Comparison of the effective core potential and model potential methods in studies of electron correlation energy in molecules: Dihalides and halogen hydrides*

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Summary. The effective core potential and model potential methods were used in post-SCF calculations on HCl, HBr, Cl_2, and Br_2 in order to gain insight into the effect of insufficient representation of inner nodes in the valence orbitals of the approximate methods. The results show that while the correlation energy may be slightly overestimated (by 1–7%), both the electric moment functions and the quantities depending on energy differences are consistently similar for the methods studied and close to the results from all-electron calculations.

Key words: Effective core potential method – Model potential method – Dihalides – Halogen halides – Electron correlation energy

1. Introduction

The methods which attempt to utilize the similarity between the valence electron shells in atoms belonging to the same family of elements in the Periodic Table in order to facilitate computational studies of the molecular structure have a history dating back to the 1930s. For an excellent, lucid review of the historical developments, see the work of Krauss and Stevens [1] and Gropen [2]; a more lengthy exposition can be found in the book by Szasz [3].

The most popular of these methods is the effective core potential (ECP) method which, by the virtue of the utilizing smooth, nodeless valence orbitals, is capable of providing substantial computational savings in the studies of large molecules and molecular systems which contain heavy atoms.

Amongst the methods which, for reasons of computational efficiency, treat explicitly only the valence electrons while replacing the core electrons by a suitably defined potential function, the model potential (MP) method [4] is capable of maintaining the nodal structure of the all-electron (AE) valence orbitals. The appeal of the model potential method, as opposed to the effective core potential method, stems from the ability of the former to reproduce the

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nodal structure of the valence orbitals with arbitrary accuracy, while the latter produces nodeless valence orbitals. The reduced number of nodes in the effective core potential techniques was associated with too large electron correlation energies [5, 6]. However, the rich nodal structure of the orbitals in heavier atoms requires a large number of primitive basis functions to span the nodes; usually, for reasons of computational efficiency, the number of primitive functions is reduced and, consequently, the inner parts of the valence MP orbitals are distorted. Furthermore, as shown in previous studies on the electron correlation effects in atoms [7], the flexible basis sets used in the MP approach may capture the core orbitals shifted into the continuum by the projector operators and lead to overestimated values of the correlation energy despite the (approximately correct) number of nodes in the valence orbitals.

The relative merits of the two approaches to the valence-electron (VE) approximation are best studied using the same program. Recently, the model potential integrals were incorporated into the GAMESS system [8] (which already contained the ECP formalism) and applied to the studies of spin-orbit effects [9]. We decided to undertake a comparative study of the two methods in the calculations on post-SCF level as applied to the molecules HCl, HBr, Cl_2 and Br_2 which were frequently used to estimate quality of the approximate methods.

2. Calculations and results

2.1. Description of one- and many-electron basis sets

Basis sets for all atoms were contracted to give triple-zeta (TZ) flexibility in the valence region: For hydrogen, Huzinaga's (5s) basis [10] was contracted to (311) and equipped with a single p-type polarization function ($\zeta_p^H = 1.0$).

The all-electron (AE) basis set for chlorine, (433/43), was taken from our compilation [11] and used in the TZ contraction of (43111/4111). The model potential (MP) valence basis of (4/4) was contracted to (211/211) [12]. The effective core potential (WH) basis set (3/3) [13] was used in the form (111/111). The compact effective potential (SBK) basis set (4/4) [14] was used in contraction (211/211). All chlorine basis sets were augmented with a diffuse p-type function ($\zeta_p^{Cl} = 0.049$) and a d-type polarization function ($\zeta_d^{Cl} = 0.47$).

For bromine, the all electron basis set (4333/433/4) [11] was contracted to (433111/43111/4). In the model potential calculations, the (5/5) basis set [12] was contracted to (311/311). The (3/3) basis for the effective core potential calculations [13] was used in the uncontracted form (111/111). A single diffuse p-type function ($\zeta_p^{Br} = 0.03$) and a single d-type polarization function ($\zeta_d^{Br} = 0.36$) were added to all basis sets for bromine.

