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Accuracy and Limitations of the Pseudopotential Method*

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Two model potential approximations to the pseudopotential operator are discussed. Suitable simple expressions for an atomic model potential with angular projection are given, the parameter values of which can be fitted to reproduce the Rydberg series rather accurately. Calculations on atomic states with several valence electrons from the first two and a half rows of the periodic system show that energies of chemical interest are accurate to 0.0–0.2 eV. The pseudo-wave functions have an accuracy of a few %.

Key words: Pseudopotentials – Model potentials – Valence shell calculations – Atoms, SCF-calculations of ~

1. Introduction

One of the disadvantages of quantum chemical *ab initio* calculations on heavy atomic molecules is the necessity to treat all the electrons of the system, although one knows from chemical experience that only the valence electrons are relevant to their static and dynamical properties. In pseudopotential theory one attempts to reduce the quantum mechanical all-electrons problem to a valence-electrons-only problem.

Given an effective one-electron operator h (h is not necessary to be a linear operator, e.g. may be some type of Hartree-Fock-operator)

$$h\phi_i = \varepsilon_i \phi_i .$$

The complete set of orbitals ϕ_i consists of the core orbitals ϕ_c and the valence and virtual orbitals ϕ_v (with core orbitals we mean those atomic orbitals, which are – in a localized orbital scheme – nearly invariant to molecular formation). In pseudopotential theory [1, 2] the following effective one-electron pseudo-Fock equation is used:

$$\tilde{h}\tilde{\phi}_v = \varepsilon_v \cdot \tilde{\phi}_v$$

where the pseudo-hamiltonian $\tilde{h}$ is given by

$$\tilde{h} = t + V_{\text{core}} + \sum_{v'}^{\text{occ}} (J_{v'} - K_{v'}) + \sum_{c}^{\text{occ}} |\phi_c\rangle (\varepsilon_v - \varepsilon_c) \langle\phi_c| \tag{1}$$

where V_{core} is the Hartree-Fock potential of the core[1].

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* This work is dedicated to the 60th birthday of Prof. H. Hartmann.

[1] More general hermitean and non-hermitean operators are derived and discussed by Schwarz [3] and Austin *et al.* [4], resp.

In the next section we discuss some problems arising from the *last term* of Eq. (1), the so called pseudopotential V_{ps}. In order to cast the pseudopotential method into an appropriate calculational scheme, it is necessary to introduce several approximations, especially into the *third term* of Eq. (1). The resulting accuracy of energies and wave-functions is investigated in Section 3 on the basis of SCF and correlation calculations on many terms of atoms and ions. In the fourth section we point out the difficulty connected with the *second term* of Eq. (1), V_{core}. In the conclusion some general statements on the accuracy and limitations of the pseudopotential method are made.

2. Model Potential Approximations

In Eq. (1) the eigensolutions of h are also eigensolutions of $\tilde{h}$. The last term of $\tilde{h}$, the pseudopotential operator V_{ps}, raises the eigenvalues of the ϕ_c up to ε_v, so that the core orbitals become degenerate with the valence orbitals, and the *lowest* eigenvalues of $\tilde{h}$ are just the *valence* orbital energies of h[2]. Therefore it is not necessary to keep the valence solutions orthogonal to the core solutions in this type of valence electron calculations. In particular one can pick out from the degenerate set $\{\phi_{c_1}, \phi_{c_2}, \ldots, \phi_v\}$ one orbital $\tilde{\phi}_v$, which resembles the canonical valence orbital outside the core, but has no nodes within the core region and is smooth there. This means that it is possible to represent one "pseudo-valence orbital", belonging to ε_v, quite accurately using a small basis set of STO's or GTO's, or to calculate this pseudo-orbital by numerical integration using a rather coarse grid[3]. By this, one selects just one smooth pseudo-orbital from the degenerate set. There will be no significant loss of accuracy in the corresponding orbital energy. However, a significant reduction of computing time may be gained, if reasonable simplifications are introduced into the exact pseudohamiltonian of Eq. (1). Two approximations for V_{ps} have often been used. The one shall be referred to as the angular projection and the other as the core projection model potential, which will now be discussed.

2.1 Core Projection Model Potential

In this approximation scheme the given form of V_{ps} is retained:

$$V_{ps}^{\text{core}} = \sum_{A} \sum_{c \in A} |\psi_c^A\rangle \, \eta_c^A \, \langle \psi_c^A| \,. \tag{2}$$

The η_c^A's are constants, which may be taken as the difference between atomic SCF core orbital energies and a representative valence orbital energy [7, 8]. The ψ_c^A's are approximations to the core orbitals ϕ_c^A of free atom A (e.g. minimal basis STO's). But now the degeneracy of core and valence orbitals is destroyed: 1) the pseudovalence orbital is no longer smooth, but has nodes as the canonical valence orbital. 2) In general one cannot prevent the lowest solution of

$$(h + V_{ps}^{\text{core}}) \, \tilde{\phi} = \tilde{\varepsilon} \tilde{\phi}$$

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[2] This statement is not exactly correct, see. Ref. [5].

