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A comparison of polarized double-zeta basis sets and natural orbitals for full configuration interaction benchmarks

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We compare several standard polarized double-zeta basis sets for use in full configuration interaction benchmark computations. The 6-31G^{**}, DZP, cc-pVDZ, and Widmark–Malmqvist–Roos atomic natural orbital (ANO) basis sets are assessed on the basis of their ability to provide accurate full configuration interaction spectroscopic constants for several small molecules. Even though highly correlated methods work best with larger basis sets, predicted spectroscopic constants are in good agreement with experiment; bond lengths and harmonic vibrational frequencies have average absolute errors no larger than 0.017 Å and 1.6%, respectively, for all but the ANO basis. For the molecules considered, 6-31G^{**} gives the smallest average errors, while the ANO basis set gives the largest. The use of variationally optimized basis sets and natural orbitals are also explored for improved benchmarking. Although optimized basis sets do not always improve predictions of molecular properties, taking a DZP-sized subset of the natural orbitals from a singles and doubles configuration interaction computation in a larger basis significantly improves results. © 2003 American Institute of Physics. [DOI: 10.1063/1.1532313]

I. INTRODUCTION

Wave function based quantum chemical methods approach the exact solution to the electronic Schrödinger equation as the basis set and the treatment of electron correlation are simultaneously improved. In recent years, considerable progress has been made in understanding convergence toward the complete basis set limit.^{1–7} It has been more challenging to investigate the convergence of electron correlation because full configuration interaction (FCI), which provides the exact solution of the electronic Schrödinger equation within a given basis set, has a computational cost that increases factorially with the number of electrons or orbitals.

Fortunately, both algorithmic advances^{8–15} and improvements in computer hardware have made full CI benchmarks less computationally expensive. Whereas full CI benchmarking in the 1980s and early 1990s focused almost exclusively on single-point energies, it is now possible to perform geometry optimizations and even frequency analysis for very small molecules using full CI to examine the effect of higher-order correlation on molecular properties.^{16–24} It is also now possible to afford enough full CI computations to generate potential energy curves,^{25–28} which are beneficial for assessing the reliability of standard quantum chemistry methods for bond-breaking reactions.

In light of these expanded possibilities, it is important to ask which basis sets are best for full CI benchmarking. Since full CI computations with basis sets larger than polarized double-zeta are rarely possible, we compare several standard basis sets of this size to determine their suitability for the computation of full CI molecular properties. Specifically, Dunning's DZP and cc-pVDZ basis sets, Pople's 6-31G^{**}

basis,³⁰ and the Widmark–Malmqvist–Roos atomic natural orbital (WMR ANO) polarized³¹ double zeta basis sets^{1,29–31} are used to compute spectroscopic constants for the ground states of the BH, CH⁺, NH, OH⁺, HF, and C₂ molecules.

The use of variationally optimized scale factors and natural orbitals are examined for their ability to provide improved one-particle spaces for the full CI. Natural orbitals (NO's) are those orbitals which diagonalize the one-particle density matrix; they provide the most rapidly convergent CI expansion in the sense that to achieve a given accuracy requires fewer configurations in a natural orbital basis than in any other orthonormal basis for a given underlying one-particle space.³² The NO's are ordered according to their occupation numbers (one-particle density matrix eigenvalues), and larger occupation numbers reflect larger contributions to the CI wave function from which the orbitals are derived. Hence, one might expect that the most important *m* orbitals from a natural orbital computation should provide a compact orbital subspace for a subsequent full CI computation. Here we investigate the efficiency of performing CI singles and doubles (CISD) computations in the large cc-pVQZ basis set and taking the *m* most important NO's, where *m* is equal to the number of orbitals present in a polarized double-zeta basis. This procedure gives far better results than any of the standard basis sets considered.

