Theor Chem Acc (1998) 100:103–111
DOI 10.1007/s002149800m39

Theoretical
Chemistry Accounts

Regular article

Core-valence correlation effects for molecules containing first-row atoms. Accurate results using effective core polarization potentials*

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Received: 11 May 1998 / Accepted: 27 July 1998 /

Abstract. The accuracy of employing effective core polarization potentials (CPPs) to account for the effects of core-valence correlation on the spectroscopic constants and dissociation energies of the molecules B_2, C_2, N_2, O_2, F_2, CO, CN, CH, HF, and C_2H_2 has been investigated by comparison to accurate all-electron benchmark calculations. The results obtained from the calculations employing CPPs were surprisingly accurate in every case studied, reducing the errors in the calculated valence D_e values from a maximum of nearly 2.5 kcal/mol to just 0.3 kcal/mol. The effects of enlarging the basis set and using higher-order valence electron correlation treatments were found to have only a small influence on the core-valence correlation effect predicted by the CPPs. Thus, to accurately recover the effects of intershell correlation, effective core polarization potentials such as the ones used in the present work provide an attractive alternative to carrying out computationally demanding calculations where the core electrons are explicitly included in the correlation treatment.

Key words: Core-valence correlation –
Core polarization potentials

1 Introduction

One of the most common assumptions in quantum chemistry involves the intuitive notion that molecular structure and energetics are primarily determined by the interactions of the valence electrons. Within this description the core electrons provide a source for the potential that is experienced by the valence electrons, but, because the core and valence electrons are concentrated in different regions of space, other effects, including intershell correlation effects, are negligible. This means that a simple orbital description would suffice for the description of the core electrons.

In 1975, Meyer and Rosmus [1] reported the first study that systematically investigated the influence of core-valence correlation on molecular properties in ab initio calculations. Their work on the first- and second-row diatomic hydrides, as well as the LiNa dimer [2], demonstrated that core-valence correlation can be nearly as important as valence correlation for alkali and alkaline earth compounds. Even for compounds containing the atoms B to F, if the goal of the calculation is the prediction of very accurate molecular structures (within thousandths of Angstroms) or energetics (better than 1 kcal/mol), then the effects of correlating the low-lying core electrons *must* be taken into account (see, for example, [3–6]). This dramatically increases the computational effort because more electron pairs must be correlated and larger basis sets must be used to simultaneously describe valence, core-valence, and core correlation effects. Of course, this level of effort is only worthwhile if the errors introduced by finite one-particle basis sets and the valence correlation treatment are smaller than the core-valence correlation effects.

A careful analysis of core-valence correlation reveals that the physical origin of this effect is principally due to the dynamic polarization of the atomic cores by the valence electrons [7]. This suggests that such effects could be taken into account by means of an effective core polarization potential (CPP). In fact this has been done for decades to improve model potentials [8–11]. However, it was again Meyer and his group who in the early 1980 s incorporated an effective core polarization potential into ab initio calculations [12–14]. They emphasized the importance of not only including the one-electron terms in such a potential, but also the proper implemention of the two-electron terms. Furthermore, they discussed different functional forms to cut-off the CPP at short distances, thus accounting for valence electrons that penetrate the cores in the determination of the polarizing field. Meyer and co-workers [12] found that the performance of the different cut-off functions

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*Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60th birthday

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was almost identical as long as the one adjustable parameter was fitted to experimental ionization potentials. This adjustment procedure was claimed to be a simple means to account for higher-order polarizabilities, as well as nonadiabatic and exclusion effects. With these CPPs they reported highly accurate spectroscopic constants for alkali and alkaline earth diatomics [13]. On the other hand, they also determined that the core-valence effect was overestimated for *d*-electrons. The latter problem was addressed by Leininger et al. [15] by introducing a nonlocal cut-off function.

Since the work of Meyer and co-workers, only a few investigations have used effective core polarization potentials within an all-electron model [16–19]. On the other hand, effective core polarization potentials have become popular in connection with pseudopotentials [20–38]. Within the pseudopotential scheme, CPPs not only account for core-valence correlation effects, but also describe the static polarization of the atomic cores by the molecular environment, an effect that is missing in standard pseudopotentials. Despite their wide use, only a few attempts have been made to compare results from such calculations with respective calculations in which the core electrons were explicitly correlated [33, 39, 40]. The findings in these investigations were always that the CPP results and those from explicitly correlating the core electrons were in reasonable correspondence, and the authors generally claimed that the agreement would probably be even better if more accurate all-electron calculations were possible.

Thus, there is considerable interest in comparing high accuracy calculations of core-valence correlation effects with similar calculations applying an effective core polarization potential. In previous benchmark studies [6, 41–43], systematic sequences of correlation consistent core-valence basis sets were used to predict the complete basis set limits for the effects of 1*s* correlation on the spectroscopic constants of several diatomics containing first-row atoms. In the present study these very accurate results, as well as other results from the literature [5, 44–47], have been used to benchmark the utility of effective CPPs in recovering the effects of intershell correlation in molecules containing first-row atoms. The motivation for this work is strongly driven by the high computational expense associated with carrying out accurate calculations correlating all of the electrons, especially in the case of polyatomic molecules. As will be demonstrated in the present study, the use of effective core polarization potentials appear to be capable of accurately reproducing core-valence correlation effects with minimal computational cost.

