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Benchmark calculations with correlated molecular wave functions

XII. Core correlation effects on the homonuclear diatomic molecules B_2-F_2

Kirk A. Peterson[1], **Angela K. Wilson**[2], **David E. Woon**[2,*], **Thom H. Dunning, Jr.**[2]

[1] Department of Chemistry, Washington State University, and the Environmental Molecular Sciences Laboratory,
Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA (e-mail: ka_peterson@pnl.gov)
[2] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA
(e-mail: ak_wilson@pnl.gov, woon@hecla.org, th_dunning@pnl.gov)

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Abstract. Using systematic sequences of the newly developed correlation consistent core-valence basis sets from cc-pCVDZ through cc-pCV6Z, the spectroscopic constants of the homonuclear diatomic molecules containing first row atoms, B–F, are calculated both with and without inclusion of 1*s* correlation. Internally contracted multireference configuration interaction (IC-MRCI) and singles and doubles coupled cluster (CCSD) theory with a perturbational estimate of connected triple excitations, CCSD(T), have been investigated. By exploiting the convergence of the correlation consistent basis sets, complete basis set (CBS) limits have been estimated for total energies, dissociation energies, equilibrium geometries, and harmonic frequencies. Based on the estimated CBS limits the effects of 1*s* correlation on D_e (kcal/mol), r_e (Å), and ω_e (cm^{-1}) are: +1.1, −0.0070, +10 for B_2; +1.5, −0.0040, +13 for C_2; +0.9, −0.0020, +9 for N_2; +0.3, −0.0020, +6 for O_2; and −0.1, −0.0015, +1 for F_2.

Key words: Molecular wave functions – Core correlation effects – Homonuclear diatomic molecules

1 Introduction

One of the most common assumptions in quantum chemistry involves the intuitive notion that molecular structure and energetics are determined solely by the interactions of the valence electrons. This leads to a much reduced computational expense and fortunately the accuracy of the resulting calculations are generally not compromised to a large extent, especially for compounds containing only first and second row atoms. However, if the goal of the calculation is the prediction of very accurate molecular structures (within thousandths of an Angstrom) or energetics (better than 1 kcal/mol), then the effects of correlating the low-lying core electrons must be taken into account in some manner. While this obviously increases the computational effort due to correlating more electron pairs, serious attention must also be given to augmenting the one-particle basis set, since these are generally developed to only describe valence-electron correlation.

In the past, the optimal number and type of additional functions necessary to accurately describe core-core and core-valence correlation effects has been very difficult to determine and one often relied upon a number of calibration tests and personal intuition (cf., Ref. [1]). Recently, however, the correlation consistent basis sets of Dunning and co-workers [2–6] have been extended to systematically describe core-correlation effects [7, 8]. Just as for the standard-valence basis sets (cc-pCV*n*Z), the new core-valence sets (cc-pCV*n*Z) appear to smoothly converge total energies and molecular properties toward an apparent complete basis set (CBS) limit.

In the present work, these new sets are benchmarked on the series of homonuclear diatomic molecules containing first row atoms: B_2, C_2, N_2, O_2, and F_2. Using highly correlated wave functions and sequences of cc-pCV*n*Z basis sets, the effects of correlating the core electrons on E_e, D_e, r_e, and ω_e have been determined. Since the calculation of these effects involves a balance between describing valence correlation and core correlation, it is essential to understand the basis set convergence characteristics of these effects in order to obtain reliable results. The systematic convergence studies reported herein for both the valence-only and all-electron CBS calculations satisfies this requirement.

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[*] *Present address*: Molecular Research Institute,
845 Page Mill Road, Palo Alto, CA 94304, USA
Correspondence to: K. A. Peterson

2 Computational details

As mentioned above, the one-particle basis sets used in the present work corresponded to the newly developed correlation consistent polarized core-valence sets of Woon and Dunning [7], denoted cc-pCV*n*Z ($x = D, T, Q$, 5), and the recently developed cc-pCV6Z sets of Wilson and Dunning [8, 9]. These sets were constructed from the standard valence cc-pV*n*Z basis sets by the addition of functions optimized explicitly for core-core and core-valence correlation in atomic calculations. For atoms of the first row (B–Ne), a 1*s*1*p* set was added to the cc-pVDZ basis set to form the cc-pCVDZ set. Likewise, a 2*s*2*p*1*d* set was added to cc-pVTZ set to form the cc-pCVTZ set, and so on.

As has been empirically observed for the valence-correlation consistent basis sets [10–20], the computed total energies converge nearly exponentially toward the apparent CBS limit. This is also found to be the case for the cc-pCV*n*Z sets, and the total energies have been fit in the present work to be standard exponential function [10, 12–14, 17]

$$\mathrm{E}_n = \mathrm{E}_\infty + \mathrm{Be}^{-Cn}, \tag{1}$$

to obtain estimates of the complete basis set limits E_∞. Estimated CBS limits for the dissociation energies have been obtained as differences between total energies extrapolated using Eq. (1). The CBS limits for r_e and ω_e, however, have been estimated from the cc-pCV5Z or cc-pCV6Z results.

Both single- and multireference correlation methods were chosen for the present work. Of the methods based on a Hartree-Fock reference function, the coupled-cluster method with single, double, and noniterative triple excitations, CCSD(T), [21–23] has been shown to be very accurate if nondynamical correlation effects are not too important (cf., Ref. [24]). For open-shell species, the spin-restricted (RCCSD) method of Knowles and Werner [25] has been used with the triples correction of Deegan and Knowles, RCCSD(T) [23]. Other methods used in this work were the internally contracted multireference configuration interaction (IC-MRCI) method of Werner and Knowles [26, 27], and IC-MRCI with the addition of the multireference analog of the Davidson correction [28–30], IC-MRCI + Q. Since the assessment of the effects of core correlation involves comparing calculations with different numbers of correlated electrons, the use of size-extensive methods is expected to produce more accurate results. This condition is satisfied by the CCSD(T) wave functions, while IC-MRCI + Q method is only approximately size extensive. For this reason, the size-extensive internally contracted averaged coupled-pair functional method, IC-ACPF [31, 32], has also been investigated. However, only the cc-pCVQZ basis set was used for these calculations.

