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Accuracy and Limitations of the Pseudopotential Method

II. First-Row Molecules

Tse-Chiang Chang*, Peter Habitz and W. H. Eugen Schwarz

Lehrstuhl für Theoretische Chemie der Universität Bonn, Wegeler Str. 12, D-5300 Bonn, Federal Republic of Germany, and Fachbereich Chemie der Gesamthochschule, D-5900 Siegen 21, Federal Republic of Germany

Molecular model potential calculations have been performed within the SCF approximation on nine di- and triatomic molecules from the first row of the periodic table. We compare the molecular constants with *ab initio* SCF values and with model potential results obtained by other authors. Our results are accurate to a few per cent. The three most significant approximations in molecular model potential theory are: 1) The molecular model potential is the sum of atomic model potentials; 2) The atomic model potential is energy-independent; 3) The electron interaction model operator is $1/r_{12}$. We arrive at the following general conclusions concerning these approximations: 1) The first approximation does not hold for strongly ionic molecules and for some highly excited molecular states. 2) Approximations 2 and 3 cancel to a large extent in molecules as they do in atoms, except in the case where approximation 1 breaks down. 3) Although various model- and pseudo-potentials yield reasonable results for atoms, not all of them are suitable for molecular calculations.

Key words: First row elements, di- and triatomic molecules consisting of ~ – Pseudopotential method

1. Introduction

The pseudo- or model-potential method reduces the all-electron molecular Schrödinger-equation to a valence-electron-only problem. Thus a series of homologous molecules from a column of the periodic table has Hamiltonians with the same structure and number of electrons. Therefore trends in the molecular properties can be simply related to changes of the model potential operators of the atoms in one column. Additionally, compared with all-electron *ab initio* methods, the computational effort is drastically reduced if we only treat the valence electrons *and* if we neglect the complicated structure of the canonical valence orbitals in the atomic core region by introducing *nodeless* pseudo-valence orbitals, which require only a small number of basis functions.

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* Present address: Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, China

In pseudopotential theory the atomic cores are represented by non-local pseudopotential operators. They are often approximated by simple expressions, the so-called effective or model potentials. These model potentials contain parameters which are determined by adjusting some atomic properties to the corresponding quantities obtained from all-electron *ab initio* calculations or obtained from experiment.

Several years ago one of us analyzed this concept [1]. A series of approximations had to be introduced in order to derive a satisfactorily simple molecular model Hamiltonian.

1) Core-Valence Separability. This means the neglect of core-valence correlation (polarization) effects. However, already in the second row of the periodic system, the core-valence pair-correlation energies are of the order of 10^{-1} eV. Their neglect will not only result in deviations of the calculated pseudo-energies but also in reorganizations of the pseudo-wavefunctions of heteronuclear molecules, producing incorrect atomic populations, dipole moments (see e.g. [42]), oscillator strengths etc. Therefore it seems recommendable to *add an empirical core-polarization potential* to the effective potential. *The simplest way of doing this is to adjust the total effective model potential to experimental data*, preferably to experimental energies. These empirical model potentials have also a further advantage in comparison with the conventional *ab initio* (non-relativistic SCF) model potentials, since they *automatically account for the significant relativistic reorganization effects in heavier atoms.*

2) Constancy of the Effective Potentials of the Atomic Cores. The model potential of the molecule is taken simply as the sum of constant effective potentials of the atomic cores, which are assumed to be independent of the energy of the valence electrons or of other surrounding cores. However, the exact pseudopotential operator depends on the *core orbitals* and also on the *core and valence orbital energies* [1]. These *energies* change considerably when we go from the separated atoms to a molecule or when we change the number of valence electrons or the configuration and state of a system. The approximation of frozen core *orbitals* seems better justified in most cases, but large deviations are expected in strongly polar molecules [1], in transition metal atoms [2], and in some excited states.

3) Neglect of Additional Projection Operators. The exact pseudo-Hamiltonian and also the exact pseudo-Fock operator contain additional core-projection operators $\mathscr{P}_c$ to be multiplied with the one- and two-electron operators in the case of several valence electrons. However, only by neglecting them can the method be made considerably faster than a full calculation. Of special importance is that the *electron interaction operator* in the pseudopotential formalism *is approximated by the usual* $1/r_{12}$ instead of the correct core-projected operator $\mathscr{P}_c(1/r_{12})\ \mathscr{P}_c$.

