Theoret. chim. Acta (Berl.) 11, 220—238 (1968)

Semi-Empirical All Valence Electrons SCF-MO-CNDO Theory

II. Interatomic Parameters and Bonding Energies*

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Received January 27, May 28, 1968

A semi-empirical SCF-MO theory is developed using the CNDO (complete neglect of differential overlap) approximation, with atomic parameters derived previously from atomic valence-state energies, interatomic electron-repulsion integrals calculated by the Mataga or Ohno formulae, and bonding parameters calibrated using the bonding parameters of binary hydrides. Bonding energies of the other molecules are calculated and found to be in much better agreement with experiment than those calculated from either the Pople-Segal CNDO/2 theory or the Extended Hückel Theory.

Es wird eine semiempirische SCF-MO-Methode unter vollständiger Vernachlässigung der differentiellen Überlappungen (CNDO) entwickelt. Kürzlich an Valenzzustandsenergien angepaßte Atomparameter werden verwendet, γ-Integrale werden nach Mataga oder Ohno bestimmt, die Bindungsparameter werden an experimentellen Daten der binären Hydride justiert. Bindungsenergien einer Vielzahl von Molekülen ergeben sich damit besser als mit der CNDO/2- oder der erweiterten Hückel-Methode.

Une théorie semiempirique SCF-MO est développée en utilisant l'approximation CNDO (négligence complète du recouvrement différentiel), aussi bien des paramètres atomiques qui étaient derivés des énergies d'état valence atomique, des integrals de la repulsion électronique interatomique calculés selon Mataga ou Ohno, et des paramètres des liaison assimilés par des paramètres de liaison d'hydrures binaires. Les énergies de liaison pour des autres molécules calculées ainsi sont en meilleur accord avec l'expérience que les valeurs calculés à l'aide des méthodes soit Pople-Segal CNDO/2 soit d'Hückel étendue.

1. Introduction

Two types of approximate Molecular Orbital Theory have been applied to all valence electrons in molecules; the independent electron molecular orbital theory as typified by the Extended Hückel Theory (EHT) [1], and the approximate self consistent field molecular orbital theory (SCF-MOT) in which the Roothaan equations are simplified by the zero-differential–overlap approximation (ZDO) [2] in which the differential overlap is assumed zero except for the same orbital.

Pople, Santry and Segal [3, 4] recently extended the ZDO approximation to molecular orbital calculations including all valence electrons, and considered its effect on the invariance properties of the wave function [3]. It is possible to make ZDO-type approximations which preserve the invariance of the wave function to orthogonal transformations among orbitals centred on the same atom. The simplest way is that of "complete neglect of differential overlap" (CNDO), in

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* Part 1 in Theoret. chim. Acta (Berl.) 7, 32 (1967).

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which, all differential overlaps of the form $\phi_K^*(l)\,\phi_L(l)$ are assumed to be zero, even when the two overlapping orbitals are centred on the same atom. A less drastic approximation is that of "neglect of diatomic differential overlap" (NDDO), in which the differential overlap of two orbitals is assumed to be zero only when they are centred on different atoms. However, NDDO has not yet been used in molecular calculations.

The intermediate INDO theory differs from the CNDO theory in the retention of the one-centre exchange integrals, and has been used to study small molecules and hydrocarbons [5–8].

Pople and Segal [9, 10] have used the CNDO approximation in molecular-orbital calculations on a number of small molecules, and compared the calculated charge distributions, dipole moments, equilibrium configurations and force constants with those obtained from the exact Roothaan equations, as well as with experiment. Santry and Segal [4] have extended this work to molecules containing atoms in the second row of the periodic table, and included the $3d$ orbitals of these atoms in the basis set. The CNDO approximation has also been used recently to study dipole moments of organic molecules [11], hyperfine coupling constants in sigma-electron radicals [12], and the electronic excited states of small molecules, and of benzene and ethylene [13].

In this paper, calculations are made using the CNDO approximation, as formulated by Pople and Segal [10]. However, the parameters in the Hamiltonian matrix elements are evaluated by different methods.

The Hamiltonian matrix elements are [9]

$$F_{kk} = U_{kk} + \left(P_{AA} - \tfrac{1}{2} P_{kk}\right) \gamma_{AA} + \sum_{B \neq A} \left(P_{BB}\, \gamma_{AB} + V_{AB}\right) \tag{1}$$

and

$$F_{kl} = -\tfrac{1}{2}\left(\beta_A^0 + \beta_B^0\right) S_{kl} - \tfrac{1}{2} P_{kl}\, \gamma_{AB}, \qquad k \neq l \tag{2}$$

where the population matrix P_{kl} is

$$P_{kl} = 2 \sum_i C_{ki}^* C_{li} .$$

The orbitals ϕ_k und ϕ_l are on atoms A and B respectively. P_{AA} is the total valence-shell electronic charge on atom A, defined by

$$P_{AA} = \sum_k^{A} P_{kk} . \tag{3}$$

The summation extends over all valence-shell orbitals on the atom. U_{kk} is the diagonal matrix element of the k^{th} orbital on atom A with respect to the kinetic energy and to the potential energy of the core of atom A; γ_{AB} represents "an average repulsion between an electron in a valence atomic orbital on A and another in a valence orbital on atom B" [3].

V_{AB} is the interaction of an orbital on atom A with the core of atom B, and must be given the same value for all orbitals on atom A in order to preserve the invariance of the Roothan equations to atomic transformations [3].

β_A^0 and β_B^0 are bonding parameters characteristic of atoms A and B respectively, and S_{kl} is the overlap integral,

$$S_{kl} = \int \phi_k^*(1)\,\phi_l(1)\,dV_1 . \tag{4}$$

The atomic parameters derived from atomic spectra using valence-state energies were derived in Part 1 [14]. In this paper the interatomic parameters, defined only with reference to molecules, are derived. The calculated molecular orbital energies are compared with experimental ionization potentials, using Koopmans' theorem in Part 3. Atomization energies of molecules are also considered, although they are given less accurately than the ionization potentials by approximate theories, since they represent small differences between two large quantities. They are sensitive to variations in β^0, and are used to evaluate them.

Dipole moments are considered in Part 4; also dealt with are nuclear quadrupole coupling constants, which depend upon charge distribution, although less directly than dipole moments.

