Theoret. Chim. Acta (Berl.) 37, 129—145 (1975)

Investigation of the Muffin-Tin Approximations for Potential and Charge Density in the MS-X_α Method by Means of Calculations of H_2O*

Ulla Mitzdorf

Lehrstuhl für Theoretische Chemie der Technischen Universität München, 8 München 2, Germany

Received August 19, 1974/October 25, 1974

By detailed analysis of results for H_2O it is shown that both approximations, the muffin-tin approximation of the potential as well as the muffin-tin approximation of the charge density, severely influence the results. Their effects are of the same order of magnitude. Good results for molecular total energies are achieved by roughly compensating the effects from the two approximations, not by minimizing them. The total energy changes drastically when radius or position of the outer sphere are varied. Equilibrium distances strongly depend on the choice of the atomic sphere radii and always are calculated too large, not due to the charge density approximation, but due to the potential approximation. In order to lay hold of angular properties, the sphere radii have to be chosen in a completely different way than for total energies.

Key words: MS-X_α method – Muffin-tin approximations – H_2O

1. Introduction

The multiple-scattering-X_α-SCF method (also called SCF-X_α-SW) has been developed during the last ten years by Slater and Johnson [1, 2]. Two basic ideas constitute this new method for calculating molecular properties: The exchange integrals are approximated by the statistical local exchange X_α [3], and the one-electron equations are solved by using the multiple-scattering formalism (MS) [4], which originally was developed in solid state physics by Korringa, Kohn and Rostoker [5].

The X_α approximation has thoroughly been investigated already in solid state calculations [6]. For molecular calculations it has been developed further by selecting the inherent parameter α from total energy criteria [7]. Test calculations have shown that this approximation does not alter the results for molecular properties significantly [8]. Especially in atomic calculations it has been shown that the resulting orbital wavefunctions are of the same quality as double-zeta functions [9].

The MS formalism represents the central point of this method. It is the reason why computing times for larger molecules don't rise as drastic as in conventional HF-methods. However its applicability presumes a local potential (achieved by using X_α), which has to be muffin-tin shaped.

---

* Extract from the dissertation of U. M., submitted to the Technische Universität München.

For ease of computation the total energy also is calculated within the muffin-tin frame; this is done by using a muffin-tin charge density in the respective formulas for the electron-nuclear-, Coulomb- and exchange-energy (E_{en}, E_c, E_x) instead of the density which results directly from the one-electron orbitals [10]. The method in its actual stage of development, in conjunction with the transition state concept [11] has proven to be successful in calculating spectroscopic data, ionization- and excitation energies, for a variety of molecules [12]. Also total energy calculations, leading to conformation- and binding-energies have yet been performed with this method: The molecules H_2, Li_2, C_2 [13], N_2 [13, 14], O_2, F_2 [14], Ne_2 [15], H_2O [10], CH_4 [16] and NH_3 [13] have been investigated with respect to equilibrium bond distances and binding energies; the rotation barriers in C_2H_6 [17], in NH_3 and H_2O_2 [18] have been calculated.

The aim of these calculations was, to reproduce the experimental data as well as possible. Hence for heteronuclear molecules the ratios of the atomic sphere radii have been varied to achieve total energies as low as possible (H_2O, CH_4), or to obtain the proper barrier height of rotation (NH_3, H_2O_2).

The aim of this paper now is not to reproduce the energies of chemical interest of the water molecule as close as possible, but to investigate the influence of the two muffin-tin approximations (MTAs). It was felt that the consequences of the MTAs have not yet received as much attention as the X_α approximation, although their effects on the results are much more suspicious. By means of detailed analyses of various calculations of the same molecule with differently chosen muffin-tin spacings the effects of the MTAs are therefore analyzed in this paper.

The H_2O molecule has been chosen for these tests for several reasons: It consists of two different kinds of atoms, H, the lightest one, and O, an atom with a $2sp$ electron shell. So the characteristic properties of the two MTAs can simultaneously be tested for H and a first row atom. As H_2O is nonlinear, it is appropriate for testing the influence on bond lengths and bond angles as well. It is a closed shell system, and problems concerning spin can be excluded. Finally there exist good *ab initio* HF-calculations for comparison of detailed results.

2. Theoretical Background and Theoretical Consequences of the Muffin-Tin Approximations

Applying the variational principle to the equation for the total energy (Rydberg energy units are used throughout this paper):

$$\begin{aligned} E_{\text{tot}} &= \sum_i \int u_i^*(1)\left(-\nabla_1^2 - \sum_\alpha \frac{2Z_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}_1|}\right) u_i(1)d\boldsymbol{r}_1 + \int\int \frac{\varrho(1)\varrho(2)}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\ &\quad + \frac{3}{4}\int \varrho(1)V_{X_\alpha}(1)d\boldsymbol{r}_1 + \sum_{\alpha<\beta} \frac{2Z_\alpha Z_\beta}{R_{\alpha\beta}} \\ &= T + E_{en} + E_c + E_x + E_{nn}, \end{aligned} \tag{1}$$

where the orbital wavefunctions u_i have been replaced already by the charge density

$$\varrho(1) = \sum_i u_i^*(1)u_i(1) \tag{2}$$

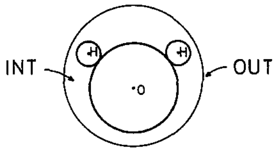

Fig. 1. Muffin-tin space partitioning for the H_2O-molecule

wherever possible, one gets to the one-electron equations

$$(-\nabla_1^2 + V(1))u_i(1) = \varepsilon_i u_i(1). \tag{3}$$

The potential herein, written explicitly, is:

$$V(1) = -\sum_\alpha \frac{2Z_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}_1|} + 2\int \frac{\varrho(2)}{r_{12}} d\boldsymbol{r}_2 - 6\alpha\left[\frac{3}{8\pi}\varrho(1)\right]^{1/3} \tag{4}$$

Multiplying Eq. (3) by $u_i^*(1)$, integrating and summing over all occupied levels i leads to the following relation:

$$\Sigma\varepsilon_i = T + E_{en} + 2E_c + \tfrac{4}{3}E_x, \tag{5}$$

or

$$T = \Sigma\varepsilon_i - E_{en} - 2E_c - \tfrac{4}{3}E_x, \tag{6}$$

and with Eq. (1) the total energy becomes

$$E_{\text{tot}} = \Sigma\varepsilon_i - E_c - \tfrac{1}{3}E_x + E_{nn}. \tag{7}$$

Comparing Eq. (5) with the respective equation of the conventional HF-formalism, one finds the correspondence:

$$\Sigma\varepsilon_{i,\text{HF}} \triangleq \Sigma\varepsilon_{i,X_\alpha} + \tfrac{2}{3}E_x, \tag{8}$$

which originates from the rigorous application of the variation principle to the two different exchange potentials. This equation will be used later to compare HF-data with results from MS-X_α calculations.

