CHEMISTRY 542

Second Exam

November 10, 2003

1. (a) Given $\mathcal{H} = a_1 I_z(1) + a_2 I_z(2)$, given that $I_z\,\alpha = (\hbar/2)\alpha$ and $I_z\,\beta = -(\hbar/2)\beta$ determine the matrix representation of $\mathcal{H}$ in the basis functions

$\psi_1 = \alpha(1)\bullet\alpha(2)$
$\psi_2 = \alpha(1)\bullet\beta(2)$
$\psi_3 = \beta(1)\bullet\alpha(2)$
$\psi_4 = \beta(1)\bullet\beta(2)$

(b) In this basis, the matrix representation of $\boldsymbol{I}(1) \bullet \boldsymbol{I}(2)$ is

$$\frac{\hbar^2}{4}\begin{array}{|c|c|c|c|}\hline 1 & 0 & 0 & 0 \\ \hline 0 & -1 & 2 & 0 \\ \hline 0 & 2 & -1 & 0 \\ \hline 0 & 0 & 0 & 1 \\ \hline\end{array}$$

Given a system described by the Hamiltonian
$\mathcal{H} = a_1 I_z(1) + a_2 I_z(2) + J\,\boldsymbol{I}(1) \bullet \boldsymbol{I}(2)$ where $a_1 = 10/\hbar$, $a_2 = 20/\hbar$ and $J = 4/\hbar^2$
Question: Determine the energies for this system.

2. Given a system with Hamiltonian
$\mathcal{H} = \mathcal{H}^{(0)} + \boldsymbol{h}$

It is known that $\mathcal{H}^{(0)}$ is represented in its own eigenfunctions $\{\phi_1, \phi_2, \phi_3, \phi_4, \phi_5\}$ by the matrix

$$\begin{array}{|c|c|c|c|c|}\hline 1 & 0 & 0 & 0 & 0 \\ \hline 0 & 2 & 0 & 0 & 0 \\ \hline 0 & 0 & 3 & 0 & 0 \\ \hline 0 & 0 & 0 & 5 & 0 \\ \hline 0 & 0 & 0 & 0 & 8 \\ \hline\end{array}$$

and that $\boldsymbol{h}$ is represented in the same basis functions by the matrix

$$\alpha\begin{array}{|c|c|c|c|c|}\hline 3 & 0 & 0 & 1 & -1 \\ \hline 0 & 5 & 0 & 0 & 0 \\ \hline 0 & 0 & -1 & 2 & 0 \\ \hline 1 & 0 & 2 & 2 & 0 \\ \hline -1 & 0 & 0 & 0 & 0 \\ \hline\end{array}$$

(where α is a small constant)

Question: Find the energies (correct to 2nd order) and wavefunctions (correct to 1st order) of the system .

2. Using the complete set of eigenfunctions of the particle in a one-dimensional box as a basis, the matrix representation of the position coordinate x is given by:

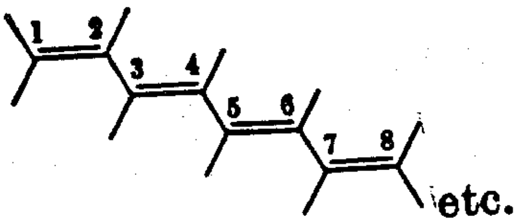
$$-(8a/\pi^2)\left|\begin{matrix}
0 & 2/9 & 0 & 4/225 & 0 & 6/1225 & 0 & \cdots \\
2/9 & 0 & 6/25 & 0 & 10/441 & 0 & 14/2025 & \cdots \\
0 & 6/25 & 0 & 12/49 & 0 & 18/729 & 0 & \cdots \\
4/225 & 0 & 12/49 & 0 & 20/81 & 0 & 28/1089 & \cdots \\
0 & 10/441 & 0 & 20/81 & 0 & 30/121 & 0 & \cdots \\
6/1225 & 0 & 18/729 & 0 & 30/121 & 0 & 42/169 & \cdots \\
0 & 14/2025 & 0 & 28/1089 & 0 & 42/169 & 0 & \cdots \\
8/3969 & 0 & 24/3025 & 0 & 40/1521 & 0 & 56/225 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots &
\end{matrix}\right|$$

(a) Determine the integral that was used to obtain the matrix element

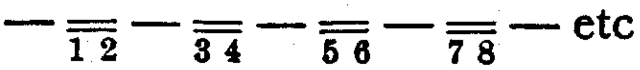
$-(8a/\pi^2)\bullet(2/9)$.

You have to write the integral explicitly, including the limits, but do not actually have to carry out the integration all the way to this numerical answer.

(b) In the so-called "free electron" model for all-trans conjugated polyenes



the polyene structure is approximated by a line (or one dimensional box):



in which the pi electrons are restricted, with the additional constraint that the electrons are <u>non-interacting</u>, except that no more than 2 may occupy the same one-electron state. The pronounced bathochromic shift (i.e., toward longer wavelengths) for an increase in chain length of the polyenes is a general experimental observation which can be predicted by the "free-electron" model.

Question: Apply the "free electron" model to 3 molecules that have 4, 6, and 8 pi electrons respectively and predict the wavelengths of the first (lowest energy) ultra-violet band. You may use an average C-C distance of 1.40 Å and add one extra C-C bond length at each end of the molecule because the electron density extends beyond the nuclei of the end carbons. For example, the butadiene "box" length is 7.00 Å, arising from 5(1.40) from —C=C—C=C—, where the extra distances at the ends are shown as —. Determine the configurations of the pi electrons of each molecule and the energy states of each of the three molecules.

(c) Given: The transitions are governed by the electric dipole mom,ent operator, such that the intensity of the observed band is proportional to the <u>square of the integral</u> :

$$\int\int\int\int\cdots\int \Psi_{\text{initial}}^{*} \textstyle\sum_j x_j \Psi_{\text{final}}\, dx_1 dx_2 \cdots$$

The dimensionless intensity measure, the oscillator stregth for the $i \rightarrow f$ transition is defined by

oscillator strength = $1.085\times10^{22}\ \underbrace{(x_{if})^2}_{cm^{2}}\ \underbrace{\omega_{if}}_{cm^{-1}}$. where $\Delta E_{if} = hc\omega_{if} = hc/\lambda$

λ means wavelength.

Question: In the free electron model for polyenes, which are trhe “allowed” (non-zero intensity) transitions?

Question: Predict the oscillator strengths for the lowest energy transitions in butadiene, hexatriene, octatriene.