Theoret. chim. Acta (Berl.) 7, 32—40 (1967)

Atomic Parameters for Semi-Empirical SCF-LCAO-MO Calculations

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Received August 19, 1966

Atomic core and electron-repulsion components of the Hamiltonian matrix elements, for *s* and *p* valence orbitals, have been evaluated from atomic valence-state energies. Atomic parameters for semi-empirical, self-consistent field, molecular-orbital calculations with the "complete neglect of differential overlap" (CNDO) approximation are given for non-transition elements of the first four rows of the periodic table. The application of these parameters to the evaluation of interatomic parameters for calculations with the CNDO approximation is discussed.

Für die Elemente der ersten vier Reihen des Periodensystems (mit Ausnahme der Übergangselemente) werden atomare Parameter für halbempirische SCF–MO Rechnungen mit der CNDO Näherung gegeben. Es wird die Anwendung dieser Parameter zur Bestimmung interatomarer Größen, die für Rechnungen mit der CNDO Näherung gebraucht werden, diskutiert.

Les énergies des états de valence atomiques sont utilisées pour évaluer les éléments de la matrice hamiltonienne dans la base des orbitales de valence *s* et *p*. Des paramètres atomiques sont fournis pour les éléments des quatre premières périodes de la table périodique (à l'exception des éléments de transition). Ces paramètres sont utilisables pour des calculs semi-empiriques dans la méthode SCF–MO avec «recouvrement différentiel nul» (CNDO). L'application de ces paramètres à l'évaluation de paramètres interatomiques pour des calculs dans l'approximation CNDO est discutée.

1. Introduction

Several authors [*4, 5, 7, 10, 12, 19—21*] have recently considered the extension of approximate self-consistent field LCAO molecular-orbital calculations to include all valence-shell electrons. A useful approximation is "complete neglect of differential overlap" (CNDO), as proposed by Pople et al. [*19*], in which differential overlap between every pair of atomic orbitals is neglected. One problem is the assignment of atomic parameters: core and electron-repulsion matrix elements over the orbitals of one atom. Pople and Segal [*20, 21*] approximated all electron-repulsion matrix elements as analytic integrals for Slater *s* orbitals. Oleari et al. [*12*] have evaluated atomic parameters from valence-state energies, but not the parameters required with the CNDO approximation. Klopman [*6*] has evaluated parameters directly from atomic spectra, but has not used valence-state energies explicitly. In this paper, atomic parameters have been evaluated from accurate valence-state energies [*2, 3*] for semi-empirical calculations with the CNDO approximation.

If the CNDO approximation is made and the results are to be invariant with respect to local transformations of the atomic orbital basis functions, then the electron-repulsion matrix element g_{ij} between the i^{th} and j^{th} orbitals, on atoms A and B respectively, must be given the same value g_{AB} for all pairs of atomic orbitals on the two atoms [*19*]. For a basis set of s and p orbitals, there are four distinct atomic electron-repulsion parameters: g_{ss}, g_{sp}, g_{pp} and $g_{pp'}$ (where p and p' are two different valence p orbitals on the same atom). In the CNDO method these must all be represented by a common value characteristic of the atom, g_{AA}, which is supposed to measure an average repulsion between two valence electrons on atom A.

This restriction, with the CNDO approximation itself, is equivalent to assuming that the energy of any valence state of the electronic configuration $(ns)^p\,(np)^q$ is the same. The valence-state data of HINZE and JAFFÉ [*2, 3*] show this to be true within 2—3 eV.

2. Parameters Evaluated from Atomic Spectra

POPLE and SEGAL [*20, 21*] assigned to g_{AA} the analytic value of the electrostatic repulsion energy of two electrons in a Slater s orbital. (If the electron-repulsion parameters are evaluated from atomic spectra, g_{ss} for most atoms is the highest of the four and not an average value.) No allowance is made for correlation energy, as is done when the parameters are evaluated from atomic spectra [*1, 16*]. Since POPLE and SEGAL used g_{AA} to compute U_{ss} and U_{pp}, where U_{ii} is the diagonal matrix element of the i^{th} atomic orbital on atom A with respect to the one-electron Hamiltonian containing only the core of atom A, any error in g_{AA} causes error in U_{ss} and U_{pp}.

