10. Second quantization: molecule-radiation interaction

Now that the full molecular (sections 7 through 9), field (2b), and interaction (2b) Hamiltonian operators are in hand, they can be combined to yield the overall molecule-radiation Hamiltonian. A quantum treatment of the radiation field results in particles (photons) which can be destroyed or createdby molecular absorption and emission.

The level of theory where matter particles are treated by a particle quantum Hamiltonian, and field particles are treated by a quantized field Hamiltonian from section 2 is referred to as "second quantization." We will consider this in detail here. The next higher level of theory also treats the matter particles with a field Hamiltonian, allowing them to be created or annihilated (e.g. electron-positron collision), and is referred to as "quantum electrodynamics."

10.1 The full quantized Hamiltonian

Adding up the field and charge-field energies from section 2b to obtain the total Hamiltonian yields

$$\begin{aligned} H_{tot} &= \sum_n \frac{\mathbf{p_n^2}}{2m_n} + V(\mathbf{r}) + \sum_{\mathbf{k},\lambda} \hbar\omega a^*_{\mathbf{k},\lambda}\, a_{\mathbf{k},\lambda} - \sum_n \frac{q}{2m_n c}(\mathbf{p_n}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p_n}) + \sum_n \frac{q_n^2}{2m_n c^2}\mathbf{A^2} \\ &= H_{\text{mol}} \qquad\qquad + H_{\text{field}} \qquad\qquad + H_{\text{interaction}} \end{aligned} \tag{10-1}$$

The quantum version of H_{mol} was derived in sections 7 through 9, and H_{field} is just a harmonic oscillator Hamiltonian. The only problem for quantization is the potential non-commutation of $\hat{p}_n$ and $\hat{A}$. However,

$$\hat{\mathbf{p}}\cdot\hat{\mathbf{A}}\Psi = \frac{\hbar}{i}\nabla\cdot(\mathbf{A}\Psi) = \frac{\hbar}{i}\{(\nabla\cdot\mathbf{A})\Psi + \mathbf{A}\cdot\nabla\Psi\} = \hat{\mathbf{A}}\cdot\hat{\mathbf{p}}\Psi \tag{10-2}$$

if we use the Coulomb gauge $\nabla\cdot\mathbf{A} = 0$. The first interaction term in eq. 10-1 simply becomes

$$H^{(1)}_{\text{int}} = \sum_n \tfrac{q}{mc}\mathbf{p}\cdot\mathbf{A} = \sum_{n,k,\lambda} \tfrac{q}{mc}\{\tfrac{hc}{Vk}\}^{1/2}\mathbf{p}\cdot\hat{\mathrm{e}}_{\mathbf{k},\lambda}\{a^+_{\mathbf{k},\lambda}e^{i\mathbf{k}\cdot\mathbf{r}} + a_{\mathbf{k},\lambda}e^{-i\mathbf{k}\cdot\mathbf{r}}\} \tag{10-3}$$

if **A** is expanded in plane waves as in eq. 2-72. Quantizing the full Hamiltonian in the Schrödinger representation,

$$\begin{aligned} \hat{H} = &\sum_n \frac{\hat{\mathbf{p}}_\mathbf{n}^2}{2m_n} + V(\mathbf{r}_n) + \sum_{\mathbf{k},\lambda}\hbar\omega(\hat{a}^+_{\mathbf{k},\lambda}\hat{a}_{\mathbf{k},\lambda} + \tfrac{1}{2}) \\ &- \sum_{n,\mathbf{k},\lambda}\frac{q_n}{m_n c}\{\frac{hc}{Vk}\}^{1/2}\hat{\mathbf{p}}_\mathbf{n}\cdot\hat{e}_{\mathbf{k},\lambda}\{\hat{a}_{\mathbf{k},\lambda}e^{i\mathbf{k}\cdot\mathbf{r_n}} + \hat{a}^+_{\mathbf{k},\lambda}e^{-i\mathbf{k}\cdot\mathbf{r_n}}\} \\ &+ \sum_{n,\mathbf{k},\mathbf{k}',\lambda}\frac{q_n^2}{m_n c^2}\{\frac{hc}{Vk}\}\{\hat{a}_{\mathbf{k}\lambda}\hat{a}^+_{\mathbf{k}'\lambda}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r_n}} + \hat{a}^+_{\mathbf{k}\lambda}\hat{a}_{\mathbf{k}'\lambda}e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r_n}} + \hat{a}_{\mathbf{k}\lambda}\hat{a}_{\mathbf{k}'\lambda}e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r_n}} + \hat{a}^+_{\mathbf{k}\lambda}\hat{a}^+_{\mathbf{k}'\lambda}e^{-i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r_n}}\} \end{aligned} \tag{10-4}$$

where the first line includes the uncoupled molecule and field, the second line includes the first order interaction Hamiltonian (linear in **A**, where **A** has been replaced by the expression derived in terms of plane waves in section 2b), and the third line includes the second order interaction operator (quadratic in **A**). As in section 2b, V is the volume of the box containing the radiation field and molecule, and λ=1,2 are two polarizations perpendicular to **k**.

In this picture, the radiation field appears like a collection of harmonic oscillators coupled to the molecule via $H^{(1)}$ and $H^{(2)}$:

$$H_{field} = \sum_{\mathbf{k},\lambda} \hbar\omega_{\mathbf{k}} (\hat{N}_{\mathbf{k},\lambda} + 1/2) \qquad 10\text{-}5$$

Each of the infinitely many combinations of wavevector **k** and polarization λ corresponds to one harmonic oscillator-like field mode, which can be populated with $N_{\mathbf{k},\lambda}$ field quanta. These field quanta are referred to as photons.

