5. Electronic Spectroscopy

We've learned the basics of molecular and electronic structure now. How does one actually "measure" the electronic structure of a molecule? This is the crux of what may be termed "electronic spectroscopy", a detailed and beautiful (and difficult) subject which we shall not have time to do justice to. (One could do an entire course—aye, two entire courses—on electronic spectroscopy.) This chapter is designed to give you a feel for the essence of electronic spectroscopy, without getting too bogged down in the details.

1. Light

To understand what happens when we shine light on a molecule, we need to consider the mathematical description of light. For our purposes, we can use the classical electrodynamic description (which you may remember from first-year physics): light is a wave, propagating in a direction, $\boldsymbol{k}$, called the wave vector, with angular frequency $\omega = 2\pi\nu$. Thus the "wave function" for light has the form:[1]

$$\psi_{light}\left(\boldsymbol{r},t\right) \sim \boldsymbol{A}\, e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-i\omega t)} \tag{5.1}$$

The important point is the effect of light: it produces an electric field[2]

$$\boldsymbol{E}\left(\boldsymbol{r},t\right) \propto 2\boldsymbol{V}\sin\left(\omega t - \boldsymbol{k}\cdot\boldsymbol{r}\right) \tag{5.2}$$

and a magnetic field

$$\begin{aligned}\boldsymbol{B}\left(\boldsymbol{r},t\right) &\propto 2\left(\tfrac{1}{\omega}\boldsymbol{k}\times\boldsymbol{V}\right)\cdot\sin\left(\omega t - \boldsymbol{k}\cdot\boldsymbol{r}\right) \\ &= 2\left(\tfrac{1}{|\boldsymbol{k}|c}\boldsymbol{k}\times\boldsymbol{V}\right)\cdot\sin\left(\omega t - \boldsymbol{k}\cdot\boldsymbol{r}\right)\end{aligned} \tag{5.3}$$

where $\boldsymbol{V}$ is a measure of the electric field strength. $\boldsymbol{V}$ is orthogonal to $\boldsymbol{k}$, and the detailed form of $\boldsymbol{V}$ depends on the polarization of the light. (For instance,

---

[1] This is not really true: a photon has a finite length (it doesn't stretch out forever), and, somewhat spookily, this length is not easily expressed in terms of the photon's frequency, but depends on how the photon was generated. It also isn't true that a photon has a single, well-defined wave length (or frequency). Mysteriously, despite the fact the "speed of light" is an accurately measured physical concept, this only is applicable to the average (sometimes called the "group") velocity of a light wave (or photon)—certain wavelengths contributing to the photon will travel faster than the speed of light (and faster than other wavelengths), as is evidenced by the way a narrow, purportedly monochromatic, beam will become more diffuse upon refraction.

[2] Here $|\boldsymbol{V}| = \tfrac{\omega}{2}|\boldsymbol{A}|$.

$\boldsymbol{V} = \frac{|\boldsymbol{V}|}{\sqrt{2}}\left[1, e^{-i\pi/2}, 0\right]$ represents right-circularly polarized light if the direction of light propagation is the z direction.)

For simplicity, we choose our axes so that the direction of light propagation is the z direction,[3]

$$\boldsymbol{k} = [0, 0, k] \tag{5.4}$$

and choose linearly polarized light in the x direction,

$$\boldsymbol{E}(\boldsymbol{r}, t) = \left[2V \sin(\omega t - kz), 0, 0\right]. \tag{5.5}$$

Owing to the properties of the cross product (remember the right-hand-rule), the magnetic field, $\boldsymbol{B}$, is qualitatively similar to the electric field, $\boldsymbol{E}$, but is orthogonal to it. Thus

$$\boldsymbol{B}(\boldsymbol{r}, t) = \left[0, \frac{2V}{c} \sin(\omega t - kz), 0\right] \tag{5.6}$$

In Eq. (5.6), c is the speed of light, $\omega = 2\pi\nu$ is its frequency, V is the electric field strength, and $k = \frac{2\pi}{\lambda}$ is the wave number, measuring the number of wavelengths of the light that can fit into a given length of space.

