the first (110) layer, Eq.(11), is larger, and $\rho^{0}(z)$ deviates less from the bulk value at this position (see fig. 1 of ref. 14). Again, the prediction, based on the magnitudes of the formation energy differences, that segregation will be more pronounced at the more open (100) surfaces is the same as that of the pair-bond model, but for a totally different reason.

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The nature of the layer coupling matrix, ϕ_{nm} , is illustrated in Table VI, using the Cs₅K₅ (100) and (110) alloy systems as examples. The qualitative features are the same for all other systems. We note first that the magnitude of ϕ_{nm} decreases rapidly as |n-m| increases, and the matrix elements coupling layers near the surface differ from the bulk layer coupling matrix elements.

The qualitative features of the layer coupling matrix can be understood

in terms of interaction potentials by including interactions out to at least the second nearest neighbor shell and taking the bond strengths from the calculated effective ionic interaction potentials (pair potentials). The bulk layer coupling matrix elements are given in terms of the pair potentials by

$$\phi_{nm} = \sum_{(j)} C_{nm}^{(j)} \left[U_{AA}(r^{(j)}) + U_{BB}(r^{(j)}) - 2 U_{AB}(r^{(j)}) \right], \quad (41)$$

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where superscript (j) specifies the j-th nearest neighbor shell, $C_{n,m}^{(j)}$ is the number of j-th nearest neighbors which an ion in layer n has in layer m, and $U_{\alpha\beta}(r^{(j)})$ is the value of the bulk pair potential between ions of species α and β evaluated for the j-th neighbor distance, $r^{(j)}$. The bulk pair potentials for the $Cs_{K_{1-\overline{X}}}$ alloys are shown in fig. 1 (see ref. 14 for a discussion of interaction potentials in the surface region). We get, for example from Eq. (41) for (100) layers using the bulk $Cs_{5}K_{5}$ pair potentials and first and second nearest neighbor interactions, $\phi_{n,n} \simeq .00158$, $\phi_{n,n\pm 1} \simeq .00250$, and $\phi_{n,\pm 2} \simeq .00039$, compared to the values .00192, .00361 and .00037 given in table VI, which were obtained from Eq. (27). It is necessary to include interactions out to at least the fifth nearest neighbor shell to get reasonably quantitative agreement with the exact calculation [i.e. Eq.(27)].

Since the formation energy difference, $f_n - f_{bulk}$, is very small in magnitude for $n \ge 2$, we may expect that the concentrations of these deeper layers will be determined primarily by the coupling between the layer concentrations. The matrix elements coupling adjacent layers are positive, thus the heat of mixing, $H_m(\bar{x}, \{\Delta x_n\})$, may be decreased if succeeding layers have alternately positive and negative Δx 's, resulting in a non-monotonic concentration profile. In fact, we find that in some cases at very low temperatures, $T < T_D$, the "concentration layering" propagates into the bulk. This bulk layering phenomenon is an artifact of the model, resulting from the neglect of local order within and between layers and the fact that fluctuations in concentration are allowed only between layers parallel to the surface plane. The model is not valid for $T \lesssim T_{D}$ in any case [see the discussion following eq. (41)].

In contrast to our psuedopotential-linear response model, the nearest neighbor pair-bond model described in section IIC will always give a monotonically decreasing concentration profile if the bulk heat of mixing is positive [see Eqs.(36) and (38)]. It is possible to obtain a non-monotonic concentration profile from a nearest neighbor pair-bond model if the bond strengths in the surface region are adjusted,^{5,7} however, this practice may be misleading since ordering may be favored in the bulk even though H_m is positive. In other words, the classification of alloys as either ordering or segregating, which is inherent to the pair-bond model, is not valid for simple metals, and is probably not valid for noble or transition metals, simply because the cohesive energy cannot be expressed as a sum over pairbonds.

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III C. Segregation Results

In this section we present and discuss the results obtained by minimizing the free energy with respect to layer concentrations. We have included twelve layers in the surface region in each case [N_s = 12, see Eq.(16)]. Figures 2, 3, and 4 show the (larger) A species concentration in the first five layers of $A_{\overline{X}} B_{1-\overline{X}}$ (100) and (110) alloy systems $Rb_{\overline{X}}K_{1-\overline{X}}$, $Cs_{\overline{X}}K_{1-\overline{X}}$, and $Cs_{\overline{X}}B_{1-\overline{X}}$ respectively, with $\overline{x} = .1$, .5, and .9. Results of the simple nearest neighbor pair-bond model (section IIC.) are shown in fig. 5 for comparison, using the $Rb_{\overline{X}}K_{1-\overline{X}}$ systems as an example. The reader is reminded that the results for temperatures near and below the "disordering temperature", $T \leq T_D$ [Eq.39, Table II], are probably not valid due to the neglect of local ordering within and between layers, as discussed in the previous sections. Concentration profiles are presented in figures 6 and 7 as histograms of species A concentration versus layer number at temperatures T = 250,200, and 150 ^OK for the $Rb_{\overline{X}}L_{1-\overline{X}}$ (100) alloy systems; fig. 6 gives the psuedopotential-linear response results, and fig. 7 is obtained from the pair-bond model.

The general features of the x_n vs T curves are in agreement with our expectations based on the formation energy differences, $f_n - f_{bulk}$, and the layer coupling matrix, ϕ_{nm} , as discussed in the previous section: £

(a) The larger, A, species always segregates to the surface layer.

- (b) Segregation is more pronounced at the more open (100) surfaces, and increases with decreasing temperature.
- (c) Segregation is more pronounced in the $Cs_{\overline{x}}K_{1-\overline{x}}$ systems where the difference in ionic size is larger.
- (d) In most cases we observe a <u>non-monotonic</u> concentration profile the concentration in the second layer is usually lower than the bulk concentration due to the high concentration in the first layer and the coupling between layer concentrations. However, in some cases [higher bulk concentration and/or (110) layers] the concentration profile

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decreases monotonically away from the surface.

- (e) At very low temperatures, T<<T_D (where the model is not valid), one can see in some cases the onset of bulk "concentration layering".
- (f) The pair-bond model gives a monotonically decreasing concentration profile, over-estimates the concentration in the surface layer, and greatly over-estimates the change in free energy upon segregation.

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IV. Conclusion

We have developed an electronic theory of surface segregation in simple metal alloys which is based on the use of local ionic psuedopotentials and linear response, and have applied this theory to the binary simple metal (solid solution) alloys composed of K, Rb, and Cs. We conclude that the segregation of the larger species to the surface layer is driven by single particle terms in the total energy expansion, i.e. by the Hartree energy terms (1-st order in the psuedopotentials) which are independent of coordination number and relative positions of ions and which depend only on the position of the surface layer with respect to the inhomogenous zeroth order electron density in the surface region. The concentration in deeper layers is determined primarily by the coupling between layer concentrations which results from interionic interactions and which may give rise to a nonmonotonic concentration profile. By comparing our electronic theory with a simple nearest-neighbor pair-bond model, in which the bond strengths are obtained from bulk thermodynamic data, we conclude that the pair-bond model is not applicable to simple metal alloy systems; the reason being that the cohesive energy cannot be expressed as a sum over pair-bonds. We speculate that the pair-bond model may not be reliable for noble or transition metal alloy systems for the same reason; this is supported by the results of Muscat¹⁰, and by the results of Connolly and Williams³¹ regarding many-body interactions and the heat of mixing in transition metal alloys. Experimental data on surface segregation in the alkali metal systems considered in this paper is not currently available; the theory can be addpted to other (nonhomovalent) simple metal systems such as Al-Li, Al-Mg, etc., and the same mechanisms discussed here must certainly be involved.

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In the current version of the theory surface relaxation¹⁸, lattice distortion due to size mismatch, and effects due to local (short range) ordering have not been considered. The inclusion of surface relaxation/lattice distortion

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effects would probabby increase the surface layer concentration of the larger species due to the fact that there is a greater freedom to relax the lattice in the surface region⁸. Short range order can in principal be included using the cluster variation method^{27,28}.

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TABLE I. Parameters used in the calculations: r_c and u_c are the psuedopotential core radius and depth (see Eq. (39)), r_s and $N^{-1}E_T$ are the electrons density parameter and bulk total energy per particle.

			<u> </u>	
Meta1	rc	u c	rs	N ⁻¹ E _T
K	3.033a	.5723	4.861a	3891Ry
Rb	3. 551a _o	.7273	5.196a ₀	3687Ry
Cs	4.112a _o	.8079	5.625a	3 449Ry

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TABLE II. Bulk alloy results: r_s is the electron density parameter, E_T is the total energy, H_m is the heat of mixing and T_D is the calculated "disordering" temperature, (Eq. 39), and T_m is the melting temperature.

			·		
$\frac{A_B}{x}$ 1-x	r	N ⁻¹ E _T	$N^{-1}H_m/\overline{x}(1-\overline{x})$	T _D	T
Rb ₁ K ₉	4.896a	3869Ry	.0018Ry	80 ⁰ K	330 ⁰ К
Rb ₅ K ₅	5.034	3785	.0017	95	310
^{Rb} 9 ^K 1	5.165 •	3706	.0016	70	310
Cs ₁ K ₉	4.948	3839	.0092	400	283
Cs5K5	5.267	3652	.0072	410	283
Cs9K1	5.556	3487	.0063	270 ´	278
Cs1Rb9	5.242	3662	.0020	90	300
Cs5 ^{Rb} 5	5.418	3563	.0019	105	282
Cs9 ^{Rb} 1	5.584	-3.471	.0017	75	293

TABLE III. Bulk formation energy, $f_{bulk} = \Delta E_H + (1 - 2\bar{x}) \Delta E_s + \Delta E_{bs}$ (see Eqs. (18) and (24-26)). The units of energy are $e^2 k_F$ where $k_F = (9\pi/4)^{1/3}/r_s$ and $r_s(\bar{x})$ is given in Table II.

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$\frac{A_B}{x^{1-\overline{x}}}$	Δε _н	ΔĒs	ΔE'bs		^r bulk
^{Rb} 1 ^K 9	.0262($e^{2}k_{F}$)	0018(e ² k _F)	.0029(e ² k _F)	.0277 ($e^{2}k_{F}$)	=.0217 Ry
Rb ₅ K ₅	.0248	 0018	.0017	.0265	=.0202 Ry
^{Rb} 9 ^K 1	.0236	0017	.0006	.0255	=.01 90 Ry
	•				
Cs ₁ K ₉	.0673	0076	.0039	.0651	≕.0 505 Ry
Cs ₅ K ₅	.0594	0074	.0002	.0596	=.0435 Ry
Cs ₉ K ₁	.0534	0071	0026	.0565	=.03 90 Ry
Cs1Rb9	.0371	0024	0004	.0347	=.0254 Ry
Cs5Rb5	.0347	0024	0012	.0335	=.0238 Ry
Cs9 ^{Rb} 1	.0327	0024	0019	.0327	=.0224 Ry

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TABLE IV. Contributions to the formation energy difference for $Cs_{\overline{x}} K_{1-\overline{x}}$ alloys, (100) layers; $[f_n - f_{bulk}] = \Delta[\Delta E_H(n)] + (1-2\overline{x}) \Delta[\Delta E'_{bs}(n)]$ where $\Delta[\Delta E_H(n)] = \Delta E_H(n) - \Delta E_H(bulk)$, etc. (see Eqs. (18) and (24-26). The units of energy are e^2k_F , where $k_F = (9\pi/4)^{1/3}/r_s$ and $r_s(\overline{x})$ is given in Table II.

x	n	$\Delta[\Delta E_{H}(n)]$	$\Delta[\Delta E_{s}(n)]$	$\Delta \left[\Delta \mathbf{E}_{\mathbf{bs}}^{\dagger}(\mathbf{n}) \right]$	[f _n -f _{bulk}]
.1	1	0122	.0007	+.0000	0116
	2	0012	.0000	0014	0001
	3	0000	0000	0001	0002
	4	0001	.0000	0000	0002
	5	.0002	.0000	0001	0000
	6	0000	0000	0001	0001
• 5	1	0098	.0006	+.0011	0087
	2	.0010	.0001	0013	0004
	3	.0001	0000	0001	+.0000
	4	0002	.0000	0000	0002
	5	.0001	.0000	0001	0000
	6	0000	0000	0000	0000
•9	1	0080	.0005	+.0018	0068
	2	.0008	.0001	0012	0005
	3	.0002	0000	0002	+.0000
	4	0002	.0000	0000	0002
	5	.0001	.0000	+.0000	+.0001
	6	0000	0000	0000	0001
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Alloy:		Rb_K x 1-x	Cs_K x1-x	Cs_Rb _{1−x}
.(100) 😿	= .1	0038 Ry	0090	0039
surface	.5	0033	0063	0033
	.9	0034	0047	0027
(110)	.1	0018 Ry	0042	0017
surface	.5	0015	0027	001.3
	.9	0012	0017	0010

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TABLE V. First layer formation energy differences, (see Eqs. 24,28).

\ n	_	0	2		e	1. 11
<u>m-n\</u>	l	2	3	4	>	bulk
			(100) sı	urface		
0	0.00329	0.00180	0.00196	0.00194	0.00190	0.00192
1	0.00388	0.00348	0.00367	0.00361	0.00364	0.00361
2	0.00050	0.00033	0.00039	0.00036	0.00038	0.00037
3	-0.00004	-0.00018	-0.00003	-0.00001	-0.00002	-0.00001
4	-0.00006	0.0	-0.00004	-0.00001	-0.00003	-0.00002
5	-0.00002	0.0	-0.00001	-0.00001	-0.00001	-0.00001
			<u>(110)</u> st	urface		
0	0.00611	0.00473	0.00465	0.00464	0.00465	0.00466
L	0.00264	0.00267	0.00267	0.00267	0.00266	0.00266
2	-0.00008	-0.00008	-0.00008	-0.00007	-0.00007	-0.00007
3	-0.00001	-0.0	-0.0	-0.00001	-0.0001	-0.0
4	-0.00002	-0.0	-0.0	-0.0	-0.0	-0.0
5	-0.00001	-0.0	-0.0	-0.00001	-0.0	0.0

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TABLE VI. Layer coupling matrix, $\phi_{nm} = \phi_{mn}$ for Cs₅K, (100) and (110) surfaces. The energy unit is $e^{2}k_{F}$.

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FIGURE CAPTIONS

- 1. Bulk pair potentials, U(R), as functions of interionic distance, R, in the $Cs_{\overline{X}}K_{1-\overline{X}}$ alloys for $\overline{x} = 0.1$, 0.5, and 0.9. Energy units are 10^{-3} Ry. The distance, R, is in units of the bcc first nearest neighbor distance R⁽¹⁾; the ratios of the first five nearest neighbor distances to R⁽¹⁾ are: 1, $\sqrt{4/3} \approx 1.15$, $\sqrt{8/3} \approx 1.63$, $\sqrt{11/3} \approx 1.91$, and $\sqrt{12/3} = 2$, respectively.
- 2. Layer concentration, x_n [Eq.(4)], and change in free energy upon segregation, ΔF_{seg} [Eq.(29)], as functions of temperature for $Rb_{\overline{x}}K_{1-\overline{x}}$ alloys with bulk concentration $\overline{x} = 0.1$, 0.5, and 0.9. The numbers 1 through 5 adjacent to the x_n versus T curves specify the layer numbers, n. These results are obtained from the <u>psuedopotential</u>-<u>linear response model</u> explained in sections IIA and B, with N_s=12 (the number of layers in the surface region).
- 3. Layer concentration, x_n , and change in free energy, ΔF_{seg} , as functions of temperature for $Cs_{\overline{X}}K_{1-\overline{X}}$ alloys, see the caption of fig. 2.

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- 4. Layer concentration, x_n , and change in free energy, ΔF_{seg} , as functions of temperature for $Cs_{\overline{x}}Rb_{1-\overline{x}}$ alloys, see the caption of fig. 2.
- 5. Layer concentration, x_n , and change in free energy, ΔF_{seg} , as functions of temperature for $Rb_{\overline{X}}K_{1-\overline{X}}$ alloys, obtained from the <u>pair-bond model</u> explained in section IIC. In this pair-bond model the layer concentrations decrease monotonically with increasing layer number (the x_n versus T curves are not labeled with layer number in this figure). See also the caption of fig. 2.
- 6. Examples of layer concentration profiles obtained from the <u>psuedopotential-</u> <u>linear response model</u>: the (100) surfaces of $Rb_{\overline{X}}K_{1-\overline{X}}$ alloys with bulk concentration $\overline{x} = 0.1$, 0.5, and 0.9 for temperatures T= 250, 200, 150 °K.
- Examples of layer concentration profiles obtained from the <u>pair-bond model</u>.
 See also the caption of fig. 6.







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Figure 2

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Figure 4

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Figure 5

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Figure 7

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B.4 <u>A Model for Atomic Hydrogen Physisorption</u>

A variational solution to a model problem of a hydrogen atom near a sharp planar surface of a semiinfinite substrate was studied. Results are presented for the ground and excited eigenstates and dipole moments of the hydrogen atom as a function of distance from the surface for two models: (a) a system in which the half-space occupied by the solid is represented by an infinite potential step, (b) a system in which the semi-infinite substrate is perfectly imaging subject to a boundary condition that excludes the atomic electron from the substrate. Model (b) is considered as an idealized model for physisorption, where the exclusion of the electron simulates the exchange repulsion originating from the overlap of the atomic and substrate electrons. Results for the physisorption holding potential as a function of distance from the plane are presented.

Variational Solutions of Simple Quantum Systems Subject to Variable Boundary Conditions*

I. A Model for Physisorption

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Abstract

A variational solution to a model problem of a hydrogen atom near a sharp planar surface of a semiinfinite substrate is studied. Results are presented for the ground and excited eigenstates and dipole moments of the hydrogen atom as a function of distance from the surface for two models: (a) a system in which the half-space occupied by the solid is represented by an infinite potential step, (b) a system in which the semi-infinite substrate is perfectly imaging subject to a boundary condition that excludes the atomic electron from the substrate. Model (b) is considered as an idealized model for physisorption, where the exclusion of the electron simulates the exchange repulsion originating from the overlap of the atomic and substrate electrons. Results for the physisorption holding potential as a function of distance from the plane are presented and discussed. Boundary conditions, as utilized in Quantum Mechanics, are usually dictated by the requirements of *physical admissibility*. For example, when considering bound states the requirement that the normalization integral converge leads to the consideration of only those solutions which are regular at the origin and are zero at infinity. For scattering states a wave function which tends to infinity as r goes to infinity corresponds to a state that has no physical meaning and must be discarded. More generally it is known that a partial differential equation possesses several arbitrary constants and it is the specification of the value of the solution, or it's normal derivative, on the boundary that yields the values of these constants.

One of the first uses of a boundary perturbation, that is a change in the boundary conditions, to *model* a physical situation was a calculation of the energy levels of a compressed hydrogen atom.^{1,2} In this calculation the effect of very high pressure on atomic hydrogen is taken into account by requiring that the wavefunction vanish - on a sphere at some finite distance from the proton. This type of calculation is, of course, only an approximate one for it only indicates the effect of repulsive forces at very high densities; but of course this is the main attraction of such an approximation in that it replaces the complicated set of interactions with only a change in the boundary conditions, which in this case is exactly solvable.³

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By changing the new boundary surface from the sphere of the previous example to an infinite plane surface, there results a situation that has been used to model several physical systems. In particular, the requirement of a vanishing wavefunction on a plane has been used⁴ to represent the exchange repulsion of atomic hydrogen physically adsorbed onto a surface.

Perhaps a more realistic use of this boundary condition in the modelling of a physical problem arises in the effective mass theory of shallow donor impurities near the surface of a semiconductor or a semiconductor-oxide interface. Because the binding energy of a shallow donor is of the order of a few milli-electron volts and the height of the surface barrier is several electron volts, the surface is essentially an infinite potential barrier and the envelope function of the donor impurity must be required to vanish on the surface. This condition on shallow impurities near semiconductor surfaces was first pointed out by Levine^{5a} and Gadzuk^{5b}.

It is the last two examples of modelling a physical problem with the use of boundary conditions that will be addressed in this series. The boundary perturbation in each case involves a change in the shape of the boundary surface while still requiring that homogeneous Dirichlet conditions be satisfied. (Recall that the isolated hydrogen atom wavefunction is required to be zero on the sphere at infinity.)

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When the surface on which the boundary conditions are to be specified is no longer a surface in a coordinate system in which the partial differential equation separates, the problem is nonseparable. This is due to the fact that even though it may be possible to separate the equation, there is no way to satisfy the boundary conditions on a surface which depends upon at least two independent variables. Because of this nonseparability, some type of approximation method must be used.

One of the first approaches to the boundary perturbation prob**lem** was made by Brillouin.⁶ By considering a displacement operator acting on the boundary he was able to construct a method that is formally similar to the standard perturbation series. However the expansion parameter in this case is the magnitude by which the boundary surface is displaced and this parameter is assumed to be small. This is clearly not satisfied by the problems we wish to solve. Other methods of treating boundary perturbations have been developed 7,8 but they all have the same restriction. That is, they can only be used when the domain of the PDE is finite and the change in the boundaries is finite. In addition to these methods, a perturbation method using Green's functions has been developed by Feshbach⁹ and also discussed by Morse and Feshbach.¹⁰ However, the method is mathematically complicated and for the problem of a change in the boundary shape while requiring homogeneous Dirichlet conditions to hold, the method cannot be used to find corrections to the energy beyond the second order.

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These considerations lead to the conviction that the variational method will yield the best approximate solutions to this type of boundary perturbation problem.

In paper I of this series a variational solution to the problem of a hydrogen atom in the presence of a planar infinite-potential wall is given. The effect of this boundary perturbation on the spectrum of the hydrogen atom is discussed. At a large distance from the plane, the isolated hydrogen atom levels are regained. When the proton lies on the boundary plane the problem is again exactly solvable⁵ and these solutions are recovered by the variational solution. Between these two limits the energy levels vary smoothly and exhibit several interesting level crossings. By using these methods, a model advanced by Bruch and Ruijgrok⁴ of the physisorption of atomic hydrogen is revisited and information with regard to excited states of the system is provided.

In paper II of this series we address the problem of a shallow donor impurity near a semiconductor surface or interface. Modifications in the variational solution due to the effect of an anisotropic effective mass are presented. Energy levels of the ground and excited states of shallow donors near the surfaces of silicon and germanium are calculated. One of the results of this model is that the total interaction energy of a shallow donor with the semiconductor surface possesses a minimum and this suggests a possible clustering of these impurities near the surface. Finally, the binding energy of a shallow donor impurity **associated** with an n-type inversion layer of a metal-oxide-semiconductor Ē

field effect transistor is calculated and compared with other recent theoretical treatments and experimental results.

The variational method of solution is described in section 1 where results for the spectrum of a hydrogen atom near an impenetrable wall are given. The introduction of images in a model of physisorption is described in section 2 and a detailed discussion of the eigenvalue spectrum and energetics of the system is given.

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2. Variational Solution - Hydrogen near an Impenetrable Wall

The variational method of solution is introduced by considering a hydrogen atom which is at some finite distance, say R, from an infinite plane surface upon which the potential is taken to be infinite. This infinite potential manifests itself by the requirement that ψ , the wavefunction of the electron, must vanish on the plane and in the half-space not containing the proton¹¹. In our treatment of the model, the Born-Oppenheimer approximation shall be used, inasmuch as the proton will be taken as being located at a fixed distance from the plane, so that there is no coupling between the nuclear and electronic motions.

The Hamiltonian of the problem is given by the usual hydrogen atom Hamiltonian

$$H = \frac{-h^2}{2m} \nabla^2 - \frac{e^2}{r}$$
(1.1)

but now the boundary condition is that ψ must be equal to zero on the plane z = R (see Fig. 1). This choice of orientation of the plane and coordinate system, which is centered on the proton, is made to simplify the following calculations.

The variational principle for eigenvalues¹² is

$$\delta[E] = \delta\left[\frac{\int \psi^* H \psi dV}{\int \psi^* \psi dV}\right] = 0 \qquad (1.2)$$

where H is an arbitrary Hermitian operator, and this leads to the eigenvalue equation

(1.3)

only when the function ψ in (1.2) obeys the same boundary conditions that are to be imposed upon the solutions of Eq. (1.3). In practical applications of the variational method, this means that the trial functions must obey the correct boundary values, independent of the choice of values of whatever variational parameters the trial function may contain. When this condition is satisfied, the trial function is said to be admissible.¹³

This requirement usually poses no problems and its importance is not often emphasized. However, in the present case when the location of the boundary surface is to be varied, and more generally when the boundary surface and conditions will be considered to be input variables, the construction of admissible trial functions can become quite cumbersome. To avoid this complication in the construction of a set of trial functions for the linear variation problem one can form the combination

$$\psi(F) = G(\vec{r}) \sum_{n} A_{n} \phi_{n}(\vec{r}) + F(\vec{r}). \qquad (1.4)$$

Here the A_n are the linear variation parameters and the set $\phi_n(r)$ is to satisfy the boundary conditions of the unperturbed problem. The n's are taken to stand for all the quantum numbers which characterize the basis set of the system. The function G(r) is such that $G(\vec{r} \text{ on } S)=0$ where S denotes the boundary surface. The function $F(\vec{r})$ is to satisfy $F(\vec{r} \text{ on } S)=X_1(S)$ for Dirichlet conditions, or $\frac{\partial F}{\partial n}$ ($\vec{r} \text{ on } S$) = $X_2(S)$ for Neumann conditions. In the present instance we are concerned

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only with homogeneous Dirichlet conditions and therefore need only consider, taking into account the coordinate system of Fig. 1 and the fact that the additional boundary surface is a plane, the combination

$$\Psi(\vec{r}) = G(z) \sum_{n} A_{n} \phi_{n} \qquad (1.5)$$

where G(R) = 0.

When the boundary surfaces are changed, there arises one more modification of the variational principle of Eq. (1.2). The range of the integrations in Eq. (1.2) is over the domain of the Eq. (1.3)and that domain is defined as the inside of the closed boundary surface on which the boundary conditions are to be satisfied. The fact that the surface is closed follows from the elliptic character of the time-independent Schrödinger equation. This means that the limits of integration in Eq. (1.2) will become dependent upon the position of the boundary surface.

Taking into account all of these considerations and using the **trial** function of Eq. (1.5) the energy of the system can be written as

$$[E] = \frac{\int_{T} [G(z)\sum_{n} A_{n} \phi_{n}]^{*} H [G(z)\sum_{n} A_{n} \phi_{n}] dV}{\int_{T} [G(z)\sum_{n} A_{n} \phi_{n}]^{*} [G(z)\sum_{n} A_{n} \phi_{n}] dV}$$
(1.6)

where the subscript T on the integrals indicates that the integration is over a truncated space and H is given by Eq. (1.1). The basis set used to expand the trial function will not in general be orthogonal, because of the factor G(z) and the integration is over a truncated space, so that the variation of the linear parameters A_n will lead to a generalized matrix eigenvalue problem

$$\underbrace{H}_{\infty} \underbrace{A}_{\infty} = E \underbrace{N}_{\infty} \underbrace{A}_{\infty}$$
(1.7)

where there now appears the overlap matrix \underbrace{N}_{\approx} . More specifically the matrix elements are given by

$$(\underbrace{H}_{\widetilde{U}})_{n'm} = \int_{T} [G(z)_{\phi_n}]^* H[G(z)_{\phi_n}] dV, \qquad (1.8)$$

and

$$(\underset{\approx}{N})_{n'n} = \int_{T} [G(z)_{\phi_n}]^* [G(z)_{\phi_n}] dV.$$
 (1.9)

Since both H and N are hermitian, the usual properties of hermitian matrices apply; except that the orthonormality of the vectors A_n is expressed as ¹⁴

$$A_{n}^{\dagger} \approx A_{n'} = \delta_{nn'}. \qquad (1.10)$$

Before the choice of the set ϕ_n is presented, the specific form of G(Z) which is zero on the boundary surface will be given. The most convenient choice is simply to set

 $G(Z) = R - Z = R - r\cos\theta$ (1.11)

Then the development of the Laplacian of the Hamiltonian (1.1) is

$$v^{2}[(R-r\cos\theta)\phi_{n}] = (R-r\cos\theta)v^{2}\phi_{n} - 2\hat{k}\cdot\nabla\phi_{n}$$

since, on noting that \hat{k} is the unit vector in the z-direction,

$$\nabla(\mathbf{R}-\mathbf{r}\cos\theta)=-\hat{\mathbf{k}},$$

and

$$\nabla^2(\mathbf{R}-\mathbf{r}\cos\theta)=0.$$

It is interesting to note that this choice yields an expression that is similar to the variational principle for unrestricted trial functions (i.e. they do not obey the boundary conditions) given by Morse and Feshbach¹⁰. Both forms involve the derivative of ϕ_n that is normal to the boundary surface; however in the present instance the integration is over the entire volume and not only over the new boundary surface.

The basis set $\phi_n(\vec{r})$, which must satisfy only the isolated hydrogen atom boundary conditions, i.e. $\psi \neq 0$ as $r \neq \infty$, is chosen to be

$$\phi_{n} \equiv \phi_{n \ell m}(\vec{r},\beta) = (2\beta)^{3/2} / \sqrt{2n} [(N-\ell-1)!/[(N+\ell)!]^{3}]^{1/2}$$

$$\times (2\beta r)^{\ell} L_{n-\ell-1}^{2\ell+1}(2\beta r) e^{-\beta r} Y_{\ell}^{m}(\theta,\phi). \qquad (1.12)$$

In Eq. (1.12) the Y_{l}^{m} are the usual spherical harmonics, the L_{p}^{k} are the associated Laguerre polynomials and r is taken to be in units of Bohr radii, $a_{0} (a_{0} = \hbar^{2}/me^{2})$. This corresponds to a scaling of the Hamiltonian (1.1) to

 $(-\nabla^2 - \frac{2}{r}) \Psi = E\Psi$

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where E is given in units of Rydbergs $(e^2/2a_0)$.

The difference between the set of functions given by Eq. (1.12) and the isolated hydrogen atom eigenfunctions is the appearance of the combination βr , where β is an additional variational parameter independent of any quantum number, rather than the combination r/n which depends upon the particular state under consideration. The advantages of this choice are twofold. First the isolated hydrogen atom orbitals do not form a complete set without the inclusion of the continuum states¹⁵. Use of the set given by (1.12) has been shown to include contributions from these states . Second, the virial theorem is automatically satisfied for any quantum mechanical system whose potential is a homogeneous function of the coordinates if a scale factor is introduced into the approximate wave function and varied so as to give the lowest energy 17, 14. The parameter β is such a scale factor and because its optimum value will be found, the properties of the states found with the approximate wave functions of Eq. (1.5) will be better than those which do not contain such a scaling.

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Since the boundary surface was chosen to be a plane perpendicular to the z-axis, there are no changes in the limits of integration over the variable ϕ . Consequently the m-quantum number remains good. This means that we can separate the problem according to the m-value of the particular level that we are interested in solving. Moreover, since the degeneracy of the two states $[n, 2, \pm m]$ is not lifted we need consider only the positive m values. The original matrix equation given Eq. (1.7) then reduces to a set of matrix equations for which m = 0, 1, 2, ..., That is

$$\underline{H}^{(m)} \underline{A}^{(m)} = E \underbrace{N}^{(m)} \underline{A}^{(m)}.$$
(1.13)

In the calculation of the matrix elements for these separate problems, the integration over the variable ϕ can now be replaced by multiplication with the factor $2\pi\delta_m$, m.