In the multireference calculations, the orbitals were taken from full valence complete active space self-consistent field (CASSCF) calculations [33, 34] in which the core orbitals were constrained to be doubly occupied. In the cases of N_2, O_2, and F_2, care was taken to remove mixing between the nominally 1*s* and 2*s* atomic orbitals. As has been discussed previously in the literature [14, 35, 36], this can lead to an artificial raising of the energy in subsequent MRCI calculations that do not correlate the core electrons. This problem is especially serious at the dissociated limits, but as in our previous work we have chosen to resolve the core orbitals via a two-step CASSCF procedure at all bond lengths. The CASSCF reference functions utilized for both the valence-only and all-electron MRCI calculations were identical.

For each species, potential energy functions were calculated by fitting seven computed energies that covered a range of $-0.3a_0 \le \Delta r \le +0.5a_0$ to sixth-order polynomials in $\Delta r = r - r_e$. For the CCSD(T) calculations, the dissociation energies were obtained by reference to calculations on the separated atoms. For these atomic cases, the symmetry equivalencing was consistent with the molecular system, e.g., for $\mathrm{B}(^2\mathrm{P})$ the calculation involved only the p_z component, consistent with dissociating to the $\mathrm{X}^3\Sigma_g^-$ state of B_2. In the IC-MRCI and IC-ACPF calculations, the dissociated limits were obtained in supermolecule calculations with $r = 50a_0$. All calculations in this work were carried out with the MOLPRO suite of ab initio electronic structure programs [37].

3 Results and discussion

The CCSD, CCSD(T), IC-MRCI and IC-MRCI + Q results for D_e, r_e, and ω_e from both valence-only and all-electron calculations are shown in Tables 1–5 for B_2–F_2, respectively, where the results are also compared to the available experimental data. Also shown in these tables are the estimated CBS limits for E_e and D_e obtained from fits of the total energies to the standard exponential function.

In each case, reasonably smooth convergence of the calculated spectroscopic constants toward the apparent CBS limits are observed. The systematic convergence of both the valence-only and all-electron quantities is illustrated in Figs. 1–3, where the CCSD(T) results for B_2–F_2 are plotted as a function of the cc-pCV*n*Z basis set used. As observed in these figures and also in Tables 1–5, the major effect of correlating the core electrons is accounted for by using the cc-pCVQZ basis set. For example, in the case of the CCSD(T) calculations on N_2, the cc-pCVQZ basis set yielded core contributions to D_e and ω_e that were better than 90% of the converged values (Table 3). Even the cc-pCVTZ set accounts for 85% of the effect on D_e and 75–80% of the effect on r_e and ω_e.

In general, B_2 and C_2 (Tables 1 and 2) exhibited the slowest convergence with respect to the calculated core-correlation effects. For example, the magnitude of the CCSD(T) bond-length contraction in B_2 upon correlating the core electrons increases from 0.0046 Å with the cc-pCVTZ basis set to 0.0058 Å with the cc-pCVQZ set. Further extension of the basis set results in additional contractions of 0.0005 Å (cc-pCV5Z) and 0.0001 Å (cc-pCV6Z). The somewhat slower convergence for B_2 and C_2 may be indicative of a bias of the cc-pCV*n*Z basis sets toward describing core-core correlation over core-valence correlation. This will be the subject of a later publication.

Table 1. Spectroscopic constants for B_2 calculated by valence-only and all-electron calculations

Method	Basis set	E_e (E_H)		D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	All	Valence	All	Δ	Valence	All	Δ	Valence	All	Δ
	Experimental				67.2 ± 1.4[a]			1.5900[b]			1051.3[b]	
CCSD	cc-pCVDZ	−49.258244	−49.329202	49.99	50.24	+0.26	1.6271	1.6255	−0.0016	1006.7	1009.0	+2.4
	cc-pCVTZ	−49.279570	−49.370935	53.55	53.87	+0.32	1.6008	1.5973	−0.0035	1031.9	1036.9	+5.0
	cc-pCVQZ	−49.285797	−49.384311	54.63	55.07	+0.44	1.5969	1.5918	−0.0051	1037.2	1044.9	+7.7
	cc-pCV5Z	−49.287383	−49.388096	54.95	55.42	+0.47	1.5960	1.5905	−0.0055	1038.5	1046.8	+8.3
	cc-pCV6Z	−49.287931	−49.389501	55.06	55.55	+0.49	1.5957	1.5901	−0.0056	1038.9	1047.4	+8.5
	Est. CBS[c]	−49.2881	−49.3901	55.1	55.6	+0.5						
CCSD(T)	cc-pCVDZ	−49.272594	−49.344046	57.87	58.22	+0.34	1.6251	1.6232	−0.0019	1017.7	1020.3	+2.6
	cc-pCVTZ	−49.297107	−49.389458	62.71	63.21	+0.50	1.5976	1.5935	−0.0040	1043.4	1048.8	+5.4
	cc-pCVQZ	−49.304207	−49.404040	64.17	64.86	+0.70	1.5932	1.5874	−0.0058	1048.8	1056.9	+8.1
	cc-pCV5Z	−49.306067	−49.408184	64.60	65.35	+0.75	1.5922	1.5860	−0.0063	1050.1	1058.8	+8.7
	cc-pCV6Z	−49.306720	−49.409725	64.77	65.53	+0.76	1.5919	1.5855	−0.0064	1050.4	1059.3	+8.9
	Est. CBS[c]	−49.3069	−49.4104	64.8	65.6	+0.8						
ICMRCI	cc-pCVDZ	−49.274919	−49.343343	59.75	60.49	+0.74	1.6293	1.6266	−0.0027	1010.7	1015.6	+5.0
	cc-pCVTZ	−49.298028	−49.386216	64.18	65.24	+1.06	1.6023	1.5975	−0.0048	1034.4	1042.8	+8.5
	cc-pCVQZ	−49.304587	−49.399927	65.43	66.71	+1.29	1.5981	1.5916	−0.0065	1039.5	1050.6	+11.1
	cc-pCV5Z	−49.306238	−49.403777	65.78	67.12	+1.34	1.5971	1.5902	−0.0070	1040.7	1052.5	+11.8
	Est. CBS[c]	−49.3070	−49.4058	65.9	67.3	+1.4						
ICMRCI + Q	cc-pCVDZ	−49.277503	−49.348502	59.46	60.02	+0.56	1.6300	1.6276	−0.0024	1008.6	1012.5	+3.9
	cc-pCVTZ	−49.301659	−49.393378	63.88	64.72	+0.84	1.6024	1.5979	−0.0046	1032.5	1039.6	+7.1
	cc-pCVQZ	−49.308446	−49.407597	65.17	66.26	+1.10	1.5982	1.5919	−0.0063	1037.6	1047.4	+9.8
	cc-pCV5Z	−49.310144	−49.411557	65.53	66.69	+1.16	1.5973	1.5905	−0.0068	1038.8	1049.3	+10.5
	Est. CBS[c]	−49.3109	−49.4136	65.7	66.9	+1.2						