2 Computational methodology

All the results reported in this paper were obtained in all-electron calculations using the coupled-cluster method with single and double substitutions (CCSD) [48, 49] and CCSD with a perturbative inclusion of triples [CCSD(T)] [50, 51]. The explicit correlation treatment was restricted to only the valence electrons, i.e., the frozen core approximation was used throughout. To describe core-valence correlation effects, we supplemented the molecular Hamiltonian with an effective core-polarization potential [12]:

$$V_{\mathrm{CPP}} = -\frac{1}{2}\sum_{\lambda} \alpha_\lambda \mathbf{f}_\lambda^2$$

$$\mathbf{f}_\lambda = \sum_{\lambda} \frac{\mathbf{r}_{\lambda i}}{r_{\lambda i}^3} g_\lambda(r_{\lambda i}) - \sum_{\mu(\neq\lambda)} \frac{Q_\mu \mathbf{r}_{\lambda\mu}}{r_{\lambda\mu}^3} g_\lambda(r_{\lambda\mu})$$

$$g_\lambda(r) = [1 - \exp(-\gamma_{\lambda n} r^2)]^n$$

The summation is over all polarizable cores λ in the molecule with the dipole polarizabilities α_λ and the electric field $\mathbf{f}_\lambda$ at the site of core λ generated by the valence electrons i and the other cores μ. The function $g_\lambda(r)$ cuts off the polarizing field inside the core region and thus prevents the CPP from becoming singular. We tested two forms of cut-off functions differing in the exponential parameter n. Calculations using $n = 1$ are subsequently denoted CPP/1, while calculations with $n = 2$ are labeled CPP/2. Since the core-polarization potential defined in this way accounts not only for core-valence correlation effects but also for the static polarization of the atomic cores in the molecular environment, we forced our cores to be spherical by taking the 1*s* orbitals from calculations on the atomic ground states and freezing these in the molecular calculations with the CPP. For the reference calculations without the CPP, the cores were allowed to relax. Thus, the difference between the two calculations is exactly the core-valence correlation contribution. The dipole polarizabilities for the 1*s* cores were taken from coupled Dirac-Fock calculations [52]. The parameters $\gamma_{\lambda\mathrm{n}}$ were adjusted as suggested by Meyer and co-workers [12] such that core-valence correlation contributions to the ionization potentials of single valence electron ions derived from experimental ionization potentials could be reproduced [53]. The CPP parameters are displayed in Table 1.

The basis sets used in the present work were those of Dunning and co-workers [54, 55], namely the correlation consistent polarized valence double-zeta through quadruple-zeta sets (cc-pV*n*Z, n = D, T, Q) and the respective sets augmented by a set of diffuse functions (aug-cc-pV*n*Z). For CO we also tested the impact of special core-valence correlation functions (cc-pCV*n*Z) [56].

Spectroscopic constants for the diatomic molecules considered in this study (B_2, C_2, N_2, O_2, F_2, CO, CN, CH, and HF) were determined by first fitting 7–9 energy points to polynomials in $\Delta r = r - r_e$ and then using the resulting polynomial coefficients to obtain minimum energies, equilibrium bond lengths, and harmonic frequencies. Results for other spectroscopic constants, e.g., vibration-rotation interaction and anharmonicity constants, are available on request from the authors. The equilibrium geometry and minimum energies of C_2H_2 were obtained by fitting a total of 13 energies to polynomials in Δr(CH) and Δr(CC). In the atomic calculations required for the determination of the dissociation energies, full symmetry equivalencing was used on the molecular orbitals. Lastly, in the case of CH, the SCF orbitals were state averaged to produce the correct $^2\Pi$ symmetry (of course, only one component was used in the subsequent correlated calculations). For the atomic and open-shell molecules, the spin-restricted RCCSD(T) method of Knowles et al. [57] was employed. All calculations were performed with the program package MOLPRO.[1]

3 Results and discussion

The 1*s* core contributions to D_e, r_e, and ω_e (ΔD_e, Δr_e, and $\Delta\omega_e$) are shown in Tables 2–11 for B_2, C_2, N_2, O_2, F_2, CO, CN, CH, HF, and C_2H_2, respectively. In each case the core-valence correlation effects on D_e, r_e, and ω_e

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[1] MOLPRO is a package of ab initio programs written by H.-J Werner and P. J Knowles with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Lloyd, W. Meyer, M. E. Mura, A. Nicklass, K. A. Peterson, R. M. Pitzer, P. Pulay, M. Schütz, H. Stoll, A. J. Stone, P. R. Taylor, and T. Thorsteinsson

Table 1. Parameters α and γ for the core polarization potentials of B through F

	α	γ (n = 1)	γ (n = 2)
B^{3+}	0.01953	1.8942	4.2385
C^{4+}	0.008919	2.8011	6.2557
N^{5+}	0.004633	3.8296	8.4652
O^{6+}	0.002639	4.9942	10.9309
F^{7+}	0.001611	6.1769	13.2663

obtained with the CPPs are given for SCF, CCSD, and CCSD(T) wave functions with the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. The CPP results are compared in these tables to the best estimates for these quantities obtained from high quality calculations reported in the literature, where all the electrons were included in the correlation treatment and large core-valence basis sets were used. In most cases these involved CCSD(T) calculations calibrated by internally contracted multireference averaged coupled pair functional (ACPF) [58] results. In three cases, CN, CH, and HF, new ACPF calculations with the cc-pCV5Z basis set were carried out to provide more accurate estimates of the core-valence correlation effects. The results obtained in these calculations have been adopted as our "best estimates" for these species. Figure 1 summarizes our present results by comparing the CPP/1 and CPP/2 1*s* core-valence contributions, ΔD_e, Δr_e, and $\Delta\omega_e$, obtained with the cc-pVQZ basis sets at the CCSD(T) level of theory to the best estimate values for these quantities.

