An SCF–MO–CNDO Study of Equilibrium Geometries, Force Constants, and Bonding Energies: CNDO/BW. Part I. Parameterization

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The semiempirical, SCF–MO theory, using the approximation of CNDO is parameterized for the prediction of potential surfaces for both open and closed shell molecules and ions. It is designated CNDO/BW. Empirical examination of the importance of core repulsion leads to the introduction of an expression for the core repulsion energy which results in the simultaneous prediction of relatively good equilibrium geometries and bonding energies for a variety of molecules. The importance of several of the CNDO parameters is examined in this context.

WITHIN the CNDO approximation,[1] the total energy of a molecule is given by (1) where N_{AB} is the repulsion

$$E_{\text{total}} = E_e + \sum_{A<B} N_{AB} \qquad (1)$$

energy between the cores A and B and E_e is the electronic energy of the valence electrons for a closed shell molecule with a single determinant wavefunction (2) in which

$$E_e = \sum_i^{\text{occ}} \varepsilon_i + \tfrac{1}{2} \sum_{k,l} P_{kl} H_{kl} \qquad (2)$$

ε_i is the orbital energy of the i^{th} MO, P_{kl} is the matrix element of the population matrix and H_{kl} is the matrix element of the one-electron core Hamiltonian operator in the CNDO approximation.[1,2] For open shells with an unrestricted wavefunction[3,4] the valence-shell electronic energy is (3) where ε_i^{α} and ε_i^{β} are the orbital

$$E_e = \tfrac{1}{2} \sum_{i=1}^{p} \varepsilon_i^{\alpha} + \tfrac{1}{2} \sum_{i=1}^{q} \varepsilon_i^{\beta} + \tfrac{1}{2} \sum_{k,l} P_{kl} H_{kl} \qquad (3)$$

energies of the i^{th} MO's associated with the electrons of α and β spins respectively.[5]

Although the total energy is sufficient for determining the relative energies of different nuclear configurations or electronic states, a chemically more interesting quantity is the bonding energy,[6] expressed as (4) where $E_e(A)$ is

$$E_{\text{bond}} = \sum_A E_e(A) - E_{\text{total}} \qquad (4)$$

the valence-shell electronic energy of atom A in the CNDO approximation, evaluated with the same parameters as the total energy.[6]

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The potential-energy curve of a diatomic molecule is determined by the attractive and repulsive contributions of E_e and N_{AB}, respectively. With a polyatomic molecule, the potential-energy curve becomes a surface because the total energy depends on the various bond lengths and bond angles. The equilibrium geometry is that set of bond lengths and angles for which E_{total} is a minimum or equivalently E_{bond} is a maximum.

There are three chemically interesting properties associated with the minimum of a potential surface: the equilibrium geometry, the bonding energy, and the force constants, which define the curvatures of the potential surface at the minimum. In order to estimate the intervening parts of the potential surface, all these quantities must be correctly estimated.

Two distinct approaches have been followed in parameterizing the SCF–MO–CNDO theory. Pople–Segal [2-4] attempt to reproduce the results of accurate minimal basis set SCF calculations, whereas Sichel–Whitehead [6,7] placed the emphasis upon agreement with experiment.

The CNDO/2 method of Pople and Segal gives reasonably good estimates for molecular geometries but is unsatisfactory for calculating bonding energies and force constants; the calculated stretching force constants of most bonds are double the observed values.[4,8]

The Sichel–Whitehead CNDO/SW calculations used the experimental equilibrium geometry as imput to the calculation and gave relatively good bonding energies for a variety of molecules.[6,9] However, the method cannot calculate geometries, since minimization of the total energy with respect to the molecular geometry leads to very small bond lengths.