[a] Ab initio prediction from Ref. [43] [b] Ref. [45] [c] Est. CBS is the estimated complete basis set limit

Table 2. Spectroscopic constants for C_2 from valence-only and all-electron calculations

Method	Basis set	E_e (E_H)		D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	All	Valence	All	Δ	Valence	All	Δ	Valence	All	Δ
	Experimental				147.8 ± 0.5[a]			1.2425[b]			1854.7[b]	
CCSD	cc-pCVDZ	−75.702651	−75.775155	113.82	113.92	+0.10	1.2647	1.2639	−0.0008	1858.2	1861.2	+3.0
	cc-pCVTZ	−75.752329	−75.848550	121.43	121.62	+0.19	1.2449	1.2429	−0.0020	1884.2	1892.0	+7.8
	cc-pCVQZ	−75.766660	−75.871694	124.37	124.62	+0.25	1.2418	1.2391	−0.0028	1893.0	1903.1	+10.1
	cc-pCV5Z	−75.770857	−75.878481	125.37	125.66	+0.29	1.2410	1.2381	−0.0029	1895.7	1906.4	+10.6
	cc-pCV6Z	−75.772347	−75.880986	125.77	126.07	+0.30	1.2407	1.2377	−0.0030	1896.9	1907.6	+10.7
	Est. CBS[c]	−75.7727	−75.8819	126.0	126.3	+0.3						
CCSD(T)	cc-pCVDZ	−75.730813	−75.803986	130.23	130.59	+0.35	1.2689	1.2680	−0.0009	1824.8	1827.7	+2.9
	cc-pCVTZ	−75.786192	−75.883829	139.90	140.61	+0.71	1.2487	1.2465	−0.0022	1848.5	1856.1	+7.6
	cc-pCVQZ	−75.801943	−75.908751	143.33	144.24	+0.91	1.2455	1.2425	−0.0030	1856.7	1866.7	+10.0
	cc-pCV5Z	−75.806599	−75.916085	144.51	145.48	+0.97	1.2446	1.2414	−0.0032	1859.1	1869.6	+10.6
	cc-pCV6Z	−75.808259	−75.918788	144.97	145.97	+1.00	1.2443	1.2411	−0.0032	1860.1	1870.7	+10.6
	Est. CBS[c]	−75.8086	−75.9197	145.2	146.2	+1.0						
ICMRCI	cc-pCVDZ	−75.728920	−75.799030	131.32	132.52	+1.19	1.2705	1.2691	−0.0015	1815.9	1823.2	+7.2
	cc-pCVTZ	−75.780798	−75.873857	140.86	142.70	+1.84	1.2500	1.2471	−0.0029	1842.5	1854.8	+12.3
	cc-pCVQZ	−75.795422	−75.897165	144.07	146.19	+2.12	1.2467	1.2430	−0.0037	1851.7	1866.2	+14.5
	cc-pCV5Z	−75.799668	−75.903965	145.12	147.32	+2.20	1.2457	1.2418	−0.0039	1854.8	1870.0	+15.2
	Est. CBS[c]	−75.8013	−75.9072	145.6	147.9	+2.3						
ICMRCI + Q	cc-pCVDZ	−75.733358	−75.806204	129.86	130.63	+0.77	1.2714	1.2701	−0.0012	1810.3	1816.2	+5.9
	cc-pCVTZ	−75.787674	−75.884760	139.19	140.52	+1.33	1.2507	1.2479	−0.0027	1836.5	1847.5	+11.0
	cc-pCVQZ	−75.802952	−75.909142	142.50	144.13	+1.63	1.2473	1.2437	−0.0035	1845.7	1858.9	+13.2
	cc-pCV5Z	−75.807366	−75.916207	143.60	145.32	+1.72	1.2463	1.2426	−0.0038	1848.6	1862.6	+14.0
	Est. CBS[c]	−75.8090	−75.9196	144.1	146.0	+1.9						

[a] Ref. [41], [b] Ref. [45], [c] Est. CBS is the estimated complete basis set limit

Table 3. Spectroscopic constants for N_2 from valence-only and all-electron calculations

