A Modification and Extension of the CNDO Method

I. Parameters for the Atoms Hydrogen to Chlorine, Potassium, Calcium, and Gallium to Bromine

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The CNDO method has been reparametrized and extended to include the third row atoms except the transition metals. The parameters have been tested on a large number of molecules. The calculated dipole moments, binding energies (heats of atomization), and ionization potentials are in most cases in good or satisfactory agreement with the experimental values. The orbital energies and configurations of the molecules and some calculated geometries and rotational barriers are reported. Some alternatives in the parametrization are also discussed.

1. INTRODUCTION

The success of CNDO in describing molecules containing first and second row atoms makes it interesting to see if CNDO or some modification of it will also be a simple, reasonably reliable method for the study of molecules including also third row atoms.

There exist now many semi-empirical sigma electron methods. Experience shows that it is very difficult to construct a method which gives good results for all properties. By careful parametrization and possibly introduction of special parameters it has been possible to get remarkably good results for a certain property in special classes of molecules. See for instance the review of all-valence electrons SCF calculations by Klopman and O’Leary. The aim of this work is, however, to make a scheme which gives good or reasonable results for many different properties in molecules containing atoms up to bromine in the periodic system. This broad scope makes it necessary to have a simple method with as few parameters as possible because of the difficulty of finding suitable standard molecules for the parameter fitting.

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The method is a modification and extension of the CNDO/1 and CNDO/2 programmes by Pople et al.\textsuperscript{1-6} The changes are the following ones: In CNDO/2 the average of the ionization potential and the electron affinity of an atomic orbital is used in the estimate of the diagonal one-center core matrix element. The difficulty to get the affinities for the atoms K to Br forced us to use the method in CNDO/1, that is, only use the ionization potential. In both CNDO/1 and CNDO/2 Slater orbital exponents are employed. These are less accurate for the third row atoms than for the first row atoms. Thus we decided to use the optimized atomic exponents from minimal basis calculations by Clementi and Raimondi\textsuperscript{18} for all the elements. This led to some modifications of the formulas as the $s$, $p$, and $d$ functions now get different radial dependence. With these changes it was necessary also to reoptimize the bonding parameter $\beta$ for all the elements from hydrogen to chlorine.

In this paper the parameters for hydrogen to chlorine, excluding neon, potassium, calcium and gallium to bromine are presented. Calculations on a large number of molecules containing these atoms are reported. The method gives quite satisfactory results for binding energies, dipole moments, and ionization potentials. Some geometries and barriers to internal rotation are also reported. The parameters for the elements scandium to zinc will be reported in a later paper.

The calculations have been performed on an IBM 360/75 at Stockholms Datacentral with a computer programme which is a modification made by us in collaboration with fil. kand. Ulf Wahlgren of the programme CNINDO in QCPE 141.

2. METHOD

The approximations in this work follow rather closely those in CNDO. The molecular orbitals are expanded in atomic orbitals on the different atomic centers in the molecule. These atomic orbitals are Slater type orbitals.

$$\psi_i = \sum_{\mu} c_{\mu i} \Phi_{\mu}$$  \hspace{1cm} (1)

The upper index $r$ indicates if the atomic orbital is an $s$, $p$, or $d$ orbital. To simplify the Roothaan equations the zero differential overlap approximation is applied. The Fock matrix elements then reduce in a closed shell case to the following expressions:

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\lambda} P_{\lambda\lambda} \gamma_{\mu\lambda}$$  \hspace{1cm} (2)

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \hspace{1cm} \mu \neq \nu$$  \hspace{1cm} (3)

The density matrix is defined as:

$$P_{\mu\nu} = 2 \sum_i c_{\mu i} c_{\nu i}$$  \hspace{1cm} (4)

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The elements of the core hamiltonian and the coulomb repulsion matrices are, respectively:

$$H_{\mu\nu} = \int \Phi_{\mu}^* \left[ -\frac{1}{2} \Delta - \sum_A V_A \right] \Phi_{\nu} \, dV = (\mu'| - \frac{1}{2} \Delta - \sum_A V_A |\nu')$$ \hspace{1cm} (5)

$$\gamma_{\mu\nu} = \int \Phi_{\mu}^* (1) \Phi_{\nu}^* (1) \frac{1}{r_{12}} \Phi_{\nu} (2) \Phi_{\nu} (2) \, dV = \gamma_{\mu\nu}^{rt}$$ \hspace{1cm} (6)

Here $-V_A$ is the potential energy operator for electron 1 in the field of the nucleus and the inner shell electrons at atomic center A. In CNDO the forms of the matrix elements are determined from their transformation properties. That question is carefully explained in the original CNDO paper \(^1\) and in the book by Pople and Beveridge.\(^6\) In this work the equations are required to be invariant under orthogonal transformations which only mix atomic functions on the same atom and with the same principal and azimuthal quantum numbers.

Thus the coulomb integrals must have the form:

$$\gamma_{\mu\nu}^{rt} = \gamma_{AB}^{rt} \hspace{1cm} \mu \in A, \hspace{0.1cm} \nu \in B$$ \hspace{1cm} (7)

The integral is therefore calculated with s functions but with the correct radial dependence of $\Phi_{\mu}^t$ and $\Phi_{\nu}^t$.

In CNDO, where the integrals are required to be invariant under transformations which include atomic hybridization one gets:

$$\gamma_{\mu\nu}^{rt} = \gamma_{AB} \hspace{1cm} \text{for all } r \text{ and } t$$ \hspace{1cm} (8)

The treatment of the matrix element $H_{\mu\nu}$ of the core hamiltonian operator falls into three separate cases.