[3] This forms the basis of the atomic pseudopotential calculations of Szasz and McGinn, see e.g. Ref. [7].

from collapsing into the core, especially for heavier atoms where only in some cases one can help by properly raising the parameters η_c[4]. 3) The core orbitals are raised into the energetic region of the excited MO's and low continuum functions and disturb the corresponding molecular states. An extreme example has been found for the He atom. It was impossible to reproduce either the low energy electron scattering cross sections or the He-Li potential curves within the core projection approximation scheme, even if the Slater exponent ζ_c in ψ_{1s}^{He} was treated as an additional adjustable parameter.

These difficulties may be overcome by choosing a suitable basis for the valence electrons to force the pseudo orbitals to be smooth and not too low in energy[5]. Corresponding molecular calculations have recently been carried out by McWeeny *et al.* [10–12] with success, although their pseudopotential core parameters and molecular results are dependent on the basis [11].

2.2 Angular Projection Model Potential

In the angular projection approximation scheme one uses the following molecular pseudopotential

$$V_{Ps}^{\mathrm{ang}} = \sum_{A} \sum_{l \in A} V_l^A(r_A) \cdot P_l^A , \tag{3}$$

where l are the angular quantum numbers of the shells in atomic core A. The projection operator P_l^A projects onto the one electron orbital subspace of angular momentum l with reference to center A. If one calculates an atomic orbital of angular momentum l, the corresponding one-dimensional equation contains only an r-dependent local potential term $V_l(r)$. Therefore the node-theorem holds and the lowest pseudovalence orbital will automatically be nodeless and smooth. Furthermore, the difficulties due to the above mentioned degeneracy can be avoided. In ansatz (3) one adjusts V_l instead of η and ψ in ansatz (2). Since the number of core shells c is usually greater than the number of different l-values, the angular projection approach needs less parameters than the core projection approach[6].

The only disadvantage of the angular projection potential is, that in molecular calculations the three-center (and some of the two-center) one-electron integrals are difficult to compute accurately [8, 14]. However, if one uses gaussian type potential functions V_l together with a gaussian lobe basis, the integrals can be calculated in a simple manner. (The corresponding formulae are given in the Appendix.) In the case of an STO basis one can apply the simple integral approximation scheme of Schwarz [2] which has been shown to give satisfactory results

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[4] McGinn [9] remarked that his atomic pseudopotential SCF-calculations on Ag did not properly converge when he used a minimal basis for the core.

[5] In this respect we remind of the analysis of valence-only calculations by Zerner [13] who explicitely introduced the presupposition of minimal basis. This means that part of the pseudopotential effect has to be taken over by the basis.

[6] Another disadvantage of the core projection is, that direct numerical integration of the Schrödinger equation, e.g. for electron scattering, is not possible but must be performed iteratively.

Table 1. SCF-results on BeH_2 ($Be-H = 2.54\ a_0$; energies in $-$a.u.)

	Full SCF	Corrected[a] energy	Pseudo-SCF	Pseudo-SCF (Integ.-approx.)	Ref. [17]
E (Valence system)	2.152	2.166	2.171	2.167	
Bond energy	0.190	0.204	0.205	0.201	
$\varepsilon(2\sigma_g)$	0.499	0.503	0.490	0.489	0.392
$\varepsilon(\sigma_u)$	0.438	0.442	0.449	0.449	0.464

[a] Corrected for core-valence correlation and relativistic effects (see Section 3.2, Eq. (4))

[15, 16]. Recently Schwartz obtained bad results in her BeH_2 and BeO calculations [17]. However, our BeH_2 calculations using both exact and approximate integrals give results in good agreement with full SCF-calculations (see Table 1).

As the conclusion of this section we find that the angular projection approximation is a quite suitable scheme.

3. Necessary Approximations in the Pseudohamiltonian

In order to be a convenient alternative to *ab initio* methods, the pseudopotential approach should lead to a significant reduction and simplification of molecular calculations. Therefore the following two approximations are introduced.

1) Frozen core approximation. Although the 2nd and 4th terms in Eq. (1), V_{core} and V_{ps}, are integral operators depending on the molecular core solutions, V_{core} and the V_l's are approximated by simple local and only r-dependent model potentials summed over the frozen atomic cores of the molecule.

2) Pseudovalence interaction approximation. To calculate the 3rd term, the valence electrons interaction, by using the exact valence orbitals v is quite time consuming. As approximation this term is calculated using the smooth pseudovalence orbitals $\tilde{v}$.