The Pariser approximation [*14*] for one-centre electron-repulsion integrals in semi-empirical calculations on π-systems is

$$g_{ii} = I_i - A_i\,, \tag{1}$$

where I_i is the valence-state ionization potential and A_i the valence-state electron affinity of the orbital. Valence-state energies are used in order to reproduce the state of the atom in a molecule.

OLEARI et al. [*12*] have generalized this method by determining parameters C, U_{ss}, U_{pp}, g_{ss}, g_{sp}, g_{pp} and $g_{pp'}$ so that the equation

$$E = C + \sum_i n_i U_{ii} + \tfrac{1}{2} \sum_i \sum_{j \neq i} n_i n_j g_{ij} + \tfrac{1}{2} \sum_i n_i (n_i - 1)\, g_{ii}\,, \tag{2}$$

where i and j are summed over all orbitals on an atom, best fits certain atomic valence-state energies as a function of orbital occupation numbers n_i.

Eq. (2) is similar to a theoretical expression for valence-state energies, except that the parameters are determined from atomic spectra. These parameters vary markedly with atomic charge [*12*] due to changes in orbital size. For use in molecular calculations, it is therefore important to evaluate the parameters from energies of valence states which are as close as possible to electroneutrality. The constant C is included so that the "core state" with all valence electrons removed is not used in evaluating the parameters. If C were set equal to zero, the core state would be fixed as the zero of energy and therefore used in determining the parameters.

The following changes have been made from the parameters of OLEARI et al.:

a) The valence-state energy data of Hinze and Jaffé [2, 3] have been used rather than those of Skinner and Pritchard [22], since the former are the result of a more complete and systematic examination of atomic spectral data, and systematic calculation of Slater-Condon parameters and non-observable states. Also the energies of all valence states needed are available [2].

b) Parameters for a given atom have been evaluated entirely from valence-state energies of that atom. Oleari et al. have adjusted their parameters to vary linearly with atomic number, since some valence-state energies had to be found by extrapolation [13]. This was unnecessary in the present work since more complete valence-state energy data were used [2].

c) The electron-repulsion integrals g_{ij} have been averaged to find the atomic parameter g_{AA}. (Section 4).

d) The atomic core matrix elements U_{ss} and U_{pp} have been adjusted *after* the averaging process for g_{AA}. (Section 4).

3. Valence State Energies used for Evaluation of Atomic Parameters

Eq. (2) contains seven atomic parameters: core integrals U_{ss} and U_{pp}; electron-repulsion integrals g_{ss}, g_{sp}, g_{pp} and $g_{pp'}$; and an additive constant C. For each atom, the core and electron-repulsion integrals have been evaluated by substituting into Eq. (2) the energies [2, 3] of seven valence states, selected according to the following principles:

a) Each electron-repulsion integral was calculated as the difference between an ionization potential and an electron affinity of the neutral atom, i.e. from energies of states differing from electroneutrality by not more than one electron.

b) For each atom, the states chosen formed a set sufficient for the evaluation of the seven parameters from Eq. (2).

c) When conditions a) and b) permitted a further choice of states, valence states with low promotion energy were preferred to more excited states, as the lower promotion energies were derived from more complete atomic spectral data and are more likely to be accurate. The lower-energy states also correspond more closely to the state of the atom in a molecule.

d) Unipositive valence states were preferred to uninegative states, since the ground-state ionization potential of most atoms is more accurately known than the ground-state electron affinity.