The calculation of the Hamiltonian matrix elements now proceeds as follows. Taking account of the truncation of the region of integration along with the above considerations the matrix elements can be written as

$$2\pi \left\{ \int_{0}^{R} \int_{0}^{\pi} H_{n',n}^{(m)} \operatorname{sineder}^{2} dr + \int_{R}^{\infty} \int_{\cos^{-1}(R/r)}^{\pi} H_{n'n}^{(m)} \operatorname{sineder}^{2} dr \right\}.$$
(1.14)

It is here, in the lower limit of the θ -integration of the second term, that the non-separability of the problem becomes apparent with the appearance of the term $\cos^{-1}(R/r)$. For future convenience we shall denote this integration as

$$\int_{T} H_{n'n}^{(m)} dV$$

The matrix elements of the Hamiltonian are now expressible as

$$H_{n'\ell',n\ell}^{(m)} = \int_{T} (R - r \cos \theta) \phi_{n'\ell'm}(\vec{r},\beta) \left\{ (R - r \cos \theta) \right\}$$

$$\times \left[-\nabla^2 - \frac{2}{r} \right] \phi_{n\ell m}(\vec{r},\beta) - 2\hat{k} \cdot \nabla \phi_{n\ell m}(\vec{r},\beta) \left\} dV, \qquad (1.15)$$

which simplifies upon using the relations

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$$(-\nabla^2 - \frac{2}{r})\phi_{n\,\ell m}(\vec{r},\beta) = \left\{ -\beta^2 + \frac{2(\beta n-1)}{r} \right\} \phi_{n\,\ell m}(\vec{r},\beta)$$
(1.16)

and

$$\hat{k} \cdot \nabla \phi_{n \ell m}(\vec{r}, \beta) = \cos \theta \quad \frac{\partial \phi_{n \ell m}}{\partial r} - \frac{\sin \theta}{r} \quad \frac{\partial \phi_{n \ell m}}{\partial \theta} \quad (1.17)$$

The expression for the overlap matrix is given simply by

$$N_{n'\ell',n\ell}^{(m)}(R) = \int_{T} \left\{ (R - r\cos\theta)^2 \phi_{n'\ell'}(\vec{r},\beta) \phi_{n\ell m}(\vec{r},\beta) \right\} dV. \qquad (1.18)$$

The numerical solution of the matrix equation (1.13) is a two step process. Because of the complicated dependence of the matrices and the associated eigenvalues on the parameter β , it is impractical to develop the variational condition $\partial[E]/\partial\beta = 0$. Therefore, at a specific distance a value of β must be assumed and then the linear problem of Eq. (1.13) can be solved, yielding the eignevalues and eigenvectors. At this point the value of β can be varied, the matrix elements calculated, and the matrix equation (1.13) is again solved. In this way one can search for the value of β that gives the best upper bound on the eigenvalue.

Before the above procedure can be applied, it must first be decided to what extent the basis set of Eq. (1.12) will be extended in the expansion of the trial function. This determines the order of the matrix equation to be solved. Since only the positive m values, one at a time, need be considered the expansion of the trial function can be written as

$$\Psi_{m}(\vec{r}) = (R-r\cos) \sum_{\substack{\Sigma \\ j=1}}^{N} \sum_{\substack{k=0}}^{j-1} A_{j+k}^{(m)} \phi_{m+j,m+k,m}(\vec{r},\beta) \qquad (1.19)$$

where m is fixed and $\phi_{n,\ell,m}(\vec{r},\beta)$ is the function given by Eq. (1.12). Once N is chosen the size of basis set, and of the matrices $\underbrace{H}_{\lambda}^{(m)}$ and $\underbrace{N}_{\lambda}^{(m)}$, is easily seen to be N(N+1)/2. Increasing N is analogous to increasing the value of the principal quantum number n that is included in the expansion of the trial function, but care has to be taken in this interpretation since the set of functions of Eq. (1.12) are not the isolated hydrogen atom wavefunctions.

The procedure of the calculation is now given by the following. First, the value of the m quantum number, which is still a good quantum number, is decided upon. Second, the eigenvalue's position in the ordered set $E_i^{(m)}(R)$ i = 1, 2, 3, ... is chosen. This is done because the optimum value of β is dependent upon exactly which eigenvalue is to be minimized. Now the value of N of Eq. (1.19) is set and the optimum value of β and the associated eigenvalue at that matrix size are calculated. Next the value of N is increased by 1, which increases the matrix size by N + 1, and again the eigenvalue is minimized with respect to p. This process is repeated until the values of the minimized energy at two successive matrix sizes agree to a certain number of significant figures. In this report most of the results presented are calculated to four significant figures, recall that the energy is in units of Rydbergs, and this was obtained by going to matrix sizes of (28 x 28). An example of convergence of the ground state for several distances is given in Table 1.

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The results of the calculation for the first four states are given in Tables 2-5. There we have tabulated the optimum value of ß and the energy for a range of distances of the proton from the plane. Also included are several properties of these states that shall be discussed later. In these tables we have labelled the states by their m-quantum number and their position in the spectrum of the reduced problem, that is the spectrum of levels having the same m-value.

The results of the ground state energy can be compared to those obtained by Bruch and Ruijgrok ⁴. These authors were mainly interested in the imaging system as a model of physical adsorption (see next section); however the results for a change of the boundary surface only are given for the ground state. Their approach to the problem is a variational one that is similar in spirit to the present one. The difference is that the problem is cast in confocal elliptic coordinates with the foci at the proton and the image proton. The trial function is then chosen as

$$\Psi_t = \exp(-\alpha k/2) \sinh(\beta k/2) \sum_{k,\ell} C_{k\ell} \sum_{n=1}^{\ell} C_{k\ell} \sum_{n=1}^{\ell} (1.20)$$

In Eq. (1.20) ξ and η are the coordinates in the confocal elliptic system, α and β are non-linear variational parameters, and the set C_{k2} constitutes the linear variational parameters. The important feature of the trial function (1.20) is that the boundary value of $\psi_t = 0$ on the plane is satisfied by the sinh($\beta n/2$) term. After converting their results to Rydbergs, the two calculations agree to as many significant figures as are reported in that paper. For example, at a distance of 1.2 Bohr radii from the plane both methods yield a ground state energy of -0.7144 Ry.

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However results are given by Bruch and Ruijgrok only for the ground state so that there is no information on the manner in which the spectrum of a hydrogen atom changes as an infinite plane potential moves in from infinity. This information is easier to interpret when it is presented as a graph showing the energy as a function of the distance of the proton from the plane. These graphs are presented in Figures 2 and 3.

It is evident from Figure 2 that when the proton is located four Bohr radii away from the plane there is very little change in the ground state energy. As the distance from the plane decreases the energy increases until, at R = 0, it is equal to -.25 Ry. This result is the expected one since when the proton is located on the plane the Hamiltonian is separable and the problem is exactly solvable. The solutions are the isolated hydrogen atom eigenfunctions restricted by the selection rule

$$|\ell - m| = \text{odd} \quad . \tag{1.21}$$

This result was first pointed out by Levine⁵, who noted its importance for the problem of a shallow donor impurity located at the surface of a semiconductor (see paper II in this series).

The correct values at the R = O limit are also obtained for the excited states in Fig. 3. In that figure the states are labelled by their m value and their position in the matrix by the notation (m,p). There are several interesting features exhibited by the spectrum presented

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in Figure 3. At $R = \infty$ there exist two states with n = 2 and m = 0, i.e. the 2s and $2p_{n}$ states. However, at R=O there exists only one state with n = 3 and m = 0 because of the selection rule (1.21) and that is the $3p_0$ state. Therefore one of the states with n = 2, m = 0at $R = \infty$ must map onto a state with n = 4 at R = 0. At R = 5 a, the state which does this is labelled by (0,3). As R decreases the energy of state (0,3) increases until it crosses the state (0,4). These two states possess the same azimuthal quantum number m and are therefore eigenvalues of the same reduced matrix problem. This appears to be a true **crossing** for two reasons. First, the eigenvalues become equal, to four figure accuracy which is the limit of accuracy in the present calculations, at a distance from the plane of approximately 3.58 a_0 . Second, the properties derived from the wavefunctions of these two states have a consistent interpretation only if such a crossing takes place. That is, the dipole in the z-direction, the average kinetic energy and the average potential energy should be continuous functions of the distance from the plane and this would not be the case if such a crossing did not occur. As the distance to the plane is decreased even further another crossing occurs. However this crossing is for states of differing azimuthal symmetry so there is no reason to suspect another symmetry of the system at this distance.

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The ground state of an isolated hydrogen atom does not possess a net dipole moment. However when the charge distribution is changed by the presence of the boundary plane this is no longer true. Because of the azimuthal symmetry, the dipole moment of the ground state will be in the z-direction and the dipole moment operator can be written as⁴

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$$\mu_{z} \equiv z = r\cos\theta \quad . \tag{1.22}$$

A positive dipole moment is directed away from the boundary plane. The convention used here is that the dipole points from the negative to the positive charge.

The manner in which the average value of μ is calculates is modified slightly due to the non-orthogonality previously discussed. First the matrix $\underline{p}^{(m)}$ is calculated, where

$$\left(\mathbb{D}^{(m)}_{\mathfrak{S}}\right)_{n'\mathfrak{L}',n\mathfrak{L}} = \int_{\mathbf{I}}^{\cdot} \phi_{n'\mathfrak{L}'m} \,^{\mu} \,\phi_{n\mathfrak{L}m} \,^{dV} , \qquad (1.23)$$

and the optimized value of β is used. The expectation value of μ for a state labelled by (m,k) is then given by

$$\overline{\mu}_{k}^{(m)} = \frac{\underline{A}_{k}^{(m)}}{\underline{A}_{k}^{(m)}} \underbrace{\underline{A}_{k}^{(m)}}_{\underline{A}_{k}^{(m)}} \underbrace{\underline{A}_{k}^{(m)}}_{\underline{A}_{k}^{(m)}}$$
(1.24)

where $\underline{A}_{k}^{(m)}$ is the optimized k-th eignevector of Eq. (1.13) and $\underline{N}_{k}^{(m)}$ is the overlap matrix. The dipole expectation values are given in Tables 2-5. As expected the influence of the boundary plane is to push the electronic charge distribution away so that its 'center of gravity' lies behind the proton and yields negative $\overline{\mu}$. Note also that the dipole moments fall off much less rapidly as a function of R for the excited states. This is due to the fact that the excited states, because of their greater spatial extent, 'feel' the presence of the plane for a further distance than does the ground state.

The average kinetic and potential energies can be calculated in a manner similar to that for the dipole. But now it is not necessary

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to calculate any additional matrices, for $\underline{J}^{(m)}$ and $\underline{V}^{(m)}$ are already available from the calculation of $\underline{H}^{(m)}$. These expectation values have also been computed and are given in Tables 2-5.

In examining the expectation values of the kinetic and potential energies of the electron given in these tables it is apparent that the relation

$$2\overline{T} = -\overline{V}$$
(1.25)

is no longer satisfied. Equation (1.25) is of course the statement of the virial theorem for an isolated system with a coulomb interaction. When the system depends upon a parameter which is assumed to be fixed, which for example can be the internuclear coordinates of a diatomic molecule in the Born-Oppenheimer approximation or the distance to the plane in the present problem, the virial theorem must be modified from the form given in Eq. (1.25). This is due to the fact that the quantity known as the 'virial'

$$-1/2 \sum_{i} \overline{r_{i}F_{i}}$$

must include *all* of the forces acting on the system. This means that since the proton is assumed to be in a fixed position some external force must be acting on it so that it remains stationary. When this external force is taken into account the correct form of the virial theorem is given by

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$$2 \overline{T} = - \overline{v} - R \frac{\partial E}{\partial R} , \qquad (1.26)$$

÷

The force acting on the proton is therefore given by the quantity $\partial E/\partial R$. Note that in the present case the Hellman-Feynman theorem is no longer valid ^{4,18}. That is

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$$\frac{\partial E}{\partial R} \neq \langle \frac{\partial H}{\partial R} \rangle$$

because the region of integration of the matrix elements is dependent upon R. This points out the importance of the virial theorem, and the choice of the basis set, if the force on the proton is to be found.

The results presented in Table 2 have been used, with the aid of Eq. (1.26), to calculate the force on the proton when the atom is in its ground state, as a function of distance. This force is presented graphically in Figure 4. The interesting features of this force is that it has a maximum at approximately 0.9 a_0 and that it is nonzero at R = 0. At R = ∞ the force is zero and at R = $-\infty$ is must also be zero for then the electron and proton have been completely separated. Therefore a maximum must exist between these two limits.

2. Image Charges and a Model of Physisorption of Atomic Hydrogen

When a gas adsorbs onto a solid surface, depending upon the magnitude of the binding energy, it is commonly said to be chemisorbed or physically adsorbed. The binding energy that is ascribed to chemical adsorption can be several electron volts while that of physisorption is of the order of a fraction of an electron-volt. The difference in binding energy magnitudes is a reflection of the different processes which are believed to occur in the two types of adsorption; in chemical adsorption a bond is formed between the adsorbed molecule or atom and the surface while in physical adsorption significant charge rearrangement associated with bond formation is absent.

Physical adsorption is usually thought to be due to a potential that is made up of an attractive long-range Van der Waals (or dispersion) potential and a short-range repulsive potential due to the overlap of the electrons of the ad-atom with those of the metal. The problem is a many electron one and has been the subject of much recent work. ^{19-22,4} However, in the case of atomic hydrogen an idealized model can be constructed, as presented by Bruch and Ruijgrok,⁴ which reduces to a one electron problem.

The model consists of replacing the metal by a perfectly imaging medium with instantaneous coulomb interactions. The effect of the exchange repulsion is modelled by the condition that the atomic electron is excluded from the metal and that its wavefunction vanish on the surface. The potential that the proton then experiences, called by Bruch and Ruijgrok the "holding potential", is given by the change in the ground state electronic energy plus the interaction of the proton with his image in the metal.

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Solving the problem of the ground state electronic energy of this system is the first step in obtaining the 'holding potential' of the atomic hydrogen. Taking into account the possibility of a finite dielectric constant for Region B of Fig. 1, the Hamiltonian for the electron can be written as

$$H = \frac{-h^2}{2m} \nabla^2 - \frac{e^2}{r}$$

$$+ \frac{(\varepsilon-1)}{(\varepsilon+1)} \frac{e^2}{[r^2+4R^2-4rR\cos\theta]^{1/2}} - \frac{(\varepsilon-1)}{4(\varepsilon+1)} \frac{e^2}{(R-r\cos\theta)}$$
(2.1)

Equation (1.3) must, of course, be solved subject to the boundary condition that $\psi = 0$ on the surface z = R. The coordinate system of Eq. (2.1) is that indicated in Figure 1 and ε denotes the static dielectric constant of region B. We shall be interested mainly in the 'metallic' limit, that is $\varepsilon \rightarrow \infty$. The last two terms in Eq. (2.1) are, respectively, the interaction of the electron with the image of the proton and the interaction of the electron with its own image, and hence the extra-factor of 1/2 (energy of assembly).

The calculation of the energy eigenvalues and properties of these states proceeds exactly as previously outlined. Now, however, there are two additional matrix elements to be included in the matrix equations. The electron-image electron term is not hard to calculate analytically but this is not true of the electron-image proton interaction given by the third term of Eq. (2.1). Because of the law of cosines denominator and the restricted region of integration given by Eq. (1.14), it has not been possible to find a closed form expression for that matrix element. There are two ways of calculating the electron-image proton matrix element. One can either use a numerical approach or, by expanding the denominator of the electron-image proton potential in the standard series of Legendre polynomials, integrate term by term. The former method was chosen because the expressions and summation of the latter method consumed a much greater amount of computer time .than a straightforward numerical integration of the matrix elements by the Gauss-Legendre and Gauss-Laguere methods.

The results of this calculation are given in Tables 6 through 9 for the first 5 states. (Recall that $m \neq 0$ states are doubly degenerate.) The ground state of this system is shown graphically in Figure 5 where the ground state of the non-imaging case has been repeated for comparison. As is apparent from this figure, and shown explicitly in Table 6 where all the energy contributions are tabulated, the interaction of the electron with the image of the proton, which is repulsive, dominates the electron-image electron interaction which is attractive. In this instance also the R = 0 value is an expected one. When R = 0, and the system is perfectly imaging, the proton and image proton charges cancel each other (as far as the electron is concerned) and the problem is now that of an electron bound by its image, which is an exactly solvable^{23,24} one-dimensional Coulomb problem, yielding a ground state energy of -0.0625 Ry.

The first excited state of the isolated atom (principal quantum number n = 2) is 4-fold degenerate. In the presence of the metal this degeneracy is partially lifted, i.e., while the 2p, $|m| = \pm 1$ states are still degenerate (due to polar angle symmetry around the normal to the metal plane), the 2s and 2p, m = 0 states mix and their energy split.

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The energy as a function of distance of the proton from the surface for the 2p, |m|=1 doubly degenerate state is given in Table 7, and those for the states originating from the 2s and 2p, m = 0 in Tables 8 and 9 respectively. These results are in good agreement with those given in Table 3 of ref. 4 (to convert to the values of ref. 4 substract from our energies the proton-image proton interaction, - 1/2R, and divide the result by 2 to convert to atomic units).

Having solved the electronic part of the problems it is possible to construct the 'holding potential' of the atomic hydrogen. The potential that the proton experiences has two contributions. First, still in the Born-Oppenheimer approximation, is the change in the electronic energy of the system as a function of distance. The second is the proton-image proton interaction which is attractive in nature.

Calculating the "holding potential" for the ground state of the system (i.e. using the energy values in table 6, subtracting from them the ground state energy at infinite separation (-1.0 Ry) and adding the proton-image proton interaction energy $(-1/_{(2R)} Ry)$ yields the potential curve shown in Fig. 6, which exhibits a potential well of depth 8.6 X 10^{-3} Ry at R = 3.44a₀ in agreement with ref. 4 (see in particular section 9.1). The various contributions to this 'holding potential' are shown in Fig. 7. The ground state expectation values of the kinetic energy and electron-proton interaction, from which the corresponding energies at R = ∞ have been subtracted are shown as curves C and A, respectively. The electron-image proton and electron-image electron interactions are denoted as curves B and D, respectively. The proton-image proton energy, given by $-1/_{(2R)}$ Ry, is denoted as curve E. The sum of the curves in Fig. 7 yields the "holding potential" curve given in Fig. 6.

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Finally we comment on the dipole expectation values given in Tables 6-9. As shown in Table 6 for the ground state the dipole moment is negative, i.e. directed inward, for locations of proton near and beyond the minimum in the holding potentials (same as found in reference 4), changing sign of the vicinity of $R=4.1a_0$. The values of the dipole moment are much larger for the excited states and falls off slower as the atom is removed from the surface reflecting the larger spatial extent of the excited states wave functions. It is of interest to **n**ote that for the distances included in the tables the dipole of the 25, m = 0 state remains negative and large even up to \sim 7.0 a₀, while for the 2p, m = 0 it changes orientation between $R = 5.0a_0$ and $5.2a_0$ and past that distance an oscillation in magnitude is observed. Similarly a reversal of sign occurs for the 2p,m=1 (doubly degenerate) state between $R=6.4a_0$ and $6.6a_0$. It has been suggested¹⁹ that the quantitative balance between contributions which determine the orientation of dipoles of physiorbed atoms may differ in light and heavy atoms, and this may be a demonstration of such an effect.⁴

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FIGURE CAPTIONS

- Fig. 1 The coordinate system of Eq. (1.1) centered at the proton and the boundary surface at $z=R=rcos\theta$.
- Fig. 2 Ground state energy as a function of distance of the hydrogen/ impenetrable wall system. In this, and the following figures energy is in units of Rydbergs and distance is in units or Bohr radii.
- Fig. 3 The first 13 excited states of the hydrogen/impenetrable wall system.
- Fig. 4 Force on the proton when the electron is in its ground state.
- Fig. 5 Ground state energy as a function of proton distance from the plane for the perfectly imaging substrate ($\varepsilon_2 \rightarrow \infty$) system.
- Fig. 6 The 'holding potential' of Bruch and Ruijgiok in which the image electron-proton interaction has not been included.
- Fig. 7 The various contributions to the interaction potential. The curve A represents the change in the expectation value of the electron-proton interaction from its value for the isolated hydrogen atom. Curve B is the average value of the electronimage proton interaction (\overline{Ve} -imp). Curve C is the change in the electron's average kinetic energy. Curve D represents the average value of the electron-image electron interaction (\overline{Ve} -ime). Curve E is the proton-image proton interaction (-1/2R).

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Convergence of the ground state energy for the hydrogen/impenetrable wall system at several distances. Distance is given in units of Bohr radii and energy is in units of Rydbergs.

•	R	0.0	0.2	0.8	4.0
	3 × 3	2500	2448	4849	9888
	6 × 6	2500	2735	5012	· 9 955
26	10 × 10	2500	2786	5042	9 969
x S1	15 × 15	•••	2800	5058	9972
atri	21 × 21	•••	2801	5064	9973
Σ	. 28 × 28	•••	2802	5065	9974

Ground state properties of the hydrogen/impenetrable wall system (m=0, p=1). Energies are in units of Rydbergs, the dipole values, $\overline{\mu}_z$ are given in units of $\frac{ea_0}{2}$ (=1.271 debye), and the distances are given in terms of Bohr radii ($a_0 = 0.529 \text{ Å}$). T and V are the expectation values of the kinetic and potential energies, respectively.

R	β	Е _О	$\overline{\mu}_z$	т	ν
0.0	1.000	-0.2500	–	0.2500	-0.2500
0.2	1.001	-0.2802	-6.383	0.3170	-0.5872
0.4	1.077	-0.3272	-5.099	0.4458	-0.7730
0.6	1.321	-0.4027	-3.735	0.6774	-1.0801
0. 8	1.537	-0.5065	-2.617	0.9527	-1.4592
1.0	1.696	-0.6172	-1.877	1.1480	-1.7652
1.2	1.795	-0.7144	-1.407	1.2375	-1.9519
1.4	1.850	-0.7912	-1.092	1.2576	-2.0488
1.6	1.872	-0.8488	-0.865	1.2429	-2.0917
1.8	1.876	-0.8911	-0.693	1.2139	-2.1049
2.0	1.870	-0.9217	-0.559	1.1811	-2.1028
2.2	1.852	-0.9438	-0.451	1.1494	-2.0933
2.4	1.822	-0.9598	-0.364	1.1211	-2.0809
2.6	1.775	-0.9712	-0.292	1.0968	-2.0680
2.8	1.719	-0.9794	-0.234	1.0765	-2.0558
3.0	1.603	-0.9853	-0.186	1.0599	-2.0452
3.2	1.554	-0.9896	-0.147	1.0465	-2.0360
3.4	1.414	-0.9926	-0.116	1.0358	-2.0284
3.6	1.290	-0.9947	-0.091	1.0274	-2.0221
3. 8	1.209	-0.9963	-0.071	1.0208	-2.0171
4.0	1.183	~0 .9974	-0.055	1.0157	-2.0131
4.2	1.161	-0.9981	-0.042	1.0118	-2.0099

Properties of the first excited state of the hydrogen/impenetrable wall system (m=0,p=2). Units as in Table 2.

R	β	E(0,2)	$\overline{\mu}_z$	T	v
0.0	0.500	-0.1111	_	0.1111	-0.2222
0.2	0.506	-0.1198	-17.171	0.1300	-0.2498
0.4	0.636	-0.1321	-15.231	0.1623	-0.2944
0.6	0.728	-0.1493	-13.148	0.2074	-0.3568
0.8	0.793	-0.1687	-11.408	0.2436	-0.4123
1.0	0.848	-0.1856	-10.172	0.2610	-0.4466
1.2	0.855	-0.1988	- 9.353	0.2669	-0.4657
1.4	0.865	-0.2087	- 8.761	0.2694	-0.4781
1.6	0.866	-0.2164	- 8.320	0.2702	-0.4866
1.8	0.868	-0.2224	- 7.974	0.2704	-0.4928
2.0	0.869	-0.2272	- 7.695	0.2700	-0.4972
2 .2	0.866	-0.2311	- 7.465	0.2693	-0. 5004
2.4	0.863	-0.2342	- 7.271	0.2684	-0.5027
2.6	0.858	-0.2369	- 7.106	0.2674	-0.5042
2.8	0.853	-0.2390	- 6.964	0.2662	-0.5052
3. 0	0.849	-0.2408	- 6.840	0.2651	-0.5058
3.2	0.843	-0.2423	- 6.732	0.2639	-0.5061
3.4	0.840	-0.2435	- 6.638	0.2627	-0.5062
3.6	0.835	-0.2446	- 6.555	0.2616	-0.5061
3.8	0.829	-0.2454	- 6.482	0.2605	-0.5059
4.0	0.823	-0.2462	- 6.417	0.2595	-0.5056
4.2	0.819	-0.2468	- 6.361	0.2585	-0.5053
4.4	0.813	-0.2473	- 6.310	0.2576	-0.5049
4.6	0.808	-0.2477	- 6.266	0.2568	-0.5045
4.8	0.800	-0.2481	- 6.227	0.2561	-0.5041
5.0	0.793	-0.2484	- 6.193	0.2554	-0.5038

TABLE 3

Properties of the second excited state (m=1,p=1) of the hydrogen/ impenetrable wall system. Units as in Table 2.

R	β	E(1,1)	$\overline{\mu}_z$	Ŧ	v
0.0	0.412	-0.1111	-	0.1111	-0.2222
0.2	0.449	-0.1150	-12.358	0.1190	-0.2340
0.4	0.486	-0.1192	-11.580	0.1282	-0.2474
0.6	0.519	-0.1239	-10.792	0.1387	-0.2626
0.8	0.559	-0.1291	- 9.999	0.1507	-0.2798
1.0	0.590	-0.1347	- 9.206	0.1643	-0.2991
1.2	0.625	-0.1409	- 8.425	0.1794	-0.3203
1.4	0.656	-0.1476	- 7.668	0.1956	-0.3431
1.6	0.687	-0.1545	- 6.948	0.2121	-0.3667
1.8	0.713	-0.1619	- 6.278	0.2282	-0.3900
2.0	0.738	-0.1693	- 5.663	0.2430	-0.4123
2.2	0.759	-0.1766	- 5.109	0.2561	-0.4327
2.4	0.779	-0.1837	- 4.613	0.2671	-0.4508
2.6	0.796	-0.1905	- 4.170	0.2758	-0.4663
2.8	0.811	-0.1968	- 3.777	0.2824	-0.4792
3.0	0.822	-0.2027	- 3.426	0.2871	-0.4898
3.2	0.831	-0.2081	- 3.113	0.2901	-0.4982
3.4	0.838	-0.2129	- 2.833	0.2918	-0.5047
3.6	0.845	-0.2173	- 2.581	0.2923	-0.5097
3.8	0.848	-0.2213	- 2.353	0.2920	-0.5133
4.0	0.851	-0.2248	- 2.147	0.2911	-0.5159
4.2	0.852	-0.2279	- 1.959	0.2896	-0.5175
4.4	0.853	-0.2307	- 1.788	0.2878	-0.5185
4.6	0.853	-0.2331	- 1.631	0.2858	-0.5189
4.8	0.851	-0.2353	- 1.488	0.2837	-0.5190
5.0	0.849	-0.2372	- 1.356	0.2815	-0.5187

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Properties of the third excited state (m=0,p=3) of the hydrogen/ impenetrable wall system. Note the discontinuity of the properties $\overline{\mu}_z$, \overline{T} and \overline{V} between the distances of $3.4a_0-3.6a_0$ which indicates a level crossing.

R	β	E(0,3)	$\overline{\mu}_{z}$	Т	V
0.0	0.268	-0.0625	-	0.0625	-0.1250
0.2	0.311	-0.0661	-32.516	0.0701	-0.1362
0.4	0.352	-0.0709	-30.202	0.0812	-0.1521
0.6	0.398	-0.0772	-27.665	0.0949	-0.1720
0.8	0.441	-0.0838	-25.323	0.1056	-0.1895
1.0	0.472	-0.0895	-23.551	0.1110	-0.2005
1.2	0.491	-0.0938	-22.314	0.1133	-0.2071
1.4	0.502	-0.0970	-21.444	0.1143	-0.2113
1.6	0.509	-0.0994	-20.804	0.1149	-0.2143
1.8	0.513	-0.1013	-20.317	0.1152	-0.2164
2.0	0.515	-0.1028	-19.932	0.1153	-0.2181
2.2	0.515	-0.1040	-19.623	0.1153	-0.2193
2.4	0.515	-0.1050	-19.365	0.1153	-0.2203
2.6	0.514	-0.1059	-19.151	0.1152	-0.2211
2.8	0.513	-0.1066	-18.968	0.1151	-0.2217
3.0	0.515	-0.1072	-18.809	0.1150	-0.2221
3.2	0.510	-0.1077	-18.676	0.1148	-0.2225
3.4	0.508	-0.1081	-18.558	0.1146	-0.2227
3.6	0.423	-0.1087	- 5.856	0.2206	-0.3294
3.8	0.449	-0.1154	- 4.709	0.2494	-0.3648
4.0	0.496	-0.1228	- 3.590	0.2791	-0.4019
4.2	0.535	-0.1310	- 2.568	0.3071	-0.4381
4.4	0.570	-0.1400	- 1.663	0.3314	-0.47 10
4.6	0.600	-0.1483	- 0.876	0.3507	~0.49 90

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R	ß	E(0,3)	$\overline{\mu}_z$	Ŧ	v
4.8	0.626	-0.1571	-0.199	0.3646	-0.5217
5.0	0.650	-0.1656	-0.383	0.3736	-0.5391

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TABLE 5

Ground state properties of the hydrogen/perfectly imaging substrate system. \overline{V}_1 , \overline{V}_2 and \overline{V}_3 denote the average values of the last three interaction terms in the Hamiltonian of Eq. (1.36). \overline{T} and \overline{V} are the expectation values of the kinetic and potential energies, respectively.

R	β	E(0.1)	$\overline{\mu}_{z}$	Ŧ	v,	\overline{v}_2	<u>v</u> 3
0.2	0.174	-0.0633	-11.408	0.0673	-0.1470	-0.1267	0.1440
Ò.4	0.399	-0.0726	- 9.597	0.1055	-0.2995	-0.1450	0.2664
0.6	0.753	-0.1039	- 6.482	0.2578	-0.5789	-0.2002	0.4174
0.8	1.142	-0.1839	- 3.671	0.6107	-1.0821	-0.2841	0.5717
1.0	1.439	-0.3049	- 2.237	0.9413	-1.5444	-0.3326	0.6308
1.2	1.621	-0.4274	- 1.532	1.1139	-1.8209	-0.3409	0.6205
1.4	1.725	-0.5309	- 1.125	1.1758	-1.9612	-0.3295	0.5848
1.6	1.780	-0.6123	- 0.856	1.1821	-2.0270	-0.3105	0.5430
1.8	1.806	-0.6748	- 0.662	1.1641	-2.0518	-0.2893	0.5024
2.0	1.813	-0.7224	- 0.514	1.1376	-2.0564	-0.2684	0.4648
2.2	1.794	-0.7589	- 0.398	1.1098	-2.0511	-0.2486	0.4311
2.4	1.751	- 0. 7870	- 0.305	1.0843	-2.0419	-0.2304	0.4009
2.6	1.690	-0.8090	- 0.231	1.0623	-2.0316	-0.2139	0.3741
2.8	1.616	- 0. 8265	- 0.172	1.0441	-2.0219	-0.1988	0.3502
3.0	1.539	-0.8405	- 0.125	1.0296	-2.0135	-0.1853	0.3287
3.2	1.466	-0.8519	- 0.088	1.0183	-2.007	-0.1731	0.3095
3.4	1.398	-0.8614	- 0.059	1.0097	-2.001	-0.1621	0.2923
3.6	1.336	- 0. 8695	- 0.037	1.0034	-1.9974	-0.1522	0.2766
3.8	1.280	- 0. 8764	- 0.021	0.9989	-1.9946	-0.1433	0.2625
4.0	1.228 .	- 0. 8825	- 0.009	0.9959	-1.9927	-0.1353	0.2497
4.2	1.182	-0.8878	- 0.0004	0.9939	-1.9916	-0.1281	0.2380
4.4	1.140	-0.8926	0.005	0.9928	-1.9911	-0.1216	0.2273
4.6	1,100	-0.8969	0,009	0.9922	-1.991	-0.1156	0.2174

R	β	E(0,1)	$\overline{\mu}_z$	Ť	۲ _۲	v ₂	\overline{v}_3
4.8	1.065	-0.9009	0.012	0.9920	-1. 9912	-0.1102	0.2084
5.0	1.033	-0.9046	0.013	0.9922	-1.9915	-0.1053	0.2001
5.2	1.003	-0.9079	0.013	0.9925	-1.9920	-0.1008	0.1924
5.4	0.977	-0.9111	0.013	0.9929	-1.9925	-0.0967	0.1853
5.6	0.951	-0.9140	0.012	0.9934	-1.9931	-0.0929	0.1787
5.8	0.931	-0.9168	0.012	0.9939	-1.9937	-0.0894	0.1725
6.0	0.912	-0.9193	0.011	0.9943	-1.9992	-0.0862	0.1668

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Properties	of th	e fi	rst	excited	state	(m=1,p	e=1),	the	2p, m =1	doubly
degenerate	state	, of	the	hydroge	en/perf	ectly	imagi	ng: s	substrate	system.

