A Theoretical Study of Atomic Oxygen on Gold Surface by Hückel Theory and DFT Calculations

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The argument of the Au-O bond energy can be also generalized by the Au-O bond order in the Au-O, Au-O-Au and O-Au-O structures as follows. For Au-O, the wave functions can be defined as

$$\Psi = c_1^{Au-O}\phi_1 + c_2^{Au-O}\phi_2 \quad \text{(S1)}$$

And the secular equation is expressed as

$$\begin{cases} (\alpha_O - E)c_1 + \beta_{O-Au}c_2 = 0 \\ \beta_{O-Au}c_1 + (\alpha_{Au} - E)c_2 = 0 \end{cases} \quad \text{(S2)}$$

The corresponding secular determinant is

$$\begin{vmatrix} \alpha_O - E & \beta_{O-\mathrm{Au}} \\ \beta_{O-\mathrm{Au}} & \alpha_{\mathrm{Au}} - E \end{vmatrix} = 0 \quad \text{(S3)}$$

And the solutions of the secular determinant for Au-O are given by

$$\begin{cases} E_1^{\text{O-Au}} = \alpha - \dfrac{-h - \sqrt{h^2+4}}{2}\beta \\ E_2^{\text{O-Au}} = \alpha - \dfrac{-h + \sqrt{h^2+4}}{2}\beta \end{cases} \quad \text{(S4)}$$

where the definition of α, β and h are given in the text.

Put the values of $E_1^{\text{O-Au}}$ and $E_2^{\text{O-Au}}$ into equation (S2), and consider the normalization of coefficient c_1 and c_2, namely,

$$c_1^2 + c_2^2 = 1 \qquad \text{(S5)}$$

So we can obtain c_1 and c_2 for Ψ_1 as,

$$\begin{cases} c_{1,1} = \dfrac{h + \sqrt{h^2+4}}{\sqrt{(h+\sqrt{h^2+4})^2 + 4}} \\ c_{1,2} = \dfrac{2}{\sqrt{(h+\sqrt{h^2+4})^2 + 4}} \end{cases} \quad \text{(S6)}$$

And for Ψ_2,

$$\begin{cases} c_{2,1} = \dfrac{h - \sqrt{h^2+4}}{\sqrt{(h-\sqrt{h^2+4})^2+4}} \\ c_{2,2} = \dfrac{2}{\sqrt{(h-\sqrt{h^2+4})^2+4}} \end{cases} \quad \text{(S7)}$$

Therefore, the wave functions for the two orbitals are

$$\begin{cases} \Psi_1 = \dfrac{h+\sqrt{h^2+4}}{\sqrt{(h+\sqrt{h^2+4})^2+4}}\phi_1 + \dfrac{2}{\sqrt{(h+\sqrt{h^2+4})^2+4}}\phi_2 \\ \Psi_2 = \dfrac{h-\sqrt{h^2+4}}{\sqrt{(h-\sqrt{h^2+4})^2+4}}\phi_1 + \dfrac{2}{\sqrt{(h-\sqrt{h^2+4})^2+4}}\phi_2 \end{cases} \quad \text{(S8)}$$

Thus, the bond order of every Au-O π-bond is obtained as

$$P_1 = \sum_i n_i c_{i,u} c_{i,v} = 2c_{1,1}c_{1,2} + c_{2,1}c_{2,2} = \frac{4(h+\sqrt{h^2+4})}{(h+\sqrt{h^2+4})^2+4} + \frac{2(h-\sqrt{h^2+4})}{(h-\sqrt{h^2+4})^2+4} \quad \text{(S9)}$$

Next, we consider the bond order of Au-O π bond of Au-O-Au. The wave function for Au-O-Au is expressed as

$$\Psi = c_1^{Au-O}\phi_1 + c_2^{Au-O}\phi_2 + c_3^{Au-O}\phi_3 \quad \text{(S10)}$$