One now hopes that the errors introduced by these approximations will, to a large extent, cancel in most cases. Of course different parametrizations of the model potentials will lead to a different extent of cancellation. In Ref. [2] we have investigated the case of atoms with different numbers of valence electrons. The following ansatz for the model potential, which describes the interaction of one valence electron with one atomic closed shell core, turned out to be quite successful in this respect:

$$V_{\text{mod}} = -\frac{Z_c}{r} - \frac{A}{r} e^{-\alpha r} + V_{\text{ang}} \tag{1}$$

$$V_{\text{ang}} = \sum_{l=0}^{l_{\max}} V_l(r) \cdot \mathscr{P}_l \tag{2}$$

$$V_l \quad = C_l \cdot \exp\left(-\gamma_l \cdot r^2\right). \tag{3}$$

The first term in Eq. (1) represents the long-range Coulomb attraction of the core with ionic charge Z_c. The second term approximates the additional attraction caused by a) the incomplete shielding of the total nuclear charge by the core electrons, b) the exchange interaction of the valence electron with the core shells, and c) the polarization of the core by the valence electron (core-valence correlation). We emphasize our finding, that in order to obtain pseudopotential results of good quality, it is very important to have an attractive potential of medium range in addition to the long-range ionic Coulomb potential. The last term in Eq. (1) is the so-called angular projection potential V_{ang}. This short-range repulsive potential prevents the variational collapse of the valence electrons. $\mathscr{P}_l$ projects onto the subspace of angular momentum l with respect to the atomic core, and $l_{\max}$ is the highest angular momentum in the atomic core. We adjust the parameters A, α, C_l, γ_l to a few low-lying experimental energies[1] of one valence electron in the field of the atomic core. The parameter values for first-row atoms are given in Table 1.

Our molecular model Hamiltonian is then given by

$$H_{\text{mod}} = -\frac{1}{2}\sum_{e} \Delta_e + \sum_{c,e} V^c_{\text{mod}}(r_{ce}) + \frac{1}{2}\sum_{e,e'}{}' \frac{1}{r_{ee'}} + \frac{1}{2}\sum_{c,c'}{}' V_{cc'}. \tag{4}$$

Here c denotes the different atomic cores and e the valence electrons. $V_{cc'}$ is the interaction potential of the two cores, the main contribution being the Coulomb repulsion $Z_c \cdot Z_{c'}/r_{cc'}$. The other contributions are rather small and are discussed in Ref. [3].

Table 1. Model potential parameters for first-row atoms (in atomic units)

	He	Li	Be	B	C	N	O	F	Ne
A	2	2	2	2	2	2	2	2	2
α	1.3	2.34	3.361	4.363	5.361	6.354	7.340	8.313	9.28
C_0	5.7	9.128	16.219	26.669	40.338	57.205	77.259	100.487	126.88
γ_0	0.7	1.5	2.8	4.6	6.9	9.7	13.0	16.8	21.1

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[1] Several authors [7, 35, 36] have emphasized that it is insufficient to use only one energy level to determine the model potential, and have recommended the adjustment of the pseudo-orbital in addition to an SCF valence orbital in one manner or another. It seems that adjusting the model potentials to a series of energies is of comparable quality.

Two questions may now be raised:

1) Will the errors in approximations 2 and 3 cancel each other to the same extent in molecules as they do in atoms?

And, more specifically:

2) Are the constant atomic model potentials additive in all types of molecules?

In order to investigate these problems, we have performed model potential SCF-calculations on a series of two and three atomic molecules with different numbers of valence electrons at different internuclear distances. In the next section we present our results. In Sect. 3 we will compare our results with those of other authors. We have, therefore, calculated molecules, which have already been treated before by other workers, in a more or less successful manner. In this paper we will restrict ourselves to first-row molecules. In spite of the fact that the model potential method will only slightly reduce the computational effort in this case, a careful test of the method should start with such molecules. Firstly, for small molecules, the most reliable all-electron *ab initio* results are available for comparison. Secondly, additional difficulties are predicted [1, 2] for molecules with the thick and soft cores of heavy atoms. Therefore, if the method fails for some light molecules, it will not be sensible to handle the corresponding heavier ones.