3.1 Homonuclear diatomics: B_2, C_2, N_2, O_2, F_2

The contributions to D_e, r_e, and ω_e from correlating the 1*s*-like core electrons in the first-row homonuclear diatomics are shown in Tables 2–6. These results demonstrate two very general trends in regards to the core-valence correlation effects predicted by the present CPPs. Firstly, the effect of valence electron correlation, while naturally having a very large impact on the total values of the spectroscopic constants, has only a relatively small effect on the 1*s* core-valence contribution to these properties as predicted by either CPP/1 or CPP/2. For example, in the case of the dissociation energy of B_2, the CPP/2 result for ΔD_e using an SCF wave function and the cc-pVQZ basis set is 0.42 kcal/mol, while using a CCSD(T) correlation treatment for the valence electrons yields a value of ΔD_e of 0.96 kcal/mol. This is to be compared to an SCF/cc-pVQZ D_e of just 21.1 kcal/mol and a CCSD(T)/cc-pVQZ value of 64.1 kcal/mol. In addition, the results for ΔD_e of F_2 are also very similar at the SCF and CCSD(T) levels (−0.04 and −0.01 kcal/mol), despite the fact that the molecule is not even

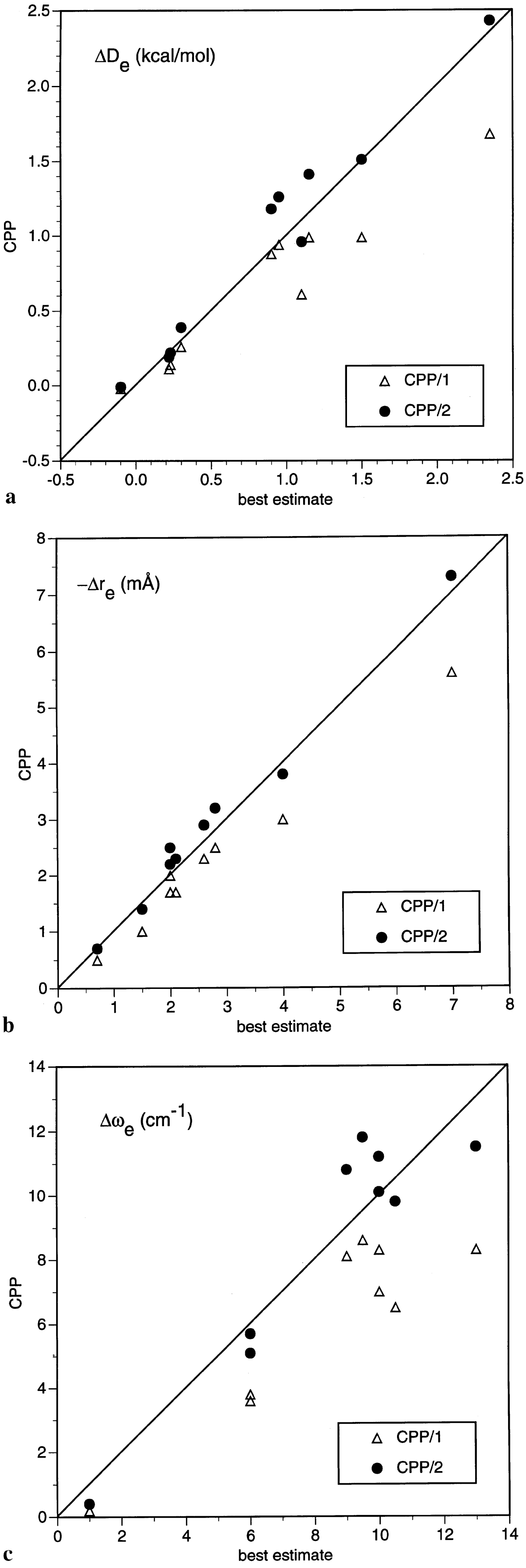

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Fig. 1a–c. The 1*s* core-valence contributions to **a** D_e, **b** r_e, and **c** ω_e obtained using effective core polarization potentials at the CCSD(T)/cc-pVQZ level of theory are compared to the best estimates obtained in large basis set, all-electrons correlated calculations. The CPP/1 results are designated by the *open symbols*, while the CPP/2 results are shown with *filled symbols*