The secular equation is given as

$$\begin{cases} (\alpha_{\mathrm{Au}} - E)c_1 + \beta_{O-Au}c_2 = 0 \\ \beta_{O-Au}c_1 + (\alpha_O - E)c_2 + \beta_{O-Au}c_3 = 0 \\ \beta_{O-Au}c_2 + (\alpha_{\mathrm{Au}} - E)c_3 = 0 \end{cases} \quad \text{(S11)}$$

And the corresponding secular determinant is

$$\begin{vmatrix} \alpha_{\mathrm{Au}} - E & \beta_{O-\mathrm{Au}} & 0 \\ \beta_{O-\mathrm{Au}} & \alpha_{\mathrm{O}} - E & \beta_{\mathrm{O}-Au} \\ 0 & \beta_{\mathrm{O}-Au} & \alpha_{Au} - E \end{vmatrix} = 0 \quad \text{(S12)}$$

The solutions of the secular determinant for Au-O-Au are given by

$$\begin{cases} E_1^{\text{Au-O-Au}} = \alpha - \dfrac{-h - \sqrt{h^2+8}}{2}\beta \\ E_2^{\text{Au-O-Au}} = \alpha \\ E_3^{\text{Au-O-Au}} = \alpha - \dfrac{-h + \sqrt{h^2+8}}{2}\beta \end{cases} \quad \text{(S13)}$$

Put the values of E_1, E_2 and E_3 into equation (S11), and consider the normalization of coefficient c_1, c_2 and c_3,

$$c_1^2 + c_2^2 + c_3^2 = 1 \quad \text{(S14)}$$

So the values of c_1, c_2 and c_3 for Ψ_1 are,

$$\begin{cases} c_{1,1} = \dfrac{2}{\sqrt{(h+\sqrt{h^2+8})^2+8}} \\ c_{1,2} = \dfrac{h+\sqrt{h^2+8}}{\sqrt{(h+\sqrt{h^2+8})^2+8}} \\ c_{1,3} = \dfrac{2}{\sqrt{(h+\sqrt{h^2+8})^2+8}} \end{cases} \quad \text{(S15)}$$

And for Ψ_2,

$$\begin{cases} c_{2,1} = \dfrac{\sqrt{2}}{2} \\ c_{2,2} = 0 \\ c_{2,3} = -\dfrac{\sqrt{2}}{2} \end{cases} \quad \text{(S16)}$$

For Ψ_3,

$$\begin{cases} c_{3,1} = \dfrac{2}{\sqrt{(h-\sqrt{h^2+8})^2+8}} \\ c_{3,2} = \dfrac{h-\sqrt{h^2+8}}{\sqrt{(h-\sqrt{h^2+8})^2+8}} \\ c_{3,3} = \dfrac{2}{\sqrt{(h-\sqrt{h^2+8})^2+8}} \end{cases} \quad \text{(S17)}$$

Therefore, the wave functions for the three orbitals are given as

$$\begin{cases} \Psi_1 = \dfrac{2}{\sqrt{(h+\sqrt{h^2+8})^2+8}}\phi_1 + \dfrac{h+\sqrt{h^2+8}}{\sqrt{(h+\sqrt{h^2+8})^2+8}}\phi_2 + \dfrac{2}{\sqrt{(h+\sqrt{h^2+8})^2+8}}\phi_3 \\ \Psi_2 = \dfrac{\sqrt{2}}{2}\phi_1 - \dfrac{\sqrt{2}}{2}\phi_3 \\ \Psi_3 = \dfrac{2}{\sqrt{(h-\sqrt{h^2+8})^2+8}}\phi_1 + \dfrac{h-\sqrt{h^2+8}}{\sqrt{(h-\sqrt{h^2+8})^2+8}}\phi_2 + \dfrac{2}{\sqrt{(h-\sqrt{h^2+8})^2+8}}\phi_3 \end{cases} \quad \text{(S18)}$$

The bond order of every Au-O π-bond in Au-O-Au is obtained as

$$P_2 = \sum_i n_i c_{i,u} c_{i,v} = 2c_{1,1}c_{1,2} + 2c_{2,1}c_{2,2} + c_{3,1}c_{3,2} = \frac{4(h+\sqrt{h^2+8})}{(h+\sqrt{h^2+8})^2+8} + \frac{2(h-\sqrt{h^2+8})}{(h-\sqrt{h^2+8})^2+8} \quad \text{(S19)}$$

Finally, we consider the bond order of Au-O π bond in O-Au-O.

