

CH651 Final Assignment, Sunday, December 15, 2013. Due Friday
December 20, 2013

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Q1 Consider the time evolution of a spin state of an electron in a magnetic field. Let the unperturbed hamiltonian be the Zeeman hamiltonian (with static field B_0 taken in the z direction): $H_0 = \gamma B_0 \hat{S}_z$, where γ is the gyromagnetic ratio and \hat{S}_z is the usual spin operator. Let the coupling hamiltonian be a time varying Zeeman interaction in the x direction, $V = \gamma B_1 \hat{S}_x \cos \omega t$, where B_1 is the strength of the perturbing magnetic field and ω is it's frequency.

(i) If the electron is initially in spin state α at $t = 0$, what is the probability of ending up in state β as a function of time t ? Take $\omega = \gamma B_0$, and use first order perturbation theory.

(ii) How does the answer to part (i) change when second order perturbation theory is used?

(iii) Now lets solve the time-dependent Schrödinger equation exactly for the same problem. To do this, first write down the coupled equations for the coefficients C_α and C_β associated with the states α and β , respectively. Now take the same limit $\omega = \gamma B_0$ in these equations. Carefully consider the time dependence of each term and neglect all terms that vary as $\exp[\pm 2i\omega t]$ in the resulting differential equations. Show that the solutions are the same as those obtained from perturbation theory (taking $\omega = \gamma B_0$) in the limit of small B_1 .

Q2 (a) Solve Heisenberg's equations of motion

$$\frac{d\hat{A}_H}{dt} = \frac{i}{\hbar} [\hat{H}_H, A_H] \quad (1)$$

for the time evolution of the raising and lowering operators $\hat{A}_H = \hat{b}_H^+$ and $\hat{A}_H = \hat{b}_H$ for a harmonic oscillator where we can write the hamiltonian as:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2 = \frac{\hbar\omega}{2}(\hat{P}^2 + \hat{Q}^2) = \hbar\omega(\hat{b}^+\hat{b} + \frac{1}{2}) \quad (2)$$

so $A_H(t) = e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar}$ and the Schrödinger operators for the transformed momentum and coordinates of the oscillator are $\hat{P} = \hat{p}/(\hbar m)^{1/2}$ and $\hat{Q} = x(m\omega/\hbar)^{1/2}$, so $\hat{b} = (\hat{Q} + i\hat{P})/\sqrt{2}$, $\hat{b}^+ = (\hat{Q} - i\hat{P})/\sqrt{2}$, and $[\hat{b}, \hat{b}^+] = 1$

(b) Show that $\hat{Q}_H(t) = Q \cos \omega t + \hat{P} \sin \omega t$.

- Q3** Consider a system of two spin-1/2 particles so that the zero order hamiltonian just contains the kinetic energy due to their spin angular momentum so $\hat{H}_0 = \hat{S}_1^2 + \hat{S}_2^2$. Suppose that in the absence of a magnetic field the two spins interact weakly (small λ) according to a spin vector dot product coupling term $V = \lambda \mathbf{S}_1 \cdot \mathbf{S}_2$ so the total hamiltonian is $H = H_0 + V$. Suppose the coupled system starts out in $|s_1, m_1, s_2, m_2\rangle = |\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\rangle$ at $t = 0$. Use first order time dependent perturbation to compute the probability that the system is in state $|s_1, m_1, s_2, m_2\rangle = |\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle$ at time t . (Hint: compute the vector dot product using angular momentum raising and lowering operators.)
- Q4** Consider an electron moving in the x-direction and suppose it is harmonically bound to a molecule so its hamiltonian has the form

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega_0^2\hat{x}^2 \quad (3)$$

The eigenstates, $|n\rangle$, of \hat{H}_0 are thus generated by the raising and lowering operators and satisfy $\hat{b}^+|n\rangle = \sqrt{n+1}|n+1\rangle$ and $\hat{b}|n\rangle = \sqrt{n}|n-1\rangle$ where

$$\begin{aligned} \hat{b} &= \left(\frac{m\omega_0}{2\hbar}\right)^{1/2} \left(\hat{x} + \frac{i}{m\omega_0}\hat{p}\right) \\ \hat{b}^+ &= \left(\frac{m\omega_0}{2\hbar}\right)^{1/2} \left(\hat{x} - \frac{i}{m\omega_0}\hat{p}\right) \end{aligned}$$