2. Evaluation of Interatomic Parameters

In Sections *A* and *B*, the evaluation of the interatomic parameters of the diagonal matrix elements F_{kk} is described: Section *A* deals with the interatomic electron-electron repulsion integral, γ_{AB}, and with the interatomic electron-core attraction integral, V_{AB}. The overlap integrals, S_{kl}, and the bonding parameters, β^0_{A}, in the off-diagonal core matrix elements, H_{kl}, are dealt with in Sections *B* and *C* respectively.

A. Interatomic Electron-Electron Repulsion Integrals

The repulsion between an electron in the k^{th} orbital of atom A, and one in the r^{th} orbital of atom B is formally defined as

$$\gamma_{kr} = (kk|rr) = \int \phi_k^*(1)\, \phi_k(1) \frac{l}{r_{12}}\, \phi_r^*(2)\, \phi_r(2)\, dV_1\, dV_2 \tag{5}$$

which may be evaluated for orbitals of a specified functional form. The γ_{kr} may then be averaged in some way to evaluate γ_{AB}. Pople and Segal [9, 10] equated γ_{AB}, for each pair of atoms, to the integral defined by equation (5) for valence-shell Slater's orbital, evaluated using formulae listed by Roothaan [15].

The CNDO approximation, however, is analogous to the ZDO approximation in π-electron theory, which is in better agreement with experiment if the interatomic electron-repulsion integrals, as well as the atomic ones, are reduced below their theoretical values [16, 17]. This is necessary because of the correlation between electrons on different atoms [16, 18–22]. The interatomic electron-repulsion integrals in the SCF-MO-CNDO theory have therefore been evaluated by empirical formulae similar to those which have been proved successful in π-electron theory, with the ZDO approximation [17, 23–25]. This procedure is tested by comparing physical properties, calculated using both the empirical and the theoretical interatomic electron-repulsion integrals, with experiment.

In the semi-empirical π-electron theory, the interatomic electron-repulsion integrals, γ_{kr}, are functions of the internuclear distance, and of the atomic electron-repulsion integrals of the two atoms. These functions behave as follows [17, 23–25]:

(i) As the internuclear distance approaches zero, the value of γ_{kr} for two π-orbitals of *similar* atoms approaches the atomic electron-repulsion integral, γ_{kk}, for a π-orbital of either atom, while for *dissimilar* atoms it approaches the arithmetic mean of the atomic electron-repulsion integrals for the π-orbitals of the two atoms.

(ii) As the internuclear distance becomes infinite, the effect of correlation becomes small, and each electron-repulsion integral approaches its theoretical value, which is, at infinite distance, the electrostatic repulsion of two point charges.

These conditions may be expressed mathematically as

$$R_{\mathrm{AB}} \overset{\lim}{\longrightarrow} 0 \qquad \gamma_{kr} = 1/2\,(\gamma_{kk} + \gamma_{rr}) \tag{6}$$

and

$$R_{\mathrm{AB}} \overset{\lim}{\longrightarrow} \infty \qquad \gamma_{kr} = 1/R_{\mathrm{AB}} \tag{7}$$

where the k^{th} and r^{th} orbital are on atoms A and B respectively. The Pariser-Parr formula is suitable only for π-systems and is not considered here [17].

Several other formulae for the interatomic integrals have been suggested, which have the correct asymptotic behaviour, and can be used at all internuclear distances. Mataga [23] used the formula

$$\gamma_{kr} = \frac{1}{R_{\mathrm{AB}} + a}, \qquad a = \frac{2}{\gamma_{kk} + \gamma_{rr}}. \tag{8}$$

In conjugated molecules [26], equation (8) leads to smaller γ_{kr} than the Pariser-Parr formula. Bloor and Brearley [27] have found that the use of equation (8) leads to more accurate predictions of the electronic spectra of alternant hydrocarbons.

Another formula is that of Ohno [24]:

$$\gamma_{kr} = \frac{1}{\sqrt{R_{\mathrm{AB}}^2 + a^2}}, \qquad a = \frac{2}{\gamma_{kk} + \gamma_{rr}}. \tag{9}$$

For conjugated hydrocarbons [26], equation (9) leads to values of γ_{kr} about equal to those found from the Pariser-Parr formula, in the range of R_{AB} in which their equation is applied. These two formulae provide a representative sample of the values of γ_{kr} used in semi-empirical molecular orbital calculations on π-electron systems [26].

Miller *et al.* [28] used theoretical interatomic electron-repulsion integrals, but modified the Slater exponent of the orbitals so that the atomic electron-repulsion integrals agreed with semi-empirical values, derived from atomic spectra. This implies that the effects of correlation, and reorganization of the σ-electrons, may be accounted for by using "effective atomic orbitals" more diffuse than actual atomic orbitals. However, interatomic electron-repulsion integrals evaluated by this method are almost identical [29] to those found from Ohno's formula, and will not be considered separately.

Three different ways of estimating electron-repulsion integrals are compared here:

(i) All the electron-repulsion integrals, both atomic and interatomic, are calculated by evaluating the theoretical integral, equation (5) for valence-shell *s* orbitals, as in the work of Pople and Segal [9, 10].

(ii) Atomic electron-repulsion integrals are evaluated from valence state energies [14] and interatomic integrals by the Mataga formula [23], which is here adapted to calculations including all valence electrons.

$$\gamma_{\mathrm{AB}} = \frac{1}{R_{\mathrm{AB}} + a}, \quad a = \frac{2}{\gamma^*_{\mathrm{AA}} + \gamma^*_{\mathrm{BB}}} \tag{10}$$

where γ^*_{AA} and γ^*_{BB} are atomic limits, defined in Paper 1 of this series [14].

(iii) Atomic integrals are evaluated as described in Paper 1 [14], and interatomic integrals by Ohno's formula [24], modified to apply to all valence electrons.

$$\gamma_{\mathrm{AB}} = \frac{1}{\sqrt{R^2_{\mathrm{AB}} + a^2}}, \quad a = \frac{2}{\gamma^*_{\mathrm{AA}} + \gamma^*_{\mathrm{BB}}}. \tag{11}$$

In this series, molecular properties are computed, using electron-repulsion integrals evaluated by all three methods. It is shown that methods (ii) and (iii) are significantly better than method (i). This justifies the use of electron-repulsion integrals derived from atomic spectra. The core attraction integrals V_{AB} are evaluated from $V_{\mathrm{AB}} = -Z_{\mathrm{B}}\,\gamma_{\mathrm{AB}}$ as in the CNDO/2 theory [10] so that the penetration integrals vanish.