In a theoretical analysis of the model potential method [2] it was shown that both approximations may result in rather large errors, which are expected to be of different signs. In the latter part of this section we will investigate the effects of these errors by numerical calculations.

3.1 Atomic Model Potentials

We adjust the model potentials to experimental atomic expectation values. Therefore V_{core} not only represents the Hartree-Fock potential of the closed shell atomic cores, but also includes core-valence electron correlation and relativistic corrections in a rough empirical way. We have tried different simple formulae and obtained the best results with a screened Coulomb potential

$$V_{\text{core}} = -Z_c/r - A/r \cdot \exp(-\alpha r).$$

Table 2. Atomic model potential parameters for the first two rows of the periodical system

Family	First row: $1s^2$-core					Second row: $1s^2\,2s^2\,2p^6$-core						
	Atom	A	α (opt)	B_0 (opt)	β_0	Atom	A	α (opt)	B_0 (opt)	β_0	B_1 (opt)	β_1
O	He	2	1.3	25	2.2	Ne	3	1.15	46	2.7	24	2.2
I	Li	2	2.3398	60.28	3.6	Na	4	1.550	91.17	3.3	48.69	2.8
II	Be	2	3.3610	115.20	5.0	Mg	5	2.125	135.31	3.9	70.47	3.4
III	B	2	4.3630	188.40	6.4	Al	6	2.625	199.4	4.5	103.7	4.0
IV	C	2	5.3608	279.33	7.8	Si	7	3.133	277.5	5.1	144.6	4.6
V	N	2	6.3537	387.85	9.2	P	8	3.660	369.0	5.7	192.9	5.2
VI	O	2	7.3405	514.46	10.6	S	9	4.210	474.1	6.3	248.45	5.8
VII	F	2	8.3132	658.60	12.0	Cl	10	4.750	591.9	6.9	310.7	6.4
VIII	Ne	2	9.282	820.8	13.4	Ar	11	5.361	724.7	7.5	381.15	7.0

Table 3. Si IV Rydberg spectrum (energies in eV below ionization limit)

Term	Exp.	Calc.
$3s$	45.142	45.141
$3p$	36.266	36.265
$3d$	25.257	25.258
$4s$	21.129	21.091
$4p$	18.071	18.067
$4d$	14.139	14.145
$4f$	13.632	13.634
$5s$	12.254	12.234
$5p$	10.856	10.866
$5d$	8.997	9.001
$5f$	8.728	8.725
$5g$	8.708	8.711
$6s$	7.996	7.987
$6p$	7.246	7.244
$6d$	6.212	6.221

Z_c is the charge of the atomic core. A should be of the order of the number of electrons in the outer shell of the core. As V_{core} simulates not only the HF-part, but also the far reaching polarization part of the effective core potential, α should be significantly smaller than twice the Slater exponent of the outer core shell. We have determined α so that the experimental Rydberg term values of the system "atomic core + one valence electron" with angular momentum $l > l_{\text{Max}}$ are reproduced. Here l_{Max} is the largest l-value in the core. In the case of the neutral rare gas cores we adjust α according to the corresponding low energy electron scattering cross section. A variation of the second parameter A has no large effect on the accuracy of the results. Therefore we have fixed it to a suitable integer number and adjusted only the parameter α. The parameter values for the first two rows of the periodical system are given in Table 2. With this V_{core} the Rydberg series can be calculated with an accuracy of about 10^{-3} as shown for Si in Table 3. By adjusting both parameters A and α, a higher accuracy could be obtained. However, many-valence-electrons states, which come out less accurate, are insensitive to such an adjustment. The normal mass effect has also not been taken into account.

Similarly the pseudopotentials V_l have been adjusted to Rydberg terms of angular momentum $l \leqq l_{\mathrm{Max}}$. A suitable ansatz is

$$V_l(r) = B_l \cdot \exp(-\beta_l \cdot r).$$

β_l describes the hardness of the core-shells with angular momentum l, into which the corresponding valence electrons are forbidden to penetrate. Therefore the β_l should be larger than α. Furthermore, because an *np* shell is more diffuse than an *ns* shell, one has $\beta_0 > \beta_1$. We have first chosen suitable values for β_l which increase linearly within one row and then optimized the remaining parameters B_l. The parameter values of B_l and β_l are given in Table 2. In addition to the $l > l_{\mathrm{Max}}$ Rydberg series, the *s* and *p* Rydberg series are also obtained with high accuracy. Our results (Table 3) are much better than other calculations which approximated the "effective potential" $V_{\mathrm{eff}}^l = (V_{\mathrm{core}} + V_l)$ by some simple formula. The reason seems to be that our ansatz can lead to a local maximum of the "effective nuclear charge" $Z_{\mathrm{eff}}^l = -V_{\mathrm{eff}}^l \cdot r$ at medium large r-values, which is necessary for a good representation of the effective potential [2].