We need to find an appropriate field basis set for the uncoupled case, and the most reasonable choice is just a product of harmonic oscillator functions, which is an eigenfunction of the field Hamiltonian.

$$H_{field}|N_{\mathbf{k}\lambda}>|N_{\mathbf{k}'\lambda'}>\cdots = H_{field}|\cdots N_{\mathbf{k}\lambda}\cdots> = \left(\sum_{\mathbf{k},\lambda} \hbar\omega(N_{\mathbf{k}\lambda} + \tfrac{1}{2})\right)|\cdots N_{\mathbf{k}\lambda}\cdots> \qquad 10\text{-}6$$

The operators $a^{+}_{\mathbf{k}\lambda}$ and $a_{\mathbf{k}\lambda}$ have the usual effect on the field eigenstates:

$$\begin{aligned} a^{+}_{\mathbf{k}\lambda}|\cdots N_{\mathbf{k}\lambda}\cdots> &= \sqrt{N_{\mathbf{k}\lambda}+1}\ \ |\cdots N_{\mathbf{k}\lambda}+1\cdots> \\ a_{\mathbf{k}\lambda}|\cdots N_{\mathbf{k}\lambda}\cdots> &= \sqrt{N_{\mathbf{k}\lambda}}\ \ |\cdots N_{\mathbf{k}\lambda}-1\cdots> \qquad 10\text{-}7 \\ [a_{k\lambda}, a^{+}_{k'\lambda'}] &= \delta_{\mathbf{kk}',\lambda\lambda'} \end{aligned}$$

For the molecular degrees of freedom, we just pick the molecular eigenfunctions $|\mathbf{r}_n>=|\varphi_{mol}>$ with energy E_n. In the uncoupled case, the total wavefunction is then just a product wavefunction

$$\Psi_{tot} = |\varphi_{mol}(\mathbf{r}_n)>|\cdots N_{k\lambda}\cdots> \qquad 10\text{-}8$$

When the molecule and field are interacting, the real wavefunction will of course be a superposition of several such states with different E_n and $N_{\mathbf{k}\lambda}$ values, until the interaction is over. The overall energy of molecule and field must however always be conserved.

10.2 Transition moments for absorption, stimulated emission, and spontaneous emission

We now use the Hamiltonian in eq. 10-4 and the basis in eq. 10-8 to calculate transition matrix elements, the squares of which yield spectral intensities. First, we review three approximations which we will make here:

i) Dipole approximation:

The molecular dimension $|\mathbf{r_n}| << \lambda$ for small molecules. In that case the exponentials in eq. 10-4 can be approximated as $|\mathbf{k}\cdot\mathbf{r}| << 1 \Rightarrow e^{i\mathbf{k}\cdot\mathbf{r}_n} \approx 1$. This is tantamount to saying that all parts of the molecule experience the same phase of the incoming electromagnetic radiation. It will be seen that this yields the well-known dipole interaction $\boldsymbol{\mu}\cdot\mathbf{E}$. For electric quadrupole or magnetic dipole interactions, which are rarely dominant in molecules (and will therefore not be considered here), one has to let at least $e^{i\mathbf{k}\cdot\mathbf{r}_n} \approx 1 + i\mathbf{k}\cdot\mathbf{r}_n$. For X-rays scattering, or optical scattering on macromolecules of size comparable to the wavelength, one has to use the full scattering phase $e^{i\mathbf{k}\cdot\mathbf{r}}$, discussed in more detail in section 12.

ii) Neglecting $H^{(2)}$

$H^{(2)}$ yields 2-proton processes in lowest order, e.g. aa results in 2-photon absorption, $aa^{\dagger}$ in scattering or Raman processes. $H^{(2)}$ is not needed to describe 1-photon processes such as absorption or spontaneous emission. We will later derive a Raman scattering formula from $H^{(1)}$,

but it should be kept in mind that this formula must be corrected by adding the contribution from $H^{(2)}$ in order to yield quantitative results.

iii) Golden Rule

For a system decaying from a single level to a dense manifold of states, the decay rate is given to first order by Fermi's Golden Rule

$$\Gamma = \frac{2\pi}{\hbar}\rho_{tot}|< \Psi_f|H^{(1)}|\Psi_i >|^2;\ \rho_{tot} \approx \rho_{field} \qquad 10\text{-}9$$

as derived from first-order time-dependent perturbation theory. Moreover, except for very small cavities, the density of field modes is much higher than the density of molecular modes, and we can approximate ρ_{tot} by just the density of field states. The Golden Rule is of course not exact at long times. A treatment without the Golden rule has been given by S. Bergmann, J. Math. Phys. **8**, 159 (1967) based on the Wigner-Weisskopf method. However, application of the Golden Rule causes one to miss only esoteric phenomena at very long fluorescence lifetimes.

Taking the expectation value of the second line of eq. 10-4 with the wavefunction in eq. 10-8 yields

$$< \Psi_f | H^{(1)} | \Psi_i >=$$
$$-\sum_{n,k,\lambda} \frac{q_n}{m_n c}\{\frac{hc}{Vk}\}^{1/2} < \varphi_f | \mathbf{p_n} | \varphi_i > \cdot \hat{e}_{\mathbf{k}\lambda}\{< N'_{\mathbf{k}\lambda} | \hat{a}_{\mathbf{k}\lambda} | N_{\mathbf{k}\lambda} > + < N'_{\mathbf{k}\lambda} | a^+_{\mathbf{k}\lambda} | N_{\mathbf{k}\lambda} >\} \qquad 10\text{-}10$$

which is the probability of making a transition between two molecular eigenstates by changing the number of photons in a single field mode (whose energy must equal the molecular energy difference in order to assure energy conservation). This is the kind of transition probability of interest if a high-resolution laser is scanned across a molecular transition. We can bring this into a somewhat more standard form by using the identity

$$[\mathbf{r_n}, H_{mol}] = [\mathbf{r_n}, \frac{\mathbf{p_n^2}}{2m_n}] = \frac{i\hbar}{m_n}\hat{\mathbf{p}}_\mathbf{n}. \qquad 10\text{-}11$$