B. Overlap Integrals

Overlap integrals for Slater orbitals, of principal quantum number 1, 2, 3 or 5 may be evaluated analytically by the methods of Mulliken *et al.* [37]. The orbital exponents Z' and the effective principal quantum numbers n' are given by Slater's rules [30].

In the hydrogen atom, there is no screening, so $Z'_{\mathrm{H}} = Z_{\mathrm{H}} = 1$, and the Slater orbital is identical to the exact wave function. In the hydrogen molecule, however, it has been found [31] that the lowest energy for an LCAO-MO wave function is obtained for $Z'_{\mathrm{H}} = 1.2$. Also, in accurate molecular calculations for other molecules [32], using the Roothaan equations, in which the hydrogen exponent has been varied, the value $Z'_{\mathrm{H}} = 1.2$ leads to lower energies than $Z'_{\mathrm{H}} = 1.0$. Physically, this is due to the fact that the contraction of the hydrogen orbital leads to more stable bonding [33]. Pople and Segal [9, 10] used $Z'_{\mathrm{H}} = 1.2$, but Hoffmann [1] in the Extended Hückel Theory used $Z'_{\mathrm{H}} = 1.0$. In the paper both values are used, and a comparison is made on the basis of computed physical properties. It will be shown that $Z'_{\mathrm{H}} = 1.2$ is preferred in the semi-empirical SCF-MO-CNDO theory, since it leads to more accurate bonding energies.

For $n = 4$, the radial function, according to Slater's rules is [30]

$$R_4(r) = N_4\, r^{2.7}\, e^{-Z'r/3.7\,a_0}. \tag{12}$$

Overlap integrals for such an orbital cannot be evaluated analytically, because of the non-integral power of r, which is present as a factor. This difficulty can be avoided by using an approximate orbital, which is a linear combination of orbitals for which overlap integrals can be evaluated. The approximate combination is obtained by assuming that R_4 can be interpolated between R_3 and R_5 in the same way that the corresponding n' is interpolated. Two forms for the approximate orbital were tried:

$$R'_4(r) = N^*_4\,(0.3\,R_3 + 0.7\,R_5) = N'_4\,(0.3\,r^2\, e^{-Z'r/3\,a_0} + 0.7\,r^3\, e^{-Z'r/4\,a_0}) \tag{13}$$

and

$$R''_4(r) = N''_4\,(0.3\,r^2 + 0.7\,r^3)\, e^{-Z'r/3.7\,a_0} \tag{14}$$

where the N's are normalization constants. The accuracy of these approximations to equation (12) may be examined by computing their overlap with the Slater orbital. The required overlap integrals are one-centre integrals, and can be computed using gamma functions. The overlap integrals of R_4 with R_4' and R_4'' are 0.99651 and 0.99979, respectively, showing that these simple interpolations are quite justified. In computations for orbitals with $n=4$, $R_4(r)$ has been replaced by $R_4''(r)$, the more accurate of the two approximations. The value of N_4'' is 1.01384531.

Leifer, Cotton and Leto [34] used series expansions of 8–10 terms each to approximate overlap integrals involving R_4, but the simpler method proposed here should be as good, since R_4'' is such a close approximation to R_4.

C. *Bonding Parameters*

No provision has yet been made for empirical evaluation of any of the parameters of the theory, using molecular properties. It was therefore decided to evaluate empirical bonding parameters for each element.

There are several molecular properties which could be used to evaluate the bonding parameters. In the Pariser-Parr theory of π-electron systems [17], the core resonance integral was evaluated using electronic spectra, while Pople [35] was concerned with ground state ionization potentials, electron affinities, resonance energies, and charge distributions. Dewar and Gleicher [36] have pointed out that, in a semi-empirical theory, ground-state properties should be calculated with parameters evaluated from ground-state properties, since the use of parameters evaluated from electronic spectra may include a correction for effects present only in excited electronic states.

In these papers, ionization potentials, molecular bonding energies, dipole moments, and nuclear quadrupole coupling constants have been computed from the SCF-MO-CNDO theory. Preliminary calculations showed that the bonding energies are most sensitive to variations in the bonding parameters (Table 1). The following procedure was therefore used to evaluate the bonding parameters:

(i) The bonding parameter for hydrogen, β_H^0, was chosen to give the correct dissociation energy for the hydrogen molecule. For hydrogen, the bonding molecular orbital is determined by symmetry to be

$$\psi = \frac{\phi_1 + \phi_2}{\sqrt{2}}. \tag{15}$$

The dissociation energy is (as shown below)

$$D_e = 2\beta_H^0 S_{12} + \tfrac{1}{2}(\gamma_{12} - \gamma_{11}) \tag{16}$$

which may be equated to the experimental value, 4.751 eV to find β_H^0, for a given choice of the interatomic electron-repulsion integrals, and of the hydrogen exponent (which determines the overlap integral S_{12}).

(ii) The bonding parameters for other elements were chosen to give the correct bonding energies of binary hydrides, AH_n. The binary hydrides were chosen as the reference molecules because they form a series including a molecule for each element of interest. The bonding energy of each hydride, AH_n, was computed for a range of values of the bonding parameter, β_A^0. The details of this calculation, and the variation of the atomization energies with β_A^0, are shown below.

Table 1. *Variation of molecular properties of* HF *and* HCl *with halogen bonding parameter* β_A^0

Physical property	HF					HCl			
β_A^0 [eV] =	20	19	18	17	Exptl.	10	9	8	Exptl.
Bonding energy [eV]	7.30	6.87	6.44	6.03	6.11[a]	5.22	4.66	4.11	4.61[b]
First ionization potential (π) [eV]	16.27	16.24	16.21	16.18	16.06[a]	13.19	13.18	13.17	12.80[a]
Second ionization potential (σ) [eV]	16.78	16.64	16.49	16.35	16.48[a]	14.27	14.09	13.89	16.28[a]
Third ionization potential (σ) [eV]	37.90	37.79	37.69	37.58	—	24.98	24.88	24.79	—
Dipole moment [D]	1.897	1.897	1.898	1.898	1.8195[c]	2.058	2.025	1.991	1.12[d]
Cl^{35} Quadrupole coupling constant [Mc/s]						85.72	86.02	86.29	67.3[e]

SCF-MO calculations with CNDO approximation.