- (i) Use the Kramers-Heisenberg expression for the polarizability matrix elements

$$(\alpha_{km})_{ij} = \frac{1}{\hbar} \sum_n \left[\frac{\langle k|\hat{\mu}_i|n\rangle\langle m|\hat{\mu}_j|n\rangle}{(\omega + \omega_{nm})} - \frac{\langle n|\hat{\mu}_i|m\rangle\langle k|\hat{\mu}_j|n\rangle}{(\omega - \omega_{nk})} \right] \quad (4)$$

and the fact that $\hat{\mu}_x = -e\hat{x}$ to show that the ground state polarizability in the x-direction is

$$(\alpha_{11})_{xx} = \frac{(e^2/m)}{(\omega_0^2 - \omega^2)} \quad (5)$$

- (ii) Compute the first excited state polarizability $(\alpha_{00})_{xx}$
 (iii) Compute the off diagonal polarizability $(\alpha_{01})_{xx}$
 (iv) Compute the off diagonal polarizability $(\alpha_{02})_{xx}$
- Q5** Consider the situation of two harmonic Born-Oppenheimer potential surfaces describing the vibrational motion of a diatomic molecule with bond length R . One surface describes nuclear motion in the lower electronic state $|\phi_m\rangle$ and the other in a higher excited electronic state $|\phi_k\rangle$. Suppose that the vibrational frequency of each harmonic surface is the same, ω_0 , but that the higher excited state potential surface is shifted by an amount, Δ , relative to the lower electronic state potential so that the normalized ground vibrational states on the different electronic surfaces have the following forms:

$$\begin{aligned} \chi_{\nu_m=0}^m &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha R^2/2} \\ \chi_{\nu_k=0}^k &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(R-\Delta)^2/2} \end{aligned}$$

Here $\alpha = (\hbar/m\omega_0)^{1/2}$.

(i) Compute the relative intensity of the electronic transition between these ground vibrational states $\nu_m = 0 \rightarrow \nu_k = 0$ as a function of the shift Δ between the two potentials.

(ii) The relative intensities of the transitions between vibrational states on two different electronic potential surfaces are given by the Franck-Condon factors $|S(\nu_m, \nu_k)|^2$ where

$$S(\nu_m, \nu_k) = \int_{-\infty}^{+\infty} \chi_{\nu_m}^{m*}(R) \chi_{\nu_k}^k(R) dR \quad (6)$$

Show that the Franck-Condon factors for the transitions from any initial vibrational state ν_m sum over all final vibrational states to give unity *i.e.*

$$\sum_{\nu_k} |S(\nu_m, \nu_k)|^2 = 1 \quad (7)$$

Q6 Consider an N electron hamiltonian, \hat{H} . Using the identity

$$[[\hat{x}_i, \hat{H}], \hat{x}_i] = 2\hat{x}_i \hat{H} \hat{x}_i - \hat{H} \hat{x}_i^2 - \hat{x}_i^2 \hat{H} \quad (8)$$

where \hat{x}_i is the operator representing the x coordinate of electron i , and assuming that the potential is independent of momentum,

(i) prove that

$$\frac{2m_e}{\hbar^2} \sum_k (E_k - E_s) |\langle k | \hat{x}_i | s \rangle|^2 = 1 \quad (9)$$

where $|k\rangle$ and E_k are the eigenfunctions and eigenvalues of the many electron hamiltonian *i.e.* $\hat{H}|k\rangle = E_k|k\rangle$. Similar expressions hold for the \hat{y}_i and \hat{z}_i coordinate operators of each electron. If the total electronic dipole moment vector operator is $\vec{\mu} = -e \sum_{i=1}^N \vec{r}_i$ then the square length of the electronic transition dipole moment, which in class we showed was proportional to the intensity of the transition between states $|k\rangle$ and $|s\rangle$, is

$$|\vec{\mu}_{ks}|^2 = e^2 \sum_{i=1}^N (|\langle k | \hat{x}_i | s \rangle|^2 + |\langle k | \hat{y}_i | s \rangle|^2 + |\langle k | \hat{z}_i | s \rangle|^2) \quad (10)$$

(ii) Use your above result together with the definition of the oscillator strength of the transition between these states

$$f_{ks} = \frac{2m_e \omega}{3\hbar e^2} |\vec{\mu}_{ks}|^2 \quad (11)$$

to prove the Thomas-Reiche-Kuhn sum rule

$$\sum_k f_{ks} = N \quad (12)$$

(iii) Note that this result is independent of initial state s . What does this imply when interpreting the intensities in the spectrum of a many electron system.