

## PROJECT ADMINISTRATION DATA SHEET



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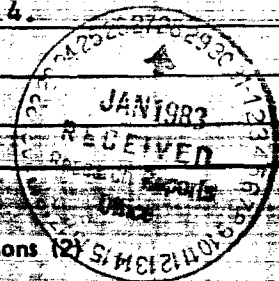
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## COMMENTS:

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FINAL REPORT

# RECOMBINATION AND REACTIONS IN DENSE IONIZED GASES

By

M. R. Flannery

Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
BOLLING AIR FORCE BASE  
WASHINGTON, D. C. 20332

Under

Grant No. AFOSR-80-0055

For Period January 1, 1980 – June 30, 1984

**GEORGIA INSTITUTE OF TECHNOLOGY**

**A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA**

**SCHOOL OF PHYSICS**

**ATLANTA, GEORGIA 30332**



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## Abstract

A list of publications of the research performed during the period 1/1/80-6/30/84 is provided. Theoretical research has been conducted (a) on ion-ion recombination in high pressure plasmas, (b) on the theory of Rydberg collisions with electrons, ions and neutrals, and (c) on the theory of ion-molecule collisions at (1 eV-4 keV)/AMU. Papers in these topics (a)-(c) have been written up and published as papers already submitted to AFOSR. In particular, a new and basic theory of ion-ion recombination in a dense gas has been developed from basic microscopic principles. The recombination rate is provided as a function of gas density and time. The theory has been published in papers already submitted to AFOSR. Appendix A of this report contains the published chapter on "Theory of Ion-Molecule Collisions at (1 eV-50 keV)/AMU".

Accomplishments due to AFOSR support

M. R. FLANNERY

School of Physics, Georgia Institute of Technology

Grant AFOSR-80-0055

Project No. 2301, Task No. A4

1.1 Full List of Refereed Publications in Scientific Journals (1980-1984)

1. "Charge-Transfer in Three-Body Ion-Ion Recombination at Low Gas Densities", Int. J. Quant. Chem.: Quant. Chem. Symp. 14, 477-482 (1980).
2. "Ion-Ion Recombination in  $(X^+ + Y^- + X)$  Systems at Low Gas Densities: I. Symmetrical Resonance Charge-Transfer Contribution", J. Phys. B: Atom. Molec. Phys. 13, 3649-3664 (1980).
3. "Three-Body Recombination of Rare-Gas Atomic Ions  $X^+$  with  $F^-$  in a Low-Density Gas  $X$ ", with T. P. Yang, J. Chem. Phys. 73, 3239-3245 (1980).
4. "Theoretical Treatment of Collisions of Rydberg Atoms with Neutral Atoms and Molecules. The Semiquantal, Impulse and Multistate-Orbital Theories", Phys. Rev. A 22, 2408-2429 (1980).
5. "Thermal Collisions of Rydberg Atoms with Neutrals", J. Phys. B: Atom. Molec. Phys., L657-663 (1980).
6. "Ion-Ion Recombination in  $(X^+ + Y^- + Z)$  Systems at Low Gas Densities. II. Elastic Ion-Neutral Collisions", J. Phys. B: Atom. Molec. Phys. 14, 915-934 (1981).
7. "Vibrational Deactivation of Oxygen Ions in Low Velocity  $O_2^+(X^3\Pi, v=1) + O_2(X^3\Sigma_g^-, v=0)$  Collisions", with T. F. Moran, K. J. McCann, M. Cobb and R. F. Borkman, J. Chem. Phys. 74, 2325-2330 (1981).
8. "Ion-Ion Recombination as a Function of Ion and Gas Densities", Chem. Phys. Letts. 80, 541-546 (1981).
9. "Exact Closed Form Solution of the Generalized Debye-Smoluchowski Equation", Phys. Rev. Letts. 47, 163-166 (1981).
10. "Cross Sections for Electron-Impact Ionization of Metastable Rare-Gas Excimers ( $He_2^*$ ,  $Kr_2^*$ ,  $Xe_2^*$ )", with K. J. McCann and N. W. Winter, J. Phys. B: Atom. Molec. Phys. 14, 3789-3796 (1981).
11. "Ion-Ion Recombination in Dilute and Dense Plasmas", Int. J. Quant. Chem.: Quant. Chem. Symp.: 15, 715-727 (1981).
12. "Theory of Ion-Ion Recombination", Phil. Trans. Royal Soc. (London) A

304, 447-497 (1982).

13. "Ion-Ion Recombination in High Pressure Plasmas", in Applied Atomic Collision Physics. Vol. 3: Gas Lasers, Eds. H. S. W. Massey, B. Bederson and E. W. McDaniel, (New York, Academic, 1982) Chapter 5, pages 141-172.
14. "Analytical Solutions of the Debye-Smoluchowski Equation for Geminate and Homogeneous Recombination and for Fluorescence Quenching", Phys. Rev. A. 25, 3403-3406 (1982).
15. "Comments on Thermal Collisions of Rydberg Atoms with Neutrals", J. Phys. B: Atom. Molec. Phys. 15, 3249-3256 (1982).
16. "Exact Closed Form Solution of the Generalized Debye-Smoluchowski Equation", Phys. Rev. Letts. 49, 1681 (1982).
17. "Theory of Rydberg Collisions with Electrons, Ions and Neutrals", in Rydberg States, Eds.: R. F. Stebbings and F. B. Dunning (Cambridge, Cambridge University Press, 1983), Chapter 11, pp. 393-454.
18. "Diffusional-Drift Influenced Chemical Reactions at all Gas Densities", Phys. Rev. Letts. 50, 1656-1659 (1983).
19. "Theory of Ion-Molecule Collisions at (1 eV-5 keV)/AMU", in Chapter 6 of Swarms of Ions and Electrons in Gases, 1984, eds. W. Lindinger, T. D. Mark and F. Howorka (Springer-Verlag), pages 103-125.

During the period (1980-1984) of the Grant AFOSR-80-0055, six copies of reports describing the above published research, #1 - #18, were submitted to AFOSR routinely as they became available. Also full details were contained in the Interim Annual Technical Reports submitted to AFOSR for the periods (a) January 1, 1980 - December 31, 1980, (b) January 1, 1981 - December 31, 1981 and (c) January 1, 1982 - December 31, 1982.

The published article #19 above entitled "Theory of Ion-Molecule Collisions at (1 eV - 5 keV)/AMU", is included as Appendix A of this Final Report.



## 1.2 Chapters in Books (1982-1984)

1. "Ion-Ion Recombination in High Pressure Plasmas", Chapter 5 of Applied Atomic Collision Physics, Vol. 3, Gas Lasers, 1982 eds., H. S. W. Massey, B. Bederson and E. W. McDaniel (New York, Academic), pages 141-172.
2. "Theory of Rydberg Collisions with Electrons, Ions and Neutrals", in Chapter II of Excited Rydberg States, 1983 eds., R. F. Stebbings and F. B. Dunning (Cambridge University Press), pages 393-453.
3. "Theory of Ion-Molecule Collisions at (1 eV-5 keV)/AMU", in Chapter 6 of Swarms of Ions and Electrons in Gases, 1984, eds. W. Lindinger, T. D. Mark and F. Howorka (Springer-Verlag), pages 103-125.

These chapters have also been included in the list (1.1) of publications but are identified explicitly here. Six copies of reprints of above articles #1 and #2 have been submitted to AFOSR when they became available. Other details were contained in the Interim Annual Reports for the periods (a) January 1, 1980 - December 31, 1980, (b) January 1, 1981 - December 31, 1981 and (c) January 1, 1982 - December 31, 1982. Chapter #3 is included as Appendix A of this report.

## 1.3 Funding History

(a) Total Number of Publications due to AFOSR support (1980-1984): 19

|             |                    |   |                    |   |                    |   |                  |
|-------------|--------------------|---|--------------------|---|--------------------|---|------------------|
| (b) Funding | FY 80              | ; | FY 81              | ; | FY 82              | ; | FY 84            |
|             | (1/1/80-12/31/80); |   | (1/1/81-12/31/81); |   | (1/1/82-12/31/82); |   | (1/1/83-6/30/84) |
|             | \$51,000           | ; | \$58,266           | ; | \$64,024           | ; | \$69,919         |

2. Invited Papers Presented at Conferences (1974-1984)

In addition to presentation of many contributed papers at the various Annual Meetings (sponsored by the American Physical Society) of the Gaseous Electronics Conference and The Division of Electron and Atomic Physics, the following Invited Papers were presented on research due to AFOSR support.

1. "Atomic and Molecular Collision Processes in High-Power Excimer Lasers", Invited Lecture presented at International Symposium on Atomic Molecular and Solid State Theory, Florida, March 11-17, 1979.
2. "Theory of Excimer Lasers", Invited Lecture for New Directions in Atomic Physics, Gordon Research Conference, Brewster Academy, New Hampshire, June 25-29, 1980.
3. "Basic Microscopic Theory of Ion-Ion Recombination", Invited Lecture presented at International Symposium on Atomic, Molecular and Solid State Theory, Florida, March 9-14, 1981.
4. "Basic Microscopic Theory of Neutralization and of Chemical Reactions in Dense Gases", Special Long Paper (30 mins.) delivered at 34 Annual Gaseous Electronics Conference, Boston, Mass., October 20-23, 1981.
5. "Basic Microscopic Theory of Chemical Reactions in Dense Gases", Invited Lecture delivered at the 3rd Annual Symposium on Atomic and Surface Plasmas, Hintermoos, Austria, February 7-13, 1982.
6. "Ion-Ion Recombination in Dense Gases", Invited Paper delivered to International Conference on Lasers '82, New Orleans, La., December 13-17, 1982.
7. "Ion-Ion Recombination", Invited Lecture in the Distinguished Invited Lectureship Series of Harvard University, Feb. 1983.
8. "Theory of Ion-Ion Recombination", Invited Plenary Lecture delivered to International Symposium on Atomic, Molecular and Solid State Theory, Florida, March 3-6, 1983.
9. "Theory of Ion-Molecule Collisions", Invited Lecture at Workshop, XVth Annual Meeting of the Division of Electron and Atomic Physics (American Physical Society), May 30 - June 2, 1984.