Table 2. Calculated spectroscopic constants of B_2 for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/cc-pCV6Z[a]		64.77	+0.76		1.5919	−0.0064		1050.4	+8.9	
Best estimate[a]			+1.1			−0.007			+10	
SCF	cc-pVDZ	19.52	0.27	0.38	1.6500	−0.0062	−0.0077	940.7	7.1	10.1
	cc-pVTZ	20.84	0.29	0.40	1.6388	−0.0066	−0.0083	936.7	7.3	10.3
	cc-pVQZ	21.07	0.30	0.42	1.6364	−0.0066	−0.0084	937.0	7.4	10.6
CCSD	cc-pVDZ	49.95	0.56	0.83	1.6290	−0.0056	−0.0070	1009.3	6.9	9.9
	cc-pVTZ	53.43	0.63	0.92	1.6031	−0.0058	−0.0073	1030.6	7.3	10.4
	cc-pVQZ	54.65	0.64	0.95	1.5972	−0.0058	−0.0074	1037.0	7.4	10.6
CCSD(T)	cc-pVDZ	57.74	0.53	0.83	1.6272	−0.0055	−0.0069	1020.3	6.6	9.5
	cc-pVTZ	62.51	0.60	0.93	1.5999	−0.0057	−0.0072	1042.1	7.0	10.0
	cc-pVQZ	64.14	0.61	0.96	1.5936	−0.0056	−0.0073	1048.6	7.0	10.1

[a] Ref. [6]

Table 3. Calculated spectroscopic constants of C_2 for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/cc-pCV6Z[a]		144.97	+1.00		1.2443	−0.0032		1860.1	+10.6	
Best estimate[a]			+1.5			−0.004			+13	
SCF	cc-pVDZ	13.97	0.51	0.67	1.2523	−0.0030	−0.0037	1914.3	9.2	12.5
	cc-pVTZ	17.65	0.63	0.82	1.2409	−0.0033	−0.0041	1904.6	10.0	13.5
	cc-pVQZ	18.40	0.65	0.85	1.2389	−0.0033	−0.0042	1905.1	10.0	13.6
CCSD	cc-pVDZ	113.80	0.93	1.36	1.2662	−0.0028	−0.0034	1861.6	7.8	10.8
	cc-pVTZ	121.02	1.02	1.47	1.2469	−0.0030	−0.0038	1881.3	8.5	11.7
	cc-pVQZ	124.35	1.03	1.49	1.2421	−0.0030	−0.0038	1892.6	8.6	11.9
CCSD(T)	cc-pVDZ	130.05	0.88	1.37	1.2705	−0.0028	−0.0035	1828.2	7.6	10.6
	cc-pVTZ	139.39	0.99	1.50	1.2507	−0.0030	−0.0038	1845.7	8.1	11.2
	cc-pVQZ	143.25	0.99	1.51	1.2458	−0.0030	−0.0038	1856.3	8.3	11.5

[a] Ref. [6].

Table 4. Calculated spectroscopic constants of N_2 for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/cc-pCV6Z[a]		226.49	+0.80		1.0991	−0.0021		2361.2	+9.9	
Best estimate[a]			+0.9			−0.002			+9	
SCF	cc-pVDZ	112.15	0.70	0.92	1.0773	−0.0018	−0.0021	2758.1	7.9	10.5
	cc-pVTZ	120.38	0.84	1.10	1.0671	−0.0020	−0.0025	2731.5	8.9	11.5
	cc-pVQZ	121.81	0.85	1.12	1.0656	−0.0020	−0.0025	2729.5	9.0	11.8
CCSD	cc-pVDZ	193.67	0.85	1.14	1.1128	−0.0018	−0.0022	2408.9	7.2	9.8
	cc-pVTZ	207.98	0.94	1.24	1.0967	−0.0020	−0.0024	2423.8	7.9	10.5
	cc-pVQZ	214.17	0.94	1.25	1.0931	−0.0020	−0.0024	2435.4	7.9	10.6
CCSD(T)	cc-pVDZ	200.69	0.79	1.07	1.1189	−0.0019	−0.0023	2339.1	7.5	10.3
	cc-pVTZ	216.70	0.88	1.18	1.1038	−0.0020	−0.0025	2346.0	8.1	10.8
	cc-pVQZ	223.17	0.88	1.18	1.1003	−0.0020	−0.0025	2356.2	8.1	10.8

[a] Ref. [6]

bound at the SCF level of theory. Very little differences are also observed between CCSD and CCSD(T) for ΔD_e, Δr_e, and $\Delta\omega_e$, implying that only modest amounts of valence electron correlation need be included when using CPPs to estimate core-valence correlation contributions. Therefore it should be stressed that in assessing the accuracy of the CPP results, they should be compared to the best estimates for the core-valence correlation effect

Table 5. Calculated spectroscopic constants of O_2 for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/cc-pCV6Z[a]		119.16	+0.22		1.2063	−0.0021		1604.1	+6.0	
Best estimate[a]			+0.3			−0.002			+6	
SCF	cc-pVDZ	25.87	0.44	0.61	1.1543	−0.0016	−0.0021	2021.1	6.3	8.5
	cc-pVTZ	32.80	0.28	0.43	1.1523	−0.0017	−0.0022	2004.2	5.3	7.4
	cc-pVQZ	34.00	0.27	0.42	1.1510	−0.0017	−0.0021	2007.8	5.1	7.1
CCSD	cc-pVDZ	98.03	0.46	0.62	1.2054	−0.0017	−0.0022	1670.1	5.4	7.4
	cc-pVTZ	105.14	0.30	0.45	1.1993	−0.0017	−0.0022	1677.2	3.8	5.7
	cc-pVQZ	108.29	0.31	0.46	1.1947	−0.0016	−0.0021	1694.8	3.8	5.6
CCSD(T)	cc-pVDZ	104.03	0.41	0.55	1.2158	−0.0018	−0.0024	1587.7	5.7	7.9
	cc-pVTZ	113.63	0.26	0.39	1.2120	−0.0018	−0.0023	1585.4	3.8	5.7
	cc-pVQZ	117.19	0.26	0.39	1.2077	−0.0017	−0.0022	1600.1	3.8	5.7