Replacing **p** in eq. 10-10 by the commutator 10-11

$$-\sum_n \frac{q_n}{m_n c} < \varphi_f | \mathbf{p_n} | \varphi_i >= -\sum_n \frac{q_n}{m_n c}\frac{m_n}{i\hbar}(< \varphi_f | \mathbf{r}_n H_{mol} | \varphi_i > - < \varphi_f | H_{mol}\mathbf{r_n} | \varphi_i >)$$
$$= \frac{-i}{\hbar c} < \varphi_f | \boldsymbol{\mu}_{\mathrm{mol}} | \varphi_i > (E_f - E_i) \qquad 10\text{-}12$$

since

$$\sum_n q_n \mathbf{r_n} = \boldsymbol{\mu}_\mathbf{mol}. \qquad 10\text{-}13$$

Inserting eq. 10-12 into eq.10-10,

$$< \Psi_f | H^{(1)} | \Psi_i >= -\sum_{\mathbf{k},\lambda} \frac{i\omega_{fi}}{c}\{\frac{hc}{Vk}\}^{1/2} < \varphi_f | \boldsymbol{\mu}_\mathbf{mol} | \varphi_i > \cdot \hat{e}_{\mathbf{k}\lambda}(< N' | a_{\mathbf{k}\lambda} | N > + < N' | a^+_{\mathbf{k}\lambda} | N >). \qquad 10\text{-}14$$

In this expression, ω_{fi} is the energy difference between the final and initial molecular states (eq. 10-12) expressed in frequency units. So $\omega_{\mathrm{mol}} = \omega_{\mathrm{fi}}$ can always be taken as positive, a (-) sign is introduced in the $a^\dagger$ term instead of letting $\omega_{em} = -\omega_{abs}$.

We previously determined the classical field operator, $E_{\mathbf{k}\lambda}$ in terms of vector potentials a and a^* (section 2b), and can now write it in terms of the quantized raising and lowering operators a and a^+. From eq. 2-72 follows

$$\begin{aligned}\hat{E} &= \frac{i\omega_{fi}}{c}\{\frac{hc}{Vk}\}^{1/2} a_{\mathbf{k}\lambda}\hat{e}_{\mathbf{k}\lambda} + \frac{i\omega_{fi}}{c}\{\frac{hc}{Vk}\}^{1/2} a^{+}_{\mathbf{k}\lambda}\hat{e}_{\mathbf{k}\lambda} \\ &= \hat{E}_{\mathbf{k}\lambda} + \hat{E}^{+}_{\mathbf{k}\lambda} \\ &= \frac{i\omega_{abs}}{c}\{\frac{hc}{Vk}\}^{1/2} a_{\mathbf{k}\lambda}\hat{e}_{\mathbf{k}\lambda} - \frac{i\omega_{em}}{c}\{\frac{hc}{Vk}\}^{1/2} a^{+}_{\mathbf{k}\lambda}\hat{e}_{\mathbf{k}\lambda}\end{aligned} \qquad 10\text{-}15$$

Clearly the field operator is analogous to the ordinary harmonic oscillator momentum operator $i(a^{\dagger} - a)$. The operator $a_{\mathbf{k}\lambda}$ allows for absorption of a photon at frequency $\omega_{abs} = \omega_{field} = kc$ of a given polarization, $a^{+}_{\mathbf{k}\lambda}$ allows for emission. Inserting eq. 10-15 into 10-14, we obtain the final formula for the matrix element

$$< \Psi_f | H^{(1)} | \Psi_i > = -\sum_{\mathbf{k},\lambda} < \varphi_f | \boldsymbol{\mu}_{\mathbf{mol}} | \varphi_i > \cdot < N'_{\mathbf{k}\lambda} | \hat{E} | N_{\mathbf{k}\lambda} > \qquad 10\text{-}16$$

which is directly analogous to the classical expression from section 8 for the interaction energy,

$$= -\sum_{\mathbf{k},\lambda} \boldsymbol{\mu}_{fi} \cdot \mathbf{E}_{\mathbf{k}\lambda} \,. \qquad 10\text{-}17$$

10.3 Molecular emission into an isotropic radiation field

In this example application of eq. 10-14, we will use the Golden Rule, assuming the field density dominates:

$$\Gamma_{f \leftarrow i} = \frac{2\pi}{\hbar}\rho_{final} | < \Psi_f | H^{(1)} | \Psi_i > |^2 \qquad 10\text{-}18$$

The molecular density of states makes a negligible contribution to ρ_{final}, which is due almost solely to photon states in the box. $\rho_{final} \to \infty$ as the volume of the box increases, but this should be exactly canceled by the $V^{-1/2}$ dependence of $H^{(1)}$ in eq. 10-14. To compute ρ_{field}, let us assume the field fills a cubic box with sides of length L (the final result should of course be independent of the shape and size of the box for large boxes). In that case k_i (i=x,y,z) takes on a discrete set of values

$$k_i = \frac{n_i \pi}{L}, \qquad n_i = 1,2,\cdots \qquad 10\text{-}19$$

According to fig. 10-1, the number of field states in an interval dk in solid angle dΩ is

$$dN = \frac{k^2 dk d\Omega}{(\frac{\pi}{L})^3} = \frac{V}{\pi^3} k^2 dk d\Omega \qquad 10\text{-}20$$

To obtain the density of modes in a given solid angle dΩ, we integrate eq. 10-20 over k while enforcing overall energy conservation by requiring that $\hbar\omega = E_f - E_i = \hbar ck$. This is strictly valid

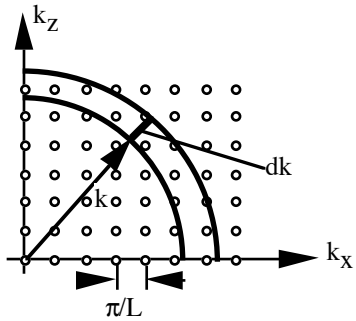

Fig. 10-1. Two-dimensional cut through the lattice of k-vectors; the incremental number of states dN is the number of lattice points in the shell dk at k.

only if the excited state has an infinite lifetime (and hence an infinitely sharp transition), but is a good approximation if the linewidth is sufficiently narrow so that the density of states does not vary much over the linewidth:

$$\begin{aligned}\frac{d\rho}{d\Omega} &= \int k^2\,dk\,\frac{V}{\pi^3}\delta(E-\hbar ck) \\ &= \frac{k^2 V}{\pi^3\hbar c}\ \text{(states per srad per unit E)}\end{aligned} \quad . \qquad 10\text{-}21$$