Bonding energies, bond lengths and force constants for a typical example, CO, calculated by these methods are compared with experiment in Table 1. The less approximate INDO method [4] results are not significantly better than the CNDO/2 results. The CNDO/SW method is better for bonds involving very electronegative elements than for bonds between weakly electronegative elements; the bond lengths of F_2 and HF are predicted to be 0·487 and 0·495 Å respectively, still far below the experimental values of 1·418 and 0·917 Å respectively. The CNDO/SW results are not significantly altered by use of the refined bonding parameters.[9]

TABLE 1

Bonding energies, bond lengths, and force constants for CO

	CNDO/2 [a]	INDO [a]	CNDO/SW [b]	Found
E_{bond}/eV	22·17	19·82	47·672	11·225
r_e/Å	1·191	1·196	$<0·001$	1·128
k_{CO}/mdyne Å^{-1}	41·3	40·5		19·0

[a] From ref. 4. [b] Minimization results with Ohno's γ_{AB} and $Z_H{}'$ 1·2. E_{bond} is 10·986 eV at r_e 1·128 Å (ref. 9).

Fischer and Kollmar [10] have introduced modifications for the core Hamiltonian matrix elements of the CNDO/2 method, and optimized the empirical parameters for a large sample of hydrocarbon molecules, to give improved bonding energies and geometries, but the stretching force constants are much too large.

Other studies adjust one or two of the empirical parameters in the CNDO/2 method to give better geometries for a particular bond length [11] or class of molecules.[12] However a general scheme to calculate good potential surfaces by the SCF–MO–CNDO theory for a variety of molecules has not been reported, although a recent theory for ethylene alone, is promising.[13] The present method is developed emphasizing the interatomic parameters of the SCF–MO–CNDO theory, and is parameterized using a minimum number of molecules, so as to be applicable to a wide range of molecular structures.

Interatomic Electron Repulsion and Core Attraction Integrals.—Previous studies [6] showed that the Ohno [14] and Mataga [15] empirical formulae for interatomic electron repulsion integrals, γ_{AB}, lead to better results for molecular properties than theoretical integrals between valence-shell Slater *s* orbitals. Theoretical γ_{AB} in which the Slater exponent is modified so that the one-centre repulsion integrals agree with semiempirical values, have been used in π electron calculations [16,17] implying that the effects of correlation and reorganization of the σ electrons may be accounted for by using effective atomic orbitals, which are more diffuse than Slater atomic orbitals.[18] The γ_{AB} values so obtained are almost identical to those from Ohno's formula for two carbon π orbitals.[19] The Mataga formula has been justified on the basis that γ_{AB} values from it agree with those obtained using the Saturno operator [20] whereas the Ohno values are larger.[21] One-centre integrals calculated with the Saturno operator approximation are lower than the semiempirical values evaluated from valence-state data [22] and, therefore, the two-centre repulsion integrals may be similarly underestimated. Consequently, γ_{AB} is evaluated from the Ohno expression, according to equation (5) where R_{AB} is the internuclear separation and $\gamma_{AA}{}^*$ and $\gamma_{BB}{}^*$ are the atomic limits [6] chosen

$$\gamma_{AB} = (R_{AB}{}^2 + a^2)^{-\frac{1}{2}},\ a = 2/(\gamma_{AA}{}^* + \gamma_{BB}{}^*) \qquad (5)$$

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to be consistent with the evaluation of the average one-centre repulsion integral[7]. The γ_{AA}^* evaluated from Hartree–Fock valence states[23] are given in Table 2 with the average one-centre repulsion integrals γ_{AA}. The corresponding core integrals are given in Table 3. Atomic parameters evaluated from Hinze and Jaffé valence-state data have been reported previously.[7]

TABLE 2

Mean electron repulsion integrals (eV)

Element	Hartree–Fock γ_{AA}	 γ_{AA}^*
C	10·017	10·221
N	11·472	11·802
O	13·663	14·009
F	15·442	15·826
Si	7·006	7·159
P	7·884	8·085
S	8·962	9·185
Cl	9·999	10·243

TABLE 3

Core integrals (eV)

Element	Hartree-Fock U_{ss}	 U_{pp}
C	−49·077	−39·246
N	−71·235	−57·409
O	−101·072	−82·421
F	−133·269	−109·495
Si	−35·957	−28·067
P	−50·589	−40·287
S	−68·245	−55·363
Cl	−88·135	−72·552

The interatomic electron-core attraction integral, V_{AB}, is evaluated from equation (6) so that penetration

$$V_{AB} = Z_B\gamma_{AB} \qquad (6)$$

terms are neglected[3].