For molecular calculations we use the ansatz

$$V_l(r) = C_l \cdot \exp(-\gamma_l \cdot r^2).$$

The resulting multi-center one-electron integrals can be easily calculated (see Appendix).

3.2 Atomic Model-Potential Calculations

With these potentials we have calculated nearly 100 many-valence-electrons terms of various atomic ions of the first two rows of the periodic system, using the Roothaan-Hartree-Fock method [6]. Some typical results are given in the following tables. To compare our model-SCF-energy values with the experimental or full SCF-results, one must keep in mind that the empirical pseudopotentials allow for core-valence correlation and some relativistic effects. That is the total model-potential valence electrons energy, E_{ps}, is assumed to represent the "corrected" energy values

$$\begin{aligned} E_{\mathrm{correct.}} &= E_{\mathrm{SCF}}(\mathrm{atom}) - E_{\mathrm{SCF}}(\mathrm{core}) + E_{\mathrm{correlat.}}^{\mathrm{core\text{-}valence}} + E_{\mathrm{relat.}}^{\mathrm{valence}} \\ &= E_{\mathrm{exp}}(\mathrm{atom} \rightarrow \mathrm{core\ ion}) - E_{\mathrm{correlat.}}^{\mathrm{intra\text{-}valence}}. \end{aligned} \tag{4}$$

The necessary $E_{\mathrm{correlat.}}$ and $E_{\mathrm{relat.}}$ values have been taken from the literature [19] or estimated.

Energy values for first row atoms are shown in Table 4. The accuracy of $E_{\mathrm{correct.}}$ and $\varepsilon_{\mathrm{correct.}}$ is estimated to be in the range of a few 0.01 eV; this should also be the accuracy of our pseudo-SCF results. According to Table 4 the errors in the total energies are within a few ‰. As predicted by Schwarz [2] the largest errors occur for systems with many valence electrons and a high Z_c-value (as

Table 4. Model-potential results for the ground states of first row atoms and ions (in negative eV)

Ion	Valence		Total valence energy			Valence orbital energies					
	Config.	State	E_{ps} (SCF)	$E_{\text{correct.}}$	Δ	$2s\,\varepsilon_{ps}$	$2s\,\varepsilon_{\text{correct.}}$	Δ	$2p\,\varepsilon_{ps}$	$2p\,\varepsilon_{\text{correct.}}$	Δ
Li	$2s$	^2S	5.39	5.39	(0.00)	5.39	5.39	(0.00)			
Be	$2s^2$	^1S	26.31	26.32	0.01	8.47	8.51	0.04			
B	$2s^2p$	$^2P^0$	69.86	69.44	−0.42	13.62	13.69	0.07	8.48	8.50	0.02
C	$2s^2p^2$	^3P	145.69	145.35	−0.34	19.31	19.31	0.00	11.90	11.87	−0.03
N	$2s^2p^3$	$^4S^0$	264.20	263.50	−0.70	25.98	26.06	0.08	15.57	15.54	−0.03
O	$2s^2p^4$	^3P	428.98	427.98	−1.00	34.32	34.37	0.05	17.29	17.30	0.01
F	$2s^2p^5$	$^2P^0$	653.60	652.02	−1.58	43.49	43.0	−0.5	19.90	19.95	0.05
F^{6+}	$2s$	^2S	185.18	185.18	(0.00)	185.18	185.18	(0.00)			
F^{5+}	$2s^2$	^1S	339.52	339.32	−0.20	154.62	154.49	−0.13			
F^{4+}	$2s^2p$	$^2P^0$	454.44	453.50	−0.94	127.65	127.36	−0.29	115.50	114.80	−0.70
F^{3+}	$2s^2p^2$	^3P	541.87	540.53	−1.34	102.80	102.41	−0.39	88.45	88.01	−0.44
F^{2+}	$2s^2p^3$	$^4S^0$	604.46	602.88	−1.58	80.13	79.70	−0.43	64.11	63.85	−0.26
F^{1+}	$2s^2p^4$	^3P	637.85	636.24	−1.61	60.47	60.04	−0.43	39.47	39.36	−0.11
F^0	$2s^2p^5$	$^2P^0$	653.60	652.02	−1.58	43.49	43.0	−0.5	19.90	19.95	0.05
Li^-	$2s^2$	^1S	5.25	5.4	0.15	0.36	0.30	−0.06			
Be	$2s^2$	^1S	26.31	26.32	0.01	8.47	8.51	0.04			
B^+	$2s^2$	^1S	61.49	61.42	−0.07	23.88	23.88	0.00			
C^{2+}	$2s^2$	^1S	110.45	110.40	−0.05	46.27	46.25	−0.02			
N^{3+}	$2s^2$	^1S	173.12	173.02	−0.10	75.53	75.46	−0.07			
O^{4+}	$2s^2$	^1S	249.48	249.34	−0.14	111.65	111.55	−0.10			
F^{5+}	$2s^2$	^1S	339.52	339.32	−0.20	154.62	154.49	−0.13			