In order to assess the effect of multiple polarization functions, CISD calculations were done for the ground state of HCl using two sets of d-type polarization functions for chlorine, $\zeta_d^{Cl} = \{0.797, 0.220\}$, and two sets of p-type functions for hydrogen, $\zeta_p^H = \{1.70, 0.45\}$.

The correlation effects were studied using MCSCF and CI wavefunctions. In the CI calculations for HCl and HBr, with the SCF electronic configuration [core]$(1\sigma^2)\{2\sigma^2 1\pi^4\}$ all configurational state functions (CSFs) generated by single and double excitations from the valence space $\{2\sigma^2 1\pi^4\}$ into the space of all virtual orbitals were taken into account. In the MCSCF calculations, the FORS wavefunctions [15] were generated in the active space $\{2\sigma^2 1\pi^4 3\sigma^0 2\pi^0\}$. In

the all-electron calculations for HCl, [core] $= [1s^2 2s^2 2p^6]$; for HBr, [core] $= [1s^2 2s^2 2p^6 3s^2 3p^2 3d^{10}]$. The core orbitals were always doubly occupied and in the valence-electron calculations they were replaced by a potential.

For Cl_2 and Br_2 with the SCF configuration [core]$(1\sigma_g^2 1\sigma_u^2)\{2\sigma_g^2 1\pi_u^4 1\pi_g^4\}$, all CSFs generated by single and double excitations from the valence space $\{2\sigma_g^2 1\pi_u^4 1\pi_g^4\}$ into the full virtual space were used in the CI wavefunction. Due to CPU limitations, the MCSCF wavefunctions were obtained by single and double excitations in the active space $\{2\sigma_g^2 1\pi_u^4 1\pi_g^4 2\sigma_u^0 2\pi_u^0 2\pi_g^0\}$.

The values of the dissociation energies for the SCF and CI wavefunctions were calculated by subtracting the value of the total energy at the equilibrium internuclear distance from the sum of the (SCF or CI) energies of the isolated atoms. For the MCSCF wavefunctions, the values of D_e were computed as the difference between the total energy at a very large (about 20 a_0) internuclear distance and the (interpolated) minimum value of the molecular total energy.

All calculations were done using a modified GAMESS code [8] running on an Amdahl 5870 and a SUN 4/370.

2.2. Results of calculations

The radial dependence of the electron correlation energy and the electric moments is very similar for the molecules studied, therefore only the results for HCl are shown here (the figures for the remaining molecules are available upon request).

The potential energy curves obtained with the MCSCF wavefunctions are presented on Fig. 1. All four methods give essentially identical overall depen-
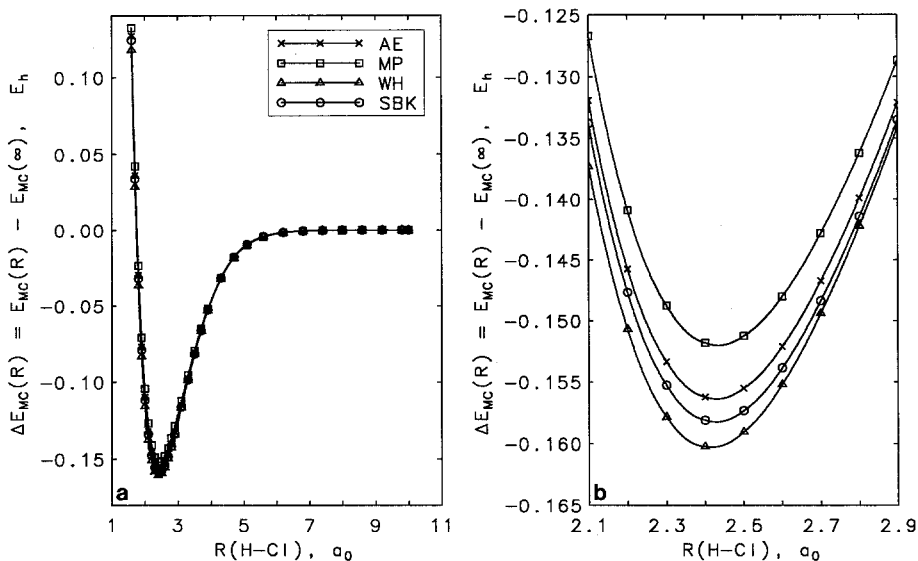