### 3. Special Highlights: New Theoretical Developments in Present Research

A new and basic theory of ion-ion recombination as a function of gas density  $N$  has been developed (M. R. Flannery, Phil. Trans. Roy. Soc. A 304, 447-497 (1982)) from basic microscopic principles. A key equation for the distribution in phase space of ion pairs had been derived together with an expression for the resulting recombination coefficient  $\alpha$ . Further development of the theory led to interesting insights to a full variation with  $N$  of  $\alpha$ , which was shown to yield the correct limits at low and high  $N$ . The recombination rate  $\alpha$  is determined by the limiting step of the rate  $\alpha_{RN}$  for ion reaction and of the rate  $\alpha_{TR}$  for ion transport to the reaction zone. An accurate analytical solution of the time-dependent Debye-Smolcuhowski equation which is a natural consequence of this theory, was provided, for the first time, for transport/reaction under a general interaction  $V$  in the cases of an instantaneous reaction ( $\alpha_{RN} \gg \alpha_{TR}$ ) and of a finite rate ( $\alpha_{RN} \sim \alpha_{TR}$ ) of reaction within a kinetic sink rendered compressible via variation of gas density. Expressions for the transient recombination rates  $\alpha(t)$  were then derived and illustrated. The exhibited time dependence lends itself to eventual experimental verification at high  $N$ .

A theory which investigated the variation of  $\alpha$  with ion density  $N^+$  was also developed. Here the ion-ion interaction  $V$  can no longer be assumed ab-initio to be pure Coulomb but is solved self-consistently with the recombination. Recombination rates for various systems were illustrated as a function of  $N$  via a simplified method for the reaction rate. Finally, two theoretical procedures for the solution of the general phase-space ion distribution were proposed.

The above work was considered to be an important advance in the field by a distinguished expert in a recent review of the subject (cf. D. R. Bates, Advances in Atomic and Molecular Physics (New York, Academic Press, 1985), vol. 20, p. 14.

## Appendix A

Theory of Ion-Molecule Collisions at  
(1 eV-5 keV)/AMU

by

M. R. Flannery

Published as a chapter in the book "Swarms of Ions and Electrons in Gases", eds. W. Lindinger, T. D. Mark and F. Howorka (Springer-Verlag, 1984) pages 103-125.

# Theory of Ion-Molecule Collisions at (1 eV–5 keV)/AMU

M. R. Flannery

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## 1. Various Aspects

In ion-molecule collisions from thermal energies, to a few eV, up to a few keV, various processes such as chemical reactions (nuclear rearrangements), charge transfer (electronic rearrangement) and rotational, vibrational and electronic transitions occur, rarely in isolation except over limited energy ranges. Inelastic scattering changes the internal state by rotational, vibrational and electronic excitation of one or both collision partners while preserving the identity of each partner, in contrast to reactive scattering (chemical reactions, three-body ion-molecule association, charge transfer, dissociation, ionization) which changes the chemical identities. There are few theories which elucidate the coupling between reactive and inelastic mechanisms, since development of feasible theoretical treatments of each of the processes in isolation presents, in itself, a considerable challenge.

The electrostatic interaction  $V(R, r, \gamma)$  between an ion  $A^+$  at relative separation  $R$  from the center of mass of the molecule BC with internuclear vector  $\hat{r}$ , depends on  $r$  which, in general, causes vibrational excitation via collision induced forces along  $\hat{r}$ ; on the angle  $\gamma$  between  $\hat{R}$  and  $\hat{r}$ , which induces (via a torque) rotational excitation, and on  $R$  which mainly controls the general variation of the corresponding inelastic differential cross sections with scattering angle. We shall see, however, that vibrational excitation can be strongly enhanced when coupled to charge-transfer channels. Within various regions of the kinetic energy  $E$  of relative motion (or center-of-mass energy), chemical reactions, charge transfer, rotational and vibrational excitation may be all or partially strongly coupled, or else be all effectively decoupled over a small ( $\sim 10$  eV) energy range. While strong couplings may exist only within all reactive mechanisms (chemical reaction and charge

transfer for  $E \lesssim 1$  eV) or only within all inelastic mechanisms (rotational and vibrational excitation) in range  $1 \lesssim E$  (eV)  $\lesssim 10$ -50, i.e., essentially in mutually exclusive energy ranges, one inelastic mechanism can be strongly coupled, for a wide range of interesting cases, with only one strong reactive scattering mechanism (as in vibrational excitation caused directly by charge transfer for  $10 \lesssim E$  (eV)  $\lesssim$  few keV).

A plausible upper limit to reaction at kinetic energy  $E$  of relative motion is the Langevin cross section,  $\sigma_L(\text{\AA}^2) = 17\alpha^{1/2}[E(\text{eV})]^{-1/2}$ , for close spiralling encounters within the orbiting radius,  $\sim(4-6)$   $\text{\AA}$  at thermal energies, centered about the center of mass of the molecule of averaged polarizability  $\alpha(\text{\AA}^3)$ . At thermal energies, the cross section  $\sigma_C$  for production [1] of  $\text{Ar}^+\text{H}^+$  in  $(\text{Ar}^+-\text{H}_2)$  collisions is  $\sigma_C(\text{\AA}^2) \sim 200$ . Also  $\text{HD}_2^+$  and  $\text{D}_3^+$  are each formed in merging beam  $(\text{D}_2^+-\text{HD})$  collisions [2] with  $\sigma_C(\text{\AA}^2) \sim 100$ , 10 and 0.1 at kinetic energies  $E$  of relative motion of 0.002, 1 and 8 eV, respectively. The  $E$ -variation of  $\sigma_C$  becomes quite precipitous for  $E \gtrsim 1$  eV, relative to the much slower  $E$ -variation of  $\sigma_L$ . Except at very low energies  $E \lesssim 1$  eV, charge transfer cross sections  $\sigma_X$  become much larger than  $\sigma_L$ , since attraction can occur from overlap forces, in addition to the weaker polarization  $R^{-4}$  attraction implicit in  $\sigma_L$ .

For  $(\text{H}^+, \text{D}_2) \rightarrow (\text{D}^+, \text{HD})$ , reaction and charge-transfer can occur for  $E$  (eV)  $\gtrsim 0.04$  assisted by direct rotational and possible vibrational excitation. For  $(\text{H}^+-\text{H}_2(v=0, J=0))$  collisions, in contrast, rotational excitation (with thresholds  $\Delta E(J=0 \rightarrow 2,4) = 0.04, 0.14$  eV) and vibrational excitation (with  $\Delta E(v=0 \rightarrow 1,2,3) = 0.516, 1.003, 1.461$  eV) are alone possible, until  $E$  reaches the threshold  $E_X \sim 1.83$  eV for charge-transfer and reaction. The cross section  $\sigma_X$  for charge-transfer [3,4] then slowly rises to a peak  $\sim 10^2 \text{\AA}^2$  at  $E \sim 1$  keV. Above  $E_D = 4.48$  eV direct dissociation, and above  $E_i \sim 11$  eV dissociation via electronic excitation, can occur, but again both peak in the keV energy region. For  $\text{Li}^+-\text{H}_2$  collisions at  $E \lesssim E_X = 10.2$  eV, only rotational and vibrational transitions and weak direct dissociation are possible.

Since the strong valence forces in  $\text{H}_3^+$  tend to expand the  $\text{H}_2$  bond length, vibrational excitation of  $\text{H}_2$  by  $\text{H}^+$  is much stronger than in  $\text{Li}^+-\text{H}_2$  collisions where short range (forced oscillator) repulsive forces are mainly responsible for the small vibrational excitation with associated excitation of high  $J'$  levels. Rotational excitation in the lighter  $\text{H}^+-\text{H}_2$  system is, however, weaker by comparison, since the torque is less and the triangular geometry of the intermediate  $\text{H}_3^+$  complex permits less flexibility for rotation of  $\text{H}_2$ .

As the ion energy or kinetic energy of relative motion  $E$  increases from  $\sim$  several eV, rotational excitation decreases since the rotational period  $\tau_{\text{rot}} \sim (10^{-11}$  for  $O_2$  -  $2 \cdot 10^{-12}$  for  $H_2$ )s becomes much greater than the duration  $\tau_{\text{coll}} \sim R(\text{\AA}) [M(\text{A.M.U.})/2E(\text{eV})]^{1/2} 10^{-14}$ s of the collision between species of reduced mass  $M(\text{A.M.U.})$  with characteristic length  $R(\text{\AA})$  for the particular process. The cross sections  $\sigma_R$  for rotational transitions (in  $Li^+-H_2$  collisions) increase from threshold, exhibit a peak  $\sim 10 \text{\AA}^2$  at 1-5 eV and then decrease [5] to  $\sim 1 \text{\AA}^2$  at 100 eV. Since the vibrational period  $\tau_{\text{vib}} \sim (10^{-13}$  for  $Br_2$  -  $10^{-14}$  for  $H_2$ )s,  $\sigma_V$  for vibrational excitation in  $Li^+-H_2$  collisions, will increase from thresholds  $\sim 1$  eV mainly via  $v, J \rightarrow v', J'$  transitions say to  $\sim 0.1 \text{\AA}^2$  and  $0.03 \text{\AA}^2$  for  $v = 0 \rightarrow 1, 2$  respectively [6] at  $E \sim 100$ -200 eV, and then decrease thereafter. The  $H^+-H_2$  ( $v=0 \rightarrow v'$ ) system involves larger vibrational cross sections with maxima,  $\sigma_V (\text{\AA}^2) \sim 6, 2.3$ , and  $0.8$  for  $v' = 1, 2$  and  $3$ , respectively, which occur [7] at  $E \sim 30$  eV.