Method	Basis set	E_e (E_H)		D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	All	Valence	All	Δ	Valence	All	Δ	Valence	All	Δ
	Experimental[a]				228.4			1.0977			2358.6	
CCSD	cc-pCVDZ	−109.268753	−109.343281	194.18	194.48	+0.30	1.1118	1.1112	−0.0006	2408.1	2411.8	+3.8
	cc-pCVTZ	−109.360335	−109.462698	208.73	209.19	+0.46	1.0952	1.0935	−0.0017	2424.9	2434.2	+9.3
	cc-pCVQZ	−109.386109	−109.498556	214.33	214.81	+0.48	1.0929	1.0908	−0.0021	2436.0	2446.7	+10.7
	cc-pCV5Z	−109.394283	−109.509695	216.38	216.90	+0.52	1.0921	1.0899	−0.0022	2440.2	2451.5	+11.3
	cc-pCV6Z	−109.397267	−109.513836	217.28	217.81	+0.53	1.0919	1.0896	−0.0023	2441.3	2452.8	+11.5
	Est. CBS[b]	−109.3977	−109.5149	217.8	218.3	+0.5						
CCSD(T)	cc-pCVDZ	−109.281483	−109.356338	201.34	201.74	+0.40	1.1179	1.1174	−0.0006	2338.3	2341.5	+3.2
	cc-pCVTZ	−109.379248	−109.482426	217.53	218.21	+0.68	1.1023	1.1006	−0.0016	2346.7	2354.6	+7.9
	cc-pCVQZ	−109.406419	−109.519837	223.38	224.11	+0.73	1.1001	1.0981	−0.0020	2356.5	2365.7	+9.2
	cc-pCV5Z	−109.415074	−109.531509	225.55	226.33	+0.78	1.0993	1.0972	−0.0021	2360.2	2370.0	+9.8
	cc-pCV6Z	−109.418247	−109.535855	226.49	227.29	+0.80	1.0991	1.0970	−0.0021	2361.2	2371.1	+9.9
	Est. CBS[b]	−109.4187	−109.5369	226.9	227.7	+0.8						
ICMRCI	cc-pCVDZ	−109.275622	−109.346913	202.59	203.36	+0.76	1.1186	1.1178	−0.0007	2328.1	2332.6	+4.5
	cc-pCVTZ	−109.366553	−109.464001	218.73	219.99	+1.25	1.1025	1.1007	−0.0018	2341.3	2350.7	+9.4
	cc-pCVQZ	−109.391780	−109.498741	224.39	225.73	+1.33	1.1003	1.0981	−0.0022	2352.0	2362.7	+10.7
	cc-pCV5Z	−109.399763	−109.509547	226.43	227.81	+1.38	1.0995	1.0972	−0.0023	2356.1	2367.4	+11.3
	Est. CBS[b]	−109.4024	−109.5139	227.3	228.8	+1.5						
ICMRCI + Q	cc-pCVDZ	−109.283923	−109.358385	201.35	201.83	+0.49	1.1193	1.1187	−0.0006	2322.3	2325.6	+3.4
	cc-pCVTZ	−109.379741	−109.482068	217.44	218.39	+0.95	1.1033	1.1016	−0.0017	2334.2	2342.3	+8.1
	cc-pCVQZ	−109.406330	−109.518705	223.35	224.40	+1.05	1.1011	1.0990	−0.0021	2344.6	2354.1	+9.5
	cc-pCV5Z	−109.414714	−109.530038	225.49	226.60	+1.11	1.1003	1.0981	−0.0022	2348.7	2358.6	+9.9
	Est. CBS[b]	−109.4175	−109.5346	226.4	227.7	+1.2						

[a] Ref. [45], [b] Est. CBS is the estimated complete basis set limit

Table 4. Spectroscopic constants for O_2 from valence-only and all-electron calculations

Method	Basis set	E_e (E_H)		D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	All	Valence	All	Δ	Valence	All	Δ	Valence	All	Δ
	Experimental[a]				120.6			1.2075			1580.2	
CCSD	cc-pCVDZ	−149.979782	−150.055246	98.13	98.27	+0.14	1.2049	1.2042	−0.0007	1670.2	1672.8	+2.6
	cc-pCVTZ	−150.115804	−150.222525	105.34	105.45	+0.10	1.1986	1.1968	−0.0018	1678.1	1684.5	+6.4
	cc-pCVQZ	−150.154350	−150.271985	108.32	108.39	+0.07	1.1944	1.1924	−0.0020	1696.2	1703.1	+7.0
	cc-pCV5Z	−150.166817	−150.287768	109.41	109.48	+0.07	1.1935	1.1914	−0.0021	1698.3	1705.6	+7.2
	cc-pCV6Z	−150.171207	−150.293457	109.99	110.06	+0.07	1.1931	1.1910	−0.0021	1700.4	1707.7	+7.3
	Est. CBS[b]	−150.1720	−150.2948	110.3	110.3	+0.1						
CCSD(T)	cc-pCVDZ	−149.991233	−150.066967	104.27	104.47	+0.20	1.2154	1.2147	−0.0007	1587.3	1589.4	+2.1
	cc-pCVTZ	−150.135896	−150.243353	113.98	114.22	+0.24	1.2114	1.2097	−0.0017	1585.9	1591.0	+5.1
	cc-pCVQZ	−150.176410	−150.294914	117.29	117.51	+0.22	1.2074	1.2055	−0.0019	1601.4	1607.0	+5.6
	cc-pCV5Z	−150.189603	−150.311465	118.51	118.74	+0.23	1.2066	1.2046	−0.0020	1602.4	1608.3	+5.9
	cc-pCV6Z	−150.194262	−150.317437	119.16	119.38	+0.22	1.2063	1.2042	−0.0021	1604.1	1610.1	+6.0
	Est. CBS[b]	−150.1950	−150.3187	119.3	119.5	+0.2						
ICMRCI	cc-pCVDZ	−149.977383	−150.048579	103.54	103.54	+0.00	1.2178	1.2168	−0.0010	1558.9	1562.0	+3.1
	cc-pCVTZ	−150.109359	−150.209357	112.48	112.55	+0.07	1.2121	1.2099	−0.0022	1568.0	1575.0	+7.0
	cc-pCVQZ	−150.146189	−150.256261	115.60	115.66	+0.05	1.2077	1.2053	−0.0024	1586.2	1593.9	+7.8
	cc-pCV5Z	−150.158122	−150.271288	116.75	116.81	+0.06	1.2068	1.2042	−0.0025	1588.6	1596.8	+8.2
	Est. CBS[b]	−150.1621	−150.2769	117.3	117.3	+0.1						
ICMRCI + Q	cc-pCVDZ	−149.993508	−150.068511	104.99	105.10	+0.11	1.2190	1.2182	−0.0008	1555.7	1558.2	+2.6
	cc-pCVTZ	−150.134388	−150.240284	114.15	114.33	+0.19	1.2143	1.2124	−0.0020	1559.4	1565.5	+6.1
	cc-pCVQZ	−150.173784	−150.290381	117.46	117.64	+0.19	1.2101	1.2078	−0.0022	1576.5	1583.4	+6.9
	cc-pCV5Z	−150.186488	−150.306324	118.67	118.88	+0.20	1.2092	1.2068	−0.0024	1578.3	1585.5	+7.2
	Est. CBS[b]	−150.1907	−150.3123	119.2	119.5	+0.2						

[a] Ref. [45]. Spin-orbit effects have been removed from the experimental D_e (see Ref. [14]), [b] Est. CBS is the estimated complete basis set limit

Table 5. Spectroscopic constants for F_2 from valence-only and all-electron calculations

