On the Application of Zero Differential Overlap Methods to Complex Molecules

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The NDDO and CNDO methods suggested by Pople *et al.* have been analyzed using Löwdin's procedure of symmetrical orthogonalization. It is concluded that it is possible to reformulate the CNDO method such that it becomes a linear method, correct to the first order in the interatomic overlap integrals. Such a reformulation is not possible for the NDDO method, except in very special cases.

Considerable attention has recently been paid to the problem of performing approximate self-consistent molecular orbital calculations on complex molecules. Encouraged by the success of the zero differential overlap (ZDO) method as applied to aromatic systems, Pople *et al.*[1] have suggested two approximate schemes in which all valence electrons may be considered: one scheme based on the complete neglect of differential overlap (CNDO method), and another scheme based on neglect only of diatomic differential overlap (NDDO method). Methods similar to the NDDO have also been used by various authors in the past, but the formulation by Pople *et al.* is especially clear.

The difference between the extended methods and the conventional ZDO method is that the former allow for several atomic orbitals per atomic center, whereas only one orbital per center (a $2p_\pi$-orbital) is allowed in the latter. It was pointed out by Löwdin[2] more than ten years ago that although the ZDO method is formulated as a zero order method, in which all overlap integrals are neglected, it can be reformulated in terms of orthogonalized orbitals, so that it becomes a linear method, *i.e.* a method which is correct through first order terms in the interatomic overlap integrals. A thorough investigation in this field has been undertaken by Fischer-Hjalmars.[3]

It is the purpose of the present paper to investigate whether the CNDO and NDDO methods can also be reformulated so that they become linear in the sense mentioned above. The conclusion is reached that the CNDO method is linear, but certain deviations from spherical symmetry are neglected in the Hartree-Fock potential. The more elaborate NDDO method can, however, not be considered as linear, except in very special cases.

MAIN FEATURES OF THE CNDO AND NDDO METHODS

In the LCAO MO description one represents the molecular orbitals of a given molecule as linear combinations of atomic orbitals χ_r. One then encounters the problem of evaluating the electrostatic interaction between charge distributions $\chi_r(1) \chi_s(1)$ and $\chi_t(2) \chi_u(2)$, i.e. integrals of the form

$$[rs|tu] = \iint \chi_r(1)\chi_s(1) \frac{e^2}{r_{12}} \chi_t(2) \chi_u(2) \, d\tau_1 d\tau_2 \qquad (1)$$

The CNDO and NDDO approximations have to do with the evaluation of such integrals. More specificly, the CNDO method assumes that the charge distribution $\chi_r\chi_s$ is zero unless χ_r and χ_s are identical, i.e.

$$[rs|tu] = \delta_{rs} \, \delta_{tu} \, [rr|tt] \qquad (2)$$

On the other hand, the NDDO method retains $\chi_r \chi_s$ if χ_r and χ_s belong to the same atomic center, but neglects this distribution if the two orbitals belong to different centers.

It was pointed out by Pople et al.,[1] that in order for the CNDO method to give a description independent of the choice of coordinate systems on the various atoms, it is necessary to replace the approximation (2) with

$$[rs|tu] = \delta_{rs} \, \delta_{tu} \, [\overline{rr}|\overline{tt}] \qquad (3)$$

where $\overline{\chi}_r$ is an s-orbital with the same radial function as χ_r. The approximation (3) makes the CNDO method a very practical one for computations.