For carbon, e.g.,

$$\begin{aligned}
g_{ss} &= E(\mathrm{C}^-, s^2ppp) - 2E(\mathrm{C}, sppp) + E(\mathrm{C}^+, ppp)\\
g_{sp} &= [E(\mathrm{C}^-, s^2ppp) - E(\mathrm{C}, sppp)] - [E(\mathrm{C}, s^2pp) - E(\mathrm{C}^+, spp)]\\
g_{pp} &= E(\mathrm{C}^-, sp^2pp) - 2E(\mathrm{C}, sppp) + E(\mathrm{C}^+, spp)\\
g_{pp'} &= [E(\mathrm{C}^-, sp^2pp) - E(\mathrm{C}, sp^2p)] - [E(\mathrm{C}, sppp) - E(\mathrm{C}^+, spp)]\\
U_{ss} &= E(\mathrm{C}, sppp) - E(\mathrm{C}^+, ppp) - 3g_{sp}\\
U_{pp} &= E(\mathrm{C}, sppp) - E(\mathrm{C}^+, spp) - g_{sp} - 2g_{pp'}\,.
\end{aligned}$$

The evaluation of the additive constant is described in Section 6.

4. Atomic Parameters for CNDO Calculations

If the full SCF–LCAO–MO equations could be simplified by the CNDO approximation, without the restrictions reviewed in the Introduction, the diagonal matrix element of the total electronic Hamiltonian for the i^{th} orbital on atom A would be

$$F_{ii} = U_{ii} + \sum_{j} P_{jj} g_{ij} (1 - \tfrac{1}{2}\,\delta_{ij}) + \sum_{k} P_{kk} g_{ik} - \sum_{\mathrm{B} \neq \mathrm{A}} V_{i\mathrm{B}} \tag{3}$$

where P_{ii} is the electronic population of the i^{th} orbital in the molecule, j is summed over all valence orbitals on atom A, and k over all valence orbitals on other atoms, denoted by B. Because of the restrictions due to invariance of the SCF equations in the CNDO Approximation, this must be modified to

$$F_{ii} = U_{ii} + g_{\mathrm{AA}} \sum_{i} P_{jj} \, (1 - \tfrac{1}{2}\,\delta_{ij}) + \sum_{k} P_{kk} g_{\mathrm{AB}} - \sum_{\mathrm{B} \neq \mathrm{A}} V_{\mathrm{AB}} \, . \tag{4}$$

These two equations are not equivalent in general but the parameters may be chosen so that they are equivalent for a specific charge distribution. In this paper the parameters are evaluated by equating the diagonal matrix elements of (3) and (4) when all the atoms in a molecule have their valence-shell electron population equally distributed among one s and three p orbitals. In this case (3) and (4) become

$$F_{ii} = U_{ii} + \frac{P_{\mathrm{AA}}}{4} \sum_{j} g_{ij} \, (1 - \tfrac{1}{2}\,\delta_{ij}) + \tfrac{1}{4} \sum_{k} P_{\mathrm{BB}} g_{ik} - \sum_{\mathrm{B} \neq \mathrm{A}} V_{i\mathrm{B}} \tag{5}$$

and

$$F_{ii} = U_{ii} + \tfrac{7}{8}\, g_{\mathrm{AA}} P_{\mathrm{AA}} + \sum_{\mathrm{B} \neq \mathrm{A}} (P_{\mathrm{BB}} g_{\mathrm{AB}} - V_{\mathrm{AB}}) \tag{6}$$

respectively, where P_{AA} is the total valence-shell electron population on atom A. The atomic terms are equal for

$$g_{\mathrm{AA}} = g^{i}_{\mathrm{AA}} = \tfrac{2}{7} \sum_{j} g_{ij} (1 - \tfrac{1}{2}\,\delta_{ij}) \, , \tag{7}$$

where the superscript indicates that the matrix element for the i^{th} orbital is used to evaluate g_{AA}. The interatomic terms are dealt with in Section 5.

Eq. (7) averages the intra-atomic valence-shell electron repulsion on an electron in the i^{th} atomic orbital for the given charge distribution, if the electronic population of each orbital is composed equally of two electrons of opposite spin, as in a molecule. As there is no reason to prefer the use of any one orbital for the evaluation of g_{AA}, (7) is averaged over all orbitals on atom A:

$$g_{\mathrm{AA}} = \tfrac{1}{4} \sum_{i} g^{i}_{\mathrm{AA}} = \frac{1}{14} \sum_{i} \sum_{j} g_{ij} (1 - \tfrac{1}{2}\,\delta_{ij}) \, . \tag{8}$$