The second ingredient in eq. 10-18 is the coupling matrix element $\langle f|H^{(1)}|i\rangle$:

$$\langle f|H^{(1)}|i\rangle = \boldsymbol{\mu}_{fi}\cdot\hat{e}_{\mathbf{k}\lambda}\{N_{\mathbf{k}\lambda}+1\}^{1/2}\left(\frac{i\omega_{fi}}{c}\right)\left\{\frac{2\pi\hbar c}{Vk}\right\}^{1/2}\ \text{for one specific } \mathbf{k},\lambda\,. \qquad 10\text{-}22$$

The rate of emission into an angle $d\Omega$ at resonance is thus:

$$\Gamma_{f\leftarrow i} = \frac{2\pi}{\hbar}\frac{k^2V}{\pi^3\hbar c}(N_{\mathbf{k},\lambda}+1)\frac{\omega^2}{c^2}\frac{2\pi\hbar c}{Vk}d\Omega|\boldsymbol{\mu}_{fi}\cdot\hat{e}_{\mathbf{k}\lambda}|^2 = \frac{4\omega^3(N_{\mathbf{k},\lambda}+1)}{\hbar\pi c^3}|\boldsymbol{\mu}_{fi}\cdot\hat{e}_{\mathbf{k}\lambda}|^2\,d\Omega \qquad 10\text{-}23$$

To obtain the isotropic emission rate, we sum over both polarizations and integrate over all angles $d\Omega$:

$$\begin{aligned}\Gamma_{tot} &= \sum_{\lambda=1,2}\int\int d\Omega\frac{4\omega^3(N_{\mathbf{k},\lambda}+1)}{\hbar\pi c^3}|\boldsymbol{\mu}_{fi}\cdot\hat{e}_{\mathbf{k}\lambda}|^2 \\ &= \frac{4\omega^3(N_{\mathbf{k},\lambda}+1)}{\hbar\pi c^3}\int_0^{\pi/2}\int_0^{\pi/2}\sin\theta d\theta d\varphi\sum_\lambda(\boldsymbol{\mu}_{fi}\cdot\hat{e}_{\mathbf{k}\lambda})(\hat{e}_{\mathbf{k}\lambda}\cdot\boldsymbol{\mu}_{fi}^\dagger) \\ &= \frac{4\omega^3(N_{\mathbf{k},\lambda}+1)}{\hbar\pi c^3}\int\int\sin\theta d\theta d\varphi\boldsymbol{\mu}_{fi}(\sum_\lambda\cdot\hat{e}_{\mathbf{k}\lambda}\hat{e}_{\mathbf{k}\lambda}\cdot)\boldsymbol{\mu}_{fi}^\dagger \\ &= \frac{4\omega^3(N_{\mathbf{k},\lambda}+1)}{\hbar\pi c^3}\int\int\sin\theta d\theta d\varphi\boldsymbol{\mu}_{fi}(I-\cdot\hat{k}\hat{k}\cdot)\,\boldsymbol{\mu}_{fi}^\dagger \qquad 10\text{-}24 \\ &= \frac{4\omega^3(N_{\mathbf{k},\lambda}+1)}{\hbar\pi c^3}\int\int\sin\theta d\theta d\varphi\{|\boldsymbol{\mu}_{fi}|^2-(\boldsymbol{\mu}_{fi}\cdot\hat{k})^2\} \\ &= \frac{4\omega^3(N_{\mathbf{k},\lambda}+1)}{\hbar\pi c^3}\int\int\sin\theta d\theta d\varphi\{|\boldsymbol{\mu}_{fi}|^2-|\boldsymbol{\mu}_{fi}|^2\cos^2\theta\} \\ &= \frac{4\omega^3(N_{\mathbf{k},\lambda}+1)}{\hbar\pi c^3}\left\{\frac{\pi}{2}|\boldsymbol{\mu}_{fi}|^2-\frac{\pi}{6}|\boldsymbol{\mu}_{fi}|^2\right\}\end{aligned}$$

The step in line 10-24 is possible because $\hat{e}_{k1}$, $\hat{e}_{k2}$, and $\mathbf{k}$ form mutually orthogonal complete set spanning three-dimensional space; $\hat{k}$ is a unit vector pointing in the same direction as $\mathbf{k}$. Note that all $\mathbf{k}$ can be recovered for positive values of the n_i (Fig. 10-1) so the $d\Omega$ integration is only over the first octant of the sphere. For simplicity we take the dipole along the z-axis, but any

oter axis yields the same result since the field uniformly fills the box. We now have an expression for the isotropic emission rate of a molecule at short times,

$$\Gamma_{tot} = \frac{4\omega^3}{3\hbar c^3}(N_{\mathbf{k},\lambda} + 1)|\boldsymbol{\mu}_{fi}|^2. \qquad 10\text{-}25$$

Even when $N_{\mathbf{k},\lambda}$=0, emission still takes place: this emission in the absence of a stimulating radiation field is known as spontaneous emission. One can think of it as being induced by the zero-point energy in the radiation field. The spontaneous lifetime is simply the inverse of 10-25 when N=0, or

$$\tau_{sp} = \frac{3\hbar c^3}{4\omega^3 |\boldsymbol{\mu}_{fi}|^2} \qquad 10\text{-}26$$

10.4 Excited state lineshape

If eq. 10-25 represents the emission rate in units of s^{-1} from an excited molecular state |f>, the population n of molecules in that state |f> will decrease as

$$\frac{dn}{dt} = -\Gamma n \text{ or } n(t) = n_0 e^{-\Gamma t} \qquad 10\text{-}27$$

Amplitude thus leaks away even though |f> is a molecular eigenstate because |f> is not an eigenstate of the molecule-field Hamiltonian. In terms of the amplitude of state |f>, we can rewrite eq. 10-27 as

$$|f(t)> = e^{-i\omega_{fi}t - \frac{\Gamma}{2}t}|f(0)> . \qquad 10\text{-}28$$

The Γ/2 arises because the population n is given by <*f*(*t*)|*f*(*t*)>, which eliminates the time evolution phase factor and restores an exp[-Γt] decay for n. Fourier transforming eq. 10-28 yields the lineshape of the transition in the frequency domain, or

$$g(\omega) = \frac{1}{\pi\hbar}\frac{\Gamma/2}{(\Gamma/2)^2 + (\omega - \omega_{fi})^2} \qquad 10\text{-}29$$

instead of $\delta(\omega - \omega_{fi})/\hbar = \delta(E - E_{fi})$, which was the lineshape initially assumed in section c) to obtain the density of states. If the lineshape is sufficiently narrow, the density of states will not vary across it as a function of energy, and the symmetrical Lorentzian 10-29 is a very good approximation. For very broad lines, the derivation in c) and d) is not self-consistent, and the variation in the density of states would have to be taken into account (e.g. Bergman reference in b-iii).