The wave function for O-Au-O is expressed as

$$\Psi = c_1^{Au-O}\phi_1 + c_2^{Au-O}\phi_2 + c_3^{Au-O}\phi_3 \quad \text{(S20)}$$

The secular equation is given as

$$\begin{cases} (\alpha_{\mathrm{O}} - E)c_1 + \beta_{O-Au}c_2 = 0 \\ \beta_{O-Au}c_1 + (\alpha_{Au} - E)c_2 + \beta_{O-Au}c_3 = 0 \\ \beta_{O-Au}c_2 + (\alpha_{\mathrm{O}} - E)c_3 = 0 \end{cases} \quad \text{(S21)}$$

And the corresponding secular determinant is

$$\begin{vmatrix} \alpha_{\mathrm{O}} - E & \beta_{O-\mathrm{Au}} & 0 \\ \beta_{O-\mathrm{Au}} & \alpha_{\mathrm{Au}} - E & \beta_{\mathrm{O}-Au} \\ 0 & \beta_{\mathrm{O}-Au} & \alpha_{\mathrm{O}} - E \end{vmatrix} = 0 \quad \text{(S22)}$$

The solutions of the secular determinant for O-Au-O are given by

$$\begin{cases} E_1^{\text{O-Au-O}} = \alpha - \dfrac{-h - \sqrt{h^2+8}}{2}\beta \\ E_2^{\text{O-Au-O}} = \alpha + h\beta \\ E_3^{\text{O-Au-O}} = \alpha - \dfrac{-h + \sqrt{h^2+8}}{2}\beta \end{cases} \quad \text{(S23)}$$

Put the values of E_1, E_2 and E_3 into equation (S21), and consider the normalization of coefficient c_1, c_2 and c_3,

$$c_1^2 + c_2^2 + c_3^2 = 1 \quad \text{(S24)}$$

So the values of c_1, c_2 and c_3 for Ψ_1 are given as

$$\begin{cases} c_{1,1} = \dfrac{2}{\sqrt{(h - \sqrt{h^2+8})^2 + 8}} \\ c_{1,2} = \dfrac{-h + \sqrt{h^2+8}}{\sqrt{(h - \sqrt{h^2+8})^2 + 8}} \\ c_{1,3} = \dfrac{2}{\sqrt{(h - \sqrt{h^2+8})^2 + 8}} \end{cases} \quad \text{(S25)}$$

For Ψ_2,

$$\begin{cases} c_{2,1} = \dfrac{\sqrt{2}}{2} \\ c_{2,2} = 0 \\ c_{2,3} = -\dfrac{\sqrt{2}}{2} \end{cases} \quad \text{(S26)}$$

For Ψ_3,

$$\begin{cases} c_{3,1} = \dfrac{2}{\sqrt{(h + \sqrt{h^2+8})^2 + 8}} \\ c_{3,2} = \dfrac{-h - \sqrt{h^2+8}}{\sqrt{(h + \sqrt{h^2+8})^2 + 8}} \\ c_{3,3} = \dfrac{2}{\sqrt{(h + \sqrt{h^2+8})^2 + 8}} \end{cases} \quad \text{(S27)}$$

Therefore, the wave functions are

$$\begin{cases} \Psi_1 = \dfrac{2}{\sqrt{(h-\sqrt{h^2+8})^2+8}}\phi_1 + \dfrac{-h+\sqrt{h^2+8}}{\sqrt{(h-\sqrt{h^2+8})^2+8}}\phi_2 + \dfrac{2}{\sqrt{(h-\sqrt{h^2+8})^2+8}}\phi_3 \\ \Psi_2 = \dfrac{\sqrt{2}}{2}\phi_1 - \dfrac{\sqrt{2}}{2}\phi_3 \\ \Psi_3 = \dfrac{2}{\sqrt{(h+\sqrt{h^2+8})^2+8}}\phi_1 + \dfrac{-h-\sqrt{h^2+8}}{\sqrt{(h+\sqrt{h^2+8})^2+8}}\phi_2 + \dfrac{2}{\sqrt{(h+\sqrt{h^2+8})^2+8}}\phi_3 \end{cases} \tag{S28}$$