Fig. 1a,b. MCSCF potential energy curves for HCl: **a** overall behaviour; **b** expanded region near the minimum. (The abbreviations denote: AE = all-electron ×—×—×, MP = model potential □—□—□, WH = effective core potential of Wadt and Hay [13] △—△—△, SBK = compact effective potential of Stevens et al. [14] ○—○—○

dence of the total energy on the internuclear distance. Both at the small and large internuclear distances the curves are very close to one another. The largest deviations occur in the region near the potential minimum, where the AE curve is bracketed by the MP curve from above (probably due to too large atomic correlation energies) and the effective core potential curves from below. The largest deviation is smaller than 5 mE_h. The curves of the dipole and quadrupole moment (Fig. 2) also show remarkably good overall agreement.

In order to assess the possible overestimation of the correlation energy by the valence electron methods, Fig. 3 presents the behavior of the correlation energy function $E_c(R) = E_{SCF}(R) - E_{MCSCF}(R)$ in the region near the potential energy minimum (where the single-determinant SCF wavefunction is a good zeroth-order wavefunction). The correlation energies from the valence-electron methods slightly overestimate (by about 2%) the all-electron values of E_c.

The electron correlation energy calculated with the CI wavefunctions is shown on Fig. 4. The MP wavefunction picks up more correlation energy than the other valence-electron methods; still, the MP method overestimates the all-electron correlation energy by only about 5%. (In the atomic calculations the origin of too large values of the correlation energy in the MP calculations could be traced to the contamination of the virtual space by core orbitals shifted up by the projector operators [7].) The effective core potential slightly underestimates the correlation energy.

The magnitude of the computed correlation energy depends on the polarization functions; the single-exponent functions used in the present calculations may favor one basis set more than another. Expanding the correlating space to two functions (Fig. 5) differentially magnifies the correlation energy by about 20 mE_h; the MP correlation energy is affected less than the WH and SBK values;
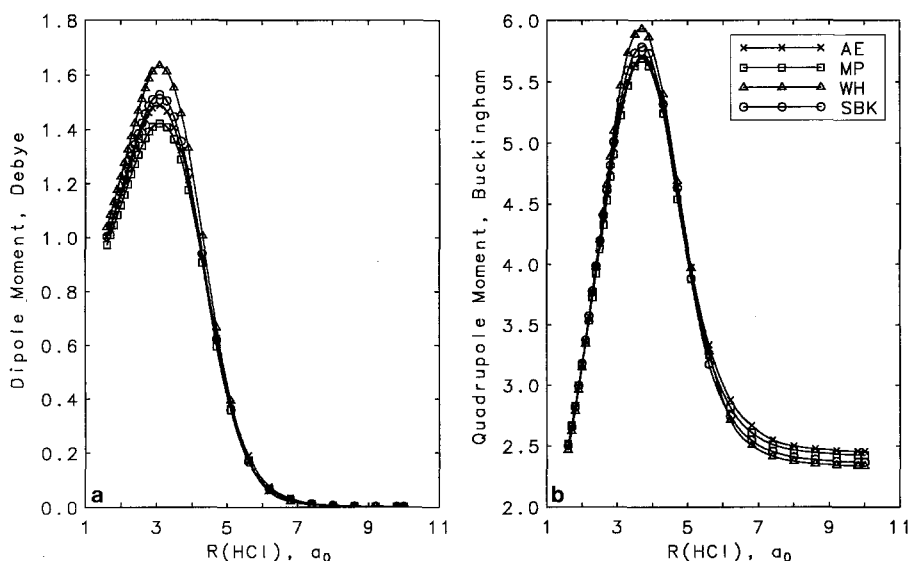

