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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 [1–6] 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.[1–14] 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.[15] 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.*[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[16] 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 β 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.

$$\psi_i = \sum_{\mu} c_{\mu i} \Phi_{\mu}^{r} \tag{1}$$

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:

$$F_{\mu\mu} = H_{\mu\mu} - \tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\lambda} P_{\lambda\lambda}\gamma_{\mu\lambda} \tag{2}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \qquad \mu \neq \nu \tag{3}$$

The density matrix is defined as:

$$P_{\mu\nu} = 2\sum_{i}^{\text{occ.}} c_{\mu i}^{*} c_{\nu i} \tag{4}$$

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

$$H_{\mu\nu} = \int \Phi_\mu{}^{r*}[-\tfrac{1}{2}\Delta - \sum_{\mathrm{A}} V_{\mathrm{A}}]\Phi_\nu{}^t \mathrm{d}V = (\mu^r| -\tfrac{1}{2}\Delta - \sum_{\mathrm{A}} V_{\mathrm{A}}|\nu^t) \tag{5}$$

$$\gamma_{\mu\nu} = \int \Phi_\mu{}^{r*}(1)\Phi_\mu{}^r(1)\frac{1}{r_{12}}\Phi_\nu{}^{t*}(2)\Phi_\nu{}^t(2)\,\mathrm{d}V = \gamma_{\mu\nu}{}^{rt} \tag{6}$$

Here $-V_{\mathrm{A}}$ 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:

$$\gamma_{\mu\nu}{}^{rt} = \gamma_{\mathrm{AB}}{}^{rt} \qquad \mu\in\mathrm{A},\ \nu\in\mathrm{B} \tag{7}$$

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

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

$$\gamma_{\mu\nu}{}^{rt} = \gamma_{\mathrm{AB}} \qquad \text{for all } r \text{ and } t \tag{8}$$

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

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

$$H_{\mu\mu} = (\mu^r| -\tfrac{1}{2}\Delta - V_{\mathrm{A}}|\mu^r) - \sum_{\mathrm{B}\neq\mathrm{A}}(\mu^r|V_{\mathrm{B}}|\mu^r) =$$

$$= U_{\mu\mu}{}^r - \sum_{\mathrm{B}\neq\mathrm{A}}(\mu^r|V_{\mathrm{B}}|\mu^r) = U_{\mathrm{A}}{}^r - \sum_{\mathrm{B}\neq\mathrm{A}}(\mu^r|V_{\mathrm{B}}|\mu^r) \tag{9}$$

The last step follows from the fact that the basis functions with the same principal and azimuthal quantum numbers are degenerate. $U_{\mu\mu}{}^r$ can be related to the energy of an electron in $\Phi_\mu{}^r$ 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:

$$E = \sum_\mu E_\mu + \sum_{\mu<\nu} J_{\mu\nu} - \sum_{\mu<\nu} K_{\mu\nu} \tag{10}$$

In the last sum the spinorbitals μ and v have parellel spins. With our approximations all exchange integrals are put equal to zero. Thus the energy reduces to:

$$E(s^m p^n d^q) = \sum_{\mu} E_\mu + \sum_{\mu<\nu} J_{\mu\nu} = \sum_{\mu} (\mu^r| - \tfrac{1}{2}\Delta - V_A|\mu^r) + \sum_{\mu<\nu} \gamma_{\mu\nu}{}^{rt}$$
$$= \sum_{\mu} U_A{}^r + \sum_{\mu<\nu} \gamma_{AA}{}^{rt} \tag{11}$$

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

$$E(A;s^m p^n d^q) = mU_A{}^s + nU_A{}^p + qU_A{}^d + \tfrac{1}{2}m(m-1)\gamma_{AA}{}^{ss} + \tfrac{1}{2}n(n-1)\gamma_{AA}{}^{pp} +$$
$$+ \tfrac{1}{2}q(q-1)\gamma_{AA}{}^{dd} + mn\gamma_{AA}{}^{sp} + nq\gamma_{AA}{}^{pd} + qm\gamma_{AA}{}^{ds} \tag{12}$$

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

$$I_A{}^s = E(A^+;\ s^{m-1}p^n d^q) - E(A,\ s^m p^n d^q) =$$
$$= -U_A{}^s - \sum_r (n_A{}^r - \delta_{sr})\gamma_{AA}{}^{sr} \qquad n_A{}^r = m,\ n,\ \text{and}\ q \tag{13}$$

The expressions for $I_A{}^p$ and $I_A{}^d$ follow immediately.

2.2 $\mu \neq \nu$ and μ and ν both on atom A.

$$H_{\mu\nu} = (\mu^r| - \tfrac{1}{2}\Delta - V_A|\nu^t) - \sum_{B\neq A} (\mu^r|V_B|\nu^t) \tag{14}$$

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 $A \neq B$

$$H_{\mu\nu} = (\mu^r| - \tfrac{1}{2}\Delta - V_A - V_B|\nu^t) - \sum_{C\neq A,B} (\mu^r|V_C|\nu^t) \tag{15}$$

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 fulfils the invariance requirements. In our case

$$\beta_{\mu\nu} = \beta_{AB}{}^{rt} S_{\mu\nu} \tag{16}$$

would do. $S_{\mu\nu}$ is the overlap integral which has the right transformation properties. The parameter $\beta_{AB}{}^{rt}$ 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.

$$\beta_{\mu\nu} = \tfrac{1}{2}S_{\mu\nu}(\beta_A + \beta_B) \tag{17}$$

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

$$(\mu_A{}^r|V_C|\nu_B{}^t) = V_{AC}{}^r \delta_{\mu\nu} \qquad A \neq C \tag{18}$$