The MTA is a space averaging procedure. The space of the molecule is partitioned into three different kinds of regions (Fig. 1): a) the atomic regions inside the atomic spheres, which are centered on the atomic sites, b) the region outside an outer sphere (OUT), which encloses all atomic spheres and c) the intersphere region (INT), which is the whole area between the atomic spheres inside OUT. The spheres may touch but not overlap in order that the MS-formalism is straight forwardly applicable.

Introducing the MTA of a function ($V(r)$ or $\varrho(r)$) now means that inside the atomic spheres and outside OUT this function is spherically averaged, and in INT it is volume averaged, i.e. in the whole intersphere region the space depending original function is replaced by one constant value (V_{INT} or ϱ_{INT}).

The MTA of the potential $V(1)$ is required to solve Eq. (3), in order that the MS-formalism can be applied; i.e. the wavefunctions $u_i(1)$ and the orbital energies ε_i are calculated via the MS-formalism for the muffin-tin potential $V_{\text{muff}}(1)$.

From these $u_i(1)$ the total charge density $\varrho(1)$ may be obtained according to Eq. (2).

Now the MTA is introduced a second time: Instead of calculating the total energy with $\varrho(1)$ (threedimensional integrals would have to be solved numerically), the muffin-tin function $\varrho_{\mathrm{muff}}(1)$ is used. This drastically simplifies the evaluation of E_{en}, E_c and E_x (the integrals become onedimensional or even less complicated [10]). The total and kinetic energy are then evaluated via Eqs. (7) and (6) in the MS-X_α programme.

Schematically this procedure may be symbolized the following way (to emphasize the MTAs, edged brackets are used):

$$\begin{tikzcd}
\langle V(\rho_{\mathrm{muff}})\rangle_{\mathrm{muff}} \arrow[rr, "\mathrm{MS}"] & & u_i\ ,\ \varepsilon_i \arrow[dll] \arrow[d, "(6)"] \\
\langle \rho \rangle_{\mathrm{muff}} \arrow[u, dashed] \arrow[r, "/10/"] & E_{en}, E_c, E_x \arrow[r, "(6)"] & T
\end{tikzcd}$$

Fig. 2. Scheme of the MS-X_α programme, indicating the influence of the two muffin-tin approximations on the various results

In the scheme also the SCF procedure of the MS-X_α method is indicated by the connection from $\langle\varrho\rangle_{\mathrm{muff}}$ back to $\langle V\rangle_{\mathrm{muff}}$.

The affection of the ε_i and $u_i(1)$ by $\langle\varrho\rangle_{\mathrm{muff}}$ via the SCF procedure is neglected completely in the following discussions. This simplifying assumption is made in order to get hold of the problem and seems justified by the fact that the dominant influences of the two MTAs can be explained by physical arguments within this framework. It is clear from this scheme then that the wavefunctions $u_i(1)$ and the energies ε_i only depend on the MTA of the potential, whereas all other quantities E_{en}, E_c, E_x and T[1] are additionally influenced by the MTA of the charge density.

The corrections to the MTAs in the terms E_{en}, E_c, E_x and T consist of second order terms: Splitting the functions into muffin-tin and non-muffin-tin parts,

$$V(1) = V_{\mathrm{muff}}(1) + \delta V(1) \tag{9}$$

$$\varrho(1) = \varrho_{\mathrm{muff}}(1) + \delta\varrho(1) \tag{10}$$

one obtains

$$\int \varrho(1)V(1)d\boldsymbol{r}_1 = \int \varrho_{\mathrm{muff}}(1)V_{\mathrm{muff}}(1)d\boldsymbol{r}_1 + \int \delta\varrho(1)\delta V(1)d\boldsymbol{r}_1\,, \tag{11}$$

because the mixed terms vanish upon integration.

---

[1] The statement that T is calculated within the same approximation as E_{en}, E_c and E_x is in contradiction to an assertion made in [10], and will therefore be explained in more detail: The argument in [10] was that T can be written in the form

$$T = \sum_i \varepsilon_i - \int \varrho(1)V(1)d\boldsymbol{r}_1\,, \tag{6a}$$

and the use of the muffin-tin potential $V_{\mathrm{muff}}(1)$ implies that the integral stays the same, if $\varrho(1)$ is replaced by $\varrho_{\mathrm{muff}}(1)$. It is, however, not compelling to use the same potential in Eq. (6a) as in (3). In contrast: like the other energy terms E_{en}, E_c and E_x, the potential in (6a) is calculated from the *new* charge density. Taking into account only the muffin-tin part of the integral in (6a) therefore is a consequence of the second MTA. This statement becomes obvious, if the integral is written in terms of the energies, as is done in Eq. (6).

In the next chapter the effects of using $V_{\mathrm{muff}}(1)$ instead of $V(1)$ on the wavefunctions and energies ε_i is investigated in detail. The influence of $V_{\mathrm{muff}}(1)$ and $\varrho_{\mathrm{muff}}(1)$ on the other results is analyzed and, whenever possible, an attempt to separate the effects of the two approximations is made.

Two consequences of the MTAs, however, can be stated already now:

1. An important assumption for the validity of the virial theorem is violated by introducing the MTA of the charge density before calculating E_{tot}, i.e. by not using Eq. (1), but the simplified form [10], which only takes into account ϱ_{muff}.

In general the virial theorem is fulfilled, if the expression for the total energy and the one-electron equation are related by the variation principle [19]. This relation is still accomplished when the local exchange potential X_α is introduced [20]. Liberman and Batra asset that the virial theorem even is still valid, when V_{muff} is used [21]. It is, however, violated by calculating E_{tot} from $\varrho_{\mathrm{muff}}(1)$ instead of $\varrho(1)$. This muffin-tin step disjuncts the wavefunctions inherent in Eq. (1) from the ones calculated in Eq. (3)[2]. Therefore the virial theorem is no more applicable to E_{tot}- and T-results of MS-X_α calcualtions.

