

MODIFIED CNDO METHOD. I. CALCULATION OF THE STRETCHING FORCE CONSTANTS FOR DIATOMIC MOLECULES

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A modified semiempirical parametrization of the approximate SCF MO CNDO treatment is presented. The new parameters, different from those used by Pople and Segal, have been chosen from various atomic data. Moreover, the two centre Coulomb integrals were calculated with the aid of Ohno's formula. The resonance integrals were approximated by using a semiempirical relation similar to that proposed by Cusachs.

The modified CNDO method has been tested on a series of diatomic molecules. Similarly as in the case of the original CNDO approach, the orbital energies are not yet adequate for the a priori calculations. However, the bond lengths and dipole moments are in reasonable agreement with experimental data. The main success of the modifications introduced seems to be in the calculation of the stretching force constants. In general, they are better than those reported previously by Segal.

1. Introduction

Until recently, most of the semiempirical theories of the electronic structure of molecules were concerned with π -electron systems. Considerable success was achieved in the interpretation of electronic properties of these molecules using the semiempirical approach due to Parr-Pariser and Pople. The source of this success seems to lie mainly in the reasonable choice of few semiempirical parameters (Parr 1965). Nevertheless, in the last years, a rapid progress has been observed in the semiempirical theories concerning both sigma and π -electrons explicitly (Klopman 1964, 1965; Newton *et al.* 1966; Pohl *et al.* 1964; Baird *et al.* 1967). The first semiempirical approach, consequently based on the Hartree-Fock-Roothaan SCF equations has been developed by Pople, Santry and Segal and is known as the so-called CNDO method (Pople *et al.* 1965, 1966).

The CNDO method, which is discussed in the next section resembles in most cases the Parr-Pariser-Pople treatment of π -electron systems. It works in the zero differential approximation and its usefulness is determined by a specific choice of semiempirical parameters for atoms and bonds in a given molecule. Although the approximations introduced

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are rather drastic, the results obtained seem to be, in general, rather good. This is the case of the charge density distribution, bond lengths, bond angles and bending force constants. Moreover, the interval between one-electron energy levels is nearly the same as that calculated with the non-empirical methods. In contrast to the calculated bending force constants, the force constants for stretching vibrations are rather poor, being 3-5 times larger than those observed ones (Segal 1967).

On the other hand, a simplified but reliable calculation of stretching force constants is needed in view of the interpretation of molecular spectra and their environmental changes.

In the present paper we develop a modified version of the CNDO method (Sadlej and Kęcki 1968) which enables us to calculate more realistic stretching force constants than those obtained by Segal by the original CNDO scheme. The modifications presented here consist in a new approximation for the Coulomb repulsion integrals and a different choice of basic parameters. This modified CNDO approach is tested on a series of diatomic molecules, and then applied in the calculation of the CN stretching force constant in acetonitrile and its complexes with metal cations.

2. The original CNDO method and its basic assumptions

In this section the original CNDO approach is presented and its main simplifying assumptions are reviewed. According to Pople *et al.*, we start with the Hartree-Fock-Roothaan self consistent field equations.

$$\sum_{\nu} F_{\mu\nu} c_{\nu i} = \sum_{\nu} S_{\mu\nu} c_{\nu i} \epsilon_i \quad (2.1)$$

for the best molecular orbitals ψ_i approximated in the LCAO form

$$\psi_i = \sum_{\mu} c_{\mu i} \Phi_{\mu}. \quad (2.2)$$

The basic set of atomic orbitals Φ_{μ} is limited to all the valence shell orbitals of all atoms constituting the molecule. The nuclei with inner shell electrons are assumed to form an unpolarizable core acting as a potential field in the so-called core Hamiltonian. The field contributed by the nucleus of atom A and its inner electrons is denoted by $V_A(\vec{r})$. Then the matrix elements $F_{\mu\nu}$ of the HFR operator for valence electrons are generally defined as