Owing to the relation[4]

$$\lambda = \frac{c}{\nu} \tag{5.7}$$

we have that

$$\omega = ck. \tag{5.8}$$

So the frequency is related to the wavelength. The other useful relationship is the "quantum mechanics" of the photon, whereby its energy is

$$E = h\nu = \hbar\omega = \frac{hc}{\lambda} = \hbar ck \tag{5.9}$$

and its momentum is[5]

---

[3]   It is interesting to digress about the polarization of light. Photons have "spin" angular momentum of $\pm\hbar$, and this is associated with the "helicity" or "polarization" of photons. While this is not especially relevant to that which follows, it does give us an insight into the nature of spin in general, and, in particular the spin of the electron. You can think of the electron's spin as measuring its helicity, or polarization. To pursue this analogy further would lead us far afield, and we would quickly enter the ethereal realms of more-or-less impractical (but very fundamental) modern physics—Elysian fields which your professor has not and never intends to visit. To those interested in further study of such things, I say "excelsior," and leave it to you to decide whether I mean this in the sense of "wood shavings used a packing material," "higher yet," or (quite possibly) both.

[4]   I remember this as the analogue of the formula from classical mechanics,

length = speed · time $\rightarrow$ wavelength = c · (period of the light)

$$\rightarrow \lambda = c\left(\frac{1}{\nu}\right).$$

$$p = \hbar k = \frac{h}{\lambda} = \hbar \left(\frac{\omega}{c} \right) = \frac{h\nu}{c}.$$
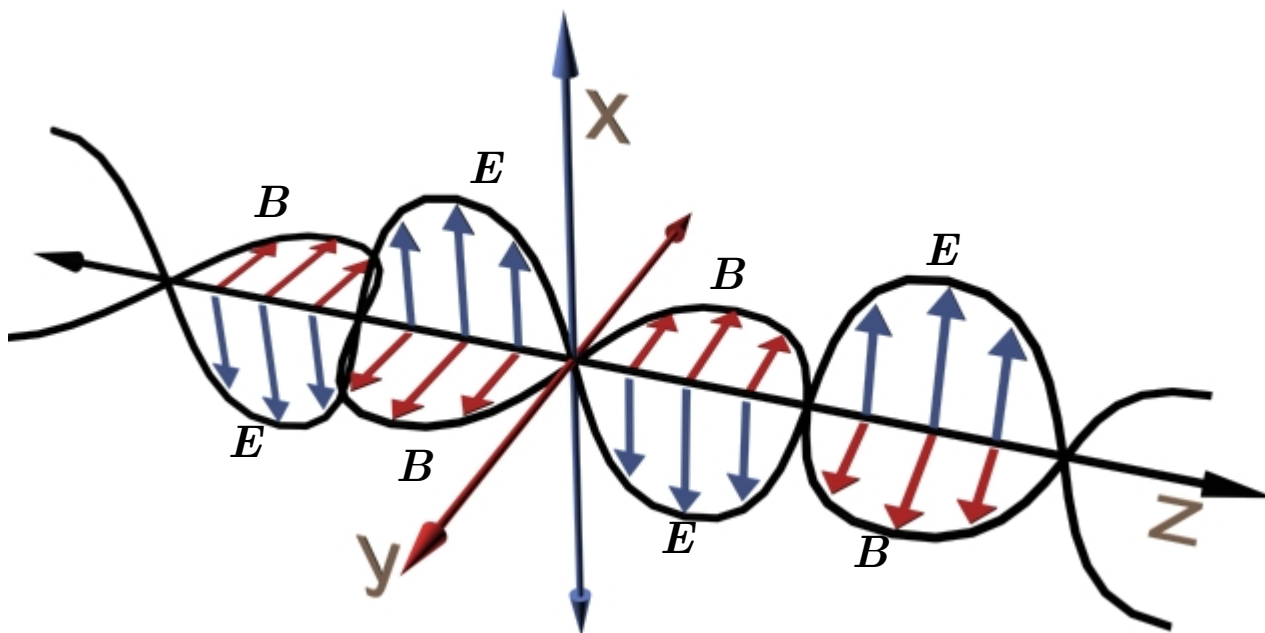
(5.10)

Figure 5.1   Adapted from <u>Molecular Spectroscopy</u> by Jeanne L. McHale (Prentice Hall, New Jersey, 1999). In this figure, the electric field oscillates "up and down" while the magnetic field oscillates "into and out of" the plane of the paper.

2. The effect of light on a molecule—General Considerations

Now we examine, in broad outline, the phenomenon of light impinging on a molecule. The first thing that should be considered is that, in general, the wavelength of the light we are interested in is much larger than the molecule of interest. For example, most fluorescence and absorption studies of molecular electronic states are done in the UV-vis range ($\lambda \sim$ 50-750 nm), while many of the larger molecules of chemical interest are no more than a few nanometers across.[6] So let's put the center of a molecule of diameter d at the position X and shine light with wavelength λ on the molecule. At any given point in

[5]   The easiest way to remember this is to remember that $E = mc^2$. Since $\text{mass} \cdot \text{velocity} = \text{momentum}$, we infer that $\frac{E}{c} = p$. (This isn't really a derivation, but just a mnemonic.)

