HW #6 Answers

1. Mixing of H 1s and 2pz due to an electric field of $e\mathcal{E}z$.

The Hamiltonian matrix is

$$\begin{pmatrix} \epsilon_{1s} & V \\ V & \epsilon_{2p_z} \end{pmatrix} \quad \text{where } V = \langle 1s | e\mathcal{E}z | 2p_z \rangle$$

$$\langle 1s | e\mathcal{E}z | 2p_z \rangle = \frac{e\mathcal{E}}{\sqrt{2}\,3a^4} \int_0^\infty e^{-3r/2a} r^4\,dr$$

$$= \frac{e\mathcal{E}}{\sqrt{2}\,3a^4} \frac{256a^5}{81} = 0.74\, e\mathcal{E}a$$

In atomic units $H = \begin{pmatrix} -1/2 & .74\mathcal{E} \\ .74\mathcal{E} & -1/8 \end{pmatrix}$

Even $\mathcal{E} = 0.001$ a.u. is a very strong electric field so PT is valid here.

$$E = -1/2 - \frac{(.74)^2\mathcal{E}^2}{3/8}$$

Note that this gives a polarizability of $\frac{16}{3}(.74)^2 = 3$ a.u.

2. For cyclobutadiene, we can exploit two symmetry planes.

$\chi_1 = 1/2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$ $\quad H_{11} = \alpha + 2\beta$

$\chi_2 = 1/2(\phi_1 + \phi_2 - \phi_3 - \phi_4)$ $\quad H_{22} = \alpha$

$\chi_3 = 1/2(\phi_1 - \phi_2 - \phi_3 + \phi_4)$ $\quad H_{33} = \alpha$

$\chi_4 = 1/2(\phi_1 - \phi_2 + \phi_3 - \phi_4)$ $\quad H_{44} = \alpha - 2\beta$

4. (7.55 from text) Matrix repr of $\hat{L}_z$ in the Y_ℓ^m basis set.

	Y_2^2	Y_2^1	Y_2^0	Y_2^{-1}	Y_2^{-2}
Y_2^2	$2\hbar$	0	0	0	0
Y_2^1	0	$1\hbar$	0	0	0
Y_2^0	0	0	0	0	0
Y_2^{-1}	0	0	0	$-\hbar$	0
Y_2^{-2}	0	0	0	0	$-2\hbar$

(7.56 from text)

What is ΔL_z for the $2p_z$ and $2p_x$ orbitals of H?

$\langle 2p_z | \hat{L}_z^2 | 2p_z \rangle - \langle 2p_z | \hat{L}_z | 2p_z \rangle^2 = 0$ since ~~L_z~~ $2p_z = 0\, 2p_z$

$\langle 2p_x | \hat{L}_z^2 | 2p_x \rangle - \langle 2p_x | \hat{L}_z | 2p_x \rangle^2 = \hbar^2 - 0 = \hbar^2$

So $\Delta L_z = \hbar$ in the latter case.

3. $A = \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}$

The eigenvalues of this matrix are $3/2 \pm \sqrt{5}/2$

For the $\frac{3+\sqrt{5}}{2}$ eigenvalue, the eigenvector is

$$\begin{pmatrix} 1 \\ \frac{-1-\sqrt{5}}{2} \end{pmatrix}$$

For the $\frac{3-\sqrt{5}}{2}$ eigenvalue, the eigenvector is $\begin{pmatrix} 1 \\ \frac{-1+\sqrt{5}}{2} \end{pmatrix}$

The corresponding normalized eigenvectors are

$$\begin{pmatrix} 1 \\ \frac{-1-\sqrt{5}}{2} \end{pmatrix} \frac{1}{\sqrt{\frac{5+\sqrt{5}}{2}}} = \begin{pmatrix} \frac{\sqrt{2}}{\sqrt{5+\sqrt{5}}} \\ \frac{-1-\sqrt{5}}{\sqrt{2}\sqrt{5+\sqrt{5}}} \end{pmatrix}$$

$$\begin{pmatrix} 1 \\ \frac{-1+\sqrt{5}}{2} \end{pmatrix} \frac{1}{\sqrt{\frac{5-\sqrt{5}}{2}}} = \begin{pmatrix} \frac{\sqrt{2}}{\sqrt{5-\sqrt{5}}} \\ \frac{-1+\sqrt{5}}{\sqrt{2}\sqrt{5-\sqrt{5}}} \end{pmatrix}$$

So $U = \begin{pmatrix} \frac{\sqrt{2}}{\sqrt{5+\sqrt{5}}} & \frac{\sqrt{2}}{\sqrt{5-\sqrt{5}}} \\ \frac{-1-\sqrt{5}}{\sqrt{2}\sqrt{5+\sqrt{5}}} & \frac{-1+\sqrt{5}}{\sqrt{2}\sqrt{5-\sqrt{5}}} \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix}$

$$U^{+} = \begin{pmatrix} U_{11} & U_{21} \\ U_{12} & U_{22} \end{pmatrix}$$

$$e^{A} = I + A + \tfrac{1}{2}AA + \ldots$$

$$U^{+}e^{A}U = I + D + \tfrac{1}{2}D^{2} + \ldots = \begin{pmatrix} e^{\lambda_1} & 0 \\ 0 & e^{\lambda_2} \end{pmatrix}$$

where D is the diagonal matrix with the eigenvalues on the diagonal.

So $e^{A} = U \begin{pmatrix} e^{\lambda_1} & 0 \\ 0 & e^{\lambda_2} \end{pmatrix} U^{+}$