[a] Ref. [6]

Table 6. Calculated spectroscopic constants of F_2 for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/cc-pCV6Z[a]		38.26	−0.07		1.4102	−0.0015		928.4	+1.6	
Best estimate[a]			−0.1			−0.0015			+1	
SCF	cc-pVDZ	−33.40	0.04	0.05	1.3477	−0.0018	−0.0023	1180.2	2.5	3.1
	cc-pVTZ	−25.32	−0.06	−0.04	1.3291	−0.0012	−0.0016	1266.9	1.2	1.8
	cc-pVQZ	−24.78	−0.05	−0.04	1.3275	−0.0012	−0.0016	1263.9	1.4	1.9
	aug-cc-pVDZ	−30.54	−0.01	0.01	1.3382	−0.0016	−0.0020	1215.8	2.1	2.7
	aug-cc-pVTZ	−24.64	−0.06	−0.04	1.3282	−0.0012	−0.0016	1270.8	1.3	1.8
	aug-cc-pVQZ	−24.48	−0.05	−0.04	1.3267	−0.0012	−0.0016	1265.9	1.4	1.9
CCSD	cc-pVDZ	22.28	0.06	0.07	1.4321	−0.0017	−0.0021	885.9	1.0	1.2
	cc-pVTZ	28.38	0.00	0.01	1.3946	−0.0010	−0.0013	1012.4	0.2	0.4
	cc-pVQZ	29.89	0.01	0.02	1.3907	−0.0010	−0.0013	1015.5	0.2	0.4
	aug-cc-pVDZ	24.58	0.02	0.03	1.4255	−0.0014	−0.0018	921.2	0.5	0.7
	aug-cc-pVTZ	29.80	0.00	0.02	1.3957	−0.0010	−0.0013	1010.7	0.3	0.5
	aug-cc-pVQZ	30.77	0.01	0.02	1.3903	−0.0010	−0.0013	1016.6	0.3	0.5
CCSD(T)	cc-pVDZ	27.24	0.02	0.02	1.4576	−0.0019	−0.0023	784.0	1.2	1.5
	cc-pVTZ	34.98	−0.02	−0.02	1.4158	−0.0010	−0.0013	919.9	0.2	0.5
	cc-pVQZ	36.92	−0.02	−0.01	1.4130	−0.0010	−0.0014	921.1	0.2	0.4
	aug-cc-pVDZ	30.03	−0.01	−0.01	1.4500	−0.0015	−0.0020	826.2	0.6	0.9
	aug-cc-pVTZ	36.65	−0.02	−0.02	1.4181	−0.0010	−0.0014	916.3	0.3	0.5
	aug-cc-pVQZ	37.90	−0.02	−0.01	1.4130	−0.0010	−0.0014	921.4	0.3	0.5

[a] Ref. [6]

and not, for instance, to just large basis set CCSD(T) results when CCSD(T) is used to correlate the valence electrons in the CPP calculations.

The second trend to be observed is the relative insensitivity of the CPP results to the basis set. It is generally observed in Tables 2–6 that the core-valence effects obtained by the CPPs are nearly completely converged with only the cc-pVTZ basis set. In the case of F_2 the effects of additional diffuse functions were also investigated by using the aug-cc-pV*n*Z basis sets. Improvements were observed at the double zeta level, but the aug-cc-pVTZ results were essentially identical to the values obtained with the standard cc-pVTZ basis set. Both of these trends are in strong contrast to the conventional method of predicting core-valence correlation effects on spectroscopic constants, where large basis sets and sophisticated correlation methods are required to obtain reliable values.

Upon comparing the core-valence correlation effects predicted by the CPP calculations with our "best estimates" from the literature (Tables 2–6 and Fig. 1), it is observed that CPP/2 is closer to the "best estimate" values compared to CPP/1 for B_2, C_2, and F_2. For these three species, the CPP/2 values differ from the "best estimates" by an average of less than 0.1 kcal/mol for ΔD_e, less than a few tenths of a mÅ in Δr_e, and less than 2 cm^{-1} in $\Delta\omega_e$. These are certainly well within the uncertainty of the best estimate values. In particular the large (positive) value of ΔD_e for C_2 is very well reproduced by CPP/2, as well as the small negative value for F_2. For each of these species, CPP/1 underestimates the core-valence correlation effects.