In the following chapter it will be shown that the virial coefficient $-T/E_{\mathrm{tot}}$ may, however, serve as a rough measure of the approximation effects from V_{muff} and ϱ_{muff}.

2. As indicated in Fig. 2, the SCF-iterations are not directly linked the conventional way in the MS-X_α method. The starting potential for the next iteration is calculated via [10]

$$u_i(1) \rightarrow \varrho_{\mathrm{muff}}(1) \rightarrow V_{\mathrm{muff}}(\varrho_{\mathrm{muff}}).$$

Although not performed explicitly, two muffin-tin steps are hidden behind this procedure:

$$u_i(1) \rightarrow \varrho(1) \Rightarrow \langle \varrho \rangle_{\mathrm{muff}} \rightarrow V(\varrho_{\mathrm{muff}}) \Rightarrow \langle V(\varrho_{\mathrm{muff}}) \rangle_{\mathrm{muff}}.$$

These intermediate muffin-tin steps imply that the iteration procedure does not necessarily lead to a truly self-consistent field. The observation of total energies, lower than the final "convergent" one, during the iterative processes of MS-X_α calculations indicate that[3].

3. Analysis of Results from Calculations of the Water Molecule

In all calculations the atomic exchange parameters α_{VT} from Schwarz [7] ($\alpha_{\mathrm{O}} = 0.74367$, $\alpha_{\mathrm{H}} = 0.97804$) and in INT and outside OUT their average $(\alpha_{\mathrm{O}} + \alpha_{\mathrm{H}})/2 = 0.86086$ have been used[4]. The SCF-convergence criterion $\left|\frac{V - V'}{V}\right| < 10^{-4}$ was

---

[2] The results of chapter 3.4 confirm this fact; namely, the rise of total energy upon enlargement of the partial wave basis contradicts the variation principle.

[3] To the author's opinion, these muffin-tin intersteps may have another consequence concerning convergence. It is possible that not only one, but several $V_{\mathrm{muff}}(1)$-functions may be related to one or more sets of wavefunctions $\{u_i\}$ via this special definition of self-consistency. If so, the programme may in the SCF-part jump from one suitable combination of $V_{\mathrm{muff}}(1)$ and $\{u_i\}$ to another, instead of iterating one special combination to convergence. This eventuality would explain some experiences made with convergence instabilities for intricate molecules.

[4] The similarity of α_{VT} and α_{HF} [7] justifies the equivalence of statistical and HF-energies, which is used later for comparison.

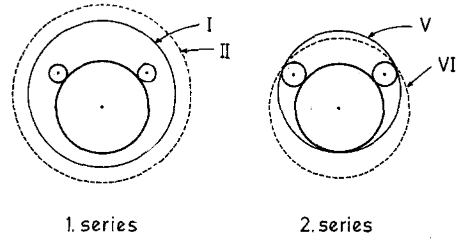

Fig. 3. Distinction between the two kinds of muffin-tin spacing, discussed in chapter 3.1

selected, and all calculations were performed with the "relaxed core" option. If not stated differently, the partial waves up to $l_O = 1$, $l_H = 0$ and $l_{OUT} = 1$ were used, and the experimental bond angle (104.5°) was taken.

3.1 *Influence of the Intersphere Region*

The most unrealistic assumption, when confining potential and charge to a muffin-tin shape, is made in the intersphere region. There both functions have steep gradients; the potential smoothly rises from its deep core-values towards zero, and the charge density, accumulated around the nuclei, descends rapidly in this area. Replacing the potential function by a constant average in the INT-region means that it is raised in the environment of the atomic spheres – thereby producing a high discontinuity step at the boarders of the atomic spheres – and is lowered further outside. For the charge density this averaging procedure is equivalent to pushing charge, located in the proximity of the atomic spheres, towards the outer sphere.

In order to investigate the consequences of these crude changes, two series of calculations were performed, where position and size of OUT have been varied; all other parameters were kept constant.

The properties within the first series are: $R_{OH} = 1.86$ a.u., $R_O/R_H = 4.83$, and OUT is placed equidistant from all three atomic spheres with $R_{OUT}(\mathrm{I}) = 2.5$ a.u., $R_{OUT}(\mathrm{II}) = 3.0$ a.u., $R_{OUT}(\mathrm{III}) = 8.0$ a.u. and $R_{OUT}(\mathrm{IV}) = 50.0$ a.u.

The properties, common within the second series: $R_{OH} = 1.84$ a.u., $R_O/R_H = 3.4$; here OUT always touches the hydrogen-spheres, therefore enlargement of R_{OUT} here mainly enlarges the intersphere region on the "lone pair side" of the oxygen atom (OXY). The sphere radius is chosen as small as possible, $R_{OUT}(\mathrm{V}) = 1.98$ a.u., so that OUT is situated concentric around OXY, $R_{OUT}(\mathrm{VI}) = 2.26$ a.u., and finally $R_{OUT}(\mathrm{VII}) = 4.14$ a.u. was selected (see Fig. 3).

Table 1 shows the detailed energy results, V_{INT} and the electron charge inside the OXY-sphere (Q_{OXY}) for the two calculations with smallest outer sphere, and their changes upon enlargement of OUT.

In all cases the total energy rises. This result was expected, as the muffin-tin charge distribution departs more and more from the correct distribution as INT is enlarged. Surprising, however, is the large amount of change: E_{tot} rises constantly with $\partial E_{tot}/\partial R_{OUT} \approx 0.6$ Ry/a.u. until $R_{OUT} \approx 6.0$ a.u. and then asymptotically approaches -148.6 Ry. This value is much higher than the free atom limit of -151.5 Ry [22].

