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Dipole Spectroscopy

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References

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Field free matter and a matter free field

Let $\hat{H}_{matter}$ denote the Hamiltonian of the electrons in the *absence* of a coupling to the electromagnetic field. If

$$\hat{H}_{matter}\psi_i = E_i\psi_i, \qquad i = 0, 1, \ldots,$$

then we will focus on the $\psi_1 \rightarrow \psi_0$ transtion. In this transition the electromagnetic field absorbs the energy $E_1 - E_0$.

Different molecular systems will have different $\hat{H}_{matter}$'s, but there is only one electromagnetic field. If the field is located in an $L \times L \times L$ box, it can be represented as a Fourier series,

$$\mathcal{E}(\boldsymbol{r}, t) = \sum_{\boldsymbol{\ell}}^{*} \sum_{\alpha} \left[\mathcal{E}_{s\boldsymbol{\ell}\,\alpha}(t) \sin(\boldsymbol{\ell} \cdot \boldsymbol{r}) + \mathcal{E}_{c\boldsymbol{\ell}\,\alpha}(t) \cos(\boldsymbol{\ell} \cdot \boldsymbol{r}) \right] \tag{1}$$

wherein $\sum_{\boldsymbol{\ell}}^{*}$ represents a sum over the wavevectors $\boldsymbol{\ell}$ with * signifying that only one of the pair $(\boldsymbol{\ell}, -\boldsymbol{\ell})$ is present in the sum. (These two terms are physically indistinguishable, so we just count them once.) $\sum_{\alpha}$ represents a sum over different *polarizations* of the field, different orientations of $\mathcal{E}_{\boldsymbol{\ell}\,\alpha}$. The values of $\boldsymbol{\ell}$ in the sum are of the form

$$\boldsymbol{\ell} = \frac{2\pi}{L}(k\boldsymbol{i} + m\boldsymbol{j} + n\boldsymbol{k}), \qquad k,\ m,\ n = 0, \pm 1, \pm 2, \pm 3, \ldots$$

We say that $\mathcal{E}(t)$ is a sum of various *modes*, the individual terms in (1).

In any region where there are no free charges,

$$\nabla \cdot \mathcal{E}(\boldsymbol{r}, t) = 0. \tag{2}$$

This requires that

$$\boldsymbol{\ell} \cdot \mathcal{E}_{s\boldsymbol{\ell}\,\alpha}(t) = 0 \quad \text{and} \quad \boldsymbol{\ell} \cdot \mathcal{E}_{c\boldsymbol{\ell}\,\alpha}(t) = 0.$$

Thus there are only two possible polarizations associated with each wavevector $\boldsymbol{\ell}$: $\mathcal{E}_{s\boldsymbol{\ell}\,\alpha}$ and $\mathcal{E}_{c\boldsymbol{\ell}\,\alpha}$ must lie in the plane perpendicular to $\boldsymbol{\ell}$. The field is made up of *transverse* waves.

The dynamical equation for the field $\mathcal{E}(\boldsymbol{r}, t)$ is the wave equation,

$$\nabla^2 \mathcal{E} = \frac{1}{c^2} \frac{\partial^2 \mathcal{E}}{\partial t^2}, \tag{3}$$

with c the speed of light. Equation (3) implies that

$$\ddot{\mathcal{E}}_{\boldsymbol{\ell}\,\alpha}(t) + \omega_{\boldsymbol{\ell}}^2\, \mathcal{E}_{\boldsymbol{\ell}\,\alpha}(t) = 0, \qquad \omega_{\boldsymbol{\ell}} = |\boldsymbol{\ell}\,|\, c = \ell c.$$

The field modes are simple harmonic oscillators. That is, they are *normal modes*.

