Practical Training on Adding Polarization Function to Basis Set for Molecular Orbital Calculation of Ethylene

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Adding a polarization function to a basis set for molecular orbital calculation is frequently useful for producing accurate representations of chemical bonding. This article explains practical training that could greatly promote intuitive understanding of the general idea of adding a 3d-type polarization function in a π-type molecular-orbital function. In the training, by using Microsoft Excel, students draw contour plots of the molecular orbitals supplemented with and without the polarization function in ethylene (CH₂ = CH₂), and visualize the effect of the addition.

Keywords: Orbital contour plot, Polarization function, Ethylene, C₂H₄, Chemical Education

1 INTRODUCTION

In the teaching of quantum chemistry, personally drawing atomic- and molecular-orbital (AO and MO) contour-plots by using Microsoft Excel greatly improves students’ intuitive understanding of the MO theory [1–7]. This article explains a part of our practical training [3–8], which is useful for the teaching of quantum chemistry.

In previous papers [4,7], we reported practical training on adding polarization and diffuse functions [9] to basis set for MO calculation in H₂+, H₂O, and H₂⁻. In the training, our students were not given any tools except for commercially available Excel, and created, right from the beginning by themselves, the plots of the MOs that essentially represented the effect of the addition. By seeing the addition, they were encouraged to master the essential physical concept underlying the addition. The concept was not a “black box” for them.

However, on adding a d-type polarization function to 2p AOs, the previous paper [7] explained only the practical training with H₂O, although examining the contribution of a d-type polarization function in a π-type bonding-MO function may also be interesting as a subject of the training. By adding 3d-type polarization functions, two 2p AOs forming the π-type bonding-MO become distorted in shape to the internuclear region. In the work presented here, we have developed a new practical-training program on adding the 3d-type polarization functions in the π-type bonding-MO function of ethylene (CH₂ = CH₂), although such a training is slightly more complex and time-consuming than that of H₂O.

2 PRACTICAL TRAINING

In a simple MO picture, the π-type bonding-MO in the ground state of planar CH₂ = CH₂ (Figure 1) is given by

\[ \phi_1 = N_1 \{ \chi_A(2pz) + \chi_B(2pz) \} \] (1)

where \( \chi_A(2pz) \) and \( \chi_B(2pz) \) respectively denote out-of-plane 2pz AOs on carbon atoms A and B, and \( N_1 \) is a normalization factor. In this paper, the internuclear direction is set to the \( x \) axis, and the \( z \) axis is set to lie perpendicular to the molecular plane. A disadvantage to \( \phi_1 \) is that the \( |\phi_1| \) values above and below the middle point of the C–C internuclear axis (dashed-oval regions in Figure 1) are less than those of the real π-type bonding-MO. In CH₂ = CH₂, the \( \chi_A(2pz) \) and \( \chi_B(2pz) \) AOs are insufficient to accurately reflect Coulomb attraction from nuclei B and A, respectively, and thus the MO \( \phi_1 \) cannot realize correct Coulomb attraction between carbon atoms A and B. Accordingly, some additional flexibility is needed to allow the 2pz AOs on the carbon atoms to be more asymmetric around the nuclei.

To allow for this asymmetry, 3dxz-type polarization functions \( \chi_A^{(3dxz)} \) and \( \chi_B^{(3dxz)} \) are respectively added to \( \chi_A(2pz) \) and \( \chi_B(2pz) \) in CH₂ = CH₂ as shown in Figure 2. The superscript p to the right of \( \chi \) means a polarization function. The orbital functions obtained by adding the polarization functions (\( \phi_A \) and \( \phi_B \)) are given by

\[ \phi_A = N_2 \{ \chi_A(2pz) + C \chi_A^{(3dxz)} \} \] (2)

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The ratio of the 3dxz-type polarization function and the original orbital
ϕ
χ
have one additional node more than
C
function (0 <