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R	β	E(1,1)	$\overline{\mu}_z$	T	ν _η	v ₂	ν ₃
0.2	0.149	-0.0602	-11.906	0.0606	-0.0506	-0.1207	0.0505
0.4	0.150	-0.0604	-11.486	0.0609	-0.0530	-0.1210	0.0527
0.6	0.152	-0.0605	-11.059	0.0614	-0.0565	-0.1213	0.0558
0.8	0.156	-0.0608	-10.624	0.0621	-0.0620	-0.1217	0.0608
1.0	0.162	-0.0611	-10.170	0.0636	-0.0717	-0.1223	0.0694
1.2	0.177	-0.0617	- 9.676	0.0671	-0.0915	-0.1234	0.0860
1.4	0.216	-0.0630	- 9.077	0.0759	-0.1287	-0.1253	0.1152
1.6	0.286	-0.0656	- 8.299	0.0920	-0.1766	-0.1288	0.1478
1.8	0.363	-0.0697	- 7.407	0.1133	-0.2234	-0.1335	0.1740
2.0	0.434	⁻ -0.0752	- 6.503	0.1372	-0.2675	-0.1386	0.1936
2.2	0.496	-0.081	- 5.656	0.1615	-0.3079	-0.1431	0.207 0
2.4	0.548	-0.089	- 4.902	0.1840	-0.3437	-0.1465	0.2167
2.6	0.593	-0.0976	- 4.248	0.2036	-0.3744	-0.1486	0.2218
2.8	0.630	-0.1058	- 3.688	0.2196	-0.3998	-0.1494	0.2238
3.0	0.660	-0.1138	- 3.207	0.2322	-0.4205	-0.1490	0.2235
3.2	0.685	-0.1215	- 2,792	0.2416	-0.4369	-0.1477	0.2215
3.4	0.705	-0.1288	- 2.432	0.2484	-0.4499	-0.1457	0.2183
3.6	0.722	-0.1356	- 2.115	0.2531	-0.4599	-0.1431	0.2143
3.8	0.735	-0.1419	- 1.836	0.2559	-0.4675	-0.1401	0.2098
4.0	0.745	-0.1476	- 1.587	0.2575	-0.4732	-0.1369	0.2050
4.2	0.753	-0.1529	- 1.364	0.2580	-0.4774	-0.1334	0.2000
4.4	0.757	-0.1576	- 1.163	0.2578	-0.4804	-0.1299	0.1949
4.6	0.760	-0.162	- 0.982	0.2570	-0.4825	-0.1263	0.1899
4.8	0.760	-0.1659	- 0.818	0.2558	-0.4839	-0.1227	0.1848
5.0	0.757	-0.1695	- 0.669	0.2544	-0.4847	-0.1191	0.1799

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R	β	E(1,1)	$\overline{\mu}_{z}$	Ť	v,	v ₂	v ₃
5.2	0.753	-0.1727	- 0.535	0.2528	-0.4852	-0.1155	0.1751
5.4	0.747	-0.1757	- 0.413	0.2511	-0.4853	-0.112	0.1705
5.6	0.739	-0.1783	- 0.303	0.2495	-0.4853	-0.1085	0.1660
5.8	0.731	-0.1808	- 0.204	0.2479	-0.4851	-0.1051	0.1616
6.0	0.722	-0.1830	- 0.116	0.2463	-0.4848	-0.1019	0.1574
6.2	0.711	-0.1850	- 0.036	0.2449	-0.4845	-0.0987	0.1533
6.4	0.700	-0.1868	- 0.034	0.2436	-0.4842	-0.0956	0.1494
6.6	0.689	- 0. 1885	- 0.096	0.2424	-0.4839	-0.0925	0.1456

Properties of the second excited state, originating from the 2s, m=0 state, of the hydrogen/perfectly imaging substrate system.

R	β	E(0,2)	$\overline{\mu}_{z}$	Ŧ	\overline{v}_1	v ₂	۷ 3
0.2	0.135	-0.0590	-12.162	0.0615	-0.0773	-0.1184	0.0756
0.4	0.144	-0.0602	-11.526	0.0622	-0.0590	-0.1207	0.0573
0.6	0.154	-0.0608	-11.052	0.0630	-0.0623	-0.1219	0.0604
0.8	0.191	-0.0616	-10.669	0.0663	-0.0836	-0.1229	0.0786
1.0	0.423	-0.0656	-10.648	0.0983	-0.2011	-0.1213	0.1586
1.2	0.537	-0.0733	-10.036	0.1239	-0.2692	-0.1207	0.1927
1.4	0.596	-0.0819	- 9.344	0.1430	-0.3128	-0.1207	0.2086
1.6	0.635	-0.0906	- 8.736	0.1587	-0.3451	-0.1203	0.2161
1.8	0.662	-0.0989	- 8.228	0.1716	-0.3700	-0.1193	0.2187
2.0	0.681	-0.1068	- 7.806	0.3897	-0.3897	-0.1176	0.2183
3.0	0.727	-0.1378	- 6.508	0.2119	-0.4430	-0.1045	0.1977
4.0	0.720	-0.1580	- 5.885	0.2230	-0.4631	-0.0899	0.1720
5.0	0.678	-0.1716	- 5.497	0.2291	-0.4730	-0.0779	0.1501
6.0	0.609	-0.1818	- 4.762	0.2368	-0.4806	-0.0722	0.1343
2.2	0.695	-0.1141	- 7.454	0.1909	-0.4053	-0.1155	0.2159
2.4	0.707	-0.1208	- 7.157	0.1979	-0.4179	-0.1130	0.2122
2.6	0.716	-0.127	- 6.907	0.2036	-0.4280	-0.1103	0.2078
2.8	0.722	-0.1326	- 6.692	0.2082	-0.4363	-0.1070	0.2028
3.0	0.727	-0.1378	- 6.508	0.2119	-0.4430	-0.1045	0.1977
3.2	0.729	-0.1425	- 6.348	0.2150	-0.4485	-0.1015	0.1925
3.4	0.729	-0.1469	- 6.209	0.2175	-0.4531	-0.0985	0.1872
3.6	0.728	-0.15 09	- 6.088	0.2197	-0.4570	-0.0956	0.1820
3.8	0.726	-0.1546	- 5.980	0.2215	-0.4603	-0.0927	0.177 0
4.0	0.720	-0.158	- 5.885	0.2230	-0.4631	-0.0899	0.1720
4.2	0.714	-0.1611	- 5.799	0.2244	-0.4655	-0.0873	0.1673

TABLE 8

R	β	E(0,2)	μ _z	T.	ν	\overline{v}_2	v ₃
4.4	.706	-0.1640	- 5.720	0.2257	-0.4677	-0.0847	0.1627
4.6	.698	-0.1667	- 5.646	0.2264	-0.4696	-0.0823	0.1583
4.8	.689	-0.1692	- 5.573	0.2280	-0.4714	-0.0800	0.1541
5.0	.678	-0.1716	- 5.497	0.2291	-0.4730	-0.0779	0.1501
5.2	.667	-0.1739	- 5.414	0.2303	-0.4745	-0.0760	0.1464
5.4	.654	-0.1760	- 5.316	0.2315	-0.4760	-0.0744	0.1429
5.6	.642	-0.1780	- 5.192	0.2329	-0.4870	-0.0731	0.1396
5.8	.625	-0.1800	- 5.020	0.2346	-0.4789	-0.0723	0.1367
6.0	.609	-0.1810	- 4.762	0.2368	-0.4806	-0.0722	0.1343

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Properties of the third excited state originating from the 2p, m=0 state, of the hydrogen/perfectly imaging substrate system.

R	β	E(0.3)	μz	T	v ₁	\overline{v}_2	\overline{v}_3
0.2	.119	0524	-14.060	.0553	0772	1058	.0753
0.4	.125	0541	-13.102	.0581	0676	1092	.0646
0.6	.131	0552	-12.395	.0594	0655	1112	.0621
0.8	.141	0562	-11.746	.0615	0707	1131	.0659
1.0	.159	0574	-11.163	.0645	0773	1144	.069 8
1.2	.176	0586	-10.495	.0656	0728	1162	.0648
1.4	.182	0595	- 9.870	.0649	0665	1179	.0601
1.6	.185	0600	- 9.354	.0645	0653	1189	.0596
1.8	.189	0605	- 8.898	.0647	0669	1195	.0612
2.0	.197	0609	- 8.469	.0654	0710	1198	.0645
2.2	.209	0614	- 8.065	.0666	0772	1199	.0691
2.4	.221	0619	- 7.684	.0682	0845	1198	.0742
2.6	.238	0625	- 7.317	.0706	0938	1194	.0815
2.8	.254	0632	- 6.952	.0737	1039	1190	.0860
3.0	.270	0640	- 6.574	.0779	1153	1187	.0921
3.2	.283	0651	- 6.158	.0840	1289	1187	.0985
3.4	.299	0665	- 5.665	.0948	1489	1196	.1072
3.6	.317	0686	- 5.027	.1165	1830	1229	.1207
3.8	.342	0722	- 4.183	.1596	2432	1305	.1420
4.0	.378	0781	- 3.197	.2198	3216	1419	.1657
4.2	.427	0862	- 2.197	.2745	3907	1526	.1825
4.4	.482	0957	- 1.271	.3149	4424	1603	.1921
4.6	.532	1059	- 0.466	.3421	4797	1651	.1969
4.8	.576	1161	- 0.211	.3589	5060	1675	.1985

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R	β	E(0,3)	$\overline{\mu}_{z}$	Ť	v,	\overline{v}_2	\overline{v}_3
5.0	.610	1260	0.773	.3677	5238	1680	.1981
5.2	.635	1354	1.236	.3705	5352	1670	.1963
5.4	.652	1441	1.611	.3690	591 8	1648	.1935
5.6	.663	1521	1.901	.3644	544 8	1616	.1899
5.8	.667	1593	2.097	.3576	5452	1575	.1858
6.0	.669	1658	2.169	.3489	5435	1523	.1811
6.2	.667	1715	2.047	. 3384	5400	1455	.1756
6.4	.667	1765	1.575	.3255	5346	1360	.1686
6.6	.669	1808	0.455	.3083	5264	1215	.1588

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Figure 3



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B.5 Shallow Donor Impurities Near Semi-conductor Vacuum and MOS Interfaces

Variational solutions to the effective mass equations describing hydrogenic donor impurities located near semiconductor-vacuum and semiconductorinsulator interfaces were obtained. Results for the ground and excited eigenstate, binding energy, spectra as a function of the location of the impurity from the semiconductor-vacuum interface are presented for Si(001) and Ge(111) surfaces. The electronic binding-energy of a hydrogenic donor impurity as a function of its distance from the interface both into the insulator or into the semiconductor were studied in detail for the Si-Si0₂ case. The effect of an external electric field on the impurity binding energy was investigated and the results are compared with other recent theoretical calculations and experimental date. Our results show that to achieve better agreement with experimental data on MOSFET, (Si-Si0₂ system), it is necessary to locate the impurity in the oxide part of the interface. In addition the importance of proper choice of the variational basis set in the calculation is demonstrated.

The method developed by us can be generalized with relative ease to treat shallow donor impurities in modulated structures.

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Variational Solutions of Simple Quantum Systems Subject to Variable Boundary Conditions

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II. SHALLOW DONOR IMPURITIES NEAR
SEMICONDUCTOR INTERFACES: Si, Ge

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Abstract

Variational solutions to the effective mass equations describing hydrogenic donor impurities located near semiconductor-vacuum and semiconductor-insulator interfaces are presented and discussed. Results for the ground and excited eigenstate, binding energy, spectra as a function of the location of the impurity from the semiconductor-vacuum interface are presented for Si(001) and Ge(111) surfaces. The electronic binding-energy of a hydrogenic donor impurity as a function of its distance from the interface both into the insulator or into the semiconductor is studied in detail for the Si-SiO₂ case. The effect of an external electric field on the impurity binding energy is investigated and the results are compared with other recent theoretical calculations and experimental data.

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The electrical and optical properties of bulk semiconductors and of semiconductor interfaces (either with vacuum of in metal-oxide-semiconductor, MOS, devices) are strongly affected by impurities.¹ In the case of a bulk semiconductor characterized by a dielectric constant ε and isotropic effective mass m^{*} the bound states associated with singly charged attractive Coulomb center impurities embedded in the semiconductor have (for a parabolic band) a hydrogenic spectrum, $E_n = -m^* e^2/2\epsilon^2 h^2 n^2$, n = 1, 2, ... with respect to the adjacent band edge. It was pointed out first by Levine,² that when the impurity is placed at the semiconductor surface the spectrum is modified. As argued by Levine, since the height of the surface barrier can be several electron-volts (and in the case of $Si-SiO_2$ about 3 eV³) and the binding energies of shallow donor impurities are of the order of mili-electron-volts the surface can be modeled as an infinite potential barrier requiring that the electron wavefunction vanish at the boundary (the effect of the infinite discontinuity approximation has been shown to be negligible⁴). In the context of the effective mass approximation, 5-7 neglecting the image potential and band bending and assuming a spherical band one obtains again for an impurity located exactly at the surface a hydrogenic energy level spectrum subject to the selection rule that only states with |l-m| = odd are allowed (i.e., s-states are excluded).

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Since that time there have been several investigations of the energies and properties of these states.⁸⁻¹³ Bell⁸ <u>et al.</u> used the selection rules of Levine and the bulk energies of silicon and germanium to calculate transition energies. Petukhov⁹ <u>et al.</u> included image charges in the effective mass Hamiltonian and performed a perturbation calculation on that system.

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Karpushin¹⁰ extended that perturbative treatment with the inclusion of linear band bending near the surface. In a later article Karpushin¹¹ used a variational method to calculate the binding energies of donors on silicon and germanium surfaces. It is important to note that all of these authors constrained the impurity to lie exactly on the surface.

Realistically the impurity will be distributed in the near-interface region, rather than being localized at the interface. The first computation which considers such a situation is that of Godwin and Teff¹⁴ who employed a simple form of the trial wavefunctions for the ground and excited states in a variational calculation. A more complete basis set, and also including the effect of an external electric field (see Section 2) has been employed by Lipari.¹⁵

Armed with the variational method which we have described in detail in the preceeding paper¹⁶ in this series, (which will be referred to as Paper I), we study in this paper¹⁷ the spectra of shallow donor impurities near semiconductor interfaces (vacuum and MOS interfaces, including the effect of electric fields) within the context of the effective mass approximation.

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In section 1 the case of a donor impurity near a semiconductor-vacuum interface is considered. Results are given for Si(001) and G(111) surfaces. In section 2 a donor impurity near a semiconductor-insulator is investigated. The impurity is embedded in the semiconductor or in the insulator. Results are given for Si-SiO₂ as a function of the location of the impurity and under the influence of an external electric field. Comparison to previous theories^{13,15} and experimental data is given.

-2-

1. A SHALLOW DONOR IMPURITY NEAR A SEMICONDUCTOR SURFACE

We consider first a donor impurity embedded in the semiconductor near, but not necessarily at, the semiconductor-vacuum interface. In constructing the model Hamiltonian for this system several simplifying assumptions shall be made. First because of the multiple minima of the conduction band in k-space, the crystallographic orientation of the surface becomes important. When considering the (001) plane of silicon or the (111) plane of germanium there exists³ two kinds of constant energy ellipsoids; those with their major axis parallel to the surface and those with their major axis perpendicular. One of the results of Karpushin¹¹ is that the ellipsoids with their major axes perpendicular give rise to a series of states which lie lower in energy than those with their major axis parallel to the surface. **Con**sequently only these types of ellipsoids will be considered, because this allows a simplification in the requirements of the boundary **co**ndition ψ = 0 on the surface plane. In addition we shall assume that there is no change in the band structure near the surface, such as the formation of a space charge layer, so that there is no band bending near the surface. Finally, we shall be working in the onevalley effective mass approximation 1^{18} .

- 3-

The preceding considerations lead to an effective mass equation given by

$$\begin{cases} \frac{-\tilde{n}^{2}}{2m_{t}^{*}} \left(\frac{\vartheta^{2}}{\vartheta x^{2}} + \frac{\vartheta^{2}}{\vartheta y^{2}}\right) - \frac{\tilde{n}^{2}}{2m_{g}^{*}} \frac{\vartheta^{2}}{\vartheta z^{2}} - \frac{e^{2}}{\varepsilon_{1}r} \\ + \frac{(\varepsilon_{2} - \varepsilon_{1})}{\varepsilon_{1}(\varepsilon_{1} + \varepsilon_{2})} \frac{e^{2}}{[r^{2} + 4R^{2} - 4rR \cos\theta]^{1/2}} \\ \frac{-(\varepsilon_{2} - \varepsilon_{1})e^{2}}{4\varepsilon_{1}(\varepsilon_{1} + \varepsilon_{2})(R - r\cos\theta)} \end{cases} F(\vec{r}) = EF(\vec{r}) . \qquad (1.1)$$

This equation must be solved subject to the boundary condition

$$F(\vec{r}) = 0$$
 when $r \cos \theta = R$. (1.2)

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The impurity is located at a distance R from the planar interface. (See Fig. 1 of paper I.) Note that equation (1.1) follows from the choice of the (001) surface for silicon or the (111) surface for germanium. In Eq. (1.1) m_t^* and m_g^* are the transverse and longitudinal effective masses, ε_1 denotes the static dielectric constant of the region containing the impurity, and in this case that is the semiconductor. The static dielectric constant of region B (see Paper I, Fig. 1) is denoted by ε_2 . This leaves open the option of solving for a semiconductor/ insulator interface or a semiconductor/vacuum interface. From Eqs. (1.1) and (12.1) it is apparent that the methods described in Paper I are applicable when $m_t^* = m_g^*$. The last two terms on the right hand side of Eq. (1.1) are the electron-image proton and the electron-image electron terms, respectively. In the following we shall be concerned with solving a scaled version of Eq. (1.1). All distances, including R, the distance of the impurity from the surface plane, are scaled to units of effective Bohr radii given by

$$a_{o}^{*} = \frac{\hbar^{2} \varepsilon_{1}}{m_{t}^{*} e^{2}} = 0.529 \left(\frac{\varepsilon_{1}m}{m_{t}^{*}}\right)^{O} A , \qquad (1.3)$$

and the energy is in units of effective Rydbergs

$$Ry^{\star} = \frac{m_{t}^{\star} e^{4}}{2h^{2} \varepsilon_{1}^{2}} = 13.6 \left(\frac{m_{t}^{\star}}{m} \frac{1}{\varepsilon_{1}^{2}}\right) eV \quad . \tag{1.4}$$

The scaled version of Eq. (1.1) is then given by

$$\left\{-\left(\frac{\partial^{2}}{\partial x^{2}}+\frac{\partial^{2}}{\partial y^{2}}+\gamma \frac{\partial^{2}}{\partial z^{2}}\right)-\frac{2}{r}+\frac{2Q}{\left[r+4R^{2}-4rR\cos\theta\right]^{1/2}}-\frac{Q}{\left[2R-r\cos\theta\right]}\right\} F(\vec{r}) = EF(\vec{r}) , \qquad (1.5)$$

where Q is given by

$$Q = \frac{(\epsilon_2 - \epsilon_1)}{(\epsilon_2 + \epsilon_1)} , \qquad (1.6)$$

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and γ is the effective mass ratio defined as $\gamma = m_t^*/m_\ell^*$. We note in passing that the effective mass equation has been scaled to the bulk semiconductor parameters rather than the surface units defined by Stern and Howard³. This scaling has been chosen for easier comparison to the bulk limit (R \rightarrow large) and because this choice yields the factor $(\varepsilon_2 - \varepsilon_1)/(\varepsilon_1 + \varepsilon_2)$. This factor always lies between -1 and 1 whereas this is not the case for surface units. This feature is a practical one since large constants multiplying matrix elements are undesirable in the solution of the matrix equations.

In the solution of Eq. (1.5) subject to the boundary conditions of Eq. (1.2) a strategy that is a combination of the methods of Paper I with a method presented by Faulkner¹⁹ is used. Since the change in the Hamiltonian of Eq. (1.5) from that of the previous paper¹⁶ is in the z-dependence only, all the symmetry properties previously discussed are valid here. In particular, m remains a good quantum number while n and ℓ do not. The difference from the R $\rightarrow \infty$ case in this situation is slightly different from that of the previous paper¹⁶. This is due to the symmetry properties of Eq. (1.5) without the boundary condition (1.2). The effective mass Hamiltonian is invariant under operations of parity and rotation about the zaxis. This means that for the bulk impurity n and 2 are no longer good quantum numbers while m is; however states of even and odd & are not mixed. Therefor, the effect of the boundary condition in this situation is to mix states of differing parity,

Since m remains a good quantum number the problem can again be reduced to the set of independent states characterized by their m Values. Using this we can write

$$F_{n}(\vec{r}) = G(z) \sum_{n \ell} A_{n+\ell} \chi_{n\ell m}(\vec{r})$$
 (17a)

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where the choice of $G(z) = R - r\cos \theta$ is as before. Now the x_{nlm} 's are

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chosen as

$$\chi_{n\ell m}(x,y,z) = \left(\frac{\alpha}{\gamma}\right)^{1/4} \phi_{n\ell m}(x,y,\left(\frac{\alpha}{\gamma}\right)^{1/2} z,\beta)$$
(1.8)

where γ is the effective mass ratio and α is another non-linear variational parameter. The $\phi_{n gm}(\vec{r},\beta)$'s are given by Eq.(11.12) and β is the variational parameter that is discussed in Paper I. The parameter α is a measure of the asymmetry induced in the wavefunction due to the asymmetric effective mass. The choice of the functions given by Eq. (1.8) was inspired by the success of the Kohn-Luttinger 5,6 form for the ground state trial wavefunction; for upon setting $\beta = 1/a$ and $\alpha = a^2 \gamma/b^2$, $x_{1,0,0}$ (x,y,z) reduces to their trial function. This basis set differs.from that used by Faulkner inasmuch as we use the combination βr rather than $\beta r/n$ in the radial function where n is the principal Therefore, for the calculation presented here quantum number. there are only two nonlinear variational parameters whereas Faulkner must use a set of such parameters the number of which depends upon **the size of the basis set used in the expansion of the trial func**tion. Of course, this means that we must calculate an overlap matrix, but as it has been shown this is not a great handicap.

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As before, the substitution of Eq. (1.7) into Eq. (1.5) will lead to a generalized eigenvalue problem of the form of Eq.(I1.7). There is a transformation that facilitates the calculation of the Hamiltonian matrix elements. These matrix elements are given by

-7-

$$\left\{ x \left\{ \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \gamma \frac{\partial^{2}}{\partial z^{2}} \right) - \frac{2}{r} + \frac{2Q}{\left[r^{2} + 4R^{2} - 4rR\cos\theta\right]^{1/2}} + \frac{Q}{2(R-r\cos\theta)} \right\}$$

$$\left\{ \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \gamma \frac{\partial^{2}}{\partial z^{2}} \right) - \frac{2}{r} + \frac{2Q}{\left[r^{2} + 4R^{2} - 4rR\cos\theta\right]^{1/2}} + \frac{Q}{2(R-r\cos\theta)} \right\}$$

$$\left\{ \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \gamma \frac{\partial^{2}}{\partial z^{2}} \right) - \frac{2}{r} + \frac{2Q}{\left[r^{2} + 4R^{2} - 4rR\cos\theta\right]^{1/2}} + \frac{Q}{2(R-r\cos\theta)} \right\}$$

$$\left\{ \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \gamma \frac{\partial^{2}}{\partial z^{2}} \right) - \frac{2}{r} + \frac{2Q}{\left[r^{2} + 4R^{2} - 4rR\cos\theta\right]^{1/2}} + \frac{Q}{2(R-r\cos\theta)} \right\}$$

$$\left\{ \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \gamma \frac{\partial^{2}}{\partial z^{2}} \right) - \frac{2}{r} + \frac{2Q}{\left[r^{2} + 4R^{2} - 4rR\cos\theta\right]^{1/2}} + \frac{Q}{2(R-r\cos\theta)} \right\}$$

$$\left\{ \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \gamma \frac{\partial^{2}}{\partial z^{2}} \right) - \frac{2}{r} + \frac{2Q}{\left[r^{2} + 4R^{2} - 4rR\cos\theta\right]^{1/2}} + \frac{Q}{2(R-r\cos\theta)} +$$

Making the substitution

$$\left(\frac{\alpha}{\gamma}\right)^{1/2}$$
 z' = z

yields

$$< n' \iota' | H^{(m)} | n\iota > = \int_{T} (R - \left(\frac{\gamma}{\alpha}\right)^{1/2} r\cos\theta) \phi_{n' \iota' m}^{*}(x,y,z,\beta)$$

$$× \left\{ - \left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \gamma \frac{\partial^{2}}{\partial z^{2}}\right) + (1-\alpha) \frac{\partial^{2}}{\partial z^{2}} - \frac{2}{\left[x^{2} + y^{2} + \frac{\gamma}{\alpha} z^{2}\right]^{1/2}}$$

$$+ \frac{20}{\left[x^{2} + y^{2} + \frac{\gamma}{\alpha} z^{2} + 4R^{2} - 4\left(\frac{\gamma}{\alpha}\right)^{1/2} rR\cos\theta\right]^{1/2}}$$

$$- \frac{0}{2(R - \left(\frac{\gamma}{\alpha}\right)^{1/2} r\cos\theta)} \right\} \left[(R - \left(\frac{\gamma}{\alpha}\right)^{1/2} r\cos\theta) \phi_{n\ell m}(x,y,z,\beta) \right] dV. \quad (1.10)$$

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The overlap matrix elements are given by

$$\langle \mathbf{n}' \mathfrak{l}' | \mathfrak{n} \mathfrak{l} \rangle = \int_{\Gamma} (\mathbf{R} - \left(\frac{\gamma}{\alpha}\right)^{1/2} \operatorname{rcos} \theta)^2 \phi_{\mathfrak{n}' \mathfrak{l}' \mathfrak{m}}^{*}(\vec{r}, \beta) \phi_{\mathfrak{n} \mathfrak{l} \mathfrak{m}}(\vec{r}, \beta) dV.$$
 (1.11)

The subscript T and T' in Eqs. (1.9 - 1.11) indicate truncated regions of integration. The effect of the transformation is seen to be a simplification of the expansion functions at the expense of dealing with more complicated operators.

The generalized matrix equation whose elements are given by Eqs. (1.10) and (1.11) shall be solved numerically. The first step in this direction is the calculation of the quantities

$$-\nabla^{2} \left(R - \left(\frac{\gamma}{\alpha}\right)^{1/2} \operatorname{rcos}_{\theta}\right) \phi_{n\ell m}(\vec{r},\beta)$$
 (1.12)

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$$(1 - \alpha) \frac{d^2}{dz^2} \left[\left(R - \left(\frac{\gamma}{\alpha} \right)^{1/2} r \cos \theta \right) \phi_{nlm}(\vec{r}, \beta) \right]$$
(1.13)

The first of these expressions (Eq.(1.12)) has already been encountered by us before (see Paper I, Eqs. (I1.11) and (I1.16)). The second yields a somewhat complicated sum of terms involving the Legendre and Laguere functions of various orders and will not be repeated here. Most of these terms can be integrated in closed form. However, for the third and fourth terms in Eq. (1.10) this was not found to be the case. Consequently, these terms were numerically integrated as previously described.

The general method of the numerical solution of the matrix equations is the same as described in the previous paper¹⁶. However, there is now an additional parameter, namely α , which must be varied

to yield an optimized energy. In practice the energy is a relatively slowly varying function of α near the optimum values of these quantities and this feature eases the problems associated with locating a minimum in the two parameter space.

Prior to discussing the results of this section, all of which are presented in effective units, the various physical constants of silicon and germanium that are relevant to this problem are presented in Table 1. The effective masses and corresponding γ values for Si and Ge are taken from references 20 and 21, respectively. The static dielectric constants of silicon and germanium are taken after Faulkner¹⁹ who determined the low temperature values of these dielectric constants by requiring that the donor spectrum calculated in the effective mass approximation have an optimum fit to the experimentally determined donor level spacing. Using these values the effective units for silicon are given by

$$a_{oSi}^{*} = \frac{\pi^{2} \epsilon_{Si}}{m_{tSi}^{*} e^{2}} = 31.7 \text{ Å},$$
 (1.14a)

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$$Ry_{Si}^{*} = \frac{m_{tSi}^{*} e^{4}}{2\hbar^{2} \epsilon_{Si}^{2}} = 1.99 \times 10^{-2} eV, \qquad (1.14b)$$

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while those for germanium are

$$a_{oGe}^{*} = 99.7 \text{ Å}$$
; $Ry_{Ge}^{*} = 4.70 \times 10^{-3} \text{ eV}$. (1.15)

Besides the introduction of an anisotropic effective mass, the major difference from the problem of the preceding paper is that the 'hydrogen atom' is now imbedded in a dielectric media and is near an interface with a media possessing a lower dielectric constant. This means that the image charges possess the same sign (positive or negative) as the charges that induce them. This can be seen from the form of the dielectric quotient given by $(\varepsilon_2 - \varepsilon_1)/(\varepsilon_1 + \varepsilon_2)$. This results in a repulsive electron-image electron interaction, while the electron-image proton interaction now becomes attractive.

The results of the 'perfectly imaging' plane show that, at least for the ground state, the absolute value of the expectation value of the electron-image proton interaction is greater than the expectation value of the electron-image electron interaction. Since the former of these quantities is negative, at a large enough distance from the surface the ground state electronic energy is expected

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to be lower than the $R = \infty$ limit when there is no image charge contribution. As the impurity is moved closer to the surface, the change in the energy due to the exclusion of the electron from the halfspace $r\cos\theta \ge R$ will begin to dominate and begin to raise (as a function of the impurity distance from the surface) the ground state energy. Therefore, we expect to see the development of a minimum in the ground state electronic energy.

The results presented in Tables 2 through 4 show that this is precisely what takes place. Table presents the ground 2 state energy of an impurity near a silicon surface for $\gamma = 1.0$; that is, as if silicon possessed a spherical conduction band. The bulk limit in this case is given by the hydrogenic -1.0 Ry*. Tables give the ground state properties of a donor impurity 3 and 4 near the (001) silicon surface and the (111) germanium surface respectively. The bulk values for these two systems, in effective Rydbergs, are given by ¹⁹

$$E_0^{Si}(R \to \infty) = -1.568 \text{ Ry}_{Si}^*$$
 (1.16a)

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$$E_{o}^{Ge}(R \to \infty) = -2.087 \text{ Ry}_{Ge}^{*}$$
 (1.16b)

As a calculational check, the energies of these ground states were computed at a distance from the surface of 100 a_0^* , yielding

$$E_{0}^{Si}(R = 100 a_{0}^{*}) = -1.571 Ry_{Si}^{*}$$
 (1.17a)

$$E_{o}^{Ge}(R = 100 a_{o}^{*}) = -2.094 Ry_{Ge}^{*}$$
 (1.17b)

which is in agreement with the bulk values, to within 0.1%.

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The ground state energies of the 'isotropic effective mass' silicon and the real silicon systems are presented graphically in Fig. 1, while the germanium system is given in There are basically three regions of different behavior **Fig.** 2. depicted in these graphs. At large R the impurity levels are approaching their indicated bulk levels. Also there now exist minima which occur at approximately 2.6 a_0^* , 1.0 a_0^* and 0.5 a_0^* for the 'isotropic' silicon, real silicon and germanium systems respectively. Finally when the impurity is close to the surface there is a steep rise in the electronic energy. The main difference in the behavior of the energy as a function of the impurity distance from the surface between these three systems lies in the location and the depth of the energy minimum. This difference is due to the changing value of γ , the effective mass ratio and can be explained in the following manner. In the bulk situation, the change in the wavefunction due to $\gamma < 1.0$ in Eq. (1.5) is to compress the wavefunction slightly in the z-direction⁶. Since the surface is perpendicular to the z-axis, this means that an impurity wavefunction for a specific value of the effective mass ratio will experience a lesser perturbation than the wavefunction corresponding to a large value of the effective mass ratio. Consequently, the minimum in energy will occur at smaller scaled distances from the surface as the value of the effective mass ratio is decreased. Note that this argument is true only for the scaled Hamiltonian, and that the minimum energy of a donor in germanium occurs at a larger distance than it does for a donor in silicon.