The Fock matrix can now be written with our formulas and some rearrangement as ($\Phi_\mu{}^r \in A$):

$$F_{\mu\mu} = -\mathrm{I}_{\mathrm{A}}^{r} - \sum_{t} n_{\mathrm{A}}^{t}\gamma_{\mathrm{AA}}^{rt} + (1 - \tfrac{1}{2}P_{\mu\mu})\gamma_{\mathrm{AA}}^{rr} + \sum_{\lambda\in\mathrm{A}} P_{\lambda\lambda}\gamma_{\mathrm{AA}}^{rt} +$$

$$+ \sum_{\lambda\in\mathrm{A}} P_{\lambda\lambda}\gamma_{\mathrm{AB}}^{rt} - \sum_{\mathrm{B}\neq\mathrm{A}}\left(\sum_{t} n_{\mathrm{B}}^{t}\gamma_{\mathrm{AB}}^{rt}\right) + \sum_{\mathrm{B}\neq\mathrm{A}}\left(\sum_{t} n_{\mathrm{B}}^{t}\gamma_{\mathrm{AB}}^{rt} - \mathrm{V}_{\mathrm{AB}}^{r}\right) \tag{19}$$

$$F_{\mu\nu} = \tfrac{1}{2}S_{\mu\nu}(\beta_{\mathrm{A}} + \beta_{\mathrm{B}}) - \tfrac{1}{2}P_{\mu\nu}\gamma_{\mathrm{AB}}^{rt} \qquad \mu \neq \nu,\ \mu\in\mathrm{A} \text{ and } \nu\in B \tag{20}$$

The fifth and sixth terms in eqn. (19) represent the net electrostatic energy for an electron in orbital Φ_{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:

$$V_{\mathrm{AB}}^{r} = \sum_{t} n_{\mathrm{B}}^{t}\gamma_{\mathrm{AB}}^{rt} \tag{21}$$

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

$$P_{\mu\nu}^{\alpha} = \sum_{i}^{\mathrm{occ}} c_{\mu i}^{\alpha *} c_{\nu i}^{\alpha} \tag{22}$$

$$P_{\mu\nu} = P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta} \tag{23}$$

The Fock matrix elements become:

$$F_{\mu\mu}^{\alpha} = -I_{\mathrm{A}}^{r} - \sum_{\mathrm{B}}\left(\sum_{t} n_{\mathrm{B}}^{t}\gamma_{\mathrm{AB}}^{rt}\right) + \left(1 - P_{\mu\mu}^{\alpha}\right)\gamma_{\mathrm{AA}}^{rr} + \sum_{\lambda} P_{\lambda\lambda}\gamma_{\mathrm{AB}}^{rt} \tag{24}$$

$$F_{\mu\nu}^{\alpha} = \tfrac{1}{2}S_{\mu\nu}(\beta_{\mathrm{A}} + \beta_{\mathrm{B}}) - P_{\mu\nu}^{\alpha}\gamma_{\mathrm{AB}}^{rt} \qquad \mu \neq \nu \tag{25}$$

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 π-electron calculations and that was used by Sichel and Whitehead [14] in a semi-empirical all-valence electrons theory, namely

$$E = \sum_{\mathrm{A}<\mathrm{B}}\left(\sum_{r,t} n_{\mathrm{A}}^{r} n_{\mathrm{B}}^{t}\gamma_{\mathrm{AB}}^{rt}\right) \tag{26}$$

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 π-electron calculation relative to the π-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 ξ^{r}, the ionization potentials I_{A}^{r}, the occupation numbers n_{A}^{r} and the betas β_{A}.

Orbital exponents. We have used the optimized exponents from the minimal basis atomic calculations by Clementi and Raimondi [16] 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 aluminium. In the third row the differences are even bigger. The optimized exponents are always the bigger ones.

However, a criterium 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 sulphur compounds seem to support this choice. The results are discussed below.

Ionization potentials. The diagonal element $U_{\mu\mu} = (\mu_A{}^r | -\frac{1}{2}\Delta - V_A | \mu_A{}^r)$ does not correspond directly to any observable property of atom A. As the function $\mu_A{}^r$ is an atomic orbital on 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 $I_A{}^s$, $I_A{}^p$ and $I_A{}^d$ 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-

lecular 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.

Atom	I_A^s	I_A^p	I_A^d
K	4.34	2.73	1.67
Ca	6.11	3.96	1.79
Ga	12.61	5.93	1.69
Ge	15.67	7.53	1.78
As	18.21	9.19	1.61
Se	17.29	10.82	3.05
Br	23.76	12.32	4.5[a]

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 2. Bonding parameter β_A in electronvolts.

Atom	$-\beta_A$	Atom	$-\beta_A$	Atom	$-\beta_A$
H	7.00				
Li	7.00	Na	3.00	K	6.00
Be	9.00	Mg	7.28	Ca	6.00
B	11.00	Al	7.00	Ga	5.50
C	15.00	Si	8.50	Ge	8.00
N	21.00	P	10.00	As	9.50
O	28.00	S	11.39	Se	11.00
F	39.00	Cl	14.70	Br	13.00

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 μ and ν. 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 hydrids AH, AH_2, AH_3, and AH_4 is good or satisfactory, except for NaH. Because only