II. THEORETICAL APPROACH

Several spectroscopic constants and dissociation energies of the ground states of BH, CH⁺, NH, OH⁺, HF, and C₂ were determined using the full CI method as implemented in the DETCI program³³ in PSI 3.0.³⁴

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TABLE I. Spectroscopic constants for $X^1\Sigma^+$ of BH.^a

Method	Energy	r_e	ω_e	$\omega_e x_e$	B_e	\bar{D}_e	α_e	D_e
FCI/DZP	-25.208881	1.2491	2339	47.6	11.700	0.12e-02	0.399	3.48
FCI/6-31G**(5d)	-25.206493	1.2346	2392	52.2	11.977	0.12e-02	0.429	3.51
FCI/6-31G**	-25.207157	1.2344	2388	52.0	11.980	0.12e-02	0.431	3.51
FCI/cc-pVDZ	-25.215324	1.2559	2340	48.8	11.574	0.11e-02	0.396	3.44
FCI/cc-pVDZ(6d)	-25.216182	1.2553	2343	49.0	11.584	0.11e-02	0.398	3.44
FCI/WMR-ANO	-25.214743	1.2675	2309	49.5	11.364	0.11e-02	0.388	3.47
FCI/6-31G**(opt)	-25.211093	1.2446	2376	52.5	11.786	0.12e-02	0.415	3.49
FCI/DZP-NO	-25.229338	1.2366	2354	50.9	11.940	0.12e-02	0.457	3.57
FCI/DZP-NO(5Z)	-25.229704	1.2362	2350	51.8	11.948	0.12e-02	0.446	3.57
Experiment		1.2324	2367	49.4	12.021	0.12e-02	0.412	3.57

^aEnergies in hartrees, r_e in Å, D_e in eV, and other quantities in cm^{-1} .

The customary rotational and vibrational energy level expressions for a diatomic molecule are

$$F_v(J) = B_v J(J+1) - \bar{D}_v [J(J+1)]^2 \cdots, \quad (1)$$

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 \cdots, \quad (2)$$

with B_v and \bar{D}_v defined as

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) \cdots, \quad (3)$$

$$\bar{D}_v = \bar{D}_e + \beta_e(v + \frac{1}{2}) + \cdots. \quad (4)$$

We have determined the harmonic vibrational frequency, ω_e , anharmonicity constant, $\omega_e x_e$, rotational constant, B_e , vibration-rotation coupling constant, α_e , and the centrifugal distortion constant, \bar{D}_e , using second through fourth-order force constants, $f_{rr} - f_{rrrr}$. The force constants were computed using tightly converged energies ($\sim 10^{-10}$ hartrees) from 5 geometries equally distributed around the equilibrium bond distance. The dissociation energies were computed using the supermolecule approach for all cases.³⁵

Computations were performed using five standard basis sets. The 6-31G** basis set is contracted as (10s4p1d/3s2p1d) and (4s1p/2s1p) for first-row elements and hydrogen, respectively.³⁰ The Huzinaga–Dunning DZP basis set^{29,36} is contracted as (9s5p1d/4s2p1d) and (4s1p/2s1p), and Dunning’s correlation consistent cc-pVDZ basis set¹ is contracted as (9s4p1d/3s2p1d) and (4s1p/2s1p). The WMR-ANO basis set is contracted as (14s9p4d/3s2p1d) and (8s4p/2s1p).³¹ The five basis sets use a different number of d functions; 6-31G**, DZP, and WMR-ANO use six Cartesian d functions, while it is cus-

tomary to use five pure angular momentum d functions for cc-pVDZ. The effect of varying the number of d polarization functions was examined by using cc-pVDZ with 6 Cartesian d functions and 6-31G** with 5 pure angular momentum d functions, designated cc-pVDZ(6d) and 6-31G**(5d), respectively.

To investigate the possibility of improving results without increasing the size of the basis, a modified 6-31G** basis for BH was constructed by optimizing a scale factor for each atom, i.e., the primitive Gaussian exponents are multiplied by the square of the scale factor (excluding the core function). This basis set is denoted 6-31G**(opt). In an alternative strategy, separate CISD/cc-pVQZ natural orbital computations were performed at each geometry and the NO’s with the largest occupation numbers were retained to form a set of molecular orbitals, denoted DZP-NO, having the same number of orbitals as cc-pVDZ (the remaining weakly occupied NO’s were discarded). Core orbitals were constrained to be doubly-occupied in all computations, and for the DZP basis the corresponding high-lying virtual orbitals were deleted.

