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On Bridging the Gap Between Extended Hückel and NDO Type LCAO-MO Theories

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The possibility of incorporating overlap effects as well as electron interaction terms in simple LCAO-MO theories is discussed. A recent suggestion by de Bruijn is criticized and a revised scheme is developed.

Key words: Orthogonalization effects in NDO theories, representation of ~.

1. Introduction

Current approximate LCAO-MO theories usually belong to one of two categories: either they are based on an explicit treatment of AO overlap, with neglect or at best a rudimentary treatment of electron repulsion, or they give up proper treatment of overlap, in which case electron interaction can be introduced into the formalism in a simple fashion. Extended Hückel theory [1], MOMO [2] and EWMO [3] are methods of the first kind, while NDO theories such as CNDO, INDO etc. [4–6] belong to the second category. Each group of theories has its characteristic shortcomings; in particular, several systematic failures of NDO theories are now well known [7–11] and most of these have recently been ascribed to an insufficient treatment of overlap effects [11]. For example, it is evident that NDO methods fail to describe the repulsion between closed shells, which is a second order overlap effect; this sometimes leads to ridiculous results, as in the case of the most stable CNDO/2 and INDO water dimers, which exhibit a partial O—O bond [8] (on the other hand, MINDO/3 apparently fails to predict any stable water dimer at all [9]). Another example is the failure [12] of standard all-valence-electrons NDO theories to predict the pairing properties [13] of alternant hydrocarbon π systems, largely due to the inclusion of spurious second neighbour terms as a result of an inadequate treatment of overlap. The development of simple MO procedures dealing effectively with overlap effects as well as

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electron interaction terms is obviously of interest. It is the aim of this communication to contribute to this development.

2. A Critique of de Bruijn's Approach [11]

Probably the most satisfactory justification of the formal NDO approximation rests on the assumption that the basis functions correspond to a set of symmetrically orthonormalized AOs [14–16]. Within this framework, de Bruijn [11] has recently analyzed the role of the one-electron two-center parameters β and emphasized that the commonly adopted functional form [6]

$$\beta_{\mu\nu} = S_{\mu\nu} f(\mu, \nu, R_{AB}) \tag{2.1}$$

where $S_{\mu\nu} = \langle \mu | \nu \rangle$ is the overlap integral, is inconsistent in the case of a polyatomic molecule, particularly with respect to second neighbour interactions. Indeed, he considered it the oversimplification responsible for most of the failures of NDO theories.

De Bruijn also suggested a revised method designed to cope with this difficulty. In this approach, which is closely related to a previous suggestion by Roby [14], the two-electron part of the Fock matrix is treated just like in traditional NDO theories, but the one-electron part is evaluated explicitly in the basis of symmetrically orthonormalized AOs (for short: the Löwdin or the λ basis). The corresponding elements are derived by the Löwdin transformation [15]

$$^{\lambda}\boldsymbol{h}^{\text{core}} = \boldsymbol{S}^{-1/2} \boldsymbol{h}^{\text{core}} \boldsymbol{S}^{-1/2} \tag{2.2}$$

from parametric matrix elements valid for Slater AOs. For some reason de Bruijn incorporates two-electron one-center terms in $\boldsymbol{h}^{\text{core}}$, an inconsistency which appears to have affected part of his general analysis but shall be of no further concern to the present discussion.

De Bruijn's analysis accurately pinpoints a number of essential problems with the NDO formalism and his ideas concerning the development of a revised method are stimulating. However, a closer look on his modified approach reveals a serious inherent inconsistency. By far the largest individual contributions to the electronic energy of a polyatomic species are the electron-core attraction and the electron-electron repulsion. Proper balancing of these dominant contributions is essential to the performance of any theoretical model, but this important principle is violated in de Bruijn's approach. The electron-core attraction terms belong to the one-electron part $\boldsymbol{h}^{\text{core}}$ and are evaluated in a basis of Löwdin orthonormalized AOs, but the two-electron terms are treated at a level which is consistent with this basis only to about first order in overlap. The approximate treatment of two-electron integrals is essential to the computational simplicity of the model and can be justified [16] in the Löwdin basis by Mulliken's approximation for overlap densities [17]; however, in a consistent and well balanced theory, the electron-core integrals must be treated at an equivalent level.