Method	Basis set	E_e (E_H)		D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	All	Valence	All	Δ	Valence	All	Δ	Valence	All	Δ
	Experimental[a]				39.0			1.4119			916.6	
CCSD	cc-pCVDZ	−199.095779	−199.172177	22.30	22.26	−0.04	1.4314	1.4306	−0.0008	887.8	890.2	+2.4
	cc-pCVTZ	−199.288659	−199.399844	28.56	28.32	−0.24	1.3933	1.3915	−0.0018	1016.7	1020.6	+3.9
	cc-pCVQZ	−199.343154	−199.466185	29.88	29.59	−0.28	1.3903	1.3883	−0.0020	1015.8	1019.9	+4.2
	cc-pCV5Z	−199.361398	−199.488012	30.61	30.32	−0.29	1.3884	1.3864	−0.0020	1021.9	1026.1	+4.2
	cc-pCV6Z	−199.367688	−199.495731	31.01	30.72	−0.29	1.3876	1.3855	−0.0021	1052.0	1056.4	+4.4
	Est. CBS[b]	−199.3688	−199.4974	30.9	30.6	−0.3						
CCSD(T)	cc-pCVDZ	−199.105806	−199.182524	27.38	27.44	+0.06	1.4571	1.4567	−0.0005	785.4	786.3	+0.9
	cc-pCVTZ	−199.307081	−199.419094	35.26	35.21	−0.05	1.4145	1.4133	−0.0012	923.9	925.3	+1.4
	cc-pCVQZ	−199.364093	−199.488097	36.95	36.88	−0.07	1.4127	1.4113	−0.0014	920.8	922.3	+1.5
	cc-pCV5Z	−199.383236	−199.510859	37.81	37.73	−0.08	1.4110	1.4095	−0.0014	926.6	928.1	+1.5
	cc-pCV6Z	−199.389859	−199.518925	38.26	38.19	−0.07	1.4102	1.4087	−0.0015	953.9	955.5	+1.6
	Est. CBS[b]	−199.3910	−199.5207	38.1	38.0	−0.1						
ICMRCI	cc-pCVDZ	−199.087932	−199.160278	26.38	26.20	−0.17	1.4648	1.4645	−0.0003	757.3	756.0	−1.3
	cc-pCVTZ	−199.272191	−199.376661	32.67	32.32	−0.35	1.4179	1.4165	−0.0014	894.4	893.3	−1.1
	cc-pCVQZ	−199.323906	−199.439260	33.95	33.54	−0.41	1.4151	1.4134	−0.0016	893.0	891.9	−1.1
	cc-pCV5Z	−199.341178	−199.459845	34.62	34.19	−0.42	1.4127	1.4110	−0.0017	900.0	899.0	−1.0
	Est. CBS[b]	−199.3468	−199.4672	34.6	34.2	−0.4						
ICMRCI + Q	cc-pCVDZ	−199.106261	−199.182295	27.76	27.70	−0.06	1.4615	1.4609	−0.0006	773.1	773.2	+0.1
	cc-pCVTZ	−199.302096	−199.412591	34.71	34.50	−0.21	1.4170	1.4154	−0.0015	911.1	911.5	+0.4
	cc-pCVQZ	−199.357477	−199.479583	36.25	35.99	−0.26	1.4145	1.4127	−0.0018	909.5	909.9	+0.4
	cc-pCV5Z	−199.375910	−199.501506	37.02	36.74	−0.27	1.4124	1.4105	−0.0019	916.4	916.9	+0.5
	Est. CBS[b]	−199.3820	−199.5095	37.1	36.8	−0.3						

[a] Ref. [45]. Spin-orbit effects have been removed from the experimental D_e (see Ref. [14]), [b] Est. CBS is the estimated complete basis set limit

Among the correlated methods used in the present work, IC-MRCI generally yields the largest effects due to correlating the core electrons; see Figs. 1–3. Presumably this is due to the nonsize extensive nature of the method. An exception is the D_e of O_2, where the IC-MRCI core contributions are similar to those obtained by CCSD. Except for this case, the addition of IC-MRCI + Q yields core-correlation effects that are smaller than the IC-MRCI predictions. The CCSD(T) method generally yields somewhat smaller core contributions than IC-MRCI + Q, and CCSD alone yields the smallest effects of all methods.

For D_e of the C_2 molecule, which has the strongest multireference character among this series, the triples correction in CCSD(T) contributes nearly 0.7 kcal/mol of the total core contribution of 1.0 kcal/mol (cc-pCV6Z). Comparison to IC-MRCI + Q, however, suggests that this is still too small by several tenths of a kcal/mol. As mentioned above, methods that are size extensive should yield the most accurate estimates of the effects of core correlation. Table 6 compares the results obtained with the cc-pCVQZ basis set for CCSD(T), IC-MRCI + Q, and IC-ACPF. While CCSD(T) is expected to yield accurate results for species dominated by the Hartree-Fock configuration, i.e., N_2, O_2, and F_2, IC-MRCI + Q and especially IC-ACPF are expected to be more reliable for B_2 and C_2. These expectations are borne out in Table 6, where IC-MRCI + Q and IC-ACPF result in similar core contributions for D_e, r_e, and ω_e for B_2 and C_2. For N_2, O_2, and F_2 IC-ACPF and CCSD(T) yield core-correlation effects of very similar magnitude, whereas IC-MRCI + Q, which is only approximately size extensive, results in values that are generally somewhat larger. The close agreement of IC-ACPF with IC-MRCI + Q for B_2 and C_2, and of IC-ACPF and CCSD(T) for the others, provides good evidence that this method yields a highly reliable description of core-correlation effects for these systems. Similar conclusions have been obtained by other workers in the cases of C_2 and N_2 [18, 19, 38].

The data from Table 6 are also shown in Fig. 4, in which the trends across the entire series can be clearly seen. For both D_e and ω_e, the C_2 molecule exhibits the largest effects from correlating the 1*s* electrons. For the equilibrium bond length, the effect for B_2 is the largest at nearly −0.007 Å. The magnitude of this effect decreases to about 0.004 Å for C_2 and approximately 0.002 Å for the other members of the series. As has been noted previously by Császár and Allen [39], the core contribution to D_e for the F_2 molecule is actually slightly negative, i.e., correlation of the core electrons lowers the energy of the atoms more than that of the molecule. However, when the effect of core correlation is accurately calculated for the whole series as shown in Fig. 4, this result for F_2 should not seem too surprising given the observed trend.