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \quad (2.3)$$

where

$$H_{\mu\nu} = \int \Phi_{\mu}^* \left(-\frac{1}{2} \Delta - \sum_A V_A(\vec{r}) \right) \Phi_{\nu} d\nu \quad (2.4)$$

$$G_{\mu\nu} = \sum_{\lambda} \sum_{\delta} P_{\lambda\delta} \left[\langle \mu\nu | \lambda\delta \rangle - \frac{1}{2} \langle \mu\delta | \nu\lambda \rangle \right] \quad (2.5)$$

$$\langle \mu\nu | \lambda\delta \rangle = \int \Phi_\mu^*(1) \Phi_\nu(1) \frac{1}{r_{12}} \Phi_\lambda^*(2) \Phi_\delta(2) dv_1 dv_2 \quad (2.6)$$

$$S_{\mu\nu} = \int \Phi_\mu^* \Phi_\nu dv \quad (2.7)$$

$$P_{\lambda\delta} = \sum_i^{\text{occ.}} 2c_{\lambda i}^* c_{\delta i} \quad (2.8)$$

In order to simplify these equations, Pople *et al.* introduce the approximations listed below.

1) As mentioned above, the inner shell electrons are treated as an unpolarizable core and are not considered explicitly.

2) The zero differential overlap (ZDO) approximation is accepted. This means that whenever the expression $\Phi_\mu \Phi_\nu$, $\mu \neq \nu$ appears as an integrand, the corresponding integral is set equal to zero. It follows that

$$\langle \mu\nu | \lambda\delta \rangle = \delta_{\mu\nu} \delta_{\lambda\delta} \langle \mu\mu | \lambda\lambda \rangle = \delta_{\mu\nu} \delta_{\lambda\delta} \gamma_{\mu\lambda} \quad (2.9)$$

$$S_{\mu\nu} = \delta_{\mu\nu} \quad (2.10)$$

Thus, the electron repulsion integrals (one and two centre exchange, hybrid and multicentre integrals) all extremely difficult to calculate disappear.

3) In order to ensure the invariance with respect to any local orthogonal transformation of a basic set of atomic orbitals, *e.g.*, with respect to the hybridization changes, a further restriction on the values of the Coulomb repulsion integrals is imposed. They all must be equal to the common value of γ_{AA} for the one-centre case and γ_{AB} for the two centre case. In other words, these integrals are independent of the type of atomic orbitals Φ_μ and Φ_ν for a given core or pair of cores, respectively.

4) Core Hamiltonian matrix elements $H_{\mu\mu}$ are evaluated by using the Goeppert-Mayer and Sklar approximation

$$\left(-\frac{1}{2} \Delta - V_A \right) \Phi_\mu = U_{\mu\mu} \Phi_\mu \quad (2.11)$$

where $U_{\mu\mu}$ denotes the energy of an electron in orbital Φ_μ of atom A in the field of the core A . Then, with approximation (2) kept in mind, the matrix element $H_{\mu\mu}$ may be written as

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} \langle \Phi_\mu | V_B | \Phi_\mu \rangle \quad (2.12)$$

5) Off-diagonal core Hamiltonian matrix elements are, in general, taken to be proportional to corresponding overlap integrals $S_{\mu\nu}$, with a proportionality constant β_{AB}^0 determined in a semiempirical way.

6) According to the approximation (1), the integrals $\langle \Phi_\mu | V_B | \Phi_\mu \rangle$ appearing in (2.12) are calculated according to the electrostatic model

$$V_{AB} = \langle \Phi_\mu | V_B | \Phi_\mu \rangle = z_B \gamma_{AB} \quad (2.13)$$

With all these assumptions, the matrix elements of the HFR operator are simplified to the following form

$$F_{\mu\mu} = U_{\mu\mu} - \left(P_{AA} - \frac{1}{2} P_{\mu\mu} \right) \gamma_{AB} + \sum_{B \neq A} (P_{BB} \gamma_{AB} - V_{AB}) \quad (2.14)$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB} \quad \text{for } \mu \neq \nu \quad (2.15)$$

where

$$P_{xx} = \sum_{\mu}^x P_{\mu\mu}.$$

As seen, they depend on the values of γ_{AA} , γ_{AB} , $U_{\mu\mu}$ and β_{AB}^0 . In the Pople approach, the mean Coulomb integrals γ_{AA} and γ_{AB} were calculated theoretically. $U_{\mu\mu}$ and β_{AB}^0 were determined from experimental data and referenced non-empirical calculations, respectively.

The problem of reasonable and effective parametrization of this method is discussed in the next section and some modifications with respect to the parameters used by Pople, are suggested.