Table 1. Results for the cases I and V and changes of these values upon enlargement of R_{OUT} (energies in Ry). The last row shows the virial coefficients

	1. Series				2. Series		
	I	→II	→III	→IV	V	→VI	→VII
R_{OUT} [a.u.]	2.5	3.0	8.0	50.0	1.98	2.26	4.14
E_{en}	−396.208	+0.23	−1.44	−2.49	−397.509	+0.92	−1.24
E_c	92.688	−0.63	−1.38	−1.38	93.356	−0.42	−1.09
E_x	− 18.265	+0.01	−0.30	−0.53	− 18.377	+0.09	−0.31
$\Sigma\varepsilon_i$	− 83.088	−0.20	+0.85	+1.56	− 83.077	+0.13	+1.66
E_{tot}	−151.825	+0.42	+2.33	+3.14	−152.230	+0.50	+2.87
T	152.019	+0.80	+5.45	+7.60	152.223	−0.06	+5.51
V_{INT}	− 1.240	+0.22	+0.87	+1.18	− 1.568	+0.27	+1.17
Q_{OXY}	7.28	+0.09	+0.76	+1.07	6.87	−0.04	+0.66
$-T/E_{tot}$	1.001	1.01	1.05	1.07	0.9995	1.003	1.056

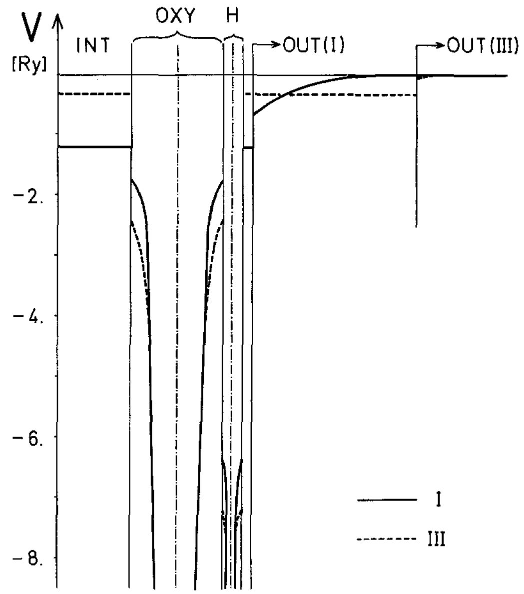

Fig. 4. Muffin-tin potential along one OH-line through the nuclei for case I ($R_{OUT} = 2.5$ a.u.) and case III ($R_{OUT} = 8.0$ a.u.)

Two typical muffin-tin potentials are shown in Fig. 4. The difference between case I and case III clearly points out that the potential deviates more and more from the exact function, as the intersphere is enlarged: The potential-steps become higher, V_{INT} rises and the atomic "craters" sink still deeper.

The electron charge inside the OXY-sphere is enlarged as the potential becomes less realistic. This effect purely originates from the change of the potential, because the MTA of the charge density does not alter the value of Q_{OXY}. This indicates an important effect: The wavefunctions u_i, calculated from a muffin-tin

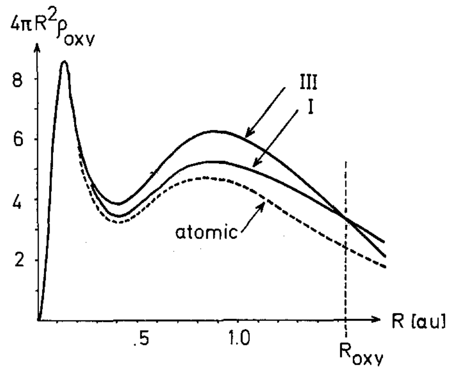

Fig. 5. Muffin-tin charge density inside the OXY-sphere for cases I and III and for the free atom

potential, are – in the average – comprimed inside the atomic spheres, i.e. in the areas of the deep potential "craters", because the adjacent V_{INT} is unfavourably high.

Fig. 5. demonstrates this effect. Even for the smallest possible outer sphere the OXY-charge is much higher than the atomic distribution, as calculated by the Herman-Skillman programme [23]. The additional charge in OXY mainly accumulates in the area of the 2*sp*-shell, not near the nucleus.

From this observation one can conclude for the deviations of molecular MS-X_α orbital energies from experimental values: Orbitals, which to a large extent are located in the INT-region, mainly π-orbitals, will be contracted towards the nuclei, i.e. towards the regions of deeper potential; their eigenvalues therefore become too low. To the σ-orbitals, which to a large extent are located inside the atomic spheres, the additional charge as well as the high V_{INT} around the spheres are of disadvantage, and their energies are calculated too high.

This general tendency can clearly be seen, for example, in the comparison of ionization energies from MS-X_α calculations with experimental data for a variety of molecules by Connolly *et al.* [24].

The preceding investigations showed how important it is to put an outer sphere tightly around the molecule in order to keep the intersphere region as small as possible. From the strong dependence of E_{tot} on R_{OUT} it follows that the energies of different molecular configurations have to be evaluated with care, as physically interesting phenomena may be hidden behind this severe approximation effect.

3.2 Variation of the Atomic Sphere Radii

Now we are going to analyze two series of calculations, which differ in the position of OUT. Within the first group the outer sphere always touches all three atomic spheres, i.e. the intersphere region is made as small as possible. Within the second group OUT is placed concentric around OXY and touches the H-spheres. For this second group Connolly and Sabin have calculated the dependence of E_{tot} on the ratio R_O/R_H and have found the minimum at $R_O/R_H = 4.83$ [10].

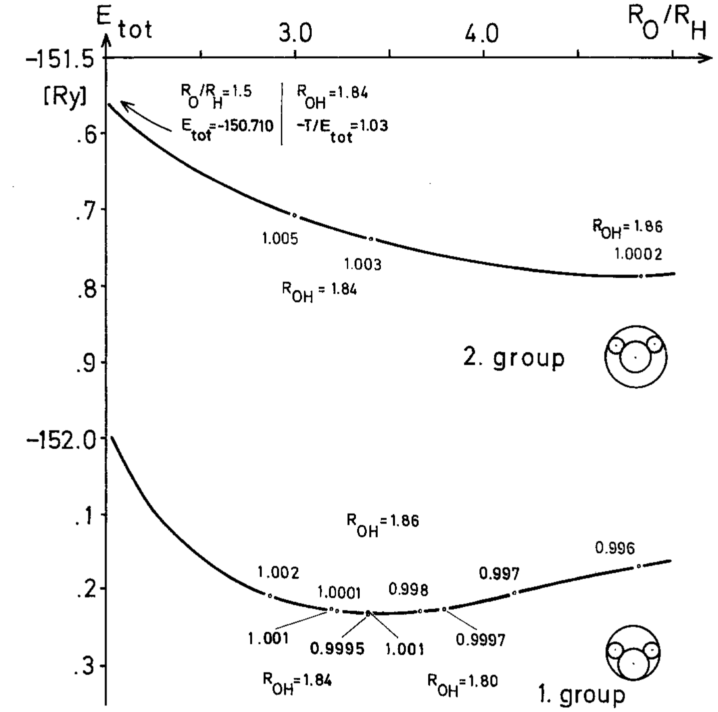

Fig. 6. Dependence of E_{tot} on the atomic sphere radii, the bond distances R_{OH} are given in the diagram, the pure numbers indicate the virial coefficients $-T/E_{tot}$

For the first group this minimum lies at $R_O/R_H = 3.4$. Fig. 6 shows the dependence of the total energy on R_O/R_H for the two groups. Other kinds of criteria for selecting R_O/R_H might be thought of: The ratio of Slater's atomic radii [25] gives $R_O/R_H = 2.4$. The atomic Herman-Skillman potentials [23] have the same values on the sphere boundaries (at experimental distance), when R_O/R_H is 1.5. The ratio of the electronic populations inside the atomic spheres Q_{OXY}/Q_H accords with the respective value of Mulliken's population analysis from HF-calculations, when R_O/R_H is about 1.27.