[6]   Molecules of biochemical interest are similar in size to light's wavelength, but their orbitals tend to be localized, so the orbitals are still much smaller than the wavelengths of light used to probe them. Bulk metals, on the other hand, are distinctly problematic.

time, the change in electric field from one side of the molecule, where $z = X - \frac{d}{2}$, to the other side, where $z = X + \frac{d}{2}$, is[7]

$$2V\left(\sin\left(\omega t + \frac{2\pi}{\lambda}\left(X + \frac{d}{2}\right)\right)\right) - 2V\left(\sin\left(\omega t + \frac{2\pi}{\lambda}\left(X - \frac{d}{2}\right)\right)\right)$$

$$= 2V\left(\sin\left[\left(\omega t + \frac{2\pi}{\lambda}X\right) + \frac{\pi d}{\lambda}\right] - \sin\left[\left(\omega t + \frac{2\pi}{\lambda}X\right) + \frac{\pi d}{\lambda}\right]\right)$$

$$= 2V\left(\cos\left(wt + \frac{2\pi X}{\lambda}\right)\sin\left(\frac{\pi d}{2\lambda}\right) - \cos\left(wt + \frac{2\pi X}{\lambda}\right)\sin\left(-\frac{\pi d}{\lambda}\right)\right)$$

$$= 2V\left(\cos\left(wt + \frac{2\pi X}{\lambda}\right)\right)\left(\sin\left(\frac{\pi d}{2\lambda}\right) - \sin\left(-\frac{\pi d}{\lambda}\right)\right)$$

$$= 2V\left(\cos\left(wt + \frac{2\pi X}{\lambda}\right)\right)\left(\sin\left(\frac{\pi d}{2\lambda}\right) + \sin\left(\frac{\pi d}{\lambda}\right)\right) \tag{5.11}$$

$$= 4V\left(\cos\left(wt + \frac{2\pi X}{\lambda}\right)\right)\left(\sin\left(\frac{\pi d}{\lambda}\right)\right)$$

$$\approx 2V\left(\cos\left(wt + \frac{2\pi X}{\lambda}\right)\right)\left(\frac{\pi d}{\lambda} - \frac{1}{3!}\left(\frac{\pi d}{\lambda}\right)^3 + \ldots\right)$$

$$\leq 4V\left(\frac{\pi d}{\lambda}\right)$$

where we have used the Taylor series for the sine function in the last step. The conclusion is that, compared to the total field strength $2V$, the field varies very little over the extent of the molecule. (For example, for a molecule one nanometer in diameter in light with wavelength $150\,nm$, the variation of the field over the breadth of the molecule never exceeds 5% of the total field strength (and it is usually substantially less than this since the cosine term is generally less than one).)

What does this mean? A molecule, sitting at the point X, does not see an appreciable spatial variation in the field. Rather, it sees a dipole that oscillates in time as the light wave moves inexorably forward. (Similarly, in our day-to-day lives we are

---

[7]   We could have jumped all the way to the third line from the bottom in Eq. (5.11) using an identity from trigonometry. I tend to remember only a few identities from trigonometry, notably

$$\cos\left(x + y\right) = \cos\left(x\right)\cos\left(y\right) - \sin\left(x\right)\sin\left(y\right)$$
$$\sin\left(x + y\right) = \cos\left(x\right)\sin\left(y\right) + \cos\left(y\right)\sin\left(x\right)$$

From these identities, for example, the useful double angle formulae follow directly (choose $x = y$). The identity we use in Eq. (5.11) is derived from

$$\sin\left(x + y\right) + \sin\left(x - y\right) = \begin{pmatrix} \cos\left(x\right)\sin\left(y\right) + \cos\left(y\right)\sin\left(x\right) \\ + \cos\left(x\right)\sin\left(-y\right) + \cos\left(-y\right)\sin\left(x\right) \end{pmatrix}$$

$$= \begin{pmatrix} \cos\left(x\right)\sin\left(y\right) + \cos\left(y\right)\sin\left(x\right) \\ - \cos\left(x\right)\sin\left(y\right) + \cos\left(y\right)\sin\left(x\right) \end{pmatrix}$$

$$= 2\cos\left(y\right)\sin\left(x\right).$$

For this derivation, we needed to remember that the cosine is an even function ($\cos\left(-x\right) = \cos\left(x\right)$) and the sine is an odd function ($\sin\left(-x\right) = -\sin\left(x\right)$).

unaware of the curvature of the earth: a Ptolemaic model whereby the sun moves in a periodic, time-dependent, fashion is quite acceptable from a local perspective.)

