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Testing the Arbitrariness and Limits of a Pseudopotential Technique through Calculations on the Series of Diatoms HF, AlH, HCl, AlF, AlCl, F_2, Cl_2

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The pseudopotential techniques present some degrees of freedom, the influence of which on molecular calculations must be tested to assess the stability and accuracy of the results. The present work uses a semi-local pseudopotential extracted from near Hartree–Fock atomic calculations; the shape of the inner part of the pseudoorbital, the analytic form of the pseudopotential are shown to have less influence than the choice of the valence basis set which must be optimized. The calculated molecular constants perfectly agree with the large basis set all-electron calculations, even for polar molecules.

Key words: Pseudopotential method, semi-local ∼ – Diatomic molecules.

1. Introduction

The past few years have seen a rapid development in the application of pseudopotential techniques to molecular calculations [1, 2]. The results obtained by most authors show that valence-electron calculations using pseudopotential formalisms reproduce all-electron values within a few percent.

The determination of pseudopotential operators in which explicit orthogonality constraints between core and valence spaces are removed implies a lot of arbitrariness. The aim of this paper is to study in molecular calculations the influence of some degrees of freedom in the determination of semi-local potentials. The first arbitrariness is the reference atomic calculation, the second one is the shape of the pseudo-orbital which reproduces the outer part of the valence orbital and the third one is the analytical expression which represents the effective potential.

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Different pseudopotentials corresponding to various choices of the above mentioned degrees of freedom were tested through molecular calculations at the SCF level using moderately extended valence basis sets. Calculations were restricted to the following closed-shell diatomic molecules HF, AlH, HCl, AlF, AlCl, F_2, Cl_2. The case of molecules containing heavier atoms was disregarded because accurate all-electron Hartree–Fock calculations are very sparse. The comparison with double-zeta type all-electron calculations would be less significant because valence orbitals are better described in valence-electron calculations than in all-electron calculations as previously discussed [3].

2. Determination of Atomic Pseudopotentials from Near Hartree–Fock Solutions

In pseudopotential methods, the total valence Hamiltonian of an atom is in atomic units (a.u.)

$$H_{ps} = \sum_{i=1}^{N_v} \left[-\frac{\Delta_i}{2} + W_{ps}(i) \right] + \sum_{i<j}^{N_v} \frac{1}{r_{ij}}. \tag{1}$$

N_v is the number of valence electrons. The pseudopotential W_{ps} is a fixed one-electron operator which takes into account the interaction of the valence electrons with the core of the atom consisting of the nucleus and the electrons of the inner shells.

Various methods have been developed to determine pseudopotentials from atomic calculations or experimental energies [1]. In this work we use new semi-local pseudopotentials derived from extended basis set Hartree–Fock–Roothaan calculations according to the scheme proposed by Barthelat and Durand [4, 5].

2.1. Pseudoorbitals

The first step in the method is the generation of a valence pseudoorbital ϕ_v for each angular momentum l. They are nodeless orbitals and they reproduce best the true Fock valence orbitals φ_v from a chosen core radius R_c to infinity. The radial part of ϕ_v must decrease monotonically towards zero as r goes from R_c to 0.

In previous work the radial parts of the pseudoorbitals were obtained by minimizing the function

$$f = \langle \phi_v - \varphi_v \mid \phi_v - \varphi_v \rangle_{R_c \to \infty} \tag{2}$$

in which the radial integration goes from R_c to infinity with the constraint $\langle \phi_v \mid \phi_v \rangle = 1$. The reference valence orbital φ_v were of double-zeta quality.

The use of such a criterion is not sufficient to yield nodeless pseudoorbitals when the true orbitals are expanded over an extended basis set. In this work we propose to eliminate spurious oscillations in the core region by using an additional constraint which enforces ϕ_v to behave like the radial part of a Slater orbital ϕ_s near the nucleus.

$$\phi_s = N r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \varphi). \tag{3}$$

This is obtained by minimizing

$$f' = \lambda f + (1 - \lambda)\langle\phi_{\mathrm{v}} - \phi_{\mathrm{s}} \mid \phi_{\mathrm{v}} - \phi_{\mathrm{s}}\rangle_{0\to R\leqslant R_c}. \tag{4}$$

λ is a weight coefficient with a typical value of $\lambda = 0.2$; R is chosen as $R_c/2$. This criterion allows us to choose the shape of the pseudoorbitals near the nucleus. This point seems to be particularly important for the s-symmetry orbitals. The choice $n = 1$ or $n = 2$ in Eq. (3) leads to a non-zero or zero amplitude for the radial part of the orbital at $r = 0$. In Fig. 1 we present the resulting s-symmetry pseudoorbitals for the aluminium atom with the various choices $n = 1$, $n = 2$ compared with the true orbital and the previously derived "double-zeta" pseudoorbitals.

