HOMEWORK ASSIGNMENT 6
QUANTUM MECHANICS
DUE APR 1, 2008

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1a. *Time-dependent perturbation theory refresher. If $a_0 = 1$ at $t = 0$, then for a weak perturbation, $\hat{H}^{(1)}(t)$, the first order perturbed wavefunction is*

$$|\Psi_0^{(1)}\rangle = \sum_{j>0} a_j(t)|\Psi_j^{(0)}\rangle \exp(-iE_j^{(0)}t/\hbar). \qquad (*)$$

Show that the expansion coefficients can be written as

$$a_j(t) \approx \frac{1}{i\hbar}\int_0^t dt'\,\langle\Psi_j^{(0)}|\hat{H}^{(1)}(t)|\Psi_0^{(0)}\rangle \exp(i\omega_{j0}t'). \qquad (**)$$

Solution. The time derivative of $(*)$ is, thanks to the product rule,

$$\frac{\partial\Psi_0^{(1)}}{\partial t} = \sum_j \Big(\dot{a}_j(t) - \frac{i}{\hbar}a_j E_j^{(0)}\Big)\Psi_j^{(0)} \exp(-iE_j^{(0)}t/\hbar).$$

Substituting into the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi_0^{(1)}}{\partial t} = (H^{(0)} + H^{(1)}(t))\Psi_0^{(1)},$$

we obtain (dropping the superscript 0 from $E_j^{(0)}$ and making $\hbar = 1$)

$$\sum_j \big(i\dot{a}_j(t) + a_jE_j\big)\Psi_j^{(0)}\exp(-iE_jt) = \sum a_j\big(E_j\Psi_j^{(0)}\exp(-iE_jt) + H^{(1)}(\Psi_j^{(0)}\exp(-iE_jt))\big),$$

or, after cancellation,

$$\sum_j i\dot{a}_j\Psi_j^{(0)}\exp(-iE_jt) = \sum a_jH^{(1)}(\Psi_j^{(0)}\exp(-iE_jt)).$$

Projection onto $\Psi_m^{(0)}$ gives

$$i\sum_j \dot{a}_j\langle\Psi_m^{(0)}|\Psi_j^{(0)}\rangle \exp(-iE_jt) = \sum_j a_j\langle\Psi_m^{(0)}|H^{(1)}|\Psi_j^{(0)}\rangle \exp(-iE_jt),$$

where we have assumed that $H^{(1)}$ commutes with multiplication by $\exp(-iE_jt)$ (this is the usual case — and always holds when $H^{(1)}$ is a potential). Using orthonormality we then get

$$i\dot{a}_m\exp(-iE_mt) = \sum_j a_j\langle\Psi_m^{(0)}|H^{(1)}|\Psi_j^{(0)}\rangle \exp(-iE_jt), \quad \text{or}$$

$$\dot{a}_m = -i\sum_j a_j\langle\Psi_m^{(0)}|H^{(1)}|\Psi_j^{(0)}\rangle \exp(-i(E_j - E_m)t).$$

Now approximate this system of ordinary differential equations by the *uncoupled* system

$$\dot{a}_m = -i\langle\Psi_m^{(0)}|H^{(1)}|\Psi_0^{(0)}\rangle \exp(-i(E_0 - E_m)t),$$

using the fact that $a_j \approx a_j(0) = \delta_{j0}$ if t is small. Integrating each of these approximate equations gives precisely the expression $(**)$ if we replace m by j, set $(E_j - E_0) = \omega_{j0}$ and restore $\hbar$.

1b. *Find the explicit form for these expansion coefficients when the perturbation is*

$$\hat{H}^{(1)}(t) = \tfrac{1}{2}\boldsymbol{E}\cdot\boldsymbol{\mu}(e^{i\omega t} + e^{-i\omega t}).$$

Solution. Introduce the dipole moment matrix element $\boldsymbol{\mu}_{j0} = \langle\Psi_j^{(0)}|\boldsymbol{\mu}|\Psi_0^{(0)}\rangle$. From part (a),

$$\begin{aligned} a_j(t) &\approx \tfrac{1}{2}\boldsymbol{E}\cdot\boldsymbol{\mu}_{j0}\left(\frac{1}{i\hbar}\int_0^t dt'\big(\exp(i\omega t') + \exp(-i\omega t')\big)\exp(i\omega_{j0}t')\right) \\ &= \frac{1}{2\hbar}\boldsymbol{E}\cdot\boldsymbol{\mu}_{j0}\left(\frac{1-\exp(i(\omega_{j0}+\omega)t)}{\omega_{j0}+\omega} + \frac{1-\exp(i(\omega_{j0}-\omega)t)}{\omega_{j0}-\omega}\right) \\ &= \frac{1}{\hbar}\boldsymbol{E}\cdot\boldsymbol{\mu}_{j0}\left(\frac{\omega_{j0}\big(1-\exp(i\omega_{j0}t)\cos(\omega t)\big) + i\omega\exp(i\omega_{j0}t)\sin(\omega t)}{\omega_{j0}^2-\omega^2}\right). \end{aligned}$$

2. (Schatz and Ratner, problem 5.5) *Consider that an electron is harmonically bound to a molecule. This means that the electronic hamiltonian is*