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-13-

The excited state energies for a donor impurity near the (001) surface of silicon and the (111) surface of germanium are presented in Figures 3 and 4. The approach to the bulk values of the energy levels of the excited states takes place at a slower rate due to the larger 'spatial' extent of these states. Note that because the states labelled (0,3) and (1,1) (recall that the first label refers to the value of the m quantum number while the second give its position in the spectrum of levels with the same m quantum number) possess different azimuthal quantum numbers, there is not, as it might appear, an avoided crossing between them.

Finally we note that using the results for the ground-state electronic energy given in Tables 2-4 the impurity-surface "holding potentials", consisting of the change in the electronic energy from its bulk value and the interaction of the positive impurity with its image, can be calculated (similar to the physisorption "holding potential" calculated in Section 2 of Paper I). The results suggest a tendency of the impurities to be concentrated near the semiconductor surface (at distances of 20-50 Å from the interface).

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2. A SHALLOW DONOR IMPURITY NEAR THE SI/SiO₂ INTERFACE OF A M.O.S. FIELD EFFECT TRANSISTOR

The acronym MOSFET is derived from the combination Metal-Oxide-Semiconductor-Field Effect Transistor. The metal gate is used to apply an electric field perpendicular to the surface of the semiconductor, from which it is insulated by an oxide layer. An n-type inversion layer can be produced in a p-type semiconductor at the surface if the energy bands near the surface are bent down enough so that the bottom of the conduction band lies near or below the Fermi level. Such a situation is referred to as an inversion layer since the majority carrier type in that region is the opposite of the bulk **majority carrier.** The band bending required to produce an inversion layer can be produced from the field applied by the metal gate.

If the electric field is strong enough, electrons in the conduction band can become quantized in the direction perpendicular to the surface, while remaining in a continuum for motion parallel to the surface. One of these quantized states is known as an electric subband and to a good first approximation these sub-band energies can be modelled as the eigenvalues of a one dimensional potential well.³ When the gate voltage is large enough, an essentially two dimension conductance can be observed between the electrodes marked source and drain.

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Recently, Hartstein and Fowler^{22,23,1} have observed an effect in the conductance, as a function of gate voltage, in a MOSFET that can be attributed to the formation of an impurity band. Briefly, the

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experiment consisted of drifting Na⁺ ions close to the Si-SiO₂ interface and then measuring the conductance of the channel as a function of gate voltage. What is observed is the appearance of a peak in the conductance below the threshold for 2-dimensional metallic conduction. By measuring the conductivity of the peak as a function of temperature, the binding energy of an electron to one of the impurities can be determined from the slope of a plot of the log of the conductivity versus the inverse of the temperature. We note here that the impurity is generally thought to be located several angstroms away from the interface into the oxide layer while the electron is in the semiconductor inversion layer.

As in the previous section, only the (001) surface of silicon shall be considered. Now, however, the dielectric constant of region B (see Fig. I.1) will be taken to be that of SiO_2 , that is $\varepsilon_2 = 3.8$. For the sake of comparison with other theoretical results, in the following the dielectric constant of silicon shall be taken as $\varepsilon_1 = 11.8$. Since the discontinuity in energy as an electron passes from the silicon to the silicon dioxide is about 3 eV,³ the boundary condition $\psi = 0$ at the interface shall again be applied ³.

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There are two modifications of the Hamiltonian of the last section to make it applicable to the present problem. First, the positively charged impurity is located in the oxide layer which changes the constant factor in its interaction with the electron; and connected with this, the image of the impurity is absent. Second, the change in the potential energy of the electron due to the presence of the electric field must be taken into account. The electric field can be a complicated function of the perpendicular distance to the

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intr:face, however a reasonable first approximation is to employ a constant field³.

These considerations lead us to a Hamiltonian given by

$$H = \frac{-\hbar^2}{2m_t^*} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \frac{\hbar^2}{2m_x^*} \frac{\partial^2}{\partial z^2} - \frac{2 e^2}{(\epsilon_1 + \epsilon_2)r} - \frac{(\epsilon_2 - \epsilon_1)e^2}{4\epsilon_1(\epsilon_1 + \epsilon_2)(R - r\cos\theta)} + eE(R - r\cos\theta) , \qquad (2.1)$$

where ϵ_1 and ϵ_2 are the dielectric constants of silicon and silicon dioxide respectively and E is the local electric field. As before this Hamiltonian is scaled to bulk units yielding

$$H' = -\left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}}\right) - \gamma \frac{\partial^{2}}{\partial z^{2}} - \frac{4\epsilon_{1}}{(\epsilon_{1} + \epsilon_{2})r}$$
$$- \frac{(\epsilon_{2} - \epsilon_{1})}{2(\epsilon_{1} + \epsilon_{2})(R - r\cos\theta)} + 2\epsilon_{1}^{3}\left(\frac{m}{m_{t}^{*}}\right)^{2} E(R - r\cos\theta) . \qquad (2.2)$$

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The Schrödinger equation with the Hamiltonian given in Eq. (2.2) is to be solved subject to the condition that $\psi = 0$ when R = rcos0. All distances are in effective Bohr radii and all energies are in effective Rydbergs (Eq. 1.14)). Once the matrix elements involving the field term have been included in the Hamiltonian matrix, the energy levels are obtained in the manner previously discussed.

The binding energy of the electron in the present case is not simply given as the absolute value of the ground state of Eq. (2.2). This is due to the fact that the electron is making a transition to the first electric sub-band and not to a bulk-like construction band. In the absence of the impurity potential the Hamiltonian (2.2)

becomes

$$H_{0} = -\gamma \frac{\partial^{2}}{\partial z^{2}} - \frac{(\varepsilon_{2} - \varepsilon_{1})}{2(\varepsilon_{1} + \varepsilon_{2})z} + K E z . \qquad (2.3)$$

In Eq. (2.3) E is to be given in electrostatic units and therefore K has the value

$$K = 1.166 \times 10^{-7} \quad \epsilon_1^3 \left(\frac{m}{m_t}\right)^2$$
 (2.4)

Of course, the electron in this system also experiences the potential jump upon entering the silicon dioxide and the boundary condition $\psi(\mathbf{o}) = 0$ must be applied.

If the repulsive image term of Eq. (2.3) were absent the system would be the exactly solvable one of a triangular potential well where the eigenfunctions are given by the Airy functions. When the image term is present a simple variational calculation yields very accurate values for the electric sub-band energy levels. A trial function of the form

$$\psi(z) = e \sum_{n=0}^{-\alpha z/2} A_n z^{n+1}$$
 (2.5)

is chosen. Notice that this trial function satisfies the correct coundary conditions. As in the previous situations, the linear variational parameters A_n lead to a matrix equation whose eigenvalues are optimized by varying the parameter α . The binding energy of the clectron is therefore given by

$$E_{\rm b} = E(H_{\rm o}) - E(H)$$
 (2.6)

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and is dependent upon the electric field through Eqs. (2.2) and (2.3).

This system has been considered by several different authors recently. Martin and Wallis¹³ have used a simple variational form to calculate binding energies only when the impurity is located on the interface. Lipari¹⁵ has utilized a basis set which is certainly correct when the impurity is on the interface but may not be so when the impurity is at a finite distance from the semiconductor/oxide interface. Hipolito and Campos²⁴ have used the variational form of Martin and Wallis to calculate the effect of electrons in the electric sub-bands screening the impurity potential and thus changing the binding energy. This screening shall not be considered further in this report.

The binding energy of an electron to a donor impurity located on the interface between the silicon and silicon dioxide as a function of electric field is presented in Fig. 5. The results of Martin and Wallis and those of Lipari, which are the same as in the present calculation are presented. Because of the simple variational form the results of Martin and Wallis are inferior, giving less binding than those of Lipari and of the present calculation. The binding energy given in Fig. 5 is larger than that found experimentally by Harstein and Fowler, but as shall be seen, when the impurity is moved off the interface and into the oxide layer the binding energy decreases.

The binding energy of the electron at zero field is exhibited in Figs. 6 and 7 as a function of impurity distance from the interface. In the first of these figures the donor impurity is located in the silicon layer while the second locates the impurity

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in the silicon dioxide layer. As can be readily seen there is a large discrepancy between the present calculation and the results of Lipari. This is most likely caused by Lipari's use of an inadmissible basis set. While noting the importance of a boundary condition $\psi = 0$ on the interface, Lipari chooses as a basis set

$$\psi_{\rm m}(\vec{r}) = \sum_{i} f_i(r) Y^{\rm m}_{\ell_i}(\theta,\phi)$$
(2.7)

where

$$f_{i}(r) = \sum_{j} C_{ij} e^{-\alpha j r}$$
(2.8)

-

and the C_{ij} and α_j are the linear and non-linear variational parameters respectively. Later it is noted that only the ℓ = odd terms contribute to the ground state in Eq. (2.7) (m=0). But this is only correct when the impurity is located on the interface and this is illustrated by the coincidence of the results of Lipari and our calculations at R = 0.0. The point to note in this connection is that the binding energy of the electron decreases more rapidly as a function of impurity distance from the interface (when in the oxide layer) than has been calculated by Lipari.

The electron binding energy to an impurity center located in the oxide layer for several electric field strengths has been calculated and these results are presented in Table 5 and Fig. 8. Also shown are the experimental results of Hartstein and Fowler who have found that for electric fields of 19.9 and 60.4 esu the binding energies are 18 and 25 meV, respectively. These results differ from those of Lipari inasmuch as distance from the interface does not turn out to be the same for both field strengths. The binding energy of 18 meV for the field strength of 19.9 esu occurs for the impurity located at approximately 10 Å, while the 25 meV binding energy at the 60.4 esu field strength occurs for the impurity at ~ 4 Å into the oxide layer. These results demonstrate that agreement with experiment is improved if the impurity ions are located at small, but finite distances from the Si-SiO₂ interface, into the insulator. In light of the approximations made in the formulation of the problem the above results should be regarded as the first step towards a theory in which effects due to screening of the impurity potential due to electrons in the inversion layer and inter-valley coupling could be quantitatively ascertained.

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FIGURE CAPTIONS

- Fig. 1. Ground state energy of a shallow donor impurity near the (001) surface of silicon. Also included are the results for an isotropic effective mass. The bulk values are given by the lines under the B. Units are those of effective Rydbergs and effective Bohr radii as defined in text.
- Fig. 2 Ground state energy of a shallow donor impurity near the (111) surface of germanium. Effective Ge units are used.
- Fig. 3 Excited states of a shallow donor impurity near the (00i) surface
 of silicon. Effective Si units are used.
- Fig. 4 Excited states of a shallow donor impurity near the (111) surface cf germanium. Effective Ge units are used.
- Fig. 5 Binding energy of an electron to a donor impurity located on the interface between the silicon and silicon dioxide as a function of electric field. Energy is in units of effective Rydbergs while the electric field is given in electrostatic units (esu).

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- Fig. 6 Binding energy at zero field as a function of impurity distance into the silicon (semiconductor) layer.
- Fig. 7 Binding energy at zero field as a function of impurity distance into the silicon dioxide layer.
- Fig. 8 Binding energy at several field strengths as a function of impurity distance into the silicon dioxide layer. The experimental results of Harstein and Fowler are also included. The curve A is at 10 esu, B at 19.9 esu and C at 60.4 esu electric field strength.

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TABLE 1

VALUES OF PHYSICAL CONSTANTS

	Ϋ́	<u>8</u>	a <mark>*</mark>	R_y *
Si	.2079	11.4	31.7Å	19.9 meV
Ge	.05134	15.36	99.7Å	4.7 meV

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Ground state properties of a shallow donor near the surface of a symmetric ($\gamma = 1$) silicon. All quantities are given in bulk units defined by Eqs. (1.3) and (1.4). E₀ denotes the ground state energy, $\overline{1}$ the average kinetic energy and \overline{V}_1 , \overline{V}_2 , \overline{V}_3 are the average values of the three potential terms in Eq. (1.5) respectively.

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R	E	Ŧ	ν ₁	v ₂	ν ₃
0.2	-0.6064	0.6373	-0.8 658	0.2380	-0.6159
0.4	-0.6507	0.7670	-1.0 594	0.2586	-0.6169
0.6	-0.7221	0.9696	-1.3522	0.2841	-0.6237
9.0	-0.8098	1.1662	-1.6626	0.3001	-0.6135
1.0	-0.8945	1.2853	-1.8972	0.3000	-0.5825
1.2	-0.9640	1.3268	-2.0379	0.2882	-0.5410
1.4	-1.0158	1.3204	-2.1092	0.2708	-0.4978
1.6	-1.0521	1.2912	-2.1381	0.2519	-0.4571
1.8	-1.0767	1.2539	-2.1434	0.2332	-0.4204
2.0	-1.0925	1.2160	-2.1364	0.2157	-0. 3878
3.0	-1.1086	1.0827	-2.0674	0.1498	-0.2736
4.0	-1.0944	1.0302	-2.0273	0.1111	-0.2084
5.0	-1.0794	1.0121	-2.0115	0.0875	-0.1 674
6.0	-1.0676	1.0057	-2.0056	0.0720	-0.1 397

TABLE 3

Ground state properties of a shallow donor near the (001) surface of silicon. ($\gamma = 0.2079$, entries and units are as in Table 2.)

R	E	ĩ	٣	v ₂	v ₃
0.2	-1.3601	1.3555	-2.0850	0.6374	-1.2679
0.4	-1.5927	1.6827	-2.7632	0.6695	-1.1817
0.6	-1.7496	1.8436	-3.1709	0.6084	-1.0307
0.8	-1.8133	1.8267	-3.2815	0.5165	-0.8750
1.0	-1.8278	1.7695	-3.2 845	0.4345	-0.7472
1.2	-1.8210	1.7255	-3.2681	0.3685	-0.6469
1.4	-1.8061	1.6701	-3.2350	0.3167	-0. 5670
1.6	-1.7890	1.6466	-3.2085	0.2762	-0.5032
1.8	-1.7722	1.6243	-3.1891	0.2441	-0.4515
2.0	-1.7568	1.6094	-3.1755	0.2183	-0.4089
3.0	-1.7013	1.5796	-3.1469	0.1425	-0.2765
4.0	-1.6697	1.5723	-3.1396	0.1060	-0.2084
5.0	-1.6499	1.5698	-3.1372	0.0845	-0.1671
·6.0	-1.6365	1,5688	-3.1361	0.0702	-0.1394

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Ground state properties of a shallow donor near the (111) surface of germanium. ($\gamma = 0.05134$, entries and units are as in Table 2.)

R	E .	Ŧ	ν V	₹2	. V ₃
0.2	-2.3 013	2. 2378	-3.7971	1.2923	-2. 0343
0.4.	-2.5389	2.4841	-4.4397	1.0238	-1.6071
0.6	-2.5485	2.4160	-4.4679	0.7463	-1.2428
0. 8	-2.5035	2.2929	-4.3725	0.5673.	-0.9912
1.0	-2.4538	2.2164	-4.3039	0.4523	-0.8185
1.2	-2.4104	2.1721	-4.2622	0.3747	-0. 6951
1.4	-2.3743	2.1460	-4.2369	0.3195	-0. 6030
1.6	-2.3447	2.1298	-4.2211	0.2785	-0. 5320
1.8	-2.3203	2.1194	-4.2108	0.2469	-0.4757
2.0	-2.2998	2.1124	-4.2038	0.2216	-0.4300
3.0	-2.2343	2.0981	-4.1896	0.1470	-0.2 898
4.0	-2.1980	2.0943	-4.1848	0.1100	-0.2183
5.0	-2.1785	2.0132	-4.1847	0.0879	-0. 1749

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TABL	E	5
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Binding energy as a function of impurity distance into the oxide layer for several values of the electric field strength.

R	E = 0.0 esu	E = 10.0 esu	E = 19.9 esu	E = 60.4 esu
0.0	0.9423	1.1949	1.2903	1.5062
0.2	0.7327	0.9723	1.0566	1.2373
0.4	0.6143	0.8437	0.9198	1.0762
0.6	0.5347	0.7553	0.8298	0.9627
8.0	0.4763	0.6891	0.7 530	0.8762
1.0	0.4311	0.6369	0.6960	0.807
1.2	0. 3949	0.5942	0.6492	0.7499
1.4	0. 3650	0.5584	0.6097	0.7017
1.6	0.3398	0.5277	0.5757	0.6602
1.8	0.3183	0.5010	0.5461	0.6239
2.0	0.2996	0.4775	0.5 199	0.5920
3.0	0.2336	0. 3 912	0.4234	0.4747



 Ψ_{i}^{l}

Figure 1



 Ψ_{1}^{i}



 M_{i}^{1}



 ${}^{1|2}_{1}$







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C. SURFACE REACTIONS

C.1 Hinderance and Modulation of the Rotations of Adsorbed Molecules

 Continuation of our studies of the quantum mechanical properties (eigenvalue and eigenfunction spectra) of hindered three dimensional rotors, corresponding to diatomic molecules bound to a surface in a microcavity or surface trough.

2. Further calculations of the hindered-to-free molecule transition probabilities as functions of surface temperature, hinderance angle and rotational angular momentum of the free molecule. The model fascilitates identification of the special role played by the zero point kinetic energy associated with the spatial localization of the adsorbed molecule. The final state distributions exhibit a highly non-equilibrium character. When plotted in the same manner as is customary in experimental studies [log $P(\pounds)$ vs. $\pounds(\pounds+1)$] to experimental data is obtained. In addition to the systems considered by us previously we have considered systems in which the symmetry of rotations around the axis normal to the surface is broken by a periodically modulating potential which possesses the local symmetry of the adsorption sites. Preliminary results indicate sensitivity of the free ejected molecule rotational distributions to the adsorption site geometry.

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3. Generalization of the model described above to include center of mass motion. Calculation of branching ratios between rotational and translational energies in the final (free) molecule as a function of hinderance angle and characteristics of the adsorbed system.

4. Detailed calculations of the eigenstate rotational spectra for molecules adsorbed in a configuration in which the internuclear axis is parallel to the surface plane and the motion of the molecule is modulated by a potential

periodic in the azimuthal angle. This potential represents the symmetry of the adsorption site. In addition to the case in which the motion of the molecule in the polar angle direction is hindered we have investigated weakly bound systems (no polar hinderance) under the influence of azimuthal modulations. The resulting spectra exhibit sensitivity to the strength of the modulating potential, and adsorption site local symmetry. These findings may become important in view of the current ability of high-resolution surface spectroscopies (electron loss and infra-red) to detect rotational modes of adsorbed molecules.

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C.2 Models of Surface Chemical Reactions: Desorption and Dissociation

An outstanding problem in the theory of chemical reactions mediated by solid surfaces is that of formulating theories in which the physical mechanisms involved in a reaction can be investigated systematically. For example, if we consider a single molecule interacting with a solid surface, it is essential to understand the relationship between the probabilities of energy transfer among the translational, vibrational, and rotational degrees of freedom of the molecule and the properties of the potential energy surface determined by the interaction between the molecule and the solid; such understanding would yield insight into the mechanisms of reactive events such as dissociation of the molecule, migration and desorption. Multiple species of gas phase molecules reacting at a solid surface present a much more complicated problem. It is important to realize, however, that, even in this case, understanding the relationship between the analogous probabilities and the potential energy of interaction is a prequisit to understanding the physics of the reaction.

Even for the simple surface mediated reactions studied to date (we use the term "reaction" to describe such changes of the chemical state of the system as chemisorption, desorption, dissociation, etc.) the complications are such that theoretical calculations have involved simplifying assumptions whose validity is difficult to ascertain. For example, a molecule chemisorbed on a solid surface is in a state whose vibrational modes are characteristic of the molecule and solid system: in other words, the effects of resonant interaction between the vibrating solid and the molecule vibrating in its chemicorption well could be important. The probability of desorption, therefore, in principle, incorporates such effects. Theoretical calculations

of desorption probabilities, however have, to date, usually utilized the Born approximation in which such resonance effects are neglected.

In what follows, we consider cases in which we have transitions between bound and propagating states of the molecule - solid system. Such cases comprise, for example, desorption and photodissociation through a quasidiscrete intermediate state. Only the vibrational degree of freedom is considered in our present model.

In order to be more specific, the potential energy of interaction in the Born-Oppenheimer approximation between a molecule and a solid, $V(\rho^{S},\rho^{m},z)$, is a function of the internal coordinates, or interatomic displacements, of the solid and molecule $(\rho^{S} \text{ and } \rho^{m}, \text{ respectively})$ and the distance, z, between the centers of mass of the solid and molecule. Assuming small oscillations of the solid atoms about their equilibrium displacements, ρ^{S}_{0} , determined from

$$\frac{\partial V}{\partial \rho_{i}} \left(\overrightarrow{\rho}_{0}^{s}, \overrightarrow{\rho}_{0}^{m}, z \right) = 0$$
(1)

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where ρ_i^s is any Cartesian coordinate, we can make the expansion

$$V(\vec{\rho}^{S},\vec{\rho}^{m},z) \cong V(\vec{\rho}_{0}^{S},\vec{\rho}^{m},z) + \frac{1}{2} \sum_{s,s'} \sum_{i,j} \frac{\partial^{2} V(\vec{\rho}_{0}^{S},\vec{\rho}^{m},z)}{\partial \rho_{i}^{S} \partial \rho_{j}^{S'}} (\rho_{i}^{S} - \rho_{0i}^{S})(\rho_{j}^{S'} - \rho_{0j}^{S'}) . \quad (2)$$

The sum in Eq. (2) extends over all the atoms of the solid, denoted by s and s', as well as over all Cartesian coordinates.

From Eq. (1), it is clear that the solid equilibrium displacement is modified by the presence of the molecule. In addition, the first term in Eq. (2) represents a potential energy of interaction in which the solid atoms are frozen in their equilibrium positions. The second term in Eq. (2),

on the other hand, corresponds to the potential energy of a system of coupled harmonic oscillators in which the force constants as well as the equilibrium positions are displaced relative to those of the isolated solid. For comparison purposes we have for the isolated systems,

$$V_{\infty}(\vec{\rho}^{S}, \rho^{m}) \equiv V(\vec{\rho}^{S}, \vec{\rho}^{m}, z \rightarrow \infty) = V_{m}(\vec{\rho}^{M}) + V_{S}(\vec{\rho}^{S}) , \qquad (3a)$$

$$V_{s}(\vec{\rho}^{s}) \stackrel{\simeq}{=} V_{s}(\vec{R}_{o}^{s}) + \frac{1}{2} \sum_{s,s'} \sum_{i,j} \frac{\partial^{2} V_{s}(\vec{R}_{o}^{s})}{\partial \rho_{i}^{s} \partial \rho_{j}^{s'}} (\rho_{i} - R_{oi}^{s})(\rho_{j} - R_{oj}^{s'})$$
(3b)

where \vec{R}_{0}^{S} denotes the equilibrium positions of atoms in the isolated solid.

The rate of desorption is given by

$$w_{des} = \frac{2\pi}{hZ} \sum_{i,f} e^{-E_i \beta} |\langle \Psi_i | H' | \phi_f \rangle|^2 \delta(E_i - \varepsilon_f), \qquad (4a)$$

$$(K_{\rm m} + K_{\rm s} + V - E_{\rm i})|\Psi_{\rm i} > = 0$$
, (4b)

$$(K_{\rm m} + K_{\rm s} + V_{\infty} + V_{\rm static} - \varepsilon_{\rm f})|\phi_{\rm f}\rangle = 0 , \qquad (4c)$$

$$H' = V - V_{\infty} - V_{\text{static}} , \qquad (4d)$$

$$Z \equiv \sum_{i}^{-\beta E} e^{i}, \qquad (4e)$$

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where K denotes the kinetic energy, V_{static} represents the first term in Eq. (2), $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant and T is the temperature. The basic point of Eqs. (4) is that if we expand V about the solid and molecule equilibrium displacements, the initial (exact) chemisorption state, $|\Psi_i\rangle$, corresponds to an eigenstate of the system of coupled solid-

molecule oscillators, while the final desorption state, $|\phi_f\rangle$, is a product of an eigenstate of the solid (corresponding to Eq. (3b)) and a state of the molecule propagating under the influence of V_{static} . Evaluation of the transition matrix element in Eq. (4a), therefore, involves as a first step the calculation of the overlap between products of harmonic oscillator states of the normal modes of the combined system and products corresponding to the normal modes of the isolated solid. Previous treatments employed the Born approximation in which $|\Psi_i\rangle$ is replaced by $|\phi_i\rangle$, a bound state of Eq. (4c), i.e., in these treatments both the initial and final states correspond to the same Hamiltonian.

In an adiabatic treatment of molecular photodissociation (or photostimulated desorption in the present context), the rate has a structure similar to that of Eqs. (4), where $|\Psi_i\rangle$ corresponds to an intermediate quasibound state of the system on the potential energy surface of an excited electronic state (within the Born-Oppenheimer approximation) and $|\phi_f\rangle$ represents the dissociative state as a product of states of the separated systems (but dependent on z through the force constants and equilibrium displacements, as in Eq. (2)) and an adiabatic state in z. In this case, also, we require overlaps between products of harmonic oscillator states corresponding to different normal modes (i.e., combined vs. separated systems).

These points are most easily appreciated by treating an atom instead of a molecule. If, for example, we treat the case of desorption, and denote the normal modes of the chemisorption system and isolated solid by $Q_{\alpha}(\vec{\rho}^{S}-\vec{\rho}_{0}^{S},\vec{z}-\vec{z}_{0})$ and $q_{a}(\vec{\rho}^{S}-\vec{R}_{0}^{S})$, respectively, then the overlap between vibrational eigenstates of the two systems is proportional to

$$\int d^{3(N-1)} \rho^{s} \begin{pmatrix} 3N & 3(N-1) \\ \pi & \Phi_{\nu}(Q_{\alpha i}) \end{pmatrix} \begin{pmatrix} \pi & \Phi_{\lambda}(q_{\alpha j}) \end{pmatrix} \propto I(\nu_{1} \cdots \nu_{3N}; \lambda_{1} \cdots \lambda_{3(N-1)}; z)$$

$$(5)$$

where I represents the overlap, v and λ are occupation numbers, we assume N + 1 atoms in the solid and have removed center of mass modes. The explicit calculation of the integral is cumbersome, which has hampered development along these lines.

We have developed a recursion method for calculating these overlaps. The methodology involves first calculating the normal modes of the two systems, expanding Q_{α} in terms of q_a , and applying simple harmonic oscillator algebra. The resulting recursion relation involves first order differential operators. For desorption of an atom from a one-dimensional solid, we have, in general for the ground state overlaps,

$$I(0 \dots 0; 0 \dots 0; z) = C_{oo} \exp(\frac{-m_o}{2h} \frac{M_T}{M} W(z - z_o)^2), \qquad (6)$$

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where m_0 is the mass of the desorbing atom, M the total mass of the chain, $M_T = m_0 + M$, the quantities W and z_0 are complicated functions of the parameters of the problem, which we do not present here. The recursion relation has the dual form

$$\sqrt{1+\nu_{\ell}} I(\nu_{1} \dots \nu_{k}+1 \dots, \nu_{N}; \lambda_{1} \dots \lambda_{N-1}; z) = \frac{1}{2} \left\{ 0_{\ell}^{+} I(\nu_{1} \dots \nu_{N}; \lambda_{1} \dots \lambda_{N-1}; z) + \sum_{a=1}^{N-1} (S_{a\ell}^{+} \sqrt{\lambda_{a}} I(\nu_{1} \dots \nu_{N}; \lambda_{1} \dots \lambda_{a-1} \dots \lambda_{N-1}; z) - S_{a\ell}^{-} \sqrt{\lambda_{a}+1} I(\nu_{1} \dots \nu_{N}; \lambda_{1} \dots \lambda_{a+1} \dots \lambda_{N-1}; z) \right\}, \quad (7a)$$

$$\frac{\sqrt{\nu_{\ell}} I(\nu_{1} \cdots \nu_{\ell-1} \cdots; \lambda_{1} \cdots \lambda_{N-1}; z) = \frac{1}{2} \left\{ 0_{\ell} I(\nu_{1} \cdots \nu_{\ell} \cdots; \lambda_{1} \cdots \lambda_{N-1}; z) + \sum_{a=1}^{N-1} (S_{\ell}^{+} \sqrt{\lambda_{a}^{+1}} I(\nu_{1} \cdots \nu_{\ell} \cdots; \lambda_{1} \cdots \lambda_{a}^{+1} \cdots; z) - S_{\ell}^{-} \sqrt{\lambda_{a}} I(\nu_{1} \cdots \nu_{\ell} \cdots; \lambda_{1} \cdots; \lambda_{a}^{+1} \cdots; z) \right\},$$
(7b)

In Eqs. (7), the 0_{g} and 0_{g}^{+} represent first order differential operators, and the S_{g} and S_{g}^{+} denote known transformation coefficients. It is well to empoasize that the form in Eq. (6) resulted from applying Eq. (7b) to the ground states of the system. All other coefficients are generated from the relations in Eq. (7) and the facility with which this procedure can be implemented results from the simplicity of relations (6) and (7). It is important to recognize that this method puts multi-phonon and single phonon states on the same footing, so that resonance effects can be examined readily Extension to the case of molecular desorption is straightforward and calculations are in progress for this case, which yields information regarding energy partitioning between the various degrees of freedom (translationa, vibrational and rotational) of the desorbing species. The calculations would also provide information concerning energy partitioning in the fragmentation of poly-atomic molecules.

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On Models of Interactive Dynamical Processes at Surfaces*

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I. INTRODUCTION

The importance of surfaces and interfaces in a variety of chemical and physical processes has been long recognized. The interest in these systems originates from coupled technological and fundamental reasons, since often the understanding and improvement of technological applications requires knowledge on a basic level. Due to the wide range of applications and phenomena ranging from chemical catalysis, corrosion research, electrochemistry and the application of surface-active agents (detergents, adhesives, etc.), to electronics and methods of crystal growth, this field of research is of an interdisciplinary nature, referred to as surface and interface science. In fact, in most of these systems we investigate interphase phenomena, i.e., the structure and interactive processes at the interface between two phases of matter, solid-gas, liquid-gas, or solid-liquid.

One of the major objectives of surface science is the understanding of the fundamental processes involved in chemical reactions catalyzed by solid surfaces. A catalyzed surface reaction may conveniently be described by a sequence of elementary kinetic steps^{1,2} such as adsorption (which may proceed via stages involving precursor states,² physisorption³ etc.); diffusion⁴ (on the surface and in certain cases through the bulk); reaction (dissociation, association, rearrangement etc.) and desorption. The traditional thermochemical analysis of reactions involving the balance of heats of the above distinct processes, such as heats of adsorption, desorption, dissociation and bond formation, provides criteria for the occurrence of certain reaction paths. However, such analysis, while determining the direction of the process in the reactants-products space, does not provide detailed information about the reaction rates and the fundamental microscopic processes which govern them. The employment of specific catalytic agents in a chemical reaction provides the means for modifying reaction paths and rates. In addition, through the use of the proper catalyst a particular reaction channel, selected from the manifold of thermodynamically allowed ones, may be enhanced. In order to enable one to choose specific catalysts with the objective of optimizing the yield of a desired reaction product it is necessary to develop an understanding of the microscopic interaction processes and to identify the physical parameters of the catalytic system (catalyst, reactants, and ambient conditions) which govern the outcome and rate of the reaction.

The evolution of a chemical reaction is conveniently described by rate data, i.e., plots of the decay or growth in time of the concentrations of the reactants and products, respectively. When treated on a phenomenological level,⁵⁻⁷ a reaction scheme is postulated and described by a set of simultaneous rate equations. In this class of studies the rate constants are regarded as parameters to

be determined by fitting the solutions of the equations to the experimental data. The functional form of the solutions to the kinetic decay and growth equations serves to catagorize reactions by their orders with respect to reactant concentrations (i.e., the exponents of the concentrations as they appear in the rate equations). However, it should be emphasized that since rate equations form the most contracted description of a chemical reaction there need not be a simple correspondence between the order and the physical mechanism of the reaction.

Understanding of chemical reactions on a more fundamental level is provided by statistical mechanical approaches,⁸⁻¹⁸ in which rate constants are evaluated using partition functions,^{5,6} stochastic methods¹⁵ or "phasespace theories" and molecular dynamics¹⁶⁻¹⁸ (i.e., classical trajectory analysis). The latter methods describe the classical evolution of the system on its potential energy surface and provide information about collision dynamics,¹⁸ energy transfer and rates. While most popular in gas-phase kinetics, these powerful statistical methods have only recently been employed in the investigations of surface reactions.