e.g. F^0) where the calculated energies are low by the order of 1 eV. Fortunately for weakly charged ions and excited states of the atom, which play a role in chemistry and chemical bonding, the energy errors are nearly equal (within 0.1 eV; compare e.g. the ground states of F^0, F^+, F^{2+}). Therefore energy differences of chemical interest can be calculated with an accuracy of about 0.1 eV. The orbital energies are obtained with the same accuracy except for fluorine.

We have also applied Sinanoğlu's Many Electron Theory [20] to the first row atoms and ions. Using the model potential approximation our preliminary results show that the internal and semiinternal correlation energies calculated for the valence electrons differ less than 0.1 eV from the exact results.

The results for the second row atoms (Table 5) look quite similar. The errors are a little larger. The orbital energies seem to be too high by about 0.2 eV. (The "corrected" energy values are accurate only within 0.1–0.3 eV because of the uncertainty of some of E_{exp} values as well as of the $E_{\text{correlat.}}$ and $E_{\text{relat.}}$ estimates.) Nevertheless, the conclusion on the term values of chemical interest still holds. To give a further example, we show the energies of the seven terms of neutral P in Table 6.

As mentioned at the beginning of Section 3 the errors in the model potential calculations have their origin in the one-electron-operator (the core and pseudopotentials are assumed to be independent of the surrounding of the atomic core) and in the two-electron operator approximations. Our calculations have shown,

Table 5. Model-potential results for the ground states of second row atoms and ions (in negative eV)

Ion	Valence		Total valence energy			Valence orbital energies					
	Config.	State	E_{ps} (SCF)	$E_{\text{correct.}}$	Δ	$2s\varepsilon_{ps}$	$2s\varepsilon_{\text{correct.}}$	Δ	$2p\varepsilon_{ps}$	$2p\varepsilon_{\text{correct.}}$	Δ
Na	$3s$	^2S	5.14	5.14	(0.00)	5.14	5.14	(0.00)			
Mg	$3s^2$	^1S	21.79	21.8_3	+0.04	7.04	7.2	0.1_5			
Al	$3s^2p$	$^2P^0$	51.82	51.8	−0.02	10.86	11.1	0.2_5	5.80	5.9	0.1
Si	$3s^2p^2$	^3P	101.21	100.9	−0.3	14.88	15.1	0.2_5	8.20	8.3	0.1
P	$3s^2p^3$	$^4S^0$	174.73	174.0	−0.7	19.18	19.4	0.2_5	10.82	10.9	0.1
S	$3s^2p^4$	^3P	273.33	272.2	−1.1	24.25	24.5	0.2	12.04	12.2	0.2
Cl	$3s^2p^5$	$^2P^0$	404.96	403.0	−2.0	29.70	29.9	0.2	13.96	14.1	0.2
Cl^{6+}	$3s$	^2S	114.30	114.30	(0.00)	114.30	113.4	0.1			
Cl^{5+}	$3s^2$	^1S	209.87	209.3	−0.6	95.71	95.8	0.1			
Cl^{4+}	$3s^2p$	$^2P^0$	277.38	276.4	−1.0	80.52	80.6	0.1	67.73	67.4	−0.4
Cl^{3+}	$3s^2p^2$	^3P	330.59	329.5	−1.1	66.22	66.3	0.1	53.55	53.2	−0.4
Cl^{2+}	$3s^2p^3$	$^4S^0$	370.36	368.4	−2.0	52.75	53.0	0.2	40.28	40.0	−0.3
Cl^{+}	$3s^2p^4$	^3P	392.99	391.0	−2.0	40.61	40.9	0.3	25.90	25.9	0.0
Cl^{0}	$3s^2p^5$	$^2P^0$	404.96	403.0	−2.0	29.70	29.9	0.2	13.96	14.1	0.2
Na^{-}	$3s^2$	^1S	4.95	5.2	0.2	0.18	0.4	0.2			
Mg	$3s^2$	^1S	21.79	21.8_3	0.04	7.04	7.2	0.1_5			
Al^{+}	$3s^2$	^1S	46.24	46.3	0.06	18.01	18.2	0.2			
Si^{2+}	$3s^2$	^1S	77.49	77.5	0.0	32.52	32.7	0.2			
P^{3+}	$3s^2$	^1S	115.22	115.2	0.0	50.35	50.5	0.1_5			
S^{4+}	$3s^2$	^1S	159.30	159.2	−0.1	71.40	71.5	0.1			
Cl^{5+}	$3s^2$	^1S	209.87	209.3	−0.6	95.71	95.8	0.1			

