MIT Department of Chemistry 5.74, Spring 2004: Introductory Quantum Mechanics II Course Instructors: Professor Robert Field and Professor Andrei Tokmakoff

## 5.74, Problem Set #1 Spring 2004 Due Date: February 18, 2003

1. Let the eigenfunctions and eigenvalues of an operator  $\hat{A}$  be  $\varphi_n$  and  $a_n$  respectively:  $\hat{A}\varphi_n = a_n\varphi_n$ . If f(x) is a function that we can expand in powers of x, show that  $\varphi_n$  is an eigenfunction of  $f(\hat{A})$  with eigenvalue  $f(a_n)$ :

$$f(\hat{A})\varphi_n = f(a_n)\varphi_n$$

- 2. For a two-level system with an Hamiltonian  $H = \begin{pmatrix} \varepsilon_a & V_{ab} \\ V_{ba} & \varepsilon_b \end{pmatrix}$ 
  - a) Show that the eigenvalues are  $\varepsilon_{\pm} = E \pm \sqrt{\Delta^2 + |V_{ab}|^2}$

where 
$$\Delta = \frac{\varepsilon_a - \varepsilon_b}{2}$$
 and  $E = \frac{\varepsilon_a + \varepsilon_b}{2}$ 

- b) If we define a transformation  $\tan 2\theta = \frac{|V_{ab}|}{\Delta}$ , find the form of the eigenvectors of the coupled states  $|\varphi_+\rangle$ ,  $|\varphi_-\rangle$ . What is the similarity transformation that takes you from the  $\{|\varphi_+\rangle, |\varphi_-\rangle\}$  to the  $\{|\varphi_a\rangle, |\varphi_b\rangle\}$  basis? Is this operator unitary?
- c) Verify that this basis is normalized and orthogonal.
- 3. Convince yourself that

$$\exp(iG\lambda)A \exp(-iG\lambda) = A + i\lambda[G, A] + \left(\frac{i^2\lambda^2}{2!}\right)[G, [G, A]] + \dots \\ + \left(\frac{i^n\lambda^n}{n!}\right)[G, [G, [G, [G, A]]] \dots] + \dots$$

where G is a Hermetian operator and  $\lambda$  is a real parameter.

4. Just as  $U(t,t_0) = \exp[-iHt/\hbar]$  is the time-evolution operator which displaces  $\psi(\bar{\mathbf{r}},\mathbf{t})$  in time,

$$D(\bar{r},\bar{r}_0) = \exp\left(-i\frac{\bar{p}}{\hbar}\cdot(\bar{r}-\bar{r}_0)\right)$$

is the spatial displacement operator that moves  $\psi$  in space.

a) Defining 
$$D(\overline{\lambda}) = \exp\left(-i\frac{\overline{p}}{\hbar}\cdot\overline{\lambda}\right)$$
, show that the transformation

$$D^{\dagger}rD = r + \lambda$$

where  $\lambda$  is a displacement vector. The relationship in Problem 3 will be useful here.

b) Show that the wavefunction of the state

$$\left|\phi\right\rangle = D\left|\psi\right\rangle$$

is the same as the wavefunction of the state  $|\psi\rangle$ , only shifted a distance  $\lambda$ . Write out  $\phi(x) = \langle x | \phi \rangle$  explicitly if  $|\phi\rangle$  is the ground state of the one-dimensional harmonic oscillator.

## 5. The Hamiltonian for a degenerate two-level system is

$$H_{o} = |a\rangle \epsilon_{0} \langle a| + |b\rangle \epsilon_{0} \langle b|$$

At time t = 0 a perturbation is applied:

$$V(t) = |a\rangle V_{ba}(t) \langle b| + |b\rangle V_{ab}(t) \langle a|$$

where  $V_{ab}(t) = V_{ba}(t)^* = V(1 - \exp(-\gamma t))$ .

- a) Does the Hamiltonian commute at all times?
- b) If the system is initially in prepared in state  $|b\rangle$  (t  $\leq 0$ ), what is the state of the system for t > 0?
- c) What is the probability of finding the system in  $|a\rangle$  for t > 0?
- d) Describe the behavior of this system in the limits  $\gamma \to 0$  and  $\gamma \to \infty$ .

## 6. <u>Time-Development of the Density Matrix</u>

(a) Using the time-dependent Schrödinger equation, show that the timedependence of the density matrix  $\rho = |\psi\rangle\langle\psi|$  is given by the Liouville-Von Neumann equation:

$$\frac{\partial \rho}{\partial t} = \frac{-i}{\hbar} \big[ H, \rho \big]$$

(b) Show that the time dependence of  $\rho$  obtained by directly integrating the Liouville-Von Neumann equation from 0 to t is the same as  $\rho(t) = U\rho(0)U^{\dagger}$ .