The most refined treatment of reaction kinetics is by microscopic models¹⁸⁻³⁸ in which the underlying physical processes, such as coupling, excitation and energy transfer, are investigated. It is via investigations on this level that one may expect to unravel the correlations between catalytic reaction kinetics and characteristic parameters of the solid substrate (geometric structure, vibrational and electronic spectra), properties of the reactants (electronic, vibrational) and ambient conditions (pressure, temperature and external fields).

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In the past two decades there has been a rapid proliferation in the development and application of spectroscopies which probe the composition, crystallographical arrangement and electronic and vibrational structure of surfaces on the atomic scale.³⁹⁻⁴⁴ At the same time theoretical formulations which allow the analysis of experimental observations and calculations of surface properties have been advanced. At this stage of development emphasis was placed on the characterization of surface systems with less work directed at the dynamics of surface interactive processes. While static information such as (i) atomic arrangement at the top-most layers of the solid and that of adsorbed species (LEED, ion scattering, SEXAFS); (ii) surface electronic structure (UPS, AES, EELS, ILEED); and (iii) vibrational structure (EELS and IR), along with theoretical studies of the

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above issues are most valuable to the understanding of surface phenomena, new methods and approaches are necessary in order to tackle successfully the dynamical aspects of surface interactions. The budding generation of new experiments (some of which are well known in gas-phase chemical dynamics⁴⁵ but novel in their employment to surface systems) such as laser-induced fluorescence studies of the rotational and vibrational-state distribution of molecules adsorbed,⁴⁶ scattered⁴⁷ and thermally desorbed⁴⁸ from metallic surfaces, rotational and vibrational state distributions obtained from analysis of optical emission from electronically excited ejected molecules,49 measurements of angular distributions of desorbed particles,⁵⁰ investigations of diffusion rates and mechanisms⁴ (FIM, FEM) provide the impetus and have profound implications on theoretical strategies for future modeling of the physical and chemical processes which underly the mechanisms and dynamics of elementary surface interactive and rate processes.

At this junction the interphase nature of interactive surface systems should be noted. Unlike gas-phase interactive systems, in the case of surface systems not all the reactants are in the same state of aggregation. The presence of a surface introduces time scales and spatial boundary conditions unique to condensed matter systems, which in turn dictate the energetics and dynamics of gas-solid interactions. Solid (and liquid) substrates possess a spectrum of electronic and vibrational excitations of an extended (and collective) nature. The degree to which an extended picture of the substrate rather than a local (cluster or embedded cluster) description should be maintained in a proper formulation of dynamical processes at surfaces depends on the class of phenomena under study. While in calculations of chemical bond formation a representation of the substrate by a finite (often small) cluster may be adequate,⁵¹ energy dissipation and redistribution mechanisms, particularly for lowenergy (thermal) processes, require an extended picture. In the latter case the validity of the Born-Oppenheimer approximation which is central to calculations of adiabatic potential energy surfaces is seriously questioned due to the availability of easily excited conduction electrons in metal substrates. Moreover, since the substrate is characterized by a continuous spectrum of electron-hole pair excitations, a description of the gas-surface interaction potential for metals in terms of a single adiabatic potential is incorrect and should be replaced by a continuous band of close-lying hypersurfaces. The strength of nonadiabatic coupling which causes transitions between these levels governs the degree of departure from the adiabatic description. The above discussion indicates the difficulties in constructing a proper potential hypersurface let alone a formulation of the evolution of the system.18

Energy dissipation and redistribution via coupling to substrate phonons is likely a dominant process.^{20,25-28,31} The substrate phonons provide a "momentum" and energy reservoir (although the energy transfer if only single-phonon processes are considered is limited to $\leq 10^{-2}$ eV, we will return to this issue in Section III). The phonons in turn may dissipate energy via electron-phonon coupling.

Of paramount importance for the understanding of reaction dynamics on a microscopic level are the mechanisms of coupling and energy exchange and redistribution between the reactants.⁵² In the case of gas phase reactions certain general conclusions with regard to the

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relative importance of translational, vibrational and rotational energies in surmounting the reaction barrier have been drawn. For example, when the barrier is encountered early in the approach of the reactants translational energy is the key factor. While for reactions in which the potential energy barrier for reaction occurs when the reactants have come to close proximity, the vibrational and rotational energy content is dominant in dictating the probability of reaction. As indicated above the formulation and theoretical analysis of surface reactions are much more complex due to the heterogeneous nature of these systems. Consequently, at this stage of development, progress may be made via model theories (employing, critically, simplifying assumptions) of coupling and excitation mechanisms of molecular species near surfaces and of the dynamical evolution leading to bond formation (sticking), bond rupture (desorption, dissociation), rearrangement and migration. The purpose of such theoretical models is to identify and elucidate the dominant mechanisms and relevant characteristic parameters which govern the dynamical physical processes. It should be noted that even though in certain cases theories can be stated in most general terms, their implementation often requires input information which for the systems under study is not yet available (such as a complete surface phonon spectrum, accurate interaction potential hypersurfaces, localized state wave functions etc., although progress in these directions is realized).

In light of the above remarks we present the elements of theoretical models developed in our laboratory for the study of certain elementary reaction processes. In Section II we derive an expression for the coupling between an adsorbed particle on a metal surface and fluctuations in the substrate. This coupling is then employed in Section III in a stochastic formulation of the temporal evolution of the system which yields results for desorption rates. In Section IV the rotational state distributions of diatomic molecules desorbing from a substrate are studied, using a simple quantum-mechanical model which emphasizes the role of the surface as a "localizing agent". We conclude in Section V, with a brief discussion of a stochastic theory of migration on surfaces and calculations of the rates of certain diffusion controlled reactions.

II. MICROSCOPIC THEORY OF DESORPTION: HAMILTONIAN AND COUPLING

(i) Hamiltonian

The first step in our formulation is a statement of the Hamiltonian of the system. The total Hamiltonian of the adsorption system may be written as

$$H = T_{e} + T_{N} + V(r, R)$$
(2.1)

where T_e and T_N represent kinetic energies of electrons and nuclei of the system (molecule and substrate) and V(r, R), various contributions to the potential energy $(r = \{r_M, r_s\}, R = \{R_M, R_s\}$, where r_M and r_s are the electronic coordinates of the adsorbed molecule and solid, respectively, and R_M , R_s the corresponding nuclear coordinates). In the adiabatic approximation⁵³ the total wavefunction is taken as

$$\psi(\mathbf{r}, \mathbf{R}) = \phi(\mathbf{r}, \mathbf{R}) \chi_{N}(\mathbf{R}). \qquad (2.2)$$

The electronic wavefunction satisfies the equation

$$[T_e + V(r, R)]\phi(r, R) = \varepsilon_e(R)\phi(r, R) \qquad (2.3)$$

solved for fixed R, where the direct interaction between

nuclei is included in V(r, R). The equation for the nuclear motion can be found variationally⁵⁴

$$\left\{-\sum_{\mu=1}^{N}\frac{1}{2M_{\mu}}\nabla_{\mu}^{2}+\left[\varepsilon_{e}(\boldsymbol{R})+V'(\boldsymbol{R})\right]\right\}\chi_{N}(\boldsymbol{R})=\varepsilon_{N}\chi_{N}(\boldsymbol{R}) (2.4)$$

where

$$V'(\boldsymbol{R}) = \sum_{\mu=1}^{N} \int d^3 \boldsymbol{r} \boldsymbol{\phi}^* \left(-\frac{1}{2M_{\mu}} \nabla_{\mu}^2 \right) \boldsymbol{\phi}, \qquad (2.5)$$

and the summations are over all the nuclei. The effective potential (expression in square brackets in Eq. (2.4)) for the nuclear notion is dominated by the electronic energy $\varepsilon_e(\mathbf{R})$ and the term $V'(\mathbf{R})$ is small. To go beyond the adiabatic approximation requires the evaluation of the non-adiabatic couplings $-(\hbar^2/M)\langle n | \nabla_{\mathbf{R}} | m \rangle \nabla_{\mathbf{R}}$ and $-(\hbar^2/2M)(n | \nabla_{\mathbf{R}}^2 | m \rangle$, where $| n \rangle$ and $| m \rangle$ are adiabatic electronic states depending upon the nuclear coordinates \mathbf{R} . While it is possible to include non-adiabatic contributions using a generalized Green's function method,⁵⁵ we do not include them in the following.

At this stage the electronic energy $\varepsilon_{\epsilon}(\mathbf{R})$ may be modeled in the following manner. First one identifies in $\varepsilon_{\epsilon}(\mathbf{R})$ those components which correspond to intramolecular bonds and to binding between atoms of the molecule and a localized region in the solid. The electronic interactions for a fixed configuration of nuclear molecular coordinates, $\{R_{M}\}$, and solid nuclear coordinates, $\{R_s\}$, determine the adsorption potential between the solid and the adsorbate. We separate the interaction into two parts: one in which the solid is kept stationary and the other where the solid is allowed to vibrate. It is via the latter contribution that an energy exchange between the molecule and solid (which may eventually yield desorption or dissociation) becomes possible. The first contribution to these "bond-potential-energies" may then be modeled by some analytical potential formulae such as a harmonic well, a Morse potential or other suggested potential formulae. The rest of $\varepsilon_{\epsilon}(\mathbf{R})$, i.e., that part which can be identified with the solid coordinates may then be replaced by a certain model of the solid (remember that internuclear interactions were included in $\varepsilon_{\epsilon}(\mathbf{R})$).

The corresponding nuclear motion equations (2.4) may then be solved with the above-mentioned model replacement for $\varepsilon_{e}(\mathbf{R})$, and their solutions provide the vibrational spectrum for the modeled system.

(ii) Coupling

In this section we derive, under certain approximations, an expression for the coupling between a point charge (of charge $+Z_{A}^{*}e$, where Z_{A}^{*} is the effective charge of the ion) adsorbed at a distance z_{1} from a metal surface and the *fluctuating* part of the metal substrate. As discussed previously, in the model which we develop the role of the electronic (including direct nuclear interactions) energy is to establish a bounded molecule-solid system characterized by, for example, a Morse potential with an equilibrium distance d_{1} of the atomic constituents from the surface, with an associated manifold of vibrational levels.

To make the calculation tractable and yet preserving the essential physical features we model the surface in the following manner. We consider an electron gas bounded by an infinite potential barrier (Fig. 1). The static ions are then placed within this potential and the first plane is positioned at a distance $L - z_0$ with $z_0 \rightarrow 0$



Fig. 1. The model adsorption system. The electron gas is bounded in a slab of linear dimension L. The first plane of substrate ions is located at $z = L - z_0$ with $z_0 \rightarrow 0$. The adsorbed ion is located at $z = L + z_1$.

from the potential barrier, where L is the linear dimension of the slab.

We now relax the static ions and allow them to fluctuate by emitting phonons. Denoting such a density fluctuation of the ions as $\delta n_b(r)$ and the electronic response to such a fluctuation as $\delta n_e(r)$, the coupling may be written as

$$v(\mathbf{r}) = \delta u_{\rm b}(\mathbf{r}) + \delta u_{\rm e}(\mathbf{r}), \qquad (2.6)$$

where $\delta u_b(r)$ and $\delta u_e(r)$ are the fluctuating ionic and electronic interaction potentials with the adsorbed charge $(+Z_A^*e)$ positioned at r, i.e.,

$$\delta u_{b}(\mathbf{r}) = Z_{A}^{*} Z_{s} e^{2} \int \frac{d\mathbf{r}' \delta n_{b}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

$$\delta u_{c}(\mathbf{r}) = -Z_{A}^{*} Z_{s} e^{2} \int \frac{d\mathbf{r}' \delta n_{c}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$
(2.7)

with Z_A^* and Z_i and atomic charges (possibly screened) of the adatom and metal ions, respectively. The position vector r of the point charge is set equal to $z_1 + L$ in Eqs. (2.6) and (2.7), where L is the thickness of the sample (Fig. 1). We choose next a wave-vector q of the fluctuating ionic background and express the single Fourier component of the density fluctuation as

$$\delta n_{\mathbf{b}}(z, \mathbf{r}_{\mathbf{i}}) = \delta n_{\mathbf{b}}(q_{\perp}, q_{\mathbf{i}}) e^{i(q_{\perp}z + q_{\mathbf{i}} \cdot \mathbf{r}_{\mathbf{i}})} + \text{c.c.}$$
(2.8)

In the following we omit writing explicitly the parallel components r_1 , q_1 from δn_b due to translational invariance in planes parallel to the surface, and denote $\delta n_b(z) \equiv \delta n_b(z, r_1)$ and $\delta n_b(q_\perp) \equiv \delta n_b(q_\perp, q_1)$. It is convenient to define an extension of $\delta n_b(z)$ by an even function $\delta n'_b(z)$ such that for z in the range [-L, 0], $\delta n'_b(z) = \delta n_b(-z)$. Treating the electrons semiclassically and solving the linearized static collisionless Boltzmann equation for the fluctuation in the electron Fermi-Dirac distribution driven by the self consistent field given by Eqs. (2.6) and (2.7) we obtain the following expression for the coupling $v(z_1 + L)^{20}$:

$$v(z_{1}+L) \equiv v(z_{1}) = \frac{Z_{\Lambda}^{*} Z_{s} e^{2} 2\pi \delta n_{b}(q_{\perp}) e^{-q_{1}}}{(q_{\perp}^{2}+q_{1}^{2})D} \times \left[1 - \frac{\lambda_{TF}^{2}}{q_{\perp}^{2}+q_{1}^{2}+\lambda_{TF}^{2}}\right]$$
(2.9)

where λ_{T}^{-1} is the Thomas-Fermi screening length of the electrons and D is given by

$$D = 1 - \frac{\lambda_{\rm TF}^2}{2(q_{\rm H}^2 + \lambda_{\rm TF}^2)^{1/2}[q_{\rm H} + (q_{\rm H}^2 + \lambda_{\rm TF}^2)^{1/2}]}.$$
 (2.10)

Within the context of the infinite surface barrier as a model for the static semi-infinite crystal the generalization of Eq. (2.9) to include crystallinity of the substrate would involve simply treating $\delta n_b(q_\perp, q_l)$ in terms of the phonon crystal propagator. In the present calculation we, however, would use a continuum Debye model of the solid.

In a continuum model of the solid the Fourier components of the positive background number density fluctuations, $\delta n_{\rm b}(q)$ see Eq. (2.8), are defined by the relation

$$\delta n_{b}(\mathbf{r}) = \sum_{\mathbf{q}} \delta n_{b}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \qquad (2.11)$$

and $\delta n_{\rm b}(\mathbf{r})$ is given as⁵⁶

$$\delta n_{\rm b}(\boldsymbol{r}) = -Z_{\rm s} n_0 \nabla \cdot \boldsymbol{D} \qquad (2.12)$$

where n_0 is the ionic number density of the solid and **D** is the displacement of the background from its equilibrium position. From Eqs. (2.11) and (2.12) it follows that

$$\delta n_{b}(q_{\perp}, q_{i}) \equiv \delta n_{b}(q_{\perp})$$

$$= Z_{s}n_{0} \sqrt{\frac{\hbar}{2M_{s}n_{0}\Omega\omega_{q}}} q(b_{q} + b_{-q}^{+}),$$
(2.13)

where M_s is the atomic mass of a solid atom, Ω is the volume of the solid and $b_q(b_q^*)$ are the annihilation (creation) operators of a phonon of wave vector q and frequency ω_q . We now express the instantaneous position of the adsorbed atom z_1 as $z_1 = d_1 + u_1$, where d_1 is the equilibrium distance of the atom from the surface, and expand the exponent, $\exp(-q_1z_1)$, in Eq. (2.9) to obtain

$$v(z_1) = v_0(q; d_1) + \delta v_1(q; u_1) + \delta v_2(q; u_1) + \cdots, \quad (2.14)$$

$$\delta v_1(\boldsymbol{q};\boldsymbol{u}_1) = \boldsymbol{g}_{\boldsymbol{q}}^{(1)} \boldsymbol{u}_1(\boldsymbol{b}_{\boldsymbol{q}} + \boldsymbol{b}_{-\boldsymbol{q}}^+), \qquad (2.14a)$$

$$\delta v_2(q, u) = g_q^{(2)} u_1^2(b_q + b_{-q}^*), \qquad (2.14b)$$

where $\delta v_1(q; u_1)$ is the potential corresponding to bilinear coupling between the vibrations of the atom and the phonons of the solid. Assuming for simplicity an acoustic continuum model for the solid, i.e., $\omega_q = sq$ where s is the sound velocity, $g_4^{(1)}$ in Eq. (2.14) is given by

$$g_{q}^{(1)} = -F \frac{q^{1/2} q_{1}}{q^{2} + \lambda_{TF}^{2}}$$
(2.15a)

$$\times \left[1 + \frac{\lambda_{TF}^{2}}{2(q_{1}^{2} + \lambda_{TF}^{2})^{1/2} [q_{1} + (q_{1}^{2} + \lambda_{TF}^{2})^{1/2}] - \lambda_{TF}^{2}} \right] e^{-q_{1} d_{1}}$$

where

$$F = 2\pi Z_{s} Z_{A}^{*} e^{2} \left(\frac{\hbar n_{0}}{2M_{s} \Omega s}\right)^{1/2}.$$
 (2.15b)

Our results can be summarized by writing the Hamiltonian for our model system as

$$H = \varepsilon_{\epsilon}^{0} + H_{\star}^{0} + H', \qquad (2.16a)$$

$$H' = \sum_{i} v(z_i), \qquad (2.16b)$$

where ε_{e}^{0} is the electronic energy (including direct nuclear-nuclear interactions) for equilibrium nuclear positions, H_{v}^{0} is the zeroth-order vibrational Hamiltonian for the adsorption system, and the last term Eq. (2.16b) in Eq. (2.16a) contains couplings between the vibrations

of intramolecular and chemisorptive bonds and fluctuations in the solid.

(iii) Transition Rate

The transition rate between vibration levels of the adsorbed system due to the coupling operator H' (Eqs. 2.16) can be evaluated to lowest order in perturbation theory using the golden rule formula⁵⁷

$$W_{v \to v'} = \frac{2\pi}{\hbar} \sum_{n_q n'_q} p(n_q) |\langle v', n'_q | H' | v, n_q \rangle|^2 \times \delta(\varepsilon_{v'} - \varepsilon_v + \varepsilon_{n'_q} - \varepsilon_{n_q}), \qquad (2.17)$$

where we sum over phonon final states n'_q and average over phonon initial states n_q using the probability distribution $p(n_q)$.

In order to evaluate $W_{e \rightarrow e^{+}}$ we need to specify the manner in which we model the vibrational spectrum of the adsorbed molecule.

(i) In the crudest approximation the vibrations are modeled by harmonic oscillators, truncated at the appropriate predissociation levels (see Section III). Keeping only terms up to bilinear coupling (δv_1 , see Eq. 2.14) allows only for single quantum transition ($v \rightarrow v \pm 1$), accompanied by the absorption (emission) of a phonon. An expression for $W_{0\rightarrow v+1}^{(b)}$ was derived (see Ref. 20).

(ii) As an improved model of the bond potential energy between an adsorbed atom and the surface we consider the Morse potential⁵⁸

$$\varepsilon_{e}(z-d_{1}) = D_{e}\{[1-\exp[-\beta(z-d_{1})]]\}^{2} - D_{e}, \quad (2.18)$$

where D_{ϵ} is the dissociation energy referred to the minimum, d_1 is the equilibrium distance of the adsorbed atom from the surface, and the parameter β determines the width of the potential. One often defines the anharmonicity parameter $x_e = h\omega_0/4D_e$ where ω_0 is the vibrational frequency for infinitesimal amplitudes (x_e is often determined empirically). Using previously derived expressions^{59,60} for the matrix elements of the deviation from equilibrium, u, the transition rates $W_{v=v+1}^{(M)}$ and $W_{v=v+2}^{(M)}$ can be derived.²⁰

III. EVALUATION OF FIRST PASSAGE TIMES FOR THE TRUNCATED HARMONIC OSCILLATOR AND MORSE-POTENTIAL MODELS

Having obtained explicit expressions for the couplings between the adsorbate and the substrate and for the rates of transitions between vibrational levels of the binding potential, induced by the couplings, we turn next to the temporal evolution of the excitations. Since for most systems of interest the allowed quanta of excitation, dictated by the characteristics of the phonon spectrum of the substrate, are much smaller than the barrier for bond rupture, an incoherent multiphonon mechanism is formulated. This, however, is applicable to systems in which the spacings between vibrational levels of the potential associated with the reaction coordinate do not exceed the maximum phonon frequencies. When the above is not satisfied coupling may occur through a mode other than the bond-rupture reaction coordinate which serves as a "door-way" state.

Consider an oscillator system with $x_n(t)$ the distribution describing the population of vibronic levels *n* at time *t*. The time evolution of this distribution is governed under certain approximations by a master equation⁶¹

$$-\frac{dx_n}{dt} = \sum_{\nu=0}^{N+1} W_{\nu n} x_n - \sum_{m=0}^{N} W_{nm} x_m, \quad n = 0, 1, \cdots, N \quad (3.1)$$

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where N is the predissociation level, and W_{nm} is the transition probability per unit time from m to n. In the above equation second-order terms due to recombination are neglected. The initial distribution (t = 0) is normalized according to

$$\sum_{n=0}^{N} x_n(0) = 1, \qquad (3.2)$$

and the $x_n(0)$'s are given by a Boltzmann distribution at temperature T, i.e.,

$$x_n(0) = e^{-\beta e_n} / \sum_{n=0}^{N} e^{-\beta e_n}.$$
 (3.3)

For the calculation of the reaction rate we will be interested in the mean time for the system specified above, to pass the N-th level for the first time — i.e., the mean first passage time, t. The distribution of first passage times P(t) is given by⁶¹

$$P(t) = -\frac{d}{dt} \sum_{n=0}^{N} x_n(t)$$
 (3.4)

and t is the first moment of P(t), i.e.,

$$\bar{t} = \int_0^\infty t P(t) dt.$$
(3.5)

An expression for the mean first passage time for an initial population distribution $x_n(0) = \delta_{n,0}$ for a truncated harmonic oscillator system and transitions between neighboring levels only, was first given by Montroll and Shuler.⁶¹ This has been generalized by Kim⁶² for the Boltzmann initial distribution (Eq. 3.3) for both a truncated harmonic and Morse oscillators with nearest and next-nearest neighbor transitions.

(i) For the truncated harmonic oscillator the result is⁶²

$$\bar{t}^{(h)} = \frac{(v+1)}{W_{v\to v+1}^{(h)}(1-e^{-\theta})} \sum_{j=1}^{N+1} j^{-1}(e^{j\theta}-1)(1-e^{-j\theta}) \quad (3.6)$$

with $\theta = h\omega_0/kT$, where ω_0 is the harmonic oscillator frequency.

(ii) To obtain an expression for the mean first passage time out of a Morse potential well, $t^{(M)}$, with transitions between nearest and next-nearest levels, we adopt the methods developed by Kim. The generalization of Kim's result [Eqs. (6.15) and (6.16) of Ref. 62] amount to taking into account that in our case the exchange of excitation is with a solid characterized by thermal occupation numbers $\bar{n}_{\omega_q} = [\exp(h\omega_q/kT) - 1]^{-1}$. Consequently, contributions corresponding to transitions between the Morse potential levels must be weighted appropriately.²⁰

In the stochastic formulation of nonequilibrium kinetics which we have employed the reaction rate, R, is given by the inverse of the mean-first-passage time t (see also discussion in Section III.B). Results for the rates of desorption of potassium and xenon from a tungsten substrate are shown in Figs. 2-4. In Fig. 2 results for the two models of the binding potential (harmonic - solid line, and Morse — dashed line) using experimentally⁶³ suggested values for the desorption energy $D_e = 2640$ meV, equilibrium distance $d_1 = 2.38$ Å and fractional charge $Z_A^* = 0.27$ e are compared, along with the experimentally obtained⁶³ rate given by R = $10^{12.8} \exp(-D_c/kT)$ (open circles). It is evident that the results for the Morse potential and truncated harmonic oscillator models yield both an Arrhenius-like straight line in the semilogarithmic plot of R vs. 1/T. The pre-exponential factors, however, differ markedly with the Morse potential in agreement with experiment. It



Fig. 2. Semilogarithmic plots of desorption rates vs. inverse temperature for the system: potassium adsorbed on tungsten. The desorption energy D_e was taken as 2.64 eV after Ref. 63. The parameters used in the calculation: fractional charge on the potassium $Z_A^* = 0.27$ e and equilibrium distance of the adsorbate from the substrate, $d_1 = 2.38$ Å, were chosen after Ref. 63; the Debye temperature of the substrate was taken as $\theta_{\rm D} = 220$ K, the electron number density of the substrate was $n_e = 38 \times 10^{22}$ cm⁻³ and $x_e = 6.5 \times 10^{-4}$; the vibrational quantum in the harmonic well was taken as $\hbar\omega_0 = 13.7 \text{ meV}$ (after L. M. Kahn and S. C. Ying, Solid State Commun., 16, 799 (1975)). The experimental points (open circles) were taken after Ref. 63, $R(T) = 10^{12.8} \exp(-D_c/kT)$. Both the Morse potential (dashed) and truncated harmonic (solid) yield linear relationships in the plot of $\ln R(T)$ vs. inverse temperature, parallel to one another (same activation energy for desorption) but with different intercepts (frequency factors). The results based on the Morse potential description of the chemisorptive bond are in better agreement with the experimentally deduced results than those derived from a truncated harmonic potential.

should be noted that the differences between the two models are less pronounced than those which were exhibited in the transition rates.²⁰ Similar results, with a somewhat less pronounced difference between the two models and in agreement with experiment,⁶⁴ are shown for xenon desorption from tungsten (with the parameters given in the figure captions) in Figs. 3 and 4. In Fig. 4 the rather weak dependence of the results for the rate of desorption on the equilibrium distance parameter is exhibited.

III.B. DISCUSSION

From the results presented in Figs. 2-4 it is apparent that the model provides a rather adequate description of desorption for both weak (Xe/W) and strong (K/W) chemisorption systems. The principal merit of this model is that it exhibits explicitly the dependencies on various microscopic quantities characteristic to the substrate and adatom. Due to the complexity of the problem our model relies on a number of simplifying assumptions certain of which we enumerate below: (a) the substrate was modeled as a continuum structureless solid, (b) surface phonons have been ignored, (c) the electron response to fluctuations of the ionic charge was calculated semiclassically (quantum interference effects neglected) and with specular boundary conditions imposed, (d) electronic band-structure effects were ignored which implies weak electron-ion coupling in the substrate, (e) bilinear



Fig. 3. Semilogarithmic plots of desorption rates R(T) vs. inverse temperature for the system: xenon adsorbed on tungsten. The characteristic parameters are: $d_1 = 2.0$ Å, $\hbar\omega_0 = 3$ meV; $Z_A^* = 0.04$ e; the desorption energy, D_e , was taken as 217 meV after Ref. 64. The experimental points (open circles) were calculated from the rate expression given in the above reference: $R(T) = 10^{12} \exp(-D_e/kT)$. Results obtained by using Morse (triangles) and truncated harmonic potentials (dots) are shown.



Fig. 4. Semilogarithmic plots of desorption rates, R(T), vs. inverse temperature for xenon adsorbed on tungsten. Characteristic parameters used: $D_e = 300 \text{ meV}$; $Z_A^* = 0.04 \text{ e}^{14}$; $\hbar\omega_n = 3.0 \text{ meV}$; $x_e = 1.25 \times 10^{-3}$. The substrate parameters are those given in Fig. 2. Results are shown for both truncated harmonic (solid and open dots) and Morse (triangles and squares) potentials. The apparent slight sensitivity of the rates to the equilibrium distance of the adsorbed atom from the surface is shown.

coupling between the nonstationary adatom and substrate was used in the numerical examples and transition rates due to these couplings were calculated using the Fermi golden rule, (f) an immobile adsorbate was assumed. The inclusion of adsorbate migration on the surface will add an extropy correction to the rate expression. While further improvements within this model are possible, the present study allows for a first evaluation of the sensitivity of desorption kinetics to the various microscopic parameters.

The standard approaches to reaction kinetics, such as Absolute Rate Theory⁵ (ART) and the various statistical methods¹⁶ (e.g., RRKM), rely upon certain criteria of applicability. The main requirement of the above is that the initial and final (or transition complex) states are uncorrelated.⁵ As discussed originally by Kramers¹⁹ and further investigated recently^{19,65} the applicability of ART is related to the strength of the fluctuating part of the coupling (friction in the nomenclature of the above studies) between the adsorbate and the adparticle. The analytical results obtained¹⁹ in the limits of small and large coupling support the assertion that the applicability of ART is limited to an intermediate regime of the coupling strength. In this regime the coupling is strong enough as to replenish instantaneously the equilibrium Maxmellian tail of particle momenta, necessary for surmounting the reaction barrier, and thus the rate becomes independent of the coupling. Outside this regime the Arrhenius behavior of the rate constant gets modified by multiplicative factors which vary with temperature. Our calculation of t in principle assumes the weak coupling regime since our transition rates $W_{v \rightarrow v+1}$ are treated to lowest order in perturbation theory. This assumption of weak coupling has internal consistency in that our low order treatment does yield good agreement with experiment. While clearly the interplay between the temperature dependence of $W_{u \rightarrow v+1}$ and the usual statistical occupations (the sum over j in Eq. (3.6)) is a complicated one and cannot rigorously reduce to the Arrhenius-like form our numerical results give a measure for the weak deviation from such a behavior. This conclusion cannot be inferred directly from the evaluated transition rates alone but requires an analysis of the rates. In this context it is important, however, to notice the dependence of the results on the model potential used (truncated harmonic vs. Morse potentials), and that the difference in rates of desorption corresponding to the two model potentials is smaller than that exhibited in the associated level transition probabilities.

The stochastic treatment of the time evolution of the vibration excitations leading to desorption which we have used, is a convenient formulation of nonequilibrium kinetic processes. In the equilibrium theory the rate constant depends only upon transitions which couple bound vibrational levels directly to the dissociated state^{61,62} ϕ_{N+1} , and similar to the basic assumption of ART there is no dependence on the details of the excitation mechanism. The first passage-time, t, calculated via the stochastic non-equilibrium formulation does not, in general, equal the reciprocal of the equilibrium rate constant.⁶² One limit in which the above equality holds is when the energy required for a transition is large compared to the available thermal energy. This condition was not obeyed in our cases. Thus, it was necessary to investigate the full stochastic behavior.

The order of coupling in our model should also be commented on. While we have used bilinear coupling, the generalizations to include higher order terms (i.e., multiphonon processes) are rather straightforward; similarly, solutions to the master equation (3.1), where transitions between any two levels are retained, can be obtained numerically or in approximated form.³¹ In this context we could argue that by a proper transformation of the coordinates $\{R_s\}$ and $\{R_M\}$ the bilinear coupling term could be removed and the frequencies of the substrate-adatom system renormalized accordingly. The coupling enters now through the new frequencies in these transformed canonical coordinates. It is now, in principle, possible to calculate desorption rates with the simple assumption of a Boltzmann occupation of these new levels, and with proper retransformation of our coordinates to define the stage of dissociation. Such a calculation is expected to yield similar results to ours (particularly in the weak coupling limit) but it is rather complex and has not as yet been carried out for the model systems discussed in this study.

Before we turn to a discussion of the state selectivity of desorbed species we comment on the application of our model to adsorbed molecular species. These systems possess additional degrees of freedom certain of which are of bond-stretching character and others which describe bond-bending, wagging, and hindered rotations. While the energies typical to molecular bond-stretching modes might (and often do) exceed in magnitude those of single phonon excitation by the solid, the energies associated with the non-stretching modes are smaller. For example, the lowest vibrational level spacings in H-H, C-H, C-O, C=C and C-C stretches are 500, 360, 210, 200 and 110 meV, respectively, while the level spacings in non-stretching modes are often 10-50 meV. Consequently it is suggested that the latter modes through their coupling to the vibrations of the solid may be excited up to high levels via an incoherent multiphonon mechanism similar to that used in the present investigation and subsequently convert these excitations into translational kinetic energy or couple via anharmonicity to the highlying, densely spaced levels of the bond-stretching modes. Once these high-lying levels have been populated, the excitation may propagate further via direct coupling to the substrate, eventually leading to fragmentation (see Fig. 5). In other words the non-stretching modes may serve as door-way states towards bond rupture via intramolecular energy redistribution. In addition localized high-frequency (in particular light impurities) modes (either intrinsic substrate impurities or induced by the adsorbed system) may participate actively in the excitation mechanism.