2.2. *Semilocal Pseudopotentials*

In a second step the atomic pseudopotentials W_{ps} are obtained by requiring that the solutions $\varepsilon'_{\mathrm{v}}$, ϕ'_{v} of the Hamiltonian of the atom (Eq. 1) should be ε_{v}, ϕ_{v}. ε_{v} is the true eigenvalue of the Fock operator and ϕ_{v} the above defined pseudoorbital. This is achieved by minimizing the norm of the operator

$$\sum_{\mathrm{v}} (\varepsilon'_{\mathrm{v}}|\phi'_{\mathrm{v}}\rangle\langle\phi'_{\mathrm{v}}| - \varepsilon_{\mathrm{v}}|\phi_{\mathrm{v}}\rangle\langle\phi_{\mathrm{v}}|). \tag{5}$$

The pseudopotentials are written in a semi-local form

$$W_{\mathrm{ps}} = -\frac{z}{r} + \sum_{l} W_l(r)P_l \tag{6}$$

in which P_l is the projector over the lth subspace of the spherical harmonics, $z = N_{\mathrm{v}}$ is the number of valence electrons and $W_l(r)$ is a radial function characterizing the l angular symmetry

$$W_l(r) = \sum_{i=1}^{n} C_i r^{n_i}\, \mathrm{e}^{-\alpha r^2}. \tag{7}$$

It must be noted that the properties of $W_l(r)$ are closely related to the analytical form of the pseudoorbital near the nucleus. For example in the case where the pseudoorbital is exactly a Slater orbital the potential would be

$$W_l(r) = \frac{n(n-1) - l(l+1)}{2r^2} - \frac{\zeta n}{r}. \tag{8}$$

For the choice $n = l + 1$, W_l behaves like $1/r$ whereas it behaves like $1/r^2$ in the other cases. Therefore it seems that the analytical dependence of $W_l(r)$ must be linked to the arbitrary shape of the pseudoorbital near the origin.

The various atomic potentials tested in this paper are reported in Table 1. The different potentials labelled I are derived from Hartree–Fock "double-zeta" wave functions and are very similar to those previously published [6]. The other ones from II to V are extracted from the near Hartree–Fock Clementi's atomic data [7].

