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The well-tempered model core potentials for the main-group elements Li–Rn

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Abstract. The well-tempered model core potential (wtMCP) parameters and valence basis sets, based on the well-tempered basis set expansion, were developed for the main-group elements Li–Rn. For the *s*–block elements, the valence space comprises the *ns* valence shell and the outermost core $(n-1)p$ shell. For the *p*-block elements, the *ns* and *np* shells together with the $(n-1)d$ shell make up the valence space. Nonrelativistic wtMCPs were developed for all atoms. Scalar-relativistic wtMCPs were prepared for all atoms heavier than Ar by using the relativistic elimination of small components to obtain the reference and core orbitals. The new potentials were tested at the restricted Hartree–Fock, second-order Møller–Plesset perturbation theory and density functional theory with Becke's three-parameter hybrid functional combined with Perdew's 1991 gradient-corrected correlation functional levels for several diatomic molecules and the results were compared with those obtained from all-electron calculations and experimental values. Excellent agreement between the results was obtained.

Keywords: Model core potentials – Well-tempered basis sets – Relativistic effects

1 Introduction

Pseudopotential methods are popular tools in computational chemistry because they are less demanding computationally than all-electron methods. In a pseudopotential method, the total number of electrons is divided into N_c core electrons and N_v valence electrons. Potentials are constructed which depend explicitly only on the coordinates of the N_v valence electrons while implicitly taking into account the influence of the chemically inert N_c core electrons. One such pseudopotential method is the model core potential (MCP) method.

The MCP method was originally proposed by Bonifacic and Huzinaga in the mid-1970s [1, 2, 3, 4, 5]. The MCP has been implemented and successfully tested in molecular calculations [6, 7, 8]. The foundations of the MCP method have recently been reviewed by Huzinaga [9, 10, 11].

The main advantage of the MCP model over other pseudopotentials is its ability to fully represent the correct nodal structures of the valence orbitals. This allows for excellent description of the valence electron distribution near the nucleus and leads to very good values of the spin–orbit coupling constants without the need for scaling [12, 13]. The MCP valence basis sets and associated parameters that were published for the main-group elements [14] and transition-metal elements [15, 16] use a small number of primitive Gaussian-type functions (pGTFs) in which the exponents are optimized via fitting to the numerical solutions of the atomic Hartree–Fock equations [17]. The number of nodes that appeared in the valence orbitals depended on the number of pGTFs used for their analytical representation.

The present paper reports results obtained with a new set of MCP parameters and a valence basis set that was developed for the main-group elements Li–Rn. For alkali and alkaline-earth metal atoms, the valence space comprises the *ns* valence shell and the outermost core $(n-1)p$ shell. For the *p*-block elements, the valence space includes the *ns* and *np* shells together with the $(n-1)d$ shells. Instead of using numerical reference functions, analytical reference functions expanded in terms of very large, high quality all-electron basis sets were used. As described in the previous paper [18], the well-tempered basis set (WTBS) [19, 20] was chosen for the present MCP development. To emphasize the relation to the WTBS, the new MCP parameterization was called the well-tempered MCP (wtMCP). Scalar-relativistic wtMCPs were developed only for the elements K–Rn, where the relativistic effects are expected to be

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significant; nonrelativistic wtMCPs were developed for the elements from Li to Rn, to allow for studies of the importance of the relativistic effects in molecules.

A description of both the MCP method and the preparation of the wtMCP parameters and basis sets is provided in Sect. 2. The quality of wtMCPs as compared with all-electron calculations and experimental data for several diatomic molecules, is illustrated in Sect. 3, and concluding remarks are given in Sect. 4.