Charge transfer collisions [8] between similar ( $AB^+-AB$ ) systems are characterized by much larger cross sections  $\sigma_X$  which decrease only very slowly as  $E$  is raised from thermal energies to a few keV; for  $N_2^+-N_2$ ,  $\sigma_X$  decreases [9] from  $\sim 70 \text{\AA}^2$  at  $E \sim 1$  eV to  $\sim 25 \text{\AA}^2$  at a few keV. Since the direct and charge transfer channels can be in near energy-resonance for symmetric systems and are closely coupled, direct vibrational excitation [8-10] is therefore characterized by large cross sections,  $\sigma_V \sim (10-20) \text{\AA}^2$ , in contrast to weaker vibrational excitation via forced oscillator collisions, which are characterized by relatively smaller cross sections  $\sim 10^{-2} \text{\AA}^2$ .

The key difference between symmetric ( $AB^+-AB$ ) and asymmetric ( $A^+-BC$ ) charge transfer collisions is that there are initially two (elastic) paths of approach in the former case, and charge transfer then arises from the phase-change caused by the different elastic scattering potentials associated with the bonding and antibonding states of the  $[AB]_2^+$ -complex (states which reduce to the gerade and ungerade states of  $A_2^+$  in  $A^+-A$  collisions). Charge-transfer in the asymmetric ( $A^+-BC$ ) case involves an electronic transition between states with different asymptotic energies ( $\sim 1.83$  eV for  $H^+-H_2$  and 11 eV for  $Li^+-H_2$  collisions), and is therefore characterized by a threshold dependent cross section which increases to somewhat lower cross section maxima ( $\sigma_X \sim 10 \text{\AA}^2$  at  $E \sim 1$  keV for  $H^+-H_2$  collisions [3]).

The variation with  $E$  of many ion-molecule processes appears as if the process were energy resonant. This is because the manifold of vibrational channels (in charge-transfer, for example) offers a band of pathways which are in near-energy resonance either with the incident channel or with a particular product (charge-transfer) channel which is strongly coupled to the incident channel.

The dominant processes for unlike systems ( $A^+-BC$ ) in the (1-100) eV range of center-of-mass energy  $E$  are elastic and rotational excitation, while for  $E \sim (1 \text{ eV} - \text{several keV})$ , the dominant process for like ( $AB^+-AB$ ), apart from direct elastic scattering, is charge-transfer with its associated direct vibrational excitation. For  $E \gtrsim \text{few keV}$ , direct electronic excitation to bound electronic and to dissociative electronic states occurs with relatively small cross sections  $\sigma_E \sim 1 \text{ \AA}^2$ . For lower  $E \lesssim 1 \text{ eV}$ , chemical reactions will compete quite strongly with any of the above processes when operative.

In the following sections, feasible and tractable semiclassical (classical path, quantal target) theories for inelastic (rotational excitation) processes alone, and for reactive processes (symmetric and asymmetric charge transfer) coupled to direct inelastic processes (vibrational excitation) will be outlined and discussed. The theories are particularly appropriate for the energy range (1 eV - several keV), since chemical reactions are specifically excluded. Full quantal treatments are not presented since their application is feasible to at most 10 eV, and since they are well documented elsewhere [11-15]. Space allows only the mention of quasi-classical trajectory methods [11,15,17], valuable for highly averaged quantities in rotational excitation in non-reactive systems, and of semiclassical S-matrix theory [13,16] and classical perturbation theory [17,18], which are all based on classical relative and internal motions and which are valuable towards realization of the conceptual power of classical mechanics. Apart from vibrational excitation in collinear collisions, the S-matrix theory, however, becomes computationally unfeasible [11,18] for three dimensional systems, even in comparison with full quantal methods.

## 2. Rotational and Vibrational Transitions in Non-Reactive Collisions

### 2.1 Quantal Methods

The traditional full quantal close coupling (CC) treatment of rovibrational transitions is the generalization [19] of the formulation [20] of Arthurs and Dalgarno for scattering of a rigid rotor (RR) by a structureless projectile to vibrating rotor (VR) collisions, and is, by now, well established. It is, however, practical only for  $E \lesssim \text{few eV}$ , since the inherent partial wave expansion for the relative motion converges only very slowly as  $E$  is increased, and excessive amounts of computer time are required. It has, as yet, only been applied [19] to rotational and vibrational excitation in  $\text{Li}^+-\text{H}_2$  collisions at 0.6 eV and 1.2 eV where coupling with the two excited vibrational channels ( $v = 1,2$ ) is extremely weak, and vibrational excitation is then at most incidental.

Many simplified quantal schemes ( $J_J$ -coupled states (CS) [21], infinite-



order sudden (IOS) [22], effective potentials [23], L-dominant [24]) based on CC have therefore been introduced for  $E \lesssim 10$  eV. These methods seek to reduce the (rotational) dimensionality of CC by assuming, for example, that the Z-axis of a rotating frame always lies along  $\hat{R}$  (as in CS [21] and in earlier rotating-atom approximation of Bates [25], where transitions are therefore restricted to zero change  $\Delta M_J$  in the Z-components of the rotational quantum number  $J$ ) or by assuming that the orientation  $\hat{r}$  of the molecule can be considered fixed during the collision (as in the sudden or adiabatic-nuclei approximation [26]). In IOS, a combination of both sudden and CS is adopted. At low energies ( $\lesssim$  few eV), vibration may either be ignored, as in rigid rotor (RR) approximations, or be treated exactly (VR), within the above methods by full solution of the vibrationally coupled equations.

Since these dimensionality-reducing (DR) schemes remain based on a partial-wave analysis they are also very time-consuming. For the transition  $J = 0 \rightarrow 2$  in  $\text{Li}^+-\text{N}_2$  collisions at 4.23 eV, which involves close-coupling of many  $J$ -levels,  $10^4$  partial waves were required in a recent IOS treatment [27]. Under the added requirement that reliable interaction potentials, in general, ab-initio, are needed as input, it is therefore not too surprising to note that only a few special systems have been studied in detail by the above quantal methods, at only a few energies chosen to coincide with measurement. For example, pure rotational and rovibrational transitions have been studied in the collisions:  $\text{H}^+-\text{H}_2$  by CS-RR [28] at 3.7 eV, by IOS-VR [29,30] at 4.67, 6 and 10 eV;  $\text{Li}^+-\text{H}_2$  by CC-RR [31], CC-VR [19], CS [32] for  $E \leq 1.2$  eV and by IOS-VR [33] at 5.54 and 8.8 eV;  $\text{Li}^+-\text{N}_2$  by IOS-VR [27] at 4.23 eV.

Comparison of the IOS-VR cross sections [29] with rotationally resolved measurements [34] for  $\text{H}^+-\text{H}_2$  ( $v=0, J=0 \rightarrow v'(0,1,2,3), J'$ ) indicates good to excellent agreement at 10 eV for the variation with scattering angle of the vibrational transition probabilities (ratio of cross sections) when summed over final levels  $J'$ , and excellent agreement for the relative differential cross sections for vibrational excitation. Only scattered agreement [30] is noted, however, for rotational excitation ( $0,0 \rightarrow 0,J'$ ) at 4.67 and 6 eV.

The agreement between IOS-VR [33] and measured [35] vibrational transition probabilities (summed over  $J'$ ) for  $\text{Li}^+-\text{H}_2$  collisions is reasonable only at 8.8 eV and very poor at 5.54 eV. When compared with the only measured absolute integral cross sections ( $\sim 4.2 \text{ \AA}^2$  [5]) for rotational excitation in  $\text{Li}^+-\text{H}_2$  ( $0,0 \rightarrow 0,2$ ) collisions at 12 eV, (and beyond), the IOS-VR cross section  $19.8 \text{ \AA}^2$  [33] at 8.8 eV is a factor of 5 higher; and the IOS-VR cross section  $\sim 0.3 \text{ \AA}^2$  [33] for vibrational excitation ( $v=0 \rightarrow 1$ ) at 8.8 eV is much in excess of the measured [6] peak values  $\sim 0.08 \text{ \AA}^2$  which are spread

over a wide range around 150 eV.

Many of the above reduced-dimensionality quantal schemes have varying degrees of success e.g., the most accurate of these, the  $J_Z$ -coupled states (CS) method [32] when compared with CC [19] predicts  $\sigma_R$  for  $\text{Li}^+-\text{H}_2$  ( $J=0 \rightarrow 2$ ) collisions to within only 33% at 0.6 - 1.2 eV, (in contrast to its success with atom-molecule collisions), and differential cross sections in substantial disagreement at intermediate angles. Also the great sensitivity [29,28] exhibited by any method to the choice of various (reasonably accurate) interactions  $V(R,r,\gamma)$  places a great premium for highly accurate (time consuming) calculations of these anisotropic surfaces [19,27,29] over an extensive range of  $(R,r,\gamma)$  parameters.

## 2.2 Semiclassical Theory (Eikonal path-Quantal target)

There is therefore some need for more accurate yet feasible treatments of the energy region,  $1 \lesssim E \text{ (eV)} \lesssim 10$ , and great need for treatments feasible in the region  $10 \text{ eV} \lesssim E \lesssim 1 \text{ keV}$ . For low energies  $\lesssim 10 \text{ eV}$  only relative differential cross sections have been measured [34-36]. Some measurements [5,6] of integral cross sections exist for rotational and vibrational excitation in  $\text{Li}^+-\text{H}_2$  collisions at center-of-mass energies  $E$  in the range (12-90 eV) for which accurate theory has not yet been applied.

