Comments on "Electron band structure of solid methane: *Ab initio* calculations"

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A recent *ab initio* band-structure calculation by Piela *et al.* for solid methane is reviewed critically. The analysis used by Piela *et al.* to determine which contributions to the Fock matrix are large is shown to be in error. This error has the effect that Piela *et al.* neglect terms in the two-center matrix element which are large and easy to evaluate and retain terms in the one-center matrix element which are small and difficult to evaluate.

Recently, Piela *et al.* have proposed a Hartree-Fock derived *ab initio* model for computing energy band structures in molecular crystals.[1] The band model derived by Piela *et al.* is obtained using considerations similar to those proposed by Gilbert[2] and the author[3] for similar type calculations. What is surprising is that the band model proposed by Piela *et al.* differs substantially from those proposed by Gilbert and by the author. In this comment, the source of this discrepancy is examined. It is seen that the results of Piela *et al.* are obtained using an erroneous criterion to determine which contributions to the Fock matrix are important.

It is quite easy to see the source of the discrepancy. Consider the Hartree-Fock density matrix ρ given in terms of molecular orbitals or local orbitals (in the present context these terms may be interchangeable) as

$$\rho(\vec{r},\vec{r}') = \sum_{\substack{Ai\\Bj}} u_i(\vec{r}-\vec{R}_A)\, S^{-1}_{Ai,Bj}\, u_j^{\dagger}(\vec{r}'-\vec{R}_B) \quad . \tag{1}$$

Here one has

$$S_{Ai,Bj} = \int u_i^{*}(\vec{r}-\vec{R}_A)\, u_j(\vec{r}-\vec{R}_B)\, d\vec{r} \quad , \tag{2}$$

where i,j refer to the pertinent molecular-orbital quantum numbers and $\vec{R}_A$, $\vec{R}_B$ refer to points in the direct lattice. It is possible to give the Fock operator F in terms of ρ. It is found to be

$$F = -\nabla^2 - \sum_A \frac{2Z_A}{|\vec{r}-\vec{R}_A|} + 2\int \frac{\rho(\vec{r}'\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}' - \frac{2\rho(\vec{r}\,\vec{r}')}{|\vec{r}-\vec{r}'|} \quad . \tag{3}$$

Rydberg units are used here. Finally, in the limit of small overlap one may use the approximation

$$S^{-1}_{Ai,Bj} = 2\delta_{Ai,Bj} - S_{Ai,Bj} + \cdots \quad . \tag{4}$$

To this point the various methods agree except for the relatively minor point (a point of absolutely no consequence for the present discussion) as to the best way to define the $u_i(\vec{r}-\vec{R}_A)$.

The next step and the most important one is to construct matrix elements of F with respect to the $u_i(\vec{r}-\vec{R}_A)$. The result of Piela *et al.* is

$$\langle u_i(\vec{r}-\vec{R}_A) \mid F \mid u_j(\vec{r}-\vec{R}_A)\rangle = \epsilon_i\delta_{ij} + \sum_{B\neq A}\langle u_i(\vec{r}-\vec{R}_A) \mid V_{CB} + V_{EB} \mid u_j(\vec{r}-\vec{R}_A)\rangle \quad , \tag{5}$$

whereas Gilbert and the author find

$$\langle u_i(\vec{r}-\vec{R}_A) \mid F \mid u_j(\vec{r}-\vec{R}_A)\rangle = \epsilon_i\delta_{ij} + \sum_{B\neq A}\langle u_i(\vec{r}-\vec{R}_A) \mid V_{CB} \mid u_j(\vec{r}-\vec{R}_A)\rangle \quad . \tag{6}$$

The author here defines

$$V_{CB} = 2\sum_k \int \frac{u_k^2(\vec{r}'-\vec{R}_B)}{|\vec{r}-\vec{r}'|}\, d\vec{r}' - \frac{2Z_B}{|\vec{r}-\vec{R}_B|}$$

and

$$\langle u_i(\vec{r}-\vec{R}_A) \mid V_{EB} \mid u_j(\vec{r}-\vec{R}_A)\rangle = \sum_k \int\int \frac{u_i^{*}(\vec{r}-\vec{R}_A)\, u_k(\vec{r}-\vec{R}_B)\, u_k^{*}(\vec{r}'-\vec{R}_B)\, u_j(\vec{r}'-\vec{R}_A)}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}' \quad .$$