2. Model Potential MO-SCF Calculations

In order to test the model theory, one should ensure that the possible deficiencies are mainly due to the theory itself, and not due to the numerical approximations of the computational technique. One can then be sure that the good results possibly obtained are not due to the fortuitous cancellation of methodical and computational errors. Therefore we have used basis sets of better than double-zeta quality. Gaussian lobe sets have been chosen. The corresponding model potential integrals are given in Ref. [2].

Since basis functions optimized in all-electron calculations are not the optimal ones for model potential calculations, we have in most cases used even-tempered basis sets with exponential factor 1/3, the exponents covering the same range as in the basis sets of Veillard [33]. Usually they were grouped into five contractions of *s* type and four contractions of *p* type, with coefficients obtained from atomic calculations according to Dunning's rules [34]. To account for polarization one or two *s–p* sets were placed at each bond center or at 1/3 and 2/3 of the bond. All-electron calculations have also been performed for comparison. The latter calculations show that with these basis sets we reach the Hartree–Fock limit within at least a few tenths of an eV and often considerably better.

In Tables 2 to 9 and Figs. 1 to 3 we present our results for nine different di- and triatomic molecules. When we compare all-electron *ab initio* SCF energies with the corresponding model potential values, we should remember that our model potentials have been adjusted to *experimental* energies and therefore account for core-valence correlation. Consequently the model orbital energies should be lower than the full SCF values by about 0.1 to 0.15 eV [2]. The model dissociation energies should also

Table 2. Molecular properties of H_2O

	Exp. Value [4]	Near HF [5]	This Work		Other model calculations					
			Full SCF	Model SCF	Switalski + Schwartz [7][b]	Simons [8]	Durand + Barthelat [35]	Linnett[c] *et al.* [9]	Barthelat[c] + Durand [39]	McWilliams + Huzinaga [40]
R_e [Å]	0.957	0.941	0.941	0.942		0.968			0.876	0.956
α [deg.]	104.5	106	109	107	~105	105	101	180	88	111
D_e [eV]	10.1	6.95	6.65	6.63				$\sim 10^2$		
Inversion barrier [eV]			1.33	1.43						
k_R [mdyn/Å]	8.4	9.8	9.6	8.6		10.3				
k_θ	0.76	0.87	0.85	0.80	~0	0.48	1.33			
$k_{R\theta}$	0.23	0.25	0.21	0.14						
$\epsilon\ 1b_1(\pi)$ [eV]	(12.6)[a]	−13.8	−13.68	−13.74	−13.56	−14.48	−11.21			−13.58
$\epsilon\ 3a'_1(n)$	(14.7)[a]	−15.8	−15.49	−15.60	−15.65	−16.33	−12.90			−15.12
$\epsilon\ 1b_2(\sigma)$	(18.5)[a]	−19.5	−19.59	−19.46	−19.42	−19.62	−17.33			−19.08
$\epsilon\ 2a_1(O2s)$	(32.2)[a]	−36.7	−36.88	−37.26	−36.42	−35.40	−34.83			−36.62
μ [Debye]	1.85	2.05	2.19	2.23						
O: $\epsilon\ 2p(^3P)$ [eV]		−17.19	−17.18	−17.23						−16.92
$\epsilon\ 2s(^3P)$		−33.86	−33.85	−34.33						−33.50
$\Delta E(^1D - {}^3P)$	1.95	2.18	2.18	2.19						
$\Delta E(^1S - {}^3P)$	4.18	5.40	5.40	5.42						

[a] Adiabatic ionization potential.

[b] The two-electron scaling parameters of the O atom are adjusted to the full SCF orbital energies of this molecule!

[c] Floating spherical Gaussian basis.

emerge slightly larger in absolute value: since the valence electron density near the cores is higher in the molecule than in the atoms, the core-valence correlation energy will be larger in the molecule. However, even after taking account of the core-valence correlation, our atomic 2*s* orbital energies tend to be too low (see Tables 2, 3, 5). This error in the atomic calculations will, of course, be carried over to the molecular calculations.