2.1. $\mu = \nu$ and $\Phi_{\mu}^t$ is located on atom A

$$H_{\mu\mu} = (\mu'| - \frac{1}{2} \Delta - V_A |\mu') - \sum_{B \neq A} (\mu'| V_B |\mu') =$$

$$= U_{\mu\mu}^t - \sum_{B \neq A} (\mu'| V_B |\mu') = U_A^t - \sum_{B \neq A} (\mu'| V_B |\mu')$$ \hspace{1cm} (9)

The last step follows from the fact that the basis functions with the same principal and azimuthal quantum numbers are degenerate. $U_{\mu\mu}^t$ can be related to the energy of an electron in $\Phi_{\mu}^t$ in the field of the core of atom A. That energy can be estimated from atomic spectral data in the following way. The energy of the valence electrons, in an atom A with the configuration $s^m p^n d^q$ and the wavefunction given by one Slater determinant expressed in orthonormal spinorbitals, is:

$$E = \sum_{\mu} E_{\mu} + \sum_{\mu < \nu} J_{\mu\nu} - \sum_{\mu < \nu} K_{\mu\nu}$$ \hspace{1cm} (10)

In the last sum the spinorbitals $\mu$ and $\nu$ have parallel spins. With our approximations all exchange integrals $\mu$ and $\nu$ have parallel spins. Thus the energy reduces to:

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\[ E(s^m p^n d^t) = \sum_{\mu} E_{\mu} + \sum_{\mu < \nu} J_{\mu \nu} = \sum_{\mu} (\mu | - \frac{1}{2} A - V_A | \mu^t) + \sum_{\mu < \nu} \gamma_{\mu \nu}^{rt} \]
\[ = \sum_{\mu} U_{\lambda}^s + \sum_{\mu < \nu} \gamma_{\lambda \lambda}^{rt} \] (11)

In the second step in eqn. (11) the spin has already been integrated out. Then the same spaceorbital can occur for two \( \mu \) values. The formula for the energy can be written:

\[ E(A; s^m p^n d^t) = m U_A^s + n U_A^p + q U_A^d + \frac{1}{2} m (m - 1) \gamma_{AA}^{ss} + \frac{1}{2} n (n - 1) \gamma_{AA}^{pp} + \]
\[ + \frac{1}{2} q (q - 1) \gamma_{AA}^{dd} + mn \gamma_{AA}^{sp} + nq \gamma_{AA}^{pd} + qmq \gamma_{AA}^{ds} \] (12)

Then an average ionization potential for an orbital can be calculated, e.g.

\[ I_A^s = E(A^+; s^{m-1} p^n d^t) - E(A, s^m p^n d^t) = \]
\[ = - U_A^s - \sum_{r} (n_A^r - \delta_{sr}) \gamma_{AA}^{sr} \]
\[ n_A^r = m, n, \text{and } q \] (13)

The expressions for \( I_A^p \) and \( I_A^d \) follow immediately.

2.2 \( \mu \neq \nu \) and \( \mu \) and \( \nu \) both on atom \( A \).

\[ H_{\mu \nu} = (\mu | - \frac{1}{2} A - V_A | \nu^t) - \sum_{B \neq A} (\mu | V_B | \nu^t) \] (14)

With \( s, p, \) and \( d \) orbitals as basis functions the first integral is zero by symmetry.

2.3. \( \mu \in A, \nu \in B \) and \( A \neq B \)

\[ H_{\mu \nu} = (\mu | - \frac{1}{2} A - V_A - V_B | \nu^t) - \sum_{C \neq A, B} (\mu | V_C | \nu^t) \] (15)

The first integral, which involves differential overlap, is not neglected. It is the so-called resonance or bonding integral \( \beta_{\mu \nu} \), which is responsible for the lowering of the energy due to interaction between the two centers. It is determined semi-empirically. It must have a form which fulfills the invariance requirements. In our case

\[ \beta_{\mu \nu} = \beta_{AB}^{\nu} S_{\mu \nu} \] (16)

would do. \( S_{\mu \nu} \) is the overlap integral which has the right transformation properties. The parameter \( \beta_{AB}^{\nu} \) could contain an explicit distance dependence, but that is already partly included in \( S_{\mu \nu} \). Furthermore we have not used the flexibility, which is implied by the indices \( r \) and \( t \). Instead the normal CNDO approximation has been used.

\[ \beta_{\mu \nu} = \frac{1}{2} S_{\mu \nu} (\beta_A + \beta_B) \] (17)

It remains to handle the core attraction integrals. The neglect of differential overlap and the transformation conditions give:

\[ (\mu_A | V_C | \nu_B^t) = V_{AC}^t \delta_{\mu \nu} \quad A \neq C \] (18)

The Fock matrix can now be written with our formulas and some rearrangement as \( (\Phi_{\mu^t} \in A) \):
\[ F_{\mu\nu} = -I_A^r - \sum_I n_A^r \gamma_{AA}^{rr} + (1 - \frac{1}{2}P_{\mu\nu})\gamma_{AA}^{rr} + \sum_{\lambda \in A} P_{\lambda\lambda} \gamma_{AA}^{rr} + \]
\[ + \sum_{\lambda \in A} P_{\lambda\lambda} \gamma_{AB}^{rr} - \sum_{B \neq A} \left( \sum_I n_B^r \gamma_{AB}^{rr} \right) + \sum_{B \neq A} \left( \sum_I n_B^r \gamma_{AB}^{rr} - V_{AB}^r \right) \]  
\[ (19) \]
\[ F_{\mu\nu} = \frac{1}{2}S_{\mu\nu}(\beta_A + \beta_B) - \frac{1}{2}P_{\mu\nu} \gamma_{AB}^{rr} \quad \mu \neq \nu, \: \mu \in A \text{ and } \nu \in B \]  
\[ (20) \]