2 Determination of wtMCPs and basis sets

In the MCP formalism, the one-electron Hamiltonian operator $\hat{h}(i)$ describes the kinetic energy of valence electron i and the potential energy arising from the interaction of valence electron i with an effective nuclear charge z_α, plus a potential for the core electrons, $\hat{V}_i^\alpha$, and a projection operator, $\hat{P}_i^\alpha$:

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \frac{z_\alpha}{r_{i\alpha}} + \hat{V}_i^\alpha + \hat{P}_i^\alpha \ . \tag{1}$$

$\hat{V}_i^\alpha$ is the spherically-symmetric local potential approximating the exact atomic nonlocal core potential and is defined in terms of radial Gaussian functions,

$$V_i^\alpha = -\frac{z_\alpha}{r_{i\alpha}} \sum_k A_{k\alpha} r_{i\alpha}^{n_{k\alpha}} e^{-\zeta_{k\alpha} r_{i\alpha}^2} \ , \tag{2}$$

where $n_{k\alpha}$ is 0 or 1, and the parameters $\{A_{k\alpha}, \zeta_{k\alpha}\}$ are specific for the atom α. This potential represents the core Coulomb and exchange potentials.

$\hat{P}_i^\alpha$ is the projection operator,

$$\hat{P}_i^\alpha = \sum_{\mathrm{c}} B_{\mathrm{c}}^\alpha \left|\phi_{\mathrm{c}}^\alpha(i)\rangle\langle\phi_{\mathrm{c}}^\alpha(i)\right| \ , \tag{3}$$

which shifts the core orbitals into the virtual space and allows for the correct representation of the nodal structure of the valence orbitals. The shift parameter B_{c}^α is defined in terms of the atomic orbital energy eigenvalue, ϵ_{c}, of the core shell, c, on atom α:

$$B_{\mathrm{c}}^\alpha = -f_{\mathrm{c}}^\alpha \epsilon_{\mathrm{c}}^\alpha \ . \tag{4}$$

A fixed value of $f_{\mathrm{c}} = 2$ was used in this work. The electronic Hamiltonian for the N_{v} electrons can thus be written as

$$\begin{aligned} &\hat{H}^{\mathrm{val}}(1, 2, \ldots, N_{\mathrm{v}}; \{A_{k\alpha}, \zeta_{k\alpha}\}) \\ &\quad = \sum_{i=1}^{N_{\mathrm{v}}} \hat{h}(i; \{A_{k\alpha}, \zeta_{k\alpha}\}) + \sum_{i=1}^{N_{\mathrm{v}}} \sum_{j>i}^{N_{\mathrm{v}}} \frac{1}{r_{ij}} \ , \end{aligned} \tag{5}$$

where the one-electron operator depends parametrically only on $\{A_{k\alpha}, \zeta_{k\alpha}\}$ and is independent of B_{c}. The values of $\{A_{k\alpha}, \zeta_{k\alpha}\}$ for a given atom α are determined in atomic calculations by fitting the MCP valence orbitals and energies to the all-electron reference set.

Before optimizing the values of $\{A_{k\alpha}, \zeta_{k\alpha}\}$, the atomic reference functions for the atoms Li–Rn were prepared. Using fully uncontracted WTBS, the generalized valence bond calculations, with both the nonrelativistic (Hartree–Fock) and the scalar relativistic (relativistic elimination of small components, RESC) [21, 22] Hamiltonians, were performed utilizing the implementation in the GAMESS-US [23, 24] computer program. All atomic calculations were carried out for the lowest state of the ground-state electronic configuration. These calculations provided the necessary analytical core functions for the projector operator in Eq. (3) and the analytical valence reference functions that are needed for the optimization of wtMCP parameters. In constructing the wtMCP basis sets, the original WTBS pGTFs for the *s* and *p* valence orbitals were used for the *s*-block elements. For the *p*-block elements, the original WTBS pGTFs were used for the *p* and *d* valence orbitals, while for the *s* orbitals a few of the pGTFs with the largest exponents were omitted. The removal of the largest exponents in the *s* space resulted in the identical number of pGTFs used for the *s* and *p* spaces that allows for effective folding of the long basis set expansions into *L* shells of functions. Table 1 compares the number of pGTFs used for the all-electron WTBS and wtMCP valence basis sets.