To emphasize that the Fourier amplitudes of the field may be taken as the *coordinates* of the field, we will rewrite (1) as

$$\mathcal{E}(\boldsymbol{r}, t) = \sqrt{\frac{2M}{\epsilon_0 V}} \sum_{\boldsymbol{\ell}}^{*} \sum_{\alpha=1,2} \omega_{\boldsymbol{\ell}} \left[q_{s\boldsymbol{\ell}\,\alpha}(t) \sin(\boldsymbol{\ell} \cdot \boldsymbol{r}) + q_{c\boldsymbol{\ell}\,\alpha}(t) \cos(\boldsymbol{\ell} \cdot \boldsymbol{r}) \right] \boldsymbol{e}_{\boldsymbol{\ell}\,\alpha}$$

with the $\boldsymbol{e}_{\boldsymbol{\ell}\,\alpha}$ unit vectors $\left(\boldsymbol{e}_{\boldsymbol{\ell}\,\alpha} \cdot \boldsymbol{e}_{\boldsymbol{\ell}\,\beta} = \delta_{\alpha\beta}\right)$ in the plane perpendicular to $\boldsymbol{\ell}$. ϵ_0 is an electrical constant associated with the SI system of units and M is a quantity with the dimensions of mass which we introduce to give the coordinate $q_{\boldsymbol{\ell}\,\alpha}$ the dimensions of length. Since the associated magnetic field must satisfy Faraday's Law,

$$\nabla \times \mathcal{E} + \frac{\partial \mathcal{B}}{\partial t} = 0,$$

the magnetic field will be

$$\mathcal{B}(\boldsymbol{r}, t) = \sqrt{\frac{2M}{\epsilon_0 V}} \sum_{\boldsymbol{\ell}}^{*} \sum_{\alpha} \frac{1}{\omega_{\boldsymbol{\ell}}} \left[\dot{q}_{s\boldsymbol{\ell}\,\alpha}(t) \cos(\boldsymbol{\ell} \cdot \boldsymbol{r}) - \dot{q}_{c\boldsymbol{\ell}\,\alpha}(t) \sin(\boldsymbol{\ell} \cdot \boldsymbol{r}) \right] \boldsymbol{\ell} \times \boldsymbol{e}_{\boldsymbol{\ell}\,\alpha}.$$

The work required to create the electromagnetic field is

$$\begin{aligned} E =& \frac{1}{2}\epsilon_0 \int dr \left[\mathcal{E}(r,t)^2 + c^2 \mathcal{B}(r,t)^2\right] \\ =& \sum_{\ell}^{*} \sum_{\alpha=1,2} \frac{1}{2} M \left\{ \dot{q}_{s\ell\,\alpha}(t)^2 + \dot{q}_{c\ell\,\alpha}(t)^2 + \omega_\ell^2 \left[q_{s\ell\,\alpha}(t)^2 + q_{c\ell\,\alpha}(t)^2 \right] \right\}. \end{aligned}$$

Introducing the canonically conjugate momenta variables $p_{\ell\,\alpha} = M\,\dot{q}_{\ell\,\alpha}$, we can produce this quantum mechanical description of the electromagnetic field:

$$\hat{H}_{field} = \frac{1}{2M} \sum_{\ell}^{*} \sum_{\alpha=1,2} \left[\hat{p}_{s\ell\,\alpha}^2 + \hat{p}_{c\ell\,\alpha}^2 + \omega_\ell^2\, M^2\, \hat{q}_{s\ell\,\alpha}^2 + \omega_\ell^2\, M^2\, \hat{q}_{c\ell\,\alpha}^2 \right] \tag{4}$$

generates the time evolution of the system and

$$\hat{\mathcal{E}} = \sqrt{\frac{2M}{\epsilon_0 V}} \sum_{\ell}^{*} \sum_{\alpha} \omega_\ell \left[\hat{q}_{s\ell\,\alpha} \sin(\ell \cdot r) + \hat{q}_{c\ell\,\alpha} \cos(\ell \cdot r) \right] e_{\ell\,\alpha} \tag{5}$$

and

$$\hat{\mathcal{B}} = \sqrt{\frac{2}{\epsilon_0 M V}} \sum_{\ell}^{*} \sum_{\alpha} \frac{1}{\omega_\ell} \left[\hat{p}_{s\ell\,\alpha} \cos(\ell \cdot r) - \hat{p}_{c\ell\,\alpha} \sin(\ell \cdot r) \right] \ell \times e_{\ell\,\alpha} \tag{6}$$

are the observables.