Fig. 2a,b. The curves of **a** electric dipole moment (in Debye units) and **b** electric quadrupole moment (in Buckingham units) of HCl calculated from MCSCF wavefunctions. (See Fig. 1 for the meaning of abbreviations)
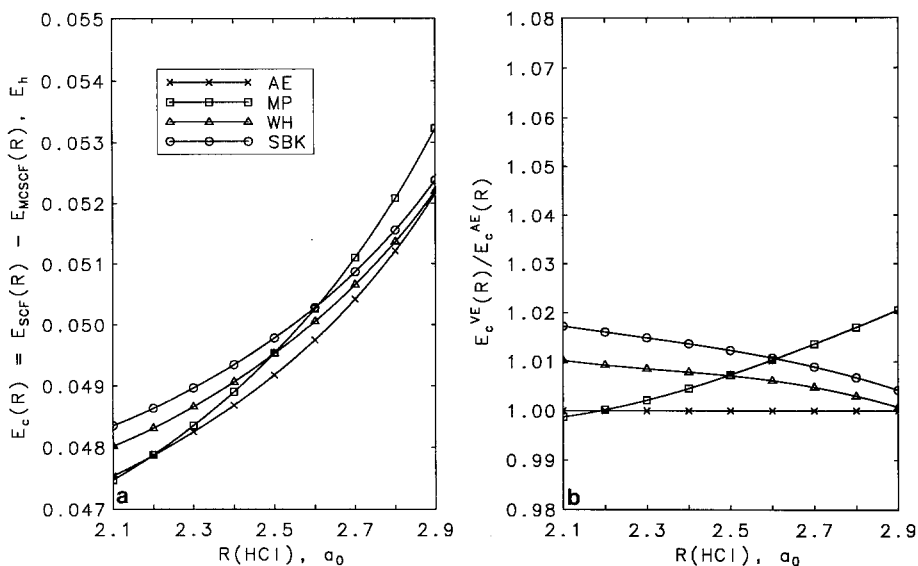
Fig. 3a,b. The MCSCF electron correlation energy in HCl: **a** absolute values; **b** values relative to the all-electron results. (See Fig. 1 for the meaning of abbreviations)
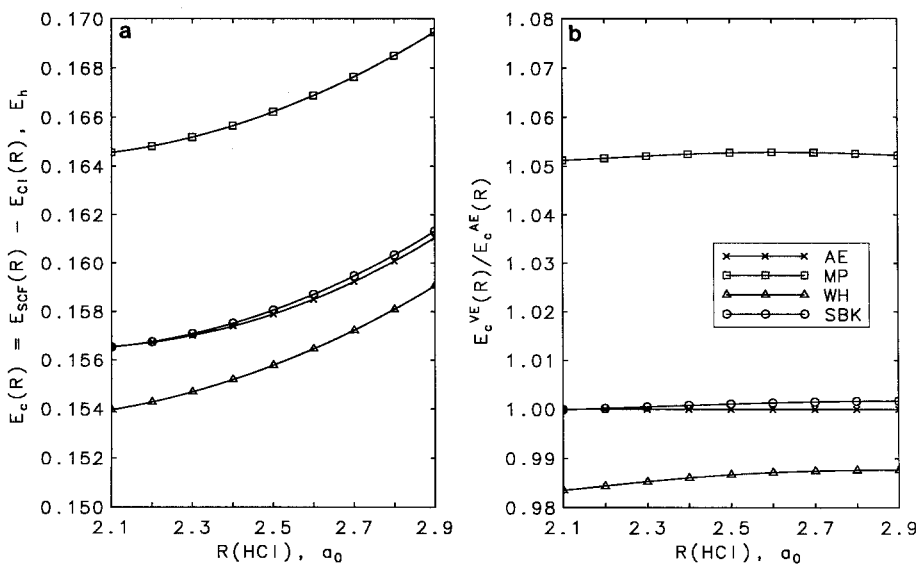