A closely related problem is the treatment of two-center penetration, i.e. the attraction of an electron by a distant neutral atom. Such terms are neglected implicitly by de Bruijn, but this approximation is not justified. First, we could argue that in a model where electron-core and electron-electron interactions are treated at different levels of accuracy, the assumption of neglect of penetration becomes quite arbitrary. Secondly and more importantly, orthogonalization effects and penetration effects are generally of the same order of magnitude but they tend to cancel [5, 16, 18] (cf. Eq. (3.11) and Eq. (3.18)). This is the most plausible justification for the commonly adopted "neglect of penetration" in NDO theories, but it is evidently inconsistent to introduce overlap and neglect penetration.

Another type of difficulty concerns the numerical stability of the parameters derived by means of the transformation indicated in Eq. (2.2). The elements of $\boldsymbol{h}^{\text{core}}$, diagonal as well as off-diagonal, are one or two orders of magnitude larger than the resulting off-diagonal elements of ${}^{\lambda}\boldsymbol{h}^{\text{core}}$. The values $\beta_{\mu\nu} \equiv {}^{\lambda}h_{\mu\nu}^{\text{core}}$ thus depend critically on the exact cancelation of large contributions, even in the case of first neighbour terms. It seems questionable whether de Bruijn's procedure is sufficiently numerically stable for the evaluation of well defined β parameters on the basis of an approximate estimate of $\boldsymbol{h}^{\text{core}}$.

In summary, there are significant difficulties with de Bruijn's modification of the NDO methods, particularly due to the unbalanced representation of attractive and repulsive Coulomb interactions. Errors are introduced which may be as large as the orthogonalization effects discussed by de Bruijn. It is possible that part of the discrepancy can be covered up by a suitable adjustment of parameters, but it is preferable to eliminate the inconsistencies of the underlying theory. This is the subject of the following section.

3. An Alternative Approach

3.1. Basic Formalism

We first reformulate the Fock operator in the following way

$$f = f^0 + f^q \tag{3.1}$$

where f^0 is the Fock operator for a hypothetical superposition of neutral atoms in their valence states, and f^q is a molecular correction term, depending on the electron displacements. For a closed shell system we have in the AO basis

$$f_{\mu\nu}^0 = t_{\mu\nu} + v_{\mu\nu} + \sum_{\lambda} n_{\lambda}[(\mu\nu, \lambda\lambda) - \tfrac{1}{2}(\mu\lambda, \nu\lambda)] \tag{3.2}$$

$$f_{\mu\nu}^q = \sum_{\lambda\sigma} (p_{\lambda\sigma} - \delta_{\lambda\sigma} n_{\lambda})[(\mu\nu, \lambda\sigma) - \tfrac{1}{2}(\mu\lambda, \nu\sigma)] \tag{3.3}$$

where $t_{\mu\nu}$ and $v_{\mu\nu}$ are matrix elements of the kinetic energy operator and the potential energy operator in the field of all atomic cores, respectively, n_{λ} is an average valence state AO occupation number, and $p_{\lambda\sigma}$ is an element of the molecular density matrix. The second and the third contribution to $f^0_{\mu\nu}$ is usually considered as a penetration term $u_{\mu\nu}$, so that f^0 may be written

$$\begin{aligned} \boldsymbol{f}^0 &= \boldsymbol{t}+\boldsymbol{u} \\ &= \boldsymbol{t}+\sum_B \boldsymbol{u}^B \end{aligned} \tag{3.4}$$

where $\boldsymbol{u}^B$ represents the potential from the neutral atom B, and the summation is over all atoms.

We then consider the transformation of $\boldsymbol{f}^0$ and $\boldsymbol{f}^q$ into the symmetrically orthonormalized Löwdin basis [15]. As discussed in detail in the literature [14, 16], all two-electron integrals tend to vanish in this basis except for one- and two-center Coulomb repulsion terms. This is considered as a justification of the NDO treatment of these integrals and we may adopt this scheme for an approximate evaluation of the elements of $\boldsymbol{f}^q$ in the Löwdin basis. These terms may be treated at any of the invariant levels of NDO approximation, such as CNDO, INDO, and NDDO [4–6]. In particular, at the CNDO level we have (μ on A, ν on B)

$$f^q_{\mu\mu}(\text{CNDO}) = -\tfrac{1}{2}q_\mu\gamma_{AA}+\sum_B Q_B\gamma_{AB} \tag{3.5}$$