These various criteria yield divergent results because of the differing properties of the constituent atoms. The divergent minima of the total energy curves (Fig. 6), however, are mainly due to a secondary effect: Enlargement of R_O/R_H is accompanied by a decrease of R_{OUT}. For the second kind of muffin-tin spacing R_{OUT} thereby decreases about twice as fast as for the first one. Bearing in mind the results of the previous chapter, we conclude that this moves the minimum further towards large values of R_O/R_H. If this secondary effect is subtracted, one arrives at a minimum value near the ratio of Slater's atomic radii for *both* groups.

The various energies change continuously (Table 2) and manifest themselves in a steady increase of the virial coefficient (Fig. 6). The energy minimum for CH_4, found by Danese [16] at a R_C/R_H slightly *smaller* than the ratio of Slater's covalent radii, is consistent with the previous findings: The covalent radius of C is larger than that of O, i.e. the charge of the $2sp$ shell is spread further there. Reducing

Table 2. Energy changes upon reduction of R_O/R_H (in Ry)

	1. Group			2. Group	
$\Delta R_O/R_H$	-0.2	-0.4	-0.8	-0.4	-1.9
ΔE_{en}	-0.088	-0.156	-0.338	$+0.069$	$+1.686$
ΔE_c	-0.033	-0.045	-0.142	-0.250	-3.429
ΔE_x	-0.024	-0.040	-0.096	-0.025	-0.187
$\Delta \Sigma \varepsilon_i$	-0.036	-0.059	-0.152	-0.222	-2.460
ΔE_{tot}	$+0.004$	-0.002	$+0.018$	$+0.031$	$+1.028$

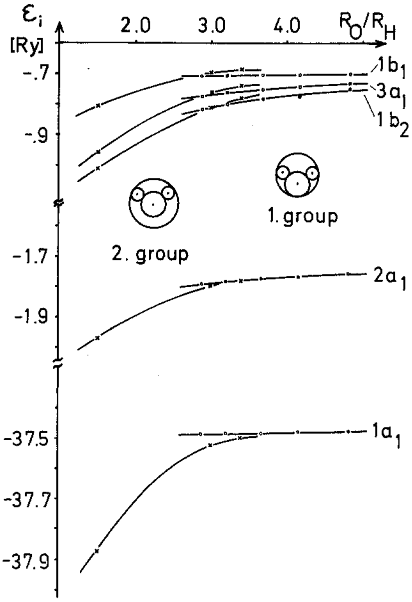

Fig. 7. Dependence of the one-electron energies on the atomic sphere radii for the first group (circles) and the second group (crosses)

the C-sphere radius therefore does not have as severe effects. The unrealistic representation of the electronic hydrogen charge (only about 0.05 e are contained in an H-sphere of 0.5 a.u. radius), on the other hand, has fourfold effects in CH_4 and tends to enlarge the hydrogen sphere radii.

The one-electron energies for CH_4 [16] and CO_2 [24] have been found to be insensitive to the choice of the atomic sphere radii. This also is true for H_2O; Fig. 7 shows the dependence of the ε_i on R_O/R_H. In the domain, where this dependence is shown for both groups simultaneously, the eigenvalues of the second group clearly show a stronger dependence than those of the first one.

3.3 Equilibrium Bond Lengths and Bond Angles

The calculations shown in Fig. 6 are based on different choices of the bond distances; although R_{OH} varies from 1.80 a.u. to 1.84 a.u., all values fit well onto the two curves. A more detailed investigation of the total energy as a function

Table 3. Equilibrium distance $R_{\mathrm{OH,min}}$ in H_2O for different values of R_O/R_H

	R_O/R_H	$R_{\mathrm{OH,min}}$ [a.u.]	$E_{\mathrm{tot}}(R_{\mathrm{OH,min}})$ [Ry]
1. Group	3.4	1.84	-152.2298
	3.2	1.87	-152.2276
2. Group	4.83	1.86	-151.7858[a]
	2.2	$\geqq 2.2$	≈ -151.70
	1.5	>2.6	≈ -151.65

[a] Ref. [10]

Table 4. Comparison of experimental equilibrium distances with results from MS-X_α calculations [a.u.]

	MS-X_α	Exp.	Error	Ref.
H_2O	1.84	1.81	2%	this paper
CH_4	2.11	2.05	2%	[16]
H_2^+	2.2	2.0	10%	[26]
F_2	4.3	2.68	160%	[14]
O_2	4.2	2.28	180%	[14]
N_2	4.1	2.07	200%	[14]

of sphere radii and bond distances now reveals that the equilibrium bond distance depends on the choice of R_O/R_H. In Table 3 a few results are listed. As the two examples of the first group show, this dependence is rather strong.

Even the smallest equilibrium distance is still larger than the experimental value. The experience has been made before with the MS-X_α method; results are summarized in Table 4.

From a first glance one would expect that the large distances originate from the MTA of the charge: The error increases as the covalent bond character increases; and a covalent bond is related to a pile-up of charge inbetween the atomic nuclei. The significant energy term E_{en}, however, does not show up in the formula for E_{tot} (Eq. 7) explicitly, but is contained in the term $\Sigma\varepsilon_i$ (Eq. 5), which is calculated prior to the charge MTA.

The large equilibrium distances as well as their strong dependence on the atomic sphere radii are rather caused by the MTA of the potential: in reality the electronic potential between atoms is lowered due to the superposition of the two atomic electron potentials. This potential valley becomes deeper, the closer the nuclei approach. The MTA lifts the potential between the atoms and lowers it on the opposite sides, nivellating exactly this potential valley. Consequently the calculated wavefunctions already lead to a charge density, which is too low between the nuclei.