The bond order of every Au-O π-bond in O-Au-O is obtained as

$$P_3 = \sum_i n_i c_{i,u} c_{i,v} = 2c_{1,1}c_{1,2} + 2c_{2,1}c_{2,2} = \frac{4(-h+\sqrt{h^2+8})}{(h-\sqrt{h^2+8})^2+8} \tag{S29}$$

According to the expressions of Au-O bond orders in O-Au (P1), Au-O-Au (P2) and O-Au-O (P3), we can describe each bond order as a function of h as shown in Figure 1S, indicating that the Au-O bond order is largest in the O-Au-O structure.

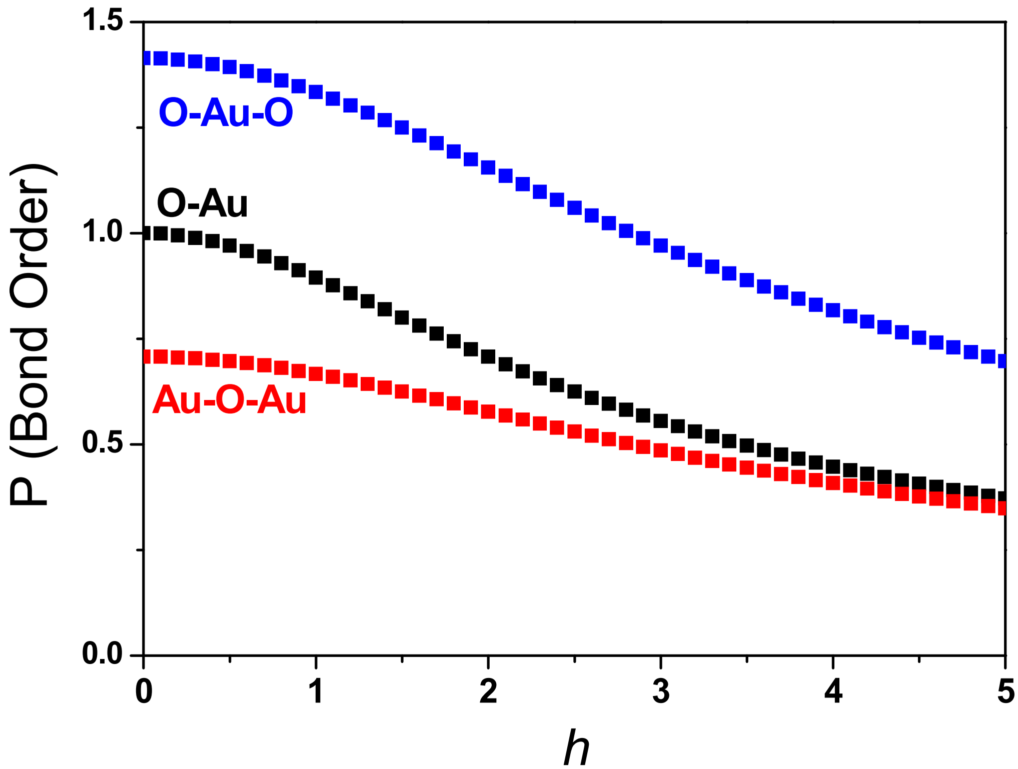

Figure 1S. The relationship between h and the bond orders of Au-O in O-Au, Au-O-Au and O-Au-O respectively.