$$f^q_{\mu\nu}(\text{CNDO}) = -\tfrac{1}{2}p_{\mu\nu}\gamma_{AB} \tag{3.6}$$

with the notation

$$q_\mu = p_{\mu\mu} - n_\mu \tag{3.7}$$

$$Q_B = \sum_\lambda^B p_{\lambda\lambda} - N_B \tag{3.8}$$

where N_B is the number of valence electrons in the neutral atom B. However, it is well known that the elements of $\boldsymbol{f}^0$ cannot be treated according to this scheme. The careful analysis by Fischer-Hjalmars [16] indicates that $\boldsymbol{f}^0$ contains just those terms that have complicated transformation properties under orthogonalization, i.e. kinetic energy and penetration terms. Moreover, according to her results, these terms are the only significant contributions to the off-diagonal elements of the one-electron operator $\boldsymbol{h}^{\text{core}}$ in the Löwdin basis, which means that we may write

$$\beta_{\mu\nu} \equiv {}^\lambda h^{\text{core}}_{\mu\nu} = {}^\lambda f^0_{\mu\nu}. \tag{3.9}$$

Hence, it is a consistent and meaningful extension of the standard NDO scheme to evaluate the elements of $\boldsymbol{f}^0$ explicitly in the Löwdin basis, i.e. via a Löwdin transformation. We thus suggest the following operational scheme for an approximate evaluation of the Fock matrix in the Löwdin basis:

$${}^\lambda\boldsymbol{f} = \boldsymbol{S}^{-1/2}\boldsymbol{f}^0\boldsymbol{S}^{-1/2}+\boldsymbol{f}^q(\text{NDO}) \tag{3.10}$$

where the elements of $\boldsymbol{f}^0$ are determined from parametric integrals valid for AOs.

Analysis of the Fock operator in terms of contributions equivalent to f^0 and f^q is certainly not new; in particular, f^0 is essentially identical to the averaged Fock operator defined by Mehrotra and Hoffmann [1]. However, as indicated above, this formalism is particularly relevant in the present connection since it allows the specific introduction of overlap effects just where they are supposed to be most important. Moreover, the scheme outlined in Eq. (3.10) avoids any of the difficulties associated with de Bruijn's approach. The Coulomb contributions to f^0 and f^q are well balanced in the sense that they involve only differences between equivalent terms; in a treatment based on Eq. (3.10) attractive and repulsive Coulomb forces are consequently treated at the same level of approximation.

3.2. Implementation

As indicated in the preceding paragraph, the elements of f^q(NDO) are easily expressed and evaluated within the standard NDO framework. We thus concentrate on the evaluation of f^0 in Eq. (3.4).

Consider the diagonal element (μ on A)

$$f^0_{\mu\mu} = t_{\mu\mu} + u^A_{\mu\mu} + \sum_{B(\neq A)} u^B_{\mu\mu}. \tag{3.11}$$

The one-center contribution to $f^0_{\mu\mu}$ can be interpreted as a valence state *AO* electronegativity closely related to Mulliken's scale [19]. This is readily seen by consideration of the atomic energy functional

$$E^A = \sum_{\mu}^{A} n_\mu (t_{\mu\mu} + v^A_{\mu\mu}) + \tfrac{1}{2} \sum_{\mu\nu}^{A} n_\mu n_\nu g_{\mu\nu} \tag{3.12}$$

where $g_{\mu\nu}$ is an effective electron interaction term. We obtain

$$\begin{aligned} -\tfrac{1}{2}(I_\mu + A_\mu) &= \tfrac{1}{2}[E^A(n_\mu)]^{n_\mu+1}_{n_\mu-1} \\ &= t_{\mu\mu} + v^A_{\mu\mu} + \sum_{\nu}^{A} n_\nu g_{\mu\nu} \\ &= t_{\mu\mu} + u^A_{\mu\mu}. \end{aligned} \tag{3.13}$$

Introducing this result in Eq. (3.11) we have

$$f^0_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + \sum_{B(\neq A)} u^B_{\mu\mu} \tag{3.14}$$

where $\tfrac{1}{2}(I_\mu + A_\mu)$ can be evaluated empirically from appropriate atomic spectral data. The two-center penetration terms $u^B_{\mu\mu}$ can be considered as a molecular correction to the AO electronegativity; the evaluation of these terms is less straightforward. As a first approximation, we may consider the second term in Eq. (3.14) as a transferable constant, at least within a series of related compounds. This approach is justified by the short-range character of penetration terms and amounts to selecting a set of molecular AO electronegativities incorporating first neighbour penetration. However, this procedure would be less adequate in a description of the formation and breaking of bonds where the distance dependence and the transformational properties of penetration terms might be significant. Assuming that the summation term in Eq. (3.14) is roughly proportional to the orthogonalization effect ${}^{\lambda}f^{0}_{\mu\mu} - f^{0}_{\mu\mu}$, an assumption which is not totally unreasonable (in view of Eq. (3.18)), we might tentatively omit this term from Eq. (3.14) and instead introduce an effective scaling of the shift of the basis orbital electronegativity on orthogonalization. The appropriate scaling factor could be derived from studies of potential energy curves and correlation diagrams.