Table 3. Molecular constants of N_2

	Exp. Value [6, 10]	Near HF [11]	This Work		Other Model Calculations	
			Full SCF	Model SCF	Switalski + Schwartz [7]^a	McWilliams + Huzinaga [40]
R_e [Å]	1.09	1.06	1.06	1.07	1.29	1.09
D_e [eV]	9.90	5.34	5.20	5.02		5.60
ω [eV]	0.29	0.34	0.34	0.32		0.31
$2\sigma_g$ ϵ [eV]	-	−17.28	−17.15	−17.25	−16.23	−17.06
I.P.	15.5	15.99	15.86	15.89		
$1\pi_u$ ϵ	-	−16.75	−17.21	−17.26	−16.23	−16.78
I.P.	16.8	15.34	15.81	15.97		
$1\sigma_u$ ϵ	-	−21.17	−20.97	−21.21	−22.38	−20.87
I.P	18.6	19.74	20.01	20.26		
$1\sigma_g$ ϵ (I.P)	(37.3)	−40.10	−41.32	−41.88	−38.61	−41.29
N^4S: ϵ (2*p*)		−15.44	−15.44	−15.57		−15.29
ϵ (2*s*)		−25.72	−25.72	−25.98		−25.53

[a] Two-electron scaling parameters for the N atom adjusted to NH_3!

Table 4. Molecular constants of BeO

	Exp. Value [10]	This Work		Model SCF [12]^a
		Full SCF^c (Near HF)	Model SCF	
R_e [Å]	1.33	1.29	1.27	
D_e [eV]	2.5	1.95	2.05	
ω [eV]	0.184	0.226	0.202	
$\epsilon^b \pi$ [eV]		−10.77	−10.84	−10.33
σ		−12.66	−12.71	−12.10
σ		−31.55	−32.24	−30.58
μ^b [Debye]		7.35	7.30	

[a] Only the Be $1s^2$ core is approximated by a model potential!

[b] At experimental bond length.

[c] Nearly identical with the results of McLean and Yoshimine [41].

Table 5. Molecular constants of LiF

	Exp. Value [30]	This Work Full SCF[c] (Near HF)	 Model SCF	Model SCF [12][a]
R_e [Å]	1.56	1.55	1.40	
D_e [eV]	5.96	4.07	4.32	
ω [eV]	0.120	0.142	0.112	
$\epsilon^b \pi$ [eV]		−12.94	−12.85	−12.69
σ		−13.63	−13.54	−12.79
σ		−37.50	−38.36	−37.09
μ^b [Debye]	6.28	6.31	6.21	
F: $\epsilon(2p)$ [eV]		−19.86	−19.81	
$\epsilon(2s)$		−42.79	−43.60	

[a] only the Li $1s^2$ core is approximated by a model potential!
[b] At experimental bond length.
[c] Nearly identical with the results of McLean and Yoshimine [41].

Table 6. Molecular constants for LiH

	Exp. Value from Ref. [13]	This Work Full SCF[b] (Near HF)	 Model SCF	Model SCF [12]
R_e [Å]	1.60	1.60	1.57	
D_e [eV]	2.52	1.48	1.55	
ω [eV]	0.174	0.178	0.175	
ϵ [eV]	(7.7)[a]	8.21_0	8.22_5	8.15
μ [Debye]	5.88	6.00	6.02	

[a] Ionization potential.
[b] Nearly identical with the results of McLean and Yoshimine [41].

Table 7. SCF calculations on BeH_2 for R(BeH) = 1.345 Å

Energies in eV	This Work Full SCF[a] (Near HF)	 Model SCF	 Model SCF Integ. Approx.	Model Potential [12]
D_e	−5.17	−5.58	−5.47	
ϵ (σ_u)	−11.92	−12.22	−12.22	−12.63
ϵ (σ_g)	−13.56	−13.33	−13.32	−10.67
ϵ (Be2s)	−8.41	−8.45	−8.45	−8.22

[a] Nearly identical with the results of Ahlrichs [38].