Table 6. Different terms of neutral phosphorus (energies in −eV)

Term		E_{ps}	$E_{\text{correct.}}$	Δ
$3s^2p^3$	$^4S^0$	174.73	174.0	−0.7
	$^2D^0$	172.75	172.1	-0.6_5
	$^2P^0$	171.47	170.8_5	−0.6
$3sp^4$	^4P	166.40	165.6	−0.8
	^2D	162.45	161.8	-0.6_5
	^2S	160.52	159.9	−0.6
	^2P	158.60	158.1	−0.5

that in most cases the pseudovalence electron interaction energy is larger than the SCF value (for an example see Table 7) and that this interaction energy difference is overcompensated by the model potential contribution. Accordingly the orbital energies have a more favorable compensation than the total energies (except in the case of F) because the electron interaction occurs twice in the orbital energies.

Finally we discuss the pseudo valence orbital functions. They reproduce the main maximum and tail of the canonical SCF quite well. Some $\langle r^n \rangle$-values for the valence orbitals are shown in Table 8. Generally the pseudo-results are smaller than the SCF results by 0.5–1.5% for $n = 1$, 2–3% for $n = 2$, 4–5% for $n = 3$, and

Table 7. Valence electron interaction energies in F and Cl-ions (in eV)

Ion	Pseudo	SCF	Δ
F^{5+}	30.28	30.40	−0.12
F^{4+}	83.63	84.05	−0.42
F^{3+}	159.37	159.74	−0.37
F^{2+}	251.88	252.07	−0.19
F^{1+}	359.03	358.88	0.15
F^{0}	466.97	466.24	0.73
Cl^{5+}	18.45	18.42	0.03
Cl^{4+}	48.53	48.62	0.09
Cl^{3+}	91.01	90.96	0.05
Cl^{2+}	143.97	143.48	0.49
Cl^{1+}	208.12	206.82	1.30
Cl^{0}	275.74	273.68	2.06

Table 8. Valence orbital $\langle r^n \rangle$-expectation values for F (^2P) and P (^4S)

n			Relativistic	Pseudo			Relativistic	Pseudo
		SCF	SCF	SCF		SCF	SCF	SCF
−2	F 2s:	8.69	8.76	1.86	P 3s:	2.71	2.78	0.42
−1		1.45	1.45	1.22		0.695	0.698	0.600
1		1.001	1.000	0.999		1.933	1.927	1.923
2		1.217	1.214	1.201		4.35	4.32	4.25
3		1.754	1.747	1.718		11.15	11.06	10.73
4		2.957	2.942	2.882		32.4	32.1	30.8
−2	F 2p:	2.395	2.398	2.420	P 3p:	0.716	0.716	0.319
−1		1.272	1.272	1.278		0.570	0.570	0.516
1		1.085	1.085	1.080		2.323	2.321	2.300
2		1.544	1.544	1.531		6.39	6.38	6.21
3		2.771	2.771	2.733		20.36	20.31	19.43
4		6.074	6.077	5.954		74.3	74.0	69.7

5–7% for $n=4$ in the second row, whereas in the first row the differences are only one half to one third of this. For $n<0$ the pseudo-results are without any sense except for $n=-1$, where they are "only" about 20% too low. For valence orbitals which have no precursors in the core as 2p in the first row atoms, the results for $n<0$ are as good as for $n>0$ and a little larger than the SCF values. All these results are quite to be expected. The model potentials are adjusted to experimental energies which are lower than the SCF-values because of the relativistic and correlation effects. Therefore the pseudo-orbitals vanish faster than the SCF-orbitals for large r-values. They should describe the valence electron density better.

4. The Frozen Core Approximation in the Case of *d* and *f* Electrons

Calculations on heavier atoms can give results of similar accuracy except in cases where *d* and *f* electrons play a role. As an example we will discuss the results of our titanium calculations. From chemical intuition one would include the 3*s* and 3*p* electrons into the core. Consequently one has to adjust the effective model potential of the Ti^{4+} core to the Rydberg spectra of Ti^{3+}. However, the corresponding pseudo-energies for different terms of Ti^{2+}, Ti^{+}, and Ti came out higher by 1–3 eV. The reason is that the frozen core approximation is not

Table 9. $\langle r^2 \rangle$ values for 3*s* and 3*p* orbitals in titanium

Ion	Config.	Term	3*s*	3*p*
Ti^{4+}		^1S	1.101	1.236
Ti^{3+}	3*d*	^2D	1.145	1.316
Ti^{1+}	$3d\ 4s^2$	^2D	1.147	1.340
Ti^{2+}	$3d^2$	^3F	1.184	1.391
Ti^0	$3d^2\ 4s^2$	^3F	1.180	1.405
Ti^{1+}	$3d^3$	^4F	1.211	1.453
Ti^0	$3d^4$	^5D	1.230	1.470