For a basis set of s and p orbitals,

$$g_{\mathrm{AA}} = \frac{1}{28} (g_{ss} + 12 g_{sp} + 3 g_{pp} + 12 g_{pp'}) \, . \tag{9}$$

The replacement of (7) by (8) destroys the equality of the atomic terms in (5) and (6). It is impossible to adjust the parameters within the framework of the CNDO approximation so as to restore this equality for all values of P_{AA}. It therefore seems best to restore the equality for the case of an exactly neutral atom, to eliminate error due to the CNDO approximations in calculations involving homopolar bonding. For calculations involving all valence-shell electrons, the total valence-shell electron population P_{AA} of an exactly neutral atom equals the core charge Z_{A}. Equality of (5) and (6) will then be restored in the case of a neutral atom by adjusting the core matrix elements in (6) for any value of P_{AA}, to

$$\bar{U}_{ii} = U_{ii} + \frac{Z_{\mathrm{A}}}{4}\left[\sum_j g_{ij}(1 - \tfrac{1}{2}\delta_{ij}) - \tfrac{7}{2} g_{\mathrm{AA}}\right] \tag{10}$$

where the bar indicates an adjusted parameter. For s and p orbitals,

$$\bar{U}_{ss} = U_{ss} + \frac{Z_{\mathrm{A}}}{4}\left[\tfrac{1}{2} g_{ss} + 3g_{sp} - \tfrac{7}{2} g_{\mathrm{AA}}\right] \tag{11}$$

and

$$\bar{U}_{pp} = U_{pp} + \frac{Z_{\mathrm{A}}}{4}\left[\tfrac{1}{2} g_{pp} + g_{sp} + 2g_{pp'} - \tfrac{7}{2} g_{\mathrm{AA}}\right]. \tag{12}$$

5. Application to Evaluation of Interatomic Electron-Repulsion Integrals

If the interatomic terms of (5) and (6) are equated and the resulting expressions averaged over all orbitals on atom A, it is found that

$$g_{\mathrm{AB}} = \frac{1}{16}\sum_i \sum_k g_{ik} \tag{13}$$

and

$$V_{\mathrm{AB}} = \tfrac{1}{4}\sum_i V_{i\mathrm{B}}. \tag{14}$$

In semi-empirical molecular orbital calculations on π-systems, two-centre repulsion integrals are usually given as a function of internuclear distance R by one of several formulae [*15*, *8*, *11*] for which

$$\lim_{R \to 0} g_{ij} = \tfrac{1}{2}(g_{ii} + g_{jj}), \tag{15}$$

where the i^{th} and j^{th} orbitals are $2p\pi$ orbitals on atoms A and B respectively. A generalization for any two valence orbitals is

$$\lim_{R \to 0} g_{ij} = \tfrac{1}{2}(g^{\mathrm{A}}_{ij'} + g^{\mathrm{B}}_{i'j}) \tag{16}$$

where $g^{\mathrm{A}}_{ij'}$ is the repulsion integral, evaluated from atomic valence-state energies as in Section 3, between an electron in the i^{th} orbital, and an electron in the valence orbital j' on atom A of the same type (s, p_x, p_y or p_z) as the j^{th} orbital on B, analogue for $g^{\mathrm{B}}_{i'j}$.

From (13) and (16),

$$\lim_{R \to 0} g_{\mathrm{AB}} = \tfrac{1}{2}(g^{*}_{\mathrm{AA}} + g^{*}_{\mathrm{BB}}) \tag{17}$$

where

$$g^{*}_{\mathrm{AA}} = \frac{1}{16}\sum_i \sum_j g_{ij}. \tag{18}$$

For a basis set of s and p orbitals

$$g^{*}_{\mathrm{AA}} = \frac{1}{16}(g_{ss} + 6g_{sp} + 3g_{pp} + 6g_{pp'}). \tag{19}$$

When one atom is hydrogen, (19) should formally be replaced by

$$g_{\mathrm{AA}}^{*} = \tfrac{1}{4}\,(g_{ss} + 3g_{sp}) \tag{20}$$

for both hydrogen and the other atom. As g_{sp} is not defined for hydrogen, it is suggested that g_{AA}^{*} be equated to g_{ss} for hydrogen, and to the value given by Eq. (19) for the other atom. Since the first of these approximations raises g_{AB} and the second lowers it, the resulting approximation is reasonable.