For the above reasons, and in order to explore the strengths of semiclassical methods which naturally focus attention on collisional time-scales and which naturally provide greater physical insight to various levels of approximation, McCann and Flannery [37-39] have developed a multistate orbital (or energy-conserving) treatment of rotational and vibrational transitions in ion-molecule and neutral-molecule collisions at intermediate and high impact energies. Rather than seeking schemes which reduce the dimensionality of the quantal CC within a phase shift analysis of the relative motion, the basis of their semiclassical treatment is initially a semiclassical description (via an eikonal or JWKB wavefunction) of the relative motion, which is then coupled to the full quantal response of the closely coupled internal modes of the collision partners, via the introduction at each  $R_\gamma$  of an interaction averaged over the quantal response of all of the internal modes. Even at low energies ( $\sim 0.6 \text{ eV}$ ) the theory realized considerable success [39] when compared with full quantal CC differential and integral cross sections [19], (Figure 1), and with measured relative differential cross sections. The procedure apparently introduces less error than does the best (CS) [32] dimensionality-reducing (DR) quantal scheme, as evidenced by comparison of CS [32] and EC [39] with CC [19] for  $\text{Li}^+-\text{H}_2$  at 0.6 eV. Within the EC method, DR approximations may in addition be made. Figure 1 indicates the excellent agreement between the semiclassical

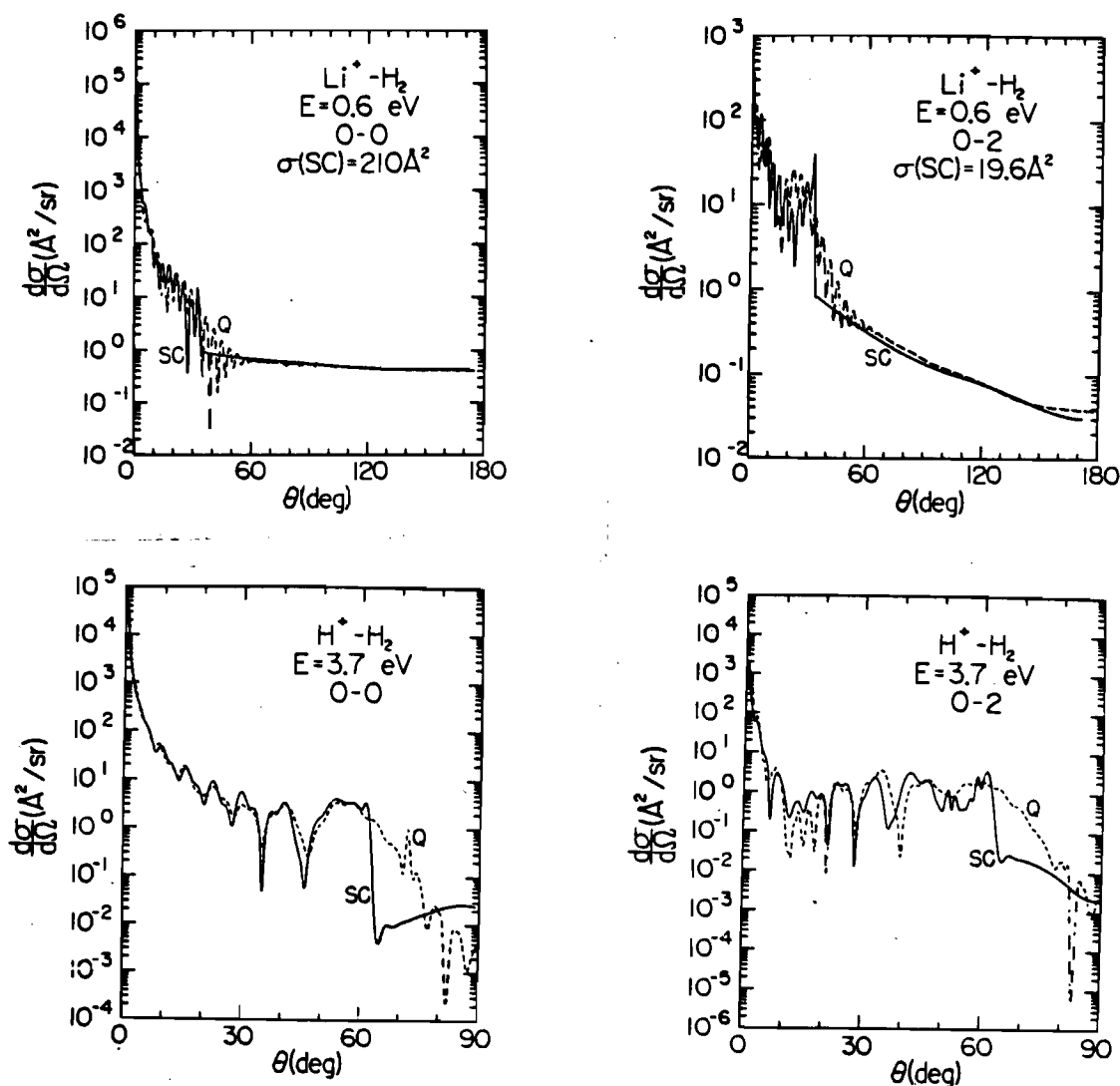


Fig. 1. Quantal [19,28] and semiclassical [39] differential cross sections for elastic ( $0 \rightarrow 0$ ) and inelastic ( $J=0 \rightarrow 2$ ) scattering in  $\text{Li}^+-\text{H}_2$  and  $\text{H}^+-\text{H}_2$  collisions.

[39] and quantal methods [28] under the common CS approximations for  $\text{H}^+-\text{H}_2$  collisions.

The method is extremely efficient and accurate in that transition amplitudes converge much faster in the impact-parameter representation than they do in the angular momentum (partial-wave) representation. It is therefore quite a natural method for (1 eV - 1 keV) inelastic collisions. It has recently been shown [40,41] to be also highly reliable for reactive collisions for  $E \lesssim 10$  eV.

### 2.3 Multistate Orbital (Energy Conserving) Method:

In contrast to customary semiclassical treatments based on a straight line, the classical path  $\mathbf{R}(t)$  for relative motion between species A (ion or atom) and BC is obtained [37] by solving Hamilton's equations

$$\partial Q_i / \partial t = \partial \langle H \rangle / \partial P_i \quad ; \quad \partial P_i / \partial t = - \partial \langle H \rangle / \partial Q_i \quad (1)$$

directly for the variation with time  $t$  of the generalized coordinates  $Q_j (\equiv X, Y, Z)$  for  $R(t)$ , the vector position of A relative to the center-of-mass of BC, and of the associated generalized momentum  $P_j(t)$  for motion under the (Ehrenfest) averaged Hamiltonian [37],

$$\langle H(R(t)) \rangle = \sum_{j=1}^3 P_j^2(R(t))/2\mu + \langle \psi(r, R(t)) | H_0(r) + V(r, R(t)) | \psi(r, R(t)) \rangle, \quad (2)$$

where  $\mu$  is the reduced mass of the (A-BC) system. The system wavefunction is therefore expanded in terms of the complete set of eigenfunctions  $\phi_n(r)$  of the unperturbed Hamiltonian  $H_0$  for the internal states of the isolated species A and BC of energy  $E_n$ , ( $H_0 \phi_n = E_n \phi_n$ ), as

$$\psi(r, R) = \sum_n A_n(R) \phi_n(r) \exp[iS_n(R) - X_n(R)] \quad (3)$$

where  $r$  denotes the collective internal coordinates of A and BC in the absence of interaction, and where  $\phi_n(r)$  separates, via the Born-Oppenheimer approximation, into associated electronic, vibrational and rotational parts. The relative motion is described by the above combination of functions  $A_n$ ,  $S_n$  and  $X_n$  which possess the following physical characteristics. The eikonal, or classical action, is the solution of the Hamilton-Jacobi equation [37-39],

$$(\nabla S_n)^2 = K_n^2(R) = k_n^2 - (2\mu/\hbar^2) V_{nn}(R) \quad (4)$$

which, of course, is the heavy-particle limit to Schrödinger's equation,

$$[-\nabla_R^2 + (2\mu/\hbar^2) V_{nn}(R)]\psi(R) = [(\nabla S_n)^2 - i(\nabla^2 S_n)]\psi(R) \equiv K_n^2\psi(R) \quad (5)$$

The wavefunction,  $\psi(R) = \exp(iS_n)$ , describes relative motion in the static channel  $n$  under interaction  $V_{nn}$ , which is a diagonal element of

$$V_{ij}(R) = \langle \phi_i(r) | V(r, R) | \phi_j(r) \rangle \quad (6)$$

where  $V(r, R)$  is the instantaneous electrostatic interaction between A and BC at separation  $R$ . The wavenumber and kinetic energy of relative motion at asymptotic  $R$  is  $k_n$  and  $\hbar^2 k_n^2/2\mu$  and the local momentum at  $R$  is  $\hbar K_n(R)$ . The phase  $X_n$  is the solution of

$$\nabla_R^2 S_n - 2(\nabla_R S_n) \cdot (\nabla_R X_n) = 0 \quad (7)$$

which represents flux conservation, ( $\nabla \cdot J_n = 0$ ), in static channel  $n$ , since the current  $J_n$  associated with the exponential factor in (3), for real  $S_n$  and  $X_n$ , is

$$J_n = \exp(-2X_n) v_n(R) \equiv (\hbar/\mu) \exp(-2X_n) \nabla S_n \quad (8)$$

when (4) is used for the local velocity  $v_n$ . Thus, flux associated with channel  $n$  of (3) is changed only via transitions to other states  $f$ , and  $A_n$  is then the probability amplitude of remaining in state  $n$ . On assuming that the eikonal  $S_n(R)$  contains the major  $R$ -variation of (3), the stationary-state Schrödinger equation with (3) inserted then yields the three-

dimensional equation [37-39],

$$i\mathbf{K}_f \cdot \nabla_{\mathbf{R}} A_f(\mathbf{R}) = (\mu/\hbar^2) \sum_{n \neq f} A_n(\mathbf{R}) V_{fn}(\mathbf{R}) \exp i(S_n - S_f) \exp(X_f - X_n) \quad (9)$$