The fifth and sixth terms in eqn. (19) represent the net electrostatic energy for an electron in orbital \( \Phi_A^r \) on atom A in the field from the total charge on atom B. The last term in eqn. (19) is the penetration term. In CNDO/1 it was found by calculating \( V_{AB}^r \) theoretically that this contribution to the total energy was overestimated. The calculated bond distances became too short. Therefore we follow the CNDO/2 prescription by putting the penetration equal to zero. That is obtained by the approximation:

\[ V_{AB}^r = \sum_I n_B^r \gamma_{AB}^{rr} \]  
\[ (21) \]

The open shell cases are calculated with unrestricted Hartree-Fock. The density matrices are defined as:

\[ P_{\mu\nu}^x = \sum_i c_{\mu i}^x c_{\nu i}^x \]  
\[ (22) \]

\[ P_{\mu\nu} = P_{\mu\nu}^x + P_{\mu\nu}^s \]  
\[ (23) \]

The Fock matrix elements become:

\[ F_{\mu\nu}^x = -I_A^r - \sum_{B} \left( \sum_I n_B^r \gamma_{AB}^{rr} \right) + \left( 1 - P_{\mu\nu}^x \right) \gamma_{AA}^{rr} + \sum_{\lambda \in A} P_{\lambda\lambda} \gamma_{AB}^{rr} \]  
\[ (24) \]

\[ F_{\mu\nu}^x = \frac{1}{2}S_{\mu\nu}(\beta_A + \beta_B) - P_{\mu\nu}^x \gamma_{AB}^{rr} \quad \mu \neq \nu \]  
\[ (25) \]

To calculate the total energy of the molecule an expression for the core repulsion energy must be given. The simple point charge model has been used in this work. The formula that is used in semi-empirical \( \pi \)-electron calculations and that was used by Sichel and Whitehead\(^4\) in a semi-empirical all-valence electrons theory, namely

\[ E = \sum_{A < B} \left( \sum_{ij} n_A^r n_B^r \gamma_{AB}^{rr} \right) \]  
\[ (26) \]

was tried too, but it did not give enough repulsion. However, the core in a CNDO type calculation is better approximated with point charges relative to the valence electrons than the core in a \( \pi \)-electron calculation relative to the \( \pi \)-electrons. Formula (26) has also a finite limiting value for \( A = B \) while it is clear that A and B cannot collapse.

3. PARAMETERS

The scheme contains the following parameters: the orbital exponents \( \xi^r \), the ionization potentials \( I_A^r \), the occupation numbers \( n_A^r \) and the betas \( \beta_A \).
**Orbital exponents.** We have used the optimized exponents from the minimal basis atomic calculations by Clementi and Raimondi\(^1\) except for hydrogen where the value 1.2 has been chosen. There are some differences between these exponents and those obtained by Slater's rules. The optimized exponents give different radial dependence for \(s\), \(p\), and \(d\) orbitals. For the first row atoms the Slater exponents are slightly bigger, but for the second row atoms the Clementi \(3s\) exponents are around 17% bigger than the Slater exponents, while the values for the \(3p\) exponents are close to the Slater values except in aluminum. In the third row the differences are even bigger. The optimized exponents are always the bigger ones.

However, a criterion must be found for determining the exponents of the polarizing functions, that is, \(3p\) and \(3d\) for Na and Mg, \(3d\) for Al to Cl, \(4p\) and \(3d\) for K and Ca and \(4d\) for Ga to Br. We decided to let the radial density maxima of the polarizing function and the highest occupied orbital coincide. Calculations on some sulfur compounds seem to support this choice. The results are discussed below.

*Ionization potentials.* The diagonal element \(U_{\mu\mu} = (\mu_\mu^* \mid -\frac{1}{2} \mathcal{A} - V_\mathcal{A} \mid \mu_\mu^* )\) does not correspond directly to any observable property of atom \(\mathcal{A}\). As the function \(\mu_\mathcal{A}^*\) is an atomic orbital on \(\mathcal{A}\), it can be related to the ionization potential of that orbital through formula \((13)\). But this formula is based on a very crude approximation and besides it contains the coulomb integrals, which depend on the choice of exponents.

In the CNDO approximation all spectroscopic levels arising from one configuration are degenerate. The energy of a certain configuration is taken as the arithmetic mean of all observed levels weighted for multiplicity. Three problems arise immediately. Which configuration of the neutral atom should be used? All required levels are not always observed. What should one do if \(I_\mathcal{A}^6\), \(I_\mathcal{A}^8\) and \(I_\mathcal{A}^4\) cannot be determined from the same configuration? The exponents we have used are optimized for the ground states of the atoms. Thus for the occupied valence orbitals we have used the ground state configurations of the neutral atoms and the resulting configurations of the ions. Sometimes those levels of the ions have not been observed and an excited configuration of the atom must then be chosen, for which the ionization process leads to an observed configuration of the ion. The ionization potentials of the polarizing functions must always be determined from excited configurations of the atoms. It is therefore impossible to obtain a set of potentials which are derived in a consistent manner. The individual values may be expected to be somewhat off from what they should be in this scheme. But it should be remembered that it is \(U_{\mu\mu}\) that originally enters into the Fock matrix element. We have studied the effects of varying some exponents and potentials separately and keeping the other parameters fixed in some molecules. The results showed that the uncertainties in the exponents are as important as the uncertainties in the potentials. Our conclusion is that, as there is no definite way of determining the exponents, and the integrals which appear in approximate molecular calculations cannot be directly related to observed atomic data, it is no use to elaborate too much on the potentials. The present way of getting them should give the correct order of magnitude. To get better results one should for a given set of exponents determine the potentials empirically by fitting the mo-

molecular calculations to accurate observed data. But that is not practical at the present time as the number of parameters would be too big. We have calculated the potentials in the above mentioned way for K to Br (Table 1) ourselves and for H to F we have used Pople's and Segal’s values \(^2\) and for Na to Cl those reported by Levison and Perkins.\(^{17}\)

