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Comments on De Bruijn's Criticisms on the Paper Entitled "An Improved LCAO SCF Method for Three-Dimensional Solids"

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As the three-dimensional solid-state method described in [1] is proving to be quite popular, it is appropriate to examine more closely the underlying philosophy and Dr. de Bruijn's criticism is, we believe, useful in this respect.

His proposal that a two-electron sphere be used in the approximation to γ_{AB}, rather than two one-electron spheres, is valid and we recommend the modification as representing an improvement. That is, instead of $d_A = 14.397/\gamma_{\lambda\lambda}$ in Eq. (2.9) (equation numbers refer to [1]), $d_A = 12/5 \times 14.397/\gamma_{\lambda\lambda}$ should be used. The other, relatively minor points regarding the dropped term C in 2.16, etc., are all valid and Fig. 1 should have R_C and R_D interchanged.

The more fundamental points raised, for example, that terms such as $\langle\lambda\lambda/\mu\sigma\rangle$ should be included if $|H - ES'| = 0$ is solved instead of $|H - E| = 0$, are less easily accepted. In the example given, the two-electron term is typical of one found in the more sophisticated approximate methods, such as MNDO or MINDO/3. The inclusion or exclusion of such terms does not depend on the nature of S'. Inclusion (as in MNDO) means that terms such as lone-pair repulsion can be considered; CNDO excludes them and thus cannot accurately predict some geometries (in fact, it is quite poor at predicting geometries).

Similarly, the criticism of our treatment of the off-diagonal terms of H is invalid. The partial retention of overlap is, as described in [1], a result of attempting to more accurately describe the phenomena present in solids. Many problems do not exist when small molecules are examined. The proposed identity regarding $h_{\mu\nu}$ is not claimed by us – we agree that to claim it would be absurd.

In general, we feel that Dr. de Bruijn has performed a service in pointing out two typographical errors and in suggesting an improvement to the approximation

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for γ_{AB}. The philosophical points are possibly less useful and, in some cases positively misleading. There is an urgent need for a workable method for calculating solid-state quantities and our approach is claimed to be a step in the right direction. We welcome any suggestions which improve the generality of the method.

Reference

1. Perkins, P. G., Marwaha, A. K., Stewart, J. J. P., Theor. Chim. Acta (Berl.) **57**, 1 (1980)

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Erratum

The Structure of the Active Oxygen Complex of Catalase: Model Calculations

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Due to the choice of an improper geometry for the structure **3** of Fe(P)(O), the results reported in the Note added in proof are erroneous. We have found that when a more realistic geometry is used for structure **3**, this one is more stable than structure **4** by about 20 kcal/mole.

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