10.5 Absorption of a monochromatic polarized plane wave by randomly oriented molecules

In high-resolution spectroscopy, a laser beam is well approximated by a plane wave with a single frequency ω, wavevector **k** and polarization λ. We derive the absorption rate in the same two steps as done for emission in c), by calculating the density of field modes and the transition matrix element. $\rho = \delta(E_{fi} - \hbar\omega)/4\pi$ is the ideal case of a truly monochromatic laser: all photons are in the same state so ∫ρdE=1, but the density of states is infinite in the infinitesimal energy interval near $\hbar\omega$. A real laser might have a finite bandwidth represented by a Gaussian or similar lineshape, but we will consider the ideal case first. The matrix element according to eq. 10-14 is

$$<f|H^{(1)}|i> = (\boldsymbol{\mu}_{fi} \cdot \hat{e}_{\mathbf{k}\lambda}) N_{\mathbf{k}\lambda}^{1/2} \left(\frac{i\omega_{fi}}{c}\right)\left(\frac{2\pi\hbar c}{Vk}\right)^{1/2} \qquad 10\text{-}30$$

and the Golden Rule rate therefore becomes

$$\Gamma_{obs} = \frac{2\pi}{\hbar}\frac{\delta(E_{fi}-\hbar\omega)}{4\pi}N_{\mathbf{k}\lambda}\frac{\omega^2}{c^2}\frac{2\pi\hbar c}{Vk}(\boldsymbol{\mu}_{fi}\cdot\hat{e}_{\mathbf{k}\lambda})^2 \qquad 10\text{-}31$$

Assuming the molecules are randomly oriented, we average over orientations by integrating over 4π steradians. Note that unlike eq. 10-24, where we averaged over all wavevector orientations in the positive octant, here we average over all possible dipole orientations. Picking the laser polarization $\hat{e}_{\mathbf{k}\lambda}$ along the z-axis

$$\begin{aligned}\Gamma_{abs} &= \frac{2\pi}{\hbar}\frac{\delta(E_{fi}-\hbar\omega)}{4\pi}N_{\mathbf{k}\lambda}\frac{\omega^2}{c^2}\frac{2\pi\hbar c}{Vk}\int_0^{\pi}\int_0^{2\pi}\sin\theta\, d\theta\, d\varphi\,|\boldsymbol{\mu}_{fi}|^2\cos^2\theta \\ &= \frac{2\pi}{\hbar}\frac{\delta(E_{fi}-\hbar\omega)}{4\pi}\delta(E_{fi}-\hbar\omega)N_{\mathbf{k}\lambda}\frac{\omega^2}{c^2}\frac{2\pi\hbar c}{Vk}\frac{4\pi}{3}|\boldsymbol{\mu}_{fi}|^2 \\ &= \frac{4\pi^2\omega}{3V}N_{\mathbf{k}\lambda}\delta(E_{fi}-\hbar\omega)|\boldsymbol{\mu}_{fi}|^2\end{aligned} \qquad 10\text{-}32$$

This can be rewritten in terms of the laser intensity. For a traveling electromagnetic wave,

$$I\left(\frac{energy}{area\cdot time}\right) = \frac{\#\,\text{photons}\cdot\text{photon energy}}{\text{beam volume}}\cdot\text{beam velocity} = \frac{N_{\mathbf{k}\lambda}\cdot\hbar\omega}{V}c \qquad 10\text{-}33$$

from which follows

$$<\Gamma_{abs}> = \frac{4\pi^2}{3\hbar c}I|\boldsymbol{\mu}_{fi}|^2\,\delta(E_{fi}-\hbar\omega), \qquad 10\text{-}34$$

the absorption rate per molecule per second.

In reality, the laser will always have a finite linewidth. So will the molecule, at the very least due to spontaneous emission. As seen in d), the delta-function lineshape then becomes the Fourier transform of an exponential decay in the simplest case, or a Lorentzian:

$$\frac{1}{\hbar}\delta(\omega-\omega_{Fi}) \rightarrow g(\omega) = \frac{1}{\pi\hbar}\frac{\Gamma/2}{(\Gamma/2)^2+(\omega-\omega_{fi})^2}. \qquad 10\text{-}35$$

The $1/\hbar$ factor is included since $\delta(E_{fi}-\hbar\omega) = \delta(\omega_{fi}-\omega)/\hbar$; the 1/π factor is a normalization factor since

$$\int_{-\infty}^{\infty}\frac{\tau^{-1}}{\tau^{-2}+\Delta\omega^2}d\Delta\omega = \pi, \text{ but } \int_{-\infty}^{\infty}\delta(\omega_{fi}-\omega)d\omega = 1 \qquad 10\text{-}36$$

The Lorentzian 10-35 thus has the same integrated linestrength as the delta-function lineshape, but spreads it over a finite frequency interval. If $\Delta\omega_{laser} << \tau_{sp}^{-1}$, and the molecular energy levels only decay by spontaneous emission, the lineshape will be completely dominated by the molecular lifetime:

$$<\Gamma_{abs}>\left(\frac{1}{\sec}\right) = \frac{\pi c^2 I}{2\omega^3\hbar\tau_{sp}}\frac{\tau_{sp}^{-1}}{\tau_{sp}^{-2}/4+(\omega-\omega_{fi})^2}\quad(\tau_{laser} >> \tau_{sp}) \qquad 10\text{-}37$$

Note that the absorption and spontaneous emission rates (inverse of eq. 10-26) are not independent of one another. This is required by detailed balance and energy conservation, and a special case of the Einstein A/B coefficients discussed further in section 11-3.