Table 8. Molecular constants of LiH^+

	Recommended Value [14]	Model Potential	
		This Work	Ref. [15]
R_e [Å]	2.19	2.17	2.4
D_e [eV]	0.15	0.14	0.09
ω [eV]	0.055	0.058	0.044
ϵ [eV]	-	13.75	13.69

Table 9. Molecular constants of Li_2^+

	Recommended Value [16]	Model Potential	
		This Work	Ref. [15]
R_e [Å]	3.16	3.10	3.14
D_e [eV]	1.29	1.28	1.23
ω [eV]	0.032	0.033	0.033
ϵ [eV]	-	6.67	6.62

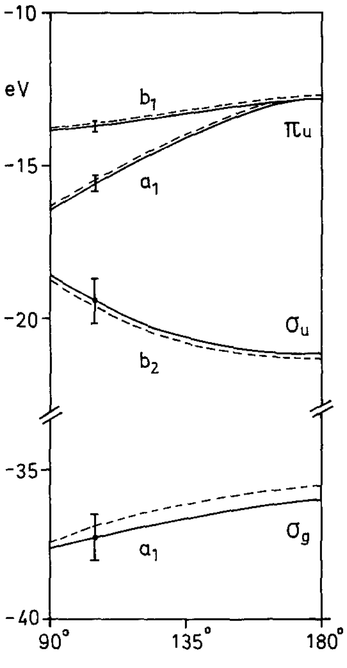

Fig. 1. Orbital energies ϵ of H_2O as a function of the bond angle for $R(OH) = 0.94$ Å. —— Model SCF, ----- full SCF. The vertical bars indicate the variation of ϵ with a 0.1 Å change of bond length

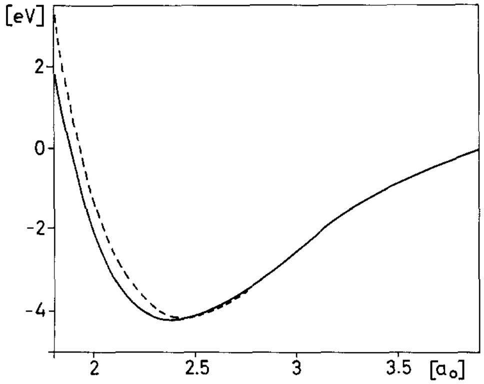

Fig. 2. Potential energy curve of BeO. — Model SCF, ----- full SCF

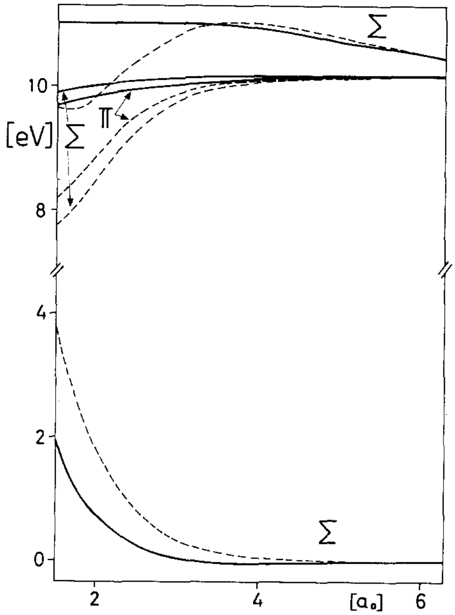

Fig. 3. Potential energy curves of HeH. — Model potential approximation, ----- full CI result [17]

Bearing these facts in mind one may find that *the model potential results show a remarkably good accuracy in general but with some typical deviations* which will be discussed below. Usually the model energies are reliable to within 0.1 to 0.2 eV, the geometric data to within a few 0.01 Å, the force constants to within 10% and the dipole moments to within 0.1 D. In some cases, the accuracy of the results lies within the accuracy of the numerical limits.

2.1 Compounds of the Non-Metals

Most molecular model potential calculations deal with covalent molecules and with hydrides. Two examples of strongly bonded molecules with many valence electrons are H_2O and N_2. Since the atoms B to F possess very small and hard cores, which remain nearly unperturbed by the valence electrons, the frozen core approximation and the assumption of the constancy of atomic model potentials in these molecules is expected to be highly accurate [1].