The potential change upon muffintinization is the more serve, the deeper the valley has been, i.e. it changes the situation more drastically for small interatomic distances; consequently the resultant equilibrium spacings are too large.

This modification of the real potential is not as servere for molecules, composed of one heavy central atom (with a deep potential crater) and light H-atoms around,

Table 5. One-electron energies ε_i [Ry]

R_O/R_H	3.4		1.5	
∢ HOH	104°	180°	104°	180°
$1a_1$—$1\sigma_g$	−37.498	−37.489	−37.873	−37.799
$2a_1-2\sigma_g$	− 1.776	− 1.772	− 1.968	− 1.941
$1b_2$—$1\sigma_u$	− 0.778	− 0.817	− 1.099	− 1.169
$3a_1$—$1\pi_u$	− 0.737	− 0.682	− 0.957	− 0.790
$1b_1$	− 0.683		− 0.806	
$\Sigma\varepsilon_i$	−82.946	−82.888	−85.406	−84.981

as it is for two adjacent heavy atoms. The different orders of magnitude of the various errors, noted in Table 4, clearly demonstrate this.

Investigation of the HOH-bond angle again confirms that the potential and charge distribution are more realistic, when the outer sphere encloses the molecule as tight as possible. This kind of muffin-tin spacing forces the main part of the intersphere charge into the region between the H-spheres, thereby screening the H-nuclei properly, and makes the bent structure more favourable than the linear one by about 0.3 Ry.

In cases where the outer sphere cannot be placed in this advantageous manner (e.g. when H_2O is contained in a larger compound), the only possibility to achieve enough screening of the H-nuclei, in order to make the bent configuration favourable, is to enlarge the hydrogen sphere radii, i.e. to make the ratio R_O/R_H smaller. Comparative calculations for both configurations have therefore been performed with various values of R_O/R_H. In order to simulate the situation, where H_2O is contained in a larger compound, the outer sphere now was placed concentric around OXY, touching the H-spheres.[5]

At $R_O/R_H=3.4$ the linear configuration ($E_{\text{tot}}=-151.86$ Ry) is favoured by 0.12 Ry. When R_O/R_H is reduced, this difference becomes smaller. From $R_O/R_H=1.5$ on the bent configuration is favoured. The total energy, however, rises drastically ($E_{\text{tot}}(R_O/R_H=1.5)=-150.71$ Ry).

The changes of the energy terms of Eq. (7), when going from the linear to the bent configuration, are given for two values of R_O/R_H (in Ry):

$$\begin{array}{rcccc} E_{\text{tot}}= & \Sigma\varepsilon_i & -E_c & -\tfrac{1}{3}E_x & +E_{nn} \\ R_O/R_H=3.4:+0.12= & -0.06 & +0.03 & +0.00 & +0.15 \\ R_O/R_H=1.5:-0.02= & -0.42 & +0.24 & +0.01 & +0.15 \end{array}$$

The bent configuration becomes more favourable, because it leads to a lower sum of one-electron energies. Table 5 shows their respective values for the C_{2v} molecular orbitals of the bent molecule and the $D_{\infty h}$ orbitals of the linear molecule.

Except for $2a_1\leftrightarrow 2\sigma_g$ they behave, as Walsh qualitatively predicts for AH_2 molecules on the general grounds of MO-theory [27]. When the muffin-tin potential is changed by reducing R_O/R_H, the C_{2v} orbital energies are lowered faster than the $D_{\infty h}$ energies, and the difference of $\Sigma\varepsilon_i$ becomes larger.

---

[5] Removing OUT completely would lead to an extremely strange situation, as then ϱ_{INT} and V_{INT} would tend to zero.

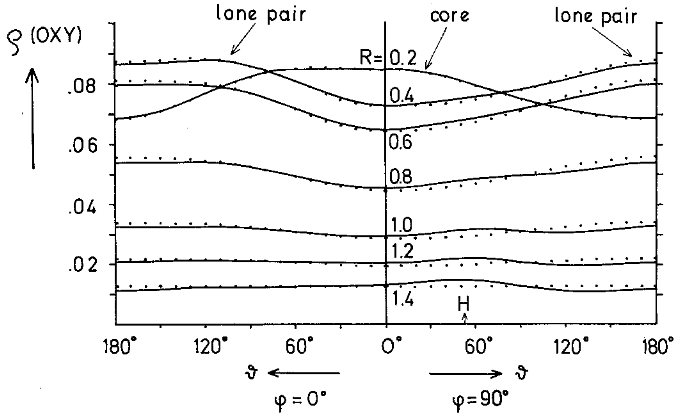

Fig. 8. Charge density inside the OXY-sphere, calculated with the small basis ··· and with the large basis —. The numbers on the $\vartheta = 0$ axis give the distance from the oxygen nucleus; ϑ is the polar angle of the OXY-sphere and φ its azimutal angle; $\varphi = 90°$ represents the HOH-plane

The preceding results are in analogy with calculations of the barriers of rotation in NH_3 and H_2O_2 [18]. There the radii of the atomic spheres had all to be taken equal, in order to reproduce the angular properties.

The disadvantage of these findings is that the angular properties have to be investigated separately with the MS-X_α method; the proper sphere radii for these calculations differ drastically from the optimal radii for calculating total energies, bond energies and equilibrium distances.

3.4 Inclusion of higher Terms in the Partial Wave Expansion

For the most suitable muffin-tin spacing, found in the previous investigations ($R_O/R_H = 3.4$, OUT minimal, $R_{OH} = 1.84$ a.u.), calculations have been performed with a basis, extended to $l_{OXY} = 2$, $l_H = 1$ and $l_{OUT} = 2$. The added functions have a severe effect on the charge distribution, resulting in smoother transitions at the sphere boarders (i.e. the continuity conditions are better fulfilled; still, however, the charge densities ϱ_{OXY}, ϱ_H and ϱ_{OUT} differ by 10 to 20% at the points, where the respective spheres touch one another). The lone pair charge accumulations inside the OXY-sphere are not markedly altered, but the charge accumulations on the O–H bond lines only show up, when the higher l-functions are added (Fig. 8).

All one-electron energies go down – as expected – by some hundredths of a Rydberg, changing $\Sigma\varepsilon_i$ by -0.252 Ry. But simultaneously E_c is lowered by 0.349 Ry. Therefore the total energy *rises* upon enlargement of the basis ($+0.083$ Ry). This unconventional change confirms the statement of Chapter 2 that this method is not properly based on the variation principle.