The Hamiltonian (4) is separable into a collection of independent simple harmonic oscillators, so the eigenvalues and eigenvectors can easily be constructed. The vacuum state Φ_0 is the state in which all the oscillators are in their ground state. Let $\Phi_{k\beta}$ represent the state in which the $k\beta$ normal mode is in its first excited state while all the other modes are unexcited. This is a state with a single *photon* (momentum $\hbar k$, polarization β) present.

Spectroscopy

To describe the complete system it is necessary to describe both the matter and the field. For the uncoupled system with Hamiltonian

$$\hat{H} = \hat{H}_{matter} + \hat{H}_{field}, \tag{7}$$

the energy eigenstates can be constructed as products of matter eigenstates and field eigenstates. The transition of interest is

$$\Psi_0 = \psi_1 \Phi_0 \;\rightarrow\; \Psi_{k\beta} = \psi_0 \Phi_{k\beta}.$$

The matter goes from the excited state to the ground state and a photon $k\beta$ appears in the electromagnetic field.

In fact Ψ_0 and $\Psi_{k\beta}$ aren't energy eigenstates because (7) ignores the coupling which is present between the field and the matter. In the case of *dipolar* coupling,

$$\hat{H} = \hat{H}_{matter} + \hat{H}_{field} + \hat{V} \tag{8}$$

with

$$\hat{V} = -\hat{\boldsymbol{d}} \cdot \hat{\mathcal{E}}. \tag{9}$$

Here $\hat{\boldsymbol{d}}$ represents the dipole moment operator of the matter and $\hat{\mathcal{E}}$ represents the electric field operator.

The problem now looks exactly like the abstract problem considered in Problem Set 8. There is a unique initial state (no photons) and many possible final states (photons with energy $\approx \hbar\omega$). If $\left\langle \Psi_{k\beta} \middle| \hat{V}\Psi_0 \right\rangle$ is a typical coupling matrix element and $\rho(E)$ is the density of possible final states, then we can write down the rate for the transition immediately as

$$\mathcal{R} = \frac{2\pi}{\hbar} \left| \left\langle \Psi_{k\beta} \middle| \hat{V}\Psi_0 \right\rangle \right|^2 \rho(E).$$

Radiation from an harmonic oscillator

For a system with one harmonically bound electron, the origin may be chosen so that $\boldsymbol{d} = -e\,\boldsymbol{r}$. If the oscillator is located at $\boldsymbol{r} = 0$,

$$\begin{aligned} \hat{V} &= -e\,\hat{\boldsymbol{r}} \cdot \hat{\mathcal{E}}(0) \\ &= -e\sqrt{\frac{2M}{\epsilon_0 V}} \sum_{\boldsymbol{\ell}}{}^{*} \sum_{\alpha} \omega_{\boldsymbol{\ell}}\, \hat{\boldsymbol{r}} \cdot \boldsymbol{e}_{\boldsymbol{\ell}\,\alpha} \hat{q}_{c\boldsymbol{\ell}\,\alpha}, \end{aligned}$$

so

$$\left\langle \Psi_{k\beta} \middle| \hat{V}\Psi_0 \right\rangle = -e\sqrt{\frac{2M}{\epsilon_0 V}} \sum_{\boldsymbol{\ell}}{}^{*} \sum_{\alpha} \omega_{\boldsymbol{\ell}} \left\langle \psi_0 \middle| \hat{\boldsymbol{r}} \cdot \boldsymbol{e}_{\boldsymbol{\ell}\,\alpha} \psi_1 \right\rangle \left\langle \Psi_{k\beta} \middle| \hat{q}_{c\boldsymbol{\ell}\,\alpha} \Psi_0 \right\rangle .$$