Parameters: γ_{AA} from atomic spectra, γ_{AB} from Mataga formula, $Z'_H = 1.2$, $\beta_H^0 = 5.4$ eV.

[a] Frost, D. C., C. A. McDowell, and D. A. Vroom: J. chem. Physics **46**, 4255 (1967).

[b] Reference [47].

[c] Weiss, R.: Physic. Rev. **131**, 659 (1963).

[d] Burrus, C. A.: J. chem. Physics **31**, 1270 (1959).

[e] Cowan, M., and W. Gordy: Physic. Rev. **111**, 209 (1958)

The chosen bonding parameters, which give the experimental bonding energies, have been rounded off to the nearest tenth of an electron volt, since greater precision would be inconsistent with the precision of most of the experimental bonding energies. Table 2 lists the bonding parameters for each choice of electron-repulsion integral and hydrogen exponent.

Since the bonding parameter for each element is evaluated with reference to its hydrides, it depends on the value of the hydrogen exponent, so that the results of calculations on molecules, which do not contain hydrogen, depend indirectly on the choice of the hydrogen exponent in the calibration. It will be shown, however, that the value $Z'_H = 1.2$, and the corresponding bonding parameters, lead to more accurate molecular energies.

Table 2. *Bonding parameters β_A^0 (in eV)*

	Code[a]	*M*1	*M*2	*O*1	*O*2	*R*1	*R*2	*PS*[b]
Parameter set	Atomic parameters	Empirical[c]	Empirical	Empirical	Theoretical[d]	Theoretical	Theoretical	Theoretical
	Interatomic γ_{AB}	Mataga[e]	Mataga	Ohno[f]	Ohno	Theoretical[d]	Theoretical	Theoretical
	Hydrogen exponent Z'_H	1.0	1.2	1.0	1.2	1.0	1.2	1.2
	Evaluation of β_A^0	Empirical[g]	Empirical	Empirical	Empirical	Empirical	Empirical	Pople and Segal[h]
	H	4.9	5.4	3.9	4.3	5.4	5.2	9
	Li	0.4	0.7	−0.9	−0.8	2.5	3.8	9
	Be	3.8	4.0	3.2	3.4	4.3	5.2	13
	B	5.8	5.6	5.2	5.0	6.2	6.5	17
	C	8.7	8.2	7.8	7.3	9.1	9.0	21
	N	9.6	8.8	8.0	7.3	11.2	10.6	25
	O	14.2	12.8	11.7	10.5	16.1	14.7	31
	F	19.2	17.2	15.7	14.1	22.6	20.4	39
	Si	5.0	5.2	4.6	4.7			
	P	6.0	6.0	5.3	5.3			
	S	6.7	6.5	5.8	5.6			
	Cl	9.3	8.9	8.1	7.8			
	Ge	4.3	4.4	3.8	4.0			
	As	4.6	4.7	4.0	4.1			
	Se	5.7	5.7	5.0	4.9			
	Br	7.3	7.2	6.4	6.3			
	Sn	3.4	3.6	1.9	2.1			
	Sb	4.5	4.7	3.9	4.2			
	Te	5.7	6.1	5.1	5.4			
	I	6.5	6.7	5.8	6.0			

[a] Arbitrary code for parameter set.
[b] CNDO/2 Method of Pople and Segal [10].
[c] From atomic spectra as described in Part 1 [14].
[d] From theoretical integral formulae of Roothan – first row only.
[e] From Eq. (10).
[f] From Eq. (11).
[g] From hydride bonding energies as described in text.
[h] By comparison with minimal-basis set calculations by Roothaan method.

The negative bonding parameter for lithium, for interatomic electron-repulsion integrals given by the Ohno approximation, indicates that the arithmetic mean of bonding parameters, used for H_{kl} [9], breaks down in this case. The use of a geometric mean would resolve this particular difficulty, but it would require extensive computation to show that a geometric mean is better for all molecules. Also, the geometric mean does not have a theoretical basis. In this series the arithmetic mean has been used, and the bonding parameter for lithium has been treated like the others, even though it has the wrong sign.

Table 2 also lists the Pople-Segal [9] bonding parameters for hydrogen and the first-row elements. The values of Santry and Segal [4] for second-row elements are not included, since they were published after the completion of the work described here. These parameters were chosen by comparing the coefficients of computed molecular orbitals, and the differences between orbital energy eigenvalues, with those obtained by accurate solution of the Roothaan equations for small molecules [9]. They are much larger than the empirical bonding parameters. A detailed comparison of the two sets of bonding parameters for first-row atoms is made by calculating molecular physical properties. It is noted here, however, that the empirical values are more consistent with the values of core resonance integrals in π-electron theories. For carbon, for example, Pople [35] showed that the resonance energy of benzene is correctly given for a carbon-carbon core resonance integral of 2.13 eV. Since the overlap integral between two carbon π-orbitals at the nearest-neighbour distance in benzene is 0.248 [37], this corresponds to a carbon bonding parameter of 8.6 eV.

Clark and Ragle [38] have recently assigned the value 11.15 eV for the bonding parameter of carbon in order to fit the electronic spectra, but they have not proposed a general empirical scheme for the evaluation of bonding parameters, as is done here, nor tested their value in calculations on a wide variety of molecules.

The exact electronic energy of a molecule can be written as [39]

$$E_{\text{elect}} = E_{\text{HF}} + E_{\text{corr}} + V_{nn} \tag{17}$$

where E_{HF} is the Hartree-Fock energy for the best single-determinant wave function and E_{corr} is the correlation energy. In the semi-empirical theory described here, the parameters are adjusted to give the correct bonding energies, including correlation energy, even though the wave function is a single determinant.