Fig. 4a,b. The CISD electron correlation energy in HCl: **a** absolute values; **b** values relative to the all-electron results. (See Fig. 1 for the meaning of abbreviations)
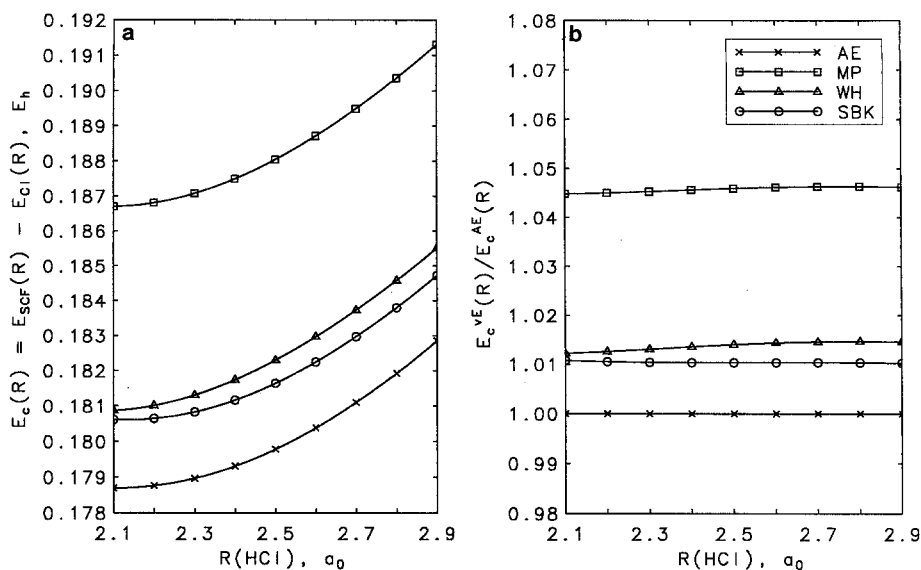
Fig. 5a,b. The CISD electron correlation energy in HCl calculated with two polarization functions: **a** absolute values; **b** values relative to the all-electron results. (See Fig. 1 for the meaning of abbreviations)

in consequence, the latter values become larger than the AE ones (as expected, due to the lack of nodes in the valence orbitals).

The values of spectroscopic constants of HCl are collected in Table 1. The overall agreement between any of the methods used and the experimental data is remarkably good, provided that atomic basis sets augmented by two polarization functions are used at the CISD level. Replacing one polarization function with two has almost identical effect for all the methods studied. The final discrepancies between the results of different methods (with the exception of $\omega_e x_e$) essentially follow the pattern established on the SCF level.

At the CISD/TZ2p level, the calculated dissociation energies are within 0.3 eV of the experimental value. (The MP result is minimally closer to the AE value than the result from the other VE methods). The equilibrium internuclear distance is overestimated by about 0.004 Å for the MP method, 0.002 Å for the AE and SBK methods, and underestimated by about 0.004 Å for the WH parametrization. For ω_e, the effective-core-potential method with the WH parametrization overestimates the experimental value by about 60 cm^{-1}; the AE and SBK results are about 20 cm^{-1} larger and the MP result almost coincides with the experimental value. The anharmonicity correction $\omega_e x_e$ is underestimated in all methods by 2–5 cm^{-1}. It appears that the discrepancies are caused by the differential effects of the polarization functions rather than by the different number of nodes in the orbitals.

The effect of the two polarization functions is to increase D_e by 0.1 eV (SCF) to 0.3 eV (CI), to shorten the bond length by 0.005–0.008 Å (SCF and CI), and to increase the harmonic vibrational frequencies by 20–50 cm^{-1}.