ORTHOGONALIZED ORBITALS

In order to throw light on the nature of the approximations of the previous section we replace the original set of atomic orbitals $\chi_1, \chi_2..., \chi_m$ with an orthonormal set $\chi_1', \chi_2',..., \chi_m'$, and we assume that this set has been obtained by Löwdin's method of symmetrical orthogonalization,[4] i.e.

$$(\chi_1' \, \chi_2'... \, \chi_m') = (\chi_1 \, \chi_2... \, \chi_m) \begin{bmatrix} S_{11}S_{12} ... S_{1m} \\ S_{21}S_{22} ... S_{2m} \\ \underline{\quad} \; \underline{\quad} \; \underline{\quad} \; \underline{\quad} \\ S_{m1}S_{m2}...S_{mm} \end{bmatrix}^{-\frac{1}{2}} \qquad (4)$$

where

$$S_{rs} = \int \chi_r(1) \, \chi_s(1) d\tau_1 \qquad (5)$$

In a theory retaining only first order terms in the overlap integrals S_{rs}, i.e. a linear theory, we may write (for S_{rs} sufficiently small [4]):

$$\chi_r' = \chi_r - \tfrac{1}{2} \sum_{s \neq r} S_{rs} \chi_s; \, r = 1, 2,...,m \qquad (6)$$

To study the implications of eqn. (6) we confine ourselves, for the moment, to a diatomic case in which there is one orbital χ_a on center a, and two mutually orthogonal orbitals, χ_{b_1} and χ_{b_2} on center b. The orthogonalized orbitals are then

$$
\begin{aligned}
\chi_a' &= \chi_a - \tfrac{1}{2} S_{a,b_1} \chi_{b_1} - \tfrac{1}{2} S_{a,b_2} \chi_{b_2} \\
\chi_{b_1}' &= \chi_{b_1} - \tfrac{1}{2} S_{a,b_1} \chi_a \\
\chi_{b_2}' &= \chi_{b_2} - \tfrac{1}{2} S_{a,b_2} \chi_a
\end{aligned}
\tag{7}
$$

and the charge distributions obtained by multiplying two of these orbitals together may now be expanded on $\chi_{b_1} \chi_{b_2}$ and normalized distributions of the type $\chi_r \chi_r$ and $\chi_r \chi_s / S_{rs}$. Retaining only first order terms in the overlap integrals we obtain:

$$
\begin{aligned}
\chi_r' \chi_s' &= \chi_r \chi_s \quad \text{when } r \text{ and } s \text{ refer to the same center} \\
\chi_a' \chi_{b_1}' &= \chi_a \chi_{b_1} - \tfrac{1}{2} S_{a,b_1} (\chi_a \chi_a + \chi_{b_1} \chi_{b_1}) - \tfrac{1}{2} S_{a,b_2} \chi_{b_1} \chi_{b_2} \\
\chi_a' \chi_{b_2}' &= \chi_a \chi_{b_2} - \tfrac{1}{2} S_{a,b_2} (\chi_a \chi_a + \chi_{b_2} \chi_{b_2}) - \tfrac{1}{2} S_{a,b_1} \chi_{b_1} \chi_{b_2}
\end{aligned}
\tag{8}
$$

If it is assumed that the Mulliken approximation [5]

$$
\chi_a \chi_b = \tfrac{1}{2} S_{ab} (\chi_a \chi_a + \chi_b \chi_b)
\tag{9}
$$

may be applied in the evaluation of two-electron integrals, we get, as far as such integrals are concerned:

$$
\begin{aligned}
\chi_r' \chi_s' &= \chi_r \chi_s \quad \text{when } r \text{ and } s \text{ refer to the same center} \\
\chi_a' \chi_{b_1}' &= -\tfrac{1}{2} S_{a,b_2} \chi_{b_1} \chi_{b_2} \\
\chi_a' \chi_{b_2}' &= -\tfrac{1}{2} S_{a,b_1} \chi_{b_1} \chi_{b_2}
\end{aligned}
\tag{10}
$$

It is noticed that the Mulliken approximation does not cause any of the charge distributions in eqn. (10) to become zero, but they can all be expressed in terms of one-center distributions.

Expressions similar to (10) can be derived in the general case with the result that charge distributions $\chi_a' \chi_b'$ involving orbitals on different centers do not vanish, as they do when there is only one atomic orbital per center.[3] There is little justification for neglecting $\chi_{b_1} \chi_{b_2}$ in eqn. (10), while retaining it in other integrals, since this charge distribution can give rise to large integral values, e.g. if χ_{b_1} and χ_{b_2} represent $2s$- and $2p$-orbitals, respectively.