Table 7. Calculated spectroscopic constants of CO for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/cc-pCV5Z[a]		257.69	+0.93		1.1306	−0.0024		2165.3	+9.8	
Best estimate[a]			+0.95			−0.0026			+10	
SCF	cc-pVDZ	176.69	0.79	1.04	1.1101	−0.0022	−0.0026	2431.6	7.5	10.2
	cc-pVTZ	183.28	0.89	1.19	1.1045	−0.0024	−0.0029	2425.0	8.9	11.7
	cc-pVQZ	184.75	0.91	1.21	1.1020	−0.0024	−0.0029	2427.3	9.1	12.0
	aug-cc-pCVDZ	178.21	0.78	1.04	1.1099	−0.0023	−0.0028	2401.8	8.5	11.3
	aug-cc-pCVTZ	183.97	0.89	1.18	1.1037	−0.0024	−0.0029	2421.0	9.0	11.9
	aug-cc-pCVQZ	184.91	0.91	1.20	1.1019	−0.0024	−0.0029	2426.5	9.1	12.0
CCSD	cc-pVDZ	235.73	0.91	1.21	1.1384	−0.0021	−0.0026	2209.2	7.0	9.6
	cc-pVTZ	244.46	0.97	1.30	1.1288	−0.0023	−0.0028	2222.9	8.1	10.9
	cc-pVQZ	248.67	0.99	1.31	1.1243	−0.0023	−0.0028	2234.8	8.2	11.0
	aug-cc-pCVDZ	235.52	0.92	1.23	1.1390	−0.0023	−0.0028	2171.7	8.0	10.8
	aug-cc-pCVTZ	245.04	0.96	1.29	1.1281	−0.0023	−0.0029	2216.7	8.1	11.0
	aug-cc-pCVQZ	248.96	0.98	1.30	1.1243	−0.0023	−0.0028	2231.7	8.2	11.1
CCSD(T)	cc-pVDZ	241.52	0.87	1.17	1.1446	−0.0022	−0.0027	2143.9	7.2	9.9
	cc-pVTZ	251.90	0.93	1.25	1.1357	−0.0024	−0.0029	2153.7	8.2	11.0
	cc-pVQZ	256.32	0.94	1.26	1.1314	−0.0023	−0.0029	2164.4	8.3	11.2
	aug-cc-pCVDZ	241.61	0.88	1.18	1.1457	−0.0023	−0.0029	2104.4	8.1	11.0
	aug-cc-pCVTZ	252.53	0.92	1.24	1.1353	−0.0024	−0.0029	2145.7	8.2	11.1
	aug-cc-pCVQZ	256.65	0.93	1.25	1.1315	−0.0024	−0.0029	2160.4	8.3	11.2

[a] Ref. [42]. The ACPF/cc-pCV5Z core-valence correlation effects from [42] were +0.90 kcal/mol, −0.0024 Å, and +9.4 cm^{-1}

Table 8. Calculated spectroscopic constants of CN for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
ACPF/cc-pCV5Z[a]		178.14	1.15		1.1754	−0.0028		2056.9	+9.5	
SCF	cc-pVDZ	80.28	0.77	1.18	1.1390	−0.0023	−0.0028	2460.9	9.1	12.8
	cc-pVTZ	86.47	0.93	1.39	1.1292	−0.0025	−0.0031	2450.7	10.2	14.0
	cc-pVQZ	87.88	0.93	1.40	1.1273	−0.0025	−0.0032	2453.3	10.1	13.9
CCSD	cc-pVDZ	150.05	0.95	1.36	1.1850	−0.0023	−0.0029	2115.8	7.8	10.9
	cc-pVTZ	160.66	1.06	1.50	1.1683	−0.0025	−0.0031	2138.3	8.7	11.9
	cc-pVQZ	165.57	1.07	1.52	1.1636	−0.0025	−0.0031	2153.5	8.5	11.8
CCSD(T)	cc-pVDZ	158.17	0.86	1.25	1.1948	−0.0024	−0.0030	2031.2	8.0	11.1
	cc-pVTZ	170.43	0.98	1.39	1.1789	−0.0026	−0.0032	2050.3	8.7	11.8
	cc-pVQZ	175.61	0.99	1.41	1.1744	−0.0025	−0.0032	2064.3	8.6	11.8

[a] This work (best estimate). Pradhan et al. [47] also reported a value for ΔD_e of 1.18 kcal/mol using ACPF wave functions

Table 9. Calculated spectroscopic constants of CH for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/cc-pCVQZ[a]		83.08	+0.13		1.1202	−0.0018		2854.1	+8.0	
ACPF/cc-pCV5Z[b]		83.41	+0.22		1.1201	−0.0021		2851.5	+10.5	
SCF	cc-pVDZ	54.65	0.02	0.08	1.1179	−0.0015	−0.0019	3048.7	5.6	8.7
	cc-pVTZ	56.76	0.05	0.12	1.1053	−0.0017	−0.0022	3036.4	6.6	9.8
	cc-pVQZ	57.13	0.04	0.12	1.1039	−0.0017	−0.0022	3043.5	6.9	10.1
CCSD	cc-pVDZ	74.95	0.08	0.15	1.1418	−0.0015	−0.0020	2831.6	5.1	8.3
	cc-pVTZ	80.72	0.12	0.20	1.1207	−0.0017	−0.0022	2859.0	6.4	9.6
	cc-pVQZ	82.24	0.11	0.19	1.1185	−0.0017	−0.0022	2873.8	6.4	9.6
CCSD(T)	cc-pVDZ	75.53	0.08	0.14	1.1431	−0.0015	−0.0020	2816.7	5.3	8.6
	cc-pVTZ	81.50	0.11	0.20	1.1224	−0.0017	−0.0023	2840.6	6.5	9.7
	cc-pVQZ	83.07	0.11	0.19	1.1202	−0.0017	−0.0023	2854.3	6.5	9.8