III. RESULTS AND DISCUSSION

Total electronic energies and spectroscopic constants are presented in Tables I (BH), II (CH⁺), III (NH), IV (OH⁺), V (HF), and VI (C₂). Experimental results are taken from Huber and Herzberg³⁷ except for CH⁺, where results are from Carrington and Ramsey³⁸ (the Huber and Herzberg value for ω_e of CH⁺, cited in many theoretical works, is more than 100 cm^{-1} too low). Experimental dissociation en-

TABLE II. Spectroscopic constants for $X^1\Sigma^+$ of CH⁺.^a

Method	Energy	r_e	ω_e	$\omega_e x_e$	B_e	\bar{D}_e	α_e	D_e
FCI/DZP	-38.004943	1.1365	2923	66.2	14.038	1.29e-03	0.503	4.02
FCI/6-31G**(5d)	-37.998840	1.1246	2939	66.9	14.334	1.36e-03	0.532	3.97
FCI/6-31G**	-38.000644	1.1241	2939	67.1	14.350	1.37e-03	0.537	3.98
FCI/cc-pVDZ	-38.002366	1.1460	2892	64.6	13.807	1.26e-03	0.492	3.97
FCI/cc-pVDZ(6d)	-38.003779	1.1449	2898	65.9	13.843	1.26e-03	0.497	3.94
FCI/WMR-ANO	-38.002902	1.1623	2805	58.8	13.421	1.23e-03	0.457	3.94
FCI/DZP-NO	-38.023851	1.1319	2840	59.3	14.153	1.41e-03	0.495	4.15
Experiment ^b		1.1309	2858	59.3	14.176	1.37e-03	0.493	4.27

^aEnergies in hartrees, r_e in Å, D_e in eV, and other quantities in cm^{-1} .

^bExperimental data from Carrington and Ramsey (Ref. 38).

TABLE III. Spectroscopic constants for $X^3\Sigma^-$ of NH .^a

Method	Energy	r_e	ω_e	$\omega_e x_e$	B_e	\bar{D}_e	α_e	D_e
FCI/DZP	-55.100022	1.0514	3246	84.3	16.217	0.16e-02	0.665	3.23
FCI/6-31G**(5d)	-55.086860	1.0452	3261	84.9	16.411	0.17e-02	0.678	3.17
FCI/6-31G**	-55.089073	1.0442	3267	85.6	16.442	0.17e-02	0.686	3.18
FCI/cc-pVDZ	-55.091952	1.0564	3188	81.8	16.065	0.16e-02	0.656	3.11
FCI/cc-pVDZ(6d)	-55.093831	1.0555	3191	82.1	16.091	0.16e-02	0.661	3.12
FCI/WMR-ANO	-55.104542	1.0608	3206	81.4	15.933	0.16e-02	0.631	3.23
FCI/DZP-NO	-55.126410	1.0400	3246	80.5	16.578	0.17e-02	0.663	3.35
Experiment		1.0362	3282	78.4	16.699	0.17e-02	0.649	3.68

^aEnergies in hartrees, r_e in Å, D_e in eV, and other quantities in cm^{-1} .

ergies D_0 have been converted to D_e using ω_e and $\omega_e x_e$ for a more direct comparison to the theoretically computed results. Table VII presents average absolute errors for the set of molecules considered.

A. Comparison of standard basis sets

In general, improved descriptions of electron correlation result in larger predicted bond lengths, while larger basis sets result in shorter predicted bond lengths. Systematic studies have shown that highly correlated methods such as CCSD(T) can require large basis sets (often triple or quadruple zeta) to provide very accurate predictions of bond lengths,^{39,40} although CCSD(T) harmonic vibrational frequencies are predicted surprisingly well by the modest DZP or cc-pVDZ basis sets.⁴¹ One might expect that full CI, representing the complete treatment of electron correlation for a given basis set, might require even larger basis sets. However, the present full CI spectroscopic constants are generally in good agreement with experiment. Bond lengths are systematically overestimated, with the most severe overestimates occurring for the WMR ANO basis (errors of about 0.03 Å for BH, CH^+ , and C_2). The average absolute errors (cf. Table VII) are around 0.01–0.02 Å for the standard basis sets except for 6-31G**, which gives lower errors of 0.007 Å. This compares to an average overestimation of 0.02 Å for single bonds in several small molecules at the CCSD(T)/cc-pVDZ level of theory reported by Martin;³⁹ hence, the basis requirements of full CI do not seem significantly different from those of CCSD(T). The rotational constant B_e , which depends on the equilibrium bond length, is likewise predicted most accurately for 6-31G** (1.2% error) and least accurately for WMR-ANO (4.3% error).