On the background of eqn. (10) it is concluded that since the charge distributions $\chi_a' \chi_{b_1}'$ and $\chi_a' \chi_{b_2}'$ depend on the overlap integrals of the system to the first order, it is not possible, along the present lines, to reformulate the NDDO method, so that it becomes linear. The only exceptions occur if no two orbitals on the same center transform in the same way under the symmetry operations of the molecule considered. Such a situation arises, for instance, if one considers the π-orbitals of a diatomic molecule, but inclusion of the σ-orbitals leads to the complication inherent in eqn. (10), since s- and p_σ-orbitals transform in the same way in the linear symmetry.

It will now be demonstrated that it is possible to construct a linear theory by making consistent approximations in the Hartree-Fock-Roothaan scheme, and that the resulting method corresponds to the CNDO method.

DERIVATION OF THE CNDO METHOD

We assume that the molecule under consideration has a closed shell structure, *i.e.* the $2n$ electrons of the molecule reside in the n doubly occupied molecular orbitals of the system, and we choose these to be the orthogonalized orbitals of eqn. (6), *i.e.*

$$\varphi_i = \sum_{r=1}^{m} C_{ri} \chi_r'; \; i = 1, 2,...,n; \; m \geq n \tag{11}$$

The expression for the Hartree-Fock operator is in this description:

$$\widehat{F} = \widehat{H}^{\text{core}} + \sum_{t,u} P_{t,u} \left([|t'u'] - \tfrac{1}{2}[u'|t']\right) \tag{12}$$

where $[|t'u']$ and $[u'|t']$ are Coulomb and exchange operators respectively associated with $\chi_t'\chi_u'$, *i.e.*

$$[|t'u'] \; \varphi(1) = \int \chi_t'(2) \, \chi_u'(2) \, \frac{e^2}{r_{12}} \, d\tau_2 \cdot \varphi(1) \tag{13}$$

$$[u'|t'] \; \varphi(1) = \int \chi_t'(2) \, \varphi(2) \, \frac{e^2}{r_{12}} \, d\tau_2 \cdot \chi_u'(1) \tag{14}$$

$P_{t,u}$ is an element of the charge and bond-order matrix:

$$P_{t,u} = 2 \sum_{i=1}^{n} C_{ti} C_{ui} \tag{15}$$

and $\widehat{H}^{\text{core}}$ includes the kinetic energy operator $\widehat{T}$ and the potential (Coulomb and exchange) from the core electrons. Adopting the Goeppert-Mayer, Sklar approximation,[6] according to which the core potential is a sum of one-center potentials $\widehat{V}_a$ associated with the various atoms a in the molecule, we have:

$$\widehat{H}^{\text{core}} = \widehat{T} + \sum_a \widehat{V}_a \tag{16}$$

For the moment we neglect the exchange terms $[u'|t']$ in eqn. (12) and define the operator

$$\widehat{F}_0 = \widehat{T} + \sum_a \widehat{V}_a + \sum_{t,u} P_{t,u} \, [|t'u'] \tag{17}$$

By inserting equations similar to (10) we get

$$\widehat{F}_0 = \widehat{T} + \sum_a (\widehat{V}_a + \sum_{t_a,u_a} B_{t_a,u_a} \, [|t_a u_a]) \tag{18}$$

where t_a and u_a refer to orbitals on center a, and the primes have been dropped in the Coulomb operator $[|t_a u_a]$, since this is now expressed in the original set of orbitals $\chi_1, \chi_2,..., \chi_m$. The coefficients B_{t_a,u_a} are, for $t \neq u$, functions of the overlap integrals of the system. For $t = u$ we have, however:

$$B_{t_a,t_a} = P_{t_a,t_a} \tag{19}$$

The expression in brackets in eqn. (18) may be interpreted as the Coulomb potential from atom a *in situ*. We proceed by replacing this potential with its spherical average around a, and comment on this approximation later. Excluding the possibility that two atomic orbitals on the same center have the same angular dependence (like $2p$ and $3p$), we get:

$$\widehat{F}_0 = \widehat{T} + \sum_a (\widehat{V}_a + \sum_{t_a} P_{t_a,t_a} \, [|\bar{t}_a \bar{t}_a])$$ (20)

where, as previously, $\bar{\chi}_{t_a}$ denotes an s-orbital with the same radial function as χ_{t_a}.

