General Paper

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

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(Received: November 30, 2016; Accepted for publication: March 21, 2017; Online publication: June 30, 2017)

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 ($\chi_A^p(3dxz)$ and $\chi_B^p(3dxz)$) 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

$$\phi_A = N_2 \chi_A(2pz) + C \chi_A^p(3dxz)$$

(2)
The ratio of the 3dxz-type polarization function and the original orbital (Eq. 1), and ϕ

have one additional node more than χ



Figure 2. Addition of 3dxz-type polarization functions to 2pz AO's on carbon atoms A and B (ϕ_A and ϕ_B, respectively). C_1 stands for the mixing ratio of the polarization function and the original orbital function (0 < C_1 < 1).

where N_2 stands for a normalization factor, and C_1 is a mixing ratio of the 3dxz-type polarization function and the original orbital function (0 < C_1 < 1). The orbital functions ϕ_A and ϕ_B are distorted in shape and have their lobes shifted toward the region above and below the internuclear middle point as shown in Figure 2. Note that the signs of the second terms in equations 2 and 3 are the reverse of each other, because the orbital functions ϕ_A and ϕ_B on carbon atoms A and B should respectively point toward the plane lying perpendicular to the molecular plane and midway between nuclei A and B, that is, toward the positive and negative x direction. As shown in Figure 2, these orbital functions ϕ_A and ϕ_B have one additional node more than χ(2pz) and χ(2pz). The π-type bonding-MO resulting from adding the polarization functions in CH_2 = CH_2 is given by

where N_3 stands for a normalization factor. The π-type bonding-MO ϕ realizing the shift of the lobes toward the internuclear region can represent the accurate Coulomb attraction between carbon atoms A and B (Figure 2).

In the present study, to support our practical training, some MO calculations have been made, and the resulting representations of the π-type bonding-MO in CH_2 = CH_2 are given in Supplementary Materials. Briefly, the addition of the polarization function greatly enhances the calculated π-electron distribution at the dashed-oval regions in Figure 1.

In our practical training, contour plots of χ(2pz), χ_A (Eq. 2), ϕ_1 (Eq. 1), and ϕ_2 (Eq. 4) in CH_2 = CH_2 are drawn with Excel. In the plot of ϕ_2, to reproduce the π-electron distribution calculated with adding the polarization function (see Supplementary Materials), the C_1 value should be taken as 0.15, so N_2 becomes 0.99 by normalizations of equations 2 and 3. To show the effect of adding the polarization function more clearly, the C_1 value should be greater than 0.15. For simplification, N_1 and N_2 are taken as 2^{-1/2}. The AO functions χ_A(2pz), χ_2(2pz), χ_A(3dxz), and χ_B(3dxz) are given by the product of the corresponding radial function and spherical harmonics function and are expressed in atomic units (au). These AO functions are then given by

where χ_1 and χ_2 are the χ functions for the 2p and 3d AO functions, respectively. According to Slater’s rule [10], Z_2p has a value of 3.25. Z_2p is taken as 4.88 according to the equation reported by Nakatsuji et al. (Z_2p = 2 = Z_2p) [11]. The C–C bond length of CH_2 = CH_2 is set to 2.53 au [12].

The contour representations of orbital amplitudes of χ_A(2pz) and ϕ_1 in CH_2 = CH_2 are thus drawn and given in Figures 3a and b, respectively. As shown, the orbital ϕ_1 is distorted in shape from χ_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 ϕ_2 (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 ϕ_1 and ϕ_2 in CH_2 = CH_2, and agree well with Figures 1 and 2, respectively. The |ϕ_1| values above and below the middle point of the C–C internuclear axis are enhanced from that of ϕ_1, so that accurate Coulomb attraction between carbon atoms A and B is represented in ϕ_2.

Thus, accurate representation of π bonding in CH_2 = CH_2 requires orbital functions (ϕ_A and ϕ_B) that incorporate the polarization functions (ϕ_A(3dxz) and ϕ_B(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 π bonding.

3 SUMMARY

In the practical training reported in this article, by using Excel, the students personally draw the contour plots of the π-type bonding-MOs supplemented with and without the polarization function in CH_2 = CH_2, 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 CH_2 = CH_2 would provide a basis for dealing with complex systems.
Figure 3. (a) Contour representation of amplitude of $\gamma_A(2p_z)$ using carbon nucleus A as coordinate origin. The grid spacing and contour interval are set to 0.2 au and 0.1, respectively. (b) $\varphi_A$. For the drawing, the $C_1$ and $N_2$ values are set to 0.15 and 0.99, respectively. (c) $\varphi_1$. (d) $\varphi_2$. 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 $\varphi_1$ and $\varphi_2$. 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.

Supplementary Materials

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.