The optimized values of the parameters $\{A_{k\alpha}, \zeta_{k\alpha}\}$ were determined through a fitting procedure by minimizing the deviations between the analytic reference and MCP orbital energies and radial functions as given by Eq. (6):

$$\begin{aligned} \delta = \sum_j \Big\{ & w_j^\epsilon \left|\epsilon_j^{\mathrm{ref}} - \epsilon_j^{\mathrm{MCP}}\right| \\ & + w_j^R \sum_k r_k^2 \left[R_j^{\mathrm{ref}}(r_k) - R_j^{\mathrm{MCP}}(r_k)\right]^2 \Big\} \ , \end{aligned} \tag{6}$$

where w_j are weight factors, ϵ_j are orbital energies, R_j are radial functions defined over a grid r_k, and j runs over all valence orbitals.

Excellent agreement was obtained between the reference and wtMCP orbital energies with energy differences smaller than 1 μE_{h}. Figures 1, 2 and 3 show the radial functions for Xe(^{1}S), comparing the 5s-, 5p- and 4d-type functions between the nonrelativistic wtMCP (NR-wtMCP) and the Hartree–Fock reference orbitals. The radial points refer to the independent logarithmic variable that expands the region near the nuclei [25]. It is clearly seen from the figures that the correct nodal structures are preserved. There is only a slight difference in the inner range of the s-type function; this deviation may be attributed to the absence of several pGTFs with

Table 1. The sizes of the primitive Gaussian-type functions for all-electron (*AE*) well-tempered basis sets (*WTBS*) and well-tempered model core potential (*wtMCP*) valence basis sets

Atoms	AE-WTBS	wtMCP
Li–Be	(20s)	(20s)
Na–Mg	(23s 13p)	(23s 13p)
K–Ca	(26s 16p)	(26s 16p)
Rb–Sr	(28s 20p 14d)	(28s 20p)
Cs–Ba	(30s 20p 17d)	(28s 23p)
B–Ne	(20s 13p)	(13s 13p)
Al–Ar	(23s 16p)	(16s 16p)
Ga–Kr	(26s 20p 14d)	(20s 20p 14d)
In–Xe	(28s 23p 17d)	(23s 23p 17d)
Tl–Rn	(28s 24p 18d)	(24s 24p 18d)