(1) *The matrix elements*

If the electron is an isotropic harmonic oscillator, the energy eigenfunction problem can be separated in Cartesian coordinates. Suppose that the initial electronic state is $\phi_0^{SHO}(x)\,\phi_0^{SHO}(y)\,\phi_1^{SHO}(z)$. Then

$$\langle \phi_0 \,|\hat{r}\phi_1\rangle = \hat{\boldsymbol{k}} \left\langle \phi_0^{SHO} \middle| z\,\phi_1^{SHO} \right\rangle = \sqrt{\frac{\hbar}{2m\omega}}\hat{\boldsymbol{k}}, \tag{11}$$

with $\hat{\boldsymbol{k}}$ a unit vector along the z-axis (*not* a wavevector). Since $\left\langle \phi_0^{SHO} | z\,\phi_n^{SHO} \right\rangle = 0$ for all $n \neq 1$, only one transition is actually possible. The fact that the SHO can only lose one quantum of energy in a dipole-coupling induced transition is called a *selection rule*.

$$\left\langle \Phi_{k\beta} \middle| \hat{V}\Psi_0 \right\rangle = -e\sqrt{\frac{M\hbar}{m\epsilon_0\omega V}} \sum_{\boldsymbol{\ell}}^{*} \sum_{\alpha} \omega_{\boldsymbol{\ell}}\, \hat{\boldsymbol{k}} \cdot \boldsymbol{e}_{\boldsymbol{\ell}\,\alpha} \left\langle \Phi_{k\beta} \middle| \hat{q}_{c\boldsymbol{\ell}\,\alpha}\Phi_0 \right\rangle .$$

The matrix elements for the field are of the same form as those in (11). Thus

$$\left\langle \Phi_{k\beta} \middle| \hat{q}_{c\boldsymbol{\ell}\,\alpha}\Phi_0 \right\rangle = \delta_{k\boldsymbol{\ell}}\,\delta_{\beta\alpha}\sqrt{\frac{\hbar}{2M\omega_{\boldsymbol{\ell}}}}.$$

Thus there is another selection rule: The only allowed transition in the field is the creation of a single photon. Energy conservation requires that this photon have $k\,c = \omega$. Combining the matter and field results gives

$$\left\langle \Psi_{k\beta} \middle| \hat{V}\Psi_0 \right\rangle = -\frac{e\hbar}{\sqrt{2m\epsilon_0 V}}\hat{\boldsymbol{k}} \cdot \boldsymbol{e}_{k\beta}$$

whence

$$\mathcal{R} = \frac{2\pi}{\hbar}\frac{e^2\hbar^2}{2m\epsilon_0 V}\left(\hat{\boldsymbol{k}} \cdot \boldsymbol{e}_{k\beta}\right)^2 \rho(E).$$

(2) *The density of states*

Since $\mathcal{R}$ is the decay rate for the matter, all possible photon states are to be used in calculating $\rho(E)$. If $\boldsymbol{e}_{k2}$ is $\perp$ to $\hat{\boldsymbol{k}}$, then only the polarization $\boldsymbol{e}_{k1}$ is possible for the created photon. If $\boldsymbol{k}$ makes an angle θ with the z-axis, $\hat{\boldsymbol{k}} \cdot \boldsymbol{e}_{k1} = \sin\theta$ and averaging over all photon orientations gives

$$\overline{(\hat{\boldsymbol{k}} \cdot \boldsymbol{e}_{k1})^2} = \overline{\sin^2\theta} = \frac{2}{3}.$$

The number of wavevectors associated with photons of energy $\leq E$ is

$$\int_0^E \rho(E')\,dE' = \sum_{|k|\leq E/\hbar c} 1 = \sum_{\sqrt{n_x^2+n_y^2+n_z^2}\leq EL/2\pi\hbar c} = \frac{4\pi}{3}\frac{E^3L^3}{(2\pi\hbar c)^3}.$$

Differentiating this expression gives

$$\rho(E) = \frac{4\pi E^2 L^3}{(2\pi\hbar c)^3} = \frac{\omega^2 V}{2\pi^2\hbar c^3}.$$