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

Molecule	Symmetry	Ionization potential eV.					Binding energy [a] eV.			Dipole moment [b] debyes			
		Calc.	Exptl.	Ref.	Ab initio	Ref.	Calc.	Exptl.[18-20]	Calc.	Exptl.	Ref.	Ab initio	Ref
H_2	$D_{\infty h}$	15.19 σ_g	15.43	25	16.18 σ_g	26	2.67	4.75					
Li_2	"	10.61 σ_g	4.96	25	4.94 σ_g	26	10.51	1.05					
B_2	"	10.38 π_u			9.78 π_u	26	8.75	3.66					
C_2	"	13.32 π_u	12.0	25	12.46 π_u	26	10.78	6.36					
N_2	"	14.29 σ_g	15.58 σ_g	27	16.75 π_u	28	14.41	9.90					
O_2	"	11.48 π_g	12.08	25	14.47 π_g	26	13.26	5.21					
F_2	"	16.76 π_g	15.63 π_g	29	17.71 π_g	26	7.39	1.65					
*LiH	$C_{\infty v}$	9.65 σ	6.5	25	8.21 σ	30	2.64	2.52	-5.88	-5.88	31	-6.00	32
BeH	"	7.88 σ	8.6	25	8.51 σ	30	2.48	2.62	-0.26			-0.28	32
*BH	"	10.76 σ	9.73	25	9.48 σ	30	4.57	3.58	2.31			1.73	32
CH	"	10.42 π	10.64	25	11.29 π	30	4.67	3.64	1.94	1.46	33	1.57	32
NH	"	12.45 π	13.10	25	14.63 π	30	4.89	3.90	1.80			1.63	32
OH	"	14.44 π	13.36	25	15.57 π	30	4.81	4.56	1.76	1.66	34	1.78	32
*FH	"	16.37 π	16.06	29	17.69 π	30	5.53	6.11	1.76	1.82	35	1.94	32
*NaH	"	8.02 σ	6.5	25	7.49 σ	36	0.94	2.3	-7.73			-6.96	32
*MgH	"	6.79 σ	6.8	36	7.06 σ	36	2.51	2.3	-3.18			-1.52	32
*AlH	"	8.69 σ	8.4	36	7.84 σ	36	3.34	3.01	-0.90			0.17	32
*SiH	"	7.69 π	8.5	25	7.78 π	36	3.58	3.32	-0.40			0.30	32
*PH	"	10.59 π	9.5	25	10.31 π	36	3.51	3.34	0.86			0.54	32
*SH	"	10.56 π	11.1	25	11.22 π	36	3.04	3.70	0.52			0.86	32
*ClH	$C_{\infty v}$	13.23 π	12.74	25	12.96 π	36	4.04	4.62	0.84	1.12	37	1.20	32
KH	"	7.97 σ					2.14	1.92	-10.01				
CaH	"	5.62 σ					1.43	≤1.70	-4.53				
GaH	"	9.18 σ					3.45	2.69	-1.29				
GeH	"	7.58 π					3.52	3.30	-0.64				
*BrH	"	11.85 π	11.87 π	29			3.85	3.92	0.83	0.83	37		
CH_2 [c]	C_{2v}	11.81 a_1					9.21		2.49				
CH_2 [d]	$D_{\infty h}$	9.44 π_u	10.40	38			6.20	7.76					
*H_2O	C_{2v}	13.40 b_1	12.61 b_1	39	13.22 b_1	23	9.52	10.06	2.10	1.87	40	2.42	23
*H_2S	"	10.36 b_1	10.42 b_1	41	10.48 b_1	42	5.95	7.5	0.75	0.97	43	0.88	23
*H_2Se	"	10.39 b_1	9.88 b_1	44	8.46 b_1	45	5.94	6.6	1.22	0.62	46		
BH_3	D_{3h}	13.45 e'	11.4	47	13.15 e'	48	12.32	12.1					
*GaH_3	"	11.49 e'			10.72 e'	45	7.26						
*NH_3	C_{3v}	12.01 a_1	10.35	49	11.07 a_1	23	13.45	12.93	2.23	1.47	50	2.14	23
*PH_3	"	11.86 a_1	10.20	51	9.99 a_1	52	10.53	10.47	1.48	0.58	53		
*AsH_3	"	11.27 a_1	10.60	54	9.39 a_1	45	10.67	9.1	0.29	0.22	55		
*CH_4	T_d	13.58 t_2	12.99	39	14.78 t_2	23	17.16	18.18					
SiH_4	"	12.21 t_2	12.20	56	13.09 t_2	57	12.75	13.87					
*GeH_4	"	12.18 t_2	12.30	56	12.65 t_2	45	12.05	12.5					
*BeO	$C_{\infty v}$	12.75 π	10.1	66	10.60 π	58	-1.38	4.69	-4.17			-7.35	59
*CO	$C_{\infty v}$	13.83 σ	14.00 σ	60	15.23 σ	58	11.01	11.23	1.25	0.11	61	-0.28	62
*CO_2	$D_{\infty h}$	11.75 π_g	13.79 π_g	63	14.80 π_g	58	14.99	16.86					
*SiO	$C_{\infty v}$	11.71 σ	10.51	25	11.72 σ	58	13.63	8.33	-4.30			-3.68	59
NO	"	9.06 π	9.25	25	9.14 π	64	13.65	6.62	0.27	0.16	65	0.50	64
SO	"	9.73 π					12.79	5.36	-2.07				
*SO_2	C_{2v}	12.37 a_1	12.52 a_1	67	12.68 a_1	42	27.01	11.18	-1.60	1.60	68	-2.17	42
BN	$C_{\infty v}$	10.61 σ			11.67 π	69	5.57	5.09	0.10			1.23	69
CN	"	12.54 σ	14.2	25	6.61 π	69	10.93	7.63	0.11				
*PN	"	12.66 σ			11.87 π	58	13.39	7.11	-4.52			-3.23	59
*LiF	"	12.49 π			12.70 π	58	-5.70	5.94	-3.87	-6.33	70	-6.30	59
*NaF	"	12.59 π			11.32 π	58	4.88	4.95	-6.93	8.16	71	-8.35	71
*KF	"	9.74 π			11.08 π	58	1.98	4.80	-9.24	8.60	71	-8.69	71
CaF	"	5.79 σ					0.29	5.42	-4.16				
*BF	"	11.91 σ			11.03 σ	58	5.64	4.38	2.91			0.88	59
*AlF	"	10.57 σ	9.5	25	9.44 σ	58	12.21	6.82	-2.23	1.53	72	-1.34	59
*GaF	"	11.37 σ			6.88 σ	45	13.89	6.24	-2.12				
SF	"	10.37 π			11.43 π	73	13.40	4.39	-0.45			-1.40	73
SeF	"	10.53 π			10.81 π	73	10.98	≈3.5	-0.42			-2.21	73
ClF	"	13.34 π			13.36 π	71	13.22	2.56	0.05	0.88	71	-1.10	71
*LiCl	"	11.49 π			10.30 π	58	2.29	4.88	-4.40	7.13	71	-7.26	71

Table 3. Continued.