Although most quantum chemical methods generally overestimate harmonic vibrational frequencies, highly correlated methods such as CCSD(T) occasionally underestimate them.³⁹ Here, too, we find that several full CI harmonic vibrational frequencies underestimate experiment. The WMR ANO basis, which gives the largest overestimations of bond lengths, usually provides the lowest predicted vibrational frequencies. The average absolute errors for harmonic frequencies are close to 1%–2% for any of the standard basis sets considered, which is again similar to the average error in CCSD(T)/cc-pVDZ harmonic frequencies reported by Martin.³⁹ Vibrational anharmonicities are predicted with roughly similar accuracies for all of the standard basis sets (4%–7%), although cc-pVDZ is best on average. Likewise, predictions of vibration-rotation interaction constants α_e are of comparable quality across the standard basis sets (3%–5% errors). These results compare to average absolute errors of 6%–9% ($\omega_e x_e$) and 5%–8% (α_e) for CCSD(T) with polarized double-zeta basis sets for a few diatomic molecules.⁴² Centrifugal distortion constants, depending on B_e and ω_e , are predicted best by 6-31G** and with roughly similar accuracy among the other standard basis sets.

Dissociation energies are more challenging to compute because accurate estimates can require very large basis sets. For example, in N_2 , i -type polarization functions were found to contribute 0.4 kcal mol⁻¹ to the dissociation energy.⁴³ For the standard polarized double-zeta basis sets considered, the errors in D_e are generally within 0.5 eV except for HF and C_2 , and the average absolute errors are 8%–10%. The 6-31G** and DZP basis sets perform slightly better on average. The full CI results underestimate D_e because the po-

TABLE IV. Spectroscopic constants for $X^3\Sigma^-$ of OH^+ .^a

Method	Energy	r_e	ω_e	$\omega_e x_e$	B_e	\bar{D}_e	α_e	D_e
FCI/DZP	-75.113655	1.0347	3173	89.8	16.606	0.18e-02	0.763	4.76
FCI/6-31G**(5d)	-75.092302	1.0323	3165	87.8	16.682	0.19e-02	0.757	4.80
FCI/6-31G**	-75.094766	1.0323	3161	86.1	16.684	0.19e-02	0.756	4.80
FCI/cc-pVDZ	-75.110738	1.0383	3123	81.8	16.492	0.18e-02	0.719	4.73
FCI/cc-pVDZ(6d)	-75.112752	1.0377	3124	81.1	16.511	0.18e-02	0.718	4.74
FCI/WMR-ANO	-75.124602	1.0397	3103	89.9	16.448	0.18e-02	0.769	4.66
FCI/DZP-NO	-75.157488	1.0287	3121	83.0	16.804	0.19e-02	0.746	5.10
Experiment		1.0289	3113	78.5	16.794	0.19e-02	0.749	5.29

^aEnergies in hartrees, r_e in Å, D_e in eV, and other quantities in cm^{-1} .

TABLE V. Spectroscopic constants for $X^1\Sigma^+$ of HF.^a

Method	Energy	r_e	ω_e	$\omega_e x_e$	B_e	\bar{D}_e	α_e	D_e
FCI/DZP	-100.242690	0.9243	4173	94.7	20.618	2.01e-03	0.794	5.74
FCI/6-31G**(5d)	-100.199160	0.9213	4171	97.2	20.750	2.05e-03	0.822	5.55
FCI/6-31G**	-100.201597	0.9214	4172	95.0	20.746	2.05e-03	0.813	5.56
FCI/cc-pVDZ	-100.228652	0.9202	4144	92.8	20.799	2.10e-03	0.806	5.49
FCI/cc-pVDZ(6d)	-100.231198	0.9200	4147	92.7	20.810	2.10e-03	0.804	5.50
FCI/WMR-ANO	-100.277950	0.9286	4068	92.5	20.428	2.06e-03	0.797	5.81
FCI/DZP-NO	-100.308531	0.9189	4126	90.5	20.862	2.13e-03	0.791	5.74
Experiment		0.9168	4138	89.9	20.956	2.15e-03	0.798	6.13

^aEnergies in hartrees, r_e in Å, D_e in eV, and other quantities in cm^{-1} .

larized double-zeta basis sets are not sufficient to accurately describe dynamic electron correlation around equilibrium.