10.6 Absorption coefficient

When light propagates through an absorbing medium, the intensity generally drops off exponentially with distance. This is due to the fact that in the absence of saturation effects, absorption over a small pathlength is proportional to the number of molecules in the path, and hence proportional to the pathlength Δz:

$$dI = -I\alpha dz \begin{cases} \Rightarrow I = I_0 e^{-\alpha z} \\ \Rightarrow \alpha = \frac{|dI|}{Idz}(\frac{1}{cm}) \end{cases}. \qquad 10\text{-}38$$

The change in intensity is given in terms of the absorption rate by

$$\begin{aligned} -dI(\tfrac{\text{energy}}{\text{cm}^2\text{sec}}) &= -c(\tfrac{\text{cm}}{\text{sec}}) \cdot du(\tfrac{\text{energy}}{\text{cm}^3}) \\ &= c < \Gamma_{abs} > (\tfrac{1}{\text{sec}}) \cdot n_0 (\tfrac{\text{molecules}}{\text{cm}^3}) dt \cdot \hbar\omega \qquad 10\text{-}39 \\ &= < \Gamma_{abs} > n_0 dz \hbar\omega \quad (cdt = dz) \end{aligned}$$

Inserting 10-34 into 10-39 and the result into 10-38 yields the absorption coefficient

$$\alpha(\omega) = \frac{< \Gamma_{abs} > n_0 \hbar\omega}{I} = \frac{4\pi^2 |\boldsymbol{\mu}_{fi}|^2 \omega n_0}{3c} g(\omega) \qquad 10\text{-}40$$

in units of inverse length.

10.7 Calculating the $\boldsymbol{\mu}_{fi}$

It remains to calculate the dipole moment expectation values $\boldsymbol{\mu}_{fi}$ from the molecular wavefunction. For electron coordinates $\mathbf{r}_e$ and nuclear coordinates $\mathbf{r}_n$, the total dipole operator is given by

$$\vec{\boldsymbol{\mu}} = -\sum_{\mathbf{e}} \mathbf{r}_{\mathbf{e}} + \sum_n Z_n \mathbf{r}_{\mathbf{n}} . \qquad 10\text{-}41$$

In the B.-O. approximation, $|\Psi_{tot}> \approx |\Psi_e> |\mathcal{M}J>$, where the second ket refers to the vibration-rotation wavefunction. Taking the matrix element of 10-41,

$$< \Psi_f | \vec{\boldsymbol{\mu}} | \Psi_i > = < \nu_f J_f | < \Psi_{ef} | \vec{\boldsymbol{\mu}} | \Psi_{ei} > | \nu_i J_i > \qquad 10\text{-}42$$

$$= < \nu_f J_f | \vec{\boldsymbol{\mu}}_{fi}(Q_n) | \nu_i J_i > \qquad 10\text{-}43$$

The electronic expectation value in eq. 10-43 gives us $\vec{\boldsymbol{\mu}}_{fi}(Q_n)$, the transition dipole operator between two electronic states as a function of nuclear coordinates. $\boldsymbol{\mu} = \boldsymbol{\mu}_{ii}(Q_n)$ is the permanent molecular dipole moment if the electronic states are one and the same.

If $\Psi_{ei} \neq \Psi_{ef}$, we have an electronic transition. If $\Psi_{ei} = \Psi_{ef}$, the result is a rotation-vibration ($\nu_f \neq \nu_i$) transition or a rotational ($\nu_f = \nu_i$, $J_f \neq J_i$) transition or a fine structure/hyperfine ($\nu_f = \nu_i$, $J_f = J_i$) transition. In all cases, the transition dipole operator can be expanded in a power series in the normal coordinates Q_n:

$$\vec{\boldsymbol{\mu}}_{fi}(Q_n) = \{\mu_{fi}(0) + \sum_n Q_n \left.\frac{\partial \mu_{fi}}{\partial Q_n}\right|_{\mathbf{Q}=0} + \cdots\} \hat{\boldsymbol{\mu}}_{fi}(\theta, \varphi, \chi) \qquad 10\text{-}44$$

where $\hat{\boldsymbol{\mu}}_{fi}$ is a unit vector pointing in the same direction as $\vec{\boldsymbol{\mu}}_{fi}(Q_n)$ to separate the rotational part of the dipole moment operator from its magnitude.

For electronic transitions, the leading term in eq. 10-44 is sufficient to yield a nonzero result for the transition intensity. Its matrix element is

$$\vec{\boldsymbol{\mu}}_{fi} \approx < \nu_f J_f | \mu_{fi}(0) \hat{\mu} | \nu_i J_i > = \mu_{fi}(0) < \nu_f | \nu_i > < J_f | \hat{\boldsymbol{\mu}}_{fi} | J_i > \qquad 10\text{-}45$$

The first factor is the electronic transition dipole moment at the equilibrium geometry. The second is the Franck-Condon factor, which requires the vibrational wavefunctions in two different electronic states to have nonzero overlap for a transition to occur. The third factor is the rotational expectation value. Which components of the vector $\hat{\boldsymbol{\mu}}_{fi}$ actually need to be included depends on the polarization of the electric field. For example, if **E** is polarized in the space-fixed z-direction, then $\hat{\mu}_Z = \mu_x \hat{\mathbf{x}} \cdot \hat{\mathbf{Z}} + \mu_y \hat{\mathbf{y}} \cdot \hat{\mathbf{Z}} + \mu_z \hat{\mathbf{z}} \cdot \hat{\mathbf{Z}}$ is the only required component in

eq. 10-45, where $\mu_x^{\ 2}+\mu_y^{\ 2}+\mu_z^{\ 2}=1$. If the transition dipole points along the molecular z axis (e.g. diatomic molecule or parallel symmetric top band), the only necessary component of $\hat{\boldsymbol{\mu}}_{fi}$ in eq. 10-45 is $\hat{\mathbf{z}}\cdot\hat{\mathbf{Z}}=\cos\theta$. In section 5 it was seen how to evaluate matrix elements of such operators.