[a] Ref. [43]. Partridge and Bauschlicher [46] have reported a values of +0.17 kcal/mol and −0.0017 Å for ΔD_e and Δr_e, respectively, using CCSD(T) wave functions

[b] This work (best estimate)

Table 10. Calculated spectroscopic constants of HF for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/cc-pCV5Z[a]		141.03	+0.18		0.9168	−0.0006		4150.0	+4.6	
ACPF/cc-pCV5Z[b]		139.89	+0.23		0.9163	−0.0007		4153.7	+6.0	
SCF	cc-pVDZ	93.72	0.13	0.20	0.9015	−0.0006	−0.0007	4440.2	4.6	6.1
	cc-pVTZ	100.06	0.13	0.20	0.8979	−0.0006	−0.0007	4481.1	4.4	5.9
	cc-pVQZ	101.19	0.13	0.20	0.8969	−0.0006	−0.0007	4476.5	4.2	5.7
	aug-cc-pVDZ	99.48	0.13	0.20	0.9002	−0.0005	−0.0007	4466.3	4.6	6.1
	aug-cc-pVTZ	101.37	0.12	0.20	0.8991	−0.0006	−0.0007	4464.8	4.3	5.8
	aug-cc-pVQZ	101.61	0.13	0.20	0.8973	−0.0006	−0.0007	4471.0	4.2	5.7
CCSD	cc-pVDZ	125.73	0.15	0.22	0.9190	−0.0005	−0.0007	4168.6	4.1	5.6
	cc-pVTZ	135.32	0.15	0.22	0.9152	−0.0005	−0.0007	4211.5	3.6	5.1
	cc-pVQZ	138.10	0.15	0.23	0.9137	−0.0005	−0.0007	4204.2	3.5	5.0
	aug-cc-pVDZ	133.40	0.15	0.22	0.9222	−0.0006	−0.0007	4115.9	4.2	5.7
	aug-cc-pVTZ	137.45	0.14	0.22	0.9182	−0.0005	−0.0007	4169.3	3.5	4.9
	aug-cc-pVQZ	138.98	0.15	0.22	0.9149	−0.0005	−0.0007	4188.6	3.5	5.0
CCSD(T)	cc-pVDZ	126.37	0.14	0.22	0.9199	−0.0005	−0.0007	4149.8	4.2	5.8
	cc-pVTZ	137.03	0.14	0.22	0.9173	−0.0006	−0.0007	4176.9	3.7	5.2
	cc-pVQZ	140.06	0.14	0.22	0.9162	−0.0005	−0.0007	4161.8	3.6	5.1
	aug-cc-pVDZ	134.52	0.14	0.21	0.9241	−0.0006	−0.0007	4080.3	4.3	5.9
	aug-cc-pVTZ	139.40	0.14	0.21	0.9210	−0.0006	−0.0007	4124.3	3.6	5.0
	aug-cc-pVQZ	141.04	0.14	0.22	0.9177	−0.0005	−0.0007	4141.3	3.6	5.1

[a] Ref. [41]
[b] This work (best estimate)

Table 11. Calculated spectroscopic constants of C_2H_2 for valence-only correlation and the changes in these values due to using core polarization potentials

Method	Basis set	D_e (HC-CH) (kcal/mol)			r_e (CC) (Å)			r_e (CH) (Å)		
		Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2	Valence	CPP/1	CPP/2
CCSD(T)/ACPF[a]			2.14 / 2.35							
SCF	cc-pVDZ	181.05	1.40	2.04	1.1918	−0.0024	−0.0029	1.0638	−0.0012	−0.0014
	cc-pVTZ	186.22	1.61	2.32	1.1801	−0.0027	−0.0033	1.0540	−0.0014	−0.0016
	cc-pVQZ	186.56	1.65	2.36	1.1792	−0.0028	−0.0033	1.0540	−0.0014	−0.0016
CCSD	cc-pVDZ	215.38	1.56	2.27	1.2227	−0.0023	−0.0028	1.0775	−0.0012	−0.0014
	cc-pVTZ	224.39	1.70	2.45	1.2032	−0.0025	−0.0031	1.0620	−0.0013	−0.0015
	cc-pVQZ	227.21	1.73	2.47	1.1999	−0.0025	−0.0030	1.0616	−0.0013	−0.0015
CCSD(T)	cc-pVDZ	220.27	1.52	2.23	1.2287	−0.0024	−0.0028	1.0789	−0.0012	−0.0014
	cc-pVTZ	230.46	1.66	2.41	1.2096	−0.0026	−0.0031	1.0637	−0.0013	−0.0015
	cc-pVQZ	233.51	1.68	2.43	1.2064	−0.0026	−0.0031	1.0633	−0.0013	−0.0015

[a] Ref. [46].