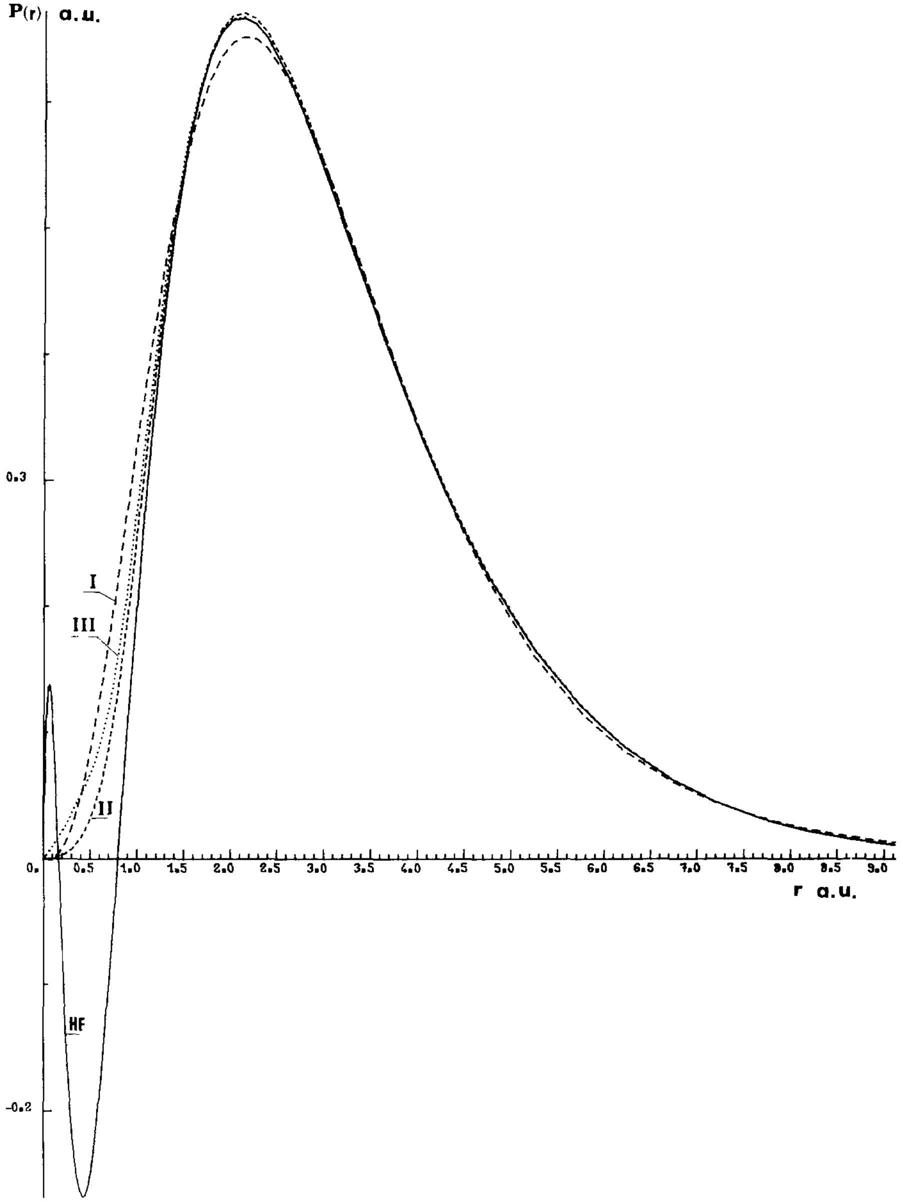

Fig. 1. Aluminium atom *s*-symmetry. HF: radial part of the valence Hartree–Fock all-electron orbital, I: radial part of the pseudoorbital determined from double-zeta atomic calculation according to previous procedure [6], II and III: radial part of the pseudoorbitals determined according to the procedure presented in this paper. II behaves as $r\,e^{-\zeta r}$ for $r \leqslant R_c/2$, III behaves as $e^{-\zeta r}$ for $r \leqslant R_c/2$

Table 1. Parameters for the radial components of the atomic pseudopotentials $W_l = e^{-\alpha r^2} \sum_i C_i r^{n_i}$

Atom	l	Type[a]	α	n_1	C_1	n_2	C_2	n_3	C_3
F	0	I	1.57675	−2	1.22780	2	−1.42491		
		II	5.76091	−2	2.54831	2	−0.59995		
		III	13.2013	−1	2.39984	0	55.6708		
		IV	14.2200	0	73.4875	2	0.0002		
	1	I	17.2852	0	−3.60619				
		II	34.0224	0	−9.20504				
		III IV	32.4647	0	−8.77959				
Al	0	I	0.40062	−2	2.50888	2	−0.09611		
		II	2.71212	−2	0.29754	0	36.7735	2	0.02726
		III	2.64035	−1	0.78427	0	18.8093	2	15.67308
		IV	2.78095	0	15.0366	2	24.4911	4	0.00012
		V	2.79336	0	9.37867	2	32.0584	4	−0.39084
	1	I	0.30587	−2	1.63343	2	−0.0385		
		II	1.87755	−2	5.60117	2	7.57783	4	−0.96018
		III IV	1.31738	−2	5.11990	2	2.45098	4	−0.69105
		V	1.91642	−2	1.22203	2	10.1706	4	−0.27317
	2	I ... V	1.13022	0	−1.00782				
Cl	0	I	0.80270	−2	3.09806	2	−0.54632		
		III	6.32177	−1	6.81352	0	−8.43637	2	279.1392
		IV	4.89029	0	42.54261	2	37.7677		
	1	I	0.75390	−2	2.13242	2	−0.33528		
		III IV	4.57212	−2	2.26586	2	67.5997	4	−8.12875
	2	I, IV	7.23767	0	−14.57895				

[a] I, from double-zeta atomic calculations; II–V, from near Hartree–Fock atomic calculations p-pseudoorbital behaves as $r\,e^{-\zeta r}$ for $r < R_c/2$; II, s-pseudoorbital behaves as $e^{-\zeta r}$ for $r < R_c/2$; III, s-pseudoorbital behaves as $re^{-\zeta r}$ for $r < R_c/2$; IV, differs from III in the analytical form of $W_l(r)$; V, from atomic calculation of the positive ion.