For HBr, the electron correlation energy calculated with the MCSCF wavefunction in the region near the equilibrium internuclear distance using the ECP

Table 1. Spectroscopic constants in the $X^1\Sigma^+$ state of $^1H^{35}Cl$[a]

Model[b]	D_e/eV	r_e/Å	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}
		SCF		
AE	3.33 (3.45)	1.277 (1.270)	3073 (3117)	40.4 (45.7)
MP	3.26 (3.38)	1.277 (1.272)	3091 (3108)	46.7 (44.4)
ECP-WH	3.41 (3.55)	1.270 (1.264)	3123 (3171)	46.1 (45.9)
ECP-SBK	3.35 (3.47)	1.277 (1.270)	3083 (3123)	42.7 (45.7)
		MCSCF		
AE	4.25	1.284	2986	47.89
MP	4.14	1.286	2976	54.87
ECP-WH	4.36	1.276	3043	51.13
ECP-SBK	4.31	1.283	3006	48.73
		CISD		
AE	4.13 (4.35)	1.284 (1.276)	2965 (3007)	46.7 (50.5)
MP	4.05 (4.31)	1.285 (1.279)	2979 (2987)	52.0 (47.5)
ECP-WH	4.17 (4.43)	1.278 (1.271)	3016 (3055)	51.4 (48.7)
ECP-SBK	4.12 (4.48)	1.285 (1.276)	2972 (3008)	48.8 (49.5)
		Experiment		
HH[c]	4.619	1.27455	2990.96	52.818

[a] The values in parentheses were obtained using two correlating functions
[b] AE: all-electron (single-ζ core, triple-ζ valence basis); MP: core-projector for model potential (single-ζ core representation, triple-ζ valence basis); ECP-WH: effective core potential (triple-ζ valence basis of Wadt and Hay [13]); ECP-SBK: effective core potential (triple-ζ valence basis of Stevens et al. [14])
[c] Experimental values from Huber and Herzberg [16]

method is about 3–8% larger than the AE values; the MP method overestimates the AE correlation energy by 2–5%. For the CI wavefunctions, the AE values of correlation energy are reproduced with good accuracy; the MP values are within 2.5% of the AE data and the WH values are slightly larger. As in the case of HCl, the discrepancy between the AE and VE values may be expected to change if two polarization functions are used rather than one. The values of the spectroscopic constants of HBr are collected in Table 2 and show good internal agreement. All the methods mimic the experimental values very well. The agreement can be improved by the use of two polarization functions.

For Cl_2, the MP values of the MCSCF correlation energy overestimate the AE values by almost 7% while the WH and SBK results underestimate them. Similar behavior of the correlation energy is observed if the CI wavefunctions are used, even though a larger virtual space is employed and the absolute values of the E_c are about four times larger than those calculated with the MCSCF wavefunctions. Despite larger differences in the absolute values of the correlation energies, the values of the spectroscopic constants, collected in Table 3, are in good agreement with each other; the changes induced by the electron correlation via the MCSCF and CI wavefunctions are similar for the four methods.

For Br_2, the MP values of the correlation energy calculated with the MCSCF wavefunction overestimate the AE values by less than 3% while the WH results are slightly larger still (2–5%). Again, this behavior may be affected by the use of two polarization functions. Very similar behavior of the correlation energy is

Table 2. Spectroscopic constants in the $X^1\Sigma^+$ state of $^1H^{81}Br$

Model[a]	D_e/eV	r_e/Å	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}
		SCF		
AE	2.87	1.410	2757	37.5
MP	2.89	1.405	2778	37.6
ECP-WH	2.84	1.417	2757	37.5
		MCSCF		
AE	3.74	1.418	2655	46.2
MP	3.78	1.413	2689	45.2
ECP-WH	3.74	1.424	2677	44.7
		CISD		
AE	3.58	1.418	2647	44.3
MP	3.63	1.414	2665	42.9
ECP-WH	3.57	1.425	2646	43.0
		Experiment		
HH[b]	3.922	1.414435	2648.975	45.2175

[a] See footnote b of Table 1
[b] Experimental values from Huber and Herzberg [16]

