Problem 1: The diagonal matrix elements of the electric dipole

Classically, the electric dipole moment associated with a pair of charges $\pm q$ is given by $\mu = qz$ where z is their separation. For an electron, we have $q = -e$. The quantum matrix representation is given by

$$\mu_{mn} = -e\langle\psi_m|z|\psi_n\rangle \tag{1}$$

The matrix element is obtained by integrating over all space (over z in this case):

$$\langle\psi_m|z|\psi_n\rangle = \int_{-\infty}^{\infty} \psi_m^* z \psi_n dz \tag{2}$$

If ψ_n has a **definite parity**, i.e. it is either even or odd under $z \to -z$, then we know that $\psi_m z \psi_n$ must be **odd** under the transformation if $m = n$. After all, an even/odd function multiplied by its complex conjugate is always even. This implies that

$$\mu_{nn} = 0 \tag{3}$$

Problem 2: Interaction of light with a two level "atomic" system

The Hamiltonian to consider is the quantum analogue of the potential energy of an electric dipole inside an electric field. This Hamiltonian acts as a perturbation to the existing Hamiltonian of the system without any interaction, which we denote by $H^{(0)}$. The perturbing Hamiltonian is

$$H^{(1)} = -\mu\mathscr{E} \tag{4}$$

where we have taken the electric field $\mathscr{E}$ to be the electric component in the same direction as the dipole moment. We are considering an electron, which has a spin of $1/2$ meaning that μ takes the form of a 2×2 matrix. As in Problem 1, we have zero diagonal elements. Furthermore we can choose the relative phase of the wavefunctions such that

$$\mu_{12} = \mu_{21} \equiv \mu_d \tag{5}$$

is real. This gives us

$$H^{(1)} = -\mathscr{E}\mu_d \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{6}$$

The unperturbed Hamiltonian is just a diagonal matrix with the energy eigenvalues of the system. The total Hamiltonian is thus given by

$$H = H^{(0)} + H^{(1)} = \begin{pmatrix} E_1 & -\mathscr{E}\mu_d \\ -\mathscr{E}\mu_d & E_2 \end{pmatrix} \tag{7}$$

We are interested in the expectation value of the electric dipole moment, which is given by

$$\overline{\langle\mu\rangle} = \mathrm{Tr}\{\rho\mu\} \tag{8}$$

Let us write

$$\rho = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \tag{9}$$

so that

$$\rho\mu = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} 0 & \mu_d \\ \mu_d & 0 \end{pmatrix} = \mu_d \begin{pmatrix} b & a \\ d & c \end{pmatrix} \tag{10}$$

and

$$\overline{\langle\mu\rangle} = \mu_d(b + c) \tag{11}$$

Next we are interested in the time evolution of the density matrix, which allows us to know the time evolution of the dipole moment. The time evolution is given by the equation of motion

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{i}{\hbar}\left[\rho, H\right] = \frac{i}{\hbar}\begin{pmatrix} -\mathscr{E}\mu_d(b-c) & -\mathscr{E}\mu_d(a-d)+(E_2-E_1)b \\ -\mathscr{E}\mu_d(d-a)+(E_1-E_2)c & -\mathscr{E}\mu_d(c-b) \end{pmatrix} \tag{12}$$

Two equations we can get from this equation are

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -i\omega_c c + \frac{i\mu_d\mathscr{E}}{\hbar}(a-d) \tag{13}$$

with $\hbar\omega_c \equiv E_2 - E_1$, which is the equation governing c (and by the hermicity of the density matrix, also b), and

$$\frac{\mathrm{d}}{\mathrm{d}t}(a-d) = \frac{2i\mu_d\mathscr{E}}{\hbar}(c-c^*) \tag{14}$$

where we have written $b \equiv c^*$, which tells us the evolution of the population diffence in both states.

This equation is equivalent to the Schrödinger equation, and we gain nothing new from it in this idealized system. The interesting part is when we consider a nonideal interactions. The **master equation** form allows us to add extra dynamics in a simpler manner, as we shall see here.

The population difference may take some value at a given time, but in the steady state we expect it to return (or **relax**) to the thermal equilibrium value we shall denote by $(a-d)_0$. Phenomenologically, this relaxation happens exponentially. The time constant is usually denoted by T_1. The equation of motion is simply modified by writing

$$\frac{\mathrm{d}}{\mathrm{d}t}(a-d) = \frac{2i\mu_d\mathscr{E}}{\hbar}(c-c^*) - \frac{(a-d)-(a-d)_0}{T_1} \tag{15}$$

The off-diagonal elements of the density matrix has a phase factor of the form $\exp\left[-i(E_u-E_v)t/\hbar\right]$ corresponding to $\left|\psi_u\right\rangle$ and $\left|\psi_v\right\rangle$. As time evolves, it is possible for the system to evolve into some state in which we have a different phase factor, say $\exp\left[-i(E_i-E_j)t/\hbar\right]$. This means that at any given time we may have an ensemble of different possibilities of different phases. The ensemble average will then average out to zero. Thus, me cna say that the off-diagonal elements of the density matrix tends towards zero. It may start at some value, but then time evolution will **relax** the value back to zero. Again, Phenomenologically this happens exponentially with a time constant denoted by T_2. This lets us write

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -i\omega_c c + \frac{i\mu_d\mathscr{E}}{\hbar}(a-d) - \frac{c}{T_2} \tag{16}$$