Project Excitation Transfer
Physics 481 / Spring 2000
Professor Klaus Schulten

Electronic Excitations of the Hexatriene, Benzene and Energy Transfer Between these Molecules.

In this problem we want to describe electronic excitations of the molecule hexatriene (see Fig. 1).

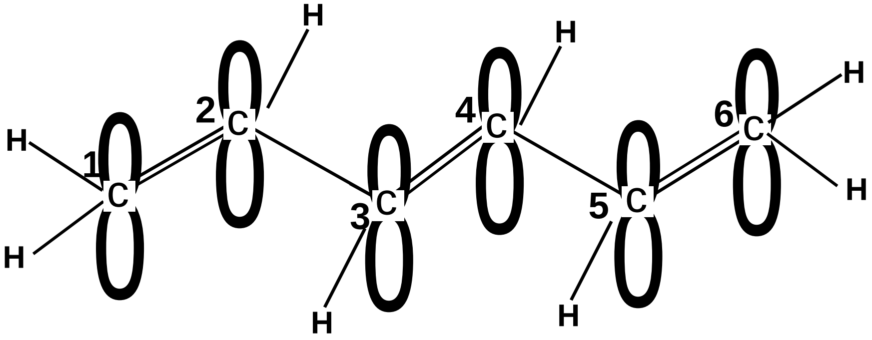

Figure 1: Hexatriene and its six atomic 2p-orbitals.

For this purpose we assume that the relevant six electrons, moving in the molecule's six 2p atomic orbitals of the six C-atoms are described by the Hubbard Hamiltonian

$$H = \sum_{\substack{r,s \\ \sigma}} t_{rs} c^\dagger_{r\sigma} c_{s\sigma} + v \sum_{r} c^\dagger_{r\alpha} c_{r\alpha} c^\dagger_{r\beta} c_{r\beta} \; . \tag{1}$$

where $c^\dagger_{r\sigma}$ generates an electron with spin σ in one of the six 2p-orbitals. t_{rs}

is described by the matrix

$$-\begin{pmatrix} I & t & 0 & 0 & 0 & 0 \\ t & I & t & 0 & 0 & 0 \\ 0 & t & I & t & 0 & 0 \\ 0 & 0 & t & I & t & 0 \\ 0 & 0 & 0 & t & I & t \\ 0 & 0 & 0 & 0 & t & I \end{pmatrix} \tag{2}$$

where we assume I = 0 and t = 2.5eV. v in (1) describes the on-site electron repulsion and a value of $v = 5eV$ is assumed. In a mathematica notebook we provide the SCF ground state $|\psi_{SCF}\rangle$ and the corresponding molecular orbitals corresponding to the creation operator:

$$d^{+}_{m\sigma} = \sum_{r=1}^{6} U_{rm} c^{\dagger}_{r\sigma} \ , \ m = 1, \ldots, 6, \ U_{rm} \in \mathbb{R} \tag{3}$$

It holds

$$h^{SCF}_{nm} = \tilde{t}_{nm} + \tilde{v}_{nm}(|\psi_{SCF}\rangle) = \epsilon^{SCF}_{n} \delta_{nm} \tag{4}$$

where

$$\tilde{t}_{nm} = \sum_{r,s=1}^{6} U_{rm} U_{sm} t_{rs} \ , \tag{5}$$

$$\tilde{v}_{nm} = v \ \sum_{r=1}^{6} (\sum_{k=1}^{3} U^{2}_{rk}) U_{rn} U_{rm} \ , \tag{6}$$

and where ϵ^{SCF}_{n} are the eigenvalues of the SCF-Hamiltonian. The corresponding SCF-ground-state is

$$|\psi_{SCF}\rangle = \prod_{m=1}^{3} d^{+}_{m\alpha} d^{+}_{m\beta} |0\rangle \tag{7}$$

where α, β denote up, down electron spins, and where the energies are ordered $\epsilon^{SCF}_{1} < \epsilon^{SCF}_{2} <$ ...

> (a) Show that Eqs.(4-6) provide the SCF-Hamiltonian to (1) in the basis of the one-electron states corresponding to the creation operators (3).

