

J07Q.3

Solution to J07Q.3 Triangular Molecule

a) In the 3s orbital basis, the one electron Hamiltonian has the following form:

$$\begin{pmatrix} \epsilon_0 & -t & -\lambda t \\ -t & \epsilon_0 & -t \\ -\lambda t & -t & \epsilon_0 \end{pmatrix}.$$

Eigenvalues ϵ are solution of the following equation:

$$(\epsilon_0 - \epsilon)^3 - t^2(2 + \lambda^2)(\epsilon_0 - \epsilon) + 2\lambda t^3 = 0 \quad (1)$$

which can be factorized,

$$(\epsilon_0 - \epsilon + \lambda t)((\epsilon_0 - \epsilon)^2 - \lambda t(\epsilon_0 - \epsilon) - 2t^2) = 0 \quad (2)$$

so the energy levels are $\epsilon_1 = \epsilon_0 + \lambda t$, $\epsilon_2 = \epsilon_0 + \frac{-\lambda + \sqrt{\lambda^2 + 8}}{2} t$, $\epsilon_3 = \epsilon_0 + \frac{-\lambda - \sqrt{\lambda^2 + 8}}{2} t$

One can easily notice that $\psi_1 = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$ (antisymmetric).

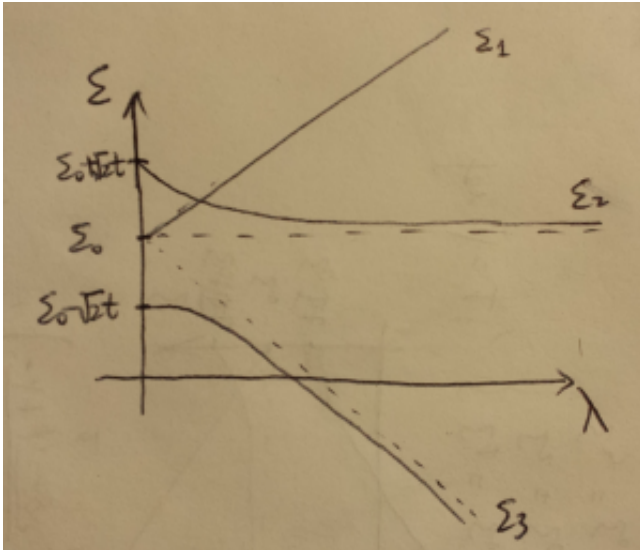
Since eigenvectors form an orthonormal basis, ψ_2 and ψ_3 should be linear combinations of $\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$ and

$$\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

So one can write $\psi_2 = \begin{pmatrix} 1 \\ a \\ 1 \end{pmatrix}$ and $\psi_3 = \begin{pmatrix} -\frac{2}{a} \\ 1 \\ 1 \end{pmatrix}$ By plugging back to the eigenvalue equation,

$$\psi_2 = \begin{pmatrix} 1 \\ \frac{4}{\sqrt{\lambda^2+8}-\lambda} \\ 1 \end{pmatrix} \text{ and } \psi_3 = \begin{pmatrix} 1 \\ -\frac{\lambda-\sqrt{\lambda^2+8}}{2} \\ 1 \end{pmatrix} .$$
 Both two states are symmetric.

Energies as function of λ are sketched:



Since the energy should be minimized, ψ_3 is the ground state.

For $\lambda = 1$, $\epsilon_1 = \epsilon_2 = \epsilon_0 + t$ (degenerate excited states) and $\epsilon_3 = \epsilon_0 - 2t$ (ground state). Moreover,

$$\psi_1 = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \psi_2 = \begin{pmatrix} 1 \\ 2 \\ 1 \end{pmatrix}, \psi_3 = \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} .$$

b) The adiabatic approximation says that, during configuration evolution, the state with the lowest energy will remain in the lowest, the intermediate in the intermediate, and the highest in the highest. For simplicity, let's only consider the intermediate state which has simple eigenvector. In A configuration, the intermediate

state corresponds to $\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

And in $(A+B)/2$ configuration, the intermediate state is $\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$. Actually, each time one pass through an

intermediate configuration, the system acquires a minus sign. Thus, eventually, the system gains a minus sign after 3 steps of evolution.

One thought on “J07Q.3”



December 17, 2013 at 2:40 am

Part (a) looks OK.

Part (b) is just sketched and requires a fuller treatment.