The first term in (2) is the kinetic energy of relative motion and, with (3) inserted, the second term reduces under the assumption that the orbits in the different channels do not differ appreciably (i.e.,  $X_n \approx X_f$ ), to the  $\mathbf{R}$ -averaged interaction [37-39],

$$\langle V(\mathbf{R}) \rangle = \sum_n [|A_n(\mathbf{R})|^2 \epsilon_n + \sum_f A_f^*(\mathbf{R}) A_n(\mathbf{R}) V_{fn}(\mathbf{R}) \exp i(S_n - S_f)] \quad (10)$$

The time  $t$  ( $\equiv s/v(\mathbf{R})$ ) is introduced as a (dummy) variable to measure distance  $s$  along the common trajectory i.e.,  $\mathbf{K}_f \cdot \nabla_{\mathbf{R}} A_f = K_f \partial A_f / \partial s \equiv (\mu/\hbar) \partial A_f / \partial t$ , and the mean momentum is

$$\frac{1}{2} \hbar (K_n + K_f) = P(\mathbf{R}) = \mu |d\mathbf{R}/dt| \quad (11)$$

so that the evolution of the eikonal difference in (9) and (10) can be written as

$$S_n(\mathbf{R}) - S_f(\mathbf{R}) = [\epsilon_{fn} t + \int_{t_0}^t \{V_{ff}(\mathbf{R}(t)) - V_{ii}(\mathbf{R}(t))\} dt] / \hbar \quad (12)$$

where  $\epsilon_{fn} = \epsilon_f - \epsilon_n$ . The amplitudes

$$C_f(t) = A_f(t) \exp[-(i/\hbar) \int_{t_0}^t V_{ff}(\mathbf{R}(t)) dt] \quad (13)$$

when inserted in (9), therefore satisfy the usual set of coupled equations,

$$i\hbar \partial C_f / \partial t = \sum_n C_n(t) V_{fn}(\mathbf{R}(t)) \exp(i\epsilon_{fn} t / \hbar) \quad (14)$$

derived for the internal response of a system to a time dependent perturbation  $V(\mathbf{r}, \mathbf{R}(t))$ . The implicit time dependence for motion under the averaged interaction (10), which reduces with the aid of (12) and (13) to, [37-39],

$$\langle V(\mathbf{R}(t)) \rangle = \sum_n [|C_n(t)|^2 \epsilon_n + \sum_f C_f^*(t) C_n(t) V_{fn}(\mathbf{R}(t)) \exp(i\epsilon_{fn} t / \hbar)] \quad (15)$$

is determined from Hamilton's equations (1), which now reduce to [37-39]

$$\partial Q_i / \partial t = P_i(t) / \mu ; \quad \partial P_i / \partial t = - \sum_n \sum_f C_f^*(t) C_n(t) [\partial V_{fn} / \partial Q_i] \exp(i\epsilon_{fn} t / \hbar) \quad (16)$$

The external relative motion (16) is therefore solved self consistently with (14), which characterizes the quantal internal response of the molecule, at all times. Two important consequences [37,39] of this procedure are that total energy is conserved at all times during the collision, ( $d\langle H \rangle / dt = \partial \langle H \rangle / \partial t = 0$ ) - energy is therefore being continually redistributed between the internal modes and the relative motion (a valuable asset) - and that total probability  $\sum_f |C_f(t)|^2$  is naturally conserved at each point on the common trajectory provided by (15) and (16).

The differential cross section per steradian is

$$\begin{aligned}\sigma_{if}(\theta, \phi) &= (k_f/k_i) |f_{if}(\theta, \phi)|^2 \\ &= (k_f/k_i) \left| (2\mu/4\pi\hbar^2) \langle \phi_f(\vec{r}) \exp(i\vec{k}_f \cdot \vec{R}) | V(\vec{r}, \vec{R}) | \psi(\vec{r}, \vec{R}) \rangle_{\vec{r}, \vec{R}} \right|^2\end{aligned}\quad (17)$$

for scattering of an incident beam directed along  $\vec{k}_i(0,0)$  into unit solid angle about  $\vec{k}_f(\theta, \phi)$ . When the main contribution to (17) arises from the stationary phase which produces the classical orbit  $\vec{R}(\theta, \phi)$ , then the scattering amplitude  $f_{if}(\theta, \phi)$  and hence differential cross section  $\sigma_{if}(\theta, \phi)$  is easily deduced from flux considerations, as [37,39]

$$f_{if}(\theta, \phi) = \lim_{R \rightarrow \infty} [A_n(\vec{R}) \exp iS'_n(\vec{R})] [\sigma_{el}^n(\theta, \phi)]^{1/2} \quad (18)$$

where  $\sigma_{el}^n(\theta, \phi)$ , the differential cross section for elastic scattering by  $V_{ff}(\vec{R})$  in channel  $f$ , or by  $\langle V(\vec{R}) \rangle$  of (15) for common trajectories  $\vec{R}_{i,f}(\theta, \phi)$ , can be determined either from classical or quantal procedures, and where

$$S'_n(\vec{R}) = S_n(\vec{R}) - \vec{k}_n \cdot \vec{R} \quad (19)$$

is the classical action along the path measured relative to the action for undeflected particles with the same wavenumber. When more than one trajectory contributes to a given scattering angle  $\theta$ , then the primitive result [37] can be suitably generalized [39] to yield (uniform) differential cross sections which exhibit the customary oscillatory structure (Fig. 1) due to interference between the classical actions  $S'_n(\vec{R})$  associated with each classical path which contributes to a specific scattering angle  $\theta$ .

Representative comparison with full CC quantum treatment at  $<1$  eV is shown in Figure 1. Implementation to higher energies ( $1 \text{ eV} \rightarrow 1 \text{ keV}$ ), for which the above treatment was mainly designed (since full CC quantal treatments then become prohibitive), is underway.

In the limit of high impact energy, the scattering becomes increasingly concentrated in the forward direction, and the classical cross section  $\sigma_{el}^n(\theta, \phi)$  if used, diverges (albeit extremely slowly). The cross section for transitions ( $J_i M_i \rightarrow J_f M_f$ ) between sublevels  $M_i$  and  $M_f$  associated with rotational levels  $J_i$  and  $J_f$ , respectively, can then be obtained directly from (17) to yield [42,43],

$$\sigma_{if}(\theta, \phi) = (k_f/k_i) \left| k_i \int_0^\infty J_\Delta(K'\rho) [C_f^{(SL)}(\rho, \infty) - \delta_{if}] \rho d\rho \right|^2 \quad (20)$$

in the heavy-particle/high-energy limit, where  $J_\Delta$  is the spherical Bessel function of order  $\Delta = (M_f - M_i)$ , where  $K'^2 = (k_i - k_f)^2 - \epsilon_{fi}/\hbar^2 v_i^2$ , and where  $C_f^{(SL)}(\rho, t)$  are the solutions of (14) evaluated using a straight line orbit, and trajectory,

$$\vec{r}(\rho, \phi) = \text{constant} ; \quad \vec{R}(t) = \vec{r} + \vec{v}_i t \quad (21a)$$

in terms of the impact parameter  $\rho$ . The integral cross section then reduces to [42,43]

$$\sigma_{if}(v_i) = 2\pi(k_f/k_i) \int_0^\infty |C_f^{(SL)}(\rho, \infty) - \delta_{if}|^2 \rho d\rho \quad (21b)$$

which permits, in contrast to the usual expression without  $\delta_{if}$ , the evaluation also of elastic scattering cross sections.

When the coupling between the classical path and quantal target can be ignored i.e., when energy conservation which results from (15) is therefore violated, the classical trajectory  $R(t)$ ,  $\theta(t)$  and orbit  $\lambda(\theta, \phi)$  at energy  $E = \frac{1}{2} \mu v_i^2$  can be assumed planar, and is determined by integration of,

$$\frac{1}{2} \mu (dR/dt)^2 = E - [\bar{V}_0(R) + E_p^2/R^2] ; \quad d\theta/dt = -\rho v_i^2/R^2 \quad (22)$$

where  $\bar{V}_0$  is either some averaged spherical interaction independent of the transition amplitudes  $C_n(t)$ , or is the spherical part of the surface  $V(r, R)$ , so that  $\phi$  remains constant.

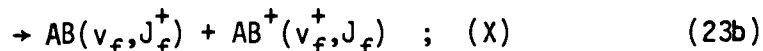
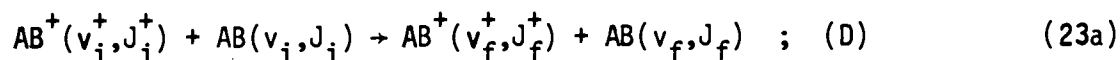
The above energy conserving (EC) classical path (CP) method reproduces the rainbow oscillatory structure and is capable of very effective description of inelastic rotational rainbows [15] characterized as structures in the final rotational distribution of differential cross sections at fixed angles for those molecular systems ( $N_2$ , CO,  $Na_2$ ) associated with small rotational constants so that many rotational levels must be included. These rotational rainbows arise from coherent superposition of scattering from different orientation angles  $\gamma$ . As the final level  $J_f$  is increased the rotational rainbows in  $J_i \rightarrow J_f$  transitions shift to larger angles due to hard collisions and have wider widths than the usual diffraction oscillations which occur from near forward scattering by the repulsive part of the interaction. The analysis of these rainbows by the pure CC quantal method is not at all feasible, and reduced dimensionality simplifications as CS and IOS may be too inaccurate.

