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 φ_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 φ_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 $H = \begin{pmatrix} \varepsilon_a & V_{ab} \\ V & \varepsilon_c \end{pmatrix}$ $\begin{pmatrix} a & a \\ V_{ba} & \varepsilon_b \end{pmatrix}$
	- 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

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

$$
+ \left(\frac{i^n \lambda^n}{n!}\right) [G, [G, [G...[G, A]]]...] + ...
$$

where *G* is a Hermetian operator and λ is a real parameter.

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

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

is the spatial displacement operator that moves ψ 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 λ is a displacement vector. The relationship in Problem 3 will be useful here.

b) Show that the wavefunction of the state

$$
\big|\phi\big>=D\big|\psi\big>
$$

is the same as the wavefunction of the state $|\psi\rangle$, only shifted a distance λ . 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 $V_{ab}(t) = V_{ba}(t)^* = V(1 - exp(-γt))$.

- a) Does the Hamiltonian commute at all times?
- b) If the system is initially in prepared in state $|b\rangle$ ($t \le 0$), 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. Time-Development of the Density Matrix

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