Table 3. Spectroscopic constants in the $X^1\Sigma_g^+$ state of $^{35}Cl_2$

Model[a]	D_e/eV	r_e/Å	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}
		SCF		
AE	0.88	2.019	612.9	1.96
MP	0.73	2.019	600.4	2.01
ECP-WH	0.76	2.011	602.0	2.06
ECP-SBK	0.87	2.018	612.3	1.97
		MCSCF		
AE	2.30	2.059	541.1	2.87
MP	2.23	2.065	524.2	2.92
ECP-WH	2.18	2.053	528.2	3.09
ECP-SBK	2.28	2.054	544.3	2.94
		CISD		
AE	1.38	2.045	569.7	2.29
MP	1.19	2.047	557.8	2.36
ECP-WH	1.24	2.041	555.4	2.44
ECP-SBK	1.34	2.045	568.1	2.29
		Experiment		
HH[b]	2.5141	1.9879	559.72	2.675

[a] See footnote b of Table 1
[b] Experimental values from Huber and Herzberg [16]

Table 4. Spectroscopic constants in the $X^1\Sigma_g^+$ state of $^{79}Br_2$

Model[a]	D_e/eV	r_e/Å	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}
		SCF		
AE	0.85	2.300	354.9	0.74
MP	0.80	2.279	354.5	0.78
ECP-WH	0.80	2.270	354.5	0.78
		MCSCF		
AE	2.09	2.334	321.7	1.09
MP	2.05	2.311	321.3	1.19
ECP-WH	2.02	2.338	312.9	1.16
		CISD		
AE	1.30	2.328	331.6	0.87
MP	1.20	2.308	330.3	0.91
ECP-WH	1.13	2.336	321.7	0.90
		Experiment		
HH[b]	2.0110	2.28105	325.321	1.0774

[a] See footnote b of Table 1
[b] Experimental values from Huber and Herzberg [16]

observed if the CI wavefunctions are used. The values of the spectroscopic constants of Br_2 are collected in Table 4. While both the MP and WH parametrizations of the valence-electron approach give results which approximate the AE data quite well, more electrons should be explicitly included in the correlated treatment to obtain agreement with the experimental D_e. Alternatively, the core-polarization potential could be added [17–19].

3. Conclusions

The comparative studies of the effective core potential (in two parametrizations) and the model potential method indicate that the improvements in parametrization schemes proposed in the recent years resulted in effective and efficient methods of studying the valence structure of molecules; the results are scattered no more than if two slightly different basis sets were used in the all-electron calculations. The smaller number of nodes in the valence orbitals provided by the effective core potential method, while leading to slightly overestimated (by a few percent) electron correlation energies, does not affect the ability of the method to accurately mimic energy differences obtained in calculations in which the number of nodes deviates less from that in the all-electron orbitals. In consequence, the spectroscopic parameters obtained with both the effective core potential method and the model potential method are very close to each other and model very well the values obtained with an all-electron approach. The agreement is good even though the (potentially present) intruder core orbitals were not removed from the virtual space spanned by the MP orbitals as done in the previous work [7]. The variations between the results of the correlated calculations often repeat the pattern found in on the SCF level. As pointed out by Schwarz and coworkers [20], better agreement with experiment may be obtained if a size-consistent multi-reference CI procedure is employed in order to include higher excitations.

The model potential method has the rare capability of correctly representing the full nodal structure of the valence orbitals. However, in practical procedures, the considerations of computationally efficiency lead to expansions containing only a few terms and, sporadically, to erratic values of $\langle r^{-3} \rangle$ [9]. Thus, while the model potential still carries the promise of an excellent description of the inner nodes and the molecular properties which depend on them, a special care will have to be exercised in the preparation of the valence orbitals to realize that prospect. In the limit, the model potential method could exactly match the all-electron orbitals; in this limit, however, the model potential valence orbital expansion would become identical with the reference all-electron basis set.

The conclusions reached depend on the relative quality of the potentials used. In this study, we used the readily available, published tabulations of the core-electron potentials and valence basis sets instead of an ideal set which would include a reference all-electron basis set and valence-electron approximations tailored to this selected all-electron reference. Still, the discrepancies between the results obtained are small enough to justify the conclusion that the effective core potential and model potential methods produce results which are essentially equivalent.

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