*NaCl	$C_{\infty v}$	11.10 σ			9.41 π	58	5.61	4.24	-7.01	9.00	71	-9.10	71
*KCl	"	10.39 π			8.93 π	58	5.56	4.39	-9.19	10.27	71	-10.46	71
*LiBr	"	10.64 π			9.18 π	58	3.97	4.34	-4.84	7.27	71	-8.98	71
*NaBr	"	10.40 σ			8.55 π	58	6.14	3.79	-7.25			-8.74	71
KBr	"	10.20 σ					6.53	3.93	-8.76				
CH_3F	C_{3v}	11.97 e	12.85 e	76	14.26 e	74	21.29	18.38	-1.57	1.86	75		
CH_3Cl	"	11.18 e	11.42 e	76			21.78	17.15	-2.47	1.87	77		
*CH_3Br	"	10.39 e	10.69 e	76			21.02	16.64	-1.91	1.80	77		
CH_3CN	"	11.31 e	12.22	78			31.32	26.59	-3.21	2.92	79		
HCN	$C_{\infty v}$	13.66 σ	13.91 π	80	13.47 π	58	15.27	13.54	-2.36	2.99	81	-3.29	59
FCN	"	12.66 π			13.56 π	58	18.57	13.53	-1.82	2.17	82	-2.28	59
H_2CO	C_{2v}	9.93 b_2	10.85 b_2	83	11.62 b_2	84	16.64	14.17	-1.58	2.34	85	-2.59	84
H_2O_2	C_2	12.40 b	10.92	86	10.65 b	87	16.61	11.09	2.01	2.26	88	1.16	87
B_2H_6	D_{2h}	10.65 b_{2g}	12.1	66	12.55 b_{2g}	89	34.18	34.85					
C_2H_6	D_{3d}	10.74 e_g	11.49	41	12.94 e_g	90	33.21	30.82					
C_3H_8	C_{2v}	10.03 b_1	11.07	41			47.77	43.56	0.00	0.08	91		
C_2H_4	D_{2h}	10.57 b_{3g}	10.48 b_{3u}	41	10.14 b_{3u}	92	25.33	24.36					
C_2H_3F	C_s	10.39 a"	10.58 a"	93	10.27 a"	92	29.06		1.29	1.43	94	1.85	92
C_2H_3Cl	"	10.42 a"	10.00 a"	95			30.09		2.70	1.44	96		
C_2H_3Br	"	9.93 a"	9.80 a"	97			29.53		2.08	1.41	96		
$C_2H_2F_2$ cis	C_{2v}	9.70 b_1			10.36	98	32.73		-2.46	2.42	99		
$C_2H_2F_2$ trans	D_{2h}	9.73 a_u			10.39	98	32.73						
HCCH	$D_{\infty h}$	12.57 π_u	11.40 π_u	100	11.24 π_u	101	18.46	17.53					
HCCF	$C_{\infty v}$	11.42 π			11.40 π	58	21.84		-0.64	0.73	102	-0.91	59
HCCCl	$C_{\infty v}$	11.56 π			10.66 π	58	22.47		-1.97	0.44	96	-0.42	59
C_6H_6	D_{6h}	9.01 e_{2g}	9.25 e_{1g}	103	10.15 e_{1g}	104	72.64	57.16					
C_6H_5F	C_{2v}	8.82 b_1	9.19	66			76.57	55.3	-1.33	1.66	96		
C_6H_5Cl	"	9.34 b_1	9.35	105			77.65		-5.45	1.75	96		
C_6H_5Br	"	9.10 b_1	8.98	106			77.10		-4.84	1.70	96		
C_6H_5OH	C_s	8.26 a"	8.46	103			80.04	61.60	1.68	1.55	96		
$C_6H_5CH_3$	C_{2v}	8.44 b_1	8.84	103			88.58	69.42	0.42	0.31	96		
$C_6H_5NH_2$	"	7.28 b_1	7.71	103			83.19	64.27	1.38	1.53	96		
HCOOH	C_s	10.02 a'	11.05	106	13.09 a'	71	23.71	20.87	0.72	1.35	96	1.49	71
$HCONH_2$	"	9.47 a'	10.25	66	11.33 a"	71	27.20	23.70	3.58	3.71	96	4.95	71
C_4H_4O	C_{2v}	8.19 a_2	8.89	106			54.48		-0.40	0.66	96		
C_4H_4S	"	8.68 b_1	8.91	103			56.52		-1.46	0.51	96		
CS	$C_{\infty v}$	11.39 σ	11.8	25			11.16	7.19	5.08	1.97	107		
SCO	"	9.77 π	11.27 π	63			17.08	14.42	-0.11	0.71	108	-0.99	59
CS_2	$D_{\infty h}$	8.84 π_g	10.11 π_g	63			18.45	11.98					
SOF_2	C_s	12.51 a'					39.71	14.45	1.26	1.62	96		
SO_4^{-2}	T_d						73.60	20.43					
SF_6	O_h	15.44 t_{1u}	16.00	67			38.39	20.83					

a. The reported binding energies are the negative of those obtained by the definition given in the text.

b. The directions of the experimental dipole moments are often not known. The calculated dipole moments are positive according to the following conventions: $A^-B_n^+$, $A^-H_n^+$, A^-BC^+, $CH_3^-X^+$, $C_6H_5^-X^+$ and $C_4H_4^-X^+$

c. Singlet

d. Triplet

σ-bonds 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 SO_2 are overstabilized by considerable *d*-populations. With the standard parameters the extreme case LiF is predicted to be unstable at the experimental equilibrium distance. The calculated bond distance is almost 1 Å longer than the experimental value. To get better results for LiF the lithium orbitals must be considerably contracted.

