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Comment on an Improved LCAO SCF Method for Three-Dimensional Solids

Steef de Bruijn

Institute of Theoretical Chemistry, University of Amsterdam, 1018 WV Amsterdam,
The Netherlands

Perkins et al. [1] modified the CNDO-method by partially including the overlap integrals and by a revised calculation of the two-electron integrals γ. Both proposed improvements are shown to be based on incorrect assumptions and to lead to absurd consequences.

Key words: CNDO – Löwdin orthogonalization – two-electron integrals.

Recently Perkins et al. [1] proposed a theoretical method for the investigation of solids, derived from CNDO by a revision of the calculation of the two-electron integrals and by an explicit consideration of overlap integrals at one stage of the procedure. Since some of their results are attractive enough to encourage further calculations along these lines I think it is useful to show that the physical model underlying their calculations cannot be accepted.

1. The Overlap Integrals

The modification of CNDO applied in [1] is based on an interpretation of CNDO as a method which *ignores* all overlap. If this interpretation were correct, we could agree with the idea that CNDO can be turned into a correct method by solving the secular determinant

$$|H-ES|=0 \qquad (1)$$

rather than Pople's $|H-E|=0$. Consistent with the choice of Eq. (1) is the introduction of a Madelung correction $M'_{\lambda\sigma}$ into $H_{\lambda\sigma}$:

$$M'_{\lambda\sigma} = \tfrac{1}{2}S_{\lambda\sigma}(M'_{\lambda\lambda} + M'_{\sigma\sigma}), \tag{2}$$

$$M'_{\lambda\lambda} = \sum_{\nu} (P_{\nu\nu} - P^{g}_{\nu\nu})\gamma_{AB}, \tag{3}$$

where $P^{g}_{\nu\nu}$ is the occupation number of the orbital χ_ν in the ground state of the free atom.

However, if we consider the aims and means of CNDO as formulated by Pople et al. [2–4] it becomes clear that overlap of AO's is not ignored; the elements of H are intended to simulate integrals over Löwdin orthogonalized orbitals, which means that we may choose either Eqs. (1)–(3) or $M'_{\lambda\sigma} = 0$ together with $|H - E| = 0$. In view of the Mulliken integral approximation [5] and of well-known justifications of ZDO [6] and NDO [7] procedures the two options are roughly equivalent, at least as far as the Madelung term is concerned. However, the necessary revision of the elements of H on going from a Löwdin basis to an overlapping basis is performed in [1] only for the rather small component M'; the main parts of $H_{\lambda\lambda}$ and $H_{\lambda\sigma}$ are taken over bodily from one representation to another. Can this step be justified? To begin with, one should not condemn a procedure solely because it deviates from CNDO. Though this method was intended to calculate H in the Löwdin basis it has been shown [8] that its implementation is so strongly inconsistent with this purpose that an arbitrary modification stands a fair chance of constituting an improvement.

In the present case the one-electron part of the diagonal elements as given by a CNDO formalism (either the original one or the version given by Armstrong et al. [9] and applied in [1]) is actually much more accurate for an overlapping basis set than for an orthogonalized one [7, 10]. Also, the choice of $-I_\lambda$ rather than $-(I_\lambda + A_\lambda)/2$ as a basic term in $H_{\lambda\lambda}$ is a considerable improvement as compared with CNDO/2 [8, 11]. However, in the two-electron part of $H_{\lambda\lambda}$, prior to orthogonalization, one looks in vain for the important terms in $(\lambda\lambda|\nu\sigma)$; here Perkins et al. combine neglect of differential overlap with retention of overlap integrals.

For the corresponding treatment of the off-diagonal elements of H there is not even a comparable partial justification. In order to avoid laborious numerical comparisons we consider only a homonuclear two-orbital case. For any one-electron operator $\hat{h}$ the matrix element is $h_{\mu\nu}$ in the overlapping basis and $(h_{\mu\nu} - Sh_{\mu\mu})(1 - S^2)^{-1}$ in the orthogonalized basis [10]. For $S \neq 0$ a supposed identity of the two expressions entails the absurd conclusion that $h_{\mu\nu} = h_{\mu\mu}S^{-1}$.

And finally the authors of [1] replace Eq. (1) by $|H - \alpha SE| = 0$, where α is an adjustable parameter. Admittedly, they have developed "a method where the non-orthogonal nature of the orbitals is, at least partially, recognized" – an expression which in view of the foregoing appears to have some unintended overtones. Also there is, at times, a correspondence between the numerical results obtained from this model and those given by *ab initio* calculations. What is lacking is a connection between the model used and the physics of the problem.

2. The Two-Electron Integrals

Perkins et al. introduce a scheme for the calculation of the two-electron integrals $\gamma_{\lambda\sigma}$, based on the approximation that the AO's can be represented by spheres with a uniform electron density inside, and zero density outside. The elaboration of the scheme consists mainly of the following errors:

1. It is stated that the relation between $\gamma_{\lambda\lambda} \equiv \langle r_{12}^{-1} \rangle$ (in eV) and the diameter d of the sphere (in Å) is given by

$$d = \frac{14.397}{\gamma_{\lambda\lambda}} \equiv \frac{C}{\gamma_{\lambda\lambda}} \tag{P 2.9}$$

(Equation numbers in [1] are identified by an additional P). Actually this expression applies to two tangent spheres, each containing one electron. For two electrons in one sphere the correct expression can be obtained by standard methods of electrostatics (cf. Appendix V of [12]):

$$d = \frac{12}{5} \times \frac{14.397}{\gamma_{\lambda\lambda}}. \tag{4}$$

2. In the calculation of the repulsion between two interpenetrating spheres with centres A and B, and radii R_A and R_B, Perkins et al. introduced R_C and R_D. R_C is the radius of the core of A, i.e. that concentric spherical part of A which is outside sphere B. With R_{12} as the distance between the centres it is obvious that both in the definitions

$$R_C = R_{12} - R_A, \qquad R_D = R_{12} - R_B \tag{P 2.10, 11}$$

and in all subsequent formulas R_C and R_D should be interchanged.

3. It is stated in [1] that the one-centre integrals γ_{AA} were calculated from (P 2.16). (Trivial correction: in the second term of this expression a factor C is lacking). Since for $R_{12} = 0$ (P 2.16) reduces to the identity $\gamma = \gamma$ [c.f. (P 2.17)] the values given for γ_{AA} are unexplained.

4. For $R_{12} > R_A + R_B$, $\gamma_{\lambda\sigma}$ is taken to be $14.397\ R^{-1}$. Though this point charge approximation is somewhat inaccurate for intermediate distances it does not constitute a serious error. Also, owing to the fortunate circumstances that (P 2.9) badly underestimates R_A, $R_{12} > R_A + R_B$ for most atom pairs. However, for neighbouring atoms it happens that $R_{12} \approx R_A + R_B$, and then it would follow from (P 2.16) and (P 2.9) that $\gamma_{AB} \approx \gamma_{AA}$. In fact for graphite $R_A = 0.719$ Å and $R_{12} = 1.421$ Å, so that with $\gamma_{AA} = 10.01$ eV we find that $\gamma_{AB} = 10.12$ eV, i.e. $\gamma_{AB} > \gamma_{AA}$.

I conclude that the treatment given in [1] does not contribute to an understanding of the investigated solids. Admittedly it is desirable to have access to a simplified but sensible MO-scheme for such complicated systems as macromolecules and solids. In my opinion the FAKE method [13], designed with precisely such applications in mind, is quite acceptable from a theoretical point of view; its practical value should be tested.

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