Within a given electronic surface, eq. 10-44 becomes

$$\boldsymbol{\mu}(Q_n)=\{\mu(0)+\sum_n Q_n\left.\frac{\partial\mu}{\partial Q_n}\right|_{\mathbf{Q}=0}+\cdots\}\hat{\boldsymbol{\mu}}(\theta,\varphi,\chi) \qquad 10\text{-}46$$

where $\boldsymbol{\mu}$ is the permanent dipole moment operator on that electronic surface. For pure rotations, the first term is again sufficient to give the leading contribution to the line intensity:

$$<\nu J_f\,|\boldsymbol{\mu}|\,\nu J_i>\approx<\nu\,|\,\mu(0)\,|\,\nu><J_f\,|\hat{\boldsymbol{\mu}}\,|\,J_i>=\mu(0)<J_f\,|\hat{\boldsymbol{\mu}}\,|\,J_i> \qquad 10\text{-}47$$

$\mu(0)$ is the permanent dipole moment, and the rotational matrix element is evaluated as discussed above.

For ro-vibrational transitions, the leading term in 10-46 makes no contribution, because vibrational wavefunctions within a given electronic state form an orthogonal set, and $\mu(0)$ is just a constant. Therefore,

$$<\nu_f J_f\,|\boldsymbol{\mu}|\,\nu_i J_i>\approx\sum_n\frac{\partial\mu}{\partial Q_n}<\nu_f\,|Q_n|\,\nu_i><J_f\,|\hat{\boldsymbol{\mu}}\,|\,J_i>+\cdots \qquad 10\text{-}48$$

The derivative times the vibrational matrix element in 10-48 is the vibrational transition moment. Note that near the bottom of the well, the vibrational eigenfunctions are nearly harmonic oscillator functions; in that case the vibrational matrix element yields a selection rule of $\Delta v=\pm 1$, e.g.:

$$<\nu_f J_f\,|\boldsymbol{\mu}|\,\nu_i J_i>\approx\sum_n\frac{\partial\mu}{\partial Q_n}\{\frac{\hbar}{2\omega_n}\}^{1/2}(\nu_i+1)^{1/2}\delta_{\nu_f=\nu_i+1}<J_f\,|\hat{\boldsymbol{\mu}}\,|\,J_i> \qquad 10\text{-}49$$

Higher vibrational eigenfunctions are not harmonic-oscillator-like due to anharmonicity, and so overtone transitions become allowed. (Q^2 terms would have to be included in the expansion in eq. 10-48 to give quantitative overtone intensities.)

10.8 Higher-order processes

We close the discussion on second quantization by briefly considering some higher order processes. There are two types:

i) Multipole transitions: $e^{i\mathbf{k}\cdot\mathbf{r}}=1+i\mathbf{k}\cdot\mathbf{r}+\ldots$ the second term leads to a matrix element $i<\varphi_f|\mathbf{p}_n\mathbf{k}\cdot\mathbf{r}_n|\varphi_i>\approx\mathbf{r}_\mathbf{n}^2\omega_{fi}$ if the same commutator trick as in eq. 10-11 is applied. Based on section 9, these terms will depend on the quadrupole moment or on the magnetic dipole moment. Such transitions are common in atoms. Molecules have lower symmetry, and are more likely to have dipole transitions. There are cases where dipole-forbidden transitions have been observed. However, their intensity is usually dominated by vibronic (non-Born-Oppenheimer) interactions with a dipole-allowed state. Thus, magnetic dipole/electric quadrupole transitions are almost never a factor in molecular line intensities, unless the molecule is a macromolecule.

ii) Multiphoton transitions: by doing second order perturbation theory on the interaction Hamiltonian 10-14, the next higher corrections to the transition moment are obtained and the Golden Rule rate becomes

$$\Gamma_{f\leftarrow i}\approx\frac{2\pi}{\hbar}\rho\left|<\Psi_f|H^{(1)}|\Psi_i>+<\Psi_f|H^{(2)}|\Psi_i>+\sum_{j\neq i,f}\frac{<\Psi_f|H^{(1)}|\Psi_j><\Psi_j|H^{(1)}|\Psi_i>}{E_i^t-E_j^t}\right|^2 \qquad 10\text{-}50$$

The first term has already been considered extensively. The second two terms involve a product of two $a_{\mathbf{k}\lambda}$ / $a^+_{\mathbf{k}\lambda}$ and are therefore two photon transitions because they change two quanta of the

field. In processes that are not one-photon resonant, the first term is usually negligible, and only the last two need be considered. Furthermore, the second term is not important in cases where transitions are enhanced by near-resonance, since $H^{(2)}$ contains no molecular coordinates or momenta. We will therefore consider the third term as an example.

In a spontaneous Raman process a laser excites the molecules initially in state $|\varphi_i\rangle$ at frequency ω, and light is emitted at a frequency ω', returning the molecule to different state $|\varphi_f\rangle$. The intermediate molecule state $|\varphi_j\rangle$ need not be resonant with the input photon as diagrammed in fig. 10-2. A photon at frequency ω could be absorbed "virtually" although no state is resonant, and then a second photon ω' could be emitted to a molecular state at higher energy than the original state (Stokes transition).

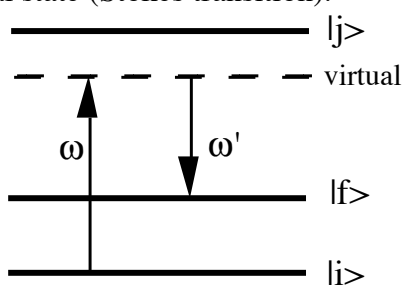

Fig. 10-2. Diagram for the two-photon spontaneous Raman process; the state E_j is nonresonant.