We shall now consider matrix elements of $\widehat{F}_0$ between the original, unsymmetrized orbitals. For the matrix element of χ_{r_a} with itself we get, from $\widehat{T}$ and the part of $\widehat{F}_0$ associated with center a:

$$(r_a|T + V_a|r_a) + \sum_{t_a} P_{t_a,t_a} \, [\bar{r}_a \bar{r}_a | \bar{t}_a \bar{t}_a]$$

We have introduced the definition

$$(r|T + V_a|s) = \int \chi_r(1)(T(1) + \widehat{V}_a(1)) \, \chi_s(1) d\tau_1$$ (21)

and utilized the fact that

$$[r_a r_a | \bar{t}_a \bar{t}_a] = [\bar{r}_a \bar{r}_a | \bar{t}_a \bar{t}_a]$$ (22)

However, χ_{r_a} cannot be replaced by $\bar{\chi}_{r_a}$ in $(r_a|T + V_a|r_a)$, because $\widehat{T}$ is a differential operator and $\widehat{V}_a$ includes important exchange terms.

The remaining terms in $\widehat{F}_0$ contributing to $(r_a|F_0|r_a)$ represent the electrostatic potential from atoms other than a. We replace this potential with its spherical average around a and discuss the justification for this later. However, we do not evaluate this average explicitly, but utilize that we can take the spherical average $\bar{\chi}_{r_a}\bar{\chi}_{r_a}$ of $\chi_{r_a}\chi_{r_a}$ instead. Strictly speaking, this is only true when exchange terms in the remaining core potentials are neglected, but it is a very good approximation to do so. We obtain therefore:

$$(r_a|F_0|r_a) = (r_a|T + V_a|r_a) + \sum_{b \neq a} (\bar{r}_a|V_b|\bar{r}_a) + \sum_t P_{t,t} \, [\bar{r}_a \bar{r}_a | \bar{t} \bar{t}]$$ (23)

According to eqn. (8) this is also the expression for $(r_a'|F_0|r_a')$.

Introducing similar approximations in evaluating $(r_a|F_0|s_a)$ with $r \neq s$ we get from eqn. (8):

$$(r_a'|F_0|s_a') = (r_a|F_0|s_a) = 0 \text{ if } r \neq s$$ (24)

because there is no matrix element between χ_{r_a} and χ_{s_a} in a spherically symmetric potential.

Finally, we find from eqn. (8) that

$$(r_a'|F_0|s_b') = (r_a|T + V_a + V_b|s_b) - \tfrac{1}{2} S_{r_a,s_b} \{(r_a|T + V_a|r_a) + (s_b|T + V_b|s_b) + (\bar{r}_a|V_b|\bar{r}_a) + (\bar{s}_b|V_a|\bar{s}_b)\}$$ (25)

provided the Mulliken approximation (9) is used in evaluating integrals arising from that part of $\widehat{F}_0$ which does not include $\widehat{T}$, $\widehat{V}_a$, and $\widehat{V}_b$.

So far as the two-electron integrals are concerned, eqns. (23—25) represent exactly what one would obtain by making the approximation

$$[r's'|t'u'] = \delta_{rs}\delta_{tu} \, [\bar{r}\bar{r}|\bar{t}\bar{t}] \tag{26}$$

i.e. the CNDO approximation. However, we have so far not included the exchange part of $\widehat{F}$ in our analysis. It is now important that the approximations made in treating $\widehat{F}_0$ fix the approximations to be made in treating the exchange terms. We must use eqn. (26) for these terms also in order to ensure, that "an electron does not interact with itself". Self-interaction occurs if the equation

$$([|\varphi_i\varphi_i] - [\varphi_i|\varphi_i]) \, \varphi_i(1) = 0 \tag{27}$$

is not fulfilled. This equation ensures that a valence electron interacts with exactly $2n-1$ electrons, as it should.