Table 10. SCF-results for titanium

Ion	Config.	Term	Valence electrons energy (in eV)		
			Full SCF	$E_{\text{correct.}}$	Pseudo
Ti^{4+}	$3d^0$	^1S	0	0	0
Ti^{3+}	3*d*	^2D	42.41	43.2_5	43.25
	4*s*	^2S	32.36	33.3	33.28
	4*p*	^2P	26.70	27.3_5	27.32
Ti^{2+}	$3d^2$	$a\,^3F$	69.11	70.8	70.82
		$a\,^1D$	67.73	69.4_5	69.46
		$a\,^3P$	67.44	69.1_5	69.17
		$a\,^1G$	66.96	68.6_5	68.70
		$a\,^1S$	63.95	65.6_5	65.68
	$3d\ 4s$	$a\,^3D$	64.35	$66._0$	66.10
		$b\,^1D$	63.84	$65._5$	65.38
Ti^{+}	$3d^3$	$b\,^4F$	81.50	84.0_5	84.10
		$a\,^2G$	80.11	82.6_5	82.74
		$a\,^4P$	80.10	82.6_5	82.74
		$a\,^2P$	79.65	82.2	82.29
		$a\,^2H$	79.65	82.2	82.29
	$3d^2\ 4s$	$a\,^4F$	81.94	$84._3$	84.50
		$a\,^2F$	81.23	$83._6$	83.43
		$a\,^2D$	80.38	$82._7$	82.80
	$3d\ 4s^2$	$c\,^2D$	77.96	$80._5$	80.21
Ti^0	$3d^4$	$a\,^5D$	83.27	86.6_5	86.77
	$3d^2\ 4s^2$	$a\,^3F$	87.47	$90._6$	90.25
		$a\,^1D$	86.17	$89._3$	88.99
		$a\,^1G$	85.45	$88._5$	88.29

applicable in this case. As the 3*d* shell is not well separated from the 3*s* and 3*p* shells, the interaction of 3*d* electrons with the 3*s* and 3*p* ones expands the core significantly (see Table 9). To account for the valence dependence of the core, the V_{core} is chosen to depend on the *d* population, n_d. We obtained an accuracy similar to other atoms like C or Si by using a parameter *A* which is a parabola quadratic in n_d. The results obtained with the potential

$$\begin{aligned} V_{\mathrm{eff}}(\mathrm{Ti}^{4+}) = & -\tfrac{4}{r} - (\underline{11.08} + \underline{0.205} \cdot n_d - \underline{0.015} \cdot n_d^2)/r \cdot \exp(-2r) \\ & + |s\rangle\, \underline{285.5} \cdot \exp(-3.6r) \langle s| + |p\rangle\, \underline{181.9} \cdot \exp(-3.2r) \langle p| \end{aligned}$$

(adjusted parameter values underlined) are given in Table 10. Although the agreement is satisfactory, the situation is not so pleasant. Firstly the number of adjustable parameters is now increased. Furthermore, in order to adjust these additional parameters one has to perform a series of calculations for several many-valence electron terms to match the *corrected* energy values [see Eq. (4)]. Therefore the determination of the model potential is rather expensive. Finally, molecular calculations are complicated by the fact that during the SCF iteration the atomic *d*-populations have to be determined in order to get a selfconsistent value for *A*. An alternative would be to treate the total *M*-shell as a valence shell [12]. But then the gain in saving the computational effort in such pseudopotential calculations is not significant enough to justify the loss in accuracy compared to a full calculation. It seems that the pseudo or model potential method is not so suitable for transition metal elements.

5. Conclusion

If high accuracy is not required, the model potential method using empirically adjusted angular projection potentials seems to be a computationally simple alternative to *ab initio* calculations on atoms and molecules (perhaps excluding systems involving transition metals).

The errors in the total SCF energy will increase from the left to the right side of the periodic system and also for the heavier atoms. Since these errors are nearly equal for ground and excited states of neutral and weakly charged atoms, they will cancel to a large extent in chemical applications. Core-valence correlation and some relativistic effects are already included in these values. Intravalence correlation can be obtained rather accurately by usual valence CI; the error of the total energy is mainly determined from the quality of the SCF result.

The valence electron distribution outside the core can also be obtained quite accurately. Therefore the pseudo-wavefunction can be applied to calculate those expectation values which mainly depend on the outer parts of the wave function as electric and magnetic polarizability or valence excitation transition probabilities.

Relativistic effects in the valence shell, especially spin-orbit interaction, begin to play a role in the third row of the periodic system. Because most terms of the Breit hamiltonian have large contributions from the core region it is not trivial to extend the model potential scheme to heavy atoms. Work on this subject is in progress.