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 SH_2, 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 SH_2 to 1.44, 1.54, 2.14, and 2.15 electrons in SO_2, SOF_2, SO_4^{-2}, and SF_6.

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

$$\bar{\mu} = \sum_{k}^{\text{nuc}} Z_k^c \bar{R}_k - 2\sum_i \sum_{\mu,\nu} c_{i\mu}^* c_{i\nu} \int \Phi_\mu^* \bar{r} \Phi_\nu \, \mathrm{d}V$$

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:

$$\bar{\mu} = \sum_{k}^{\text{nuc}} \{(Z_k^c - \sum_{\mu \in k} P_{\mu\mu})\bar{R}_k - 2 \sum_{\substack{\mu<\nu \\ \mu,\nu \in k}} P_{\mu\nu} \int \Phi_\mu^* \bar{r} \Phi_\nu \, \mathrm{d}V\}$$

The same expression is obtained in the case of an open shell with $P_{\mu\nu} = P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta$. 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 hydrids 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 H_2S and H_2Se have smaller dipole moments than H_2O, and that PH_3 and AsH_3 have smaller dipole moments than NH_3 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

systems it is seen that in the molecules with F, OH, NH_2, and CH_3 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 C_α 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 C_β and the opposite effect on C_α. Chlorine on the other hand is mainly π-electron accepting. Compared to the fluorine case it pulls π-electrons from C_β to C_α and itself, and C_β 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 C_α 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.[21] In B_2H_6 the *z*-axis is through the boron atoms and the *y*-axis through the bridge hydrogen atoms. Planar C_{2v} 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 $\sigma^2\sigma^2\pi_\alpha\sigma^2\pi^3{}_{\alpha\beta}\pi_\alpha$ and MgH as $\sigma_\alpha\sigma_\beta\sigma_\alpha$. The orbital order may even be reversed for α- and β-spin, *e.g.* in O_2: $\sigma_g{}^2\sigma_u{}^2\pi_{u\alpha}{}^2\sigma_g{}^2\pi_{u\beta}{}^2\pi_{g\alpha}{}^2$. 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 π-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.

H_2	
σ_g	15.19
Li_2	
σ_g	10.61
B_2	
π_u	10.38
σ_u	11.40
σ_g	20.77
C_2	
π_u	13.32
σ_u	15.29
σ_g	28.66
N_2	
σ_g	14.29
π_u	15.95
σ_u	21.75
σ_g	37.41
O_2	
$(\pi_g)^2$	11.48
$(\pi_u)^2$	15.06
$(\sigma_g)^2$	17.92
$(\pi_u\alpha)^2$	20.25
$(\sigma_u)^2$	28.26
$(\sigma_g)^2$	41.97
F_2	
π_g	16.76
σ_g	17.74
π_u	20.56
σ_u	37.06
σ_g	44.88
LiH	
σ	9.65
BeH	
σ_α	7.88
σ_β	13.03
σ_α	13.87
BH	
σ	10.76
σ	16.88
CH	
$\pi_\alpha{}^2$	10.42
$(\sigma)^2$	12.85
$(\sigma)^2$	21.56
NH	
$(\pi_\alpha)^2$	12.45
$(\sigma)^2$	14.64
$(\sigma)^2$	27.24
OH	
$(\pi)^3$	14.43 $\alpha^2\beta$
$(\sigma)^2$	16.41
$(\sigma)^2$	33.44
FH	
π	16.37
σ	18.31
σ	40.86
NaH	
σ	6.02
MgH	
σ_α	6.79
σ_β	10.39
σ_α	12.02
AlH	
σ	8.69
σ	12.97
SiH	
$\pi_\alpha{}^2$	7.69
$(\sigma)^2$	10.71
$(\sigma)^2$	16.43
PH	
$(\pi_\alpha)^2$	10.59
$(\sigma)^2$	13.10
$(\sigma)^2$	20.05
SH	
$(\pi)^3$	10.56 $\alpha^2\beta$
$(\sigma)^2$	13.10
$(\sigma)^2$	21.23
ClH	
π	13.23
σ	15.67
σ	25.42
KH	
σ	7.97
CaH	
σ_α	5.62
σ_β	8.65
σ_α	10.59
GaH	
σ	9.18
σ	13.88
GeH	
$\pi_\alpha{}^2$	7.58
$(\sigma)^2$	10.76
$(\sigma)^2$	16.70
BrH	
π	11.85
σ	14.49
σ	24.01
CH_2 singlet	
a_1	11.81
b_2	13.90
a_1	23.26
CH_2 triplet	
$(\pi_u)^2$	9.44
$(\sigma_u)^2$	15.63
$(\sigma_g)^2$	22.76
H_2O	
b_1	13.40
a_1	14.65
b_2	16.27
a_1	34.62
H_2S	
b_1	10.36
a_1	12.62
b_2	13.37
a_1	21.99
H_2Se	
b_1	10.39
a_1	12.43
b_2	13.53
a_1	19.00
BH_3	
e'	13.45
a_1'	19.95
GaH_3	
e'	11.49
a_1'	16.02
NH_3	
a_1	12.01
e	14.88
a_1	30.55
PH_3	
a_1	11.86
e	13.14
a_1	21.20
AsH_3	
a_1	11.27
e	12.52
a_1	20.38
CH_4	
t_2	13.58
a_1	25.93
SiH_4	
t_2	12.21
a_1	18.78
GeH_4	
t_2	12.18
a_1	18.85
BeO	
π	12.75
σ	13.21
σ	33.88
CO	
σ	13.83
π	16.73
σ	20.96
π	39.54
CO_2	
π_g	11.75
σ_u	15.44
π_u	20.02
σ_g	20.48
σ_u	38.08
σ_g	39.45
SiO	
σ	11.67
π	14.84
σ	17.08
σ	35.83
NO	
$\pi_\sigma{}^3$	9.06
$(\pi)^3$	15.60 $\alpha\beta^2$
$(\sigma)^2$	16.22
π_α	19.94
$(\sigma)^2$	24.38
$(\sigma)^2$	40.59
SO	
$(\pi_\alpha)^2$	9.73
$(\pi_\beta)^2$	14.06
$(\sigma)^2$	14.19
$(\pi_\alpha)^2$	16.44
$(\sigma)^2$	21.27
$(\sigma)^2$	35.81
SO_2	
a_1	12.37
b_2	13.30
a_2	14.25
b_1	16.37
b_2	16.51
a_1	18.11
a_1	21.99
b_2	36.08
a_1	37.39
BN	
σ_σ	10.61
$(\pi)^3$	14.01 $\alpha^2\beta$
σ_β	14.35
σ_α	16.36
σ_α	31.14
σ_β	31.28
CN	
σ_σ	12.54
$(\pi)^4$	14.72
σ_β	17.00
σ_α	18.98
σ_α	33.41
σ_β	33.64
PN	
σ	12.66
π	13.73
σ	19.17
σ	31.09