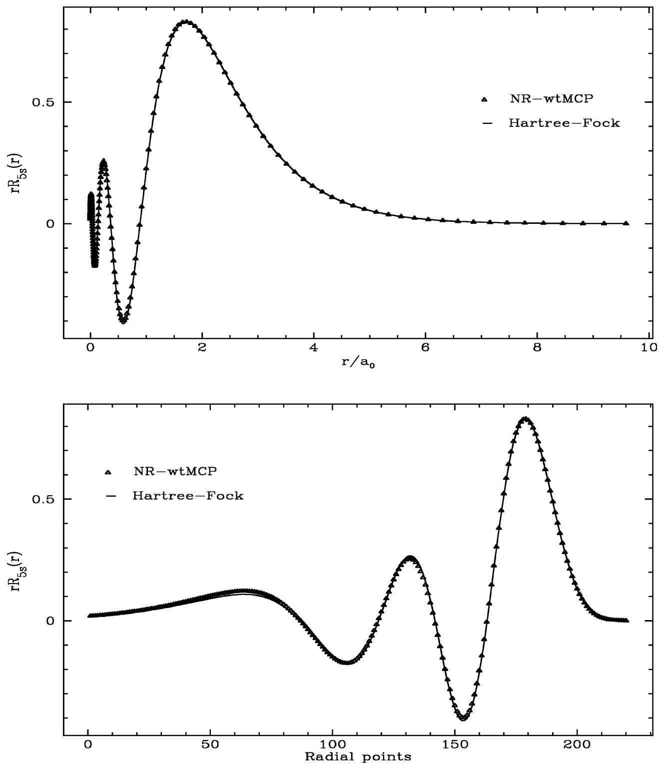

Fig. 1. Nonrelativistic Xe(^{1}S) 5s radial distribution function

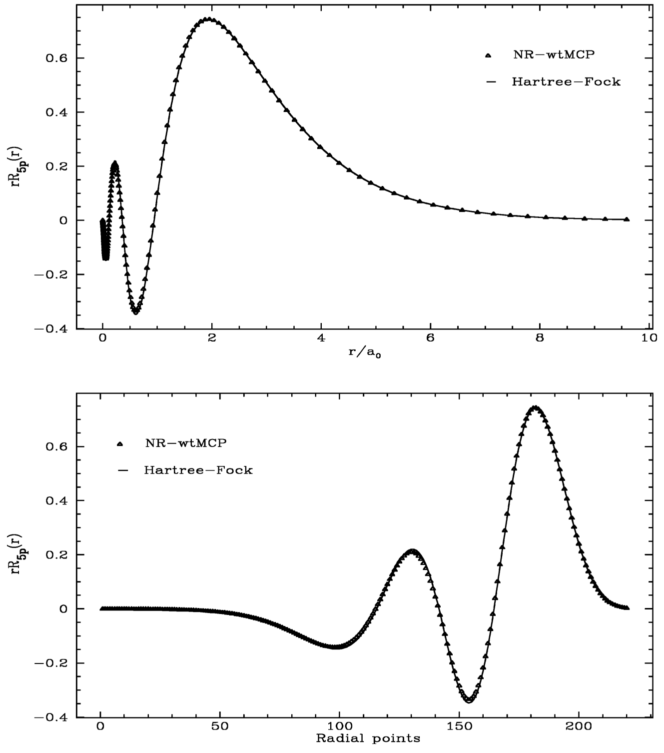

Fig. 2. Nonrelativistic Xe(^{1}S) 5p radial distribution function

the highest exponents in the valence basis set. The same excellent agreement was also observed between the scalar-relativistic wtMCP (SR-wtMCP) and the RESC reference functions.

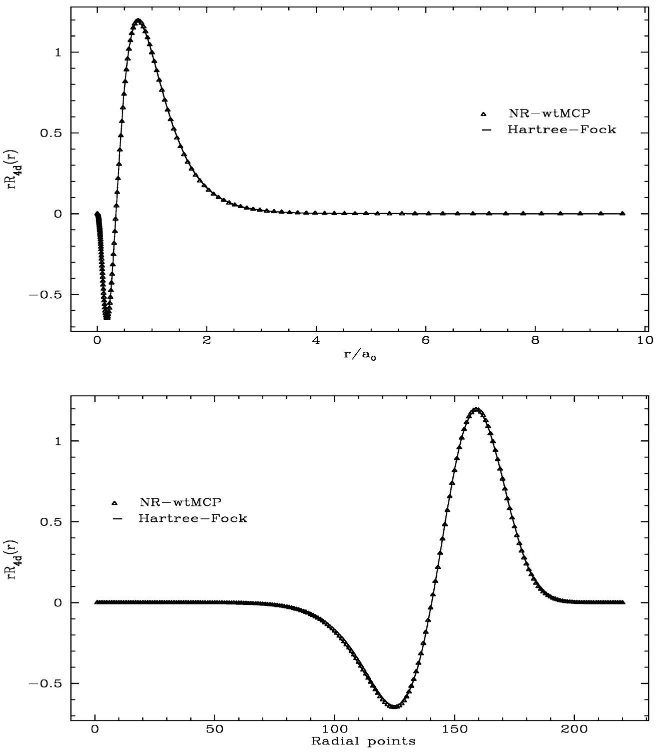

Fig. 3. Nonrelativistic Xe(^{1}S) 4d radial distribution function

Table 2. Parameters of the nonrelativistic (*NR*) wtMCP for iodine. See Eq. (2) for the definition of the symbols

k	$n_{k\alpha}$	$A_{k\alpha}$	$\zeta_{k\alpha}$
1	0	1.660360	296.720130
2	0	0.221558	2.122267
3	0	0.049118	1.011422
4	1	21.266578	4053.042800
5	1	10.288802	36.861737
6	1	0.017616	3.479541

The optimized wtMCP parameters for iodine are collected in Table 2 and the corresponding basis set is shown in Table 3. (The data for other main-group elements Li–Rn are available from the authors upon request.)

