Theoret. chim. Acta (Berl.) 31, 289–295 (1973)

On Bridging the Gap between the INDO and the NDDO Schemes

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Received March 20, 1973/June 4, 1973

A series of approximate LCAO–SCF methods intermediate between the INDO and the NDDO schemes is proposed. The suggestion is based upon the decomposition of integrals in multipole-multipole type interactions.

Key words: Approximate LCAO–SCF – Multipole-multipole interactions – INDO – DRINDO – NDDO

1. Introduction

In recent years considerable efforts have been dedicated to studies of the CNDO (Complete Neglect of Differential Overlap) and the INDO (Intermediate NDO) approximate LCAO–SCF schemes [1–4]. On the other hand, only a few calculations have been performed using the less approximate NDDO (Neglect of Diatomic DO) scheme [1, 4]. Apparently the complications of the latter are judged to be disproportionately large compared with the gain expected in the reliability of the calculation. Most of the many additional integrals to be computed are unimportant, and they do not appear to be readily accessible to parameterization.

Of the few attempts made so far in bridging the gap between the INDO and the NDDO approximation schemes most have been plagued by the inadequacy of their not being invariant to the choice of local coordinate systems. The PNDO (Partial NDO) method [5] offers an example of this [4].

In the present paper a number of approximation schemes, all of which lie between the INDO and NDDO levels of approximation and all of which possess the desired invariance properties, is presented.

2. Proposals

The basis of the schemes to be proposed is the multipole expansion of the potentials from one-center charge distributions. To remove two-center charge distributions, the NDDO approximation is initially invoked. The remaining two-electron integrals are either integrals involving orbitals from only a single atom, or integrals which may be interpreted as representing the electrostatic interaction energy of two reasonably well separated one-center charge distributions (ϱ_A and ϱ_B). The former integrals are all retained, as in the INDO method, while for the latter the following expression is obtained when the usual expansion of $1/r_{12}$ [6a] (around center A, say) is employed:

$$\begin{aligned} I(\varrho_{\mathrm{A}},\varrho_{\mathrm{B}}) &\equiv \int\int \varrho_{\mathrm{A}}(r_1)\varrho_{\mathrm{B}}(r_2)/r_{12}\,dv_1\,dv_2 \\ &= \sum_{l=0}^{\infty}\int \varrho_{\mathrm{B}}(r_2)\left\{\frac{4\pi}{2l+1}\int r_<^l\,\varrho_{\mathrm{A}}(r_1)\sum_{m=-l}^{+l} Y_{lm}^*(\theta_1,\varphi_1)\frac{Y_{lm}(\theta_2,\varphi_2)}{r_>^{l+1}}\,dv_1\right\}dv_2\,. \end{aligned} \tag{1}$$

For non-overlapping charge distributions ($r_< = r_1$ and $r_> = r_2$), the expression in parentheses is the l^{th} term in the classical multipole expansion of the potential from ϱ_{A} [6b]. The fact that charge distributions do overlap in molecular integrals will not affect the argument given below.

When approximations are introduced into (1) the problem of coordinate invariance arises. The value of the integral should not depend upon the position of the origin and upon the orientation of the coordinate system chosen to describe the charge distributions and $1/r_{12}$. Since the integral is calculated exactly in the NDDO scheme, all coordinate systems will yield identical results in that case. For the INDO or the CNDO method, on the other hand, only the spherical term (the $l=0$, or the monopole term) is retained. The integral is assigned a non-zero value only if the spherical average of ϱ_{A} (and of ϱ_{B}) around the chosen origin differs from zero [7]. This truncation of the multipole expansion destroys the origin invariance. (This may easily be seen by considering the interaction of two point charges.) However, the problem is not serious when two atomic charge distributions are involved. In this case the natural choice for an origin is at either of the nuclear positions. It follows that computations with these two origins should yield the same result, and this implies in general, except for cases where the two charge distributions are identical and symmetrically arranged, that the integral must be calculated from the spherical averages of the two charge distributions around the respective centers. The orientation of the coordinate system employed in such a calculation is obviously immaterial; a spherical object looks the same in any direction from the center.