In the case of N_2, and to a lesser extent O_2, the core-valence correlation effect is overestimated by CPP/2. For N_2 the CCSD(T)/cc-pVTZ results using CPP/2 are 1.18 kcal/mol, −0.0025 Å, and +10.8 cm^{-1} for ΔD_e, Δr_e, and $\Delta\omega_e$, respectively. These can be compared to best estimates of +0.9 kcal/mol, −0.002 Å, and +9 cm^{-1}. For O_2 the largest discrepancy is the value of ΔD_e predicted by CPP/2, which is probably too large by about 0.1 kcal/mol. The core-valence contributions to r_e and ω_e, however, are in good agreement for CPP/2. The source of these errors, which also occur in CO and CN (see below), is not yet understood, but the restriction to frozen, spherical cores in the CPP calculations could perhaps give rise to these overestimations. Work is currently in progress to remove this restriction. Other forms of the cutoff function are also being investigated. Given the large computational expense, however, to accurately calculate core-valence correlation effects using standard correlation methods, errors of a few tenths of a kcal/mol would appear to be very acceptable when there are essentially no additional costs beyond the usual valence-only calculation.

3.2 CO and CN

The results for CO and CN given in Tables 7 and 8 show very similar trends as were discussed above for the homonuclear diatomics. In the case of CO, very similar observations as noted for N_2 can be made. For example, the value of ΔD_e obtained using CPP/2 is too large by about 0.3 kcal/mol out of 1 kcal/mol. The effects of using basis sets that include tight *d* and *f* functions designed to recover core-core and core-valence correlation effects were also investigated for CO. The results of these calculations, which actually used the aug-cc-pCVDZ through aug-cc-pCVQZ basis sets (extra diffuse and tight functions), are also shown in Table 7 and, as with the diffuse augmented sets alone, result in very few benefits. The results for CN are intermediate in accuracy between C_2 and CO, e.g., ΔD_e is too large by about 0.2 kcal/mol and Δr_e is too negative by about 0.0005 Å).

3.3 CH and HF

For both CH and HF, CPP/2 yields very accurate values for the core-valence contributions to D_e, r_e, and ω_e (Tables 9 and 10). In the all-electron benchmark calculations, the previous CCSD(T) results [43, 46] for CH yielded core-valence correlation effects somewhat smaller than those obtained by the ACPF method. The values obtained from the latter calculations are in very good agreement with the ones from CPP/2, i.e., within 0.03 kcal/mol, 0.0002 Å, and 1 cm^{-1} for ΔD_e, Δr_e, and $\Delta\omega_e$, respectively. Similar excellent agreement between CPP/2 and our best estimates are also observed for HF. In this case, it has been observed previously [59, 60] that extra diffuse functions were very important for obtaining accurate dissociation energies and harmonic frequencies. However, as also shown above for F_2, the addition of these functions to the basis set have a negligible influence on the core-valence correlation effect predicted by the CPPs.

3.4 C_2H_2

The last example considered in the present work was the acetylene molecule. Initially this was chosen in an attempt to show that the short, triple bond in N_2 (and CO) was responsible for the overestimation of the core-valence effects by CPP/2 in that molecule. The results shown in Table 11 for C_2H_2, however, indicate that this is probably not a valid explanation since excellent results are obtained by CPP/2. The core-valence effect on D_e(HC-CH) is surprisingly large, as first shown by Partridge and Bauschlicher [46]. Use of CPP/2 reproduces their ACPF result (+2.35 kcal/mol) to within 0.1 kcal/mol. In contrast, CPP/1 strongly underestimates the core-valence contributions. Our calculations also yield core-valence contributions to the two bond lengths in C_2H_2, predicting bond length contractions (CPP/2) of 0.0031 and 0.0015 Å for r_e(CC) and r_e(CH), respectively. These should be accurate to within 0.2 mÅ.

4 Conclusions

The core-valence correlation contributions to the spectroscopic constants (D_e, r_e, ω_e) of several molecules containing first-row atoms have been investigated using effective CPPs. In each case the CPP results reproduced well the best estimates of these quantities, which were obtained in extensive calculations where all of the electrons were included in the correlation treatment. The use of the CPP method reduced the error in the calculated valence D_e values (relative to the all-electron D_e values) from a maximum of nearly 2.5 kcal/mol to just 0.3 kcal/mol. Similar error reductions were found for r_e and ω_e.

As shown in Fig. 1, this study indicates that the choice of the cut-off function in the CPP plays a more important role than anticipated by Meyer and coworkers [12]. In contrast to their claim that their different cut-off functions performed equally well as long as the parameters were carefully adjusted, we found CPP/2 to outperform CPP/1 in nearly all cases. This was especially true when the core-valence effects became sizeable. However, it should also be mentioned that the fitting procedure devised by Meyer is obviously better suited for alkali and alkaline earth elements. For elements to the right of the periodic table, the one valence-electron ions used in the fitting procedure for the cut-off function have little similarity to the atoms in the neutral molecules of the present study. So it is somewhat surprising that one of the cut-off functions (CPP/2) does so well, while CPP/1 exhibits significant deviations. Gaining more insight into the role of the cut-off function is the topic of an ongoing investigation.

In general, the minimal computational expense and apparent high accuracy of the CPPs in reproducing the core-valence correlation effects should result in a more widespread and routine use of these operators in molecular calculations.

Acknowledgements. It is a pleasure to dedicate this paper to Prof. Wilfried Meyer on the occasion of his 60th birthday. This work was supported by the National Science Foundation (CHE-9501262) and the Chemical Sciences Division in the Office of Basic Energy Sciences of the U.S. Department of Energy at Pacific Northwest National Laboratory, a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830. The authors thank Dr. Thom H. Dunning, Jr. for helpful discussions during the course of this work.

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