The above EC-CP method can also be extended [44] to cover vibrational transitions and vibrational rainbows. For vibrational excitation simpler time-dependent semiclassical schemes based on an uncoupled classical path (21a), (22) or its three-dimensional equivalent, have been adopted [45-48]. Billing [49] has treated vibrational excitation by assuming that rotation and relative motion can be determined classically from various Hamiltonians which include an asserted average over the one-dimensional quantal vibrational response, but which are not, however, consistent with energy conservation.

### 3. Charge-Transfer and Associated Vibrational Excitation

In contrast to charge transfer in ( $B^+-C$ ) collisions [50] involving atomic species, theoretical development of viable descriptions of  $AB^+-AB$ ,  $A^+-BC$ ,  $BC^+-A$ ,  $AB^+-CD$  charge-transfer collisions are relatively scarce [8-10,51-61]. This is mainly due to great difficulty of accurate determination of the various electronic interaction matrix elements which are, in general, anisotropic and which involve orbitals based on three and four centers. The added complexity introduced by acknowledgement of vibrational and even rotational transitions (which proceed via the anisotropic part of the interaction) is however tractable, and given the electronic interactions, semiclassical multistate calculations, although time-consuming, are feasible. Bates and Reid [8] have realized the first tractable and simplified multi-vibrational level treatment of charge-transfer between like systems ( $AB^+-AB$ ) which do not involve an electronic transition. Hedrick *et al.* [60] have provided the first detailed account of  $A^+-BC$  and  $BC^+-A$  charge-transfer collisions which involve an electronic transition and have shown (as with Bates and Reid [8]) that direct vibrational excitation is greatly enhanced by coupling with the charge-transfer channel.

In the collision,

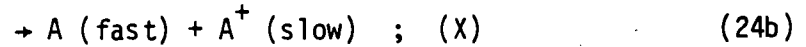
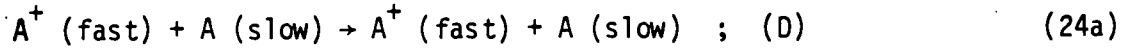


at low and intermediate  $E \lesssim \text{few keV}$ , it can be assumed that only the ground electronic states of each species participate, so that the  $[AB]_2^+$  complex has only two possible electronic states. These represent the active electron remaining either attached to the slow, neutral target  $AB$  - the direct (D) channel, (23a) - or attached to the (fast) projectile ion - the exchange channel (X), (23b). The kinetic energy  $E$  of relative motion of two species each of mass  $M$  (A.M.U.) and moving with relative speed  $u$  (a.u.) is  $\sim 25 M u^2$  (keV) such that for  $E$  sufficiently high  $\gtrsim 10$  eV when the collision duration  $\tau_{\text{coll}} \gg \tau_{\text{rot}}$ , the rotational period, electron-transfer may be considered to occur at a fixed orientation  $\chi$  of each internuclear axis, so that for spherical interactions, rotation of the target and projectile remains unaffected i.e.,  $J_i = J_f$  and  $J_i^+ = J_f^+$ . Vibrational transitions  $v_i^{(+)} \rightarrow v_f^{(+)}$  are however important since  $\tau_{\text{coll}} \gtrsim \tau_{\text{vib}}$ , the vibrational period.

#### 3.1 Two-State Treatment for ( $A^+-A$ ) and $AB^+-AB$ Charge-Transfer

Of all the charge transfer processes involving molecules, (23) is closest in spirit to the symmetric resonance process [50],





between atomic species, insofar as (23b) proceeds via the time-varying field generated by the energy splitting  $\epsilon^+(R) - \epsilon^-(R)$  associated with the bonding and antibonding eigenfunctions, the electronic states of the  $[AB^+-AB]$  complex, which become symmetric or antisymmetric with respect to the mid-point of the separation  $R$  between the center of masses of  $AB^+$  and  $AB$ , only when internuclear vectors  $R_p$  and  $R_T$  of  $AB^+$  and  $AB$ , respectively, are equal and parallel.

Since the bonding-antibonding splitting becomes naturally decoupled, via the Born-Oppenheimer approximation, from the Franck-Condon factors which couple the vibrational states of ion and neutral, (23a) also permits feasible detailed study of characteristics of convergence in the number of vibrational states used in the wavefunction expansion. Also, direct vibrational excitation (23a) is achieved via its close coupling with the charge-transfer channel (23b) normally characterized by large cross sections  $\sim 10 \text{ \AA}^2$  at  $\sim 100 \text{ eV}$ .

For straight line relative motion, the cross section for (24b), which lays the conceptual groundwork for (23b) is [50,8,9]

$$\sigma_{el}^X = 2\pi \int_0^\infty \sin^2 \eta_{el}^X(\rho) \rho d\rho \quad (25)$$

where the phase difference between elastic scattering in each of the gerade and ungerade channels (which are acknowledged by expanding the system wavefunction as a linear combination of gerade (+) and ungerade (-) eigenfunctions of  $A_2^+$ ) is [50,9]

$$\eta_{el}^X = (1/2\hbar) \int_{-\infty}^{\infty} [\epsilon^+(R(t)) - \epsilon^-(R(t))] dt \quad (26)$$

When either an LCAO (linear combination of atomic orbitals) is used for the gerade and ungerade states of  $A_2^+$ , or when the system wavefunctions is expanded in terms of atomic states  $\phi_i^D$ ,  $\phi_f^X$ , based on each center, then (25) follows, with [50,9]

$$\eta_{el}^X = (1/\hbar) \int_{-\infty}^{\infty} V(R(t)) dt \quad (27)$$

where the exchange interaction is given, in general, by [50,9]

$$[1 - |\langle \phi_i^D | \phi_i^X \rangle|^2] V(R) = [\langle \phi_f^X | V^D | \phi_i^D \rangle - \langle \phi_f^X | \phi_i^D \rangle \langle \phi_i^D | V^D | \phi_i^D \rangle], \quad (28a)$$

$$= [\langle \phi_i^D | V^X | \phi_f^X \rangle - \langle \phi_i^D | \phi_f^X \rangle \langle \phi_f^X | V^X | \phi_f^X \rangle], \quad (28b)$$

The initial and final wavefunctions for the active electron attached to the target and projectile ionic cores are  $\phi_i^D(r_1)$  and  $\phi_f^X(r_2)$  respectively, with

$r_2 = R + r_1$ , and  $i = f$  for energy resonance. The electrostatic interaction for the direct (D) channels associated with the fast ion and slow target is  $V^D(r_1, R)$  and, for the exchange (X) channels associated with a fast neutral and slow ion, is  $V^X(r_2, R)$ . Since the bra-ket  $\langle | \rangle$  denotes integration over the coordinate  $r_1$  (or  $r_2$ ) of the active electron, the integrations in (28) involve, in general, one-electron two center integrals. For symmetric resonance processes, the diagonal terms in (28a) and (28b) are equal.

By comparison of (26) and (27), the gerade-ungerade splitting for electronic states in the LCAO approximation may be approximated as

$$\epsilon^+(R) - \epsilon^-(R) = 2V(R) \quad (29)$$

On assuming in (23) that only one pair ( $v_i^+ = v_f^+$ ,  $v_i = v_f$ ) of vibrational levels participate, then on separating the wavefunction for the isolated neutral and ionic molecular systems into their electronic, vibrational and rotational parts (via the Born-Oppenheimer approximation), the charge transfer cross section for (23b) is [52]

$$\sigma^X = 2\pi \int_0^\infty \sin^2 [P_{ii} n_{e1}^X] \rho dp \quad (30)$$

where  $P_{ii}$  is the diagonal element of the matrix  $P$  with element

$$P_{fn} = \langle v_f^+ | v_n \rangle \langle v_n^+ | v_f \rangle \equiv F_{fn} F_{nf} \quad (31)$$

where each (Franck-Condon) positive or negative amplitude  $F_{in}$  is the vibrational overlap for the  $AB^+(v_i^+) \rightarrow AB(v_n)$  transition. The electronic interaction  $V(R)$  in (27) now involves, in general, orbitals on four centers.

The above expression (30), derived originally by Gurnee and Magee [52], is valid in the low energy limit only when the ground vibrational levels of both ion and neutral alone participate in an energy-resonant process. It is the natural generalization of the electronic result (25) for this case. For vibrationally excited ions and ground neutrals, initially, accidental degeneracy can occur when a band of various pairs of ( $v_f^+, v_f$ ) vibrational states is in close energy-resonance with the original pair ( $v_i^+, v_i = 0$ ) so that (30) is inadequate, even at low energies  $E$ . Moreover, as  $E$  is raised, an increasing number of vibrational levels participate in the processes (23).