(3) *The rate of spontaneous emission*

With this orientational averaging and this evaluation of the density of states, the rate becomes

$$\mathcal{R} = \frac{2\pi}{\hbar}\frac{e^2\hbar^2}{2m\epsilon_0 V}\frac{2}{3}\frac{\omega^2 V}{2\pi^2\hbar c^3} = \frac{e^2\omega^2}{3\pi m\epsilon_0 c^3}.$$

To simplify this expression it is useful to introduce the *dimensionless* constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = 0.00729720\ldots = \frac{1}{137.0388\ldots},$$

the *fine structure* constant. Using α to eliminate ϵ_0 gives

$$\mathcal{R} = \frac{2\alpha}{3}\frac{\hbar\omega^2}{mc^2}.$$

(4) *Other electronic transitions*

If the electron starts in state ψ_n, the rate of transition into the state ψ_f will be

$$\mathcal{R} = \frac{4\alpha\omega^3}{3c^2}\left|z_{fn}\right|^2.$$

This rate is only non-zero when $f = n-1$ when

$$z_{n-1,n} = \sqrt{\frac{n\hbar}{2m\omega}}.$$

Thus

$$\mathcal{R}_{n\to n-1} = \frac{2\alpha}{3}\frac{\hbar\omega^2}{mc^2}n. \tag{12}$$

The emission rate is proportional to the excitation energy.

Induced transitions

In deducing (12) we assumed that the *field* started in its ground state. If, however, all the states into which the photon was emitted were initially occupied by n_f photons, the radiation rate will be *increased*. Since

$$\sqrt{\frac{\hbar}{2M\omega_\ell}} \to \sqrt{\frac{\hbar(n_f+1)}{2M\omega_\ell}},$$
$$\mathcal{R} = \frac{2\alpha}{3}\frac{\hbar\omega^2}{mc^2} \to \frac{2\alpha}{3}\frac{\hbar\omega^2}{mc^2}(n_f+1).$$

The $n_f = 0$ rate is the *spontaneous* emission rate while the rate $\propto n_f$ is the *induced* emission rate. When we look at the reverse process the matrix elements are proportional to $\sqrt{n_f}$. There is no spontaneous absorption but there is an induced absorption out of the field.

In practice, of course, induced absorption and radiation are not produced by a field in which all the modes of the electromagnetic field are excited. Only modes with energy $\approx \hbar\omega$ need be excited and the geometry of practical experiments usually limits the inducing photons to having $\boldsymbol{k}$ values aligned along a beam and polarizations can also be limited.

Problem Set #9

1. For the 3D harmonic oscillator, show that the matrix element $\left\langle \phi_0^{SHO} | z\, \phi_1^{SHO} \right\rangle$ can be written as the ground state expectation of some operator, i.e., that

$$\left\langle \phi_0^{SHO} | z\, \phi_1^{SHO} \right\rangle = \left\langle \phi_0^{SHO} | \hat{Q} \phi_0^{SHO} \right\rangle .$$

   Give a physical interpretation for $\hat{Q}$.

2. The decay rate out of the first excited state for a simple harmonic oscillator is just dependent upon the classical frequency of oscillation = the frequency of the emitted radiation. Make a plot of $\log_{10}$ (the lifetime of the state) as a function of $\log_{10}$ (the emission frequency).

3. Let $\psi_{n\ell m}(r, \theta, \phi)$ be the n^{th} state, $n = 1, 2, \ldots$ with total angular momentum $\ell\hbar$, counting up in energy with $n = 1$ being the lowest energy for the electron in a spherical box. If the dipole moment is

$$\boldsymbol{d} = -e\boldsymbol{r},$$

   the dipole spectroscopy is determined by the matrix element $\langle \psi_{n'\ell'm'} | \boldsymbol{r} \psi_{n\ell m} \rangle$. Show that this matrix element is a product of three one-dimensional integrals. Show that there is a *selection rule*

$$m \to m' = m, m \pm 1.$$

   Use the recurrence relation for Associated Legendre polynomials (see *Abramowitz and Stegun*, §8.5) to show that there is a selection rule on $\ell \to \ell'$ also. Superimpose arrows upon the level diagram made for Problem 7.2 which show what the allowed transitions would be.