3 Test calculations and discussion

3.1 Comparison of all-electron and wtMCP results at the restricted Hartree-Fock level

One of the main goals of the wtMCP or any pseudopotential is to reduce the amount of computation time for molecular systems without sacrificing too much of the accuracy of the results. The wtMCP valence basis sets and corresponding pseudopotentials must be tested in order to assess their efficacy in reproducing the all-electron results.

Molecular calculations were performed at the restricted Hartree–Fock (RHF) level for homonuclear

Table 3. NR valence basis set for iodine

i	ζ_i	c_i^s	c_i^p	c_i^d
1	161092.9700000	0.00005989	−0.00000055	
2	59231.1270000	0.00007098	−0.00000233	
3	23530.8440000	0.00037507	−0.00001075	
4	9991.8892000	0.00081129	−0.00004787	−0.00000314
5	4487.6664000	0.00242272	−0.00019010	−0.00002098
6	2110.9230000	0.00507285	−0.00068804	−0.00008495
7	1030.6417000	0.01055268	−0.00197482	−0.00043744
8	518.1956500	0.01365231	−0.00598735	−0.00183141
9	266.4983600	0.00956916	−0.01018417	−0.00580880
10	139.4022900	0.00043308	−0.02118083	−0.01205981
11	73.8324560	−0.08844354	−0.02744321	−0.05594621
12	39.4525690	−0.06640292	0.01348612	−0.10699146
13	21.2112860	−0.01433314	0.04974148	−0.12190219
14	11.4509230	0.22365880	0.11307494	−0.10494222
15	6.1981301	0.31363026	0.02627737	0.10023304
16	3.3603620	−0.17996321	−0.17401213	0.34557314
17	1.8235681	−0.51037716	−0.23507663	0.38779415
18	0.9901049	−0.40548312	−0.09375228	0.24409634
19	0.5377146	0.17961764	0.19743282	0.07970811
20	0.2920600	0.53709011	0.37547326	0.01832313
21	0.1586394	0.48471485	0.37538545	
22	0.0861699	0.15469738	0.20181108	
23	0.0468060	0.01250074	0.05084538	

diatomic molecules of representative *p*-block elements. The ground electronic states of the second-row molecules were used in calculating their structural parameters. Similar electronic states were used for the corresponding diatomic molecules in the group. The pGTFs described in Table 1 were fully uncontracted and used as basis functions for both all-electron and wtMCP calculations. The present MCP code in GAMESS-US allows only for the energy evaluation; hence, the equilibrium internuclear distances, r_e, were obtained through the modified Powell method of searches along conjugate directions, while the harmonic vibrational frequencies, $\bar{\omega}_e$, were obtained by fitting (with fourth- to sixth-degree polynomials) the total energies computed at several (5–7) points bracketing the minimum on the potential-energy curve.

Tables 4 and 5 show a comparison of equilibrium geometries and vibrational frequencies between the NR-wtMCP and the SR-wtMCP with the corresponding all-electron nonrelativistic RHF and scalar-relativistic RESC RHF results. The mean errors in r_e and $\bar{\omega}_e$ were evaluated by using Eq. (7):

$$\sigma(X) = \sum_{i=1}^{N} \frac{\left|X_i^{\text{calc}} - X_i^{\text{ref}}\right|}{N} \quad , \tag{7}$$

where N is the number of molecules studied and $X = r_e, \bar{\omega}_e$.

The wtMCP values showed excellent agreement with all-electron WTBS results: $\sigma(r_e) = 0.005$ Å, $\sigma(\bar{\omega}_e) = 1.0\,\text{cm}^{-1}$ for nonrelativistic and $\sigma(r_e) = 0.008$ Å, $\sigma(\bar{\omega}_e) = 0.4\,\text{cm}^{-1}$ for scalar relativistic levels.