They were derived from different choices of the inner part of the pseudoorbital according to the criterion (4) with different analytical forms for W_l. The characterization of these various potentials is indicated in Table 1.

3. Atomic Calculations. Determination of Gaussian Valence Basis Sets

The above described procedure leads to pseudoorbitals which are expanded over the whole all-electron basis set. Therefore it is necessary to determine valence basis sets in order to take advantage of the pseudopotential representation of the core electrons. Since our molecular programs work with Gaussian functions we optimized Gaussian valence basis sets in the valence atomic calculations using the various effective potentials given in Table 2. For each symmetry, a set of four Gaussian exponents was derived in order to minimize the total valence energy of

Table 2. Hartree–Fock reference one electron energies $\varepsilon_{\mathrm{HF}}$ in atomic units and deviation $\Delta\varepsilon$ resulting from the resolution of valence Hamiltonians using effective potentials I–V

Calculation characterization[a]		Fluorine		Aluminium		Chlorine	
$\varepsilon_{\mathrm{HF}}$[b]		−1.57254	−0.72388	−0.39340	−0.21002	−1.07311	−0.50652
$\Delta\varepsilon$[c]	I 44	−5.95	6.23	−0.48	0.24	−0.83	0.34
	II 44	5.15	4.93	0.27	0.24		
	II 55	2.37	3.24	—	—		
	III 44	5.66	6.65	−0.24	−0.06	−1.48	0.58
	III 55	3.65	4.36	—	—	−2.20	0.26
	IV 44	10.52	4.80	−0.31	0	1.86	0.70
	IV 55	3.68	3.95	—	—	0.65	−0.04
	V 44	—	—	0.18	0	—	—

[a] Pseudopotential type (see Table 1) and number of Gaussian primitives in symmetry *s* and *p*.
[b] In atomic units.
[c] In 10^{-3} atomic units.

the atom. The deviations of the Fock valence operator eigenvalues from the corresponding Hartree–Fock one-electron levels are reported in Table 2. The greater discrepancies occur in the case of the fluorine atom but this is essentially due to the use of a limited number of Gaussian functions instead of Slater functions as shown by the equivalent all-electron results obtained with Gaussian basis sets [8]. It is not surprising that very similar results are obtained with effective core potentials extracted either from double-zeta basis sets or extended basis sets; since in both cases the all-electron reference results are as accurate for such atoms. However this would not be true for heavier atoms, particularly for *d*-orbitals in transition metal atoms. On the other hand a better reproduction of the all-electron valence orbital in the valence region is obtained with the procedure presented in this paper (see Fig. 1). Moreover it must be noticed that the resolution of the atomic valence Hamiltonian with the Gaussian basis set yields orbitals which reproduce well the given pseudo-orbitals. Graphical representations do not put into evidence any differences and are not reproduced in this paper.

4. Molecular Results

The different expressions of the effective core potentials were used in SCF calculations of the diatomic molecules HF, HCl, AlH, AlF, AlCl, F_2, Cl_2, which were carried out with the modified version of the IBMOL [6] or HONDO [9] programs.

For the hydrogen atom we used the 4*s*3*p* Gaussian basis set reported in Ref. [10]. In the case of F, Al and Cl atoms we used the various optimized *s* and *p* valence basis sets corresponding to each effective core potential augmented with one or two *d* polarization functions. The single *d* exponents are taken from Roos [11]; two *d* exponents are derived by multiplying the second p exponent in ascending order by 0.5 and 2.0. For the sake of brevity the different basis sets are not included here but are available upon request.

4.1. Comparison of the Different Expressions of the Pseudopotential Operator

For each molecule Table 3 displays the spectroscopic constants obtained from a parabolic fit of three calculated points around the minimum of the potential curves. The results correspond to a constant quality valence basis set of four uncontracted Gaussian functions for F, Al and Cl augmented with one d polarization function. All Gaussian functions are kept free for the hydrogen atom.