**Table 1.** Ionization potentials in electronvolts for potassium, calcium and gallium to bromine.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(I_A^a)</th>
<th>(I_A^b)</th>
<th>(I_A^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>4.34</td>
<td>2.73</td>
<td>1.67</td>
</tr>
<tr>
<td>Ca</td>
<td>6.11</td>
<td>3.96</td>
<td>1.79</td>
</tr>
<tr>
<td>Ga</td>
<td>12.61</td>
<td>5.93</td>
<td>1.69</td>
</tr>
<tr>
<td>Ge</td>
<td>15.67</td>
<td>7.53</td>
<td>1.78</td>
</tr>
<tr>
<td>As</td>
<td>18.21</td>
<td>9.19</td>
<td>1.61</td>
</tr>
<tr>
<td>Se</td>
<td>17.29</td>
<td>10.82</td>
<td>3.05</td>
</tr>
<tr>
<td>Br</td>
<td>23.76</td>
<td>12.32</td>
<td>4.8(^a)</td>
</tr>
</tbody>
</table>

Values rounded off to two decimals.

\(^a\) Estimated value as the appropriate configuration is not observed.

As mentioned in the introduction CNDO/1 and CNDO/2 differ in the way \(U_{\mu\mu}\) is estimated. For molecules with only first row atoms we tried both methods. The two methods gave similar results with respect to the order and spacing of the orbitals. But the orbital energies obtained with \(U_{\mu\mu}\) given by the CNDO/1 prescription were less negative and were in better agreement with the experimental ionization potentials when Koopmans' theorem was applied. The spectral data are taken from Ref. 24.

**Occupation numbers.** The occupation numbers which enter into the formulas are simply the occupation numbers giving the ground state configurations of the atoms.

**The bonding parameter beta.** To optimize the betas we have deviated from the original CNDO method, that is, solely calibrating the results against minimal basis ab initio calculations. Firstly, as some empirical elements are introduced into the theory by the betas and the ionization potentials, it is doubtful if the results obtained in ab initio all-electron calculations by minimizing the total energy should be the only standard. Secondly, the number of suitable molecules with second and third row atoms treated by such a method is limited. Some of these molecules have open shells in the ground state. As this CNDO method uses unrestricted Hartree-Fock, while many ab initio calculations are made with restricted Hartree-Fock a precise comparison is not possible for such cases. We have chosen to look both at the order and spacing of SCF orbitals, without trying to reproduce the expansion coefficients, and at experimental data such as ionization potentials, dipole moments and binding energies whenever possible. The optimum for the beta in each case is determined by an “overall judgement” of these properties. It was our experience

that the results were much more sensitive to the betas in open than closed shell cases.

The betas are collected in Table 2. The molecules which have been used to determine the betas are marked * in Table 3 with the results of the calculations.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$-\beta_A$</th>
<th>Atom</th>
<th>$-\beta_A$</th>
<th>Atom</th>
<th>$-\beta_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>7.00</td>
<td>Li</td>
<td>7.00</td>
<td>Na</td>
<td>3.00</td>
</tr>
<tr>
<td>Be</td>
<td>9.00</td>
<td>Mg</td>
<td>7.28</td>
<td>Ca</td>
<td>6.00</td>
</tr>
<tr>
<td>B</td>
<td>11.00</td>
<td>Al</td>
<td>7.00</td>
<td>Ga</td>
<td>5.50</td>
</tr>
<tr>
<td>C</td>
<td>15.00</td>
<td>Si</td>
<td>8.50</td>
<td>Ge</td>
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<td>N</td>
<td>21.00</td>
<td>P</td>
<td>10.00</td>
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<tr>
<td>O</td>
<td>28.00</td>
<td>S</td>
<td>11.39</td>
<td>Se</td>
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</tr>
<tr>
<td>F</td>
<td>39.00</td>
<td>Cl</td>
<td>14.70</td>
<td>Br</td>
<td>13.00</td>
</tr>
</tbody>
</table>

4. RESULTS

The experimental geometries have been used except in a few cases. For the substituted benzenes the standard benzene ring has been used. BH$_3$ and GaH$_3$ are calculated with assumed geometries.$^3,45$

a. Binding energies. The binding energy is calculated as the total energy of the molecule minus the sum of the atomic energies. These are the ground state energies of the atoms calculated in the CNDO approximation with the standard parameters. The calculated binding energies should not be expected to be very accurate for several reasons. In a true Hartree-Fock solution the correlation energy is still missing and the CNDO approximation is far from a Hartree-Fock description of the valence electrons. Further, the form of the resonance integral, $\beta_{\mu\nu} = \frac{1}{2} S_{\mu\nu}(\beta_A + \beta_B)$, is probably not flexible enough to describe accurately the relative magnitudes of the different contributions to the bond between A and B, for instance, it does not take into account the energies of the orbitals $\mu$ and $\nu$. The inclusion of the polarizing functions makes the molecular and atomic calculations not directly comparable. The energy is very sensitive to the exponents of the polarizing functions. A high population in a polarizing function generally, but not always, gave a much too negative binding energy (in Table 3 minus the binding energy is reported). Calculations without polarizing functions predicted less stable molecules. That is, the polarizing function not only influences the charge distribution in total and the division of charge between the valence orbitals on its own center, but it also stabilizes the molecule in bond formation. In similar molecules the deviations from the correct values due to the above mentioned difficulties are hopefully of the same magnitude.