We consider now electronically excited states of hexatriene, i.e., not the ground state. These states can be expressed in the basis of the following states ($m \in \{1, 2, 3\}$; $n \in \{4, 5, 6\}$):

$$|^{0,0}\Psi_m^n\rangle = \frac{1}{\sqrt{2}}(d_{n\alpha}^+ d_{m\alpha} + d_{n\beta}^+ d_{m\beta})|\psi_{SCF}\rangle \tag{8}$$

$$|^{1,0}\Psi_m^n\rangle = \frac{1}{\sqrt{2}}(d_{n\alpha}^+ d_{m\alpha} - d_{n\beta}^+ d_{m\beta})|\psi_{SCF}\rangle \tag{9}$$

$$|^{1,1}\Psi_m^n\rangle = d_{n\alpha}^+ d_{m\beta}|\psi_{SCF}\rangle \tag{10}$$

$$|^{1,-1}\Psi_m^n\rangle = d_{n\beta}^+ d_{m\alpha}|\psi_{SCF}\rangle \tag{11}$$

(b) Show that the basis excited state (8) is a singlet state and that the basis states (9-11) are triplet states.

We will evaluate now the Hamiltonian (1) in the basis

$$\begin{aligned} \mathcal{B} = \{|\psi_{SCF}\rangle\} \ &\cup \{|^{0,0}\Psi_m^n\rangle, m \in \{1,2,3\};\ n \in \{4,5,6\}\} \\ &\cup\{|^{1,0}\Psi_m^n\rangle, m \in \{1,2,3\};\ n \in \{4,5,6\}\} \\ &\cup\{|^{1,1}\Psi_m^n\rangle, m \in \{1,2,3\};\ n \in \{4,5,6\}\} \\ &\cup\{|^{1,-1}\Psi_m^n\rangle, m \in \{1,2,3\};\ n \in \{4,5,6\}\} \\ &. \end{aligned} \tag{12}$$

For his purpose we need to determine the matrix elements ($\langle I|H|J\rangle$) for $|I\rangle, |J\rangle \in \mathcal{B}$, as given in (14).

The resulting Hamiltonian matrix has the form

$$- \begin{pmatrix} E_{SCF} & 0 & 0 & 0 & 0 \\ 0 & H_1 & 0 & 0 & 0 \\ 0 & 0 & H_2 & 0 & 0 \\ 0 & 0 & 0 & H_2 & 0 \\ 0 & 0 & 0 & 0 & H_2 \end{pmatrix} \tag{13}$$

where H_1, H_2 are 9×9 matrices describing singlet, triplet states and where the zeros represent vanishing matrix elements.

(c) Show that (13) should be the form of the Hamiltonian.

(d) Prove that

$$\langle {}^{0,0}\Psi^{n}_{m} | H | {}^{0,0}\Psi^{n'}_{m'} \rangle = \begin{cases} E_0^{SCF} + h_{nn}^{SCF} - h_{mm}^{SCF} + & , \text{for } n = n' \text{and } m = m' \\ +v \sum_{r=1}^{6} U_{rm} U_{rn} U_{rm} U_{rn} & \\ & \\ v \sum_{r=1}^{6} U_{rm'} U_{rn'} U_{rm} U_{rn} & , \text{otherwise} \end{cases} \tag{14}$$

where E_0^{SCF} is the SCF ground state energy of the molecule, and it can be set to zero[1].

(e) Using the mathematica notebook provided in web-address http://www.ks.uiuc.edu/Services/Class/PHYS481/CI/PS10.nb determine numerically the matrix H_1 as defined in (13).

(f) Note that the matrix H_1 is block diagonal if one orders the states as follows:

$$\begin{aligned} &\{ |{}^{0,0}\Psi^{4}_{1}\rangle, |{}^{0,0}\Psi^{6}_{1}\rangle, |{}^{0,0}\Psi^{5}_{2}\rangle, |{}^{0,0}\Psi^{4}_{3}\rangle, |{}^{0,0}\Psi^{6}_{3}\rangle \} \\ &\quad \cup \{ |{}^{0,0}\Psi^{5}_{1}\rangle, |{}^{0,0}\Psi^{4}_{2}\rangle, |{}^{0,0}\Psi^{6}_{2}\rangle, |{}^{0,0}\Psi^{5}_{3}\rangle \} \end{aligned} \tag{15}$$

Explain this on the basis of a symmetry of the states with respect to rotation around the 2-fold axis shown in Fig. 2. [If you cannot do this don't worry and go ahead]

For this purpose characterize first the states corresponding to $d^{\dagger}_{n\sigma}$ by plotting U_{nr}, $r = 1, 2, \ldots, 6$, for $n = 1, 2, \ldots, 6$. Do this for a few different values of v (the on site electron repulsion). How does U_{nr} depend on v? Explain this dependence.

A program to calculate excited state wavefunctions $|\phi_i\rangle$, and corresponding transition dipole moments $\vec{D}_i = \langle \phi_0 | \vec{d} | \phi_i \rangle$ (see chapter 8) is made available at
www.ks.uiuc.edu/∼ritz/form1.html

(g) Use the program for hexatriene, as described by Hamiltonian (1,2) with stated parameters. Verify that the Hamiltonian constructed by the program and the mathematica program are numerically identical.