Core Repulsion Energy.—If the atomic cores, Z_A and Z_B of atoms A and B, are assumed to be point charges, or nonpolarizable nonpenetrating spherical charge distributions, then the core repulsion energy is the classical electrostatic repulsion between point charges, given by equation (7). If penetration integrals are neglected,

$$N_{AB} = Z_AZ_B/R_{AB} \qquad (7)$$

this approximation leads to a net electrostatic repulsion between two neutral atoms in the CNDO approximation.

The simplest alternative is to assume that the net electrostatic interaction between two neutral atoms vanishes as in equation (8) where γ_{AB} is the two-centre electron repulsion integral discussed above.

$$N_{AB} = Z_AZ_B\gamma_{AB} \qquad (8)$$

Extensive calculations[24] on a variety of molecules within the framework of the CNDO/SW method showed that neither approximation is satisfactory for the calculation of good potential surfaces due to underestimation of N_{AB} at short R_{AB} by equation (8) and overestimation by equation (7). A suitable form would be intermediate between the above approximations, equation (9), where λ_{AB} is a new empirical parameter.

$$N_{AB} = \lambda_{AB}\,(Z_AZ_B/R_{AB}) + (1 - \lambda_{AB})\,Z_AZ_B\gamma_{AB} \qquad (9)$$

General observations[24] are illustrated by the potential energy curves for CO with N_{AB} calculated from equations (7)—(9) which are compared with the empirical Morse potential[25] in Figure 1. The atomic parameters are evaluated from Hinze and Jaffé valence states,[7] γ_{AB} from equation (5), and V_{AB} from equation (6) in each calculation.

The inadequacy of equation (8) is apparent from Table 1. The point-charge approximation (7) is somewhat better, as shown in Figure 1, where the bonding parameter β_{CO} has been adjusted so that the calculated bonding energy agrees with experiment at the experimental r_e, but the calculated force constant of 36·7 mdyne Å^{-1} is too high. If β_{CO} is increased to give the correct C–O bond length, both the bonding energy and force constant are seriously overestimated. Better results are obtained with N_{AB} evaluated from equation (9) with β_{CO} and λ_{CO} chosen to give the experimental E_{bond} at r_e. The calculated curve with β_{CO} 24·808 and λ_{CO} 0·3738 compares very well in the bonding region with the Morse curve which is a satisfactory representation of the experimental curve near the minimum.[26] The relatively good value of 22·6 mdyn Å^{-1} for the force constant suggests this should be a useful procedure for calculating potential energy surfaces. However at large internuclear separations, equation (9) leads to

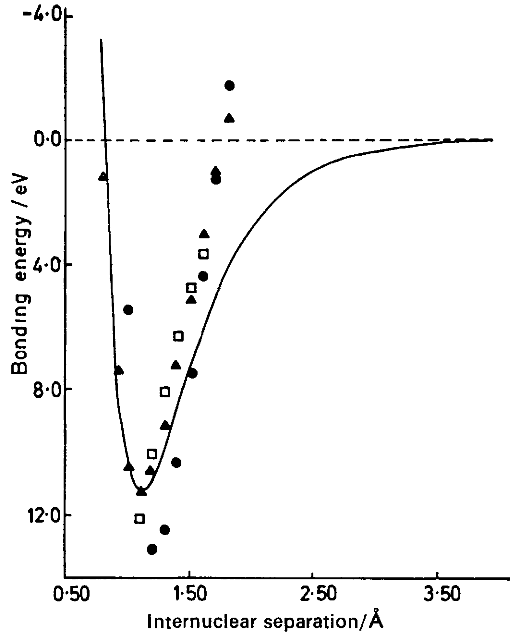

FIGURE 1 Calculated and Morse potentials of CO; Full circles $N_{AB} = Z_AZ_B/R_{AB}$; open squares $N_{AB} = Z_AZ_B\gamma_{AB}$; and closed triangles $N_{AB} = \lambda_{AB}(Z_AZ_B/R_{AB}) + (1 - \lambda_{AB})Z_AZ_B\gamma_{AB}$

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excessive repulsions which result in large bond lengths and angles for polyatomic molecules.