The parameters for iodine (Tables 2, 3) were used to illustrate the reduction in computation time due to the use of the MCPs. Using the GAMESS-US program, Hartree–Fock energy calculations were performed for the I_2 molecule at the experimental [26] internuclear distance of 2.666 Å. The direct self-consistent-field (SCF) method was used, as it would be the approach applicable in large molecular systems. The basis set of Table 3 was used in Raffenetti's general contraction [27] (23,1,1,1,1, 1/23,1,1,1,1,1/17), while the well-tempered basis for iodine [20] was contracted to (28,28,28,28,28,1,1,1,1, 1/23,23,23,23,1,1,1,1,1/17,17). In both cases, the SCF iterations converged in ten steps; the all-electron calculations took nearly 15.5 h, while the wtMCP run was completed in less than 11 min – almost 85 times faster

Table 4. Restricted Hartree–Fock (*RHF*) optimized bond lengths (Å) of homonuclear diatomic molecules

Molecule	Method			
	AE-NR	NR-wtMCP	AE-RESC	SR-wtMCP
C_2	1.257	1.256		
Si_2	2.133	2.133		
Ge_2	2.185	2.180	2.176	2.169
Sn_2	2.576	2.568	2.548	2.542
Pb_2	2.751	2.743	2.656	2.650
N_2	1.084	1.082		
P_2	1.938	1.935		
As_2	2.065	2.057	2.057	2.049
Sb_2	2.469	2.458	2.446	2.435
Bi_2	2.660	2.651	2.576	2.568
O_2	1.194	1.194		
S_2	2.004	2.003		
Se_2	2.144	2.139	2.140	2.133
Te_2	2.556	2.545	2.540	2.530
Po_2	2.763	2.754	2.695	2.690
F_2	1.379	1.379		
Cl_2	2.132	2.129		
Br_2	2.291	2.287	2.288	2.282
I_2	2.704	2.694	2.692	2.680
At_2	2.922	2.914	2.862	2.855

Table 5. RHF vibrational frequencies $\bar{\omega}_e$ (cm^{-1}) for diatomic molecules

Molecule	Method			
	AE-NR	NR-wtMCP	AE-RESC	SR-wtMCP
C_2	1812.7	1808.7		
Si_2	552.6	551.0		
Ge_2	345.7	344.8	344.0	343.6
Sn_2	227.3	226.6	225.7	225.1
N_2	2563.4	2560.5		
P_2	797.1	795.7		
As_2	507.9	508.1	506.4	506.6
Sb_2	326.6	326.5	325.8	325.8
Bi_2	226.9	227.3	229.6	231.0
O_2	1829.0	1825.2		
S_2	699.5	699.6		
Se_2	436.9	437.1	435.4	435.3
Te_2	283.0	283.9	281.3	281.6
Po_2	203.3	203.6	204.5	204.5
F_2	1189.2	1188.5		
Cl_2	550.1	550.2		
Br_2	349.5	349.3	348.7	348.6
I_2	231.9	232.5	231.3	231.5
At_2	165.5	165.9	166.2	166.8

than the all-electron one. (Calculations were done on an Athlon computer with 1.8-GHz clock.)

3.2 Comparison between experimental data and wtMCP results

In the previous section, it was demonstrated that the RHF results obtained using the wtMCP can match the results of all-electron WTBS calculations with great accuracy. Often, however, predicting molecular properties using an ab initio method requires the inclusion of electron correlation. If the wtMCP method is to be used as an alternative to the all-electron approach for modeling real chemical systems, it is necessary to determine how well it reproduces known experimental data.