Careful consideration of the off-diagonal elements of f^0 (μ on A, ν on B)

$$f^{0}_{\mu\nu} = t_{\mu\nu} + u^{A}_{\mu\nu} + u^{B}_{\mu\nu} + \sum_{C(\neq A,B)} u^{C}_{\mu\nu} \tag{3.15}$$

is essential since these terms are largely responsible for covalent bonding; in particular, the lowering of the kinetic energy term under bond formation is of overriding importance [16, 20, 21]. $f^{0}_{\mu\nu}$ is essentially a local term and in our approximate theory we may adopt the functional relationship

$$f^{0}_{\mu\nu} = \tfrac{1}{2}S_{\mu\nu}(f^{0}_{\mu\mu} + f^{0}_{\nu\nu})[1 + k_{\mu\nu}(R_{AB})] \tag{3.16}$$

where $k_{\mu\nu}(R_{AB})$ is an analytical function of the internuclear distance, to be determined according to a semi-empirical strategy; e.g., one conceivable criterion could be the ensurance of the pairing properties of alternant π systems [13].

It is convenient to have a rough guide to the relation between ${}^{\lambda}f^{0}_{\mu\nu}$ and $f^{0}_{\mu\nu}$. Under the assumption that $f^{0}_{\mu\mu} = f^{0}_{\nu\nu}$ for all μ and ν we obtain to second order in $\Delta_{\mu\nu} \equiv S_{\mu\nu} - \delta_{\mu\nu}$

$${}^{\lambda}f^{0}_{\mu\nu} = f^{0}_{\mu\mu}\left[\delta_{\mu\nu} + \Delta_{\mu\nu}k_{\mu\nu} - \tfrac{1}{2}\sum_{\lambda}\Delta_{\mu\lambda}\Delta_{\lambda\nu}(k_{\mu\lambda} + k_{\lambda\nu})\right] \tag{3.17}$$

where the distance dependence of $k_{\mu\nu}$ is implicit. Keeping only the most significant terms leads to the expressions

$${}^{\lambda}f^{0}_{11} \approx f^{0}_{11}\left[1 - \sum_{\lambda}^{\substack{\text{neigh-}\\ \text{bours}}} S^{2}_{1\lambda}k_{1\lambda}\right] \tag{3.18}$$

$${}^{\lambda}f^{0}_{12} \approx f^{0}_{11}S_{12}k_{12} \tag{3.19}$$

$${}^{\lambda}f^{0}_{13} \approx f^{0}_{11}[S_{13}k_{13} - \tfrac{1}{2}S_{12}S_{23}(k_{12} + k_{23})]. \tag{3.20}$$

For second neighbour interactions to vanish in alternant π systems, thereby ensuring the pairing symmetry, we have from Eq. (3.20) the condition

$$k_{13}/k_{12} \approx S^{2}_{12}/S_{13} \tag{3.21}$$

constituting a bound on the distance dependence of $k_{\mu\nu}$.

In this paragraph we have discussed possible implementations of the scheme outlined in Eq. (3.10); the final choice must depend on the results of actual numerical calculations. The increase in computation time relative to conventional NDO theories is insignificant; the Löwdin transformation need only be carried out once and requires about the same time as one SCF cycle.

4. Concluding Remarks

The central part of the theory presented in the preceding section is associated with the operator f^0 which can be considered as a superposition of Fock operators for neutral atoms in the molecule. Indeed, if the displacement operator f^q is neglected, we are left with essentially an extended Hückel problem based on Mulliken AO electronegativities, yielding in effect the tempered orbital energies defined by Mehrotra and Hoffmann [1]. In emphasizing the AO electronegativity the method is similar to a CNDO/2 type theory [5, 6], to which it reduces if the Löwdin transformation in Eq. (3.10) is omitted, two-center penetration terms are neglected, and f^q is approximated by Eq. (3.5) to Eq. (3.8) with all n_μ equal to unity. Hence, the approximate MO theory presented in this paper is effectively a fusion of the two general types of theory mentioned in the introduction and it can hopefully be expected to unite their advantages and at the same time avoid some of their shortcomings.