The good stability of the results with respect to the different core potentials can be noticed. The bond length in the molecules containing an aluminium atom is slightly shortened by the use of the present form of effective potential, and it is the only general trend which appears from Table 3. This can be related to a better reproduction of the valence orbital in the present technique as shown in Fig. 1. On the one hand it is satisfactory to note the insensitivity of the spectroscopic constants when different analytical expressions are used to describe the core potential corresponding to a given pseudoorbital (pseudopotentials III and IV). On the other hand little deviations result from a different choice of the inner part of the pseudoorbital as it

Table 3. Comparison between valence electron molecular results obtained with various effective potentials

Molecule	Pseudo-potential type	r_e Å	ω_e cm^{-1}	D_e eV	μ_e D
HF	I	0.901	4432	4.38	1.92
	II	0.898	4460	4.38	1.91
	III	0.900	4481	4.34	1.88
	IV	0.900	4479	4.32	1.87
AlH	I	1.666	1723	2.32	0.18
	II	1.650	1676	2.34	0.25
	III	1.647	1671	2.35	0.25
	IV	1.647	1670	2.35	0.25
	V	1.650	1667	2.31	0.24
HCl	I	1.274	3198	3.57	1.27
	III	1.275	3159	3.47	1.28
	IV	1.275	3160	3.47	1.28
AlF	I, I	1.698	908	4.96	1.63
	IV, III	1.668	869	5.04	1.69
AlCl	I, I	2.194	526	4.17	1.98
	IV, III	2.177	617	4.11	1.98
FF	I	1.344	1071	−1.28	—
	III	1.323	1035	−1.31	—
ClCl	I	1.995	571	1.04	—
	III	2.003	562	0.81	—

can be seen in the comparison between the II and III cases for AlH and HF. Nevertheless the differences remain in the range of 1–2 per thousand. These calculations do not allow any preference between the different shapes of the *s*-pseudo-orbital. Moreover in the case of AlH the core potential extracted from an aluminium positive ion (*V*) does not really modify the calculated molecular constants. This supports the validity of the frozen core approximation even for an atom with a few valence electrons.

4.2. *Comparison with Elaborate All-Electron Results*

The reference to the elaborate all-electron (AE) [12–15] results and to the corresponding experimental data [16] are to be found in Table 4. Note first that spectroscopic constants are sensitive to the number of points used to represent the potential curves as shown by the three points and five points interpolated values given for HF and AlH. Therefore, in order to compare the valence electron (VE) results of Table 3 with the AE values, spectroscopic constants were recalculated from a parabolic fit of three points around the minimum when AE calculations were available.

4.2.1. Hydrides

The comparison between the results reported in Tables 3 and 4 shows that VE calculations give results close to those obtained by Meyer [12] with extended Gaussian basis sets in AE calculations. It can be noticed that in the VE calculations we used very few polarization functions as compared to the AE calculations [12]. Nevertheless it is rather surprising that in the case of the hydrogen fluoride molecule the description of the valence orbital of fluorine by five Gaussian functions (results in Table 4) instead of four is sufficient to obtain a potential curve quite identical to the AE one. The lack of polarization functions has greater effects on the second-row hydrides. A better description of the valence orbital of the chlorine atom does not change the VE results but the introduction of two *d* polarization functions improves significantly the comparison with AE results. Note that the important value of the derivative of the dipole moment function at r_e explains the apparently great discrepancy found for the dipole moment of AlH.

4.2.2. AlF

The two AE reference calculations [13, 14] were done with the same extended basis set of Slater functions except for the exponent of one *d* polarization function. The different results obtained emphasize the role of the polarization functions. Moreover in the VE calculations the replacement of the *d* polarization exponent of aluminium by two exponents leads to results in satisfactory agreement with the AE reference values.