Results of preliminary tests with electron correlation are reported in this section. Molecular calculations were performed at the second-order Møller–Plesset perturbation theory (MP2) and density functional theory with Becke's three-parameter hybrid functional combined with Perdew's 1991 gradient-corrected correlated functional (DFT-B3P91) levels of theory for the ground electronic state $^1\Sigma^+$ of group 13 halides (BF, AlCl, GaBr, InI), group 14 sulfides AS (A = C, Si, Ge, Sn) and interhalogen diatomic compounds. RHF calculations were also performed to serve as a reference in the absence of electron correlation. The locally modified version of the CADPAC [28] computer package was used for all the calculations. Analytical gradients and numerically determined Hessians were used for obtaining the optimized geometries and harmonic vibrational frequencies, respectively.

The wtMCP basis functions given in Table 1 were contracted in the manner shown in Table 6. A set of double d-type polarization functions, taken from Sadlej's medium-sized polarized basis sets [29, 30], was used for the elements of the first two rows of the periodic table.

Table 6. Contractions of the atomic wtMCP basis set used in the correlation studies. The notation 4s (8,2,1,2) denotes 4s-type basis functions, the first of which is an eight-term contracted function, followed by a two-term contracted function, an uncontracted function and the last being a two-term contracted function

Atom	Basis set
B–F	4s (8,2,1,2) 4p (8,2,1,2)
Al–Cl	5s (8,3,2,1,2) 5p (8,3,2,1,2)
Ga–Br	5s (12,3,2,1,2) 5p (12,3,2,1,2) 3d (10,2,2)
In–I	5s (13,5,2,1,2) 5p (13,5,2,1,2) 3d (11,4,2)

Table 7. Comparison of wtMCP and experimental bond lengths and vibrational frequencies for group 13 halides (*NR* and *SR* represent NR-wtMCP and SR-wtMCP, respectively)

Molecule	Method	r_e/Å		$\bar{\omega}_e$/cm^{-1}	
		NR	SR	NR	SR
BF	RHF	1.246		1491.7	
	MP2	1.267		1401.0	
	DFT	1.266		1346.8	
	EXP	1.263		1402.1	
AlCl	RHF	2.164		467.5	
	MP2	2.165		469.6	
	DFT	2.154		449.2	
	EXP	2.130		481.3	
GaBr	RHF	2.394	2.394	255.8	253.4
	MP2	2.349	2.346	272.1	270.7
	DFT	2.359	2.359	260.9	259.2
	EXP	2.352		263.0	
InI	RHF	2.846	2.830	163.3	161.7
	MP2	2.776	2.756	176.2	176.3
	DFT	2.790	2.774	171.5	170.7
	EXP	2.754		177.1	

For the diatomic molecules, Tables 7, 8 and 9 show a comparison of NR-wtMCP and SR-wtMCP results, along with the corresponding experimental values taken from the compilation of Huber and Herzberg [26]. The mean errors, calculated using Eq. (7), were also evaluated and are tabulated in Table 10.

The calculated bond lengths, r_e, at the RHF level alone showed very close agreement with experimental values. A noticeable improvement is seen when correlated methods are used. The average errors in bond lengths are about 0.02 Å at the MP2 level and 0.01 Å at the DFT level using NR-wtMCP and SR-wtMCP valence basis sets.

Table 8. Comparison of wtMCP and experimental bond lengths and vibrational frequencies for group 14 sulfides (*NR* and *SR* represent NR-wtMCP and SR-wtMCP, respectively)

Molecule	Method	r_e/Å		$\bar{\omega}_e$/cm^{-1}	
		NR	SR	NR	SR
CS	RHF	1.525		1406.9	
	MP2	1.559		1264.1	
	DFT	1.543		1294.9	
	EXP	1.535		1285.1	
SiS	RHF	1.936		797.9	
	MP2	1.978		717.9	
	DFT	1.949		744.1	
	EXP	1.929		749.6	
GeS	RHF	2.002	1.997	627.5	625.8
	MP2	2.032	2.028	570.5	569.2
	DFT	2.010	2.006	585.0	583.6
	EXP	2.012		575.8	
SnS	RHF	2.203	2.195	539.0	535.0
	MP2	2.236	2.228	491.3	488.0
	DFT	2.210	2.204	500.2	496.4
	EXP	2.209		487.3	