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[1] This is obviously equivalent to redefining the origin of the energy scale.

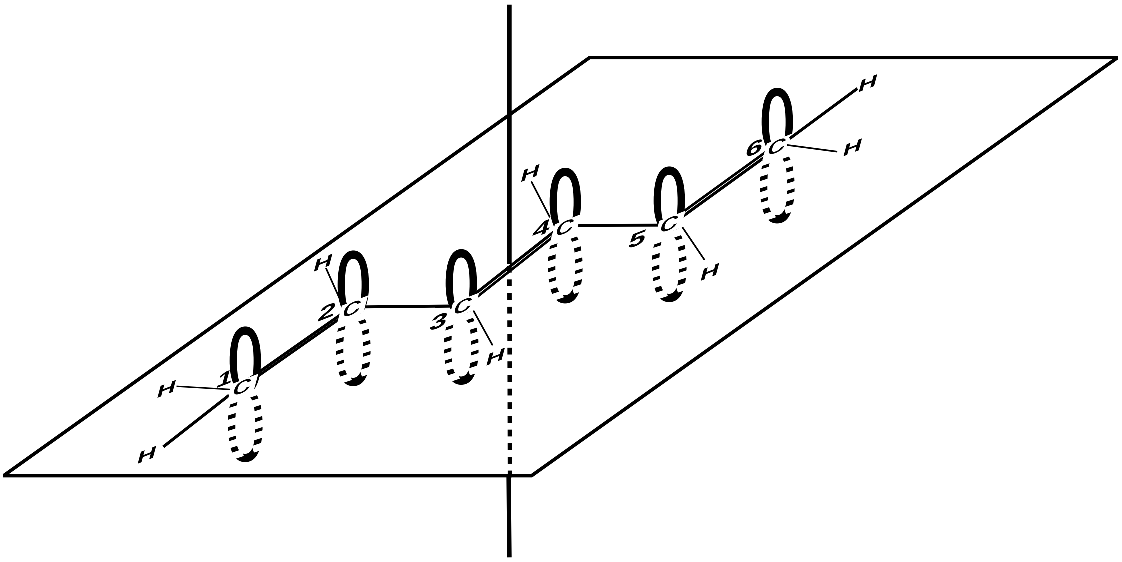

Figure 2: 2-fold symmetry of Hexatriene and its six atomic 2p-orbitals.

> (h) By means of the program provided calculate transition dipole moments of the first three excited states of hexatriene and benzene (for the case of benzene Hamiltonian (2) needs to be modified).

We want to describe now how electronic excitations can be transferred from benzene to hexatriene. Consider the lowest excited state of benzene. When an excited benzene molecule is brought into contact with e.g., a hexatriene molecule, energy transfer between the two molecules might occur. The initially excited benzene molecule (i.e. excitation donor) can transfer its excitation energy to the hexatriene molecule, which was initially in its ground state. The rate of this energy transfer is described by Fermi's golden rule (see chapter 8)

$$k_{DA} \;=\; \frac{2\,\pi}{\hbar}\,|U_{DA}|^2\,J_{DA}\;. \tag{16}$$

Here, J_{DA} depends on spectral properties of the donor and acceptor (benzene and hexatriene in this case), and U_{DA} can be approximated as

$$U_{DA} \;=\; \frac{\vec{D}_D \cdot \vec{D}_A}{{r_{DA}}^3} - \frac{3(\vec{r}_{DA} \cdot \vec{D}_D)\,(\vec{r}_{DA} \cdot \vec{D}_A)}{{r_{DA}}^5}\,. \tag{17}$$

Here $\vec{D}_D$, $\vec{D}_A$ are the transition dipole moments of donor and acceptor excited states involved in excitation transfer, and $\vec{r}_{DA}$ is a distance vector between the donor and acceptor centers of masses.

> (i) Calculate the rate (and time $\tau_{DA} = 1/k_{DA}$) of excitation energy transfer between a benzene molecule, and a hexatriene molecule assuming that $J_{DA} = 1eV^{-1}$. Use $\vec{D}_D$, $\vec{D}_A$ of the two lowest excited states of benzene and hexatriene respectively, as calculated from the provided program. The benzene and hexatriene coordinates (with center of mass placed at the origin of the coordinate system) will emerge as an output of the program provided. Assume that the centers of mass of benzene and hexatriene are shifted by $\vec{r}_{DA} = 15\ \AA\,\hat{x}$ ($\hat{x}$ is the unit vector along the x-axis).

This project needs to be handed in by Friday, May 12, 2000 into the mail box of Gheorghe-Sorin Paraoan in Loomis.