Since the basis set requirements for CI singles and doubles (CISD) are less severe than for full CI, it is possible for CISD to be more accurate than full CI when a polarized double-zeta basis set is used. For the CISD/cc-pVDZ level of theory, the average absolute errors in spectroscopic constants of the first row hydrides⁵ are 0.013 Å (r_e), 0.7% (ω_e), 3.0% ($\omega_e x_e$), 2.2% (B_e), 3.7% (α_e), and 11% (D_e). These results are comparable to and in some cases slightly better than our present full CI results due to a cancellation of errors between the CISD approximation and the limited cc-pVDZ basis set. This error cancellation cannot happen for full CI, since the treatment of electron correlation is exact. Fortunately, however, this lack of error cancellation between full CI and polarized double-zeta basis sets does not lead to large errors in predicted spectroscopic constants. This suggests that basis sets of this size are already large enough for meaningful benchmark studies on the effects of higher levels of electron correlation on molecular properties.

In the present study, 6 d functions were used for the 6-31G**, DZP, and WMR-ANO basis sets. One might suppose that the additional d function could offer a slight advantage to these basis sets. This possibility was explored by performing additional computations with the cc-pVDZ basis using 6 d functions, denoted cc-pVDZ(6d); spectroscopic constants changed very little compared to 5 d functions, with bond lengths shortening by about 0.001 Å or less and frequencies changing by just a few cm^{-1} . This suggests that 6 d functions offer very little advantage over 5, while the computational cost of adding an additional d function per heavy atom will increase the cost of the full CI significantly. The differences between 6-31G**(5d) and 6-31G**(6d) are

also insignificant, thus supporting the idea of using pure angular momentum d functions if limited by computational resources.

Overall, the average absolute errors in Table VII show that full CI properties computed with the 6-31G** basis are generally better than for the other standard basis sets considered, while the WMR ANO basis gives some of the largest errors compared to experiment. However, except for bond lengths, there is not a large difference among the basis sets considered.

B. Variationally optimized basis sets

We investigated the possibility of obtaining better results using optimized basis sets. For BH, the 6-31G** basis was modified by optimizing the scale factors for the boron and hydrogen valence functions to give the lowest full CI energy at $R(\text{B-H})=1.20$ Å. The scale factors thus obtained were 0.93 (B) and 0.92 (H), and the optimized basis sets multiplied the primitive Gaussian exponents by the square of the scale factor except for the primitives comprising the B 1s function. The resulting spectroscopic constants in Table I, labeled 6-31G**(opt), are improved in some cases, but worse for others compared to the regular 6-31G** basis. The equilibrium bond length prediction is made worse by 0.01 Å.

C. Using natural orbitals to obtain correlating orbitals for full CI benchmarks

As discussed in the Introduction, natural orbitals can provide a very compact orbital subspace for use in CI computations. Here we obtained CISD/cc-pVQZ natural orbitals and deleted the most weakly occupied NO's to achieve the

TABLE VI. Spectroscopic constants for $X^1\Sigma_g^+$ of C_2 .^a

Method	Energy	r_e	ω_e	$\omega_e x_e$	B_e	\bar{D}_e	α_e	D_e
FCI/DZP	-75.731641	1.2695	1813	13.3	1.743	6.44e-06	0.017	5.74
FCI/6-31G**(5d)	-75.723459	1.2603	1859	13.1	1.769	6.40e-06	0.017	6.00
FCI/6-31G**	-75.726127	1.2596	1859	13.2	1.771	6.43e-06	0.017	5.99
FCI/cc-pVDZ	-75.729852	1.2727	1813	13.5	1.734	6.35e-06	0.017	5.67
FCI/cc-pVDZ(6d)	-75.732244	1.2717	1814	13.6	1.737	6.37e-06	0.017	5.69
FCI/WMR-ANO	-75.732305	1.2793	1766	15.8	1.716	6.49e-06	0.018	5.44
FCI/DZP-NO	-75.766448	1.2500	1834	12.8	1.797	6.90e-06	0.017	5.99
Experiment		1.2425	1855	13.3	1.820	6.92e-06	0.018	6.33

^aEnergies in hartrees, r_e in Å, D_e in eV, and other quantities in cm^{-1} .