In order to obtain better results it is necessary to modify equation (9) so as to reduce long range interactions by making λ_{AB} dependent on R_{AB} so that, at large R_{AB}, N_{AB} approaches the electron repulsion approximation in equation (8) and all long range interactions between neutral atoms vanish. In order to avoid short bond lengths, N_{AB} should approach the point-charge repulsion energy at very short R_{AB}. At the time that a suitable functional form for λ_{AB} was being considered, Dewar and Haselbach [27] reported the results of a semiempirical method based on the INDO approximation [28] in which the core repulsion energy is evaluated from on expression equivalent to equation (9) with

$$\lambda_{AB} = e^{-\alpha_{AB}R_{AB}} \qquad (10)$$

The potential energy curve for CO with α_{CO} 2·3313 and β_{CO} 11·9081 eV is compared in Figure 2 with the constant λ_{CO} results discussed above. The result at large R_{CO} is much better, with *ca.* 75% of the excess repulsion energy at 1·6 Å being eliminated. The calculated force constant of 19·9 mdyn $Å^{-1}$ is in good agreement with the experimental value of 19·0 mdyn $Å^{-1}$. Equation (10) leads to a significant improvement for polyatomics. This improvement has been achieved without any increase in the number of empirical parameters. In view of the results of Dewar and Haselbach [27] and the above observations, the core repulsion energy is calculated in this work from equations (9) and (10).

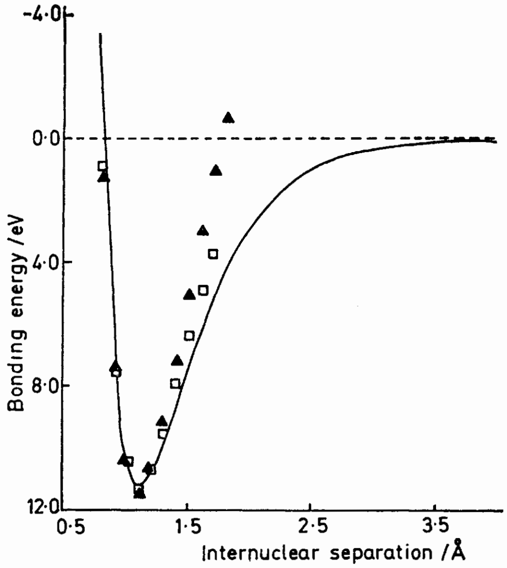

FIGURE 2 Comparison of λ_{AB} = constant (closed triangles) with $\lambda_{AB} = e^{-\alpha_{AB}R_{AB}}$ (open squares) for the potential of CO. The Morse potential is shown as a full line

Evaluation of the Bonding and Core Repulsion Parameters.—For each pair of interacting atoms A and B, there are two molecular parameters, α_{AB} and β_{AB}, which depend only on the nature of the two atoms. These parameters are chosen to give the correct bond length of an AB bond and bonding energy of a molecule containing one or more such AB bonds. The molecules for which the most accurate information is available are used. Wherever possible diatomic molecules are used.

Previous SCF–MO–CNDO calculations [6] have considered the effect of using different orbital exponents for hydrogen and different methods for evaluating γ_{AB}. In this work comparative calculations are made to determine the effect of including valence-state ionization potentials in the evaluation of the resonance integrals. Hence calculations are made using equations (11) and (12).

$$H_{kl} = -\beta_{AB}S_{kl} \qquad (11)$$

$$H_{kl} = -\beta_{AB}'(I_k + I_l)S_{kl} \qquad (12)$$

The effect of the atomic parameters on calculated properties is also considered. Calculations with atomic parameters evaluated from Hinze and Jaffé valence states [7] are compared with calculations based on atomic parameters evaluated from Hartree–Fock valence states.[23] The valence-state ionization potentials used in equation (12) are given in Table 4 for the two sets of valence-state data.