The two types of intermediate processes in such a case can be diagrammed as

$$\begin{array}{ccccc} & & E_j^{(tot)}=E_j-\hbar\omega & & \\ & \nearrow & |\varphi_j\rangle|\cdots,N_{\mathbf{k}\lambda}-1,0,\cdots\rangle & \nwarrow & \\ |\varphi_i\rangle|\cdots,N_{\mathbf{k}\lambda},0,\cdots\rangle & & & & |\varphi_f\rangle|\cdots,N_{\mathbf{k}\lambda}-1,1,\cdots\rangle. \\ & \searrow & |\varphi_j\rangle|\cdots,N_{\mathbf{k}\lambda},1,\cdots\rangle & \swarrow & \\ & & E_j^{(tot)}=E_j+\hbar\omega' & & \end{array} \qquad 10\text{-}51$$

In the upper path, photon ω is absorbed before photon ω' is emitted, and the converse occurs in the lower path. Note that the number of modes in the box containing the molecule is typically so great, that $N_{k\lambda}' \approx 0$ for any given mode if only black body radiation is present. In the spontaneous Raman process, the intermediate state is usually an excited electronic state, so $\mu_{ji} \approx \mu_{ji}(0) < v_j | v_i >< J_j | \hat{\boldsymbol{\mu}}_{ji} | J_i >$. Near resonance, the third term in eq. 10-50 is largest and yields

$$\Gamma_{f\leftarrow i} = \frac{2\pi}{\hbar}\rho\left|\sum \frac{\hat{e}_{k'\lambda'}\cdot\boldsymbol{\mu}_{fj}\boldsymbol{\mu}_{ji}\cdot\hat{e}_{k\lambda}}{E_i-(E_j-\hbar\omega)}\frac{i\omega_{ji}}{c}\{\frac{hc}{Vk}\}^{1/2}\sqrt{N_{k\lambda}}(\frac{i\omega_{fj}}{c})\{\frac{hc}{Vk'}\}^{1/2}\sqrt{1}+\right.$$
$$\left.\sum \frac{\hat{e}_{k'\lambda'}\cdot\boldsymbol{\mu}_{fj}\boldsymbol{\mu}_{ji}\cdot\hat{e}_{k\lambda}}{E_i-(E_j+\hbar\omega')}(\frac{i\omega_{ji}}{c})\{\frac{hc}{Vk'}\}^{1/2}\sqrt{1}(\frac{i\omega_{fj}}{c})\{\frac{hc}{Vk}\}^{1/2}\sqrt{N_{k\lambda}}\right|^2 \qquad 10\text{-}52$$

If the input laser is polarized, the output intensity may not be isotropic due to alignment of the excited molecular dipoles. Otherwise, the total density of states is approximately the product of the laser density of states at frequency ω and the density of states available in the box (black body cavity) where the experiment is done:

$$\begin{aligned}\rho &\approx \rho_{laser}(\omega)\rho_{box}(\omega') \\ &\approx \frac{\delta(\omega_{laser}-\omega)}{4\pi}\cdot\frac{k'^2 V}{\pi^3\hbar c} \quad (\text{units: Joule}^{-1}\text{Hz}^{-1})\end{aligned}. \qquad 10\text{-}53$$

Note that one of the densities of states is expressed as "states per frequency interval" instead of "states per energy interval" (factor of $\hbar$ difference) for the next step. Inserting eq. 10-53 into eq. 10-52

$$\Gamma_{fi}(s^{-1}\mathrm{Hz}^{-1}) = \frac{2\pi}{\hbar}\left\{\frac{\delta(\omega_{laser}-\omega)}{4\pi}\cdot\frac{k'^2 V}{\pi^3\hbar c}\right\}\frac{h^2\omega\omega' N_{k\lambda}}{V^2}\,|\,\hat{e}_{k'\lambda'}\cdot \mathrm{R}\cdot\hat{e}_{k\lambda}\,|^2, \qquad \text{10-54a}$$

$$= \frac{2\omega'^3}{\hbar\pi c^4}\left\{\frac{c\hbar\omega N_{k\lambda}}{V}\delta(\omega_{laser}-ck)\right\}|\,\hat{e}_{k'\lambda'}\cdot \mathrm{R}\cdot\hat{e}_{k\lambda}\,|^2, \qquad \text{10-54b}$$

$$= \frac{2\omega'^3}{\pi\hbar c^4}\bullet I(\omega)\left(\frac{energy}{area\bullet time\bullet Hz}\right)\bullet|\,\hat{e}_{k'\lambda'}\cdot \mathrm{R}\cdot\hat{e}_{k\lambda}\,|^2\ (cm^6) \qquad \text{10-54c}$$

where R is the polarizability tensor

$$\mathrm{R}\ (\mathrm{cm}^3) = \sum_j\left\{\frac{\cdot\boldsymbol{\mu}_{fj}\boldsymbol{\mu}_{ji}\cdot}{E_{ji}-\hbar\omega}+\frac{\cdot\boldsymbol{\mu}_{fj}\boldsymbol{\mu}_{ji}\cdot}{E_{ji}+\hbar\omega'}\right\}\frac{\omega_{fj}\omega_{ji}}{\omega\,\omega'} \qquad \text{10-55}$$

and $I(\omega)$ is the input laser intensity per unit bandwidth of the laser (i.e. the energy per unit area and unit time, per 1 Hz of laser bandwidth). Expressing the laser intensity per frequency interval instead of the total laser intensity is particularly useful if the laser has a finite bandwidth, i.e. it is not the ideal delta function electric field in 10-54b. Note that Γ is the rate per unit frequency bandwidth of the pump laser, and $s^{-1}Hz^{-1}$ is unitless. Note that the prefactor in eq. 10-54c can differ slightly if the experimental geometry is changed. However, absolute Raman transition rates are never measured in practice, and the important factors are that the signal depends on the cube of the scattering frequency (favoring a blue rather than a red pump laser since $\hbar\omega' = \hbar\omega + E_{ji}$), that the signal depends linearly on the pump laser intensity, and on the square of the polarizability tensor R.

The intensity term in eq. 10-54c could be split into two electric field contributions yielding

$$H^{(2)} \sim (\mathrm{E}\hat{e}\cdot\mathrm{R})\cdot\mathbf{E} = \boldsymbol{\mu}_{ind}\cdot\mathbf{E}\ . \qquad \text{10-55}$$

One can therefore think of the spontaneous Raman effect as being due to an off-resonant field at frequency ω inducing a dipole moment in the molecule, which then interacts as usual with the field.