Table 9. Comparison of wtMCP and experimental bond lengths and vibrational frequencies for diatomic interhalogen compounds (*NR* and *SR* represent NR-wtMCP and SR-wtMCP, respectively)

Molecule	Method	r_e/Å		$\bar{\omega}_e$/cm^{-1}	
		NR	SR	NR	SR
ClF	RHF	1.614		905.3	
	MP2	1.674		769.2	
	DFT	1.657		797.9	
	EXP	1.628		786.2	
BrF	RHF	1.729	1.729	764.3	762.0
	MP2	1.783	1.782	662.8	662.0
	DFT	1.768	1.768	678.7	678.2
	EXP	1.759		670.8	
BrCl	RHF	2.146	2.144	482.5	481.7
	MP2	2.167	2.165	449.2	448.7
	DFT	2.151	2.150	449.1	448.4
	EXP	2.136		444.3	
IF	RHF	1.882	1.886	694.9	687.6
	MP2	1.927	1.930	617.7	612.6
	DFT	1.919	1.922	617.3	612.7
	EXP	1.910		610.2	
ICl	RHF	2.330	2.328	416.1	414.3
	MP2	2.345	2.343	392.0	390.6
	DFT	2.335	2.334	386.0	384.9
	EXP	2.321		384.3	
IBr	RHF	2.485	2.477	288.6	288.0
	MP2	2.491	2.483	272.1	271.9
	DFT	2.485	2.479	267.0	268.1
	EXP	2.469		268.6	

For the vibrational frequencies, the RHF results are too large by about 10–120 cm^{-1}, using either the NR-wtMCP or the SR-wtMCP. This reflects the fact that RHF wavefunction usually does not dissociate to correct atomic states, therefore leading to potential-energy curves that are too steep near the minimum. Again, a significant improvement is seen in results obtained with the correlated methods, where the spread in vibrational frequencies is relatively smaller. At the same time, it is interesting to note that SR-wtMCP valence basis sets show better performance than their NR-wtMCP counterparts. At the MP2 level, errors in $\bar{\omega}_e$ ranged between 1 and 30 cm^{-1} using NR-wtMCP and between 1 and 10 cm^{-1} using the SR-wtMCP. At the DFT-B3P91 level, the range of errors in $\bar{\omega}_e$ is about 2–55 and 1–10 cm^{-1} for NR-wtMCP and SR-wtMCP, respectively. On average, the MP2 results show a slightly better agreement with experimental values than the DFT ones.

Table 10. Mean errors in bond lengths (Å) and vibrational frequencies (cm^{-1}) using NR-wtMCP(NR) and SR-wtMCP(SR) valence basis set for diatomic molecules

Method	Mean errors, σ			
	r_e/NR	r_e/SR	$\bar{\omega}_e$/NR	$\bar{\omega}_e$/SR
RHF	0.023	0.025	56.1	42.0
MP2	0.025	0.017	9.5	4.6
DFT	0.014	0.011	11.3	4.7

4 Conclusions

The results presented in this paper clearly show that the wtMCP can reproduce very well both results from all-electron calculations and experimental data. Despite treating explicitly the valence electrons only, the new wtMCPs have the capability of reproducing accurate molecular geometries and vibrational frequencies.

The wtMCPs use large uncontracted valence basis sets that are designed to be very flexible so that the levels of contraction can be tailored to the requirements of the computation for specific chemical application. Although the basis set is large, the sharing of the exponents between the *s* and *p* spaces has the computational advantage of being conveniently folded into a contracted *L*-shell basis set. Efficient routines for the evaluation of integrals over *L*-shells are available in many computer programs [23, 24, 28].

The new wtMCPs are designed for use in systems which would be difficult or even impossible to deal with using all-electron basis sets without sacrificing accuracy. The preliminary results for the test molecules are promising and encouraging. Further testing is being done to validate the effectiveness of wtMCPs in reproducing other molecular properties for polyatomic molecules.

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