4.2.3. AlCl

Because of the lack of extended basis set AE calculations the VE results can only be compared to experimental data. By analogy with the AlF case we might expect a

Table 4. Comparison between all-electron (AE) results, valence electron (VE) results and experimental data

			r_e Å	ω_e cm^{-1}	D_e eV	μ_e D
HF	exp[a]		0.917	4139	6.12	1.83
	AE[b]		0.898	4476	4.32	1.90
		(3)[l]	0.901	4473		
		(5)	0.897	4502		
	VE[c]	(3)	0.901	4471	4.32	1.89
		(5)	0.897	4499		
AlH	exp[a]		1.646	1683	3.01	
	AE[b]		1.647	1731	2.38	0.11
		(3)	1.654	1765		
		(5)	1.648	1725		
	VE[d]	(3)	1.647	1670	2.35	0.25
		(5)	1.645	1706		
HCl	exp[a]		1.275	2991	4.62	1.09
	AE[b]		1.266	3141	3.49	1.2
		(3)	1.268	3116		
	VE[e]		1.275	3164	3.47	1.26
	VE[f]		1.272	3145	3.49	1.22
AlF	exp[a]		1.654	802	6.89	1.53
	AE[g]		1.658	942		
	AE[h]		1.638	831		
	VE[i]		1.654	863	5.29	
AlCl	exp[a]		2.13	481	5.08	1–2
	VE[j]		2.176	502	4.19	
FF	exp[a]		1.417	892	1.44	
	AE[k]		1.338	1259	−1.11	
	VE[d]		1.323	1035	−1.31	
ClCl	exp[a]		1.988	560	2.48	
	AE[k]		1.991	603	1.16	
	VE[d]		2.003	562	0.81	

[a] Ref. [16].

[b] Ref. [12].

[c] Effective potential III, basis set 5*s*/5*p*/1*d* for fluorine.

[d] Same as Table 3.

[e] Effective potential III, basis set 5*s*5*p*1*d* for chlorine.

[f] Effective potential III, basis set 4*s*4*p*2*d* for chlorine.

[g] Ref. [13].

[h] Ref. [14].

[i] Same as in Table 3 but 4*s*4*p*2*d* basis set for aluminium.

[j] Same as in Table 3 but 4*s*4*p*2*d* basis set for chlorine.

[k] Ref. [15].

[l] Number of points used to represent the potential curve.

calculated equilibrium distance shorter than the experimental one. The VE results do not agree with this conjecture but the addition of a second polarization function to the chlorine atom significantly lowers the calculated bond length. The same improvement of the valence aluminium basis set would probably be efficient. Because of the only qualitative character of the comparison additional calculations have not yet been performed.

4.2.4. F_2, Cl_2

Due to the inadequacy of the SCF description of the bonding for these molecules comparisons are rather difficult to make since SCF results are very dependent on the basis set [3]. Nevertheless the comparison between AE and VE calculations seems satisfactory. There is no evidence for specific problems similar to those reported by Hay et al. [17]. We may notice that our *d* effective potential does not present any artifactual attractive tail despite a derivation of *d* potential from excited states of the chlorine atom.

4.3. Contractions of the Basis Set

The effects of the contractions of the basis sets described in Sect. 1 were investigated in a limited number of cases. Two main conclusions arise from the results displayed in Table 5:

1) For a given contraction the variation due to the use of the different forms of the effective core potential are similar to those obtained with uncontracted basis sets.
2) Triple-zeta basis sets provide a representation flexible enough for the valence orbitals.

Table 5. Influence of basis set contraction on the calculated spectroscopic constants

	Atom 1		Atom 2	r_e Å	ω_e cm^{-1}	D_e eV
	Al		H			
I[a]	31/31/1[b]		31/3	1.676	1785	2.30
II	31/31/1		31/3	1.662	1707	2.29
III	31/31/1		31/3	1.664	1724	2.29
IV	31/31/1		31/3	1.664	1721	2.29
III	211/31/1		31/3	1.658	1694	2.31
IV	211/211/1		31/3	1.658	1696	2.31
III	211/211/1		31/3	1.649	1668	2.33
III	211/211/1		211/3	1.651	1669	2.34
	Cl		H			
III	31/31/1		31/3	1.281	3221	3.41
III	211/211/1		211/3	1.275	3163	3.45
	Al		F			
I	31/31/1	I	31/31/1	1.715	941	4.80
IV	31/31/1	III	31/31/1	1.695	935	4.94

[a] Potential type, see Table 1.

[b] Number of primitives in each contracted function. Symmetry *s p d*.