In comparing the results of Tables 1–5 with experimental results the all-electron IC-MRCI + Q results yield r_e and ω_e values in excellent agreement. Indications from Table 6 are that the use of IC-ACPF would even slightly improve upon these results. Similar behavior concerning IC-MRCI + Q for N_2 has been noted previously in other

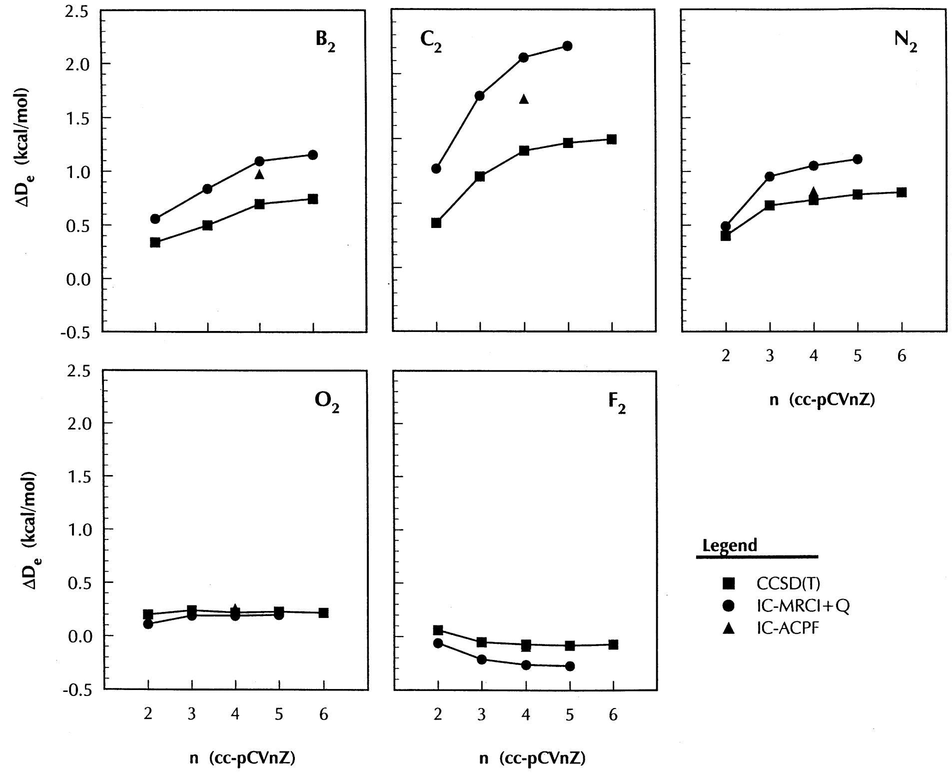

Fig. 1. Convergence of ΔD_e for B_2–F_2 as a function of the cc-pCV*n*Z basis set. Results are plotted for the CCSD(T), IC-MRCI + Q, and IC-ACPF (cc-pCVQZ set only) methods

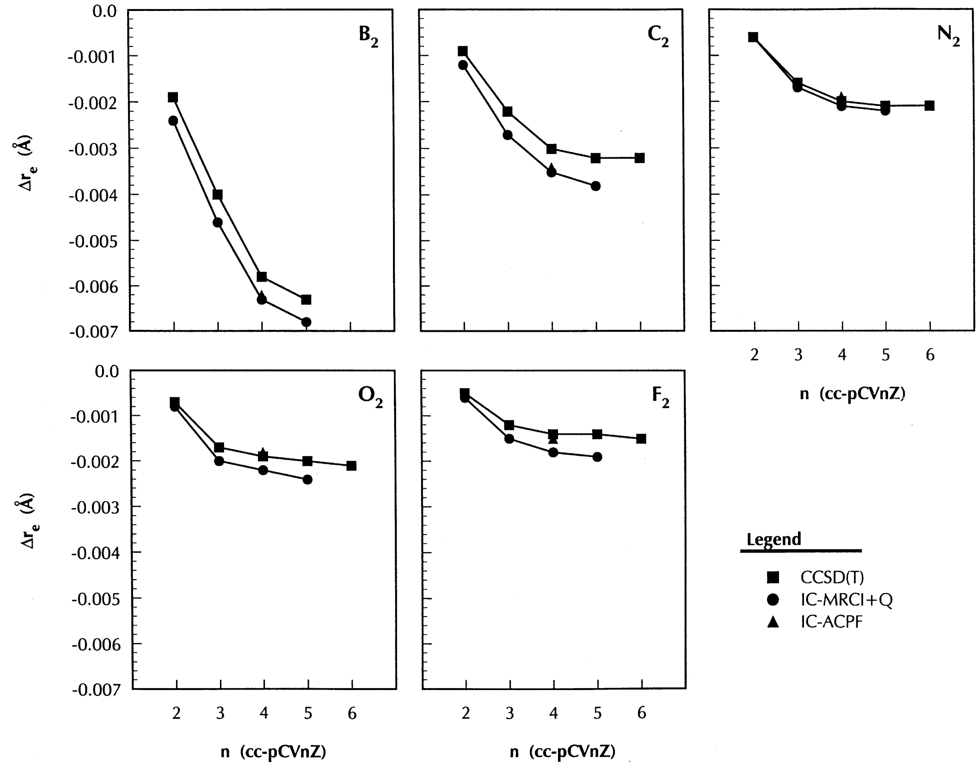

Fig. 2. Convergence of Δr_e for B_2–F_2 as a function of the cc-pCV*n*Z basis set. Results are plotted for the CCSD(T), IC-MRCI + Q, and IC-ACPF (cc-pCVQZ set only) methods

work [18, 36]. The CCSD(T) method generally yields bond lengths that are too small and harmonic frequencies that are too large when all the electrons are correlated. This is also true for IC-MRCI, but to a lesser extent in the case of ω_e. After extrapolating to the CBS limit, the accuracy of the dissociation energies calculated by IC-MRCI + Q is also very good for all of the species except C_2 and F_2. In the case of C_2, it has been shown [14, 40] that IC-MRCI provides a more accurate description of the energetics of this species compared to IC-MRCI + Q. Applying our estimated core contribution for D_e of 1.5 kcal/mol (see below) to the CBS limit valence-only IC-MRCI result (145.6 kcal/mol) yields 147.1 kcal/mol, which is in good agreement with the