We make this picture more quantitative by writing

$$
\begin{aligned}
E_x(\boldsymbol{r},t) &= 2V\sin(\omega t - kz) \\
&= 2V\sin(\omega t)\cos(kz) - 2V\cos(\omega t)\sin(kz) \\
&= 2V\sin(\omega t)\cos\left(\tfrac{\omega z}{c}\right) - 2V\cos(\omega t)\sin\left(\tfrac{\omega z}{c}\right)
\end{aligned}
\tag{5.12}
$$

If, then we assume that field varies very little from one position in the molecule, $\boldsymbol{r}$, to another, $\boldsymbol{r}'$, then we can assume that the electric field doesn't change over the extent of the molecule and write $\boldsymbol{E}(\boldsymbol{r},t) \approx E(\boldsymbol{r}_0,t)$, where $E(\boldsymbol{r}_0,t)$ is the value of the field at some representative place in the molecule. If we put the center of the molecule at the origin, for instance, we might take

$$
\begin{aligned}
E_x(\boldsymbol{r},t) &\approx E_x(0,t) \\
&\approx 2V\sin(\omega t)\cos(0) - 2V\cos(\omega t)\sin(0) \\
&\approx 2V\sin(\omega t)
\end{aligned}
\tag{5.13}
$$

and so, referring back to Eq. (5.5),

$$
\boldsymbol{E}(\boldsymbol{r},t) \approx [2V\sin(\omega t), 0, 0]
\tag{5.14}
$$

Equation (5.14) will be our model for describing the interaction between atoms and molecules and radiation: a molecule tends to see light as an "oscillating dipole field". There are, of course, other effects: the effect of the oscillating magnetic field, the "quadrupole" and other terms that were neglected in the long-wavelength approximation, etc.. The largest of these terms, however, is still a factor of $\frac{1}{\lambda}$ smaller than the oscillating dipole term,[8] and so these effects are difficult to observe—they are often thousands of times weaker than the dipole field transition. To my mind, the important thing is to recognize that there are corrections to the long-wavelength approximation, and these

---

[8] The electric quadrupole term comes from considering the spatial variation of the electric field in z, as through Eq. (5.11). We have

$$
E_x(\boldsymbol{r},t) = 2V\sin(\omega t)\left(0 + \tfrac{(kz)^2}{2!} + \ldots\right) - 2V\cos(\omega t)\left(kz - \tfrac{(kz)^3}{3!}\right)
$$

$$
= 2V\sin(\omega t) - 2V(kz)\cos(\omega t) + 2V\tfrac{(kz)^2}{2}\sin(\omega t) - \ldots
$$

and the first term is the "dipole" field, the second the quadrupole field, the third the octupole field, etc..

Sometimes it is the spatial dependence of the magnetic field which interacts with a system in such a way as to stimulate transitions between energy levels. Consequently, the leading order term for magnetic dipole transitions is also proportional to the variation in the field over the length of the atom, and thus proportional to k. The interaction energy is $-k\boldsymbol{B}\cdot\boldsymbol{\mu} = -\tfrac{2Vk}{c}\sin(\omega t)\mu_y$, where μ_y is the y-component of the system's magnetic moment.

justify the existence of low-intensity spectral lines. However, the approach taken here, which avoids the Lagrangian altogether, is really not the right way to treat the finer points of spectroscopy.

3. Time-Dependent Perturbation Theory

We are now in possession of the tools we need to obtain a theoretical description for electronic spectroscopy. To this end, let us first review the physical situation: we are given a molecule, Q, in some initial state i, described by the time-independent wave function $\Phi_i\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N; \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P\right)$. (Here $\left\{\boldsymbol{r}_i\right\}_{i=1}^N$ are the positions of the electrons and $\left\{\boldsymbol{R}_\alpha\right\}_{\alpha=1}^P$ are the positions of the nuclei.) We place this molecule in the presence of electromagnetic radiation. Presuming the wavelength of the radiation is much larger than the size of the molecule and presuming the radiation is linearly polarized and propagates in the z-direction, we can describe the radiation as an time-dependent electric field, $E_x = 2V \sin \omega t$, ignoring its magnetic component and its spatial dependence.