Door-way state models have been instrumental in explaining certain types of nuclear reactions⁶⁶ and laser induced dissociation.⁶⁷ The role of rotational (and translational) modes in vibration relaxation of impurity molecules in host crystalline matrices has been proposed and investigated.⁶⁸⁻⁷⁰ In particular the participation of local modes in the relaxation mechanism has been emphasized.^{68.69} These studies were motivated by the observation⁶⁸ which implied breakdown of a proposed energy gap law,^{71,72} in the same spirit as we were motivated to introduce the door-way state model by the mismatch in the frequencies of bond-rupture modes and solid phonons.

Quantitative analysis of the proposed door-way state thermal desorption requires first calculation of initial state wave functions for the modes of the coupled admolecule (or adatom)-crystalline substrate system. In



Fig. 5. Schematic picture of the door-way state model for thermal surface desorption or dissociation reaction mechanism. A characteristic Debye phonon density of states, $\rho(\omega)$, is shown on the left and right. Excitation of a low-frequency, door-way, mode of vibration (typically a nonstretching mode) occurs via an incoherent multiphonon mechanism. Upon achieving the level E_{ϵ} the excitation is transferred to the high-lying levels of a stretching mode (or combination of such modes) via anharmonic coupling. Further excitation in the dense vibrational manifold corresponding to the bond-rupture coordinate can occur via direct incoherent multiphonon excitations induced by thermal coupling to the substrate. The predissociation level is denoted by E_{N+1} . Having achieved this level the reaction proceeds through coupling to possible final state channels, such as dissociation or migration.

the resulting modes one may identify modes which are characterized as bond stretching (intra admolecule, admolecule-surface and substrate vibrations), and those which are of rotational (or hindered rotational) character. In addition, modes localized at the vicinity of the admolecule can be identified. The final state may correspond to a number of possible desorption scenarios (e.g., molecular desorption, dissociative desorption). The potential which causes transfer of excitations can now be written in terms of the actual distances of adatoms from the substrate:

$$V = \sum_{i=1}^{n} \sum_{j=1}^{p} v_{ij} \left(\left| \vec{r}_{i} - \vec{R}_{j} \right| \right)$$

where *n* is the number of atoms in the admolecule, *P* goes over the substrate atoms interacting with the admolecule (dictated by the range of the potentials v_{ij}) and \vec{r}_i , \vec{R}_j are adatom and solid atom position vectors. Expansion of v_{ij} around the equilibrium positions $(\vec{r}_i^o, \vec{R}_j^o)$ yields an expression which consists of coupling terms such as (see Eq. 2.14)

$$g_{\nu,\omega}^{(1)}(b_{\nu}+b_{\nu}^{+})(a_{\omega}+a_{\omega}^{+}), \quad g_{\nu,\omega}^{(2)}(b_{\nu}+b_{\nu}^{+})(b_{\nu'}+b_{\nu'}^{+})(a_{\omega}+a_{\omega}^{+})$$

where b_{\star} , b_{\star}^{+} are creation and annihilation operators for phonon-like modes and a_{ω} , a_{ω}^{+} for molecular-like modes (ν and ω include local modes). The rate of desorption to a specific final state can then be evaluated using the apppropriate final-state wave function using the golden rule expression, and averaging over the thermal population in the initial state.

Another approach to the door-way state (dual ladder) model is to consider the system as consisting of two manifolds, one consisting of the low-frequency modes (usually non-stretching) and the second consisting of stretching modes. The two are coupled through anharmonic terms when near degeneracy⁷³ (or accidental degeneracy leading to Fermi resonances). The resulting modes are admixtures of the two manifolds. When such coupling occurs at energies where the resulting level

spacings are within the range of phonon frequencies, direct excitation by the substrate becomes possible. In this scheme the excitation evolution may be evaluated using the stochastic formulation described in Section III.A.

In both schemes of calculation the three-dimensional character of the system is essential. Besides allowing the description of desorption in strongly bonded systems (circumventing the use of low-probability coherent multiphonon excitations) the model suggests the possibility of angular distributions of the desorbed flux which reflect the symmetry of the admixed modes (dependent on bonding site geometry, force constants and modecoupling strength).

IV. STATE SELECTIVITY

A detailed investigation of reaction mechanisms requires an analysis of the reaction products in the form of state selective measurements^{45,47-50} (filling in the elements of the S-matrix). Such data consists of product identification, their center of mass translational energy, excitations of internal degrees of freedom and angular distributions. In this section we present first a simple quantummechanical model for rotational state distributions of diatomic molecules thermally desorbed or ejected from a surface, followed by brief comments on final-state product branching and angular distributions.

IV.A. A SOLVABLE HINDERED ROTOR MODEL FOR ROTATIONAL DISTRIBUTIONS OF MOLECULES EJECTED FROM A SURFACE

The role played by the rotational degrees of freedom of diatomic molecules which are dynamically coupled to solid surfaces has been the focus of several recent experiments.46-49 Laser-induced-fluorescence (LIF) studies of the rotational-state distribution of NO molecules scattered,47 thermally desorbed48 or ejected from metallic surfaces suggest highly non-equilibrium⁴⁹ behavior in either event. Concurrently, rotational excitation of H₂, D₂, and HD physisorbed⁴⁶ on Ag(111) and Cu(100) surfaces has been observed in electron-energyloss-spectroscopy (EELS), showing loss features very similar to those seen in free molecules, suggesting that at least on these particular surfaces the rotations are unhindered.74

These experiments demonstrate the necessity for models beyond the usual one-dimensional ones involving only nuclear translations or vibrations normal to the surface. On purely theoretical grounds, it has already been suggested that the coupling of hindered rotations ("door-way states") to the stretching vibrational modes associated with the chemical bond between the adsorbate and the surface serves as the energy flow pathway for substrate phonon pumping up the vibrational ladder towards dissociative (desorption) continuum states (see Section III.B and Ref. 20), a mechanism also requiring a multi-dimensional microscopic picture.

With the above in mind, at least two distinctly different theoretical approaches are suggested which can enhance our insights into the actual behavior. First, one can write and solve some relevant set of classical Langevin equations for the coupled motion in the manner pursued by Tully.¹⁸ Certainly this has been a highly illuminating direction, as he has demonstrated. Nonetheless there are motivations for complimentary model studies on isolated and idealised components of the complex system, the We present the main features and illustrative numerical consequences of a highly idealized but mathematically intriguing model for a hindered 3-dimensional rotor. The characteristic of our model is that free rotations are possible only within a conical domain bounded at some critical polar angle $\beta \le \pi/2$ by an infinitely repulsive wall, and as such the model is a spherical coordinate system analog of a textbook infinite-square well. It is to be stressed that this model was first put forth more because of its interesting analytical properties than because it is a realistic approximation to a currently identifiable lab system. Nonetheless its easily illustrated physics seem quite similar to the opaque physics involved in much more complex systems, hence its usefulness.

Specifically the model facilitates identification of the special role played by the zero point kinetic energy associated with the spatial localization of the rotor, both on ground state properties and on the excitation spectrum. This can be contrasted with the harmonically constrained rotor in which the effects of localization are distributed between kinetic and potential energy.^{76,77}

The model will be outlined in Section (i) and the mathematical properties of the eigenstates presented in (ii). Section (iii) is devoted to the numerical consequences. Eigenvalues are shown as a function of hinderance angle and are correlated with free rotor states in the $\beta = \pi/2$ limit by means of a "surface-selection rule," for nodal wavefunctions.78 Sudden removal of the hindering potential⁷⁹ (constrained \rightarrow free rotor transition as might be experienced in thermal desorption) results in a nonequilibrium population within the manifold of free rotational states whose distribution is determined by rotational Franck-Condon factors. Apparent free rotational temperatures, differing from the equilibrium temperature of the hindered state due to the conversion of zero point kinetic energy into free rotational energy, are investigated as a function of equilibrium temperature and hinderance angle. Oscillating and "plateau" structures in the state distribution due to Franck-Condon interferences⁸⁰ are found. Implications with regards to scattering and desorption experiments are discussed. An extension of the model to include center of mass motion is discussed in (iv).

(i) Model

We will be concerned with the two mathematically equivalent models displayed in Fig. 6, in which a rigid dumbell executes free rotations within the conical space defined by $\theta < \beta$, $0 < \phi \leq 2\pi$. In Fig. 6a the rotations are about an origin placed at the center of mass. This geometry could simulate a hindered rotor embedded within an anisotropic void or in an "atomic trough" on a surface. The rotor shown in Fig. 6b simulates an adsorbed diatomic in which one end might be clamped to a surface via a chemical bond. For the present, vibrational motion along the rotor axis will be neglected.

The model is characterized by the standard angular part of the Schrödinger equation:

$$\begin{cases} \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \\ + \frac{2I}{\hbar^2} (\varepsilon - V(\theta, \phi)) \end{cases} \psi^{\text{rot}}(\theta, \phi) = 0$$
(4.1)

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Fig. 6. The hindered rotor in an infinite conical well: (a) and (b) are two possible realizations of the model.

with $I = \sum_{i} m_{i} r_{i}^{2}$. For the ϕ -independent "infinite conical well,"

$$V(\theta, \phi) = \begin{cases} 0, & \theta \leq \beta \\ \infty, & \theta > \beta \end{cases}$$

so not only is the total rotational wavefunction separable as

 $\psi^{\text{rot}}(\theta,\phi) = P(\theta)v(\phi) \text{ with } v(\phi) = (2\pi)^{-1/2} \exp(im\phi)$

but also $P(\theta) = 0$ for $\theta > \beta$.⁸¹ With the above choice for $V(\theta, \phi)$, it is a textbook exercise to reduce the θ part of Eq. (4.1), in terms of the auxiliary variable $x = \cos \theta$, to

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left(\frac{2I}{\hbar^2} - \frac{m^2}{1-x^2}\right)P = 0 \qquad (4.2)$$

valid in the domain $\cos \beta \le x \le 1$. Equation (4.2) is exactly Legendre's equation when the eigenvalues are written in the form

$$\varepsilon = B\nu(\nu+1); \qquad B = \hbar^2/2I. \tag{4.3}$$

(ii) Mathematical Consequences

The eigenstates of the hindered rotor are solutions of Eq. (4.2) with the boundary conditions that P(x) is finite at x = 1 and zero at $x = \cos \beta$. With the eigenvalue written in the form $\nu(\nu + 1)$ where ν is a continuous (usually non-integer) positive "quantum number," the eigenfunctions are associated Legendre functions of arbitrary order,⁸² that is,

$$\psi_{\nu m}^{not}(\theta,\phi) = \begin{cases} \frac{A_{\nu m}}{\sqrt{2\pi}} P_{\nu}^{|m|}(\cos\theta) e^{im\phi}, & 0 \leq \theta \leq \beta \\ 0, & \beta \leq \theta \leq \pi \end{cases}$$
(4.4)

with $m^2 < \nu(\nu + 1)$ and $A_{\nu m}$ a normalization constant. The eigenvalues are numerically determined by the condition

$$P_{\nu}^{m}(\cos\beta) = 0 \tag{4.5}$$

together with Eq. (4.3), and the normalization by

$$\frac{1}{|A_{rm}|^2} = \int_{\cos\beta}^1 dx |P_{\nu}^{mi}(x)|^2 = \frac{-(\nu+m)}{2\nu+1} P_{\nu-1}^{m}(\cos\beta) \left[\frac{dP_{\nu}^{m}(\cos\beta)}{d\nu}\right].$$
(4.6)

Lastly, the overlap integral between an arbitrary function, conveniently expanded in a free space

$$Y_{lm'}(\theta,\phi) = \frac{A'_{l,m'}}{\sqrt{2\pi}} P_l^{m'}(\cos\theta) e^{im'\phi} \quad (l = \text{integer})$$

basis, and $\psi_{\nu m}(\theta, \phi)$ is easily evaluated using the relationship

$$\langle Y_{lm} \mid \psi_{\nu m} \rangle = \frac{\delta_{m,m} A_{\nu m} A_{lm}}{\nu + l + 1} \left(\frac{\nu + m}{\nu - l} \right) P_l^m(\cos\beta) P_{\nu-1}^m(\cos\beta)$$

$$(4.7)$$

valid for $\nu \neq l$.

An interesting limiting case occurs for $\beta = \pi/2$, that is, when the rotor is constrained to a half infinite space. The boundary condition, Eq. (4.5), requires that the eigenfunctions have nodes on the plane separating the half spaces. But solutions of Eqs. (4.2) and (4.5) are just the subset of usual Y_{im} 's satisfying the "surface-selection rule" invoked in the nodal-hydrogenic wavefunction papers.⁷⁸

That rule states that only Y_{lm} 's obeying the condition

$$(l+m) = \text{odd} \tag{4.8}$$

are permissible, Some important consequences follow from Eq. (4.8):

(i) The $\beta = \pi/2$ confined rotor ground state is a non-degenerate *p*-state with $l = \nu = 1$, m = 0.

(ii) The zero point energy associated with localization of the rotor to a half space is $E_{sp}(\beta = \pi/2) = \hbar^2/I$.

(iii) The *l*'th level is *l*-fold degenerate rather than 2l + 1 as in the unhindered rotor.

(iv) The $\beta < \pi/2$ -confined-rotor eigenstates are related to the half-space states via $E_{zp}(\beta < \pi/2) > \hbar^2/I$ and the *l*-fold degeneracy, for different *m* states, is increasingly lifted as ν increases with decreasing β from the integer value it takes on at $\beta = \pi/2$.

This exact analytic limit provides a useful numerical as well as intuitive check on our computer results reported in the next section.

(iii) Results

The lowest four eigenvalues of the hindered rotor, obtained by numerical solution of Eqs. (4.2), (4.3), and (4.5), are displayed in Fig. 7 in the form of ν vs. β plots. These values apply to both models suggested in Fig. 6, though the moments of inertia differ, appearing only as a scale factor in the eigen-energy expression, Eq. (4.3). The



Fig. 7. The four lowest restricted rotor quantum numbers, ν , as a function of the cone angle, β .

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 $\beta = \pi/2$ values are those of the free rotor, subject to the constraints of the " $\nu + m = \text{odd}$ " rule. Each non-zero m state is 2-fold degenerate. Note, however, that the degeneracies of various m states, for given $\nu = l$, $\beta = \pi/2$, is lifted as the cone is closed up. This is due to the m-dependent reduction of the " ϕ -repulsion" $(m^2/(1-x^2) \text{ in Eq. } (4.2))$ relative to the "kinetic energy" term which depends upon wavefunction curvature, as the cone angle decreases and hence the curvature (kinetic energy) increases.

The general form of the results shown in Fig. 7 are in accord with our intuition. As β decreases, the zero point kinetic energy associated with the increased localization increases dramatically, as does the scale of the excitation spectrum. To illustrate the significance of this effect, consider a rotor constrained to a cone with $\beta = 10^{\circ}$, as a model for a diatomic molecule adsorbed in an upright configuration on a surface.83 Using established values for free space rotational constants ($B_r = \hbar^2/2kI$), with $B^{N_2} =$ 2.89 K and $B^{H_2} = 87.5$ K, the zero point rotational energies are ~ 0.025 and 1.0 eV, respectively, which in the case of H₂ significantly influences possible chemistry.⁸⁴ This, of course, is not surprising in view of the properties of the H2-molecular solid75 and explains why the nearly spherical H₂ molecule does not orient in the condensed phase.

The stimulus for the LIF desorption⁴⁸ (and perhaps trapping regime of the scattering⁴⁷) studies is the hope that determination of the rotational state distribution of the free rotor (desorbed molecule) will provide information pertaining to the dynamics of energy flow in the desorption process of the initially hindered rotor. Certain aspects of the hindered-to-free rotor transition which must occur in desorption are illuminatingly illustrated with the present model. Consider the following scenario for a desorption event. As a first approximation an upright molecule executes hindered rotations of the type shown in Fig. 6b which are taken to be decoupled from the rigid molecule vibrations associated with the chemical bond between the "pinned" atom and the surface. The rotational potential energy surface depends parametrically on the vibrational/translational quantum state of the molecule via a standard Born-Oppenheimer separation of slow (rotational) and fast (vibrational) degrees of freedom. Desorption occurs by climbing the vibrational ladder through a series of (assumed) impulsive kicks from the underlying substrate atoms.^{20,85,86} Focus on the final collision in which sufficient energy is transferred from the substrate to the molecule to induce a bound (adsorbed) to continuum (desorbed) transition. From the point of view of the rotor, this corresponds to a switching of rotational potential energy surfaces, from an initial one with the hindering potential to that of the free rotor. Within the sudden approximation,79 which is not unreasonable due to the impulsive collisions, the probability for ending up in the l'th free rotor state is just a sum of rotational Franck-Condon factors between Y^{tree} and $\psi_{\nu,m}^{\text{rot}}$, given by Eq. (4.4), weighted by appropriate thermal factors. In the case of desorption, however, not only is the hindering potential turned off but also the atom tied down to the surface (Fig. 6b) is released, thus permitting free translation of the molecular center of mass. Thus the kinetic energy of the hindered rotor would be partitioned between translational and rotational energy of the free particle and to a first approximation, both free translation and rotational energies would appear cooler than the background temp-

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erature, in agreement with observations⁴⁸ (see subsection (iv)).

For present purposes consider the more limited problem of the rotor in Fig. 6a, executing hindered rotations about the center of mass. Following the discussion of the previous paragraph, if the hindering potential is suddenly switched off, then free rotations are permitted, but with no rotational to translational transitions possible. The probability for excitation of the *l*'th free rotor state is then

$$P(l) = \frac{1}{Z_{\min}} \sum_{\nu > 1, m, m'} \exp\left(-\frac{B\nu}{kT}(\nu+1)\right)$$
$$\times |\langle Y_{jm}^{\text{tree}} | \psi_{\nu m}^{\text{rot}} \rangle|^2$$
(4.9)

where T is the ambient temperature and Z_{hin} the hindered rotor partition function. The probability for observing the l'th state thus depends both upon the overlap of the ν 'th hindered state with the particular free state and also upon the probability that the ν 'th state is occupied. The overlap integrals are a measure of the kinetic energy distribution associated with the localization. If $B/kT \ge 1$, one would expect that the population of high *l* states results mainly from their overlap with low-lying ν states, not from a one-to-one correspondence with thermally excited ν states. In other words the final state rotational energy derives from the zero point energy, not from thermal excitation. Consequently the more narrow the cone, the "hotter" the final state distribution, independent of ambient temperature. Furthermore, as the cone narrows, "gaps" in the excitation spectrum increase thus reducing the role of thermal excitation for the same reasons that the specific heats of ortho and para-hydrogen differ.75.87

The expectations just mentioned are borne out by our calculations. State distributions given by Eq. (4.9), using values of ν and the overlap integral determined from Eqs. (4.5)-(4.7), for a "typical" value of B/kT = 0.05 (corresponding to say $B_r \approx 15$ K, $T \approx 300$ K) and treating β parametrically are shown in Fig. 8. As anticipated, the smaller the hinderence angle, the greater the population of higher energy rotational states.

Laser-induced-fluorescence data^{47,48} is often plotted in the form $\log(P(l))/(2l+1)$ vs. l(l+1), which yields a straight line with slope = $-B/kT_R$ if the rotational distribution of the interrogated molecules corresponded to



Fig. 8. Rotational state distributions, P(l), for the suddenly unhindered rotor (Fig. 1), as a function of the free rotor rotational quantum number, l.

an equilibrium state at some rotational temperature T_{R_r} . In fact Kleyn et al.⁴⁷ observe two regimes in rotational distributions of NO scattered from Ag. For $l \leq 20$, the distribution is Maxwellian over two orders of magnitude, showing a T_R which is basically independent of the surface temperature. For $l \geq 20$, a plateau structure whose breadth depends upon the kinetic energy of the incident beam is observed. This structure has been attributed to a rotational rainbow. Cavanagh and King⁴⁸ also observed a linear distribution over an order of magnitude, for NO thermally desorbed from Ru, again with T_R apparently unrelated to the surface temperature from which the NO desorbed.

Guided purely by the just-mentioned experimental convention for data presentation, we have plotted our state distributions, obtained from Eq. (4.9), semilogarithmically. The somewhat astonishing results are shown in Fig. 9 where each panel corresponds to a different hinderance angle and \dot{B}/kT is treated parametrically within a panel. Note that all the distributions show basically two distinctly different regimes. First, for low l $(\leq 20-30)$, a rather linear decrease occurs over 2 to 3 orders of magnitude whose inverse slope could be represented by a free rotational temperature. As depicted in Fig. 9, for given hinderance angle β , $T_{\rm R}$ appears to be independent of T (for $\beta \leq 45^{\circ}$). Furthermore, as β decreases (increasing zero point kinetic energy and excitation energies) the inverse slope or apparent rotational temperature increases. Both of these characteristics support our conjecture that conversion of zero-point, rather than thermal kinetic energy into free rotational energy is the mechanism responsible for population of the free rotor excited states, at least within the context of our model problem; hence the apparent T-independence of the low-l state distribution. For the model (Fig. 6a) treated here, $T_{\rm R}$ is always greater than 2B/k, the minimum possible zero point energy (for $\beta = \pi/2$). Thus the distribution appears "hot." As already mentioned,



for a desorption event, center-of-mass motion is also possible, in which case the rotation zero point energy is split between translation and free rotations, which would have the effect of cooling our distribution.⁸⁸ The remarkable properties of this first regime of the state distributions are that they are linear over so many decades, thus permitting identification of a $T_{\rm R}$, and that the break from the linear form to a second regime occurs in the region $l \sim 20$, where the population is down by ~ 3 orders of magnitude, just as observed by Kleyn et al.⁴⁷

The second (high 1) region displays qualitatively different behavior. At some critical l value, the state distribution drops precipitously from the linear form, then rises, and displays an oscillatory structure which is most pronounced for low T. The origin of this structure is interference effects within the Franck-Condon factors which are certainly enhanced in the "infinite-conicalwell" model. The oscillations, which show a periodicity in l varying as $180^{\circ}/\beta$, are thermally washed out, though still leaving a plateau or smoothly varying distribution at high l which is quite different from the low l range. This is emphasized in Fig. 10, where again $\log(P(l)/(2l+1))$ is plotted vs. l(l+1), but now on an expanded scale. Although it is unlikely that the oscillatory behavior would survive in a real laboratory system, the plateauing should. Already such an effect has been observed in beam experiments.^{47,49} The fact that such data was interpretable in terms of rotational rainbows⁸⁹ suggests that there could be an intimate connection between the physics responsible for rainbows and the physics implicitly contained within our Franck-Condon factors. This possible connection is under investigation.

(iv) Extension to Include Center of Mass Motion

In the model presented above the center of rotation and the center of mass of the admolecule were assumed to coincide. In this section we present an extension in which this restriction is lifted. We present a brief outline of the model and sample results for rotational state



Fig. 10. Same as Fig. 9, for several cone angles, β , for a range of $0 \le l(l+1) < 1000$.

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distribution for the case of desorption caused by incident radiation (photon, electron or atomic induced desorption). To facilitate our discussion we restrict our discussion to a molecule AB bound to the surface in an infinite cone well potential with the nuclei A, B and the apex (O) of the cone collinear.⁹⁰ This system can be regarded as a limiting case of a general triatomic molecule ABO with the force constant corresponding to bending (deviation from linearity) approaching an infinite value. Denoting the position vector to the center of mass of the molecule (with reference to the apex of the cone, which need not be located, in general, at the surface) by \vec{R}_{cm} and assuming rigidity with respect to stretching (fixed bond length AB = a, and fixed center of mass distance to the apex, d), the initial state nuclear wave function may be written as

$$|\nu, m; \beta\rangle \equiv \psi_{i} \tag{4.10a}$$

$$= N_i \psi_{\nu m}^{\rm res}(\theta, \phi) \delta(R_{\rm cm} - d) \delta(\hat{R}_{\rm cm} - \hat{r}) \delta(r - a)$$

and the nuclear final state as

$$|k, l, m'\rangle \equiv \psi_l$$

= $N_l e^{i \vec{k} \cdot R_{cm}} Y_{lm'}(\theta, \phi),$ (4.10b)

where N_i and N_t are normalization constants, k is the wave vector of the center of mass translation in the final state and the $\psi_{\nu m}(\theta, \phi)$ are the restricted-rotor wave functions of the initially adsorbed molecule, discussed in the previous subsections. The delta functions in the wave-function should be regarded as symbolic (operationally they represent the limiting process mentioned above) in calculations of the required matrix elements, $\langle \vec{k}, l, m' | \nu m; \beta \rangle$. These matrix elements enter the evaluation of the required probability for the final state to be found in rotational state l, P(l). To calculate the matrix element we use the expression of the plane wave

$$e^{i\vec{k}\cdot\vec{R}_{\rm cm}} = 4\pi \sum_{l'=0}^{\infty} \sum_{n=-l'}^{\infty} (i)^{l'} j_{l'}(kR_{\rm cm}) j_{l'}(kR_{\rm cm})$$
$$\times Y_{l'n}^{*}(\theta_{k},\phi_{k}) Y_{l'n}(\theta_{\rm cm},\phi_{\rm cm})$$
(4.11)

where (θ_k, ϕ_k) are the angles specifying the direction of the center of mass wave vector in the final state, \vec{k} , with reference to the normal to the surface. In addition we employ the expansion of the restricted-rotor wave function $\psi_{im}^{res}(\theta, \phi)$ in terms of spherical harmonics

$$\psi_{\nu m}^{res}(\theta,\phi) = \sum_{l=|m|}^{\infty} \langle lm \mid \nu m; \beta \rangle Y_{lm}(\theta,\phi) \qquad (4.12)$$

where the coefficients in the expansion are the overlap integrals entering the Franck-Condon factors discussed in the previous subsection. Using (4.11) and (4.12) and the relation (where the Wigner 3j symbols are used)

$$\int Y_{l_1m_1}^*(\Omega) Y_{l_2m_2}^*(\Omega) Y_{l_3m_3}(\Omega) d\Omega$$

= $\left[\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi} \right]^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}$ (4.13)
 $\times \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & -m_2 & m_3 \end{pmatrix} (-1)^{m_1+m_2}$

yields an expression for $\langle \vec{k}, l, m' | \nu m; \beta \rangle$.

Having obtained the overlap integral, expressions for final-state probabilities may be derived.

(a) The probability for finding the free molecule with rotational state l and center-of-mass wave vector \vec{k} is calculated using the golden rule,

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$$P_{\omega}(l,\vec{k}) = \frac{2\pi}{\hbar} N_{1} \sum_{\nu,mm'} \frac{\exp[-B_{r}\nu(\nu+1)/k_{B}T_{s}]}{Z_{hin}}$$

$$\times |\langle \vec{k}, l, m'| \nu m; \beta \rangle|^{2}$$

$$\times \delta \left[D + B_{r}\nu(\nu+1) + \hbar\omega - B_{t}l(l+1) - \frac{\hbar^{2}k^{2}}{2m} \right]$$

$$B_{r} = \hbar^{2}/2I_{r}, \qquad B_{t} = \hbar^{2}/2I_{t}; \qquad (4.14)$$

 N_1 contains numerical normalization factors and an averaged magnitude squared matrix element of the interaction due to the radiation evaluated between the initial and final Born-Oppenheimer electronic states. The delta function expresses the conservation of energy, with D the desorption energy. We define now the threshold incident radiation energy, $\hbar\omega_c$, as the amount of excitation energy which will result in an l = k = 0 desorbed molecule, at low surface temperature when the only state of the hindered rotor populated is ν_g , i.e.,

$$\hbar\omega_{\rm c} = -D - B_{\rm r}\nu_{\rm g}(\nu_{\rm g} + 1). \tag{4.15}$$

We may now define Δ as the incident radiation energy above the threshold,

$$\Delta = \hbar (\omega - \omega_c). \tag{4.16}$$

In terms of Δ the δ -conservation may be written as

 $\delta\{B_r[\nu(\nu+1) - \nu_s(\nu_s+1)] + \Delta - B_t l(l+1) - \hbar^2 k^2/2m\}.$ Thus we study the final state probabilities as functions of Δ .

(b) The probability for final state (l, k), integrated over directions,* is

$$P_{\Delta}(l,k) = N_2 \int d\Omega_k P_{\Delta}(l,\vec{k}). \qquad (4.17)$$

Finally

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(c) The probability for final state (l) regardless of direction and translational energy is given by

$$P_{\Delta}(l) = N_3 \int k^2 P_{\Delta}(l,k) dk. \qquad (4.18)$$

In Figs. 11a and 11b we present sample results for $P_{\Delta}(l)$, Eq. (4.18), for a value of $B_t/k_BT = 0.9$ (for example H_2 , and T = 100 °K) and $d = 0.5 \hbar/(mk_BT)$. Results are shown for hinderance angles $\beta = 30^\circ$, 60° and 90° and several values of Δ/k_BT . In Fig. 11a we show $P_{\Delta}(l)/P_{\Delta}(0)$ vs. *l* and in Fig. 11b, $\log[P_{\Delta}(l)/(2l+1)P_{\Delta}(0)]$ vs. *l*(*l*+1). From the results in Fig. 11a it is seen that upon increasing Δ (the incident energy above the desorption threshold) the peak in the distribution of rotational states of the desorbed molecule shifts to higher *l*-values, for all hinderance angles. It is also seen that in general the probabilities for the higher angles are larger. The results in Fig. 11b exhibit an overall non-Boltzmann behaviour. Nevertheless, venturing straight line fits to judiciously chosen regions on the curves shown in Fig. 11b results in

* The expression for the absolute square of the overlap matrix element integrated over the solid angle Ω_k is given by (see U. Landman, C. L. Cleveland, R. N. Barnett and J. W. Gadzuk, to be published)

increasing rotational temperatures for higher incident excitation (higher Δ). These effective rotational temperatures are not necessarily higher than the temperature of the substrate with which the initial hindered molecule is in equilibrium.

In Table 1 we present ratios of the average rotational energies of the free (desorbed) and hindered molecule, $\langle E_{ROT}^t \rangle \langle E_{ROT}^r \rangle$, and of the average rotational energy of the free molecule to its center-of-mass translational energy, $\langle E_{ROT}^t \rangle / \langle E_{CMT}^t \rangle$. These ratios are given for $\beta =$ 30°, 60° and 90° and various values of Δ for the system described in Fig. 11. Comparing results for different angles β it is seen that for small hinderance angles a higher excitation energy, Δ , is needed in order to increase the rotational energy content in the final state over that of the adsorbed molecule.

The branching ratios of rotational to center-of-mass translation energy in the final state demonstrate that overall more of the excitation energy is converted into the center-of-mass translation than into rotational energy. However, note the difference in trend as a function of Δ , for different angles, β . While the ratio peaks at an intermediate value of Δ for $\beta = 30^{\circ}$ and 60° , it decreases monotonically for $\beta = 90^{\circ}$. For a strongly hindered adsorbed molecule, (small β) and at low excitation energy, Δ , above the desorption threshold, coupling to the center-of-mass translational degree of freedom is dominant. As the hinderance cone angle increases the



Fig. 11. (a) Plots of $P_{\Delta}(l)/P_{\Delta}(0)$ vs. l for the bindered rotor desorption with center-of-mass motion for hindrance angles $\beta = 30^{\circ}, 60^{\circ}$ and 90° for values of Δ (energy above the excitation threshold in units of $k_{\rm B}T$), 1, 40, 80, 160 and 240. (b) Plots of $\log[P_{\Delta}(l)/(2l+1)P_{\Delta}(0)]$ vs. l(l+1) for hindrance angles $\beta = 30^{\circ}, 60^{\circ}$ and 90° and various values of Δ .

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	$\beta = 30^{\circ}$				$\beta = 60^{\circ}$					$\beta = 90^{\circ}$				
$\frac{\Delta/k_{\rm B}T}{\langle E'_{\rm ROT}\rangle/\langle E'_{\rm ROT}\rangle}$ $\langle E'_{\rm ROT}\rangle/\langle E'_{\rm CMT}\rangle$	$ 1 9.5 \times 10^{-8} 1.2 \times 10^{-6} $	40 0.82 0.36	80 1.47 0.31	160 2.74 0.28	240 3.97 0.27	$ 1 3.9 \times 10^{-2} 0.14 $	40 2.75 0.27	80 5.34 0.263	160 10.52 0.258	240 15.66 0.255	1 0.23 0.60	40 5.01 0.26	80 9.90 0.256	160 19.67 0.254

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transfer of excitation energy to the rotational degree of freedom becomes increasingly efficient.