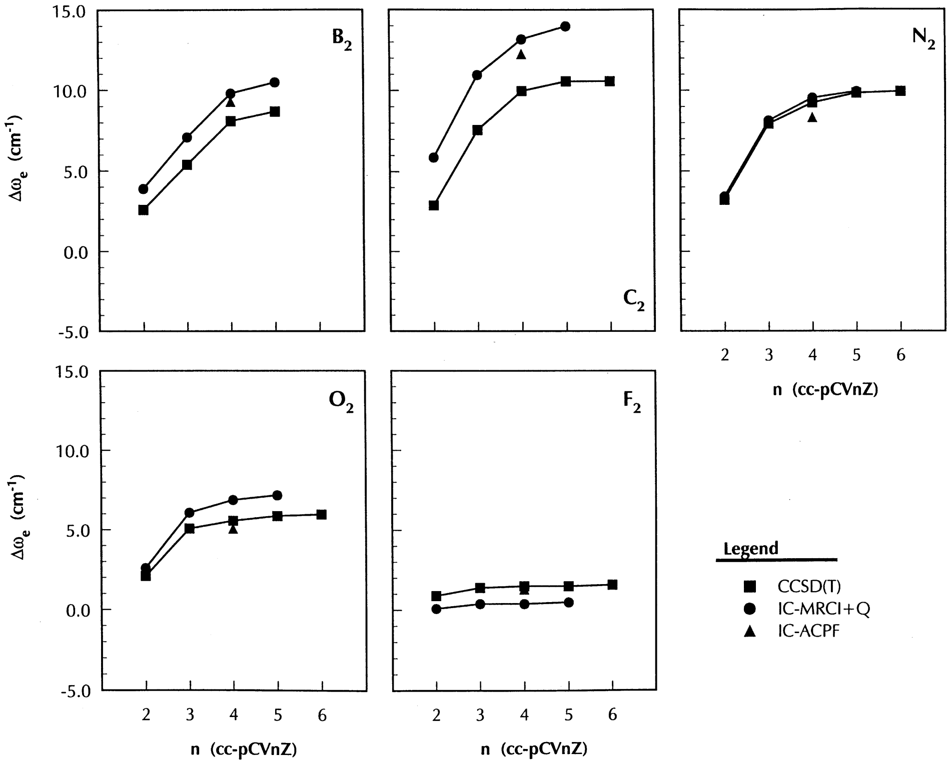

Fig. 3. Convergence of ΔW_e as a function of the cc-pVnZ basis set used

Table 6. Comparison of core-valence correlation effects calculated by IC-ACPF with IC-MRCI + Q and CCSD(T) using the cc-pCVQZ basis set

Species	Method	D_e (kcal/mol)			r_e (Å)			ω_e (cm^{-1})		
		Valence	All	Δ	Valence	All	Δ	Valence	All	Δ
B_2	ICACPF	65.24	66.22	+0.98	1.5982	1.5919	−0.0062	1038.2	1047.4	+9.3
	ICMRCI + Q	65.17	66.26	+1.10	1.5982	1.5919	−0.0063	1037.6	1047.4	+9.8
	CCSD(T)	64.17	64.86	+0.70	1.5932	1.5874	−0.0058	1048.8	1056.9	+8.1
C_2	ICACPF	142.78	144.09	+1.31	1.2472	1.2437	−0.0034	1846.7	1859.0	+12.3
	ICMRCI + Q	142.50	144.13	+1.63	1.2473	1.2437	−0.0035	1845.7	1858.9	+13.2
	CCSD(T)	143.33	144.24	+0.91	1.2455	1.2425	−0.0030	1856.7	1866.7	+10.0
N_2	ICACPF	223.41	224.22	+0.81	1.1010	1.0990	−0.0019	2345.5	2353.8	+8.3
	ICMRCI + Q	223.35	224.40	+1.05	1.1011	1.0990	−0.0021	2344.6	2354.1	+9.5
	CCSD(T)	223.38	224.11	+0.73	1.1001	1.0981	−0.0020	2356.5	2365.7	+9.2
O_2	ICACPF	117.24	117.50	+0.26	1.2102	1.2083	−0.0018	1575.8	1580.9	+5.1
	ICMRCI + Q	117.46	117.64	+0.19	1.2101	1.2078	−0.0022	1576.5	1583.4	+6.9
	CCSD(T)	117.29	117.51	+0.22	1.2074	1.2055	−0.0019	1601.4	1607.0	+5.6
F_2	ICACPF	36.19	36.10	−0.09	1.4151	1.4135	−0.0015	908.5	909.8	+1.3
	ICMRCI + Q	36.25	35.99	−0.26	1.4145	1.4127	−0.0018	909.5	909.9	+0.4
	CCSD(T)	36.95	36.88	−0.07	1.4127	1.4113	−0.0014	920.8	922.3	+1.5

experimental value 147.8 ± 0.5 kcal/mol of Urdahl et al. [41]. For the D_e of F_2, most of the deviation from experimental results at the IC-MRCI level was shown previously [14] to be due to a poor cancellation of the internal contraction error in F_2 with that of F atom for a valence CAS reference function. In this case, the CCSD(T) D_e is in much better agreement with the experiment. Surprisingly, however, at the all-electron CBS limit D_e[CCSD(T)] is still smaller than the experimental data by 1.0 kcal/mol.

In order to accurately predict the magnitude of the core correlation effect on D_e, r_e, and ω_e for all five species of this series, we take the estimated CBS limits from IC-MRCI + Q calculations for B_2 and C_2 (Tables 1 and 2) and from CCSD(T) calculations for the others (Tables 3–5) and combine these with the differences between these methods and IC-ACPF from Table 6. The effects of 1s correlation on D_e (kcal/mol), r_e (Å), and ω_e (cm^{-1}) are thus estimated to be: +1.1, −0.0070, +10 for B_2; +1.5, −0.0040, +13 for C_2; +0.9, −0.0020, +9 for N_2; +0.3, −0.0020, +6 for O_2; and −0.1, −0.0015, +1 for F_2.