TABLE VII. Average absolute error of the molecular test set.^a

Method	r_e	ω_e	$\omega_e x_e$	B_e	\bar{D}_e	α_e	D_e
FCI/DZP	0.013	1.6	7.3	2.2	5.1	2.6	7.7
FCI/6-31G** (5d)	0.007	1.2	8.0	1.3	2.1	4.4	7.8
FCI/6-31G**	0.007	1.1	7.3	1.2	2.0	4.6	7.7
FCI/cc-pVDZ	0.017	1.3	3.9	2.9	6.3	2.6	9.6
FCI/cc-pVDZ (6d)	0.016	1.3	4.2	2.8	6.3	2.8	9.6
FCI/WMR-ANO	0.025	2.2	6.9	4.3	6.7	3.1	9.0
FCI/DZP-NO	0.003	0.7	2.7	0.6	0.7	3.4	4.5

^aErrors in bond lengths are in Å and other quantities are in %.

same number of orbitals as in a polarized double-zeta basis set like cc-pVDZ. Full CI computations were then performed in this truncated natural orbital set denoted DZP-NO.

The equilibrium full CI energies are much lower with the DZP-NO orbitals than for any of the standard basis sets, and the spectroscopic constants are much more reliable on average. The average absolute error in r_e drops to a mere 0.003 Å, while for ω_e it is reduced to 0.7%. Similarly, B_e , \bar{D}_e , and the dissociation energy are all improved substantially. The quality of the DZP-NO results does not appear to improve significantly by using a larger basis to generate the natural orbitals. For BH, the natural orbitals were also obtained from the cc-pV5Z basis, yielding a set labeled DZP-NO (5Z) in Table I; the results are very similar to the cc-pVQZ generated DZP-NO values.

IV. CONCLUSIONS

Several standard polarized double-zeta basis sets have been compared for their suitability in full configuration interaction benchmarking by determining their reliability for the spectroscopic constants of several diatomics. The performance of the basis sets is similar, but 6-31G** is better on average. Although full CI might be expected to have very large basis set requirements, the predicted spectroscopic constants are in good agreement with experiment and exhibit errors similar to those of CCSD(T) and not much worse than CISD with similar basis sets. This suggests that the effects on molecular properties of electron correlation beyond CCSD(T) can be reasonably examined in DZP-sized basis sets. The optimization of basis scaling factors did not significantly improve spectroscopic constants for BH. The use of DZP-sized sets of natural orbitals gave results far superior to those of the standard basis sets and may provide considerably more rapid convergence to the complete basis set limit for highly correlated wave functions.

