5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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Chemistry 5.76
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Problem Set #1

1. Given $[x_k, p_j] = (x_k p_j - p_j x_k) = i\hbar\delta_{jk}$

   and

   $$\vec{L} \equiv \vec{r} \times \vec{p} \equiv \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

   Show that

   (a) $[L_i, L_i] = 0 \qquad i = x, y, z$

   (b) $[L_i, L_j] = i\hbar L_k \qquad (i, j, k) = (x, y, z)$ and cyclic permutations.

2. Consider the Hamiltonian matrix constructed in the $\{\phi\}$ basis.

   $$\mathbf{H} = \begin{pmatrix} -\alpha & \beta & 0 \\ \beta & -\alpha & \beta \\ 0 & \beta & 2\alpha \end{pmatrix} \qquad \boldsymbol{\phi} = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix}$$

   α, β are real numbers.

   (a) Give eigenvalues, their corresponding eigenvectors, and the unitary transformation which brings $\mathbf{H}$ to diagonal form

   $$(\mathbf{U}^{\dagger}\mathbf{H}\mathbf{U})_{ij} = E\delta_{ij}.$$

   (HINT: Use trigonometric form of solution for cubic equation.)

   (b) Can the eigenvalues be evenly spaced for clever choice of α, β?

   (c) Can two of the eigenvalues ever be degenerate for nonzero β?

3. Carry out the angular momentum algebra and show explicitly that $\langle \ell\ell_z|\mathbf{j}_x|\ell\ell_z\rangle = 0$, and that $\left\langle \mathbf{J}_x^2 \right\rangle - \langle \mathbf{J}_x \rangle^2 \neq 0$.

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

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

   and

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

   where $\beta = 4\pi^2 m\omega/h$, and $\omega = \frac{1}{2\pi}[k/\mu]^{1/2}$ is the vibrational harmonic frequency.
   Evaluate the nonzero matrix elements of $\mathbf{x}^2$, $\mathbf{x}^3$, and $\mathbf{x}^4$; 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 part a, evaluate the average values of $\mathbf{x}$, $\mathbf{x}^2$, $\mathbf{x}^3$, and $\mathbf{x}^4$ in the vth vibrational state. Is it true that $\overline{x}^2 = (\overline{x})^2$, or that $\mathbf{x}^4 = (\mathbf{x}^2)^2$? What conclusions can you draw about the results of a measurement of x in the vth vibrational state?