The calculated and experimental$^{18-20}$ binding energies are listed in Table 3. The binding energies in the homonuclear diatomic molecules are exaggerated except in the hydrogen molecule. The fit to experimental data in the hydrides AH, AH$_2$, AH$_3$, and AH$_4$ is good or satisfactory, except for NaH. Because only

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## Table 3. Calculated ionization potentials, binding energies and dipole moments compared to experimental data and ab initio NBO calculations.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ionization potential (eV)</th>
<th>Binding energy (eV)</th>
<th>Dipole moment (debyes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>15.95 eV</td>
<td>15.43 eV</td>
<td>25</td>
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<tr>
<td>N₂⁺</td>
<td>16.80 eV</td>
<td>16.89 eV</td>
<td>25</td>
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<tr>
<td>O₂</td>
<td>15.28 eV</td>
<td>15.28 eV</td>
<td>25</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>16.80 eV</td>
<td>16.89 eV</td>
<td>25</td>
</tr>
<tr>
<td>CS₂</td>
<td>14.39 eV</td>
<td>14.39 eV</td>
<td>27</td>
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<tr>
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<tr>
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<td>25</td>
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<tr>
<td>CH₂Cl₂</td>
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<td>22.45 eV</td>
<td>25</td>
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<td>CH₂Cl₃</td>
<td>23.50 eV</td>
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<td>23.50 eV</td>
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Note: The table continues with similar data for other molecules.
Table 3. Continued.

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|       |       |       |       |       |       |       |       |       |       |� between the hydrogen 1 s-orbitals and the orbitals on atom A are
involved, one could expect, that a single β-value for each atom would be enough
to describe the binding energies in this series of molecules. Of the oxides only
the carbon oxides, which have been used in the parameter fitting, come out
right. The second row oxides SiO, SO, and SO₂ are overestabilized by considereable
d-populations. With the standard parameters the extreme case LiF is
predicted to be unstable at the experimental equilibrium distance. The calcu-
lated bond distance is almost 1 Å longer than the experimental value. To
get better results for LiF the lithium orbitals must be considerably contracted.

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But these lithium parameters were not suitable in LiH. The second and third row fluorides have fairly big d-populations and big binding energies. The general trend within the group methyl halides and methyl cyanide is very well described, but the absolute values are somewhat too high. Thus the methyl halides are incorrectly predicted to have bigger binding energies than methane. The calculated energies for methane, ethane, propane, ethylene, and acetylene are close to the experimental values. But the corresponding halogen substituted compounds are predicted to have higher binding energies contrary to what the experimental values indicate in the cases where they are given. The energy of benzene is too high but the relative energies in the series benzene, phenol, aniline, and toluene are well described. The sulphur compounds, except SH and SH₂, are stabilized by the sulphur d-function. The difference between the theoretical and experimental binding energies increases with the d-population. This population goes from 0.06 and 0.13 electrons in SH and SH₂ to 1.44, 1.54, 2.14, and 2.15 electrons in SO₂, SOF₂, SO₄⁻², and SF₆.

b. Dipole moments. In the case of a closed shell the expression for the dipole moment vector

\[ \vec{\mu} = \sum_{h} Z_{h} \vec{R}_{h} - 2 \sum_{i} \sum_{\mu,\nu} c_{i\mu} c_{i\nu} \int \Phi_{\mu}^{*} r \Phi_{\nu} \, dV \]

is simplified by neglecting two-center overlap but retaining one-center overlap, that is the sp and pd one-center dipoles are kept. The final expression is thus:

\[ \vec{\mu} = \sum_{h} (Z_{h} - \sum_{\mu \in h} P_{\mu \mu}) \vec{R}_{h} - 2 \sum_{\mu, \nu \in h} P_{\mu \nu} \int \Phi_{\mu}^{*} r \Phi_{\nu} \, dV \]

The same expression is obtained in the case of an open shell with \( P_{\mu \nu} = P_{\mu \nu}^{s} + P_{\mu \nu}^{p} \). The dipole moment is a test of how well the calculated wavefunction predicts the charge distribution in the molecule.

For the molecules where experimental data exist the calculated dipole moments with a few exceptions are very satisfactory. The pd dipoles play an important role in the molecules with second and third row atoms. The difference in dipole moment between first and second row hydrides AH is the big pd contribution in the series NaH to ClH. With the sign conventions in Table 3 the total charge dipole varies from -1.24 D to 1.32 D, the sp dipole from -4.34 D to 1.03 D and pd dipole from -2.15 D to -1.51 D in NaH to ClH. The variations are not monotonic. The same trends are seen in the series KH to BrH. The experimental facts that H₂S and H₂Se have smaller dipole moments than H₂O, and that PH₃ and AsH₃ have smaller dipole moments than NH₃ are reproduced in the calculations including pd dipoles. These dipoles oppose the contributions from the total charge and the sp dipoles. The ab initio SCF calculations predict a much bigger dipole moment for SiO then for CO. The same thing is predicted in this semi-empirical theory and it is due to the big pd dipole on Si. In the alkali halides, which are very polar molecules the order of the calculated dipole moments comes out very well, though the magnitudes are somewhat low in some cases. In the conjugated