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- ¹T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ²V. Termath, W. Klopper, and W. Kutzelnigg, *J. Chem. Phys.* **94**, 2002 (1991).
- ³R. A. Kendall, T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ⁴D. E. Woon and T. H. Dunning, *J. Chem. Phys.* **99**, 1914 (1993).
- ⁵K. A. Peterson, R. A. Kendall, and T. H. Dunning, *J. Chem. Phys.* **99**, 1930 (1993).
- ⁶J. W. Ochterski, G. A. Petersson, and J. A. Montgomery, *J. Chem. Phys.* **104**, 2598 (1996).
- ⁷A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* **286**, 243 (1998).
- ⁸J. Olsen, B. O. Roos, P. Jørgensen, and H. J. Aa. Jensen, *J. Chem. Phys.* **89**, 2185 (1988).
- ⁹R. J. Harrison and S. Zarrabian, *Chem. Phys. Lett.* **158**, 393 (1989).
- ¹⁰A. V. Luzanov, A. L. Wulfov, and V. O. Krouglov, *Chem. Phys. Lett.* **197**, 614 (1992).
- ¹¹G. L. Bendazzoli and S. Evangelisti, *Int. J. Quantum Chem., Quantum Chem. Symp.* **27**, 287 (1993).
- ¹²A. O. Mitrushenkov and Y. Y. Dmitriev, *Chem. Phys. Lett.* **235**, 410 (1995).
- ¹³A. Povill and J. Rubio, *Theor. Chim. Acta* **92**, 305 (1995).
- ¹⁴S. Evangelisti, G. L. Bendazzoli, R. Ansaloni, and E. Rossi, *Chem. Phys. Lett.* **233**, 353 (1995).
- ¹⁵H. Dachsel, H. Lischka, R. Shepard, J. Nieplocha, and R. J. Harrison, *J. Comput. Chem.* **18**, 430 (1997).
- ¹⁶C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.* **86**, 858 (1987).
- ¹⁷C. W. Bauschlicher, *J. Phys. Chem.* **92**, 3020 (1988).
- ¹⁸C. W. Bauschlicher, S. R. Langhoff, H. Partridge, and D. P. Chong, *J. Chem. Phys.* **89**, 2985 (1988).
- ¹⁹J. Olsen, A. M. Sánchez de Meras, H. J. Aa. Jensen, and P. Jørgensen, *Chem. Phys. Lett.* **154**, 380 (1989).
- ²⁰H. Koch and R. J. Harrison, *J. Chem. Phys.* **95**, 7479 (1991).
- ²¹J. M. Galbraith, G. Vacek, and H. F. Schaefer, *J. Mol. Struct.* **300**, 281 (1993).
- ²²J. M. Anglada and J. M. Bofill, *Theor. Chim. Acta* **92**, 369 (1995).
- ²³C. D. Sherrill, M. L. Leininger, T. J. Van Huis, and H. F. Schaefer, *J. Chem. Phys.* **108**, 1040 (1998).
- ²⁴M. L. Leininger, C. D. Sherrill, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **108**, 6717 (1998).
- ²⁵T. van Mourik and J. H. van Lenthe, *J. Chem. Phys.* **102**, 7479 (1995).
- ²⁶J. Olsen, P. Jørgensen, H. Koch, A. Balková, and R. J. Bartlett, *J. Chem. Phys.* **104**, 8007 (1996).
- ²⁷H. Larsen, J. Olsen, P. Jørgensen, and O. Christiansen, *J. Chem. Phys.* **113**, 6677 (2000).
- ²⁸A. Dutta and C. D. Sherrill, *J. Chem. Phys.* (in press).
- ²⁹T. H. Dunning, *J. Chem. Phys.* **53**, 2823 (1970).
- ³⁰P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973).
- ³¹P.-O. Widmark, P.-Å. Malmqvist, and B. O. Roos, *Theor. Chim. Acta* **77**, 291 (1990).
- ³²P. O. Löwdin, *Phys. Rev.* **97**, 1474 (1955).
- ³³C. D. Sherrill and H. F. Schaefer, "The configuration interaction method: Advances in highly correlated approaches," in *Advances in Quantum Chemistry*, edited by P.-O. Löwdin (Academic, New York, 1999), Vol. 34, pp. 143–269.
- ³⁴T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, M. L. Leininger, R. A. King, S. T. Brown, C. L. Janssen, E. T. Seidl, Y. Yamaguchi, W. D. Allen, Y. Xie, G. Vacek, T. P. Hamilton, C. B. Kellogg, R. B. Remington, and H. F. Schaefer III, PSI 3.0, development version, PSITECH, Inc., Watkinsville, GA 30677, U.S.A., 1999.
- ³⁵CISD is not size consistent, so the quality of CISD natural orbitals will degrade at extended geometries. Computing dissociation energies by a fragment approach makes predictions even better on average; the difference ranges from 0.04 eV for BH to 0.32 eV for HF. The performance of CISD natural orbitals beyond equilibrium remains to be fully explored.
- ³⁶S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ³⁷K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ³⁸A. Carrington and D. A. Ramsey, *Phys. Scr.* **25**, 272 (1982).
- ³⁹J. M. L. Martin, *J. Chem. Phys.* **100**, 8186 (1994).

- ⁴⁰T. Helgaker, J. Gauss, P. Jørgensen, and J. Olsen, *J. Chem. Phys.* **106**, 6430 (1997).
- ⁴¹J. R. Thomas, B. J. DeLeeuw, G. Vacek, and H. F. Schaefer, *J. Chem. Phys.* **98**, 1336 (1993).

- ⁴²M. O. Sinnokrot and C. D. Sherrill, *J. Chem. Phys.* **115**, 2439 (2001).
- ⁴³J. Almlöf, B. J. DeLeeuw, P. R. Taylor, C. W. Bauschlicher, and P. Siegbahn, *Int. J. Quantum Chem., Quantum Chem. Symp.* **23**, 345 (1989).