In order to determine the bonding energy of a molecule accurately from a single-determinant wave function, without using empirical parameters, it would be necessary to first determine E_{HF} from a complete SCF-MO calculation, and then either to calculate the exact energy by superposition of configurations [39], or to estimate the correlation energy, as in the approximate theory of Hollister and Sinanoglu [40]. The present method is much simpler, however, and can therefore be applied to larger molecules. Its validity is tested by examining the accuracy of bonding energies calculated in this way for molecules other than those used in the calibration of the bonding parameters.

3. Calculation of Bonding Energies from the SCF-MO-CNDO Theory

For a closed shell molecule with a single-determinant wave function the total electronic energy [35, 3] is

$$E_{\text{total}} = \tfrac{1}{2}\,\mathrm{tr}\,P\,H + \sum_i E_i + V_{nn} \tag{18}$$

where P is the population matrix, H the core Hamiltonian matrix, E_i the orbital energy eigenvalue and V_{nn} the expectation value of the internuclear potential energy for a fixed nuclear configuration. Hence the bonding energy [41] is

$$E_{\mathrm{B}} = \sum_{\mathrm{A}} E_{\mathrm{A}} - E_{\mathrm{total}} \,. \tag{19}$$

Thus

$$E_{\mathrm{B}} = \sum_{\mathrm{A}} E_{\mathrm{A}} - E_e - V_{nn} \tag{20}$$

where

$$E_e = \tfrac{1}{2} \operatorname{tr} P(H + F) = \tfrac{1}{2} \operatorname{tr} P H + \sum E_i \,. \tag{21}$$

The atomic energy, E_{A}, is the energy to remove all the valence-shell electrons from atom A, and E_e the energy to remove the valence-shell electrons from the molecule. The successive ionization of electrons, from both atoms and molecules, requires increasing amounts of energy because:

(i) the electrostatic repulsion of other electrons acting on the electron to be ionized decreases. This effect is incorporated into any SCF theory, since the variation of the electrostatic potential with charge distribution is explicitly included.

(ii) as electrons are removed, the remaining electrons are less screened from the nucleus. The orbitals are re-organized with a greater probability density near the nucleus, and the expectation value of the nuclear attraction is increased. This effect is not accounted for in SCF-MO calculations with a minimum basis, since the orbital parameters are assigned fixed values. The parameters evaluated from atomic spectra [14] are valid only for valence states close to electroneutrality. If the energy required to remove all the valence electrons from an atom is calculated from these parameters, it differs from the sum of experimental ionization potentials by [44], for example, 24.5 eV for C, and 171.0 eV for F.

If, in calculating the bonding energy from equation (20), atomic energies were equated to the sum of the appropriate experimental ionization potentials, the effect of orbital reorganization would be included only in the atomic energy, and not in the molecular energy, so that the bonding energy would be seriously in error. Therefore the atomic and molecular energies must be calculated using the same approximations and parameters, so that the errors cancel.

In the CNDO approximation, the energy of an atomic state is

$$E = C^0 + \sum_k n_k \bar{U}_{kk} + \tfrac{1}{2} \Big(\sum_k n_k\Big) \Big(\sum_k n_k - 1\Big) \gamma_{\mathrm{AA}} \tag{22}$$

where n_k is the number of electrons in the k^{th} orbital, and the summations extend over all the valence-shell orbitals. Relative to the core state, when C^0 becomes zero, and for a state with n_s s-electrons and n_p p-electrons, this becomes

$$E = n_s \bar{U}_{ss} + n_p \bar{U}_{pp} + (n_s + n_p)(n_s + n_p - 1) \gamma_{\mathrm{AA}} \,. \tag{23}$$

The internuclear potential energy, V_{nn}, is [3, 10]

$$V_{nn} = \sum_{\mathrm{A}>\mathrm{B}} Z_{\mathrm{A}} Z_{\mathrm{B}} R_{\mathrm{AB}}^{-1} \,. \tag{24}$$

The net electrostatic interaction between any two atoms is consequently

$$E_{\mathrm{AB}} = V_{nn} + P_{\mathrm{AA}} V_{\mathrm{AB}} + P_{\mathrm{BB}} V_{\mathrm{BA}} + P_{\mathrm{AA}} P_{\mathrm{BB}} \gamma_{\mathrm{AB}} \tag{25}$$

where

$$V_{\mathrm{AB}} = -Z_{\mathrm{B}} \gamma_{\mathrm{AB}} \,. \tag{26}$$

Thus for two neutral atoms, with atomic populations P_{AA} and P_{BB} equal to the atomic core charges Z_A and Z_B, the use of the pointcharge expression, equation (24), leads to a net electrostatic repulsion,

$$E_{AB}^0 = Z_A Z_B (R_{AB}^{-1} - \gamma_{AB}) \tag{27}$$

which makes it impossible to predict accurate bonding energies for any reasonable choice of parameters.

The matrix elements H_{11} and H_{12} for hydrogen are [10, 9]

$$H_{11} = U_{11} - \gamma_{12} \tag{28}$$

and

$$H_{12} = -\beta_H^0 S_{12} . \tag{29}$$

Combining these with equations for F_{11} and F_{12}, where $F_{11} = U_{11} + \frac{1}{2}\gamma_{11}$ and $F_{12} = -\beta^0 S_{12} - \frac{1}{2}\gamma_{12}$, the electronic energy is

$$E_e = 2U_{11} + \tfrac{1}{2}\gamma_{11} - \tfrac{3}{2}\gamma_{12} - 2\beta_H^0 S_{12} + V_{nn} \tag{30}$$

and the bonding energy is

$$E_B = 2\beta_H^0 S + \tfrac{3}{2}\gamma_{12} - \tfrac{1}{2}\gamma_{11} - V_{nn} \tag{31}$$

since for hydrogen, the atomic energy E_H equals the local core-Hamiltonian matrix element U_{11}. If the internuclear potential energy has the point-charge form, the bonding energy is then

$$E_B = 2\beta_H^0 S + \tfrac{3}{2}\gamma_{12} - \tfrac{1}{2}\gamma_{11} - R_{AB}^{-1} . \tag{32}$$

If Eq. (32) is solved simultaneously with the equation for the ionization potential of hydrogen (Paper 3),

$$I = 7.171 + \beta_H^0 S + \tfrac{1}{2}\gamma_{12} \tag{33}$$

then for the experimental bonding energy and ionization potential, with γ_{11} determined from the Pariser approximation [45], and $Z'_H = 1.2$, the interatomic electron-repulsion integral γ_{12} equals 28.052 eV, and the bonding parameter β_H^0 is -5.748 eV. These values are absurd, however, since γ_{12} is much higher than even the theoretical γ_{11} for hydrogen, 20.408 eV, and the bonding parameter has the wrong sign, which implies that the anti-bonding orbital is the occupied orbital.