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systems it is seen that in the molecules with F, OH, NH₃, and CH₃ substituents the calculated dipole moments are in good agreement with the experimental ones, while Cl and Br substituents lead to much too big values. Taking fluoro- and chloroacetylene as two examples the calculations indicate that chlorine should be more negative than fluorine and at the same time Cₓ gets more electrons in the chlorine compound. There are different effects for the σ- and the π-electrons in the two cases. Fluorine accepts more σ-electrons than it donates π-electrons. It also polarizes the C—C bond leading to a pile up of both σ- and π-electrons on Cβ and the opposite effect on Cₓ. Chlorine on the other hand is mainly π-electron accepting. Compared to the fluorine case it pulls π-electrons from Cβ to Cₓ and itself, and Cβ increases its σ-population, mainly taken from the hydrogen. One would, of course, expect fluorine and chlorine to behave more or less in the same way. Part of the explanation is that there is no d-function on fluorine, which is therefore forced to be π-donating instead of π-accepting as might be expected from electronegativity values. Another factor is the choice of exponents. The chlorine one-center coulomb repulsion integrals and the repulsion integrals between Cₓ and Cl are smaller than corresponding integrals in the fluorine case. An increase of the chlorine exponents and thus an increase of these integrals leads to a better result for the dipole moment. These comments also apply to the ethylenes and the benzenes. In the methyl halides the dipole moments are better since this long range polarization over a chain of atoms is not possible. Similar effects are also present in thiophene and furan. The big dipole moment of CS is due to a big pd dipole.

c. Ionization potentials and configurations. The ionization potentials are calculated with Koopmans’ theorem, that is, the energy required to remove an electron from an orbital is assumed to be equal to minus the orbital energy. This approximation is not completely accurate. It is less accurate for the deeper lying orbitals. Even the orbital order may be reversed. In a semi-empirical theory, however, it is possible to adjust the parameters to improve the results for classes of molecules. The theoretical values should be compared to observed vertical potentials if possible. The orbital symmetries are given according to the conventions in the book by Cotton. In B₃H₄ the z-axis is through the boron atoms and the y-axis through the bridge hydrogen atoms. Planar Cₓ molecules lie in the yz-plane and in propane the carbon atoms lie in the yz-plane. In Table 3 the highest occupied orbital is reported and in Table 4 all the orbital energies with symmetry and occupation are given. The orbitals within a symmetry are not numbered. A subindex α or β indicate α- or β-spin when necessary for the following reason. Because the open shell cases are calculated with unrestricted Hartree-Fock, corresponding alpha- and beta-orbitals may be non-degenerate, e.g. NO is calculated as σ²σ₂πₓσ₂π₂βασ₂ and MgH as σ₂σβσ₂. The orbital order may even be reversed for α- and β-spin, e.g. in O₂: σ²σ₂π₂σ₂π₂σ₂π₂π₂σ₂π₂. The orbital order is sensitive to the parametrization. The calculated energy value for the highest occupied orbital is generally in very good or reasonable agreement with the experimental value when the latter one is given. In the alkali chlorides and bromides, where the orbital order changes, it should be noted that the highest σ- and π-orbitals are almost degenerate. One problem arises in the conjugated systems. Both ethylene and benzene are incorrectly predicted to have σ-orbitals on

the top. But the substituted ethylenes and benzenes have \(\pi\)-orbitals as the highest occupied orbitals in agreement with the general interpretation of the experimental data.

d. **Geometries and rotational barriers.** One important field of application of this type of method is the investigation of molecular structure. The geometry is determined by minimizing the total energy with respect to the geometrical

**Table 4.** Orbital energies and configurations. The orbital energies are multiplied by minus one. The occupation number of the orbitals are only given in molecules with open shells. Energies in eV. The symmetries of the molecules are given in Table 3.

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<th>C8H8</th>
<th>PF3</th>
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parameters. In CNDO/1, where the integrals $V_{AB}$ were calculated theoretically, the penetration contribution to the energy became too big and the bond distances too short. That was cured in CNDO/2 by choosing $V_{AB}$ so the penetration terms became zero. CNDO/2 has been very successful in determining geometries but the binding energies are too high as well as the force constants. Fischer and Kollmar have got very good results for both binding energies and geometries in hydrocarbons. Their calculated force constants are better too. Thus they have got good descriptions of the energy hypersurfaces, which is necessary for the study of reactions. They use a somewhat more complicated formula for $V_{AB}$:

$$V_{AB} = Z_B \left\{ (1 - \alpha) \gamma_{AB} + \alpha \sqrt{R_{AB}^2 + \frac{1}{\xi_A^2}} \right\}, \alpha = 0.22$$  \hspace{1cm} (27)

By using this extra parameter they could adjust the shape and the location of the energy hypersurface. Formula (27) goes into the CNDO/2 formula when $\alpha = 0$. They also use another expression for the bonding parameter:

$$\beta_{\mu\nu} = - \frac{1}{2} S_{\mu\nu} (k_A I_{\mu} + k_B I_{\nu}), \mu \in A, \nu \in B$$  \hspace{1cm} (28)

As the present scheme spans the periodic table up to bromine (with the exception for the transition metals so far), it was desirable to have as few parameters as possible. The analysis of energy-geometry to determine the extra parameter $\alpha$ would be too complicated in our case, unless a single $\alpha$-value would do in all combinations of atoms. Our calculated geometries for a small group of test molecules are reported in Table 5. In some of the molecules only