3. Some remarks on the basic assumptions and the semiempirical parameters

It should be pointed out that the CNDO method, similarly as the Parr-Pariser-Pople approach for π -electron systems, is based to a great extent on the ZDO approximation. It is usually said that the CNDO treatment is valid if the AO's used are treated as the Löwdin orthogonalized orbitals (Fischer-Hjalmar 1965). Then, the HFR equations in their simplified form are nearly correct due to small the values of the neglected integrals. However, in this case the basic parameters $U_{\mu\mu}$, γ_{AA} , γ_{AB} and β_{AB}^0 do no longer have the typical one or two centre character (Cook *et al.* 1967). Moreover, they depend on the topology of a given molecule and the problem of transferability of these parameters cannot be correctly solved.

It is very hard to say *a priori* how involved such a treatment is and what the general rules for reasonable parametrization are. The apparent attestation is to make a comparison of the final results with experimental data. Thus, there are many ways in which the parameters may be chosen. One of them was used by Pople *et al.*

The parameter $U_{\mu\mu}$ has been taken partly from atomic data (I_{2s} and I_{2p} ionization potentials) and depends on the assumption regarding the mean value of γ_{AA} Coulomb integrals. According to the approximation (2), which allows us to neglect all one-centre exchange and hybrid integrals, the formulas for $U_{\mu\mu}$ are given for the configuration $X(2s^m 2p^n)$ by

$$U_{2s,2s} = -I_{2s} - (m+n-1)\gamma_{AA} \quad (3.1)$$

$$U_{2p,2p} = -I_{2p} - (m+n-1)\gamma_{AA}. \quad (3.2)$$

Some comments should be devoted to the Coulomb integrals γ_{AA} and γ_{AB} . As mentioned above, such an approximation is forced upon us by the invariance principle for the HFR equations. It seems to be quite good in the case of two centre integrals γ_{AB} for interatomic

distances typical of molecules. It is supported by numerical values of various Coulomb integrals calculated for the CO molecule by Hurley (1960). If we assume $\gamma_{\mu\nu}$ to be the mean value of γ_{AB} , then the error introduced seems to be fairly small in view of the approximate nature of the CNDO theory. However, the same statement should not be true for the one-centre Coulomb integrals and it would seem better to find a reasonable semi-empirical relation for γ_{AB} integrals with correct asymptotic behavior. A similar procedure has been successfully applied in the theory of π -electron systems.

More arbitrary is the case of off-diagonal core Hamiltonian matrix elements. In the Pople method they were chosen to be proportional to the corresponding overlap integrals. This approximation is partly due to the mentioned invariance principle. The frequently used approximate formulas of Wolsberg-Helmholz (1952) and Cusachs (1965) are not invariant with respect to any local orthogonal transformation of the reference system. However, we have applied a modified Cusachs type formula for $H_{\mu\nu}$ integrals despite the inaccurate transformation properties. It seems that this incorrectness is of little importance for our final results. On the other hand the proposed formulas reproduce fairly well the shapes of molecular energy curves.

4. Modified parametrization of the CNDO method

In order to determine the one-centre core Hamiltonian matrix elements $H_{\mu\mu}$ and one-centre Coulomb repulsion integrals γ_{AA} and γ_{AB} we have extensively used experimental data. Apart from the "experimental" values of I_{2s} and I_{2p} ionization potentials evaluated by Pople *et al.*, we introduce a third experimental quantity, $U_{2s,2s}$. According to its physical meaning, this quantity may be taken as equal to the last valence ionization potential of a given atom A . Knowledge of $U_{2s,2s}$ together with Eq. (3.1) allows us to determine the "experimental" mean value of integral γ_{AA} , and then from Eq. (3.2) the value of $U_{2p,2p}$.

All these quantities for a series of first row atoms are listed in Table I.

The matrix elements $U_{\mu\mu}$ and integrals $\gamma_{\mu\mu}$ (in a.u.)

TABLE I

	Li	B	C	N	O	F
$U_{\mu\mu} \ 2s$	-0.1981	-1.3936	-2.3970	-3.5965	-5.0753	-6.8026
$U_{\mu\mu} \ 2p$	-0.1301	-1.1823	-2.0474	-3.1411	-4.4678	-6.0110
γ_{xx}	0.1678	0.4386	0.5517	0.6641	0.7771	0.8875

It should be pointed out that our values of $U_{2s,2s}$ and $U_{2p,2p}$ are higher (in absolute value) than those obtained previously by other authors (Sichel *et al.* 1967). On the other hand, the integrals γ_{AA} are slightly lower than the theoretical values. One may expect both of these effects to include to some extent the errors due to the ZDO approximation. Once we are forced to manipulate with semiempirical theory, it seems better to use the experimental data as far as possible in order to reduce the errors introduced by incorrectness of the theory.