If, on the other hand, the bonding parameter is chosen to give the correct dissociation energy for reasonable values of γ_{12}, then the bonding parameter is 14.074 eV, and 10.759 eV, when γ_{12} is determined by the Mataga, and by the Ohno formula respectively. The calculated ionization potentials are then 20.53 eV, and 19.78 eV, in the two cases, in very poor agreement with the experimental value of 15.45 eV.

The point-charge form for V_{nn} is therefore unsatisfactory. Dewar and Klopman [6] have suggested that this is because the method of assignment of atomic parameters fails to allow for the reorganization of atomic orbitals, and changes in the effective nuclear charges, upon molecule formation, and that this error must be compensated by altering the form of V_{nn}.

The simplest satisfactory assumption is that the net electrostatic interaction between two neutral atoms, E_{AB}^0, vanishes, so that

$$V_{nn} = \sum_{A>B} Z_A Z_B \gamma_{AB} \tag{34}$$

as assumed by Chung and Dewar for π-electron systems [51]. The electrostatic interaction between any two atoms is then simply the interaction of net charges.

$$E_{\mathrm{AB}} = (P_{\mathrm{AA}} - Z_{\mathrm{A}})(P_{\mathrm{BB}} - Z_{\mathrm{B}})\,\gamma_{\mathrm{AB}}\,. \tag{35}$$

With this choice of V_{nn}, accurate bonding energies and ionization potentials can be obtained for reasonable parameter values. For hydrogen, substitution of Eq. (33) into Eq. (30) leads to the bonding energy

$$E_{\mathrm{B}} = 2\beta_{\mathrm{H}}^{0} S + \tfrac{1}{2}(\gamma_{12} - \gamma_{11}) \tag{36}$$

which may be solved simultaneously with Eq. (32) for the ionization potential to give $\gamma_{12} = 10.766$ eV and $\beta_{\mathrm{H}}^{0} = 4.293$ eV (for $Z'_{\mathrm{H}} = 1.2$).

Dewar and Klopman [6] have objected to the use of Eq. (34) in calculations including all valence electrons, since they have found that a net repulsive interaction between neutral atoms at short internuclear distances is necessary in order to predict potential energy minima. In this paper, however, it is found that Eq. (34) leads to satisfactory prediction of bonding energies at experimental bond lengths.

The final formula used to compute bonding energies from the semi-empirical SCF-MO theory is found by substituting Eq. (18) and (34) into Eq. (20) so that

$$E_{\mathrm{B}} = \sum_{\mathrm{A}} E_{\mathrm{A}} - \tfrac{1}{2}\,\mathrm{tr}\,P H - \sum_{i} E_{i} - \sum_{\mathrm{A}>\mathrm{B}} Z_{\mathrm{A}} Z_{\mathrm{B}}\,\gamma_{\mathrm{AB}} \tag{37}$$

where E_{A} is given by Eq. (23).

4. Comparison of Calculated Bonding Energies with Experiment

The experimental data for bonding energies were taken from the JANAF Interim Thermochemical Tables [47] and anharmonicity corrections were neglected, since the effect on E_{B} is only 0.004 eV in hydrogen, less for other diatomics [47], and unknown for most polyatomics.

For molecules not listed in the JANAF tables, the vibrational frequencies were taken from Herzberg [46, 48] and the heats of formation at 298 °K were taken from National Bureau of Standards data [57] for BrCl, ICl, C_2H_6, C_3H_8, ICN, CH_3CN, CH_3Cl, CH_3Br, and CH_3I. The heats of formation of Group IV, V, VI hydrides were determined by Gunn and Green [49] using an explosive decomposition method, and the dissociation energies of ClF, BrF, and IF were found from appearance potentials by Irsa and Friedman [50].

The vibrational energy of propane was extrapolated from that of methane and ethane, since the vibrational frequencies are not all known [48]. The unknown vibrational frequencies of IF and BrCl were assumed to be equal to the arithmetic mean of the corresponding pure halogen frequencies, since this approximation is accurate within 50 cm^{-1} for the other four interhalogen molecules [47, 57].

The experimental bonding energies of the binary hydrides used to calibrate the bonding parameters have been rounded off to their probable precision. For other molecules, the bonding energies are given to 0.001 eV from the experimental data, although this exaggerates their precision in many cases.

Bonding energies calculated from SCF-MO theory using empirical bonding parameters are shown in Table 3, for molecules other than those used in calibration. The energies are fairly accurate on the whole, in contrast to those calculated using the Pople-Segal bonding parameters so that the theory includes correlation energy reasonably accurately.

The bonding energies calculated for $Z'_H = 1.2$ are more accurate than those for $Z'_H = 1.0$. When electron-repulsion integrals evaluated from atomic spectra are used, the bonding energies for $Z'_H = 1.2$ (Columns $M2$ and $O2$) are more accurate for all the molecules considered, except SO_2, I_2, IF, IBr, CH_3I, and (for interatomic γ_{AB} calculated from the Mataga formula only) LiF. When theoretical electron-repulsion integrals are used, more accurate bonding energies are predicted for $Z'_H = 1.2$ (Column $R2$), except for LiF, CH_3F, and F_2. The value 1.2 is therefore chosen as the better value for the Slater exponent of hydrogen in the SCF-MO calculations.