To find the wavefunction of the molecule in the presence of the electric field, we need to construct the Hamiltonian. Recall that the force due to an electric field is

$$\boldsymbol{F} \equiv q\boldsymbol{E} \tag{5.15}$$

where q is the charge of the particle on which the field acts and recall that the relationship of the force to the potential is

$$\boldsymbol{F}\left(\boldsymbol{r}, t\right) = -\nabla V\left(\boldsymbol{r}, t\right). \tag{5.16}$$

Then, from Eq. (5.13),

$$qE_x = 2Vq \sin\left(\omega t\right) = -\nabla V\left(\boldsymbol{r}, t\right) \tag{5.17}$$

and so, to within an arbitrary constant,

$$V\left(\boldsymbol{r}, t\right) = -2Vqx \sin\left(\omega t\right). \tag{5.18}$$

The total Hamiltonian for a molecule exposed to electromagnetic radiation, then, is

$$
\begin{aligned}
\hat{H} = &\sum_{\alpha=1}^P \left(-\frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^P \frac{e^2}{4\pi\varepsilon_0} \left(\frac{Z_\alpha Z_\beta}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|} \right) \right) + \sum_{i=1}^N \left(-\frac{1}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^P \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right) \right) \\
&+ \sum_{\alpha=1}^P \sum_{i=1}^N -\frac{Z_\alpha e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|} + \left(\sum_{i=1}^N 2Vex_i \sin\left(\omega t\right) - \sum_{\alpha=1}^P 2VZ_\alpha eX_i \sin\left(\omega t\right) \right)
\end{aligned}
\tag{5.19}
$$

Based on our prior experience, we expect that perturbation theory would be an appropriate method for treating this Hamiltonian. Perturbation theory is only reliable if the perturbation is small, however, which is only true if potential induced by the electric fields

is much smaller than the other terms in the Hamiltonian. In particular, it is necessary that the external electric field be small compared to the electric field due to the other terms in the Hamiltonian, because then the electromagnetic force will merely cause a slight alternation in the electrons' and nuclei's motion, which can be reliably modeled with perturbation theory.

Coulomb's law tells us that the magnitude of the force between two particles in the molecule (whether they be nuclei or electrons) will be

$$|\boldsymbol{F}| = \frac{q_1 q_2}{4\pi\varepsilon_0 \left|\boldsymbol{r}_1 - \boldsymbol{r}_2\right|^2} \tag{5.20}$$

where q_1 and q_2 are the charges on the particle. In a molecule, the magnitude of the charges is no smaller than the electric charge, and the average spacing between a particle and the next closest particle is on the order of 1 Bohr.[9] The magnitude of the field felt by an electron or nucleus in an isolated molecule, then is

$$|\boldsymbol{E}| \approx \frac{\left(1.602 \cdot 10^{-19}\right)\mathrm{C}}{4\pi \cdot 8.5 \cdot 10^{-12} \frac{\mathrm{C}^2}{\mathrm{Nm}^2} \left(.5 \cdot 10^{-10}\mathrm{m}\right)^2} = 6 \cdot 10^{11} \, \tfrac{\mathrm{V}}{\mathrm{m}} \tag{5.21}$$

This may be compared with the typical electric fields we encounter in the laboratory, ranging from a brightly lit lab bench (suitable for observing the color of a transition-metal complex) ($|\boldsymbol{E}| \approx 30 \frac{\mathrm{V}}{\mathrm{m}}$) to a laboratory-grade laser ($|\boldsymbol{E}| \approx 10^7 \frac{\mathrm{V}}{\mathrm{m}}$). In any case, these fields are quite weak compared to the typical fields experienced by an electron in an atom, and so treating electromagnetic radiation with perturbation theory is definitely justified.