5. Conclusion

This work presents a procedure to extract elaborate pseudopotentials from accurate analytical atomic calculations. The pseudopotential receives a given semi-local analytical form; starting from a near Hartree–Fock all-electron calculation performed in a large Slater orbital basis set, the HF energy levels and the outer part of the HF orbitals must be reproduced by the valence Hamiltonian solution using somewhat smaller basis sets. A few arbitrary points are inherent to this procedure, namely the inner part shape of the valence pseudoorbital and the analytical form of the potential. The numerous tests performed in the present work show the stability of the molecular results with respect to these degrees of freedom. This verification is only done for the precise algorithm of the Barthelat–Durand pseudopotentials but we believe that it remains valid for the whole class of semi-local potentials extracted from both the energy and the wave-function, such as those proposed by Kahn et al. [18] and Topiol et al. [19].

A more important point concerns the quality of the valence basis set. Double-zeta valence basis sets optimized in valence atomic calculations provide reliable results. The simulation of accurate all-electron results is possible but requires the enlargement of the valence basis set somewhat diminishing the practical advantage of the pseudopotential technique.

From a more general point of view, one may notice the existence of two possible pseudopotential strategies;

1) The first one which is followed in the present paper tries to extract from the best atomic calculation the best pseudopotential which will give the right answer to valence basis set extensions; with such a pseudopotential, no accident is to be expected in the molecular calculation but its counterpart is the requirement of a sufficiently large basis set. This procedure remains interesting for spectroscopic studies of small molecules, but at the present stage it cannot provide a reasonable answer for heavy atoms containing large molecules, the size of which prevents from going beyond the minimal basis level.
2) An alternative strategy would consist in extracting the pseudopotential using a poor description of the valence pseudoorbital (for instance a three-contracted Gaussian description) but the correct energy level. Such a pseudopotential could not give the right answer to basis set extensions but when applied in a molecule with the same minimal basis set as that used in the extraction procedure, it should give at lower cost better results than all-electron calculation performed with a minimal basis set. This strategy is under investigation and should make feasible calculations on large molecules according to the original spirit of pseudopotential research.

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References

1. Dixon, R. N., Robertson, I. L., in: Theoretical chemistry, Vol. III, p. 100. London: The Chemical Society 1978
2. Barthelat, J. C., Durand, Ph.: Gaz. Chim. Ital. **108**, 225 (1978)
3. Teichteil, Ch., Malrieu, J. P., Barthelat, J. C.: Mol. Phys. **33**, 181 (1977)
4. Durand, Ph., Barthelat, J. C.: Theoret. Chim. Acta (Berl.) **38**, 283 (1975)

5. Barthelat, J. C.: Thèse, Université de Toulouse (1977)
6. Barthelat, J. C., Durand, Ph., Serafini, A.: Mol. Phys. **33**, 159 (1977)
7. Clementi, E., Roetti, C.: Atomic data and nuclear data tables 14, 177 (1974)
8. Mezey, P. G., Kari, R. E., Csizmadia, I. G.: J. Chem. Phys. **66**, 964 (1977)
9. Dupuis, M., Rys, J., King, H. F.: J. Chem. Phys. **65**, 111 (1976) Pseudopotential adaptation by J. P. Daudey to be submitted to Q.C.P.E.
10. Pelissier, M., Malrieu, J. P.: J. Chem. Phys. **67**, 5963 (1977)
11. Roos, B., Siegbahn, P.: Theoret. Chim. Acta (Berl.) **17**, 199 (1970)
12. Meyer, W. E., Rosmus, P.: J. Chem. Phys. **63**, 2356 (1975)
13. McLean, A. D., Yoshimine, M.: IBM J. Res. Develop. **12**, 206 (1968)
14. So, S. P., Richards, W. G.: J. Phys. B **7**, 1973 (1974)
15. Straub, P. A., McLean, A. D.: Theoret. Chim. Acta (Berl.) **32**, 227 (1974)
16. International tables of selected constants, Vol. 17: Spectroscopic data relative to diatomic molecules, Ed. B. Rosen. Oxford: Pergamon 1970
17. Hay, P. J., Wadt, W. R., Kahn, L. R.: J. Chem. Phys. **68**, 3059 (1978)
18. Kahn, L. R., Baybutt, P., Truhlar, D. G.: J. Chem. Phys. **65**, 3826 (1977)
19. Topiol, S., Moskowitz, J. W., Melius, C.: J. Chem. Phys. **68**, 2364 (1978)

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