Table 3. *Bonding energies calculated by* SCF-MO *theory with* CNDO *approximation and empirical bonding parameters*

Parameter set	$M1$	$M2$	$O1$	$O2$	$R1$	$R2$	Exptl. (eV)
N_2	12.325	10.480	12.402	10.839	12.997	11.566	9.903
CO	13.838	11.931	13.798	12.166	14.136	12.579	11.225
CS	8.093	7.414	8.660	7.970			7.190
CO_2	22.032	18.981	21.310	18.592	22.578	20.160	16.856
OCS		16.142	17.968	15.984			14.417
CS_2	14.154	13.012	14.262	13.090			11.980
NNO			17.401	14.986	18.899	16.634	11.724
SO_2	11.085	9.494	11.255	9.761			11.177
O_3	11.995	9.804	11.009	9.034			6.345
C_2H_2	19.333	17.724	19.969	18.264	20.003	19.448	17.530
C_2H_4	25.290	24.250	25.609	24.366	25.169	24.831	24.357
C_2H_6	31.603	31.032	31.650	30.799	31.077	30.867	30.818
C_3H_8	46.431	45.230	46.250	44.705	45.699	45.373	43.563
B_2H_6	28.657	27.706	27.523	26.580	28.398	27.652	26.004
LiF	5.970	5.551	6.557	6.290	4.101	3.822	5.940
F_2	2.887	2.060	2.627	1.983	0.991	0.064	1.653
Cl_2	3.491	3.178	3.398	3.170			2.508
Br_2	2.767	2.687	2.774	2.695			1.991
I_2	1.677	1.837	1.750	1.907			1.557
ClF	3.882	3.191	3.604	3.079			2.668
BrF	3.369	2.799	3.216	2.778			2.682
BrCl	2.997	2.804	2.977	2,826			2.334
IF	1.524	1.153	1.570	1.295			2.91
ICl	2.382	2.307	2.405	2.368			2.190
IBr	2.162	2.201	2.212	2.251			1.928
CH_3F	19.558	18.634	19.126	18.234	18.813	17.847	18.384
CH_3Cl	17.680	17.329	17.669	17.211			17.154
CH_3Br	16.808	16.608	16.891	16.532			16.640
CH_3I	15.789	15.733	15.944	15.727			15.931
HCN	16.113	14.705	16.367	14.996	16.410	15.603	13.537
CH_3CN			30.866	28.710			26.586
FCN	19.703	17.167	19.265	17.113	20.114	18.199	13.529
ClCN		15.262	17.159	15.468			12.310
BrCN	16.051		16.183	14.589			
ICN	14.868	13.333	15.094	13.658			11.159

On comparing the results in Table 3 for $Z'_H = 1.2$ and different choices of electron-repulsion integrals, the bonding energies calculated using theoretical integrals are less accurate than those calculated using integrals evaluated from atomic spectra, except for C_2H_6 and B_2H_6, for which the bonding energies calculated using theoretical integrals are more accurate than those obtained using the Mataga formula, but not the Ohno formula.

Table 4. *Bonding energies calculated by* SCF-MO *theory with* CNDO *approximation and Pople-Segal bonding parameters*

Parameter set	*MP*[a]	*OP*[a]	*RP*[a]	Experimental (eV)
H_2	14.700	13.209	14.398	4.751
LiH	9.542	10.509	7.987	2.6
BeH_2	25.117	27.240	23.591	6.9
BH_3	44.931	48.392	43.312	12.1
CH_4	62.505	67.602	61.033	18.18
NH_3	47.787	52.018	45.279	12.93
H_2O	32.552	35.672	31.020	10.06
HF	17.639	19.271	16.366	6.11
N_2	51.344	55.082	48.316	9.903
CO	46.269	49.706	44.377	11.225
CO_2	78.196	83.951	74.404	16.856
NNO	76.386	82.387	70.354	11.724
O_3	45.767	50.183	38.955	6.345
C_2H_2	79.055	85.021	78.328	17.530
C_2H_4	96.015	103.204	93.889	24.357
C_2H_6	113.428	121.945	110.297	30.818
C_3H_8	167.580	179.622	163.209	43.563
B_2H_6	110.206	117.628	105.457	26.004
LiF	15.955	17.300	12.639	5.940
F_2	11.672	12.850	8.308	1.653
CH_3F	66.474	71.449	63.159	18.384
HCN	63.955	68.801	61.784	13.537
CH_3CN	118.383	126.709	114.546	26.586
FCN	73.472	78.570	69.548	13.529

[a] *MP* Mataga γ_{AB}, Pople and Segal bonding parameters.
OP Ohno γ_{AB}, Pople and Segal bonding parameters.
RP Theoretical γ_{AB}, Pople and Segal bonding parameters.
$Z'_H = 1.2$ in all calculations.

The bonding energies do not provide a conclusive choice between the Mataga and Ohno formulae for interatomic electron-repulsion integrals, since each leads to more accurate bonding energies for about the same number of molecules. As in the calculation of molecular ionization potentials, it seems that the exact values of the interatomic integrals do not matter, provided that the atomic integrals, and the atomic limit of the interatomic integrals, are evaluated from atomic spectra.

Table 4 shows that the Pople-Segal bonding parameters are completely inadequate for the calculation of total molecular energies, since the predicted bonding energies are higher than the experimental by factors ranging from 3 to 8. The bonding energies calculated using theoretical electron-repulsion integrals (Column *RP*) are slightly better than the others, $MP =$ Mataga and $OP =$ Ohno) but the difference is negligible in view of the magnitude of the errors of all the calculated energies in Table 4. It should be noted that, since the bonding energies are too high rather than too low, the errors cannot be blamed on the omission of correlation energy, but are due simply and solely to the large values of the Pople-Segal bonding parameters [9].

5. Comparison with Extended Hückel Theory

In the Extended Hückel Theory, E_e cannot be evaluated from Eq. (21), since the one-electron Hamiltonian, h^0_{eff}, is not separated into core and electron-repulsion terms. Hoffmann and Lipscomb [1, 52] equated the total electronic energy of closed-shell molecules to twice the sum of occupied orbital energies, as in the Hückel π-electron theory [53, 54].

$$E_{\mathrm{elect}} = 2 \sum_i E_i \,. \tag{38}$$

From Eq. (38) and (19), the bonding energy is given by

$$E_{\mathrm{B}} = \sum_{\mathrm{A}} E_{\mathrm{A}} - 2 \sum_i E_i \,. \tag{39}$$

The internuclear potential energy, V_{nn}, is not included in this calculation of the bonding energy, since Hoffmann [1] found that the EHT predicts potential energy minima for most stable molecules (although not hydrogen), which vanish when V_{nn} is included. He assumed therefore that

> "the method of guessing the matrix elements simulated within the electronic energies the presence of nuclear repulsions at small distances," [1]

and suggested that this effect is due to a rough cancellation of electron-electron and nuclear-nuclear repulsions, neither of which is included explicitly in the EHT. Allen and Russell [55] have shown that bond angles are predicted correctly from Hartree-Fock calculations, using a simple sum of orbital energies as in Eq. (38), except for highly ionic molecules; so that the EHT may also be expected to predict bond angles correctly. This does not apply, however, to bond lengths [55].