The bonding and core repulsion parameters for H–H interactions are evaluated for H_2. With an exponent of 1·0 for the hydrogen 1*s* orbital, the experimental bonding energy of 4·751 eV and equilibrium bond length of 0·7413 Å are predicted correctly if α 2·3844 and β_{HH} 4·8524 eV. The effect of varying the orbital exponent Z_H' through the range of values commonly used in semiempirical calculations [24] showed that better results are obtained with the theoretical value of 1·0 for Z_H' than with the higher values commonly used. The calculated force constant of 6·4 mdyn $Å^{-1}$ and ionization potential of 16·18 eV agree well with the experimental values of 5·7 mdyn $Å^{-1}$ and 15·98 eV respectively. The CNDO/2 method with Z_H' 1·20 gives 20·82 eV for the ionization potential and 10·4 mdyn $Å^{-1}$ for the force constant and the Fischer–Kollmar refinement of the CNDO/2 method gives k_{HH} 9·5 mdyn $Å^{-1}$ with Z_H' 1·16. The results obtained in the present work are, therefore, relatively good.

TABLE 4

Valence-state ionization potentials (eV)

Element	Valence state	Hartree–Fock		Hinze and Jaffé	
		I_s	I_p	I_s	I_p
H	s			13·595	
B	spp			14·912	8·421
C	$sppp$	20·013	9·953	21·012	11·273
N	s^2ppp	24·213	13·069	25·588	13·946
O	$s^2p^2p\mathbf{p}$	31·812	16·443	32·297	17·274
F	$s^2p^2p^2\mathbf{p}$	40·095	19·937	39·391	20·862
Si	$sppp$	15·968	7·521	17·307	9·190
P	s^2ppp	18·123	9·466	18·612	10·733
S	$s^2p^2p\mathbf{p}$	22·751	11·821	21·135	12·396
Cl	$s^2p^2p^2\mathbf{p}$	27·770	14·374	25·227	15·037
Br	$s^2p^2p^2\mathbf{p}$			23·735	13·101
I	$s^2p^2p^2\mathbf{p}$			20·833	12·670

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The above observations for H_2 are not changed if H_{kl} is evaluated from equation (12). The bonding parameters are related by equation (13) where I_s is the valence-state ionization potential of the hydrogen 1*s*

$$\beta_{HH}' = \frac{\beta_{HH}}{2I_s} \qquad (13)$$

orbital, and the core repulsion parameters are identical. This is true for H_2 since the basis set consists of 1*s* orbitals only. In general, the basis set consists of valence shell *s* and *p* orbitals which have different VSIP values and, therefore, β_{AB} and β_{AB}' are not related by a simple transformation.

Interatomic bonding parameters * and core repulsion parameters for many atom pairs are listed in Tables 5 and (6) respectively. The data used to evaluate the parameters are contained in Parts II and III. An orbital exponent of 1·0 for the hydrogen 1*s* orbital has been used for all calculations involving hydrogen.

Table 5

Interatomic bonding parameters [a] β

	Parameter set			
Atomic parameters	(I) Hinze–Jaffé	(II) Hartree–Fock	(III) Hinze–Jaffé	(IV) Hartree–Fock
Resonance integrals	Eqn. (12)	Eqn. (12)	Eqn. (11)	Eqn. (11)
Interaction	β_{AB}'		β_{AB}	
H–H	0·1785	0·1785	4·8524	4·8524
H–B	0·2298		5·6410	
H–C	0·2619	0·2717	7·3991	7·3824
H–N	0·2519	0·2694	7·1976	7·4831
H–O	0·2974	0·3220	9·8721	10·3629
H–F	0·3276	0·3746	12·8798	14·1823
H–Si	0·2194	0·2299	5·5035	5·4655
H–P	0·2488	0·2348	6·2843	5·5872
H–S	0·2491	0·2565	6·7560	6·7730
H–Cl	0·2741	0·2900	8·2425	8·4952
H–Br	0·2566		7·1329	
H–I	0·2765		7·4005	
B–B	0·3478		6·9957	
B–F	0·3430		12·1506	
C–C	0·3510	0·4025	9·6295	9·9158
C–N	0·3269	0·3745	9·6170	10·0735
C–O	0·3735	0·4075	11·9081	12·0627
C–S	0·3899	0·4157	9·8821	9·7059
N–N	0·3166	0·3524	9·5896	9·9593
N–O	0·3483	0·3767	11·4812	11·7046
O–O	0·5360	0·5732	17·2597	17·3807
O–S	0·4423	0·4719	13·5001	13·6999
F–F	0·5399	0·5462	17·4031	18·1766
F–Cl	0·5250	0·6274	16·0521	16·5577
F–Br	0·5014		15·0796	
F–I	0·5229		15·9541	
S–S	0·4187	0·4363	10·3386	10·1342
Cl–Cl	0·4674	0·4803	12·0979	11·5893
Cl–Br	0·4805		12·4191	
Cl–I	0·4416		10·6447	
Br–Br	0·4893		9·9051	
Br–I	0·4886		9·8086	
I–I	0·4475		9·1744	