Even though the effect of radiation on a molecule can be treated as a perturbation, radiation is a time-dependent perturbation, which requires a generalization of the usual perturbation theoretic approach (which is only valid for time-independent perturbations). Based on the previous discussion, we consider the molecule to be resting, in isolation, until the time $t = 0$, at which point in time we turn on our light source. The resulting perturbation is

---

[9] The average spacing is much less in the region near the nuclear centers, but if we are concerned with excitations of the valence electrons, this is a reasonable estimate. Near the nuclear centers, the forces between the electrons and nuclei tend to cancel one another out, so that the magnitude of the average instantaneous force felt by a nucleus is not unreliably estimated by an expression like Eq. (5.21). However, the force felt by core electrons in heavy atoms is many times greater than that in Eq. (5.21), owing to the high nuclear charge and the small radius of the core orbitals.

$$V\left(\boldsymbol{r},t\right) = \begin{cases} 0 & t \leq 0 \\ -2Vqx\sin\left(\omega t\right) & t > 0, \end{cases} \tag{5.22}$$

and so the total molecular Hamiltonian can be written as

$$\begin{aligned} \hat{H} &\equiv \hat{H}_{molecule} + \sum_{i=1}^{N} V\left(\boldsymbol{r}_i,t\right) + \sum_{\alpha=1}^{P} V\left(\boldsymbol{R}_\alpha,t\right) \\ &\equiv \hat{H}_{molecule} + \hat{V}. \end{aligned} \tag{5.23}$$

Here, $\hat{H}_{molecule}$ is the Hamiltonian of the molecule in isolation and, once the light source is turned on, the total Hamiltonian has the form of Eq. (5.19). Until the light source is turned on, we assume that the molecule is resting in the ith excited state, with wave function $\Psi_i\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N;\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_P;t\right)$.[10] (In what follows, we shall frequently omit the variables on which a function depends, including them only when they are of special importance to the phenomenon being considered.)

Since the perturbation is time-dependent, the wave functions will change in time and we need to solve the time-*dependent* Schrödinger equation,

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}. \tag{5.24}$$

Of course, it is, in almost all circumstances of practical interest, impossible to solve Eq. (5.24) directly. However, suppose we know the solutions to the time-*independent* Schrödinger equation for the isolated molecule,

$$\hat{H}_{molecule}\Phi_k = E_k\Phi_k. \tag{5.25}$$

For $t \leq 0$, there is no perturbation, and so Eq. (5.25) gives a complete description of our system.

Once the perturbation is turned on, we use the usual method of expanding the energy and wave functions as Taylor series in terms of the perturbation strength, V. Unlike the time-independent case, however, both the wave functions and energies now depend on the time. So

$$E\left(t\right) = E\left(V=0\right) + \left(V-0\right)\frac{\partial E(t)}{\partial V} + \frac{V^2}{2!}\frac{\partial^2 E(t)}{\partial V^2} + \ldots \tag{5.26}$$

and

$$\Psi\left(t\right) = \Psi\left(t=0\right) + \left(V-0\right)\frac{\partial \Psi(t)}{\partial V} + \frac{V^2}{2!}\frac{\partial^2 \Psi(t)}{\partial V^2} + \ldots. \tag{5.27}$$

When the magnitude of the perturbation is zero, we know that the perturbation will not stimulate any change in the system's initial state, which allows us to identify $E\left(V=0\right) = E_i$ and $\Psi\left(V=0\right) = \Psi_i$. Thus,

---

[10] In mathematical terms, this provides the "initial condition" for the time-dependent Schrödinger equation.

$$E\left(t\right) = E_i + V \left.\frac{\partial E(t)}{\partial V}\right|_{V=0} + \frac{V^2}{2!} \left.\frac{\partial^2 E(t)}{\partial V^2}\right|_{V=0} + \ldots \tag{5.28}$$

and

$$\Psi\left(t\right) = \Psi_i + V \left.\frac{\partial \Psi(t)}{\partial V}\right|_{V=0} + \frac{V^2}{2!} \left.\frac{\partial^2 \Psi(t)}{\partial V^2}\right|_{V=0} + \ldots. \tag{5.29}$$

We now substitute Eqs. (5.28) and (5.29) into the time-dependent Schrödinger equation, Eq. (5.24). We obtain

$$\left(\hat{H}_{molecule} + \hat{V}\right)\left(\Psi_i + V \left.\frac{\partial \Psi(t)}{\partial V}\right|_{V=0} + \frac{V^2}{2!} \left.\frac{\partial^2 \Psi(t)}{\partial V^2}\right|_{V=0} + \ldots\right) = i\hbar \frac{\partial \left(\Psi_i + V \left.\frac{\partial \Psi(t)}{\partial V}\right|_{V=0} + \frac{V^2}{2!} \left.\frac{\partial^2 \Psi(t)}{\partial V^2}\right|_{V=0} + \ldots\right)}{\partial t}$$

$$\hat{H}_{molecule}\Psi_i + \left(\hat{H}_{molecule}V \left.\frac{\partial \Psi(t)}{\partial V}\right|_{V=0} + \hat{V}\Psi_i\right) + \left(\hat{H}_{molecule} \frac{V^2}{2!} \left.\frac{\partial^2 \Psi(t)}{\partial V^2}\right|_{V=0} + \hat{V} \cdot V \left.\frac{\partial \Psi(t)}{\partial V}\right|_{V=0}\right) + \ldots \tag{5.30}$$

$$= i\hbar \left(\frac{\partial \Psi_i}{\partial t} + V \left.\frac{\partial^2 \Psi(t)}{\partial V \partial t}\right|_{V=0} + \frac{V^2}{2!} \left.\frac{\partial^3 \Psi(t)}{\partial V^2 \partial t}\right|_{V=0} + \ldots\right)$$

