

## 5.73 Problem Set 5

1. Consider a system that evolves under the Hamiltonian

$$\hat{H} = \omega \hat{J}_z.$$

Compute the average values  $\langle \hat{J}_x(t) \rangle$ ,  $\langle \hat{J}_y(t) \rangle$  and  $\langle \hat{J}_z(t) \rangle$  given fixed initial values for each average. What is the vector  $\vec{J} = \langle \hat{J}_x(t) \rangle \vec{i} + \langle \hat{J}_y(t) \rangle \vec{j} + \langle \hat{J}_z(t) \rangle \vec{k}$  doing? What aspects of the evolution are quantum mechanical and what aspects are classical?

2. Consider a particle with the wavefunction:

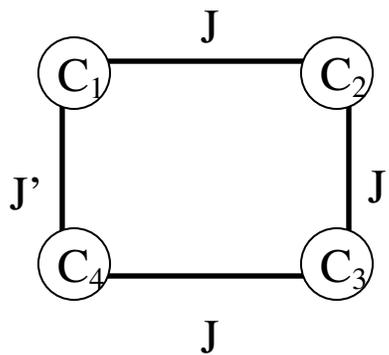
$$\langle r, \theta, \phi | \psi \rangle = N R(r) (1 - \cos^3 \theta) \sin \theta \cos \phi$$

where  $N$  is a normalization constant.

- If one performs a measurement of  $\hat{L}^2$  and  $\hat{L}_z$  for this state, what are the possible outcomes?
  - The dipole moment operator is  $\hat{\mu} = e\hat{r}$ . Does this state possess a dipole moment along the x, y or z directions? You need not compute the values of the x, y or z components; merely determine if they are zero.
  - What about the quadrupole moment  $\hat{M} = e(3\hat{z}^2 - \hat{r}^2)$ ? Is it non-zero?
3. The idea behind Lewis Dot Structures is that bonds are formed when two  $S=1/2$  electrons from different atoms “pair” to form a state with  $S_{\text{tot}}=0$ . First, notice that for an isolated pair of electrons, this is accomplished by an “exchange” Hamiltonian

$$\hat{H} = J \hat{S}_i \cdot \hat{S}_j$$

where  $\hat{S}_i$  and  $\hat{S}_j$  are the spin operators of the two electrons and  $J$  is a constant that determines the strength



of the “bond”.

In this problem, we will consider a Lewis-dot model of the bonding in cyclobutadiene. We are only interested in the 4  $\pi$ -electrons, so we can write

$$\hat{H} = J\hat{S}_1 \cdot \hat{S}_2 + J'\hat{S}_2 \cdot \hat{S}_3 + J\hat{S}_3 \cdot \hat{S}_4 + J'\hat{S}_4 \cdot \hat{S}_1$$

where, as the picture implies,  $J' \geq J$ .

- Compute the eigenfunctions and eigenvalues of this Hamiltonian for  $J = 1$ ,  $J' = 2$ .
- Compute the eigenfunctions and eigenvalues of this Hamiltonian for  $J = J' = 3/2$ .
- Develop a measure for the “strength” of the bond and show that in a) the C<sub>1</sub>-C<sub>2</sub> and C<sub>3</sub>-C<sub>4</sub> bonds are weaker than the other two while in b) the bonds are all equivalent.

4. Consider the low energy reaction of atomic hydrogen with singlet oxygen to yield hydroxyl radical and atomic oxygen:



At low energy, the transition state complex [HO<sub>2</sub>·] has no rotational angular momentum. Given that the H atom is spin-1/2, O<sub>2</sub><sup>\*</sup> is spin-0, OH is spin-1/2, O is spin-1 and total angular momentum is conserved, what are the relative yields of O atoms with  $m_S = +1, 0, -1$ ? That is, will one of the  $m_S$  values be preferred over the others? Would it be possible for the products to be OH( $m_S = +1/2$ ) + O( $m_S = +1$ )? Why or why not?

5. Consider an anharmonic potential of the form

$$V(\hat{q}) = \frac{1}{2}k\hat{q}^2 - \alpha\hat{q}^3 + \beta\hat{q}^4$$

use perturbation theory to compute the eigenvalues of this potential to lowest non-vanishing order in  $\alpha$  and  $\beta$ . [Hint: the cubic and quartic terms will contribute at different orders] Express your result in the standard vibrational form:

$$E(n) = E_0 + \omega_e \left(n + \frac{1}{2}\right) - \omega_e x_e \left(n + \frac{1}{2}\right)^2 + \omega_e y_e \left(n + \frac{1}{2}\right)^3$$

Compare this result to the variational prediction you made in a previous problem set (which assumed the particular values  $\alpha = .045$ ,  $\beta = .00107$ ). Is perturbation theory accurate for this potential?