In the case of the mean two-centre Coulomb repulsion integrals γ_{AB} we use the semiempirical formula of Ohno (1964), successfully applied in the theory of π -electron systems,

$$\gamma_{AB} = e^2 (R_{AB}^2 + a_{AB}^2)^{-1/2} \quad (4.1)$$

where R is the interatomic distance and a_{AB} is a parameter derived from the asymptotic properties determined by the relation

$$\left| \frac{e^2}{a_{AB}} \right| = \left(\left| \frac{e^2}{a_A} \right| + \left| \frac{e^2}{a_B} \right| \right), \quad a_x = \gamma_{xx}^{-1}. \quad (4.2)$$

The formula of Mataga and Nishimoto (1957) studied in a previous paper (Sadlej, Kecki 1968), rather gives too large bond distances in diatomic molecules and has been omitted in these calculations.

A reasonable choice of non-diagonal core Hamiltonian matrix elements is more complicated. The approximation used by Pople *et al.* is not justified very well as the $H_{\mu\nu}$ integrals are proportional rather to $S_{\mu\nu}^2$ than to $S_{\mu\nu}$. The most suitable formula seems to be that of Cusachs,

$$H_{\mu\nu} = \frac{1}{2} S_{\mu\nu} (2 - |S_{\mu\nu}|) (I_{\mu\nu} + I_{\nu\nu}). \quad (4.3)$$

Similarly, as had been done by Pople, we have introduced the mean values of $I_{\mu\mu}$ for all valence orbitals of atom A . Thus

$$H_{\mu\nu} = \frac{1}{2} S_{\mu\nu} (2 - |S_{\mu\nu}|) (\beta_A^0 + \beta_B^0) \quad (4.4)$$

where

$$\beta_x^0 = \frac{1}{2} (I_{2s} + I_{2p}).$$

Numerous calculations with various approximations for γ_{AB} and $H_{\mu\nu}$ indicate that our parameters are optimal in view of the obtained molecular energy curves.

Finally, it should be noted that overlap integrals were calculated with the use of Slater-type atomic orbitals and the same orbital exponents as those used by Pople *et al.*

5. Some details of numerical calculations

The simplified CNDO equations were solved by using the iteration procedure. The initial set of molecular orbitals was obtained from the diagonalization of the core Hamiltonian matrix and there from the zeroth order P matrix was formed. Using this matrix, the CNDO Hamiltonian matrix elements were set up and the entire process was repeated, until selfconsistency of the P matrix with an accuracy equal to 0.0001 was achieved. The potential

energy curve was constructed with the points calculated in the range of $3/2 h\nu_e$ above the minimum energy. The steps were chosen to be equal to 0.02 a.u. of length.

From the calculated energy values of various bond distances, the molecular energy curve was approximated with the best polynomial of the order $n \leq 10$. This procedure was performed in a selfconsistent manner, increasing the order of the polynomial by one in each following step. The selfconsistency was achieved when the difference between the coefficients at R^2 in two successive steps became negligible.

All calculations were programmed for the Gier Computer in Gier-Algol-3 algorithmic language.

6. Results for diatomic molecules

In this section we should like to present our results for the series of diatomic molecules with $^1\Sigma^+$ ground state. We compare these results with those obtained by Pople and those calculated according to non-empirical approaches. This comparison concerns the orbital energies, charge density distribution and the shape of molecular energy curves.

Similarly to the original Pople treatment, the orbital energies are in general more negative than those calculated in a non-empirical way with the same restriction for AO basis set. However, their relative values, *i. e.* the orbital energy intervals $\Delta\varepsilon = \varepsilon_i - \varepsilon_j$, agree sufficiently with a priori results. This is shown in Table II.

Comparison of molecular orbital energy intervals (in a.u.)