As in the SCF theory, the atomic and molecular energies must be calculated using the same approximations and parameters, so that there is a cancellation of errors in the bonding energy. By analogy with Eq. (38), the valence-shell energy of an atom with n_s *s*-electrons and n_p *p*-electrons is

$$E_{\mathrm{A}} = n_s h_{ss} + n_p h_{pp} \,. \tag{40}$$

Hoffmann and Lipscomb [1, 56] have used instead

$$E_{\mathrm{A}} = (n_s - 1) h_{ss} + (n_p + 1) h_{pp} \tag{41}$$

for boron and carbon, since they found that the ratios of bonding energies for different boron hydrides are correctly predicted using Eq. (41) in a preliminary calculation [56] with all off-diagonal matrix elements given by

$$h_{kl} = K S_{kl} \,, \qquad K = 21 \text{ eV} \,. \tag{42}$$

This procedure is not justified, however, since Eq. (40) and not Eq. (41) refers to the ground state of an atom. Table 5 shows that the procedure of Hoffmann and Lipscomb is not only theoretically invalid, but also leads to much less accurate bonding energies than are obtained using Eq. (40).

The bonding energies calculated using the Extended Hückel Method are given in Table 6. The results for some molecules are quite accurate, but the theory is seriously in error for the binary hydrides, and especially hydrogen, just as in the prediction of ionization potentials. For the hydrides, the differences between the results for the two values of Z'_H are insignificant in view of the errors. For organic molecules, however, the bonding energies are predicted relatively accurately by the EHT, and the values for $Z'_H = 1.0$ (Column H 1) are more accurate than those for $Z'_H = 1.2$. Thus it seems that the best value for the Slater exponent of hydrogen in molecules is 1.2 in the SCF-MO theory as claimed by Pople and Segal [9], and 1.0 in the EHT, as used by Hoffmann [1]. Since the value of Z'_H determines the behaviour of the molecular orbitals near a hydrogen nucleus, it should not depend on the theory used to calculate the orbitals, but the difference is probably due to a cancellation of errors in one theory or the other.

Table 5. *Comparison of* EHT *bonding energies* ($Z'_H = 1.0$) *with those calculated as per Hoffmann and Lipscomb*

	This work	As per Hoffmann and Lipscomb	Experimental (eV)
CH_4	19.552	29.291	18.18
C_2H_2	19.792	39.270	17.53
C_2H_4	24.883	44.361	24.36
C_2H_6	30.781	50.259	30.82
C_3H_8	42.037	71.254	43.56
BH_3	16.398	22.889	12.1
B_2H_6	23.475	36.457	26.00

It is interesting to compare the bonding energies for BH_3 and B_2H_6 in the two theories. In the SCF-MO theory, the bonding energy of B_2H_6 is predicted as accurately as that of many other molecules, despite the possible uncertainty due to the use of the unstable molecule, BH_3, to calibrate the bonding parameter for boron. The EHT, on the other hand, predicts incorrectly that B_2H_6 is unstable with respect to BH_3, even though the EHT was originally developed for calculations on boron hydrides [56, 52]. This is another example of the unreliability of the EHT.

In summary, therefore, the best of the theories considered for the calculation of bonding energies is the SCF-MO-CNDO theory with empirical bonding parameters, a Slater exponent for hydrogen of 1.2, and electron-repulsion integrals evaluated from atomic spectra and either the Mataga or the Ohno formula.

Acknowledgements. This research was supported by the National Research Council of Canada, to whom JMS is appreciative for Scholarships from 1964—1967. We wish to thank the McGill Computing Centre for machine time and assistance.

Table 6. *Bonding energies calculated by extended Hückel theory*

	*H*1[a]		*H*2[a]	Experimental (eV)
H_2	35.814		32.096	4.751
LiH	8.696		8.576	2.6
BeH_2	12.752		12.439	6.9
BH_3	16.398		17.265	12.1
CH_4	19.552		21.697	18.18
NH_3	15.640		17.051	12.93
H_2O	13.191		13.843	10.06
HF	8.923		9.103	6.11
SiH_4	23.418		23.725	13.87
PH_3	16.611		17.231	10.47
H_2S	11.252		11.565	7.5
HCl	6.421		6.469	4.61
GeH_4	23.542		23.583	12.5
AsH_3	16.353		17.011	9.1
H_2Se	11.109		11.281	6.6
HBr	5.545		5.576	3.92
SnH_4	24.261		23.898	11.0
SbH_3	17.172		17.740	8.3
H_2Te	10.925		10.828	5.8
HI	5.840		5.710	3.20
N_2		10.182		9.903
CO		10.760		11.225
CS		7.780		7.190
CO_2		19.745		16.856
OCS		16.832		14.417
CS_2		12.985		11.980
NNO		15.785		11.724
SO_2		17.287		11.177
O_3		7.133		6.345
C_2H_2	19.792		20.071	17.530
C_2H_4	24.883		26.770	24.357
C_2H_6	30.781		34.298	30.818
C_3H_8	42.037		46.994	43.563
B_2H_6	23.475		25.947	26.004
LiF		15.503		5.940
F_2		2.404		1.653
Cl_2		2.309		2.508
Br_2		1.610		1.991
I_2		2.447		1.557
ClF		4.238		2.668
BrF		5.392		2.682
BrCl		2.130		2.334
IF		6.771		2.91
ICl		2.753		2.190
IBr		2.073		1.928
CH_3F	21.413		23.005	18.384
CH_3Cl	17.272		19.140	17.154
CH_3Br	16.167		18.052	16.640
CH_3I	16.395		18.228	15.931
HCN	16.420		16.442	13.537
CH_3CN	28.070		29.533	26.586
FCN		15.851		13.529
ClCN		14.473		12.310
BrCN		14.113		
ICN		14.348		11.159

[a] *H*1 Extended Hückel Theory with $Z'_H = 1.0$.
*H*2 Extended Hückel Theory with $Z'_H = 1.2$.

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