Clearly, this last term is second order in overlap, small compared to the terms retained in Eqs. (5) and (6), and as small as other terms rejected in forming Eq. (5)[2,3] for the one-center term. The ϵ_j's are the expectation values of the Fock operator for the system at site A with the function $u_j(\vec{r}-\vec{R}_A)$. The differences here are not important in that the term involving V_{EB} in Eq. (5) is second order in overlap of the same order of smallness as other terms neglected by Piela,[1] Gilbert,[2] and the author.[3]

Severe differences occur in the two-center terms. Here Piela *et al.* find

$$\langle u_i(\vec{r}-\vec{R}_A) \mid F \mid u_j(\vec{r}-\vec{R}_B)\rangle = (\epsilon_i+\epsilon_j)\, S_{Ai,Bj} + \langle u_i(\vec{r}-\vec{R}_A) \mid \nabla^2 \mid u_j(\vec{r}-\vec{R}_B)\rangle \quad , \tag{7}$$

whereas Gilbert and the author find

$$\langle u_i(\vec{r}-\vec{R}_A) \mid F \mid u_j(\vec{r}-\vec{R}_B)\rangle = (\epsilon_i+\epsilon_j)\, S_{Ai,Bj} + \langle u_i(\vec{r}-\vec{R}_A) \mid \nabla^2 \mid u_j(\vec{r}-\vec{R}_B)\rangle$$

$$+ \sum_{k,l} 2S_{AkBl} \int\int u_l^*(\vec{r}-\vec{R}_A)\, \frac{u_k(\vec{r}-\vec{R}_A)\, u_l^*(\vec{r}'-\vec{R}_B)\, u_j(\vec{r}'-\vec{R}_B)}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}'$$

$$\approx S_{Ai,Bj}\left[\epsilon_i+\epsilon_j+(2/|\vec{R}_A-\vec{R}_B|)\,\delta_{i=\mathrm{occ}}\,\delta_{j=\mathrm{occ}}\right] + \langle u_i(\vec{r}-\vec{R}_A) \mid \nabla^2 \mid u_j(\vec{r}-\vec{R}_B)\rangle \quad . \qquad (8)$$

(This approximation is valid as given here only for nonionic crystals and is appropriate to the case considered by Piela *et al.*) It is clear that the extra term in Eq. (8) is large and of the same order of magnitude as the terms retained by Piela *et al.* in Eq. (7).

It is easy to see where the differences between Eqs. (5) and (6) and Eqs. (7) and (8) arise. They arise from a different set of criterion for determining which terms are negligible in forming matrix elements of the Fock operator. The criterion adopted by Piela *et al.* is to remove "small" terms from ρ. Piela *et al.* do this by setting S^{-1}_{AiBj} in Eqs. (1) and (4) equal to δ_{AiBj}. Doing this leads at once to Eq. (5). It leads also to Eq. (7) if one also sets the three center terms equal to zero. That is, Piela *et al.* set the terms of the form

$$\langle u_i(\vec{r}-\vec{R}_A) \mid V_{CC}+V_{EC} \mid u_j(\vec{r}-\vec{R}_B)\rangle = 0 \quad . \qquad (9)$$

This may be reasonable, but one must note that the term involving V_{CC} is actually a first order in overlap term but is not likely to be of comparable size to the terms retained by Piela *et al.*[2,3]

The difference between Eqs. (7) and (8) is severe and arises because Piela *et al.* used an improper criterion for removing small terms from the matrix elements of the Fock operator. In the work of Gilbert[2] and the author[3] the criterion used is to form ρ correctly and then form the matrix element of F with respect to the basis and then reduce the matrix element to its dominant terms. When this is done one obtains Eq. (8) subject to a few simplifying assumptions clearly discussed by Gilbert.[2] The importance of this extra term in Eq. (8) when compared to Eq. (7) is great. This term arises because "small" terms in ρ neglected by Piela *et al.* yield a "large" contribution to F. The criterion of removing "small" terms in ρ when forming the matrix for F is improper since we have seen that these "small" terms in ρ yield "large" terms in F. We therefore argue that the proper criterion is to form the matrix elements of F first and then eliminate "small" terms in F since doing otherwise has been clearly shown here to produce substantial errors in the matrix elements of F. Furthermore, a simple tight-binding calculation for the case of CH_4 considered by Piela *et al.* is sufficient to show that the effect of including the final term in Eq. (8) is sufficient to reduce the width of the $2a_1$ band by about 0.02 Ry on about 25% of its width. The effect on the $1t_{2x}$, $1t_{2y}$, $1t_{2z}$ bands will be even greater. Clearly, then the term omitted by Piela *et al.* in their reduction of F is non-negligible in its effect.

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