Eq. (14) is of no use in evaluating V_{AB} since semi-empirical values of $V_{i\mathrm{B}}$ are not known. POPLE and SEGAL [*21*] have put

$$V_{\mathrm{AB}} = Z_{\mathrm{B}}\, g_{\mathrm{AB}} \tag{21}$$

so that penetration contributions to F_{ii} vanish. This is especially important if g_{AB} is evaluated from atomic spectra, since if in this case V_{AB} were evaluated analytically as in the original CNDO method [*20*] the penetration contributions would be quite large.

6. Results

Tab. 1 shows $\overline{U}_{ss}$, $\overline{U}_{pp}$, g_{AA} and g_{AA}^{*} evaluated from Eqs. (11), (12), (9) and (19) respectively. The additive constant is denoted by C^0 since it is chosen so that

Table 1. *Semi-empirical atomic parameters* (in eV)

Element	$\overline{U}_{ss}$	$\overline{U}_{pp}$	g_{AA}	g_{AA}^{*}	C
H	−13.595	—	12.848	12.848	13.595
Li	−4.999	−3.673	3.469	3.458	4.999
Be	−15.543	−12.280	5.935	5.953	25.151
B	−30.371	−24.702	8.000	8.048	61.444
C	−50.686	−41.530	10.207	10.333	123.517
N	−70.093	−57.848	11.052	11.308	204.291
O	−101.306	−84.284	13.625	13.907	335.908
F	−129.544	−108.933	15.054	15.233	487.697
Na	−4.502	−3.247	2.982	3.031	4.502
Mg	−13.083	−9.603	4.623	4.656	21.544
Al	−22.828	−18.592	5.682	5.680	47.203
Si	−36.494	−30.375	6.964	7.015	92.438
P	−58.610	−50.940	9.878	9.886	172.095
S	−66.796	−58.008	9.205	9.260	227.860
Cl	−86.774	−75.681	10.292	10.366	335.847
K	−3.170	−3.115	3.702	3.560	3.170
Ca	−9.842	−7.696	3.977	3.979	15.707
Ga	−25.032	−19.807	5.936	5.942	52.063
Ge	−35.844	−29.973	6.608	6.634	92.527
As	−50.151	−44.485	8.399	8.361	150.653
Se	−66.005	−57.927	9.121	9.156	227.686
Br	−76.413	−65.412	8.823	8.838	294.760
Rb	−3.555	−2.804	2.495	2.384	3.555
Sr	−9.430	−7.074	3.749	3.761	15.110
In	−23.056	−17.663	5.530	5.582	47.185
Sn	−26.981	−21.869	4.297	4.304	72.317
Sb	−47.427	−40.923	7.657	7.761	141.347
Te	−64.464	−57.144	8.985	9.039	223.174
I	−76.905	−69.091	9.448	9.382	301.030

valence-state energies are given by

$$E = C^0 + \sum_i n_i \bar{U}_{ii} + \tfrac{1}{2} \left(\sum_i n_i\right) \left(\sum_i n_i - 1\right) g_{\mathrm{AA}} \tag{22}$$

relative to the ground state of the neutral atom. This is chosen as the zero of energy, rather than the core with all valence electrons removed, since the higher ionization potentials of some of the heavier elements are uncertain or unknown [*9*]. C^0 is evaluated by equating the energy of the most stable neutral valence state to its promotion energy [*2*, *3*].

7. Discussion

The parameters in this paper are chosen so that, for a specific charge distribution, the diagonal Hamiltonian matrix elements, which are a measure of the atomic orbital electronegativities in the molecule, have the same values as if the use of a common value for all atomic electron-repulsion parameters retained in the CNDO approximation were not required. It is impossible, however, for the matrix elements to have the same variation with charge distribution as they would have without this restriction.