### 3.2 Multilevel Treatment for ( $AB^+ - AB$ ) Charge-Transfer

The wavefunction for the time dependent response of the internal modes (represented collectively by  $r$ ) of the ( $AB^+ - AB$ ) system under the influence of their mutual electrostatic interaction  $V(r, R(t))$  is expanded as [8]

$$\Psi(r, t) = \sum_{\alpha=D, X} \sum_n A_n^\alpha(t) \phi_n^\alpha(r) \exp(-iE_n^\alpha t/\hbar) \quad (32)$$

in terms of  $\phi_n^\alpha(r)$  which form a complete set of molecular eigenfunctions (with electronic, vibrational and rotational parts) of the unperturbed

Hamiltonian  $H_0$  for the isolated molecular systems with total internal energy  $E_n$  at infinite center-of-mass separation  $R$ . The index  $\alpha$  denotes whether the labelled quantities are associated with the direct (D) channels (23a) or with the charge-transfer (X) channels (23b). Insert (32) into the time-dependent Schrodinger equation, and assume that electronically averaged quantities such as the overlap

$$S(R) = \langle \psi_{el}^D | \psi_{el}^X \rangle_R \quad (33)$$

between the electronic parts  $\psi_{el}^{D,X}$  of the wavefunctions  $\phi_n^{D,X}$  for the D and X channels, and the diagonal distortion (secular) terms

$$V^{DIS}(R) = \langle \psi_{el}^{D,X} | V(R) | \psi_{el}^{D,X} \rangle_R \quad (34)$$

are all independent of each of the internal nuclear separations  $R_P$  and  $R_T$  of the projectile P and target molecules T i.e.,  $S$  and  $V^{DIS}$  are spherical in  $R$  so that rotational state of P and T remains unchanged. By working to lowest order in  $S$ , Bates and Reid [8] then found that the amplitudes,

$$C_n^\alpha(t) = A_n^\alpha(t) \exp(i/\hbar) \int_{-\infty}^t V^{DIS}(R(t)) dt \quad (35)$$

satisfied the following set of coupled equations [8]

$$i\hbar \partial C_f^\alpha / \partial t = V(R) \sum_n P_{fn} \bar{C}_n^\alpha(t) \exp(i\epsilon_{fn} t / \hbar) \quad (36)$$

where

$$V(R) = \langle \psi_{el}^D | V(R) | \psi_{el}^X \rangle - S(R) V^{DIS}(R) \quad (37)$$

is assumed spherical, where  $P_{fn}$  is the product (31) of Franck-Condon amplitudes  $F_{fn}$ , and where  $\epsilon_{fn}$  is the difference ( $\epsilon_f - \epsilon_n$ ) between the combined energies  $\epsilon_f$  of the vibrational levels of the ion and neutral (the small difference between the rotational energies in the D and X channels being neglected). The label  $\bar{\alpha}$  in (36) is D when  $\alpha$  is X and vice versa, i.e., the D channel cannot proceed without participation of the X channels and vice versa. For straight line relative motion, (21a) along the Z-axis, the cross section for charge-transfer ( $\alpha = X$ )

$$\sigma_{if}^\alpha(E) = 2\pi \int_0^\infty |C_f^\alpha(\rho, t \rightarrow \infty)|^2 \rho d\rho \quad (38)$$

reduces to (30) for the energy resonant case, ( $v_i^+ = v_f^+$ ,  $v_i = v_f$ ).

Once the solutions  $\bar{C}_n^\alpha$  are obtained from (36) subject to  $C_f^D(\rho, t \rightarrow \infty) = \delta_{ni}$ ,  $C_f^X(\rho, t \rightarrow \infty) = 0$ , differential cross sections are given by (20) with  $\Delta = 0$ . The use of (21b), rather than (38), permits the additional evaluation of direct elastic integral cross sections. Also the assumption of straight-line relative motion may be removed by the orbital (or energy-conserving method) of McCann and Flannery [37] so that extension to the lower (eV) energies can be obtained [56,40]. It is worth noting that the above

treatment ignores electron translational factors  $\exp(i\mathbf{u} \cdot \mathbf{r})$ , which arise from the momentum change introduced as the active electron jumps from the target to the projectile ion and which become important mainly in the keV region.

At low impact speeds  $u$ , when only these levels  $n$  which form a band in near energy resonance with the initial channel need be included, (since, otherwise the exponent in (36) oscillates rapidly to yield negligible contribution), and at high  $u$ ,  $\exp(i\epsilon_{fn} Z/\hbar u)$  in (36) is effectively unity, the set (36) may then be solved analytically by diagonalization techniques [8].

At high energies this procedure yields [8],

$$\sigma_{if}^X = P_{fi}^2 \sigma_{el}^X(E) \quad ; \quad \sigma_{if}^D = 0 \quad (i \neq f) \quad ; \quad (39)$$

such that the charge transfer cross section  $\sigma_{if}^X$  when summed over all final vibrational levels  $f$  is simply  $\sigma_{el}^X$ , as in the atomic case (25) - (27).

Thus, near energy-resonant channels ( $\epsilon_{fi} \approx 0$ ) with reasonable vibrational overlaps  $P_{fi}$  control the process, at low  $E$ , while  $\sigma_{if}^X$  at large  $E$  is mainly determined by  $P_{fi}$ ; dependence at intermediate  $E$  results from coupling between energy defects  $\epsilon_{fi}$  and  $P_{fi}$ .

The main limitation to application of this theory [(36) and (39)] is the inherent complexity of calculation of the exchange interaction (37) which involves orbitals based on four centers and anisotropic  $V$ . Bates and Reid [8] extended the method of Firsov for the splitting (29) and calculated the D and X cross sections for  $H_2^+(v) - H_2(v=0)$  collisions in the (C.M.) energy range  $1 \text{ eV} \lesssim E \lesssim 25 \text{ keV}$ . Flannery and associates [9,10,51,53-56] investigated, in detail,  $N_2^+-N_2$ ,  $CO^+-CO$ ,  $NO^+-NO$  and  $O_2^+-O_2$  collisions by adopting a prescription due to Sato for (29); and  $H_2^+-H_2$ ,  $D_2^+-D_2$ ,  $T_2^+-T_2$  collisions by using the Bates-Reid interaction. Up to 100 vibrational channels may be coupled. The similar vibrational frequencies of the neutral and ionic species ( $N_2$ ,  $CO$ ) results in a grouping of the energy defects for different vibrational channels into different "bands" separated by approximately one vibrational quanta. The largest vibrational overlaps  $F_{ij}$  are in the near resonant band. Dissimilar vibrational frequencies for the ionic and neutral species ( $NO$ ,  $O_2$ ) prevent this grouping, and large vibrational overlaps are spread over a moderate number of product channels. For ( $H_2$ ,  $D_2$ ,  $T_2$ ), the ionic and neutral vibrational frequencies are dissimilar but the energy defects do, however, exhibit band structure and the vibrational overlaps are spread over a large number of product channels. These characteristics (energy defects versus vibrational overlaps) of these various systems are reflected in the variation of the calculated cross sections [9,10,53-56] with energy  $E$ .

Some calculated cross sections [54] are illustrated in Figure 2 for the

first ten D and X channels with the smallest energy defects for  $H_2^+$  ( $v_i^+ = 0$ ) +  $H_2$  ( $v_i = 0$ ) collisions. At low E, the channels in close energy resonance have the largest cross sections as expected from (30). Above 100 eV-ion energy, the vibrational overlaps start to play an important role and the cross sections are influenced considerably by energy defect and overlap, until at high energies ( $\sim 5$  keV), the vibrational overlaps, in accord with (39), control the relative cross sections which increase with increasing overlap (Figure 2).

Quantitative comparison of theory and measurements is difficult in that the vibrational population of the reactant ions, produced in many experiments by high-energy electron impact, can be questionable due to competition between direct ionization and autoionization. Figure 3 illustrates comparison of theoretical charge transfer cross sections for reactant ions  $H_2^+$  ( $v_i^+ = 0, 1$ ) with various measurements for ions produced mainly in the lower levels ( $v_i^+ = 0, 1$ ) by 16 eV electron impact. At low energies ( $\sim 1$  eV) rearrangement channels which produce  $H_3^+$  and which are not included in the above theory, seriously compete with charge-transfer. Comparison between theory and measurements for other systems may be found in the review by Moran [51].

Within the Bates-Reid method, Smirnov and associates [57] determined the matrix element  $V(R)$  of (37) by asymptotic methods (which are based on the assumption that electron transfer occurs at distances R large compared with molecular dimensions). They were then able to extract both the spherical and anisotropic parts of  $V(R)$  from Hartree-Fock one electron wavefunctions for a wide range of systems.

Since the main limitation to application of the Bates-Reid method is a lack of reliable data on the exchange interaction, Borkman and Cobb [69] have recently computed ab-initio potential-energy curves for the  $H_2^+-H_2$  complex using SCF (self consistent field) and CI (configuration interaction) techniques. This is the only comprehensive study yet available for  $AB^+-AB$  system, is extremely time consuming, and indicates that the interaction  $V(R)$  is extremely anisotropic. Rotational excitation is therefore expected to be important for  $E \lesssim 100$  eV or so. Lee and De Pristo [70] have recently found agreement between their simple model of  $V(R)$  and the ab-initio results.

De Pristo [40] adopted the orbital (or energy-conserving) method of McCann and Flannery [37,56], rather than the straight-line relative motion, within the Bates-Reid treatment, and has shown good-excellent agreement with the

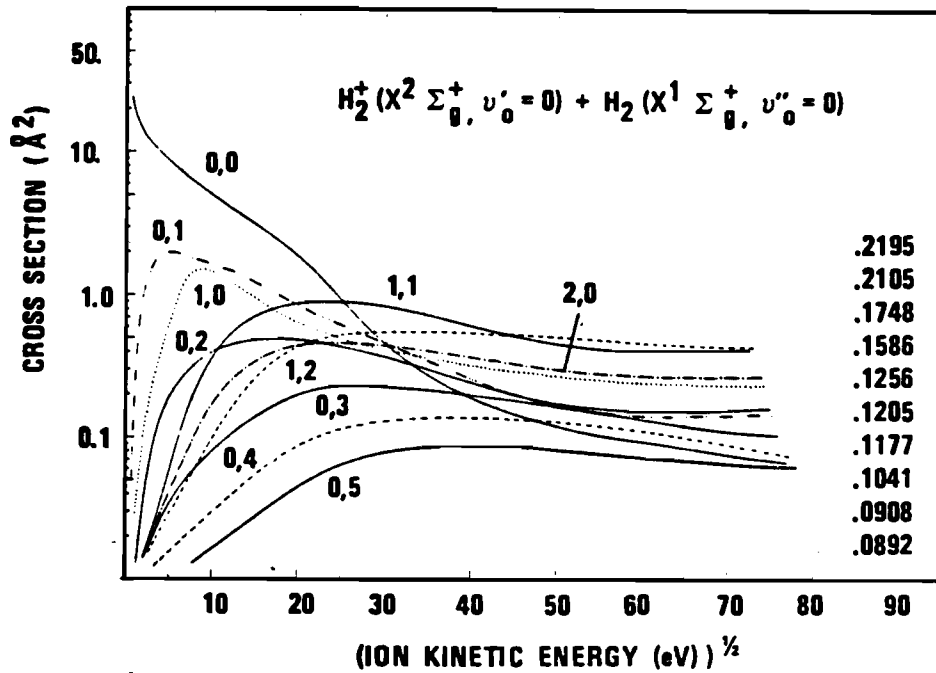


Fig. 2. State-to-state ( $v_i^+ = 0, v_i = 0$ )  $\rightarrow$  ( $v_f, v_f^+$ ) charge-transfer cross sections; ( $v_f, v_f^+$ ) label each curve which at high energy become arranged in order of the indicated vibrational overlaps  $P_{fi}$  (from [54]).