[a] Values of β_{AB}' for parameter sets (I) and (II) are dimensionless. Values of β_{AB} for parameter sets (III) and (IV) are in electron volts.

Molecular geometries were specified in terms of internal valence co-ordinates (IVC) which are the displacements in the bond lengths and bond angles in the molecule. The potential surface minimum was found by allowing the IVC values to vary subject to certain symmetry constraints imposed in order to reduce the amount of computation and based on experimental knowledge of the various molecules. The symmetry constraint corresponds to the symmetry of the equilibrium geometry or subgroup thereof. For example, AB_2 molecules were specified in terms of two IVC values: the A–B bond length and the B–A–B bond angle. In this case the symmetry constraint is C_{2v} since the two AB bond lengths are assumed to be equal and the equilibrium geometry may be either C_{2v} or $D_{\infty h}$. Calculations without such constraints, on selected molecules, showed that the constraints did not alter the results. The equilibrium values of the IVC values were found by polynomial interpolation.[5]

Table 6

Core repulsion parameters α

	Parameter set [a]			
	α			α
Interactions	(I)	(II)	(III)	(IV)
H–H	2·3844	2·3844	2·3844	2·3844
H–B	1·6641		1·7250	
H–C	1·9125	1·9563	2·0063	2·0500
H–N	2·4406	2·5437	2·7922	2·7922
H–O	2·4906	2·4984	2·8781	2·8797
H–F	2·6406	2·4672	2·9609	2·8594
H–Si	1·1813	1·1938	1·2391	1·2531
H–P	1·1656	1·4406	1·2734	1·5191
H–S	1·5047	1·5711	1·6352	1·7086
H–Cl	1·5523	1·5527	1·7022	1·7441
H–Br	1·3623		1·4951	
H–I	0·8418		0·9417	
B–B	0·9453		1·0844	
B–F	2·1086		2·2785	
C–C	1·4750	1·3844	1·6062	1·5500
C–N	2·0641	1·9820	2·2078	2·1422
C–O	2·1102	2·0820	2·3313	2·3270
C–S	1·2434	1·2785	1·4144	1·4801
N–N	2·4625	2·3890	2·6609	2·5844
N–O	2·2625	2·2250	2·5094	2·4813
O–O	1·5938	1·5656	2·0250	2·0250
O–S	1·4984	1·5023	1·7916	1·8156
F–F	1·8699	1·8966	2·4672	2·3953
F–Cl	1·4351	1·2749	1·9141	1·9084
F–Br	1·3860		1·8379	
F–I	1·2051		1·6660	
S–S	1·0260	1·0621	1·2195	1·2940
Cl–Cl	1·0754	1·1121	1·3838	1·4761
Cl–Br	0·9438		1·1621	
Cl–I	0·8862		1·1606	
Br–Br	0·8491		1·2051	
Br–I	0·7183		1·0498	
I–I	0·6414		0·9153	

[a] Parameter sets are defined in Table 5.

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* Referred to as interatomic in order to distinguish them from the one-centre bonding parameters discussed in ref. 9.