Appendix

The multicenter one-electron model potential integral

$$\mathrm{Int} = \langle \psi_B | l)\; V_l^A (l | \psi_C \rangle$$

with gaussian lobe orbitals at centers B, C and gaussian model potential at center $A \neq B, C$ can be solved in closed form. With $AB = \boldsymbol{R}_B$ and $AC = \boldsymbol{R}_C$ it explicitely reads as

$$\begin{aligned}\mathrm{Int} = \sum_{m',m''} \mathscr{D}^{(l)}_{m'm''}(0, \widehat{BAC}, 0) \cdot \int_0^\infty r_A^2 \cdot dr_A \cdot \{B_l \exp(-\beta_l \cdot r_A^2)\} \\ \cdot \{\textstyle\int\int d\cos\vartheta'_A \cdot d\phi'_A \cdot Y_{lm'}(\vartheta'_A, \phi'_A) \cdot \exp(-\zeta_B(\boldsymbol{r}'_A - \boldsymbol{R}_B)^2)\} \\ \cdot \{\textstyle\int\int d\cos\vartheta''_A \cdot d\phi''_A \cdot Y_{lm''}(\vartheta''_A, \phi''_A) \cdot \exp(-\zeta_c(\boldsymbol{r}''_A - \boldsymbol{R}_c)^2)\}\end{aligned}$$

where ϑ'_A, ϕ'_A refers to the axis AB and ϑ''_A, ϕ''_A to AC and $\boldsymbol{r}'_A$ means $r_A \cdot (\sin\vartheta' \cos\phi'; \sin\vartheta' \sin\phi'; \cos\vartheta')$. Using the formula

$$e^{-\zeta_B(\boldsymbol{r}_A - \boldsymbol{R}_B)^2} = e^{-\zeta_B(r_A^2 + R_B^2)} \cdot \sum_{l'=0}^{\infty} (2l'+1) \cdot P_{l'}(\cos\vartheta_A) \cdot M_{l'}(2\zeta_B R_B \cdot r_A)$$

where P_l is the Legendre polynomial and M_l the modified spherical Bessel function of the first kind, one obtains

$$\begin{aligned}\mathrm{Int} &= B_l \cdot P_l(\cos\widehat{BAC}) \cdot e^{-\zeta_B R_B^2 - \zeta_C R_C^2} \cdot 4\pi(2l+1) \\ &\quad \cdot \int_0^\infty r_A^2\, dr_A \cdot e^{-(\beta_l + \zeta_B + \zeta_C) r_A^2} \cdot M_l(2\zeta_B R_B \cdot r_A) \cdot M_l(2\zeta_C R_C \cdot r_A) \\ &= B_l \cdot P_l(\cos\widehat{BAC}) \cdot [\pi/(\beta_l + \zeta_B + \zeta_C)]^{1,5} \cdot (2l+1) \cdot \exp(-\varDelta) \\ &\quad \cdot M_l[2\zeta_B \zeta_C R_B R_C/(\beta_l + \zeta_B + \zeta_C)]\end{aligned}$$

with

$$\varDelta = [(\beta_l + \zeta_C)\,\zeta_B R_B^2 + (\beta_l + \zeta_B)\,\zeta_C R_C^2)]/[\beta_l + \zeta_B + \zeta_C]\,.$$

Here we have used formula No. 15.31 from Ref. [18].

In order to obtain an accuracy of better than 10^{-13} the following formulae are suitable

$$M_0(Z) \approx 1 + Z^2/3! + Z^4/5! \quad \text{if} \quad Z < 0.025\,,$$

otherwise

$$\exp(-\varDelta)\, M_0(Z) = 1/2Z \cdot [\exp(Z - \varDelta) - \exp(-Z - \varDelta)]$$

$$M_1(Z) \approx Z \cdot (2/3! + 4Z^2/5! + 6Z^4/7! + 8Z^6/9!) \quad \text{if} \quad Z < 0.1\,,$$

otherwise

$$\exp(-\varDelta)\, M_1(Z) = -1/2Z^2 \cdot ((1 - Z) \cdot \exp(Z - \varDelta) - (1 + Z) \cdot \exp(-Z - \varDelta))$$

$$M_2(Z) \approx Z^2 \cdot (2 \cdot 4/5! + 4 \cdot 6Z^2/7! + 6 \cdot 8Z^4/9! + 8 \cdot 10Z^6/11! + 10 \cdot 12Z^8/13!) \quad \text{if} \quad Z < 0.37\,,$$

otherwise

$$\exp(-\varDelta) M_2(Z) = 3/2Z^3 \cdot ((1 - Z + Z^2/3) \cdot \exp(Z - \varDelta) - (1 + Z + Z^2/3) \cdot \exp(-Z - \varDelta))$$

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