

5.74, Problem Set #3
 Spring 2004
 Due Date: March 10, 2004

1. Confirm that the classical interaction Hamiltonian $H = \frac{1}{2m} [\bar{\mathbf{p}} - q\bar{\mathbf{A}}(\bar{\mathbf{r}}, t)]^2$ is consistent with the Lorentz equation for the force on a charged particle $\mathbf{F} = q(\bar{\mathbf{E}} + \bar{\mathbf{v}} \times \bar{\mathbf{B}})$. To do this, first find the force on a particle in the x direction $F_x = m\ddot{x}$ with the help of $\dot{p}_x = -\partial H/\partial x$ and $\dot{x} = -\partial H/\partial p_x$. Then show that this is the same result you get directly from the Lorentz equation. (This problem is taken from McHale, but Appendix III in CTDL is probably the most useful reference).

2. Magnetic Dipole and Electric Quadrupole Transitions

In the interaction Hamiltonian

$$V(t) = -\sum_i \frac{q_i}{m_i} \bar{\mathbf{A}} \cdot \bar{\mathbf{p}}_i$$

$$\bar{\mathbf{A}} = A_0 \hat{\mathbf{e}} \exp[-i(\bar{\mathbf{k}} \cdot \bar{\mathbf{r}} - \omega t)] + c.c.$$

the second term in the expansion

$$e^{i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}} = 1 + i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}} + \dots$$

leads to magnetic dipole and electric quadrupole transitions. We can use the identity

$$(\boldsymbol{\varepsilon} \cdot \bar{\mathbf{p}})(\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}) = \hat{\boldsymbol{\varepsilon}} \cdot (\bar{\mathbf{p}}\bar{\mathbf{r}}) \cdot \bar{\mathbf{k}}$$

$$= \frac{1}{2} \hat{\boldsymbol{\varepsilon}} (\bar{\mathbf{p}}\bar{\mathbf{r}} - \bar{\mathbf{r}}\bar{\mathbf{p}}) \bar{\mathbf{k}} + \frac{1}{2} \hat{\boldsymbol{\varepsilon}} (\bar{\mathbf{p}}\bar{\mathbf{r}} + \bar{\mathbf{r}}\bar{\mathbf{p}}) \bar{\mathbf{k}}$$

to separate $V(t)$ into two terms where the first leads to the magnetic dipole transitions, and the second leads to electric quadrupole transitions.

(continued)

- a) From the first term, express the magnetic dipole interaction in terms of the magnetic field \vec{B} and the orbital angular momentum \vec{L} . What is the form of the magnetic dipole moment?

$$\text{A useful vector identity is } (\mathbf{A} \times \mathbf{B}) \cdot (\mathbf{C} \times \mathbf{D}) = (\mathbf{A} \cdot \mathbf{C})(\mathbf{B} \cdot \mathbf{D}) - (\mathbf{A} \cdot \mathbf{D})(\mathbf{B} \cdot \mathbf{C})$$

- b) From the second term, derive the matrix elements for electric quadrupole transitions in analogy to the electric dipole moment, and show that it is a tensor quantity.

3. Using Fermi's Golden Rule for the rate of transfer from an initial state $|\ell\rangle$ to a continuum of states $|k\rangle$ under a constant perturbation V , show that the rate $\bar{w}_{k\ell}$ can be written in a interaction picture representation as a correlation function in the time-dependent perturbation

$$\bar{w}_{k\ell} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \langle V_I(t) V_I(0) \rangle dt$$

$$\text{Note: } \delta(\omega) = (1/2\pi) \int_{-\infty}^{+\infty} \exp(i\omega t) dt .$$

4. Numerical calculation of correlation function from a trajectory

On the 5.74 site you will find an ASCII file that contains a trajectory of instantaneous transition frequencies $\omega_i(t)$ for a molecule in a fluctuating environment. The file is a set of 3000 consecutive frequencies in cm^{-1} for points separated by 30 femtoseconds. We will calculate the correlation function using the time-averaging expression for a single molecule valid for an ergodic system.

- (a) Write the integral version of $\delta\omega(t) \delta\omega(0)$ as an explicit summation over all pairs of points for a finite discrete data set.
- (b) Calculate and plot the correlation function for the frequency fluctuations $C_{\delta\omega\delta\omega}(t)$ using this expression. What is ω_0 ? What is the correlation time τ_c for these fluctuations?