In order for this equation to be satisfied, terms with the same dependence on V must all be equal. That is, we must have that

$$\hat{H}_{molecule}\Psi_i = i\hbar \frac{\partial \Psi_i}{\partial t}$$

$$\hat{H}_{molecule}\left(V \left.\frac{\partial \Psi(t)}{\partial V}\right|_{V=0}\right) + \hat{V}\Psi_i = i\hbar \left(V \left.\frac{\partial^2 \Psi(t)}{\partial V \partial t}\right|_{V=0}\right)$$

$$\hat{H}_{molecule}\left(\frac{V^2}{2!} \left.\frac{\partial^2 \Psi(t)}{\partial V^2}\right|_{V=0}\right) + \hat{V}\left(V \left.\frac{\partial \Psi(t)}{\partial V}\right|_{V=0}\right) = i\hbar \left(\frac{V^2}{2!} \left.\frac{\partial^3 \Psi(t)}{\partial V^2 \partial t}\right|_{V=0}\right) \tag{5.31}$$

$$\vdots$$

We can solve the zeroth order equation in V by separation of variables, followed by integration. First, write the wave function as a time-independent and time-dependent piece (separation of variables),

$$\Psi_i\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;\boldsymbol{R}_1,\ldots,\boldsymbol{R}_P;t\right) = \Phi_i\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N;\boldsymbol{R}_1,\ldots,\boldsymbol{R}_P\right)\chi_i\left(t\right) \tag{5.32}$$

Substituting Eq. (5.32) into the first equation (5.31), we have

$$\hat{H}_{molecule}\Psi_i = i\hbar \frac{\partial \Psi_i}{\partial t}$$

$$E_i \Phi_i \chi_i = i\hbar \frac{\partial \Phi_i \chi_i}{\partial t}$$

$$E_i \Phi_i \chi_i = i\hbar \Phi_i \frac{\partial \chi_i}{\partial t}$$

$$\frac{1}{i\hbar}E_i dt = \frac{1}{\chi_i} d\chi_i \tag{5.33}$$

$$\frac{-i}{\hbar} \int E_i dt = \int \frac{1}{\chi_i} d\chi_i$$

$$-\frac{iE_i t}{\hbar} = \ln\left(\chi_i\right) + (\text{constant})$$

$$\chi_i = e^{-iE_i t/\hbar + \phi}$$

where ϕ is an phase factor, which can be taken to be zero in the absence of specific information about the phase of the wave function. We conclude that the wave function for a pure state, in the absence of a time-dependent perturbing potential, is simply

$$\Psi_i = \Phi_i e^{-iE_i t/\hbar} \tag{5.34}$$

where Φ_i is the eigenfunction of the time-independent Schrödinger equation with eigenvalue E_i:

$$\hat{H}_{molecule}\Phi_i = E_i\Phi_i. \tag{5.35}$$

The interpretation of Eq. (5.34) is that any system, even one in a stationary state, has a characteristic frequency of oscillation, which is related to its energy. One can think of this as a "standing wave." an oscillation which is constant in time (so it represents a stationary state), but which is an oscillation nonetheless. Some additional insight is obtained by recalling that for light (or any "free particle"), the wave function resembles a plane wave. So $\Psi_{free}(\boldsymbol{r},t) \sim Ae^{i\boldsymbol{k}\cdot\boldsymbol{r}}e^{-i\omega t}$. For a photon (and, similarly, for a free particle), $E = \hbar\omega$, which gives $\Psi_{free}(\boldsymbol{r},t) \sim Ae^{i\boldsymbol{k}\cdot\boldsymbol{r}}e^{-\frac{iEt}{\hbar}}$, in direct analogy to Eq. (5.34).