In order to see the influence of higher l-functions on angular properties, the two water calculations with OUT concentric around OXY and $R_O/R_H = 1.5$ were repeated with the larger basis: Now the linear configuration becomes more favourable again, even at this small sphere ratio; i.e. a larger basis does not improve the situation.

Table 6. Comparison of HF- and MS-X_α-results (Ry)

	HF[a]	MS-X_α	HF → MS-X_α	HF[b]	MS-X_α	HF → MS-X_α
R_{OH} [a.u.]	1.81	1.81		1.80	1.80	
R_O/R_H	—	3.4		—	3.4	
E_{tot}	−152.1040	−152.2280	−0.12	−152.1187	−152.2274	−0.11
T	152.1037	152.3788	+0.27	152.0188	152.4308	+0.41
V	−304.2079	−304.6068	−0.40	−304.1376	−304.6581	−0.52
$E_c + E_x$	75.5554	75.1837	−0.37	75.6957	75.2522	−0.44
E_{en}	−398.1530	−398.1702	−0.02	−398.3102	−398.3905	−0.08
$\Sigma\varepsilon_i(+\frac{2}{3}E_x)$[c]	− 94.9392	− 95.4218	−0.48	− 94.8732	− 95.4530	−0.58

[a] Ref. [28] [b] Ref. [29] [c] This comparison is based on Eq. (8).

3.5 Comparison of the Energy Terms with ab initio HF-*Results*

By this comparison, finally, some quantitive statements can be made about the deviations of the absolute values of the various energy terms, caused by the MTAs.

The two *ab initio* calculations referred to were performed by Diercksen [28] at $R_{OH} = 1.81$ a.u. with a Gauss basis (11 7 1/6 1), contracted to [3 4 1/5 1], and by Neumann and Moskowitz [29] at $R_{OH} = 1.80$ a.u. with an uncontracted Gauss basis (10 6 2/4 2). Both calculations are very accurate, as a comparison of the total energies with the HF-limit (−152.126 Ry [30]) demonstrates.

In Table 6 these results are compared with corresponding MS-X_α calculations, which are optimal concerning the choice of the outer sphere (R_{OUT} minimal) and the atomic sphere radii.

The total energies from the MS-X_α calculations look very contenting; and the difference to the free atom limit (−151.5210 Ry [22]) of 0.707 Ry agrees well with the experimental bond energy (0.699 Ry). Inspection of the detailed energy results, however, reveals that these good values are not obtained, because the approximations have negligible influence on the data, but that their effects just compensate in E_{tot}.

The largest difference to the *ab initio* values appears in the one-electron energies and is caused by the MTA of the potential (Fig. 2). For less proper muffin-tin spacings the resulting $\Sigma\varepsilon_i$ might be higher than the HF-value (enlargement of OUT, Chapter 3.1) or even more negative (diminuation of R_O/R_H, Chapter 3.2).

The deviation of $E_c + E_x$ is of the same order of magnitude. Here the comprimation of charge inside the OXY-sphere due to the potential approximation (raising E_c somewhat), is of minor importance, whereas the MTA of the charge influences this quantity strongly by reducing its size: Simple electrostatic considerations show that the Coulomb interaction of a system of negative charge, contained in a definite volume, strongly diminishes, when this charge, accumulated at some certain places, becomes equally distributed over the whole volume. In molecules the electronic charge distribution does not only have steep gradients in the direction away from the nuclei, but there also appear other charge accumulations (lone pairs, covalent bonds, π-orbitals). These fluctuations, however,

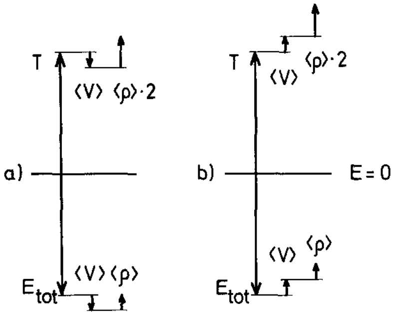

Fig. 9a and b. Schematic demonstration of the influence of the two muffin-tin approximations on total and kinetic energy

are nivellated by the averaging procedure of the charge MTA before E_c is calculated. Therefore the resultant Coulomb energies always are too low.

The electron-nuclear interaction E_{en} deviates least from the HF-value, although it represents the largest quantity. It is influenced by both MTAs, but neither strongly, nor in the same direction: The contraction of charge in the $2sp$ shell inside OXY – due to the muffin-tin potential – lowers E_{en} slightly. The charge MTA has no effect inside the atomic spheres; it raises E_{en} mainly due to the transfer of intersphere charge towards OUT.

The virial coefficient $-T/E_{\text{tot}}$ reflects the influence of the MTAs on the results. A large virial coefficient indicates strong influence (Tab. 1). This becomes obvious through Eqs. (6) and (7) and is illustrated in Fig. 9 under two different assumptions: a) supposing that the potential approximation $\langle V\rangle$ lowers $\Sigma\varepsilon_i$ and b) supposing that it raises $\Sigma\varepsilon_i$. The dominant effect of the charge approximation $\langle\varrho\rangle$ was found to be a lowering of E_c. The variation of E_{en} is neglected here, because it only appears in T, and its size is small, its direction may not uniquely be determined.

Thus in the MS-X_α method the virial coefficient may be helpful for a rough estimate of the errors due to the MTAs.

4. Concluding Remarks

In general the following conclusions can be drawn:

1. The use of a muffin-tin potential in Eq. (3) leads to wavefunctions which are squeezed into the atomic spheres. This makes E_{en} and the contributions to E_c inside the atomic spheres somewhat too large.

2. The one-electron energies ε_i are not strongly affected, as they are overall properties of the whole molecule, and therefore reflect some averaging ability over the different regions, where the potential is assumed too high and too low, respectively. As a rule of thumb it can be stated that the eigenvalues of σ-orbitals are calculated too high, those of π-orbitals too low.

3. The use of a muffin-tin charge density (to compute E_c, E_{en} and E_x) most severely changes E_c. The resulting Coloumb interaction is much too small, as all the gradients in the intersphere region as well as all spherical pile-up of charge

inside the atomic spheres are not taken into account. The electron-nuclear interaction also decreases, mainly due to the volume averaging in INT. This error, however, does not influence E_{tot}, as E_{en} does not contribute explicitly in Eq. (7).