CH2 = CH2 is given by

\[ \chi_A(2pz) = 4^{-1/2}Z_{2p}^{3/2}x_\chi^2 \exp(-Z_{2p}x_\chi^2/2) \]

\[ \chi^pB(3dxz) = (2/\sqrt{81})Z^{2/2}x_{x'}^2z_{x'}^2 \exp(-Z_{3d}x_{x'}^2/3) \]

where \( X = A \) or \( B \), \( r_x \) denotes the distance from nucleus \( X \), and \( x \) and \( z \) are the values of the \( x \) and \( z \) coordinates using nucleus \( X \) as the coordinate origin. \( Z_{2p} \) and \( Z_{3d} \) stand for the effective nuclear charges for the 2p and 3d AO functions, respectively. According to Slater’s rule [10], \( Z_{2p} \) has a value of 3.25. \( Z_{3d} \) is taken as 4.88 according to the equation reported by Nakatsuji et al. \( Z_{2p}/Z_{3d} = 2 = Z_{2p}/3 \) [11].

The C–C bond length of CH2 = CH2 is set to 2.53 au [12].

Several sample plots obtained in our training are provided in
Figures 3a and b, respectively. As shown, the orbital \( \phi_A \) is distorted in shape from \( \chi_A(2pz) \) and the two charge-centers are shifted away from points on the 2p-orbital axis to the positive \( x \) direction. Similar charge-center shifts to the negative \( x \) direction are also realized in \( \phi_B \) (Figure not shown).

As expected above, these charge-center shifts are consistent with Figure 2.

Figures 3c and d show the contour representation of orbital amplitude of \( \phi_1 \) and \( \phi_2 \) in CH2 = CH2, and agree well with Figures 1 and 2, respectively. The \( |\phi_1| \) values above and below the middle point of the C–C internuclear axis are enhanced from the \( |\phi_1| \) values (Figures 3c and d). Figure 3e shows contour representation of the difference in electron distribution between \( \phi_1 \) and \( \phi_2 \). The electron distribution of \( \phi_2 \) above and below the internuclear middle point is also enhanced from that of \( \phi_1 \), so that accurate Coulomb attraction between carbon atoms A and B is represented in \( \phi_2 \).

Thus, accurate representation of \( \pi \) bonding in CH2 = CH2 requires orbital functions (\( \phi_A \) and \( \phi_B \)) that incorporate the polarization functions \( \chi^pA(3dxz) \) and \( \chi^pB(3dxz) \). In this way, the drawings of the orbital functions as contour plots could greatly help students to better understand the general ideas of the d-type polarization function and \( \pi \) bonding.

3 SUMMARY

In the practical training reported in this article, by using Excel, the students personally draw the contour plots of the \( \pi \)-type bonding-MOs supplemented with and without the polarization function in CH2 = CH2, and visualize the effect of the addition. Several sample plots obtained in our training are provided in Supplementary Materials. Ideas developed in treating simple molecules such as CH2 = CH2 would provide a basis for dealing with complex systems.
Some computational representations of the $\pi$-type bonding-MO in CH$_2$=CH$_2$, and Excel files for drawing the contour plots of the MOs supplemented with and without some function in our practical training.

**Supplementary Materials**

Figure 3. (a) Contour representation of amplitude of $f_{CA}(2p_z)$ using carbon nucleus A as coordinate origin. The grid spacing and contour interval are set to 0.2 au and 0.1, respectively. (b) $\phi_A$. For the drawing, the $C_1$ and $N_2$ values are set to 0.15 and 0.99, respectively. (c) $\phi_1$, (d) $\phi_2$. Here, the $C_1$ and $N_2$ values are again set to 0.15 and 0.99, respectively. Under the conditions, the $\pi$-electron distribution calculated with adding the polarization function (see Supplementary Materials) is reproduced as described in the text. (e) Difference in electron distribution between $\phi_1$ and $\phi_2$. The grid spacing and contour interval are set to 0.2 au and 0.02, respectively. The carbon nuclear positions are shown in the figure.

**REFERENCES**


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