IV.B. COMMENTS ON PRODUCT BRANCH RATIOS AND ANGULAR DISTRIBUTIONS

We have already remarked on the possible scenarios of a desorption event which may include molecular or dissociative desorption with the products possibly in excited vibrational, rotational or electronic (through curve crossing) excited states, or surface bound products corresponding to recapture or surface diffusional states. The final-state product branching ratios may be calculated using a formalism similar to that used in studies of autoionization," and predissociation"-" phenomena and applied also in the study of radiationless transitions in molecules^{95,96} and photodissociation.⁹⁷⁻⁹⁹ Employing such formalisms we have treated, phenomenologically, the configurational mixing of the ϕ_{N+1} state of the initial vibrational ladder with several final state manifolds and have derived²⁰ expressions for the time dependence of final-state probabilities, decay rates and product branching ratios.

Measurements of the angular and energy distributions of desorbed species, and particularly joint measurements, may reveal useful information concerning the dynamical mechanism of the desorption processes and provide a test for theoretical models. Experimental measurements of angular distributions have been performed using (a) molecular beams,^{100,101} (b) permeation experiments¹⁰² and (c) flash desorption.¹⁰³ The results show deviations of the angular distributions, $N(\theta)$, from Knudsen's cosine law, an enhancement in $\langle E(\theta) \rangle$ above the $2k_BT$, value (expected for an equilibrated desorbed gas with a surface at temperature T_s) in the normal to the surface direction, and a decrease in $\langle E(\theta) \rangle$ for angles θ which approach $\pi/2$.

Features in the angular and energy distributions of desorbed molecules may be attributed to different processes characteristic to the adsorption system and reflecting the desorption mechanism. We have already commented in the context of our proposed door-way state model of desorption on the possibility that the admixture of different modes of the adsorbed species in the processes of excitation (ladder climbing) would yield an angular distribution characteristic of the shape of the potential surface, and coupling constants in the initial state. Such a situation is most likely to occur for a chemisorbed species whose desorption does not involve precursor states. On the other hand, for certain desorption systems where desorption may involve passage through an intermediate weakly bound state (which may allow mobility parallel to the surface and thus energy equi-partitioning) we expect that the angular distribution will reflect less characteristics of the symmetries of motions in the initially bound state and will be influenced more by kinematics of passage through the potential field normal to the surface.104,105

V. STOCHASTIC THEORIES OF SURFACE DIFFUSION AND CERTAIN DIFFUSION CONTROLLED REACTIONS

Diffusion processes on or in the vicinity of surfaces are of importance in many surface controlled, or driven, physical and chemical phenomena. Such phenomena include crystal growth, surface phase transformations, annealing and recovery of damage, surface and interfacial segregation and chemical processes, heterogeneously catalyzed by surfaces.

rios of refined theoretical studies, and methods of analysis.^{4b} The objective of these studies is to understand on a microscopic level the mechanism, kinetics, dynamics and energetics (all of which are related) of surface diffusion. It is convenient to classify the theoretical approaches as: (a) stochastic processes, (b) dynamical simulations, and (c) energetics. Our discussion will focus on several selected topics (mainly within the context of a stochastic approach) chosen to illustrate certain of the issues which are encountered in this field. g such y, the *Stochastic Theory of Diffusion and Reactions — Multiinitial* state Random Walks The degree of microscopic detail with which we study a physical system is dictated by characteristics of the system (relaxation times, correlation lengths, etc.) and by experimental resolution. While single particle diffusion

The advent, development and application of experi-

mental techniques such as Field Ion Microscopy (FIM)⁴ and Field Emission Microscopy (FEM)⁴ provide quan-

titative information about the microscopic nature of

surface diffusion processes and serve as the impetus for

system (relaxation times, correlation lengths, etc.) and by experimental resolution. While single particle diffusion on a perfect lattice is commonly described in terms of a random walk process, generalizations of the formalism are needed in order to describe complex diffusion mechanisms and diffusion on defective lattices.⁴⁶ A stochastic description of diffusion processes which incorporates a detailed set of states (and corresponding transition rates), through which the system evolves, allows the investigation of atomistic mechanism of diffusion in complex systems. When applied to the analysis of experiments of sufficient resolution the method provides a means of determining the "spectroscopy of internal states". The internal states may correspond to the energetics of the motion (i.e., they may represent selected points on the energy surface), spatial configurations (as in the description of cluster diffusion) or other characteristic internal states which may participate in the migration mechanism. We have shown^{4b} that for a number of varied transport systems the set of allowable states can be mapped onto lattices, possibly with multiple sites in each unit cell. The stochastic time development of these systems, which may be semi-Markovian or non-Markovian, can be treated as a continuous-time random walk (CTRW) process on these lattices. In the following we outline the method and demonstrate it for the study of dimer channeled diffusion and certain unimolecular and bimolecular diffusion controlled reactions on surfaces.

The diffusive motion of adatoms and clusters of adatoms on surfaces has been dramatically revealed by Field Ion Microscope $(FIM)^{106-110.4a}$ studies. Field Ion Microscopy which was conceived and developed by E. W. Muller in the early 1950's was used first for the investigation of adatom migration on surfaces by Ehrlich and Hudda¹¹¹ in 1966. Later studies revealed that adatoms on metal surfaces can become correlated to move as a single cluster.¹¹²⁻¹²¹ One example we will analyze in detail is the motion of rhenium dimers on a W(211) surface.¹¹²

The FIM is, under certain conditions, able to give images from which one can determine the distance traveled by an adatom in a time t at a temperature T. For example, the motion of a *single* tungsten adatom on a W(211) surface is seen to occur¹¹¹ (away from boundaries) as a one-dimensional random walk with symmetric nearest-neighbor hopping. Standard random walk theory

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gives for the mean squared displacement, $\sigma^2(t)$, after a time t,

$$\sigma^2(t) = \lambda L^2 t \tag{5.1}$$

where λ is the hopping transition rate, L is the lattice spacing, and $\sigma^2(t)$ can be obtained from FIM pictures. The transition rate λ is seen to be in the Arrhenius form

$$\lambda = \nu \exp(-E/kT) \tag{5.2}$$

since a semilogarithmic plot of $\sigma^2(t)L^2t$ vs. 1/kTyields a straight line of slope -E and ordinate intercept log ν . Thus, an analysis of the FIM pictures can yield the activation energy, E, for diffusion, as well as the frequency factor ν . We will now discuss how the maximum amount of information can be extracted from FIM data when the motion of a cluster occurs and several transition rates are involved. This will lead us to the study of random walks with several internal states.

The nature of the motion of a cluster on a surface depends on the substrate composition and morphology as well as on the type and number of atoms in the cluster. For example, rhenium dimers¹¹² are seen to undergo one-dimensional motion on W(211) by alternating between straight and staggered configurations, as shown in Fig. 12. If only one staggered position is allowed, the center of mass motion of the dimer can be mapped onto a perfect lattice with two states per unit cell (Fig. 12b), and



Fig. 12. One-dimensional dimer migration. (a) Three possible spatial configurations of a dimer (filled circles connected by heavy line) moving along the x direction (the allowed equivalent marror-image configurations are not included): if only states 1 and 2 are allowed, a 2-state dimer; if all states are allowed, a 3-state dimer. The location of the dimer centroid is marked \times . (b) Random-walk lattice describing the motion of the centroid of a 2-state dimer in (a). States in the unit cell are denoted by numbered circles. Lettered arrows indicate transitions to and from states. Note the transition rates connecting states can be different for transitions to the left or right (i.e., $a \neq \alpha, b \neq \beta$). (c) Random-walk lattice for the 3-state dimer shown in (a). Note that the centroid location is the same for states 1 and 3; however, they are distinguished by different transition rates.

the motion is characterized by the transition rates, a, α , b, and β . If there is no bias caused by, say, an external electric field then $\alpha = a$ and $b = \beta$. We express the rates in activated form:

$$a = v_a \exp[(-E_a + V)/kT],$$

$$\alpha = v_a \exp[(-E_a - V)/kT], \quad \text{etc.} \qquad (5.3)$$

As seen, a and α are not independent quantities even in the presence of a biasing electric potential V. Thus the dimer motion in Fig. 12b is characterized by only two transition rates. If a third more extended (nondissociated) state is allowed then the center of mass motion can be mapped onto a lattice with three states per unit cell (two of which overlap) as shown in Fig. 12c. The motion is then characterized by the four transition rates a, b, c, and d. If the dimer can move in two dimensions then the center of mass motion can be mapped onto a two-dimensional lattice, as shown in Fig. 13, characterized by four transition rates, i.e., four activation energies and four frequency factors.

Mathematical Formalism of Random Walks with Internal States

We will now develop the mathematical formulation of random walks on these lattices with internal states and show how to relate the unknown transition rates in terms of the known FIM observables, such as diffusion distances and equilibrium occupation probabilities of the different internal states. Our generating (Green's) function analysis will be based on the semi-Markov continuous time random walk of Montroll and Weiss¹²² and its generalizations.^{123-125,46} In addition this approach has been shown to be equivalent to a generalized master approach.¹²⁶

In the course of our study many probabilistic quantities will be introduced in order to calculate the values of FIM observables. Let us first introduce $R_{ij}(\vec{l}, t | \vec{l}_0)$ which is the probability density for reaching site \vec{l} in internal state *i*, (\vec{l}, i) , exactly at time *t* given that (\vec{l}_0, j) was attained at t = 0. This quantity satisfies the following recursion relation,¹²⁵ and identifies *R* as a Green's function propagator:

$$R_{ij}(\vec{l},t \mid \vec{l}_{0}) = \sum_{l'} \sum_{m} \int_{0}^{l} \Psi_{im}(\vec{l}-\vec{l}',\tau) R_{mj}(\vec{l},t-\tau \mid \vec{l}_{0}) dt + \delta_{\vec{l},\vec{l}_{0}} \delta_{ij} \delta(t),$$
(5.4)

where $\Psi_{im}(\vec{l},t)$ is the probability density that at time t a



Fig. 13. Two-dimensional dimer migration: (a) spatial configurations; (b) random-walk lattice.

single jump occurs from (0, m) to (\overline{l}, i) given that the state (0, m) was attained at t = 0. It there are s internal states then **R** and Ψ are $s \times s$ matrices and in matrix notation Eq. (5.4) becomes

$$\mathbf{R}(\vec{l}, u \mid \vec{l}_{0}) - \sum_{\vec{l}'} \Psi(\vec{l} - \vec{l}', u) \mathbf{R}(\vec{l}', u \mid \vec{l}_{0}) = \delta_{\vec{l}, \vec{l}_{0}} \mathbf{1} \quad (5.5)$$

where we have Laplace-transformed over time $(t \rightarrow u)$. To proceed further one must examine the waiting time density matrix Ψ . We write

$$\Psi_{ij}(\vec{l},t) = p_{ij}(\vec{l})\psi_{i}(t)$$
 (5.6)

where $\psi_i(t)$ is the probability density that a transition occurs at time t from an internal state j which was attained at time t = 0. To keep a matrix notation we treat ψ_i as the *jj* element of a diagonal matrix. The probability that this jump goes into an internal state i is given by $p_{ij}(\vec{l})$. The waiting time distribution function is a most basic element of the CTRW formalism. This function may represent the on-site stochastic process governed by characteristics of the site binding potential and the dynamics of the hopping mechanism, or it may be used to simulate randomness in transition rates between sites. Such is the case for diffusion in a disordered media where jump distances and/or activation barriers may be randomly distributed.¹²³ Using_Eq. (5.5) in Eq. (5.6) and Fourier transforming $(\vec{l} \rightarrow \vec{k})$ over all lattice sites \vec{l} we arrive at the matrix relation

$$\mathbf{R}(\vec{k}, u \mid \vec{l}_0) = [\mathbf{1} - \mathbf{p}(\vec{k}) \mathbf{\Psi}(u)]^{-1} \exp((+i\vec{k} \cdot \vec{l}_0)). \quad (5.7)$$

In our notation, functions of u have always been Laplace-transformed over time, and functions of \vec{k} have been Fourier-transformed over the lattice space.

The probability for being at (\bar{l}, i) at time i, $P_{ij}(\bar{l}, t | \bar{l}_0)$, when the stochastic process began at (\bar{l}_0, j) is related to $R_{ij}(\bar{l}, t | \bar{l}_0)$ by

$$P_{ii}(\vec{l},t \mid \vec{l}_{0}) = \int_{0}^{t} R_{ii}(\vec{l},t-\tau \mid \vec{l}_{0}) \left[\int_{\tau}^{\infty} \psi_{i}(\tau')d\tau' \right] d\tau$$

$$\equiv \int_{0}^{t} R_{ii}(\vec{l},t-\tau \mid \vec{l}_{0}) \Phi_{i}(\tau)d\tau$$
(5.8)

where the factor Φ takes into account that the system may have reached (\vec{l}, i) at an earlier time $t - \tau$, and no transition out of (\vec{l}, i) occurs in the remaining time τ .

All the quantities one wishes to calculate are derivable from $P_{ij}(\vec{l}, t | \vec{l}_0)$ which in turn only depends on $\Psi_{ij}(\vec{l}, t)$, as can be seen from Eqs. (5.7) and (5.8). We choose Ψ to be normalizable, i.e.,

$$\sum_{i} \sum_{l} p_{ij}(\vec{l}) = 1, \quad \int_{0}^{\infty} \psi_{i}(\tau) d\tau = 1.$$
 (5.9)

We now show how to calculate positional moments and equilibrium occupation probabilities from a knowledge of Ψ .

The positional moments of the probability distribution are given by

$$\langle l_{r}^{n}(t) \rangle = \sum_{\vec{l}} \sum_{i,j} (\vec{l}_{r})^{n} P_{ij}(\vec{l},t \mid 0) f_{i}$$
(5.10)

where f_i is the probability that an internal state j is occupied initially. Since from Eq. (5.8)

$$\mathbf{P}(\vec{k},t) = \mathscr{L}^{-1}\left(u^{-1}[1-\boldsymbol{\psi}(u)]\sum_{\vec{l}}e^{i\vec{k}\cdot\vec{l}}\mathbf{R}(\vec{l},u)\right) \quad (5.11)$$

where \mathcal{L}^{-1} is the inverse transformation and r = x, y, or z, we see that Eq. (5.10) can be rewritten as

 $\langle l_{i}^{n}(t)\rangle = (5.12)$ $\lim_{\vec{k}\to 0} \mathcal{L}^{-1}\left\{ (-i)^{n} \sum_{ki} \partial^{n} R_{ij} (\vec{k}, u \mid 0) / \partial k_{i}^{n} u^{-1} [1 - \psi_{i}(u)] f_{i} \right\}$

where $\mathbf{R}(\vec{k}, u \mid 0)$ is given in terms of Ψ in Eq. (5.7).

Note that the matrix **R** is the inverse of the matrix $[1 - \mathbf{p}(\vec{k})\mathbf{\psi}(u)]$ (see Eq. 5.7). Performing the matrix inversion we write **R** as

$$\mathbf{R}(\vec{k}, u) = \mathbf{M}(\vec{k}, u)\Delta^{-1}(\vec{k}, u)$$
(5.13)

where Δ is the determinant of the cofactors in M. All the physical quantities in which we will be interested are in the $t \rightarrow \infty$ limit and will only involve **R** and its derivatives in the limit of both \vec{k} and u going to zero. In this limit¹²⁷ the elements of M will approach constants, while Δ will diverge as u^{-1} . Thus $\partial^2 \mathbf{R} / \partial k^2$ in Eq. (5.12) (which enters the calculation of the variance $\sigma^2(t)$) will diverge as u^{-2} causing the mean-squared displacement of the random walker to grow linearly with time, as was given in Eq. (5.1). This is the standard diffusion limit ($t \rightarrow \infty$) result. It can be shown¹²⁷ that in the diffusion limit Eq. (5.12) for $\sigma^2(t)$ reduces to

$$\sigma^{2}(t) = \langle l^{2}(t) \rangle - \langle l(t) \rangle^{2}$$
$$= \lim_{\mu \to 0} \lim_{k \to 0} \frac{u^{2}}{\Delta^{2}} \frac{\partial^{2} \Delta}{\partial k^{2}} t.$$
(5.14)

Thus one only needs to calculate Δ and one does not have to perform the tedious matrix inversion to calculate **M**.

Another quantity of interest, which can be obtained from FIM data on cluster motion by simply counting the number of micrographs in which the cluster is found in the various spatial configurations, is the equilibrium probability of occupying an internal state j, $P_{j,eq}$. This quantity is defined as

$$P_{j,\text{eq}} = \lim_{t \to \infty} \sum_{i} \sum_{l} P_{ji}(\vec{l}, t \mid 0) f_{i}.$$
 (5.15)

The rhs can be written in Laplace space as

$$P_{j,eq} = \lim_{t \to \infty} \sum_{i} \sum_{l} u P_{il}(\vec{l}, u \mid 0) f_{l}.$$

Since $\lim_{k\to 0} P_{\mu}(\vec{k}, u \mid 0) = \sum_{\vec{l}} P_{\mu}(\vec{l}, u \mid 0)$, we can express $P_{j,eq}$ as

$$P_{j,eq} = \lim_{u \to 0} \lim_{\vec{k} \to 0} \sum_{i} R_{ji} (\vec{k}, u | 0) [1 - \psi_j (u)] f_i.$$

Except in extreme cases where the mean time to make a transition between states is infinite, R_{β} will not depend on the initial state *i*, so

$$P_{j,eq} = \lim_{u \to 0} \lim_{k \to 0} R_{ji} (\vec{k}, u \mid 0) [1 - \psi_j (u)].$$
(5.16)

Dimer Diffusion in 1D

The set of transition rates $\{a\}$ connecting the different internal states of a cluster are assumed to be in an activated form, $a = v_a \exp(-E_a/kT)$.

To find all the individual activation energies and frequency factors characterizing the diffusion we need to consider a random walk with internal states.

Consider first the two-state dimer in Fig. 12. The effect of a bias can be incorporated by choosing $a \neq \alpha$, $b \neq \beta$. The total rate of leaving state 1 is $A = a + \alpha$, and the probability that the transition is to the right is a/A, and the probability that the transition is to the left is α/A . We

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choose $a = \alpha$, $b = \beta$. The waiting time density matrix is then given by

$$\boldsymbol{\psi}(l,t) = \tag{5.17}$$

$$\begin{pmatrix} 0 & \frac{1}{2}B\exp\left(-Bt\right)\left(\delta_{t,0}+\delta_{t,1}\right)\\ \frac{1}{2}A\exp\left(-At\right)\left(\delta_{t,0}+\delta_{t,-1}\right) & 0 \end{pmatrix}$$

where, if the transition is within the unit cell, l does not change value, and it changes by +L depending on whether the transition moves the dimer centroid to the unit cell on the right or the left. We will measure lengths in units of the unit cell size L. Constructing the matrix **R** (Eq. (5.7)), we obtain, in the diffusion limit $(t \rightarrow \infty)$ using Eq. (5.14),

$$\sigma^{2}(t) = \frac{1}{2}L^{2}\frac{AB}{A+B}t = L^{2}\frac{ab}{a+b}t.$$
 (5.18)

From the knowledge of Ψ , detailed balance relations, Eq. (5.16) can be calculated to give

$$\frac{P_{1,eq}}{P_{2,eq}} = \frac{b}{a} \equiv R_{12}(T).$$
(5.19)

Equations (5.18) and (5.19) allow us to solve for the individual rates, i.e.,

$$\nu_a \exp\left(-E_a/kT\right) = a = L^{-2}t^{-1}\sigma^2(t)[1+R_{12}(T)], \quad (5.20)$$

$$\nu_b \exp(-E_b/kT) = b = L^{-2}t^{-1}\sigma^2(t)[1+R_{12}^{-1}(T)]. \quad (5.21)$$

Experimentally $\sigma^2(t)$ and $P_{1,eq}(T) = 1 - P_{2,eq}(T)$ are measurable and L^2t is known. Thus, a semilogarithmic plot of the rhs of Eq. (5.20) vs. 1/kT would yield a straight line of slope $-E_a$, and ordinate intercept log ν_a . Similarly, the same plot for Eq. (5.21) would yield E_{b} and v_b . Note that for this case, merely plotting $\log \sigma^2(t)$ vs. 1/kT (where $\sigma^2(t)$ is the variance of the dimer centroid position) does not allow the determination of E_a , ν_a , E_b and v_b . Such a plot would in fact yield a "curved" Arrhenius line, as can be seen by substituting activated forms for a and b in Eq. (5.18) for $\sigma^2(t)$. However, in a limited temperature range a plot of $\log \sigma^2(t)$ vs. 1/kT may appear to be a straight line, but its slope and intercept will not characterize the individual transition rates of the dimer motion. We emphasize that full use of all the FIM data, such as both $\sigma^2(t)$ and detailed balance relations $R_{12}(T)$, must be employed to calculate the individual dimer transition rates. Reed and Ehrlich¹¹⁵ have also obtained Eq. (5.18) for the positional variance using Kolmogorov birth and death equations for the study of dimer motion. In a later paper pertaining to the motion of rhenium dimers on W(211) Graham, Stolt and Ehrlich¹¹² find $E_a = 17.5 \pm 0.4$ kcal/mol, while $E_b = 18.2 \pm 0.3$ kcal/mol, where as by just plotting log $\sigma^2(t)$ for the dimer centroid vs. 1/kT yields a "straight line" with slope 18.0 ± 0.3 kcal/mol. This demonstrates the spectroscopic kinetic information available from such studies. We note that our matrix continuous-time random walk approach can be applied to a system with any number of states per unit cell, even if different states of the cluster have the same center of mass. This point was an obstacle to extending the approach of Reed and Ehrlich.

Diffusion Controlled Reactions on Surfaces

(i) Unimolecular Reactions: What is a Reaction Rate? The evolution of many physical systems can be viewed as unimolecular, bimolecular, or pseudounimolecular (if from two reactive species one species is vastly more abundant than the other) reactions. Unimolecular decay reactions involve the irreversible loss of independent reactants. McQuarrie¹²⁸ has reviewed the master equation approach to unimolecular and bimolecular reactions. This stochastic approach allows the calculation of fluctuations, which deterministic equations do not. McQuarrie's solutions are in terms of rate constants, but he does not discuss how to calculate these rate constants from first principles. In this section, we show that the rate constants are conditional first passage (coincidence) probability densities and we relate them to the probability that the lifetime of a reactant is greater than a time t.

The master equation governing unimolecular decay is

$$\frac{dP(N,t)}{dt} = K(t)[P(N+1,t) - NP(N,t)], \quad (5.22)$$

where N is a random variable representing the number of reactants which have not yet reacted (decayed). The solution of Eq. (5.22) for the mean is

$$\langle N(t)\rangle = N_0 \exp\left[-\int_0^t K(\tau)d\tau\right]$$
 (5.23a)

where N_0 is the initial number of reactants, and N(t) satisfies the equation

$$\frac{d\langle N(t)\rangle}{dt} = -K(t)\langle N(t)\rangle.$$
(5.23b)

The major task involved with Eq. (5.22) is to calculate the reaction rate K(t) which contains all the physics of the reaction under study.

The quantity K(t) is the conditional probability of a reaction occurring, of a particular reactant, in the interval (t, t + dt), given that no reaction occurred in the interval (0, t). We assume the stochastic process began at t = 0. The quantity K(t)dt says that the stochastic process began at t=0 and that at time t one has the information that the particular reactant of interest has not yet decayed, and then asks with what probability will the decay occur at time t + dt. Thus, K(t) is a prediction at time t of what will happen at time t + dt, given the information that the resonant did not decay in (0, t). The conditional first passage density K(t) can be related to the unconditional first passage density F(t). The quantity F(t)dt says that the stochastic process began at time t = 0 and then asks for the probability that the decay takes place in the interval (t, t + dt). So F(t) is a prediction at time t = 0 of what will happen at time t + dt.

To calculate K(t), we first define P(L > t) to be the probability that the lifetime of a particle is greater than t, i.e., that the decay takes place in the interval (t, ∞) :

$$P(L > t) = \int_{t}^{\infty} F(\tau) d\tau.$$
 (5.24)

Now, P(L > t + dt) can be written in terms of a conditional probability

$$P(L > t + dt) = P[L > t + dt | \text{no decay in } (0, t)]$$

× P(L > t). (5.25)

where the last factor on the rhs is the probability that no decay has occurred in the interval (0, t). Dividing both sides of Eq. (5.25) by P(L > t) and expanding P(L > t + dt) in a Taylor series about t, we find

$$P[L > t + dt | \text{no decay in } (0, t)]$$

= 1 + dt(d/dt)log P(L > t) + O(dt)². (5.26)

Now.

$$K(t)dt = P[L \le t + dt | \text{no decay in } (0, t)]$$

= 1 - P[L > t + dt | no decay in (0, t)] (5.27a)

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$$K(t) = -(d/dt)\log P(L > t)$$

= $F(t) / \int_{t}^{\infty} F(\tau) d\tau.$ (5.27b)

Using Eq. (5.27a) in (5.23a) yields the intuitive result

$$\langle N(t)\rangle/N_0 = \exp\left[-\int_0^t K(\tau)d\tau\right] = \int_t^\infty F(\tau)d\tau$$
 (5.28)

and shows the connection between the unconditional and conditional first passage distributions.

We see that if $P(L > t) \sim \exp(-\lambda t)$ as $t \to \infty$, then $K(t) \to \lambda$, a constant. This is the reason why constant reaction rates can often be used in Eq. (5.22). Note that

$$K(t) = -(d/dt)\log(\langle N(t)\rangle/N_0), \qquad (5.29)$$

which is similar in structure to Eq. (5.27b). In Eq. (5.29), one used experimental results to find K(t), while in Eq. (5.27), one uses assigned microscopic parameters to predict K(t). Together, Eqs. (5.27) and (5.29) allow a determination of the microscopic parameters governing K(t).

(ii) Calculation of a Diffusion Controlled Unimolecular Reaction Rate. Consider now the situation where Eq. (5.22) represents N_0 reactants per active site at t = 0, and where there is one active site per V lattice sites. A reaction occurs at the instant when a reactant reaches an active site on our periodic lattice. We divide our system into identical unit cells each initially with N_0 reactants and an active site at the origin of a unit cell with V sites. Periodic boundary conditions are used in each unit cell, so the study of one cell will yield the kinetics of the concentration of the reactants C(t) = N(t)/V. We could endow our reactants with internal states (energetic, configurational, spin, etc.) and the lattice with various types of defects (promoters or inhibitors of diffusion) using our matrix renormalized propagator.⁴⁶ However, we will choose for simplicity a single particle on a perfect 2D square lattice governed by nearest neighbor jumps and $\psi(t) = A \exp(-At)$. This model is then similar to Montroll's129 and Lakatos-Lindenberg, Heminger and Pearlstein's¹³⁰ studies of exciton trapping.

Given $\Psi(\vec{l}, t) = \psi(t)p(\vec{l})$ we now calculate the unconditional first passage time F(t) for a reactant initially at a non-active site. The probability density $f(0, t | \vec{l}_0)$, for reaching the active site $\vec{l} = 0$ at time t for the reactant starting at \vec{l}_0 , enters the following equation:

$$\sum_{I_0 \neq 0} R(0, t \mid \vec{l}_0) g(\vec{l}_0) = \sum_{I_0 \neq 0} \int_0^t f(0, t - \tau \mid \vec{l}_0) g(\vec{l}_0) R(0, \tau \mid 0) d\tau$$
(5.30)

where we have averaged over the initial probability of occupying \vec{l}_0 , and the rhs takes into account that for the reactant to reach the origin at time t it could have reached there at an earlier time $t - \tau$ and returned to the origin (any number of times) in the remaining time τ . Here we are treating the origin as a normal site and calculate the first passage into $\vec{l} = 0$. Equation (5.30) may be solved by Fourier and Laplace transforms to yield an expression⁴⁶ for

$$F(t) = (V-1)^{-1} \sum_{l \neq 0} f(0, t \mid \vec{l}_0).$$

Montroll has analyzed the behavior of the random-walk Green's function for return to the origin, $R(\vec{l} = 0, u|0)$ in the long-time (small Laplace variable u) limit. Using Montroll's results we obtain in 2D

$$F(u) \sim 1 - SV[1 - \psi(u)] + O[1 - \psi(u)]^{3/2} \quad (5.31)$$

where $S = S_1 \log V + S_2 + S_3 / V + S_4 / V^2 + \cdots$ and the values of S_1, \dots, S_4 are of the order of 0.1 to 1.0 and differ for hexagonal, square, and triangular lattices. In our example $1 - \psi(u) \sim u(t)$ where $\langle t \rangle = \int_0^{\infty} t \psi(t) dt$ is the mean time between jumps. In the long time limit F(t) and $\psi(t)$ will have the same form, and

$$\int_0^\infty tF(t)dt = SV \int_0^\infty t\psi(t)dt.$$
 (5.32)

Hence, approximately SV steps are taken before the reaction occurs. Thus we arrive at the equation for the concentration of reactants C(t) in the long time limit

$$\frac{C(t)}{C(0)} = \exp\left(-\frac{A}{SV}t\right).$$
(5.33)

For shorter times the reaction rate (K(t) = A/SV) will be time-dependent. The structure of the substrate enters the rate through the quantity S. Using Montroll's values for S_1, S_2, \cdots , it can be shown that the rates order as $K_{tri} > K_{tq} > K_{hex}$, which is the same ordering as the coordination numbers. The structural effect is more pronounced for large V (low active site concentrations). For V = 10, K_{tq} and K_{tri} are 23% and 29% larger, respectively, than K_{hex} .

(iii) Diffusion Controlled Bimolecular Reactions. Bimolecular reactions on a surface can be treated in a similar fashion as unimolecular reactions, but they are inherently more difficult.131 First, the bimolecular master equation (Eq. (5.34)) is more complicated than the simple unimolecular one. Secondly, the calculation of K(t)involves conditional first pair coincidences rather than first passage times. Thirdly, a single reactant upon reaching a reactive site will leave if the second reactant (which is necessary for the reaction) does not arrive in sufficient time. It is likely that the transition rate for a single particle to leave the reactive site is different than for it to leave a non-reactive site. In this case single particles will migrate on a defective lattice in the bimolecular reaction due to the nature of the reactive site, but not in the unimolecular reaction where they immediately react at the reactive (defective) site.

The bimolecular reaction master equation for identical particles $A + A \rightarrow 2A$ is¹²⁸

$$\frac{dP(N,t)}{dt} = K(t) \left[\binom{N+2}{2} P(N+2,t) - \binom{N}{2} P(N,t) \right]$$
(5.34)

where N is the number of reactants which have not decayed at time t. We assume N is initially even, and changed by two after a reaction. For two different species $A + B \rightarrow C$ a similar master equation can be written.