Thus, by making suitable approximations in taking matrix elements of $\widehat{F}_0$ and letting the exchange terms follow the Coulomb terms in order to avoid self-interaction, we have arrived at the following expressions for the matrix elements of $\widehat{F}$:

$$(r_a'|F|r_a') = (r_a|T + V_a|r_a) + \sum_{b \neq a} (\bar{r}_a|V_b|\bar{r}_a) + \sum_t P_{t,t} \, [\bar{r}_a\bar{r}_a|\bar{t}\bar{t}]$$
$$- \tfrac{1}{2} P_{r_a,r_a} \, [\bar{r}_a\bar{r}_a|\bar{r}_a\bar{r}_a] \tag{28}$$

$$(r_a'|F|s_a') = - \tfrac{1}{2} P_{r_a,s_b} \, [\bar{r}_a\bar{r}_a|\bar{s}_a\bar{s}_a], \; r \neq s \tag{29}$$

$$(r_a'|F|s_b') = (r_a'|F_0|s_b') = \tfrac{1}{2} P_{r_a,s_b} \, [\bar{r}_a\bar{r}_a|\bar{s}_b\bar{s}_b] \tag{30}$$

with $(r_a'|F_0|s_a')$ given by eqn. (25).

The equations (28—30) show that the CNDO method suggested by Pople *et al.*[1] can be interpreted as a linear method and the equations also supply theoretical expressions for the matrix elements of $\widehat{H}^{\text{core}}$. They are derived for the orthogonalization scheme (6), based on small overlap integrals. The Mulliken approximation (9) has also been used along with the process of spherical averaging. Some comments are necessary to justify the averaging process, and we concentrate these in three points.

1. The spherical parts of the potentials considered are likely to be the predominant parts.

2. The deviations from spherical symmetry are probably not well represented by the Mulliken approximation (9). Hence, by only retaining the spherical parts of the potentials, the consequences of that approximation are taken.

3. Similar deviations from spherical symmetry are neglected in detailed and successful calculations on solids.[7]

These points indicate that the CNDO scheme is likely to be a sound and consistent scheme for approximate quantum chemical calculations on complex molecules.

Eqns. (28—30) provide theoretical expressions for the matrix elements of the core operator. In the calculations by Pople *et al.* these matrix elements are considered as parameters of the theory, but on the basis of the present

analysis they may as well be calculated. From the conventional ZDO method it is known that the two procedures yield very similar results. This conclusion is important, because the number of parameters tends to become excessive when atomic orbitals of high quantum numbers are involved.

In a forthcoming report [8] on molecular orbital theories of transition metal complexes the theoretical expressions have been used for the matrix elements of $\hat{H}^{core}$ and it is also shown that the CNDO approximation may be justified on the basis of other orthogonalization schemes than the symmetrical one.

REFERENCES

1. Pople, J. A., Santry, D. P. and Segal, G. A. *J. Chem. Phys.* **43** (1965) S129.
2. Löwdin, P. O. *Svensk Kem. Tidskr.* **67** (1955) 380.
3. Fischer-Hjalmars, I. *J. Chem. Phys.* **42** (1965) 1962.
4. Löwdin, P. O. *Phil. Mag. Suppl.* **Vol. 5** (1956) No. 17.
5. Mulliken, R. S. *J. Chim. Phys.* **46** (1949) 497, 675.
6. Goeppert-Mayer, M. and Sklar, A. L. *J. Chem. Phys.* **6** (1938) 645.
7. Slater, J. C. *Advan. Quantum Chem.* **1** (1964) 35.
8. Dahl, J. P. and Ballhausen, C. J. *Advan. Quantum Chem.* **4** (1967). *In press.*