### Table 5. Calculated and experimental geometries.

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<td>R(S–H) 1.43</td>
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<td>BH₃</td>
<td>D₃ₙ</td>
<td>R(B–H) 1.31</td>
<td>1.18</td>
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<td>GaH₃</td>
<td>D₃ₙ</td>
<td>R(Ga–H) 1.64</td>
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<tr>
<td>CH₄</td>
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<td>BN</td>
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<td>R(B–N) 1.49</td>
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<td>CN</td>
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<td>R(C–N) 1.27</td>
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<td>KBr</td>
<td>Cᵥ</td>
<td>R(K–Br) 2.81</td>
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<td>CH₃F</td>
<td>Cᵥ</td>
<td>R(C–F) 1.41</td>
<td>1.385</td>
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<td>-1.62</td>
<td>1.86</td>
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<td>CH₃Cl</td>
<td>Cᵥ</td>
<td>R(C–Cl) 1.68</td>
<td>1.782</td>
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<td>-3.00</td>
<td>1.87</td>
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<td>CH₃Br</td>
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<td>1.938</td>
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<td>1.80</td>
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<tr>
<td>C₂H₆</td>
<td>D₆d</td>
<td>R(C–C) 1.61</td>
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<tr>
<td>HCCN</td>
<td>D₁₃h</td>
<td>R(C–N) 1.32</td>
<td>1.204</td>
<td>110</td>
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<tr>
<td></td>
<td></td>
<td>R(C–H) 1.18</td>
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<td>110</td>
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<tr>
<td>HCCF</td>
<td>Cᵥ</td>
<td>R(C–F) 1.38</td>
<td></td>
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<td>-1.12</td>
<td>0.73</td>
<td>102</td>
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<tr>
<td>HCCCl</td>
<td>Cᵥ</td>
<td>R(C–Cl) 1.66</td>
<td>1.68</td>
<td>109</td>
<td>-2.04</td>
<td>0.44</td>
<td>96</td>
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</tr>
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</table>

One geometrical parameter has been varied while the others have been kept fixed. The experimental distances of BH₃ and GaH₃ are only assumed values. The dipole moment is the property which is most sensitive to geometrical variations. In SO₄, though the charges are the same, the opening of the OSO angle results in a much smaller dipole moment. Using the observed geometries gives better descriptions of the molecules. Generally the calculated bond distances are a little longer than the experimental ones. The gain in total energy by varying the geometry was in most cases less than 0.5 eV. The exceptions are BN and H₂CO, where the lowering of the energy was around 2 eV.

Another problem, which has been studied with different theoretical methods, is barriers to internal rotation in molecules. The results obtained with semiempirical methods have been of varying agreement with the observed values. The experimental barriers are very small, up to a few tenths of an eV (1 eV = 23 kcal/mol). It should be remembered firstly, that CNDO only handles the electron interaction in an approximate way and secondly, that within the given approximation it is very difficult to reach the optimal parametrization. Gordon and Fischer and Kollmar have tried to analyse the total energy in different physical terms to deepen the understanding of these problems. A few barriers are reported in Table 6. The results are comparable to those of other semi-empirical methods.

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Table 6. Barriers to internal rotations (kcal/mol).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Calc.</th>
<th>Exptl.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄⁺</td>
<td>1.53</td>
<td>2.875</td>
<td>111</td>
</tr>
<tr>
<td>C₂H₆⁺</td>
<td>1.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂NCOH⁺</td>
<td>15.94</td>
<td>18 ± 3</td>
<td>112</td>
</tr>
<tr>
<td>HCOOH</td>
<td>4.89 cis</td>
<td>13.4</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td>3.14 trans</td>
<td>Ref.</td>
<td></td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>5.21</td>
<td>7.0 cis</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1 trans</td>
<td></td>
</tr>
</tbody>
</table>

*a* Experimental geometry. *b* R(C-C) calculated equilibrium distance. *c* Rotation of NH₄⁺ group. The molecule planar in the ground state. *d* The molecule is calculated to be trans planar in its ground state. The experimental dihedral angle is 111.5° for the ground state. *e* Rotations from the cis, respectively the trans configurations. *f* Rotations from the equilibrium configuration over the cis, respectively the trans configurations. *g* The trans form should be at least 4 kcal/mol above the cis form according to D. R. Lide, Jr., Ann. Rev. Phys. Chem. 15 (1964) 234.

e. Alternatives in the parametrization. Taking into account the simplicity of the method and its broad field of application, the results are rather satisfactory. However, the less good results in some cases, of course, raise the question if some simple modification of the parameters might improve the results. Two things were investigated. The bonding parameter beta and the exponent of the polarizing function.

The binding energies and to a lesser extent the stabilization of the orbitals are sensitive to the betas. With the standard parameters reported in this paper calculated binding energies of SH, SH₂, BN, and CO are in good agreement with experimental data, while SO₂, CN, and NO are predicted to have too high binding energies. Generally the molecules only having σ-bonds are well described by the standard parameters. SO₂ differs from SH₂ by having both σ- and π-orbitals and CN and NO from BN and CO by having one extra π-orbital. The standard parameters also predict the wrong order between σ- and π-orbitals in ethylene and benzene.