Table 4. Continued.

LiF	
π	12.49
σ	13.21
σ	36.81
NaF	
π	12.59
σ	13.23
σ	36.86
KF	
π	9.74
σ	10.52
σ	33.57
CaF	
σ_α	5.78
$(\pi)^4$	13.47
σ_β	14.10
σ_α	14.20
σ_β	38.11
σ_α	38.16
BF	
σ	11.90
π	19.32
σ	21.01
σ	45.54
AlF	
σ	10.57
π	15.45
σ	16.30
σ	39.97
GaF	
σ	11.37
π	16.62
σ	17.73
σ	41.72
SF	
$(\pi)^3$	10.37 $\alpha^2\beta$
$(\sigma)^2$	16.38
π_β	17.61
$(\pi)^3$	18.55 $\alpha^2\beta$
$(\sigma)^2$	22.20
$(\sigma)^2$	42.42
SeF	
$(\pi)^3$	10.53 $\alpha^2\beta$
$(\sigma)^2$	15.29
π_β	17.37
$(\pi)^3$	18.23 $\alpha^2\beta$
$(\sigma)^2$	19.79
$(\sigma)^2$	41.84
LiCl	
π	11.49
σ	11.57
σ	23.61

NaCl	
σ	11.10
π	11.16
σ	22.95
KCl	
π	10.39
σ	10.44
σ	22.28
LiBr	
π	10.64
σ	10.82
σ	22.88
NaBr	
σ	10.40
π	10.46
σ	22.34
KBr	
σ	10.20
π	10.24
σ	22.36
CH_3F	
e	11.97
a_1	15.80
e	18.68
a_1	24.99
a_1	41.86
CH_3Cl	
e	11.18
a_1	13.41
e	16.08
a_1	22.53
a_1	28.25
CH_3Br	
e	10.39
a_1	12.69
e	15.68
a_1	21.92
a_1	27.59
CH_3CN	
e	11.31
a_1	12.34
e	17.06
a_1	17.67
a_1	28.57
a_1	33.07
HCN	
σ	13.66
π	14.03
σ	20.88
σ	33.01

FCN	
π	12.66
σ	14.96
π	20.86
σ	21.75
σ	33.47
σ	45.13
H_2CO	
b_2	9.93
b_1	13.94
a_1	15.05
b_2	19.20
a_1	22.85
a_1	37.68
H_2O_2	
b	12.40
a	12.88
a	14.24
a	17.40
b	18.20
b	29.65
a	39.18
B_2H_6	
b_{2g}	10.65
a_g	12.78
b_{2u}	14.87
b_{3u}	15.71
b_{1u}	17.63
a_g	27.28
C_2H_6	
e_g	10.73
a_{1g}	12.17
e_u	16.58
a_{2u}	21.75
a_{1g}	30.21
C_3H_8	
b_1	10.03
b_2	10.28
a_1	10.42
a_2	13.05
b_2	14.27
a_1	16.54
b_1	18.24
a_1	21.32
b_2	25.88
a_1	32.80
C_2H_4	
b_{3g}	10.57
b_{3u}	11.25
a_g	12.99
b_{2u}	18.13
b_{1u}	20.88
a_g	29.89

C_2H_3F	
a''	10.39
a'	11.37
a'	12.87
a'	16.65
a''	18.20
a'	19.60
a'	21.95
a'	29.55
a'	42.90
C_2H_3Cl	
a''	10.42
a'	11.06
a'	11.50
a''	14.53
a'	14.65
a'	18.28
a'	21.34
a'	25.17
a'	31.58
C_2H_3Br	
a''	9.93
a'	10.40
a'	10.93
a''	13.71
a'	14.15
a'	17.96
a'	21.06
a'	24.16
a'	31.11
$C_2H_2F_2$	
b_1	9.69
a_1	11.58
b_2	13.04
b_2	16.78
a_2	17.25
a_1	17.98
b_1	19.65
a_1	21.47
b_2	21.91
a_1	29.28
b_2	42.19
a_1	44.28
$C_2H_2F_2$	
a_u	9.73
a_g	11.13
a_g	14.83
b_u	14.95
b_g	17.44
a_g	19.37
a_u	19.72
b_u	19.94
b_u	23.14
a_g	28.81
a_g	43.32
b_u	43.57