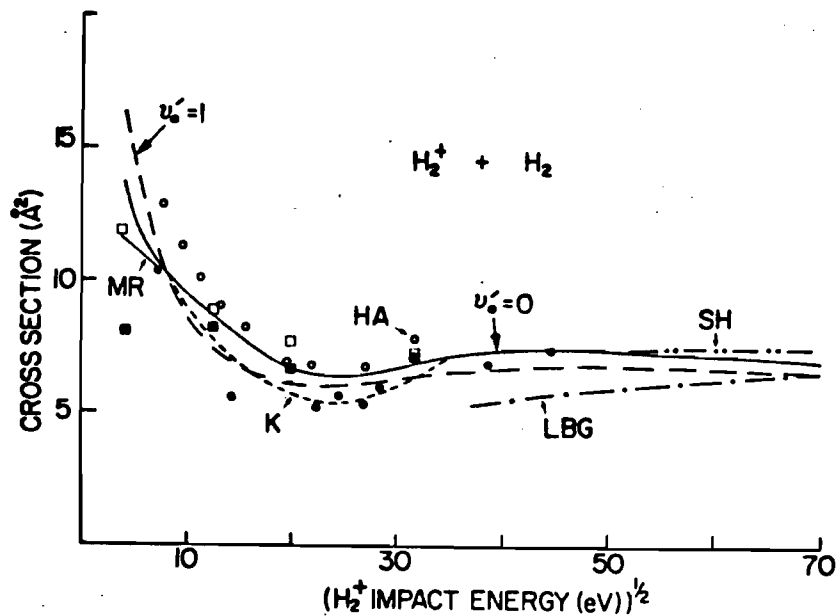


Fig. 3. Present theoretical (labelled  $v_0' = 0, 1$ ) and various experimental (SH [62], K [63], MR [64], LBG [65], HA [66],  $\bullet$  [67], ( $\blacksquare$ ,  $v_0' = 0$ ;  $\square$ ,  $v_0' = 1$ ) [68]) cross sections for  $H_2^+(X^2 \Sigma_g^+, v_0') - H_2(X^1 \Sigma_g^+, v_i = 0)$  charge-transfer collisions (from [51] and [54]).

only full quantal treatment performed by Becker [59] for  $O_2^+-O_2$  charge transfer collisions at 8 and 36 eV (C.M.). Finally Sears and De Pristo [58] have recently developed a simple number scaling relationship in which they assert that the entire set of unknown state-to-state cross sections can be generated from one cross section and two parameters based on overlaps, energy defects and collision durations. It essentially represents an effort to extend the exact parametric dependence (39) at high energies down to lower energies by acknowledging interplay between  $\epsilon_{fi}$  and  $P_{fi}$ .

### 3.3 Multistate Treatment of $(A^+-BC)$ and $(BC^+-A)$ Charge Transfer

For unlike (asymmetric) systems, Hedrick *et al.* [60] expand the system wavefunction as (32) and find that the amplitudes  $A_n^{D,X}(t)$  satisfy the set of coupled equations,

$$i\hbar[\dot{A}_f^X + S_{21} \sum_n \dot{A}_n^D F_{fn} \exp(iE_{fn}^{XD}t/\hbar)] = V_{21}^D \sum_n A_n^D F_{fn} \exp(iE_{fn}^{XD}t/\hbar) + V_{22}^X A_f^X \quad (40a)$$

$$i\hbar[\dot{A}_f^D + S_{12} \sum_n \dot{A}_n^X F_{nf} \exp(iE_{fn}^{DX}t/\hbar)] = V_{12}^X \sum_n A_n^X F_{nf} \exp(iE_{fn}^{DX}t/\hbar) + V_{11}^D A_f^D \quad (40b)$$

where  $F_{fn}$  is the Franck-Condon amplitude  $\langle v_f^+ | v_n \rangle$  for  $BC^+(v_f^+) \rightarrow BC(v_n)$  transitions, and where  $E_{fn}^{\alpha\beta} = E_f^\alpha - E_n^\beta$ , the combined electronic and vibrational energy defects between the D and X channels. The matrix elements

$$\left. \begin{aligned} \langle \phi_f^D | V^D(\underline{r}, \underline{R}) | \phi_n^D \rangle_{\underline{r}} &= [\langle \phi | V^D | \phi \rangle \equiv V_{11}^D(R)] \delta_{vib} \delta_{rot} \\ \langle \phi_f^D | V^X(\underline{r}, \underline{R}) | \phi_n^X \rangle_{\underline{r}} &= [\langle \phi | V^X | \psi_X \rangle \equiv V_{12}^X(R)] F_{nf} \delta_{rot} \\ \langle \phi_f^D | \phi_n^X \rangle_{\underline{r}} &= [\langle \phi | \psi_X \rangle \equiv S_{12}(R)] F_{nf} \delta_{rot} \end{aligned} \right\} \quad (41a)$$

$$\left. \begin{aligned} \langle \phi_f^X | V^X(\underline{r}, \underline{R}) | \phi_n^X \rangle_{\underline{r}} &= [\langle \psi_X | V^X | \psi_X \rangle \equiv V_{22}^X(R)] \delta_{vib} \delta_{rot} \\ \langle \phi_f^X | V^D(\underline{r}, \underline{R}) | \phi_n^D \rangle_{\underline{r}} &= [\langle \psi_X | V^D | \phi \rangle \equiv V_{21}^X(R)] F_{fn} \delta_{rot} \\ \langle \phi_f^X | \phi_n^D \rangle_{\underline{r}} &= [\langle \psi_X | \phi \rangle \equiv S_{21}(R)] F_{fn} \delta_{rot} \end{aligned} \right\} \quad (41b)$$

represent various  $\underline{r}$ -averages of the direct interaction  $V_D$  between  $A^+$  and BC, and of the exchange interactions  $V^X$  between A and  $BC^+$  over post and prior electronic wavefunctions ( $\phi$  for BC alone,  $\psi$  for  $BC^+$ ,  $\chi$  for the one-electron orbital of A), and over vibrational and rotational wavefunctions for BC and  $BC^+$ . The incident speed as before (§ 3) is sufficiently large that rotational transitions are neglected (and  $V_{ij}$  are assumed to be independent of orientation of the internal internuclear vectors of BC and  $BC^+$  and hence of the orientation of  $\underline{R}$ , the relative channel vector between  $A^+$  and BC). In contrast to the elastic bonding and antibonding channels in the  $AB^+-AB$  case (§ 3.2), charge-transfer occurs here via an electronic

transition between distinct electronic states 1 and 2 of different asymptotic energies and represented by electronic wavefunctions  $\phi$  and  $\psi_X$ . Also  $V_{11}^D \neq V_{22}^X$ ,  $V_{21}^D \neq V_{12}^X$ , in contrast with the symmetric case (§ 3.2), and the overlap  $S_{12}$  cannot in general be neglected. We note, with the aid of (34) that the set (40) reduces to (36) for equal distortion terms  $V_{jj}^{D,X} (\equiv V_{jj}^{DIS}, j = 1, 2)$  in the D and X channels, when the electronic overlap  $S_{if}$  is neglected, and when  $F_{fn}$  is naturally replaced by  $P_{fn}$ . For the case of one (incident) D channel and n-X channels, (40) reduces to a simplified set [60].

Hedrick et al. [60] calculated differential and integral cross sections (20) and (21) from the solution of (40) for  $\text{Ar}^+ - \text{H}_2$  collisions at ion energies between 0.9 and 3.5 keV. The interactions in (41) were computed directly from simple analytical electronic wavefunctions for  $\text{H}_2$  and  $\text{H}_2^+$  and from an analytic fit to the numerical 3p-orbital for Ar. Fair agreement with experiment was obtained.

More recently, Sidis and de Bruijn [61] have given similar theory as above but used asymptotic methods to determine the various interactions for  $\text{H}_2^+ - \text{Mg}$  collisions.

#### 4. Conclusion

We have therefore discussed, in § 1 of this Chapter various aspects of ion-molecule collisions. We have then presented in § 2 a theory suitable for differential and integral cross sections for rotational transitions with extension to vibrational transitions. In § 3, a theory which couples reactive (charge-transfer) and inelastic (vibrational excitation) scattering is described for charge-transfer and vibrational excitation in like ( $\text{AB}^+ - \text{AB}$ ) and unlike ( $\text{A}^+ - \text{BC}$ ) systems. A natural combination of the treatments in § 2 and § 3 would permit the additional coupling of rotational transitions to the present theory in § 3. This coupling would be mainly important for collision energies  $E < 100$  eV, but would, however, place great emphasis on accurate determination of ion-molecule bonding and antibonding anisotropic interactions, which at this stage are only (partially) known for the  $\text{H}^+ - \text{H}_2$  [29],  $\text{Li}^+ - \text{H}_2$  [19],  $\text{Li}^+ - \text{N}_2$  [27] and  $\text{H}_2^+ - \text{H}_2$  [69] systems.

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