Recently, the C_2 and N_2 molecules have been the subject of several studies, some of which have included

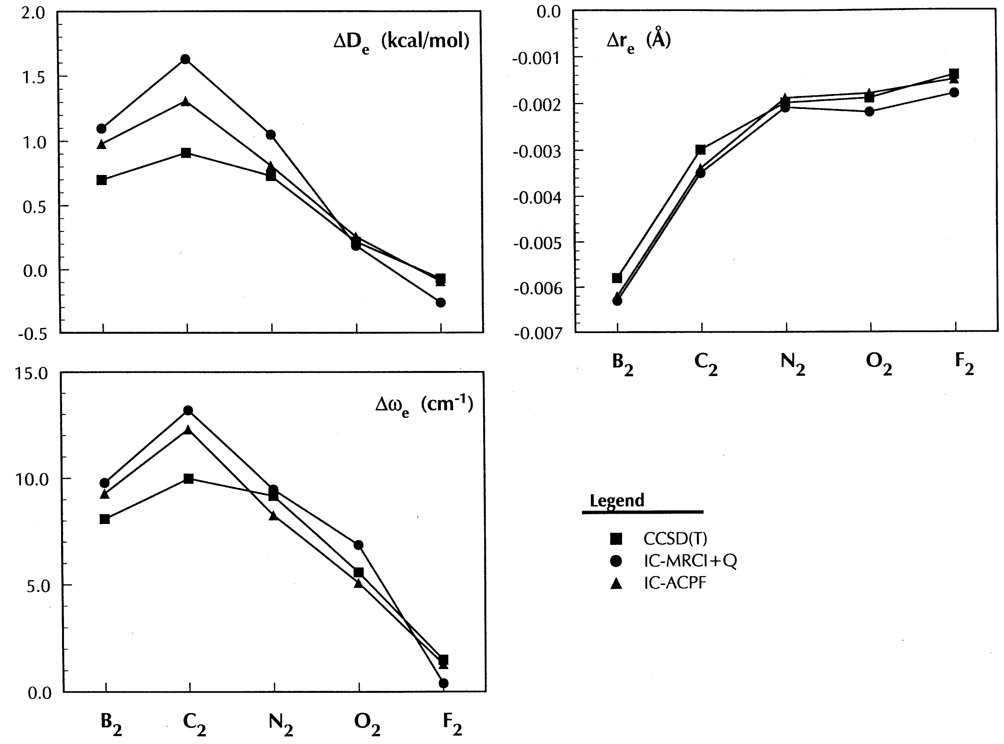

Fig. 4. A comparison of calculated core-correlation contributions to D_e, r_e, and ω_e using the cc-pCVQZ basis set with the CCSD(T), IC-MRCI + Q, and IC-ACPF methods for the set of homonuclear diatomics containing first two atoms

the effects of correlating the core electrons. For the N_2 molecule, recent work has included IC-MRCI calculations by Werner and Knowles [36] and the work of Bauschlicher and Partridge [18] where several correlation methods were employed and compared. In neither case were the basis sets used systematically extendable. However, these sets, which were based on atomic natural orbitals (ANO) [42], were significantly flexible to yield excellent agreement with our present cc-pCVQZ results. This was also found to be the case for C_2, where recent studies by Pradhan et al. [19] and Partridge and Bauschlicher [38] used a basis set similar to the one used by Bauschlicher and Partridge for N_2. In the present case, the systematic convergence of the cc-pCV*n*Z basis sets allows the estimation of the all-electron CBS limits, which results in somewhat larger core contributions, especially for D_e.

The current work appears to be the first accurate study of the core-correlation effects in B_2. Previous work [43] had proposed a maximum core contribution to D_e of 0.7 kcal/mol based upon comparison to calculations on BH. The present IC-MRCI + Q and IC-ACPF calculations, however, predict that the actual core contribution should be about 1.1 kcal/mol. Adding this result to our valence-only IC-MRCI CBS limit D_e, which is expected to be the most accurate based on a previous full CI calibration [14], yields a prediction for D_e of 67.0 kcal/mol. The uncertainty in this value is estimated to be less than 1 kcal/mol based on the estimated residual errors in the one- and *n*-particle treatments. This is in very good agreement with earlier ab initio predictions of 67.2 ± 1.4 [43] and 66.9 kcal/mol [14].

For the other members of this series, Császár and Allen [39] have presented results at the CCSD(T) level of theory using basis sets similar to those used by Bauschlicher and Partridge. Their results tend to be in good agreement with our cc-pCVQZ values. Likewise, similar effects of core correlation on the spectroscopic properties of several small molecules that included N_2 and F_2 were obtained in a study by Martin [44], where the cc-pCVTZ and ANO-based basis sets were used.

Table 7. Best estimates of the core and core-valence correlation effects on D_e, r_e, ω_e for the B_2–F_2 series

Species	D_e (kcal/mol)	r_e (Å)	ω_e (cm^{-1})
B_2[a]	+1.1	−0.007	+10
C_2[a]	+1.5	−0.004	+13
N_2[b]	+0.9	−0.002	+9
O_2[b]	+0.3	−0.002	+6
F_2[b]	−0.1	−0.0015	+1

[a] Based on IC-MRCI + Q results at the estimated CBS limit with corrections from IC-ACPF/cc-pCVQZ. See the text

[b] Based on CCSD(T) results at the estimated CBS limit with corrections from IC-ACPF/cc-pCVQZ. See the text

4 Conclusions

The effects of correlating the 1*s*-like core electrons in the homonuclear diatomics containing first row atoms have been studied using several methods for treating electron correlation and systematic sequences of core-valence correlation consistent basis sets. The regular convergence characteristics of these sets allowed for estimates of both the valence-only and all-electron CBS limits for each property with each correlation method. This facilitated the accurate prediction of the core contributions to D_e, r_e, and ω_e for each species. The IC-MRCI + Q and, in particular, IC-ACPF methods provided reliable results for B_2 and C_2, while IC-ACPF and CCSD(T) produced reliable estimates of the core contributions for N_2, O_2, and F_2.

The best estimates for the core- and core-valence correlation effects on D_e, r_e, and ω_e for the B_2–F_2 series are given in Table 7. As can be seen, the effects decrease dramatically, but not quite uniformly, from B_2 to F_2 for D_e and ω_e, the effect of including the 1*s* electrons in the calculations is actually largest for C_2. Clearly, however, core- and core-valence correlation effects must be taken into account if high accuracy is required.

Convergence of the core- and core-valence effects with basis sets is reasonably rapid. Calculations with the cc-pVQZ set yield more than 90% of the estimated CBS limits. Even the cc-pCVTZ set provides reasonable estimates of the core- and core-valence effects for D_e, r_e, and ω_e.

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