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2x^2$$

where x is the electronic coordinate and ω_0 is the frequency of oscillation. The electronic wavefunctions in this case are simplya harmonic oscillator states, and the energy levels are $E_n = \hbar\omega_0(n+\frac{1}{2})$. Show that the Rayleigh polarizability for this system is

$$\alpha = \frac{e^2/m}{\omega_0^2-\omega^2}.$$

Solution. We start from formula (5.125) of Schatz and Ratner, which gives the polarizability for a system in a stationary state in terms of the energy spectrum and the dipole coupling involving this state and all others. Adjusting the notation to avoid confusion with the mass m, and realizing that the problem is one-dimensional, so the outer product $\boldsymbol{\mu}_{mn}\boldsymbol{\mu}_{nm}$ in (5.125) reduces to the product of two complex conjugate scalars, we have for the polarizability in state k the value

$$\alpha_{kk} = \frac{1}{\hbar}\sum_n |\mu_{kn}|^2\frac{2\omega_{nk}}{\omega_{nk}^2-\omega^2}, \qquad (\dagger)$$

where $\mu_{kn} = \langle k|\mu|n\rangle$, with $\mu = -ex$. To find μ_{kn} we use the explicit form of the wavefunction,

$$\psi_n = A_ne^{-u^2/2}H_n(u), \quad \text{with } u = x\sqrt{\frac{m\omega_0}{\hbar}} \text{ and } A_n = \frac{1}{\sqrt{2^nn!}}\sqrt[4]{\frac{m\omega_0}{\pi\hbar}}.$$

We know from the dipole selection rules that the integral $\int_{-\infty}^{\infty}\psi_k u\psi_n\,du$ (for $k \le n$) vanishes unless $n = k+1$. Mathematica gives

$$\int_{-\infty}^{\infty} e^{-u^2/2}H_k(u)\cdot u\cdot e^{-u^2/2}H_{k+1}(u)\,du = 2^k\sqrt{\pi}\,(k+1)!,$$

so

$$\mu_{k,k+1} = -eA_nA_{n+1}2^k\sqrt{\pi}\,(k+1)!\,\frac{\hbar}{m\omega_0},$$

where the last factor comes from the scaling $u \mapsto x$. Simplification leads to

$$\mu_{k,k+1} = -e\sqrt{\frac{\hbar(k+1)}{2m\omega_0}} = \mu_{k+1,k}.$$

From this, ($\dagger$) and the equalities $\omega_{k,k-1} = -\omega_{k,k+1} = \omega_0$ we obtain

$$\alpha_{kk} = \frac{1}{\hbar}|\mu_{k,k+1}|^2\frac{2\omega_0}{\omega_0^2-\omega^2} + \frac{1}{\hbar}|\mu_{k,k-1}|^2\frac{-2\omega_0}{\omega_0^2-\omega^2} = \left(e^2\frac{k+1}{2m\omega_0} - e^2\frac{k}{2m\omega_0}\right)\frac{2\omega_0}{\omega_0^2-\omega^2} = \frac{e^2/m}{\omega_0^2-\omega^2}.$$

In particular, the polarizability does not depend on the state k.

3a. (Schatz and Ratner, problem 5.4) *When high-intensity radiation interacts with matter, the induced dipole* μ^{ind} *is related to the field* E_ω *by*

$$\mu^{\text{ind}} = \alpha E_\omega + \beta E_\omega^2 + \gamma E_\omega^3 + \cdots$$

which includes terms that depend nonlinearly on E_ω*. The first nonlinear term is proportional to the hyperpolarizability* β*. Allowing the induced dipole moment from this term to interact iwth another radiation field* $E_{\omega'}$ *leads to the interaction*

$$V_{\text{int}} = -E_{\omega'} \cdot \beta \cdot E_\omega^2.$$

Using the semiclassical theory of radiation and the long-wavelength approximation, find the term in V_{int} *that causes Stokes-hyper-Raman scattering (i.e., absorption of two* ω *photons, emission of one* ω' *photon with* $\omega' < 2\omega$*).*

Solution. We rewrite the expression of V_{int} as

$$V_{\text{int}} = -\beta(\boldsymbol{E}_{\omega'}, \boldsymbol{E}_\omega, \boldsymbol{E}_\omega) \tag{‡}$$

to emphasize that β is a trilinear form (rank-three tensor). Let the two fields be

$$\boldsymbol{E}_\omega = \frac{A_0\omega}{c}\boldsymbol{\varepsilon}\cos\omega t \quad \text{and} \quad \boldsymbol{E}_{\omega'} = \frac{A_0'\omega'}{c}\boldsymbol{\varepsilon}'\cos\omega' t.$$

Substituting in (‡) we get

$$\begin{aligned} V_{\text{int}} &= -\Big(\frac{\omega A_0}{c}\Big)^2 \frac{A_0'\omega'}{c}\beta(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon}, \boldsymbol{\varepsilon})(\tfrac{1}{2})^3(e^{i\omega t} + e^{-i\omega t})^2(e^{i\omega' t} + e^{-i\omega' t}) \\ &= -U\big(e^{2i\omega t} + 2 + e^{-2i\omega t}\big)\big(e^{i\omega' t} + e^{-i\omega' t}\big) \\ &= -U\big(e^{i(2\omega+\omega')t} + 2e^{\omega' t} + e^{i(-2\omega+\omega')t} + e^{i(2\omega-\omega')t} + 2e^{-\omega' t} + e^{i(-2\omega-\omega')t}\big), \end{aligned}$$

where we have set

$$U = \frac{1}{8}\Big(\frac{\omega A_0}{c}\Big)^2 \frac{A_0'\omega'}{c}\beta(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon}, \boldsymbol{\varepsilon}).$$

The term responsible for Stokes-hyper-Raman scattering is the one involving $e^{i(-2\omega+\omega')t}$, if $\omega' < 2\omega$.

3b. *What other transitions does* V_{int} *cause?*

- absorption of an ω' photon and emission of two ω photons;
- absorption of an ω' photon and absorption of two ω photons;
- emisssion of an ω' photon and emission of two ω photons;
- absorption or emisssion of a single ω' photon (with absortion-emission of an ω photon).

In each case, one should regard the order in which photons are absorbed or emitted as indeterminate.