TABLE II

Molecule	Interval	$\Delta\varepsilon$ (CNDO)	$\Delta\varepsilon$ (a priori)	Table Ref.
BH	$3\sigma - 2\sigma$	0.4169	0.3020	[1]
	$4\sigma - 2\sigma$	1.2391	1.1150	
FH	$3\sigma - 2\sigma$	0.8317	0.9108	[1]
	$4\sigma - 2\sigma$	1.9315	1.9535	
CH ⁺	$3\sigma - 2\sigma$	0.3452	0.3935	[2]
	$4\sigma - 2\sigma$	1.0144	1.9200	
N ₂	$2\sigma_u - 2\sigma_g$	0.6967	0.7217	[1]
	$3\sigma_g - 2\sigma_g$	0.9071	0.9076	
	$3\sigma_u - 2\sigma_g$	2.1742	1.5633	
	$1\pi_g - 1\pi_u$	0.8658	0.8524	
BF	$4\sigma - 3\sigma$	0.8996	0.9140	[1]
	$5\sigma - 3\sigma$	1.2787	1.2880	
	$6\sigma - 3\sigma$	2.2052	2.2491	
	$2\pi - 1\pi$	0.9187	0.8298	

In order to test the correctness of the calculated charge density-bond order matrix P we have calculated the total dipole moments μ_{app} for heteronuclear diatomic molecules using the approximate method proposed by Pople *et al.*

According to this method, the total dipole moment is defined as the sum of μ_Q , representing the contribution of atomic charge densities, and μ_{sp} , the dipole moment due to atomic dipole. Corresponding values of the total dipole moment μ_{app} , μ_Q and μ_{sp} together with experimental data are listed in Table III. As one may see from this Table, the results obtained here are not worse than those found by Pople or even by nonempirical calculations with limited AO basis.

TABLE III

Dipole moments (in debyes) (negative values are for A+B⁻)

Molecule	CNDO calculation, this work			Observed [3]	Table Ref. calc. [1]
	μ_Q	μ_{sp}	μ_{app}		
LiH	-1.86	-4.23	-6.09	-5.90	-6.41
BH	-0.77	2.75	1.97	—	1.00
FH	0.39	0.90	1.29	1.91	0.88
LiF	-1.21	-1.42	-2.63	-6.60	-2.94
BF	0.41	3.97	4.38	—	2.16

The main attention is turned in this paper to the calculation of the potential energy curves and especially to the reasonable semiempirical determination of the harmonic force constants. In the paper published recently by Segal, the CNDO calculated harmonic force constants were three to five times larger than the experimental ones. The present parametrization of the CNDO method allows us to obtain more realistic values of stretching force

TABLE IV

Potential energy curve parameters for diatomic molecules

Molecule	CNDO this work R_{\min} (Å)	exp [4] R_{\min} (Å)	CNDO this work $k_e \cdot 10^5$ dyns/cm	exp [4] $k_e \cdot 10^5$ dyns/cm	Table Ref. [5] $k_e \cdot 10^5$ dyns/cm
LiH	1.550	1.595	1.99	1.026	1.92
BH	1.337	1.232	6.71	3.044	9.3
FH	1.147	0.917	13.48	9.657	19.7
CH ⁺	1.760	1.131	3.05	4.6 [6]	12.5
OH ⁻	1.255	0.970	7.60	7.791[7]	—
Li ₂	2.758	2.672	0.63	0.255	—
N ₂	1.264	1.092	34.19	22.94	53.8
LiF	1.606	1.510	10.55	2.783	—
BF	1.426	1.264	20.64	8.071[8]	—

constants for diatomic molecules. However, these are still only qualitatively comparable with experimental data. On the other hand, the bond distances agree rather well with measured values. These results, *i e.* the calculated bond lengths and harmonic stretching force constants, are presented in Table IV.

In the course of our calculations we have found the harmonic stretching force constant to be drastically dependent on the value of β_{AB}^0 and γ_{AB} . For example, if one chooses the mean value of β_A^0 as equal to I_{2s} of atom A , then the harmonic force constant increases rapidly. The opposite dependence of the approximation of the integrals γ_{AB} follows from the comparison of the present results and those previously performed based on the MN formula. However, the bond lengths obtained with the MN approximation for the integrals γ_{AB} were too far from the experimental ones. This was the reason why we decided to use the Ohno formula for the approximation of two-centre electron repulsion integrals γ_{AB} .

7. Final remarks

The results obtained here are not very satisfactory, especially in the case of calculated harmonic force constants. However, the non-empirical calculations even with the limited AO basis are more time consuming and their results are in general of the same quality.

Assuming the results presented above to be quite satisfactory, we consider in the next part of this paper some problems of intermolecular interactions in acetonitrile electrolyte solutions.

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