HCCH	
π_u	12.57
σ_g	14.40
σ_u	20.44
σ_g	28.67
HCCF	
π	11.42
σ	15.95
π	19.97
σ	20.88
σ	28.89
σ	44.31
HCCCl	
π	11.56
σ	14.44
π	15.90
σ	19.69
σ	26.21
σ	30.43
C_6H_6	
e_{2g}	9.01
e_{1g}	9.41
e_{1u}	13.08
b_{1u}	14.47
b_{2u}	14.59
a_{2u}	17.31
a_{1g}	21.32
e_{2g}	22.82
e_{1u}	29.16
a_{1g}	39.10
C_6H_5F	
b_1	8.82
b_2	8.98
a_2	9.84
a_1	9.95
b_2	13.14
b_2	13.40
a_1	13.91
a_1	15.63
b_1	15.65
b_2	17.73
b_1	19.58
a_1	21.05
a_1	22.79
b_2	23.98
a_1	28.33
b_2	29.67
a_1	39.10
a_1	43.52

C_6H_5Cl	
b_1	9.34
b_2	9.55
a_1	9.64
a_2	10.21
b_2	11.39
b_1	12.76
a_1	13.36
b_2	13.83
a_1	15.00
b_2	16.04
b_1	18.49
a_1	20.07
a_1	22.84
b_2	23.96
a_1	25.39
b_2	30.07
a_1	30.55
a_1	39.90
C_6H_5Br	
b_1	9.10
a_1	9.35
b_2	9.39
a_2	10.13
b_2	10.66
b_1	11.93
a_1	13.12
b_2	13.75
a_1	14.84
b_2	15.75
b_1	18.29
a_1	19.91
a_1	22.69
b_2	23.79
a_1	24.67
b_2	29.96
a_1	30.11
a_1	39.79
C_6H_5OH	
a''	8.26
a'	8.83
a'	9.50
a''	9.62
a'	12.66
a'	13.16
a'	13.40
a''	14.19
a'	14.83
a'	17.18
a''	18.52
a'	20.22
a'	22.42
a'	23.76
a'	27.66
a'	29.45
a'	37.51
a'	40.18

Table 4. Continued.

$C_6H_5CH_3$	
b_1	8.44
a_1	8.68
b_2	8.73
a_2	9.37
b_2	11.92
a_1	12.41
b_2	13.01
b_1	14.07
a_1	14.22
b_2	16.01
b_1	18.18
a_1	19.13
a_1	22.09
b_2	23.37
a_1	25.71
b_2	29.25
a_1	31.71
a_1	39.29

$C_6H_5NH_2$	
b_1	7.28
b_2	8.66
a_1	9.13
a_2	9.43
b_2	12.54
b_1	12.82
b_2	12.94
a_1	12.95
a_1	14.56
b_2	17.02
b_1	18.08
a_1	19.79
a_1	22.18
b_2	23.62
a_1	26.82
b_2	29.23
a_1	34.71
a_1	39.48

HCOOH	
a'	10.29
a''	11.38
a'	12.86
a'	17.06
a''	17.51
a'	18.98
a'	22.95
a'	35.55
a'	40.14

$HCONH_2$	
a'	9.47
a''	9.54
a'	12.59
a'	15.85
a''	16.12
a'	18.99
a'	22.18
a'	32.76
a'	37.76

C_4H_4O	
a_2	8.19
b_1	10.42
b_2	10.89
a_1	11.22
a_1	11.62
b_2	12.69
b_1	18.98
a_1	20.51
a_1	20.83
b_2	21.06
b_2	26.92
a_1	31.17
a_1	43.97

C_4H_4S	
b_1	8.68
a_2	9.21
a_1	9.48
b_2	10.72
b_2	11.71
a_1	12.15
b_1	16.64
a_1	18.64
b_2	19.44
a_1	20.66
a_1	25.26
b_2	27.47
a_1	37.09

CS	
σ	11.39
π	12.31
σ	18.34
σ	26.19

SCO	
π	9.76
σ	14.33
π	18.76
σ	19.74
σ	26.41
σ	40.08

CS_2	
π_g	8.84
σ_u	12.67
π_u	15.26
σ_g	17.53
σ_u	23.80
σ_g	28.32

SOF_2	
a''	12.51
a''	14.12
a''	14.47
a''	16.19
a'	17.20
a''	18.28
a''	20.09
a'	20.13
a'	20.34
a'	23.75
a'	37.07
a''	42.67
a'	43.41

SF_6	
t_{1u}	15.44
t_{1g}	16.73
t_{2u}	17.37
e_g	17.65
t_{1u}	22.57
t_{2g}	23.33
a_{1g}	25.88
e_g	43.28
t_{1u}	43.75
a_{1g}	46.59

SO_4^{2-}	
t_1	+6.65
t_2	+4.84
e	+0.94
t_2	+0.07
a_1	-2.90
t_2	-16.67
a_1	-19.03

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 [13] 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}:

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

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:

$$\beta_{\mu\nu} = -\tfrac{1}{2}S_{\mu\nu}\{k_A I_\mu + k_B I_\nu\},\ \mu \in A,\ \nu \in B \tag{28}$$

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 α would be too complicated in our case, unless a single α-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.