For most atoms, electron-repulsion parameters evaluated from atomic spectra decrease in the order $g_{ss} > g_{sp} \approx g_{pp} > g_{pp'}$, so that $g^s_{\mathrm{AA}} > g_{\mathrm{AA}} > g^p_{\mathrm{AA}}$. The approximation $g^s_{\mathrm{AA}} = g_{\mathrm{AA}} = g^p_{\mathrm{AA}}$, which is made in this paper, gives too high a value for the electronegativity of s orbitals, and too low a value for that of p orbitals, when these orbitals have an electron population greater than $\frac{1}{4} Z_{\mathrm{A}}$. The reverse is true when they have an electron population less than $\frac{1}{4} Z_{\mathrm{A}}$.

Table 2. *Valence-state ionization potentials recalculated from parameters* (in eV)

Ionization Process	Valence State Ionization Potential		
	From atomic spectra	From parameters in this paper	From parameters of Pople and Segal
C($sppp \rightarrow ppp$)	21.008	20.065	22.078
C($sppp \rightarrow spp$)	11.269	10.909	13.579
F($s^2p^2p^2p \rightarrow sp^2p^2p$)	39.389	39.220	45.116
F($sp^2p^2p^2 \rightarrow p^2p^2p^2$)	38.244		
F($s^2p^2p^2p \rightarrow s^2p^2pp$)	18.109	18.609	23.924
F($sp^2p^2p^2 \rightarrow sp^2p^2p$)	18.514		
F($s^2p^2p^2p \rightarrow s^2p^2p^2$)	20.860		

Table 3. *Valence-state electron affinities recalculated from parameters* (in eV)

Process	Valence State Electron Affinity		
	From atomic spectra	From parameters in this paper	From parameters of Pople and Segal
C($sppp \rightarrow s^2ppp$)	8.917	9.858	6.023
C($sppp \rightarrow sp^2pp$)	0.345	0.702	− 2.456
F($sp^2p^2p^2 \rightarrow s^2p^2p^2p^2$)	24.372	24.166	19.428
F($s^2p^2p^2p \rightarrow s^2p^2p^2p^2$)	3.497	3.555	− 1.764

The accuracy of atomic parameters for CNDO calculations may be partially assessed by comparing valence-state ionization potentials and electron affinities found from Eq. (22) with more accurate values [*2*, *3*]. Tab. 2 and 3 show these quantities for common valence states of carbon and fluorine, as examples of elements usually participating in relatively homopolar and heteropolar bonds respectively. The ionization potentials and electron affinities calculated from the parameters in Tab. 1 are accurate within about 1 eV, except for the relatively unimportant ionization potential, $s^2p^2p^2p \rightarrow s^2p^2p^2$, of the singly occupied p orbital in fluorine. The ionization potentials and electron affinities derived from the final parameters of Pople and Segal [*21*] are in error by several eV, since their electron-repulsion integrals were not determined from atomic spectra.

The parameters in this paper are calculated by considering the charge distribution in which the valence-shell electrons on each atom are equally distributed among the valence orbitals. If only s and p orbitals are included, this is a rough approximation to the charge distribution in actual molecules, so that the parameters obtained are reasonable for molecular calculations. For elements whose d orbitals are only involved in bonding to a minor extent in most molecules, inclusion of d orbitals on the same basis as s and p orbitals would be a much worse approximation.

A possible criticism of the procedure is that Eq. (9) is not itself invariant to a change in basis set. It was found for several atoms, however, that g_{AA} varies by only a few tenths of an electron volt if a hybrid basis set is used in its evaluation, so that a value found from s–p valence-state energies is adequate for MO calculations with a basis set of hybrid orbitals. It is better to evaluate the parameters from s–p valence-state energies, rather than energies for a hybrid set because

a) the valence-state promotion energies come more directly from spectral data and are more accurate, and

b) the core Hamiltonian off-diagonal matrix elements between pure s, p, d, ... orbitals vanish for reasons of symmetry. The off-diagonal matrix elements between hybrid orbitals are non-zero, and cannot be evaluated by the procedure of Section 3.

We are currently considering the application of these parameters to calculations of the charge distribution in simple organic molecules.

Acknowledgements. We wish to thank Dr. N. C. Baird for helpful discussions, and the National Research Council of Canada for the award of a studentship to one of us. (J.M.S.)

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