The approximations involved in the INDO method may be considered as an operator approximation for $1/r_{12}$ suitably corrected to fullfill invariance requirements. However, one may adopt another point of view by expanding each of the charge distributions in spherical harmonics around the respective centers:

$$\varrho_{\mathrm{A}}(r) = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} R_{lm}(r)\,Y_{lm}(\theta,\varphi) \equiv \sum_{l=0}^{\infty}\varrho_{\mathrm{A}}^{(l)}(r) \tag{2}$$

and similarly for ϱ_{B}. Inserting these expansions into (1) one obtains

$$I(\varrho_{\mathrm{A}},\varrho_{\mathrm{B}}) = \sum_{k,l}\int\int \varrho_{\mathrm{A}}^{(l)}(r_1)\varrho_{\mathrm{B}}^{(k)}(r_2)/r_{12}\,dv_1\,dv_2 \equiv \sum_{k,l} I_{kl} \tag{3}$$

with

$$I_{kl} = \int \varrho_{\mathrm{B}}^{(k)}(r_2)\left\{\frac{4\pi}{2l+1}\int r_<^l\,\varrho_{\mathrm{A}}^{(l)}(r_1)\sum_{m=-l}^{+l} Y_{lm}^*(\theta_1,\varphi_1)\frac{Y_{lm}(\theta_2,\varphi_2)}{r_>^{l+1}}\,dv_1\right\}dv_2\,. \tag{4}$$

The two-center interactions retained in the INDO scheme, I_{00}, may be characterized as monopole-monopole types. However, the expansion of integrals in multipole-multipole type interactions may be continued to any order without loss of coordinate invariance. This follows directly from the addition theorem for spherical harmonics [6a]:

$$P_l(\cos\alpha) = \frac{4\pi}{2l+1} \sum_{m=-l}^{+l} Y_{lm}^*(\theta_1, \varphi_1)\, Y_{lm}(\theta_2, \varphi_2)\,. \tag{5}$$

The angle α between the radius vectors of the two points does not depend upon the coordinate system as long as the origin is fixed. Thus by inserting (5) into (4) all explicit reference to the coordinate system is removed. Each term in the double sum in (3) is therefore coordinate system invariant and the summation itself may be truncated in any manner. Of course, in molecular calculations the truncation must be symmetric in the sense that inclusion of I_{kl} implies that I_{lk} also be included. Thus the interactions retained are classified according to the multipole-multipole type.

The above analysis leads to the following proposal for the assignment of values to two-center integrals:

Firstly, the total charge of each of the charge distributions is calculated. The corresponding monopole-monopole type interaction energy, defined in such a way that it depends only upon the nature of the two atoms, is then computed. In addition, an analysis is made of whether or not the charge distributions have any multipole moments relative to their respective centers. For any that have the corresponding multipole-multipole (*i.e.* monopole-dipole, dipole-dipole, monopole-quadrupole, *etc.*) interaction energies of given types are added. These should, of course, depend upon the relative orientation of the multipoles, but otherwise only upon the atoms involved and the distance between them.

Such a procedure will be coordinate invariant. It may be shown to be invariant under hybridization transformations as well [3].

When the detailed form of the atomic charge distributions is taken into account it can be seen that for a finite basis set the expansion in (2) must terminate at some finite l. For a basis set containing *s*- and *p*-orbitals only, the highest non-vanishing term that may occur in (2) is the quadrupole term ($l = 2$). This is easily seen using the coupling rule for spherical harmonics [8]. Thus a calculation retaining interactions up to and including the quadrupole-quadrupole type in this case would be equivalent to the NDDO scheme. As a consequence, the decomposition of integrals into multipole-multipole interactions will give rise to only a finite number of approximation schemes that are intermediate between the INDO and the NDDO schemes.

3. The DRINDO Scheme

In the simplest of the approximate LCAO–SCF schemes proposed above monopole-dipole interactions are included in addition to the monopole-monopole terms. This scheme may be given the name DRINDO (Dipoles Retained INDO). The field which is made self-consistent in the DRINDO scheme is constructed taking into account the main effects of the polarization of atoms in molecular environments.

In the following a basis set of unhybridized atomic orbitals (AO's) consisting only of s- and p-orbitals is assumed. The symbols ν and λ denote general AO's, while s, σ and i (or j) denote specific AO's. For atom A, s_A is the s-orbital, σ_{AB} is the p-orbital pointing towards atom B, and i_A, $i = x, y, z$, are the p-orbitals directed along the axis of the local coordinate system on A.