However, one type of deviation is found in the H_2O model calculations. The error in the energy of the lowest valence MO, $\epsilon(2a_1)$, varies slightly with bond angle and decreases for bent geometry (see Fig. 1). However, the other model orbital energies are parallel to the SCF curves. Also the model result for the "inversion barrier", $E_{\min}$ (180°) $- E_{\min}$ (105°), is too large by 0.1 eV (see Table 2). This can be explained in the following way: In linear geometry the $2a_1$ MO has no O2*p* contribution whereas in bent geometry it has. The atomic 2*s* model orbital energy is too low, but the 2*p* result is correct. Therefore the error of $E(2a_1)$ is expected to decrease upon bending. In other words, the reason is that the correct two-electron operator in pseudopotential theory is of the type $V_{\mathrm{ang}}(1/r_{12})V_{\mathrm{ang}}$, which differs from the simple $1/r_{12}$ and results in angular dependent deviations.

2.2 Compounds of the Electropositive Metals

The electropositive atoms Li and Be have large and soft cores. Their uppermost core orbital energies are rather high and are comparable with the lowest valence orbital energies of electronegative atoms. E.g. in LiF the Li 1*s* core orbital is mixed with a 2% F2*s*-valence orbital at the molecular equilibrium distance. At shorter distances the mixing rises sharply. Correspondingly the correct molecular valence orbital also contains varying contributions from the core AO's which exceed the contribution caused by the orthogonality constraint. It has been pointed out in Ref. [1] that this *mixing of core and valence AO's may lead to considerable deviations of the model results* from the correct values (e.g. ground-state energies might turn out too low), especially for small internuclear distances.

In Tables 4 and 5 and in Fig. 2 we present results on two strongly polar molecules (BeO, LiF) and in Tables 6 to 9 results on the less-polar hydrides (BeH_2, LiH, LiH^+) and on a non-polar molecule (Li_2^+). Large deviations occur in the two polar molecules, especially in LiF. The model potential curves are too low at small internuclear distances. As a consequence, the equilibrium distance R_e emerges too short, the minimum of the potential curve, $-D_e$, is too low, and the vibrational frequency is too small. At the equilibrium distance the *orbital energy* of the lowest valence MO is too low. This deviation is larger than in the case of the 2*s* AO's in the free O or F atoms. For shorter bond lengths the error of the MO energy increases. However, this error is considerably less pronounced than the error of the *total* (binding) *energy*. The sum of the orbital energies differs from the total energy in the two-electron part. It is then evident that the errors introduced by approximations 2 and 3, which refer to the one- and two-electron part of the Hamiltonian, respectively, do not cancel each other to a sufficient extent in these strongly polar metal compounds.

Since the H1*s* orbital energy does not lie as low as the energy of the O2*s* or F2*s* orbitals, the above-mentioned deviations are much smaller in the hydrides.

2.3 *HeH*

Finally we present results for the HeH molecule, which possesses the extremely soft He$1s^2$ core. In Fig. 3 the four lowest model potential curves are compared with reasonable *ab initio* CI results [17]. The ground-state curve deviates as expected: the energy becomes considerably lower for internuclear distances smaller than $4a_0$. The next higher potential curves show an even more dramatic failure of the model potential approximation. This may easily be explained by the softness of the He core: in an all-electron calculation [17] the sudden drop of the upper curves is related to configuration mixing of He$1s^2$-H$2sp$ with He$1s2sp$-H$1s$. In other words, the positive nuclear charge of the hydrogen atom, especially in its excited state, is only weakly shielded and can strongly polarize the He$1s^2$ shell. Therefore at smaller internuclear distances and especially at *higher energies* the frozen core approximation and the core-valence separability breaks down, because the exact wavefunctions contain significant contributions from core-excited configurations. The molecular pseudopotential operator is no longer the sum of the pseudopotentials of the free atoms. Whereas the ground-state energy will usually be lowered by these approximations, the reverse may hold for excited states (see Fig.3).

3. Discussion

In recent years a considerable number of model potential calculations have been performed more or less successfully[2]. The most systematic investigations have been done, among others, by Switalski and Maurice Schwartz [7], by Dixon and Hugo [18], and by McWilliams and Huzinaga [40], and, more recently, by Durand and coworkers [35, 45] and by Kahn *et al.* [36] during the course of our own work. These model potential calculations differ in several respects, concerning limited basis sets, approximations of the model potential integrals, and the type and parametrization of the model potential used. Therefore the question may be raised whether the quality of the model potential results obtained is determined a) by the numerical approximations applied, b) by the chosen parametrization of the model potential, or c) by defects inherent in any type of model potential.

