Nov. 9, 2009

Chem. 2430

Problem Set 2, Nov. 16, 2009.

1) In class we studied quantum dynamics according to the two-level system (TLS):

$$i\hbar\begin{pmatrix}\dot{c}_1(t)\\ \dot{c}_2(t)\end{pmatrix} = \boldsymbol{H}\begin{pmatrix}c_1(t)\\ c_2(t)\end{pmatrix}\ ;\ \boldsymbol{H} \equiv \begin{bmatrix}E_1 & \Delta\\ \Delta & E_2\end{bmatrix} \qquad [1]$$

a) Show that the substitution $\begin{pmatrix}c_1(t)\\ c_2(t)\end{pmatrix} = \exp\left[-i(E_1+E_2)t/2\hbar\right]\begin{pmatrix}b_1(t)\\ b_2(t)\end{pmatrix}$ converts Eq. [1] into the equivalent form:

$$i\hbar\begin{pmatrix}\dot{b}_1(t)\\ \dot{b}_2(t)\end{pmatrix} = \tilde{\boldsymbol{H}}\begin{pmatrix}b_1(t)\\ b_2(t)\end{pmatrix}\ ;\ \tilde{\boldsymbol{H}} \equiv \begin{bmatrix}\varepsilon & \Delta\\ \Delta & -\varepsilon\end{bmatrix} \qquad [2]$$

with $\varepsilon = (E_1 - E_2)/2$.

b) Starting from Eq. [2], show that for the initial conditions $c_1(0) = 1$, $c_2(0) = 0$, then:

$$|c_1(t)|^2 = |b_1(t)|^2 = 1 - \frac{\Delta^2}{\Delta^2+\varepsilon^2}\sin^2(\sqrt{\varepsilon^2+\Delta^2}\ t/\hbar)$$

2) In class we studied the motion of an optically driven TLS, governed by the matrix Schrödinger Eq.:

$$i\hbar\begin{pmatrix}\dot{c}_1(t)\\ \dot{c}_2(t)\end{pmatrix} = \boldsymbol{H}(t)\begin{pmatrix}c_1(t)\\ c_2(t)\end{pmatrix}\ ;\ \boldsymbol{H}(t) \equiv \begin{bmatrix}E_1 & \mu_0\mathcal{E}_0\cos(\omega_0 t)\\ \mu_0\mathcal{E}_0\cos(\omega_0 t) & E_2\end{bmatrix} \qquad [3]$$

We developed an approximate solution to these equations of motion in the case of large light-source frequency ω_0 and small detuning of the light source from resonance between molecular energy levels E_1, E_2. We called the result of this analysis the Rotating Wave Approximation (RWA). For the case of zero detuning, i.e., $\hbar\omega_0 = E_2 - E_1$, probability shuttles back and forth completely between the two basis states in a sinusoidal fashion. Given initial preparation in state 1, i.e., $c_1(0) = 1$, $c_2(0) = 0$, what is the earliest time that the probability to find the system in state 2 is unity, according to the RWA?

3) The electric dipole moment of a system comprised of a set of point charges is $\vec{\mu} = \sum_{\alpha} q_{\alpha} \vec{r}_{\alpha}$, where q_{α} , $\vec{r}_{\alpha}$ are the charge and position of charge α . If we specialize to a single charge moving in one dimension (say, the x-direction), then $\mu = qx$.

Consider a one dimensional harmonic oscillator with charge q and mass m moving in the potential energy well $V(x) = \frac{1}{2}\kappa x^2$, where $\kappa > 0$ is the constant characterizing the restoring force. Calculate the dipole operator matrix elements:

a) $\int_{-\infty}^{\infty} dx \phi_0(x) \hat{\mu} \phi_0(x)$

b) $\int_{-\infty}^{\infty} dx \phi_0(x) \hat{\mu} \phi_1(x)$,

where $\phi_n(x)$ is the standard unit-normalized harmonic oscillator energy eigenfunction corresponding to energy eigenvalue $E_n = \hbar \sqrt{\frac{\kappa}{m}} (n + 1/2)$.