Concerning the properties of chemical interest, it can be stated:

4. As the total energy strongly depends on the muffin-tin spacing, especially on the radius of the outer sphere, the results for conformation and binding energies are unreliable. Potential curves in polyatomic molecules rise too steep and approach values far above the sum of the energies of the two fragments. Only the potential curve for *simultaneous* enlargement of all bonds leads to reasonable results.

5. The equilibrium distances are calculated too large, by some percent for A–H bonds, by about a factor of two for covalent bonds between heavier atoms.

6. In order to reproduce angular properties, the muffin-tin spacings have to be chosen in a completely different way; i.e. separate calculations are necessary for such investigations.

The present study shows that the MS-X_α method does not fulfil the requirements of an *ab initio* method for calculating conformation and binding energies. The arbitrariness in choosing the muffin-tin parameters and their great influence on the results confine it to semiempiricism.

Further development of the method by correcting the muffin-tin charge alone does not seem to make sense, as it only removes one of the two equally important approximations. Complete departure from both muffin-tin assumptions, on the other hand, would lead beyond the multiple-scattering formalism – the central point of the method, which brings about all its advantages.

As the MS-X_α method is the first one, which promises applicability to biological macromolecules and other large compounds due to its advantageous computer time requirements, it seems worthwhile to further investigate its potentialities. When its limitations are clearly known and the optimal sets of muffin-tin parameters for various compounds are found, it may serve as a powerful new semiempirical method for spectroscopic data as well as conformation- and binding-energies.

Acknowledgement. I wish to thank Professor G. L. Hofacker for discussions and for the opportunity of working in his institute. I also thank Dr. N. Rösch, Professor V. H. Smith, Jr., and Professor J. Ladik, for discussions of the subject, and Professor K. H. Johnson for the permission to use the MS-X_α programme. The calculations have been performed on the TR 440 of the Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaften München.

The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

1. Slater, J. C.: Advan. Quantum Chem. **6**, 1 (1972)
2. Johnson, K. H.: Advan. Quantum Chem. 7, 143 (1973)
3. Slater, J. C.: Phys. Rev. **81**, 385 (1951); Gaspar, R.: Acta Phys. Hung. **3**, 263 (1954); Kohn, W., Sham, L.: Phys. Rev. **140**, A1133 (1965)
4. Johnson, K. H.: J. Chem. Phys. **45**, 3085 (1966); Johnson, K. H.: Intern. J. Quantum Chem. **1S**, 361 (1967)
5. Korringa, J.: Physica **13**, 392 (1947); Kohn, W., Rostoker, N.: Phys. Rev. **94**, 1111 (1954)
6. Slater, J. C.: Quantum theory of molecules and solids, IV. New York: McGraw-Hill 1974

7. Lindgren, I.: Arkiv Fysik **31**, 59 (1966); Slater, J.C., Wood, J.H.: Intern. J. Quantum Chem. **4**S, 3 (1971); McNaughton, D.J., Smith, V.H., Jr.: Intern. J. Quantum Chem. **3**S, 775 (1970); Berrendo, M., Goscinski, O.: Phys. Rev. **184**, 10 (1969); Kmetko, E.A.: Phys. Rev. A**1**, 37 (1970); Schwarz, K.: Phys. Rev. B**5**, 2466 (1972)
8. Baerends, E.J., Ros, P.: Chem. Phys. **2**, 52 (1973)
9. Schwarz, K., Connolly, J.W.D.: J. Chem. Phys. **55**, 4710 (1971)
10. Connolly, J.W.D., Sabin, J.R.: J. Chem. Phys. **56**, 5529 (1972)
11. Slater, J.C., Mann, J.B., Wilson, T.H., Wood, J.H.: Phys. Rev. **184**, 672 (1969)
12. Johnson, K.H., Norman, J.G., Connolly, J.W.D.: In: Herman, F., McLean, A.D., Nesbet, R.K. (Eds.): Computational methods for large molecules and localized states in solids, p. 161. New York: Plenum Press 1973
13. Connolly, J.W.D., unpublished results, mentioned in [12]
14. Weinberger, P., Konowalow, D.D.: Intern. J. Quantum Chem. **7**S, 353 (1973)
15. Konowalow, D.D., Weinberger, P., Calais, J.-L., Connolly, J.W.D.: Chem. Phys. Letters **16**, 81 (1972)
16. Danese, J.B.: Intern. J. Quantum Chem. **6**S, 209 (1972)
17. Wahlgren, U., Johnson, K.H.: J. Chem. Phys. **56**, 3715 (1972)
18. Wahlgren, U.: Chem. Phys. Letters **20**, 246 (1973)
19. Hurley, A.C.: In: Löwdin, P.O., Pullman, B. (Eds.): Molecular orbitals in chemistry, physics and biology, p. 161. New York: Academic Press 1964; Löwdin, P.O.: J. Mol. Spectry. **3**, 45 (1959)
20. Slater, J.C.: J. Chem. Phys. **57**, 2389 (1972); Ross, M.: Phys. Rev. **179**, 612 (1969)
21. Liberman, D.A., Batra, I.P.: J. Chem. Phys. **59**, 3723 (1973)
22. Mann, J.B.: Atomic structure calculations, I. Hartree-Fock energy results for the elements hydrogen to lawrencium (Los Alamos Scientific Laboratory Report, LA. 3690, 1967); the main results are given in [9]
23. Herman, F., Skillman, S.: Atomic structure calculations, Englewood Cliffs, N.J.: Prentice Hall 1963
24. Connolly, J.W.D., Siegbahn, H., Gelius, U., Nordling, C.: J. Chem. Phys. **58**, 4265 (1973)
25. Slater, J.C.: J. Chem. Phys. **41**, 3199 (1964)
26. Smith, F.C., Johnson, K.H.: Phys. Rev. Letters **22**, 1168 (1969)
27. Walsh, A.D.: J. Chem. Soc., 2260 (1953)
28. Diercksen, G.H.F., private communication
29. Neumann, D., Moskowitz, J.W.: J. Chem. Phys. **49**, 2056 (1968)
30. Meyer, W.: Intern. J. Quantum Chem. **5**S, 341 (1971)

Dr. U. Mitzdorf
Lehrstuhl für Theoretische Chemie der
Technischen Universität München
D-8000 München 2
Arcisstraße 21
Federal Republic of Germany