The formula for the beta which has been used in this paper,

\[ \beta_{\mu \nu} = \frac{1}{2} S_{\mu \nu} (\beta_A + \beta_B) \]  

(17)

does not take into account the energies of the orbitals involved. Santry and Segal⁴ improved their results by multiplying the expression on the right hand side in formula (17) with a factor k equal to 0.75 if μ and or ν belong to a second row atom and equal to 1.0 otherwise. As an alternative we tried a Wolfsberg-Helmholz type of relation.

\[ \beta_{\mu \nu} = - \frac{1}{2} S_{\mu \nu} (k_A I_{\mu} + k_B I_{\nu}), \; \mu \in A, \; \nu \in B \]  

(28)

The k’s were optimized with respect to the binding energies in H₂, SH, SH₂, SO₂, BN, CN, CO, and NO. The k’s obtained were also tested on CS and C₂H₄⁺. The results are collected in Table 7. The values obtained for k_A lead to a bigger “β_A” for an s-orbital and a smaller value for a p-orbital than the standard β_A. As can be seen in the table, the overall agreement between calculated and observed properties is not improved by the new beta formula. In SH

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Table 7. Comparison of the results obtained with the two different types of bonding parameter.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Binding energy eV</th>
<th>Dipole moment D</th>
<th>Ionization potential eV</th>
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<td></td>
<td>I</td>
<td>II</td>
<td>expvl</td>
</tr>
<tr>
<td>H₂</td>
<td>4.75</td>
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<td>SH</td>
<td>3.04</td>
<td>3.04</td>
<td>3.70</td>
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<td>SH₂</td>
<td>5.95</td>
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<td>7.5</td>
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<tr>
<td>SO₂</td>
<td>12.02</td>
<td>27.01</td>
<td>11.18</td>
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<tr>
<td>BN</td>
<td>4.97</td>
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<tr>
<td>CN</td>
<td>6.95</td>
<td>10.93</td>
<td>7.63</td>
</tr>
<tr>
<td>CO</td>
<td>8.28</td>
<td>11.01</td>
<td>11.23</td>
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<tr>
<td>NO</td>
<td>6.74</td>
<td>13.65</td>
<td>6.62</td>
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<tr>
<td>CS</td>
<td>9.83</td>
<td>11.16</td>
<td>7.19</td>
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<tr>
<td>C₂H₄</td>
<td>35.63</td>
<td>25.33</td>
<td>24.36</td>
</tr>
</tbody>
</table>

I  : \[ \beta_{\mu \nu} = \frac{1}{2} S_{\mu \nu} (k_A I_\mu + k_B I_\nu) \]
II : \[ \beta_{\mu \nu} = \frac{1}{2} S_{\mu \nu} (\beta_A + \beta_B) \]

and SH₂ the polarities increase and the pd dipoles decrease leading to very big dipole moments. In SO₂ the \( \alpha_2 \) orbital is destabilized compared to the standard calculation by having less \( d \)-character. The \( \pi \)-orbital (\( b_{3w} \)) in ethylene gets a higher energy as the bonding parameter between the \( p \)-orbitals is less negative now. But the highest \( \sigma \)-orbital (\( b_{3g} \)) is almost degenerate with it and the binding energy for ethylene is now around 11 eV too high. This is due to the fact, that so many of the resonance integrals involve \( s \)-functions in this molecule and what was said above about "\( \beta_A \)" for \( s \)-functions. To get the right orbital order in conjugated systems Del Bene and Jaffe ¹ had separate bonding parameters for \( \sigma \)- and \( \pi \)-bond contributions. Probably this would be needed here too. A completely new parametrization might give the correct results.

The second point of investigation was the polarizing function. Santry and Segal ⁴ found that the 3d functions were not necessary to explain the shape of molecules containing second row atoms but the inclusion of them stabilized the molecules and improved the charge distributions. We have chosen some sulphur compounds, SH, SH₂, SO₂, CS, SOF₂, and SF₆ as test molecules. With the standard parameters the binding energies in SO₂, SOF₂, and SF₆ and the dipole moment in CS were exaggerated while the other results for these test molecules were satisfactory. A set of six calculations was made on each molecule. First the sulphur \( d \)-function was excluded from the basis set and then, while keeping the ionization potential fixed, the values 3.00, 2.05, 1.8273 (standard value), 1.50 and 0.5 were given to the \( d \)-exponent, corresponding to a variation from a very contracted to a very diffuse 3d-orbital. It turns out, that the results are very sensitive to the \( d \)-function. The exponent equal to 1.50, that is, a function a little more diffuse than the 3p-orbital, gave the biggest stabilization. In fact, in the extreme cases SOF₂ and SF₆, the binding energies were 50.52 eV and 89.03 eV with \( d \)-populations of 1.84 and 2.47, while without \( d \)-functions the energies were 5.29 eV and 3.90 eV. The experimental values are 14.45 eV and 20.43 eV. In SH the variation is only 3.47

eV to 2.27 eV. The stabilization is accompanied by an increase of electrons on the sulphur atom in SO₂, SOF₂, and SF₆ and the reversed process in the other cases. The dipole moments calculated with the exponent equal to 1.50 are rather bad, being −0.05 D, 0.06 D, −0.63 D, 5.97 D, and 1.35 D in SH, SH₂, SO₂, CS, and SOF₂, respectively. With the standard parameters the values are 0.52 D, 0.75 D, −1.60 D, 5.08 D, and 1.26 D. The calculations without d-functions led to much too big dipole moments in SH and SH₂. The conclusion is that the standard parameters, though SO₂, SOF₂, and SF₆ are overestimated, give the most reasonable results. The criterion for choosing the d-exponent, letting the radial density maxima for the highest occupied atomic orbital and the polarizing function coincide, was obtained by Roos and Siegbahn by minimizing the energy in ab initio calculations. The criterion works here in connection with our parameters, but not by giving the lowest energy. Finally it should be pointed out, that the orbital order depends on
the d-function is some cases.

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