Molecule	Symmetry	Geometrical parameter Å and degr.	Calc.	Exptl.	Ref.	Dipole moment D Calc.	Exptl.	Ref.
H_2O	C_{2v}	R(O–H)	1.07	0.957	18	2.06	1.87	40
		∠HOH	102°	104°31′	18			
H_2S	C_{2v}	R(S–H)	1.43	1.336	18	0.68	0.97	43
		∠HSH	93°	92°13′	18			
H_2Se	C_{2v}	R(Se–H)	1.50	1.460	18	1.32	0.62	46
		∠HSeH	95°	90°55′	18			
BH_3	D_{3h}	R(B–H)	1.31	1.18	3			
GaH_3	D_{3h}	R(Ga–H)	1.64	1.551	45			
CH_4	T_d	R(C–H)	1.20	1.0934	18			
SiH_4	T_d	R(Si–H)	1.54	1.4798	18			
GeH_4	T_d	R(Ge–H)	1.60	1.527	18			
SO_2	C_{2v}	R(S–O)	1.46	1.4321	18	−0.72	1.60	68
		∠OSO	136°	119°21′	18			
BN	$C_{\infty v}$	R(B–N)	1.49	1.281	18	0.17		
CN	$C_{\infty v}$	R(C–N)	1.27	1.172	18	0.04		
KBr	$C_{\infty v}$	R(K–Br)	2.81	2.821	18	−8.71		
CH_3F	C_{3v}	R(C–F)	1.41	1.385	18	−1.62	1.86	75
CH_3Cl	C_{3v}	R(C–Cl)	1.68	1.782	18	−3.00	1.87	77
CH_3Br	C_{3v}	R(C–Br)	1.79	1.938	18	−2.41	1.80	77
H_2CO	C_{2v}	R(C–O)	1.33	1.210	18	−2.11	2.34	85
		R(C–H)	1.20	1.102	18			
		∠HCH	118°	121°6′	18			
C_2H_6	D_{3d}	R(C–C)	1.61	1.534	110			
HCCH	$D_{\infty h}$	R(C–C)	1.32	1.204	110			
		R(C–H)	1.18	1.058	110			
HCCF	$C_{\infty v}$	R(C–F)	1.38			−1.12	0.73	102
HCC Cl	$C_{\infty v}$	R(C–Cl)	1.66	1.68	109	−2.04	0.44	96

one geometrical parameter has been varied while the others have been kept fixed. The experimental distances of BH_3 and GaH_3 are only assumed values. The dipole moment is the property which is most sensitive to geometrical variations. In SO_2, 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 H_2CO, 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 [22] and Fischer and Kollmar [13] 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.

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

Molecule	Calc.	Exptl.	Ref.
C_2H_6[a]	1.53	2.875	111
C_2H_6[b]	1.17		
H_2NCOH[c]	15.94	18 ± 3	112
HCOOH	4.89 *cis*[e]	13.4	113
	3.14 *trans*[e]	Ref.[g]	
H_2O_2[d]	5.21	7.0 *cis*[f]	114
		1.1 *trans*[f]	114

[a] Experimental geometry. [b] R(C—C) calculated equilibrium distance. [c] Rotation of NH_2 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, SH_2, BN, and CO are in good agreement with experimental data, while SO_2, 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. SO_2 differs from SH_2 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,

$$\beta_{\mu\nu} = \tfrac{1}{2} S_{\mu\nu}(\beta_A + \beta_B) \tag{17}$$

does not take into account the energies of the orbitals involved. Santry and Segal [4] 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.

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

The k's were optimized with respect to the binding energies in H_2, SH, SH_2, SO_2, BN, CN, CO, and NO. The k's obtained were also tested on CS and C_2H_4. 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

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

Molecule	Binding energy eV			Dipole moment D			Ionization potential eV		
	I	II	exptl.	I	II	exptl.	I	II	exptl.
H_2	4.75	2.67	4.75				16.13 σ_g	15.19 σ_g	15.43
SH	3.81	3.04	3.70	1.83	0.52		10.47 π	10.56 π	11.1
SH_2	7.53	5.95	7.5	2.29	0.75	0.97	10.18 b_1	10.36 b_1	10.42 b_1
SO_2	12.02	27.01	11.18	−1.66	−1.60	1.60	10.86 a_2	12.37 a_1	12.52 a_1
BN	4.97	5.57	5.09	1.54	0.10		10.27 σ	10.61 σ	
CN	6.95	10.93	7.63	0.65	0.11		11.78 σ	12.54 σ	14.2
CO	8.28	11.01	11.23	1.03	1.25	0.11	13.14 σ	13.83 σ	14.00 σ
NO	6.74	13.65	6.62	−0.04	0.27	0.16	10.79 π	9.06 π	9.25
CS	9.83	11.16	7.19	2.41	5.08	1.97	11.03 σ	11.39 σ	11.8
C_2H_4	35.63	25.33	24.36				10.56 b_{3u}	10.57 b_{3g}	10.48 b_{3u}
							10.59 b_{3g}	11.25 b_{3u}	12.50

I $\beta_{\mu\nu}=\frac{1}{2}S_{\mu\nu}\ (k_A I_\mu + k_B I_\nu)$
II $\beta_{\mu\nu}=\frac{1}{2}S_{\mu\nu}\ (\beta_A + \beta_B)$
$k_H = 0.654$, $k_B = 1.21$, $k_C = 1.16$, $k_N = 1.04$, $k_O = 1.21$, and $k_S = 0.92$

and SH_2 the polarities increase and the *pd* dipoles decrease leading to very big dipole moments. In SO_2 the a_2 orbital is destabilized compared to the standard calculation by having less *d*-character. The π-orbital (b_{3u}) in ethylene gets a higher energy as the bonding parameter between the *p*-orbitals is less negative now. But the highest σ-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 "β_A" for *s*-functions. To get the right orbital order in conjugated systems Del Bene and Jaffe [7] had separate bonding parameters for σ- and π-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 3*d* 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, SH_2, SO_2, CS, SOF_2, and SF_6 as test molecules. With the standard parameters the binding energies in SO_2, SOF_2, and SF_6 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 3*d*-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 3*p*-orbital, gave the biggest stabilization. In fact, in the extreme cases SOF_2 and SF_6, 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 SO_2, SOF_2, and SF_6 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, SH_2, SO_2, CS, and SOF_2, 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 SH_2. The conclusion is that the standard parameters, though SO_2, SOF_2, and SF_6 are overstabilized, 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 [23] 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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