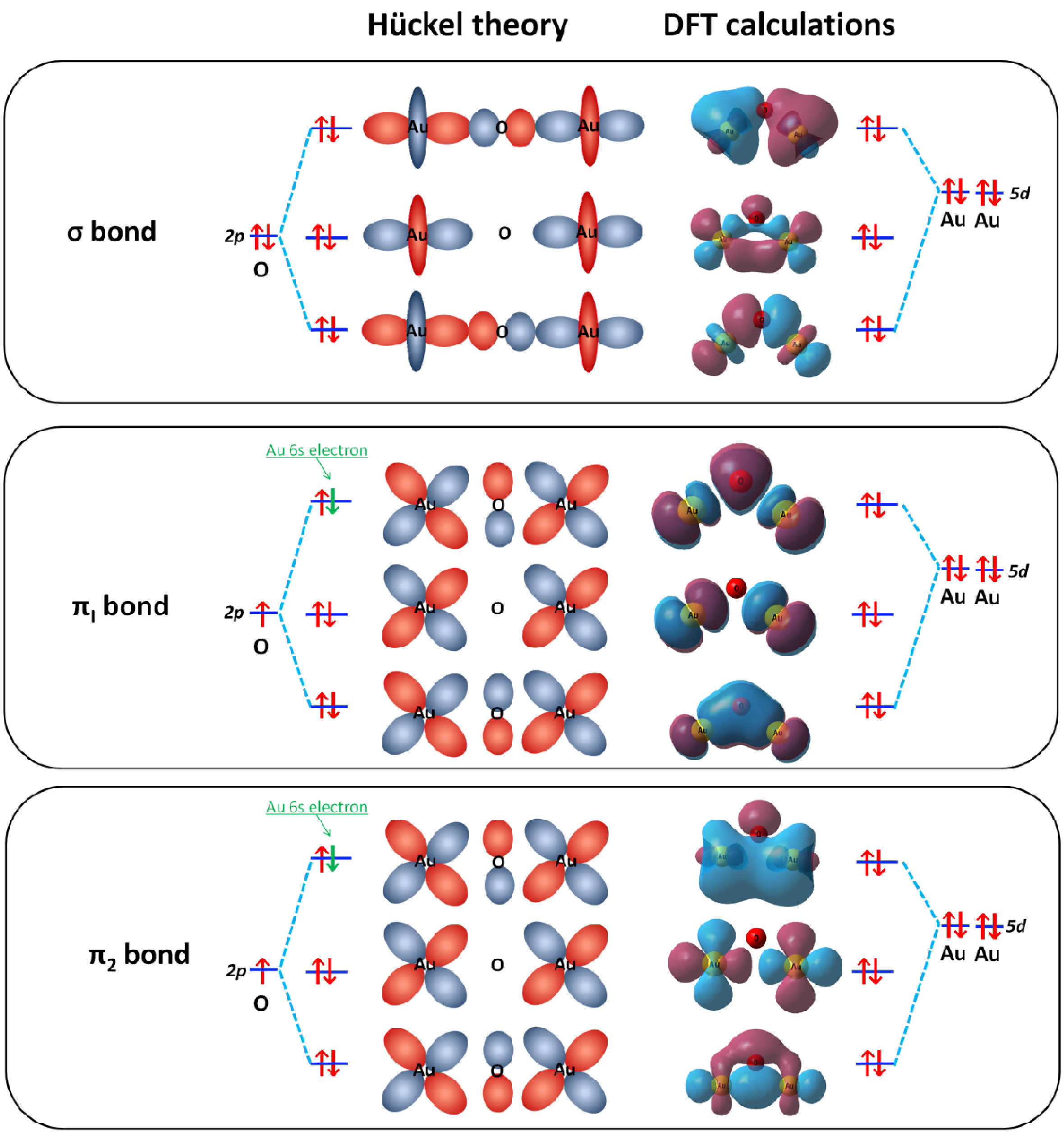

Figure 2S. The molecular orbitals of Au-O-Au from Hückel theory and DFT calculations. The tiny difference in the shapes of the molecular orbitals comes from the difference angle of Au-O-Au in Hückel theory and DFT calculations. To clarity, the 6s electrons of Au in the results of Hückel theory are marked as green color.