With this basis set, the two-electron, two-center integrals which, according to the DRINDO procedure, should be retained are:

$$\begin{aligned}[\nu_A \nu_A|\lambda_B \lambda_B] &= \gamma_{AB} \\ [s_A i_A|\lambda_B \lambda_B] &= \delta^B_A(e_{Ai}\cdot e_{AB})\end{aligned} \tag{6}$$

e_{Ai} and e_{AB} are unit vectors directed along the i-axis on A and from A towards B respectively. If it is assumed that the s- and p-orbitals have the same radial dependence the expression for δ^B_A is:

$$\delta^B_A = [s_A \sigma_{AB}|s_B s_B] .$$

As noted by Dixon [9], it would be inconsistent to include the integrals (6) while neglecting the monopole-dipole interactions with the atomic cores. Thus the integrals

$$\langle s_A|V_B|i_A\rangle = d^B_A(e_{Ai}\cdot e_{AB})$$

where V_B is the attractive core potential from atom B, must also be included, d^B_A being given by

$$d^B_A = \langle s_A|V_B|\sigma_{AB}\rangle .$$

The matrix elements of the Fock operator in the DRINDO approximation are now readily constructed. Using superscripts to indicate the centers of the orbitals the following expressions are obtained for the one-center elements:

$$\begin{aligned}F^{AA}_{\nu\nu} &= F^{INDO}_{\nu\nu} + \sum_{B\neq A} 2\delta^A_B\left(e_{BA}\cdot\sum_j P^{BB}_{sj}e_{Bj}\right), \\ F^{AA}_{si} &= F^{INDO}_{si} + e_{Ai}\cdot\sum_{B\neq A} e_{AB}(P_{BB}\delta^B_A + d^B_A) .\end{aligned}$$

Here $F^{INDO}_{\nu\lambda}$ is the corresponding matrix element in the INDO approximation, $P^{BB}_{\nu\lambda}$ denotes an element of the charge and bond order matrix, while the gross electronic population P_{BB} on atom B is defined as:

$$P_{BB} = \sum_\lambda P^{BB}_{\lambda\lambda} .$$

The two-center matrix elements are given in a similar notation by:

$$\begin{aligned}F^{AB}_{ss} = F^{INDO}_{ss} &- \tfrac{1}{2}\delta^B_A\Big(e_{AB}\cdot\sum_i P^{AB}_{is}e_{Ai}\Big) \\ &- \tfrac{1}{2}\delta^A_B\Big(e_{BA}\cdot\sum_j P^{AB}_{sj}e_{Bj}\Big)\end{aligned}$$

$$
\begin{aligned}
F_{sj}^{\mathrm{AB}} &= F_{sj}^{\mathrm{INDO}} - \tfrac{1}{2}\delta_{\mathrm{A}}^{\mathrm{B}}(\boldsymbol{e}_{\mathrm{AB}} \cdot \sum_{i} P_{ij}^{\mathrm{AB}} \boldsymbol{e}_{\mathrm{A}i}) \\
&\quad - \tfrac{1}{2}\delta_{\mathrm{B}}^{\mathrm{A}} P_{ss}^{\mathrm{AB}}(\boldsymbol{e}_{\mathrm{BA}} \cdot \boldsymbol{e}_{\mathrm{B}j}) \\
F_{ij}^{\mathrm{AB}} &= F_{ij}^{\mathrm{INDO}} - \tfrac{1}{2}\delta_{\mathrm{A}}^{\mathrm{B}} P_{sj}^{\mathrm{AB}}(\boldsymbol{e}_{\mathrm{AB}} \cdot \boldsymbol{e}_{\mathrm{A}i}) \\
&\quad - \tfrac{1}{2}\delta_{\mathrm{B}}^{\mathrm{A}} P_{is}^{\mathrm{AB}}(\boldsymbol{e}_{\mathrm{BA}} \cdot \boldsymbol{e}_{\mathrm{B}j}) .
\end{aligned}
$$

The above expressions do not describe the manner in which the result of corresponding INDO and DRINDO calculations differ. However, an investigation of how two atoms, one of which is a hydrogen atom, interact in the two schemes does yield informations on this point. It is well-known that the total energy expression in the INDO approximation can be partitioned into monatomic and diatomic contributions [3]. This is retained in the DRINDO scheme. Since the additional integrals included in the DRINDO approximation all involve two centers, it follows that the monatomic terms are unchanged. If h denotes the hydrogen 1s-orbital, the difference between the diatomic contributions from the atom pair A and H is:

$$E_{\mathrm{AH}}^{\mathrm{DRINDO}} - E_{\mathrm{AH}}^{\mathrm{INDO}} = 2P_{s\sigma}^{\mathrm{AA}} \left\{ P_{\mathrm{HH}}[hh|s\sigma] - \langle s| \frac{e^2}{r_{\mathrm{H}}} |\sigma\rangle \right\} - P_{sh}^{\mathrm{AH}} P_{\sigma h}^{\mathrm{AH}} [hh|s\sigma] . \quad (7)$$

The charge distributions (hh) and $2P_{s\sigma}^{\mathrm{AA}}(s\sigma)$ can, for the present discussion, be regarded as a point charge and a point dipole respectively. Thus the first term on the right-hand side describes the electrostatic interaction between the net charge on the hydrogen atom and the effective dipole on A.

