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5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1977

Problem Set #1
Due February 14, 1977

1. Carry out the angular momentum algebra indicated in Section 2 (of Steinfeld, Chapter 1); that is, show explicitly that $\langle 11_z|\mathbf{j}_x|11_z\rangle = 0$, and that $\left\langle \mathbf{J}_x^2\right\rangle - \langle \mathbf{J}_x\rangle^2 \neq 0$.

2. (a) Given the matrix elements of the coordinate x for a harmonic oscillator:

$$\langle v|\mathbf{x}|v'\rangle = \int \psi_v^\star x \psi_{v'}\, dx = 0 \text{ unless } v' = v \pm 1$$

and

$$\langle v+1|\mathbf{x}|v\rangle = (2\beta)^{-1/2}(v+1)^{1/2}$$
$$\langle v-1|\mathbf{x}|v\rangle = (2\beta)^{-1/2}(v)^{1/2}$$

where $\beta = 4\pi^2 m\omega/h$, and ω is the vibrational frequency.
Evaluate the non-zero matrix elements of x^2, x^3, and x^4; that is, evaluate the integrals

$$\langle v|\mathbf{x}^r|v'\rangle = \int \psi_v x^r \psi v'\, dx$$

for $r = 2, 3$, and 4 (without actually doing the explicit integrals, of course!).

(b) From the results of (a), evaluate the average values of x, x^2, x^3, and x^4 in the v^{th} vibrational state. Is it true that $\overline{x}^2 = (\overline{x})^2$, or that $x^4 = (x^2)^2$? What conclusions can you draw about the results of a measurement of x in the v^{th} vibrational state?

3. Let

$$\mathbf{H} = \begin{vmatrix} H_{11} & 0 & 0 \\ 0 & d & V \\ 0 & V & -d \end{vmatrix} \qquad \text{in the } \phi_i \text{ basis, and}$$

$$\mathbf{U} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & cos\theta \end{vmatrix}$$

$$\cos\theta = \left[1/2 + \frac{d}{2(d^2+V^2)^{1/2}}\right]^{1/2} \qquad \sin\theta = \left[1/2 - \frac{d}{2(d^2+V^2)^{1/2}}\right]^{1/2}$$

(a) Calculate $\mathbf{U}^\dagger\mathbf{H}\mathbf{U}$.

(b) List the three energy eigenvalues and associated eigenfunctions expressed as the linear combinations of the ϕ_i basis functions.

(c) Show that the eigenfunctions are normalized and mutually orthogonal.

(d) Suppose that $\boldsymbol{\mu}$ is the electric dipole transition moment operator, and that its matrix representation in the ϕ_i basis is

$$\boldsymbol{\mu} = \begin{vmatrix} 0 & \mu_{12} & \mu_{13} \\ \mu_{12} & 0 & 0 \\ \mu_{13} & 0 & 0 \end{vmatrix}.$$

Express $\boldsymbol{\mu}$ in the energy eigenbasis.

(e) What are the transition probabilities between energy eigenstates, expressed in terms of μ_{12}, μ_{13}, V, d, and H_{11}?

(f) There are several interesting limiting cases. Suppose ϕ_2 and ϕ_3 are "unperturbed" states which have equal transition probabilities, $|\mu_{12}|^2 = |\mu_{13}|^2$, from ϕ_1. V is a perturbation term which causes ϕ_2 and ϕ_3 to mix. The U_{23} and U_{32} elements are the mixing coefficients.

(i) Let $|d/V| \gg 1$. The perturbation is turned off. What are the $\psi_1 \rightarrow \psi_2$ and $\psi_1 \rightarrow \psi_3$ transition probabilities?

(ii) Let $|d/V| \ll 1$. The perturbation is on full strength. What are the $\psi_1 \rightarrow \psi_2$ and $\psi_1 \rightarrow \psi_3$ transition probabilities? Note that one transition has accidentally become forbidden, even though the final state is composed of equal parts of two basis functions, each of which have allowed transitions from $\phi_1 = \psi_1$. This is a quantum interference effect that is often observed experimentally.

(iii) Let $d > 0$, $V > 0$, and $\mu_{12} = \mu_{13}$. Which transition is allowed, the one to the upper or lower of the mixed levels?

(iv) Note that if $\mu_{12} = -\mu_{13}$, the opposite transition becomes allowed. What happens when the sign of V is switched? What happens when the sign of d changes? Answer in terms of transitions to *upper* vs. *lower* eigenstates rather than ψ_2 or ψ_3.

(v) Comment on when changing the sign of an off-diagonal matrix element might be expected to have observable consequences.

4. Several methods for computer diagonalization of large matrices are discussed in the handout "Notes on matrix Methods" pages 12–18. Unfortunately there are several typographical errors.

(a) What is the error in Equation 3.10?

(b) The discussion of Method IIB is rather confused. Describe the procedure for construction of a tridiagonal matrix. Which matrix element is annihilated first? How does the rotation differ from that performed in Method IIA? Why is it possible to arrange for annihilation of various elements without spoiling any of the previously zeroed off-diagonal elements? Why is it not possible to reduce the matrix beyond tridiagonal form?

(c) Suppose you have a 5×5 tridiagonal matrix and apply Method IIA to annihilate the M_{34} and M_{43} elements. What happens to the elements outside of the 2×2 $(3, 4)$ block?