3.1 *Model Potential Integral Approximations*

In Tables 4–7 are listed the model potential orbital energies of Maurice Schwartz (M.S.) [12]. His results deviate quite considerably from the full SCF values. There are three differences between M.S.'s and our calculations: M.S. used a smaller basis set, a different ansatz and parametrization of the model potential, and finally he did not compute the one-electron model potential integrals exactly but used the approximation scheme of W. H. E. Schwarz [1, 19]. In order to test whether the deviations in M.S.'s results are caused by this integral approximation, we performed calculations on BeH_2

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[2] It should be noted that workers in this field often state that their pseudopotential results are not particularly inferior to full *ab initio* calculations and that agreement is very good, even in the case where qualitative trends are only roughly reproduced [7, 8, 12, 28, 43].

(Table 7), in which case M.S. obtained the wrong order of the orbital energies. We found that although the approximated one-electron integrals differ by up to several per cent from the exact ones, the SCF results are only insignificantly influenced. Therefore the deviation seems to be mainly caused by the different ansatz and parametrization of the model potential (see below). That the integral approximation of Ref. [1] works quite well is also demonstrated by the corresponding calculations of M.S. [15] on LiH^+ and Li_2^+ (see Tables 8 and 9).

Contrary to this, the integral approximation of Linnett *et al.* [9], by which the angular dependence of the model potential is simply averaged out, seems much too crude (see Table 2). That their unreasonable results are not caused by the Floating Gaussian basis, as suspected by the authors, may be seen from the recent FSG calculations with proper integral handling by Barthelat [39] (see Table 2). The different behavior of the model potentials for different angular momenta has to be treated explicitly, especially if finer details, e.g. correlation effects [26], are to be accurately reproduced (see also Ref. [27]). Therefore we are not sure that an l-independent model potential, as used by several authors, will always give reasonable results.

3.2 *Parametrization of the Model Potentials*

Kahn *et al.* [36] and Durand *et al.* [37] have argued that it is essential to fit the model potentials to properties of the neutral atoms and not to those of highly charged one-valence electron ions (as we do), and furthermore to fit not only the energies but also the wavefunctions.[3] However, the quality of the corresponding model potential results of Kahn [36] on HF and F_2 and of Durand [35] on F_2, HF and H_2O (see Table 2) is comparable to our model potential results on H_2O and N_2.

On the other hand, the *ab initio* model potentials of Schwartz *et al.* [7, 12], which were adjusted to SCF energies and wavefunctions, gave unsatisfactory results (see Tables 2-7). In order to correct for the deficiency of those model potentials, they introduced a scaling procedure of the two-electron integrals, following a suggestion of Simons [20]. Two extra parameters are introduced for each first-row atom, which are adjusted so that the orbital energies of the corresponding hydride *molecules* are approximately reproduced. These parameters are then used in the calculation of other molecules. The orbital energies for a series of molecules were then at least qualitatively correct (correct order), however, the deviations are still up to ±3 eV (see e.g. Table 3). In the case of H_2O and N_2, they also reported properties of the potential curves, which again were not very accurate (see Tables 2 and 3). Simons [20], who proposed the scaling of $1/r_{12}$, has also calculated the water molecule, using yet another ansatz for the model potential. His results [8] (see Table 2) also do not show good agreement with the full SCF values. This demonstrates that different forms of the model potential,

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[3] Of course, in this case the determination of the model potentials has to be performed on the *ab initio* SCF level which is more laborious than our scheme. Furthermore the core-valence correlation and the relativistic reorganization of the inner shells cannot easily be handled in this way.

even though they reproduce several atomic properties satisfactorily, may behave quite differently in molecular calculations. A very drastic effect of this kind has also recently been observed by M.S. (private communication, [44]). M.S. changed *pairs* of his *ab initio* model potential parameters to some degree by using a different kind of adjustment to the SCF orbitals in such a manner that the atomic valence energy levels did not change. Nevertheless, his molecular results could be considerably improved in this way.