The last term in (7) is a bond term of second order. This term will be important only if the two atoms are bound together. In a localized description where both bond orders involved may be derived from a single molecular orbital describing the bond we have:

$$P_{sh}^{\mathrm{AH}} P_{\sigma h}^{\mathrm{AH}} = P_{\mathrm{HH}} P_{s\sigma}^{\mathrm{bond}} . \quad (8)$$

The bond term thus removes from the electrostatic term half of the interaction between the electronic charge on hydrogen and that part of the dipole on A which is due to the two bonding electrons. The electron does not interact with that portion of the dipole which it has produced itself.

For atoms far apart, the difference (7) is dominated by the pure electrostatic interaction. For atoms bound together, however, the situation is reversed. In this case the bond term which involves the gross electronic population rather than the net charge will usually play the major role. This term describes an attraction between the two atoms which, according to (8), increases with increasing sp-mixing in the bonding hybrid.

The above analysis indicates that the results of a DRINDO calculation will deviate from those from the corresponding INDO calculation by having:

1. Enhanced hybridization and thus increased polarization of atoms.
2. Smaller computed bond distances, in particular for short bonds (AH-bonds) where monopole-dipole interactions are largest.
3. Larger electron density on atoms bound to polarized (highly electronegative) atoms such as nitrogen, oxygen and fluorine. This will lower the electrostatic

repulsion between the atoms by roughly twice the amount with which the bond attraction is decreased.

The quantities δ_A^B and d_A^B which constitute the difference between the DRINDO and the INDO schemes may be treated in various ways. They are easily calculated theoretically [10], but they may also be parameterized semiempirically. For example, corresponding to the Ohno-Klopman expression [11, 12]:

$$\gamma_{AB} = e^2[R_{AB}^2 + (\varrho_A + \varrho_B)^2]^{-\frac{1}{2}}$$

one may use

$$\delta_A^B = e^2\{[(R_{AB} - \Delta_A)^2 + (\varrho_A + \varrho_B)^2]^{-\frac{1}{2}} - [(R_{AB} + \Delta_A)^2 + (\varrho_A + \varrho_B)^2]^{-\frac{1}{2}}\}.$$

This expression behaves correctly in the limits $R_{AB} \to \infty$ and $R_{AB} \to 0$. Δ_A is an atomic parameter which may be either treated as such or calculated theoretically from

$$\Delta_A = \tfrac{1}{2}\left|\int s_A r_A p_A \, dv\right|.$$

4. Concluding Remarks

The approach employed in the present work differs somewhat from that followed by Pople and co-workers. These latter authors were concerned about the form of the individual charge distributions in the integral (1). Here, on the other hand, attention has been focussed on the types of interactions *between* the charge distributions. The emphasis has thus been shifted from attempts to approximate charge distributions to attempts to approximate integrals.

The second member of the series of approximations proposed above is the scheme in which dipole-dipole and monopole-quadrupole type interactions are included. These both decrease asymptotically proportionally to the inverse third power of the distance. Of the additional terms included the dipole-dipole type will probably be the most important, since no cancellation between electron-electron and electron-core interactions takes place in this case.

When quadrupoles are introduced the inconvenience that charge distributions (even from an unhybridized basis set) may possess both a monopole and a quadrupole arises. Invariance with respect to rotation of local coordinate systems requires that *all* quadrupoles be retained. On the other hand, the inclusion of monopole-quadrupole terms leads to a difference between the direct interactions of *s*- and *p*-electrons with the surroundings. This difference has been asserted to be important by several authors [5, 13]. Rather complex local transformations of *d*-type functions have to be performed in this case. However, problems of this kind do not constitute major obstacles to the applicability of the approximation scheme, and it appears that the multipole-multipole decomposition of integrals is a convenient way of approaching the NDDO level of approximation in a manner which, by its very nature, suggests a detailed semiempirical parameterization scheme.

Acknowledgement. The author wishes to thank Dr. Å. E. Hansen for his stimulating interest in the present work.

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