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References

1. Hoffmann, R.: J. Chem. Phys. **39**, 1397 (1963); Mehrotra, P. K., Hoffmann, R.: Theoret. Chim. Acta (Berl.) **48**, 301 (1978) and literature cited
2. Lykos, P. G., Schmeising, H. N.: J. Chem. Phys. **35**, 288 (1961); Bartlett, R. J., Öhrn, Y.: Theoret. Chim. Acta (Berl.) **21**, 215 (1971); Maksić, Z. B., Rubčić, A.: J. Am. Chem. Soc. **99**, 4233 (1977)
3. Linderberg, J., Öhrn, Y.: Propagators in quantum chemistry, p. 82. London: Academic Press 1973; Linderberg, J., Öhrn, Y., Thulstrup, P. W. in: Quantum science – methods and structure, Calais, J.-L., Goscinsky, O., Linderberg, J., Öhrn, Y. eds., p. 93. New York: Plenum Press 1976
4. Pople, J. A., Santry, D. P., Segal, G. A.: J. Chem. Phys. **43**, S129 (1965)
5. Pople, J. A., Segal, G. A.: J. Chem. Phys. **44**, 3289 (1966)
6. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory, New York: McGraw-Hill. 1970
7. Baird, N. C.: J. Chem. Soc. D. Chem. Commun. **1970**, 199; Mol. Phys. **18**, 39 (1970)
8. Gregory, A. R., Paddon-Row, M. N.: J. Am. Chem. Soc. **98**, 7521 (1976); Thiel, W.: Theoret. Chim. Acta (Berl.) **48**, 357 (1978)
9. Zielinski, T. J., Breen, D. L., Rein, R.: J. Am. Chem. Soc. **100**, 6266 (1978); Klopman, G., Andreozzi, P., Hopfinger, A. J., Kikuchi, O., Dewar, M. J. S.: J. Am. Chem. Soc. **100**, 6268 (1978)
10. Bantle, S., Ahlrichs, R.: Chem. Phys. Letters **53**, 148 (1978)
11. De Bruijn, S.: Chem. Phys. Letters **54**, 399 (1978); erratum: Chem. Phys. Letters **61**, 420 (1979)
12. Ellis, R. L., Jaffé, H. H.: J. Mol. Spectr. **50**, 474 (1974); Jørgensen, P., Poulsen, J. C.: J. Phys. Chem. **78**, 1420 (1974); Obbink, J. H., Hezemans, A. M. F.: Chem. Phys. Letters **50**, 133 (1977)
13. Coulson, C. A., Rushbrooke, G. S.: Proc. Camb. phil. Soc. math. phys. Sci. **36**, 193 (1940); Pariser, R.: J. Chem. Phys. **24**, 250 (1956); for experimental proof of the near-validity of the pairing theorem see, *e.g.*, Gerson, F.: High resolution E.S.R. spectroscopy, Weinheim/Bergstr.: Verlag Chemie 1970; Shida, T., Iwata, S.: J. Am. Chem. Soc. **95**, 3473 (1973); Tseng, K. L., Michl, J.: J. Am. Chem. Soc. **98**, 6138 (1976); Jordan, K. D., Burrow, P. D.: Acc. Chem. Research **11**, 341 (1978); van Paridon, M. W., Koning, R. E., Zandstra, P. J.: Chem. Phys. Letters **61**, 258 (1979)
14. Roby, K. R.: Chem. Phys. Letters **11**, 6 (1971), **12**, 579 (1972)
15. Löwdin, P.-O.: J. Chem. Phys. **18**, 365 (1950), **21**, 496 (1953)

16. Fischer-Hjalmars, I.: J. Chem. Phys. **42**, 1962 (1965)
17. Mulliken, R. S.: J. Chim. Phys. **46**, 497 (1949)
18. Jørgensen, N. H., Pedersen, P. B., Thulstrup, E. W., Michl, J.: Intern. J. Quantum Chem. **S12**, 419 (1978)
19. Mulliken, R. S.: J. Chem. Phys. **2**, 782 (1934)
20. Ruedenberg, K.: Rev. Mod. Phys. **34**, 326 (1962); Advan. Quantum Chem. **5**, 27 (1970); Feinberg, M. J., Ruedenberg, K.: J. Chem. Phys. **54**, 1495 (1971)
21. Kutzelnigg, W.: Einführung in die Theoretische Chemie, Bd. 2, pp. 24–27. Weinheim/Bergstr.: Verlag Chemie 1978; Pearson, R. G.: Theoret. Chim. Acta (Berl.) **52**, 253 (1979)

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Note Added in Proof

A detailed re-examination of the justification of NDO approximations has been published recently by G. S. Chandler and F. E. Grader, Theoret. Chim. Acta (Berl.) **54**, 131 (1980), including additional references to the literature on the subject.