Equation (5.34) can be solved by generating function techniques¹²⁸ to yield

$$\langle N(t) \rangle = \sum_{N=2}^{N_0} A_N \exp\left[-2^{-1}N(N-1)\int_0^t K(\tau)d\tau\right]$$
 (5.35)

where

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$$A_{N} = \frac{1-2^{N}}{2^{N}} \left[\frac{\Gamma(N_{0}+1)\Gamma\left(\frac{N_{0}-N-1}{2}\right)}{\Gamma(N_{0}-N+1)\Gamma\left(\frac{N_{0}+N+1}{2}\right)} \right]$$

and N is even. Here K(t)dt is the conditional probability distribution that a reaction takes place between two particular reactants in the interval (t, t + dt) given that the reaction did not occur before in (0, t). As before we will be interested in diffusion controlled reactions at reactive sites which we take to be the origins of the defect superlattice cells of volume V with periodic boundary conditions. In analogy to Eq. (5.30), to find the probability density for a first coincidence at the reactive site $\vec{l} = 0$, at time t, $f(0, t | \vec{l}_1, \vec{l}_2)$ of two reactants which were at \vec{l}_1 and \vec{l}_2 at t = 0, we first need to calculate the probability density of any coincidence $C(0, t | \vec{l}_1, \vec{l}_2)$ of two particles which initially were situated at sites \vec{l}_1 and \vec{l}_2 and coincide at the origin of their unit cell at time t:

$$C(t) = \sum_{\vec{l}_2} \sum_{\vec{l}_1}' C(0, t \mid \vec{l}_1, \vec{l}_2) g(\vec{l}_1) g(\vec{l}_2)$$
(5.36)
$$= \sum_{\vec{l}_2} \sum_{\vec{l}_1}' \int_0^t f(0, t - \tau \mid \vec{l}_1, \vec{l}_2) g(\vec{l}_1) g(\vec{l}_2) C(0, \tau \mid 0, 0) d\tau$$

where we have averaged over all initial positions of the two particular reactants, except for both being at the origin initially.¹³² The above equation can be solved for the first coincidence density f to give

$$F(t) = \sum_{\vec{l}_1} \sum_{\vec{l}_2}' f(0, t \mid \vec{l}_1, \vec{l}_2) g(\vec{l}_1) g(\vec{l}_2)$$

= $\mathcal{L}^{-1}[C(u)/C(0, u \mid 0, 0)].$ (5.37)

To proceed further we need to specify the allowable states of the reactants and the probability distributions governing transitions. We will treat the simplest case where all reactants are of the same type and have the waiting time density $\psi(t) = A \exp(-At)$ for hopping, and only nearest neighbor jumps occur. We also consider that the release rate from the reactive site is unchanged from that of the normal site when only one reactant is there at the origin. A reaction will occur at time t if one reactant already resides on the reactive site (having arrived there earlier) and a second reactant arrives there at exactly time t, or vice versa. Remembering that R is the probability density for just arriving at a site, and P is the probability for being at a site, we have

$$C(t) = \frac{2}{V(V-1)} \sum_{\vec{l}_1} \sum_{\vec{l}_2}' P(0,t \mid \vec{l}_1) R(0,t \mid \vec{l}_2). \quad (5.38)$$

Thus for large V we have

$$F(t) = \mathcal{L}^{-1}\left(\frac{P(\vec{k}=0, u \mid 0)R(\vec{k}=0, u \mid 0)}{P(\vec{l}=0, u \mid 0)R(\vec{l}=0, u \mid 0)}\right).$$
 (5.39)

Again using Montroll's asymptotic $(u \rightarrow 0)$ results for the terms in the denominator we find for the rate constant in Eq. (5.35)

$$\lim_{t \to \infty} K(t) = A/2SV \tag{5.40}$$

where S is given in Eq. (5.31). Note that this rate is one half of the unimolecular reaction rate. For reaction between two species whose transition rates are characterized by rates A and B we find for large t the rate

$$K(t) = (A + B)/(SV[2 + A/B + B/A]).$$
(5.41)

Note again the structure dependence of the rates through the parameter S.

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$$\varepsilon_{\rm rot}^{\rm hin} = \frac{1}{2}mV^2 = Z_{\rm hin}^{-1} \sum_{\nu,m} B\nu(\nu+1) \exp(-B\nu(\nu+1)/k_{\rm B}T)$$

= $B\nu_g(\nu_g+1).$

At t = 0 the hindering potential and that bounding the molecule to the surface are switched off. In the free state the molecule is now rotating about its translating center of mass. The total energy is

$$\varepsilon_{\text{tree}} = \varepsilon_{\text{cm}} + \varepsilon_{\text{rot}}^{\text{tree}} = \frac{1}{2}(m_1 + m_2) \frac{V^2}{4} + \frac{1}{2}(m_1 + m_2) V_r^2,$$

which with $m_1 = m_2$ and $\varepsilon_{\text{bin}} = \varepsilon_{\text{rece}}$ (a consequence of the sudden approximation) yields $V_r = V/2$, or $\varepsilon_{\text{rot}}^{\text{tree}} = \varepsilon_{\text{rot}}^{\text{bin}/2}$. Consequently if

$$B\nu_{\rm g}(\beta)(\nu_{\rm g}(\beta)+1) < 2k_{\rm B}T$$

the molecules will emerge rotationally cooler than if they were in equilibrium with the substrate. For example, for $\beta = 10^{\circ}$, with $B/k_{\rm B} = 3K$ (N₂ or NO), $B\nu_{\rm g}(\nu_{\rm g} + 1)/k_{\rm B} = 500$ K which is much less than $2T \sim 1000$ K as in the desorption experiment described in Ref. 48. Under these conditions the above equation is well satisfied and we would anticipate rotationally cool desorbed molecules as observed experimentally.⁴⁴ For further discussion see Section (iv) and J. W. Gadzuk, U. Landman, E. Kuster, C. L. Cleveland and R. N. Barnett, J. Elect. Spect. (in press) and U. Landman et al. (to be published).

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Infinite Conical Well: An Analytic Model for Quantum Mechanical Hindered Rotors

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The rotational quantum mechanics of a new analytic model for a hindered rotor is presented, and rotational-state distributions of the hindered rotor are given in terms of unhindered rotor states.

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The role played by the rotational degrees of freedom of diatomic molecules which are dynamically coupled to solid surfaces has been the focus of several recent experiments in which the observed rotational-state distributions of diatomic molecules scattered,¹ desorbed,² and sputtered³ from surfaces bear no obvious relationship to equilibrium state distributions inferred from surface temperatures. In this communication we present the main features and illustrative numer-

ical consequences of a model for a hindered threedimensional rotor, which provides considerable insight into possible mechanisms responsible for the reported state distributions. The model in which a rigid dumbbell executes free rotations within a conical domain bounded at some critical polar angle $\beta \leq \pi/2$ by an infinitely repulsive wall, and as such is a spherical-coordinate-system analog of a textbook infinite square well, is displayed in the inset of Fig. 1. In Fig. 1(a) the rotations are about an origin placed at the center of mass. This geometry could simulate a hindered rotor embedded within an anisotropic void or in an "atomic trough" on a surface. The rotor shown in Fig. 1(b) simulates an adsorbed diatomic molecule in which one end might be clamped to a surface via a chemical bond. As will become apparent, the model facilitates identification of the special role played by the zero-point kinetic energy associated with the spatial localization of



FIG. 1. The four lowest rotational quantum numbers as a function of the cone angle. The azimuthal quantum numbers are labeled on the left. Inset: Infinite conicalwell model treated here. The left and right models are referred to as 1(a) and 1(b), respectively.

the rotor, both on ground-state properties and on the excitation spectrum. This can be contrasted with the harmonically constrained rotor in which the effects of localization are distributed between kinetic and potential energy.^{4.5}

The model is characterized by the standard angular part of the Schrodinger equation:

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{2I}{\hbar^2}\left[\epsilon - V(\theta,\varphi)\right]\right\}\psi^{\text{rot}}(\theta,\varphi) = 0,\tag{1}$$

with $I = \sum_{i} m_{i} r_{i}^{2}$. For the φ -independent "infinite conical well," we have

$$V(\theta,\varphi) = \begin{cases} 0, & \theta \leq \beta, & 0 \leq \varphi \leq 2\pi, \\ \infty, & \theta > \beta; \end{cases}$$

so not only is the total rotational wave function separable as

$$\psi^{\text{rot}}(\theta,\varphi) = P(\theta)v(\varphi) \text{ with } v(\varphi) = (2\pi)^{-1/2} \exp(im\varphi)$$

but also $P(\theta) = 0$ for $\theta > \beta$. With the above choice for $V(\theta, \varphi)$, it is a textbook exercise to reduce the θ part of Eq. (1), in terms of the auxiliary variable $x = \cos \theta$, to

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left(\frac{2I\epsilon}{\hbar^2} - \frac{m^2}{1-x^2}\right)P = 0 \qquad (2)$$

valid in the domain $\cos\beta \le x \le 1$. Equation (2) is exactly Legendre's equation when the eigenvalues are written in the form

$$\epsilon = B \nu (\nu + 1) \tag{3}$$

with $B \equiv \hbar^2/2I$ and ν a continuous (usually noninteger) positive "quantum number." For the free rotor in which $\cos\beta = -1$, the quantum numbers ν take on integer values only and the eigenfunctions ψ_{rot} are the familiar spherical harmonics $Y_{1.m}$. The eigenstates of the hindered rotor, solutions of Eq. (2) with the boundary conditions that P(x) is finite at x = 1 and zero at $x = \cos\beta$, are associated Legendre functions of arbitrary order,⁶ that is

$$\psi_{\nu m}^{\text{rot}}(\theta,\varphi) = \begin{cases} A_{\nu m}(2\pi)^{-1/2} P_{\nu}^{|m|}(\cos\theta) \exp(im\varphi), & 0 < \theta < \beta, \\ 0, & \beta \leq \theta \leq \pi, \end{cases}$$
(4)

with $m^2 < \nu(\nu + 1)$ and $A_{\nu m}^{0}$ a normalization constant. The eigenvalues are numerically determined by the condition

$$P_{\nu}^{m}(\cos\beta) = 0 \tag{5}$$

together with Eq. (3), and the normalization by

$$|A_{\nu m}|^{-2} = \int_{\cos\beta}^{1} dx |P_{\nu}|^{m} (x)|^{2} = \frac{-(\nu+m)}{(2\nu+1)} P_{\nu-1}^{m} (\cos\beta) \left[\frac{dP_{\nu}^{m} (\cos\beta)}{d\nu} \right].$$
(6)

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(7)

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(8)

Lastly, the overlap integral between a free space

$$Y_{lm}(\theta,\varphi) = \left[A_{lm}'/(2\pi)^{1/2}\right]P_l^{m}(\cos\theta)e^{im\varphi} \quad (l = \text{integer})$$

and $\psi_{vm}(\theta,\varphi)$ is easily evaluated with the relationship

$$\langle Y_{lm'} | \psi_{\nu m} \rangle = \frac{\delta_{m,m'} A_{\nu m} A_{lm'}}{\nu + l + 1} \left(\frac{\nu + m}{\nu - l} \right) P_l^m (\cos \beta) P_{\nu - 1}^m (\cos \beta)^{2}$$

valid for $\nu \neq l$. Derivations and detailed discussion of the mathematics leading to Eqs. (3)-(7) will be presented in a much expanded article.

An interesting limiting case occurs for $\beta = \pi/2$, that is, when the rotor is constrained to a halfinfinite space. The boundary condition, Eq. (5), requires that the eigenfunctions have nodes on the plane separating the two half spaces. But solutions of Eqs. (2) and (4) are just the subset of usual Y_{im} 's satisfying the "surface-selection rule"⁷

l + m = odd

which has as some consequences the following:

(i) The $\beta = \pi/2$ confined-rotor ground state is a nondegenerate p state with $l = \nu = 1$, m = 0.

(ii) The zero-point energy associated with localization of the rotor to a half space is $E_{zp}(\beta = \pi/2) = \hbar^2/I$.

(iii) The *l*th level is *l*-fold degenerate rather than (2l+1)-fold as in the unhindered rotor.

The lowest four eigenvalues of the hindered rotor, obtained by numerical solution of Eqs. (2), (3), and (5), are displayed in Fig. 1 in the form of ν versus β plots. These results are in accord with our intuition. As β decreases, the zero-point kinetic energy associated with the increased localization increases dramatically, as

$$P(l) = \frac{1}{Z_{\text{hin}}} \sum_{\nu > 1, \dots, m'} \exp\left[-B\nu(\nu+1)/kT\right] \left| \langle Y_{lm'}^{\text{free}} | \psi_{\nu m}^{\text{free}} \rangle \right|^2,$$

where T is the ambient temperature and Z_{hin} the hindered-rotor partition function. If $B/kT \gg 1$, one would expect that the population of high-lstates results mainly from their overlap with lowlying ν states, not from a one-to-one correspondence with thermally excited ν states. In other words the final-state rotational energy derives from the zero-point energy, not from thermal excitation. Consequently the more narrow the cone, the "hotter" the final-state distribution, independent of ambient temperature. State distributions given by Eq. (8), with values of ν and the overlap integral determined from Eqs. (5)-(7), for a "typical" value of B/kT = 0.05 (corresponding to say $\theta_{\tau}\simeq 15$ K, $T\simeq 300$ K) and treating β parametrically are shown in Fig. 2. As

does the scale of the excitation spectrum. To illustrate the significance of this effect, consider a rotor constrained to a cone with $\beta = 10^{\circ}$, as a model for a diatomic molecule adsorbed in an upright configuration on a surface. With established values for free space rotational constants of N₂ and H₂, the zero-point rotational energies are ~0.025 and 1.0 eV, respectively, which in the case of H₂ significantly influences possible chemistry.⁵ Moreover, even for N₂ the lowest excitation energy ~0.04 eV ~ 500 K, which suggests that most properties of the hindered N₂ will appear temperature independent if the ambient temperature is less than ~500 K.

Now consider a model dynamics problem in which the hindering potential in Fig. 1(a) is suddenly switched off⁸ (constrained \rightarrow free rotor transition as might be experienced in thermal desorption), resulting in a nonequilibrium population of free rotational states due to the conversion of initial zero-point kinetic energy into free rotational energy about the rotor center of mass. The probability for ending up in the *l*th free rotor state is just a sum of rotational Franck-Condon factors between $Y_{lm'}$, free and $\psi_{\nu,m}$ rot, given by Eq. (4) weighted by appropriate thermal factors⁸; that is,



FIG. 2. Rotational-state distributions for the suddenly unhindered rotor of Fig. 1(a), as a function of the free-rotor rotational quantum number.

anticipated, the smaller the hindrance angle, the greater the population of higher-energy rotational states.

Laser-induced-fluorescence data¹⁻³ are often plotted in the form $\log[P(l)/(2l+1)]$ vs l(l+1), which yields a straight line with slope = -B/kT, if the rotational distribution of the interogated molecules corresponded to an equilibrium state at some rotational temperature T_r . In fact Kleyn, Luntz, and Auerbach¹ observe two regimes in rotational distributions of NO scattered from Ag. For $l \leq 20$, the distribution is Maxwell-Boltzmann, over two orders of magnitude, showing a T_{\star} which is basically independent of the surface temperature. For $l \ge 20$, a plateau structure whose breadth depends upon the kinetic energy of the incident beam is observed. This structure has been attributed to a rotational rainbow.⁹ Cavanagh and King² also observed a linear distribution over an order of magnitude, for NO thermally desorbed from Ru, again with T_{\star} apparently unrelated to the surface temperature from which the NO desorbed. Efstathiou and Thomas³ observed distributions similar to those of Kleyn, Luntz, and Auerbach for sputtered N_2 from Si.

Guided purely by the just-mentioned experimental convention for data presentation, we have plotted our state distributions, obtained from Eq. (8), semilogarithmically. The somewhat astonishing results are shown in Fig. 3 where each panel corresponds to a different hindrance angle and B/kT is treated parametrically within a panel. Note that all the distributions show basically two distinctly different regimes. First, for low $l (\leq 20-30)$, a rather linear decrease occurs over 2 to 3 orders of magnitude whose inverse slope could be represented by a free rotational temperature, as observed.¹⁻³ As depicted in Fig. 3, for given hindrance angle β , T_r appears to be independent of T (for $\beta \leq 45^\circ$). Furthermore, as β decreases the inverse slope or apparent rotational temperature increases. Both of these characteristics support our conjecture that conversion of zero-point rather than thermal kinetic energy into free rotational energy is the mechanism responsible for population of the free-rotor excited states, at least within the context of our model problem; hence the apparent T independence of the low-l state distribution. For model 1(a) treated here (see Fig. 1), T_r is always greater than 2B/k, the minimum possible zero-point energy (for $\beta = \pi/2$). Thus the distribution appears "hot." In the case of desorption, however, not only is the hindering potential turned off but also



FIG. 3. Rotational-state distributions for the suddenly unhindered rotor of Fig. 1(a), plotted in the form $\log [P(l)/(2l+1)] vs l(l+1)$.

the atom tied down to the surface is released, thus permitting free translation of the molecular center of mass. The addition of this "new" degree of freedom in the final state requires that the rotational zero-point energy is split between translations and free rotations, which would have the effect of cooling our distributions. In fact a simple classical sudden approximation (removal of hindrance and release of tied down atom) on homonuclear model 1(b), with only the consequences of energy and angular momentum conservation, yields the result that $T_r = T/2$, as observed by Cavanagh and King.²

The second (high l) region displays qualitatively different behavior. At some critical l value, the state distribution drops precipitously from the linear form, then rises, and displays an oscillatory structure which is most pronounced for large B/kT. The oscillations, which show a periodicity in l varying as $180^{\circ}/\beta$, are diminished as B/kT decreases, though still leaving a plateau or smoothly varying distribution at high l which is quite different from the low-l range. Already such an effect has been observed in beam¹ and sputtering experiments.³ The fact that the beam data were interpretable in terms of rotational

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rainbows suggests that there could be an intimate connection between the physics responsible for rainbows and the physics implicitly contained within our Franck-Condon factors.

In summary we have presented a model for a hindered diatomic-molecule rotor, worked out its quantum mechanics, and applied the results to a model dynamics problem involving a sudden release of the hindering potential. Conversion of zero-point kinetic energy into free rotational energy results in highly nonequilibrium final rotational-state distributions which have a striking resemblance to state distributions observed in several recent experiments involving different, but related, dynamic surface processes.

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ROVIBRATIONAL EXCITATION WITHIN THE INFINITE CONICAL WELL: DESORPTION OF

DIATOMIC MOLECULES

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ABSTRACT

An analytic model for the hindered rotational states of a diatomic molecule adsorbed upright on a solid surface is discussed. Various model dynamics situations, within the sudden approximation, designed to simulate desorption are presented and rotational state distributions are calculated including both rotational and translational degrees of freedom. Criteria are established for observing rotationally cool desorbed molecules.

INTRODUCTION

Stimulated by several recent experimental studies in which the rotational state distributions of diatomic molecules scattered or desorbed from metallic surfaces have been measured (refs. 1), we have constructed a simple, analytic model for a quantum mechanical hindered rotor, (ref. 2) designed to simulate the rotational states of a diatomic molecule hindered by a solid state or surface environment. Consideration of both the energy levels and dynamics associated with this model should lead to insights useful for the understanding of the reported experiments. The single most striking feature of the model study was the recognition of the role played by the zero-point kinetic energy resulting from the spatial localization of the rotor. If the hindered rotor is subjected to a dynamical situation in which the hindering potential is switched off, such as occurs in desorption, the ultimate disposal or redistribution of the zero-point energy can strongly influence the characteristics of observed rotational state distributions, as will be shown.

In this paper, various aspects and extensions of our previous work are described. The model is presented in the next section followed by some illustrative numerical consequences. Next, a simple classical analysis of the partitioning of available energy between rotational and translational degrees of freedom in desorbed molecules is given. Finally, drawing upon analogies with gas phase photodissociation of polyatomic molecules, some preliminary results for

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electron and photon stimulated desorption are presented.

MODEL

In order to describe the quantum mechanics of a hindered rotor in a reasonably tractable manner we have adopted a philosophy inspired by papers on two topics, one being nodal hydrogenic surface impurity wavefunctions (refs. 3) and the other the quantum mechanics of gears (ref. 4). In both of these works, simple and elegant results have been obtained for the quantum mechanical properties of familiar systems in which not-so-familiar boundary conditions are imposed, in the first case a plane surface on the spherical Coulomb problem and in the second, the constraints of mutually compatible rotational states (dictated by wheel radii, gear teeth ratio, chatter, etc.) of two free rotators.

The related characteristics of the present model are displayed in the inset of Fig. 1. Free rotations of a rigid dumbell (diatomic molecule) are allowed about some point on the molecular axis (Left: about center of mass; Right: about one end) provided the polar angle lies within the domain $0<\theta<\beta$. In other words, the angle-dependent hindering potential is an infinite-conical well, the spherical coordinate analog of a Cartesian coordinate infinite-square well. The special features of this potential stem from the fact that the angular part of the Schrodinger equation is identical with that of the free rotor, the distinction lying solely in the boundary conditions. The polar eigenvalue equation is just Legendre's equation (with x = cos θ)

$$(1-x^{2}) \frac{d^{2}p}{dx^{2}} - 2x \frac{dP}{dx} + (v(v+1) - \frac{m^{2}}{1-x^{2}}) P = 0$$
(1)

subject to the unusual boundary condition $P(x=\cos \beta) = 0$, that is the wavefunction must vanish at the infinitely repulsive cone wall. The resulting rotational eigenfunctions are

$$\psi_{\upsilon}^{\mathsf{rot}}(\theta,\phi) = \begin{cases} \mathsf{A}_{\upsilon m} (2\pi)^{-1/2} \mathsf{P}_{\upsilon}^{|m|}(\cos\theta) \exp(\mathrm{i}m\phi) & 0 \le \theta < \beta \\ 0 & \beta \le \theta < \pi \end{cases}$$
(2)

and the energy eigenvalues

$$\varepsilon = Bv(v+1) \tag{3}$$

with B = $f_1^2/2I$, I the moment of inertia, and A_{vm} a normalization constant. If $\beta = \pi$, then ψ_{vm} are just the familiar Y_{gm} 's and v takes on integer values only. If $\beta = \pi/2$, the eigenfunctions are still the Y_{gm} 's but now only those states satisfying l+m = odd are allowed as this condition picks out those states with nodes on the boundary (refs. 3). For $\beta < \pi/2$, although the quantum numbers v are generally non-integers, P_u^[m] remains an associated Legendre function (of

arbitrary order) (ref. 5).

The lowest four quantum numbers numerically obtained from Eq. 1 are shown in Fig. 1 as a function of the cone angle. These intuitively appealing results show that as β decreases, not only does the zero-point kinetic energy associated with the increased localization increase dramatically, but also so do the excitation energies. For instance, with $\beta \approx 10^{\circ}$ (an upright adsorbed diatomic) the zero point energy ≈ 180 B and the lowest lying excitation energy is ~ 160 times that of the equivalent free rotor.





SUDDEN UNHINDRANCE: ROTATIONAL HEATING

A model dynamics problem can be envisioned in which the hindering potential is suddenly switched off, as might occur when a molecule is ejected from the solid state environment responsible for the hindrance. Under these circumstances, the zero-point kinetic energy of the hindered rotor must influence the dynamics and/or final state energy distributions. In fact for hindered rotations about the center of the mass (left side in Fig. 1 inset), sudden release of the hindering potential will result in purely hindered to free rotational transitions (no center of mass translational energy), producing a final free rotational state distribution which appears "hot" due to conversion of zero point to free rotational energy. Within the sudden limit (refs. 6), the rotational state distribution is given by a sum of rotational Franck-Condon factors between $Y_{gm'}$ free and $\psi_{v,m}$ rot, weighted by appropriate thermal factors, that is

$$P(\ell) = \frac{1}{Z_{hin}} \sum_{\nu>1,m,m'} \exp[-B_{\nu}(\nu+1)/k_{b}T] |\langle Y_{\ell m'}, \psi_{\nu m}\rangle|^{2}$$
(4)

where T is the ambient temperature and Z_{hin} the hindered-rotor partition function. The Franck-Condon factors have been calculated analytically for the

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infinite conical well and these results will be reported separately (refs. 2,7). We note that if $B\nu_g(\nu_g+1)/k_bT >> 1$ (ν_g is the ground state quantum number), the expected heating effect will be due to conversion of zero-point energy, not thermal excitation. Consequently, the more narrow the cone, the "hotter" the real-temperature-independent free rotor distribution. State distributions obtained from Eq. 4, for a "typical" value of $B/k_bT = 0.05$ ($\theta_{rot} = B/k_b = 5$ K, $T \approx 100$ K say) are shown in Fig. 2. As expected, the smaller the hindrance angle, the greater the population of high & states



Fig. 2. Rotational-state distribution for the suddenly unhindered rotor on the left in Fig. 1, as a function of the free-rotor rotational quantum number.

Fig. 3. Rotational-state distributions for the suddenly unhindered (left) rotor, plotted in the form $log[P(\ell)/(2\ell+1)]$ vs. $\ell(\ell+1)$.



It is also enlightening to plot the distributions in the form $\log[P(l)/(2l+1)]$ vs. l(l+1), as has been done in Fig. 3. Two distinctly different regimes appear. For $l \leq 20-30$, a linear behavior is seen in which T_r , an effective "rotational temperature", can be identified by equating the slope of the curves to $-B/k_bT_r$. For the rather narrow cones characterized by large quantum numbers, T_r is fairly independent of T, the actual ambient temperature. Furthermore as β decreases, the inverse slope or apparent rotational temperature increases. Both of these characteristics support our conjecture that conversion of zero-point rather than thermal kinetic energy into free rotational energy is the mechanism responsible for population of the free-rotor excited states within our model problem. We will not comment here on the high l behavior other than to note that the periodicity in l, varying as $1B0^{\circ}/\beta$, is related to the commensurability between free and hindered rotations (ref. 2).

CLASSICAL ROTATIONAL COOLING

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As appealing as the ideas of the last section are, they deal with only half of the relevant physics pertaining to desorption of a hindered diatomic molecule, for not only is the hindering potential switched off but also the bond which "clamps" one end of the molecule to the surface is broken. Thus in addition to free rotation, free center-of-mass translation is also permitted in the final state. For the example already discussed (left model in Fig. 1), the only possibility is hindered-to-free rotational energy flow since the center-of-mass is always at rest. For desorption (right model in Fig. 1), the hindered rotational energy divides between rotational and translational due to the addition of the extra degree of freedom in the final state. This is not easy to work with within a clean quantum mechanical model due to algebraic complications arising from a space-fixed vs. body-fixed axis description of the hindered and free rotor (refs. 8).

Nonetheless a simple classical model, again in the sudden limit, demonstrates the essential features. Consider the 3 steps in "desorption" shown in Fig. 4.





Originally at time $t=0^{\circ}$, the loose end of the rotor is moving in the cone with a velocity v due to the zero point energy as shown in Fig. 4a. For a homonuclear molecule, the center-of-mass is also moving with velocity v/2. Thus the initial energy is

$$\varepsilon_{\text{rot}}^{\text{hin}} = \frac{1}{2} mv^2 = \frac{1}{Z_{\text{hin}}} \sum_{\nu,m} B_{\nu}(\nu+1) \exp(-B_{\nu}(\nu+1)/k_b T) \simeq B_{\nu}(\nu_g+1).$$
(5)

At time t=0, the potential is switched off and the bound atom released, as in Fig. 4b. Sometime later (t>0), the situation is as shown in Fig. 4c, where not only is the center-of-mass translating, but also the molecule is rotating about the center-of-mass. The total energy is

$$\varepsilon_{\text{free}} = \varepsilon_{\text{cm}} + \varepsilon_{\text{rot}}^{\text{free}} = \frac{1}{2} (m_1 + m_2) \frac{v^2}{4} + \frac{1}{2} (m_1 + m_2) v_r^2$$

with $m_1 = m_2$ and $\epsilon_{hin} = \epsilon_{free}$ (a consequence of the sudden approximation), yielding $v_r = v/2$ or $\epsilon_{rot}^{free} = \epsilon_{rot}^{hin}/2$. Consequently, if

 $Bv_{a}(\beta) (v_{a}(\beta) + 1) < 2 k_{b}T,$

the molecules will emerge rotationally cooler than if they were in equilibrium with the substrate. For example, if $\beta \approx 10^{\circ}$, then with $B/k_b \approx 3$ K (approximately N₂ or NO), $Bv_g(v_g + 1)/k_b \approx 500$ K, which is much less than 2T ~ 1000 K, as in the Cavanagh-King thermal desorption experiment.¹ Under these conditions, Eq. 6 is well satisfied, so we would anticipate the rotationally cool desorbed molecules observed experimentally (ref. 1).

(6)

PHOTODISSOCIATION/STIMULATED DESORPTION

The final topic focuses on the formal similarities which exist between the photodissociation of a triatomic molecule, due to electronic excitation (ref. 9), and photo (or electron) stimulated desorption (ref. 10) in the limit in which the fragment "atom" is taken to be infinitely massive (the substrate). In either case, emphasis is placed on total system Franck-Condon factors associated with the switch from an initial to final state potential surface dictated by the implicit electronic transition. The Franck-Condon factors order the importance of various allowed final channels via the partitioning of available energybetween vibrational, rotational, and translational (VTR) degrees of freedom. Within Golden Rule perturbation theory, the transition rate induced by radiation of energy ω to some final state is

$$P_{\omega}(fin) = \frac{2\pi}{\hbar} \int \psi_{fin}^{VTR}(Q) \quad V_{\omega}(Q) \quad \psi_{in}^{VTR}(Q) \, dQ \, |\,^{2} \delta(\epsilon_{f} - \epsilon_{i} - \hbar\omega)$$

$$\approx \frac{2\pi}{\hbar} |\tilde{V}_{\omega} f \psi_{fin}^{VTR}(Q) \quad \psi_{in}^{VTR}(Q) \, dQ \, |\,^{2} \delta(\epsilon_{f} - \epsilon_{i} - \hbar\omega)$$
(7)

with

$$V_{\omega}(\underline{0}) = \langle \phi_{f}(\underline{x};\underline{0}) | V_{\omega}(\underline{x}) | \phi_{i}(\underline{x};\underline{0}) \rangle_{x} \simeq \overline{V}.$$

In Eq. 7, ψ^{VTR} describes nuclear motion states in terms of abstract coordinates $Q, \phi(x; Q)$ are Born-Oppenheimer electronic states, $V_{\omega}(x)$ is the interaction due to the radiation, and \bar{V} is assumed constant with Q over the range spanned by the integrand.

To apply Eq. 7 to desorption, consider the limit in which both the diatomic as well as chemical bond are taken to be rigid (no explicit vibrational motion)

so that the initial and final state wavefunctions may be written as

$$\psi_{in}^{TR}(Q) \rightarrow |\nu,m;\beta\rangle = N_i \psi_m^{rot}(\theta,\phi) \delta(R_{cm} - R/2) \delta(\hat{R}_{cm} - \hat{r})$$
(8a,b)
and

$$\psi_{fin}^{TR}(Q) \rightarrow |k, \ell, m' \ge N_f e^{ik \cdot B_{Cm}} Y_{\ell m'} (\theta, \phi)$$

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where N₁ and N_f are normalization constants, \underline{k} is the wave vector of the center of mass translation in the final state, \underline{R}_{cm} is the position vector of the center-of-mass, and ψ_{vm}^{rot} are given by Eq. 2. If we define $\hbar\omega_c$ as the threshold radiation to produce an $\ell = \underline{k} = 0$ desorbed molecule from the hindered rotor ground state and $\Delta = \hbar(\omega - \omega_c)$ as the excess radiation energy above threshold, then the probability for desorption into a free rotational state ℓ with center-of-mass wavevector k, thermally averaged over initial states, is given by

$$P_{\omega}(\ell,k) = \frac{2\pi}{\hbar} |\bar{v}|^2 \sum_{\nu,m,m'} \frac{\exp(-B_{\text{hin}}\nu(\nu+1)/k_bT)}{Z_{\text{hin}}} |\langle k,\ell,m'|\nu,m;\beta\rangle|^2$$
(9)

$$x\delta[B_{hin}(v(v+1)-v_g(v_g+1) + \Delta-B_{free}^{\ell(\ell+1)} - \hbar^2k^2/2M]$$

and the probability for final state ℓ , regardless of direction or translational energy by

$$P_{\Delta}(\ell) = N f P_{\omega}(\ell, k) d^{3}k.$$
(10)

Explicit calculation of the Franck-Condon factors is a formidable job which has been detailed elsewhere (refs. 7,11). Using these reported results, some examples for $P_{\Delta}(k)$ are shown in Fig. 5, plotted in the normalized form $\log[P_{\Delta}(k)/((2k+1) P_{\Delta}(0)]$ vs. k(k+1) for a value of $B_{free}/k_bT = 0.9$ (for example H_2 and T = 100 K), hindrance angles $\beta = 30^{\circ}$, 60° , and 90° , and several values of Δ/k_bT . Although the results in Fig. 5 exhibit an overall non-Boltzmann behavior, if we venture straight line fits to judiciously chosen regions, we could identify increasing rotational temperatures for higher incident excitation (large Δ), which are not necessarily higher than the temperature of the substrate. Furthermore, for fixed (large) k and Δ , smaller β (more zero point energy) yields distributions somewhat more populated at large k than does the larger β initial state. Two simple generalizations can be made from these observations. First, the greater the excitation energy, the hotter the rotational temperature and secondly, the larger is the initial zero point energy, the hotter is the final state. Work is in progress to extend these preliminary studies to the point where more useful

intuitive guidelines can be uncovered.





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