So far we have discussed calculations using the V_{ang} type of model potential. Another type is the "core orbital projection potential"

$$V_{\mathrm{orb}} = \sum_{c}^{\mathrm{occ.}} |c\rangle a_c \langle c| \tag{5}$$

where c denotes some approximation to the occupied core orbitals, and a_c adjustable parameters. Although V_{orb} is formally more similar to the exact pseudopotential operator [21], this model potential leads to theoretical difficulties [2] and sometimes to problems in numerical calculations [2, 22]. However, it seems that, in practice, these difficulties can be handled by a "balanced" choice of the basis [18, 23, 24]. Indeed, in recent calculations of this type, on first- and second-row molecules, Huzinaga *et al.* [25, 40] obtained very promising results (see Tables 2 and 3).

Summarizing, the quality of molecular model potential results strongly depends on "suitable" parametrization of the atomic model potential. One can only judge the superiority of a special type of "semiempirical" or "*ab initio*" model potential by its capability of reproducing a large amount of atomic *and* molecular data. This situation introduces some amount of empiricism into any kind of model potential method.

3.3 Defects of Any Model Potential Method

One of the main problems with the model potential approach is that both the one- and the two-electron parts of the Hamiltonian can only be determined approximately. Consequently, specific deviations will occur in orbital energies and total energies (concerning correlation energies and singlet-triplet splittings, see Refs. [45, 46]). These deviations can be minimized by a "suitable" parametrization of the model potential. *Nonpolar and weakly polar compounds can then be calculated with quite high accuracy.* This also seems to hold for heavier species. Small errors in the molecular results are caused by corresponding errors in the model description of the atoms. E.g. angular dependent properties may behave slightly incorrect if the hybridization changes with bond angle.

Some time ago, based on a thorough theoretical investigation [1], the largest deviations had been predicted in *polar molecules* with atoms from the left side and lower part of the periodic system. The upper core orbitals of these atoms have rather high orbital energies. They may be polarized in the molecular environment and can mix with valence AO's from a strongly electronegative atom (core shell binding). The trend we have found in this work, using a special type of model potential, confirms this general prediction. The ground-state potential curves of such species emerge too low at small internuclear distances. The error is expected to increase for *heavier atoms.* These errors and similar ones in *transition metal compounds*[4] [2, 29, 36, 43] may also be overcome, however, by explicitly treating the electrons from those atomic shells which are usually termed the highest core shells, as the $1s$ shell in Li or the $3sp$ shell in third-row transition metal atoms. Of course this is a conceptual drawback, since the number of "valence electrons" is now significantly increased.

4. Summary

In conclusion, the model potential approach will give excellent results, at least for the *lower states* (where core excitations do not yet play a role), of molecules consisting of atoms from the right and upper parts of the periodic system, that is mainly of the non-metallic elements and hydrogen. Furthermore, the model potential method is also expected to give correct results for polar molecules containing atoms from the lower and right part of the periodic table (electropositive and transition metals) if we also explicitly treat the electrons of the "highest core shell". For molecules with heavier atoms the model potential method is the only simple device to take the strong influence of the relativistic core contraction on the valence shells into account. The "empirical" version of the model potential method can also simulate the influence of core-valence correlation. Therefore, from the practical point of view, the model potential approach is still very promising.

Appendix

Corrections to Part I of this series (Ref. [2])

In Table 4 of Part I, the $2s$ $\epsilon_{\text{correct}}$ (and Δ) values for N $2s^2p^3$ and O $2s^2p^4$ should read 25.86 (–0.14) and 34.02 (–0.30) instead of 26.06 (+0.08) and 34.37 (+0.05). The headline of Table 5 should read $3s$ and $3p$ instead of $2s$ and $2p$. $3s$ $\epsilon_{\text{correct}}$ for Cl^{6+} $3s$ should read 114.4 instead of 113.4; the corresponding Δ-value is, however, correct.

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[4] A typical failure of this kind has been found by Osman *et al.* [43] in the case of Ni(CO)_4, although the opposite is stated in the text (mainly based on a misprint of the *ab initio* values in their own table). The two most important molecular orbitals for chemical bonding in the complex are the $8a_1$ and $8t_2$ types. The $8t_2$ is half an eV above the $8a_1$, and the CO π orbitals are lying between them. Treating the Ni $3sp$ electrons as inert core electrons, Osman *et al.* find the $8a_1$ and $8t_2$ levels just reversed. Another failure is discussed by Demuynck: Chem. Phys. Letters **45**, 74 (1977).

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