With this insight, it is reasonable to write the first-order correction to the wave function, $V\frac{\partial\Psi}{\partial V}\big|_{V=0}$, as a linear combination of the solutions of the time-dependent Schrödinger equation in the *absence* of a perturbation,

$$\begin{aligned} V\tfrac{\partial\Psi}{\partial V}\big|_{V=0} &= \sum_{k=0}^{\infty} c_k^{(1)}\Psi_k \\ &= \sum_{k=0}^{\infty} c_k^{(1)}\Phi_k e^{-iE_k t/\hbar}. \end{aligned} \tag{5.36}$$

Substituting this result into the second equation in Eq. (5.31),[11] we obtain

$$\hat{H}_{molecule}V\tfrac{\partial\Psi(t)}{\partial V}\Big|_{V=0} + \hat{V}\Psi_i = i\hbar V\tfrac{\partial^2\Psi(t)}{\partial V\partial t}\Big|_{V=0}$$

$$\hat{H}_{molecule}\sum_{k=0}^{\infty} c_k^{(1)}\Phi_k e^{-iE_k t/\hbar} + \hat{V}\Psi_i = i\hbar\frac{\partial\sum_{k=0}^{\infty} c_k^{(1)}\Phi_k e^{-iE_k t/\hbar}}{\partial t}$$

$$\sum_{k=0}^{\infty} c_k^{(1)}E_k\Phi_k e^{-iE_k t/\hbar} + \hat{V}\Phi_i e^{-iE_i t/\hbar} = i\hbar\sum_{k=0}^{\infty}\left(\Phi_k e^{-iE_k t/\hbar}\frac{\partial c_k^{(1)}}{\partial t} + c_k^{(1)}\Phi_k\left(\tfrac{-iE_k}{\hbar}\right)e^{-iE_k t/\hbar}\right) \tag{5.37}$$

$$\sum_{k=0}^{\infty} c_k^{(1)}E_k\Phi_k e^{-iE_k t/\hbar} + \hat{V}\Phi_i e^{-iE_i t/\hbar} = i\hbar\sum_{k=0}^{\infty}\Phi_k e^{-iE_k t/\hbar}\frac{\partial c_k^{(1)}}{\partial t} + \sum_{k=0}^{\infty} c_k^{(1)}E_k\Phi_k e^{-iE_k t/\hbar}$$

$$\hat{V}\Phi_i e^{-iE_i t/\hbar} = i\hbar\sum_{k=0}^{\infty}\Phi_k e^{-iE_k t/\hbar}\frac{\partial c_k^{(1)}}{\partial t}$$

Multiplying both sides by Φ_f, integrating over the spatial variables, and using the orthogonality of the spatial wave functions $\langle\Phi_f|\Phi_k\rangle = \delta_{fk}$, we obtain

---

[11]　This is first-order perturbation theory since each term being considered has a linear (V^1) dependence on the field strength.

$$\left\langle \Phi_f \left| \hat{V} \right| \Phi_i \right\rangle e^{-iE_i t / \hbar} = i\hbar \sum_{k=0}^{\infty} \left\langle \Phi_f \middle| \Phi_k \right\rangle e^{-iE_k t / \hbar} \frac{\partial c_k^{(1)}}{\partial t}$$

$$\left\langle \Phi_f \left| \hat{V} \right| \Phi_i \right\rangle e^{-iE_i t / \hbar} = i\hbar e^{-iE_f t / \hbar} \frac{\partial c_f^{(1)}}{\partial t} \tag{5.38}$$

$$\frac{\partial c_f^{(1)}}{\partial t} = \frac{1}{i\hbar} \left\langle \Phi_f \left| \hat{V} \right| \Phi_i \right\rangle e^{it \frac{(E_f - E_i)}{\hbar}}$$

Because $\frac{E_f - E_i}{\hbar}$ is the characteristic angular frequency for light that causes a transition between the states i and f, one typically introduces descriptive notations for the characteristic angular frequency, $\frac{E_f - E_i}{\hbar}$, and frequency, $\frac{E_f - E_i}{h}$:

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$

$$\nu_{fi} = \frac{E_f - E_i}{h} = \frac{\omega_{fi}}{2\pi}. \tag{5.39}$$

To recognize what we have achieved, it is instructive to insert the specific form of the perturbation under consideration, Eq. (5.22),

$$\frac{\partial c_f^{(1)}}{\partial t} = \begin{cases} \dfrac{1}{i\hbar} \left\langle \Phi_f \left| 0 \right| \Phi_i \right\rangle e^{it \frac{(E_f - E_i)}{\hbar}} & t \leq 0 \\[2ex] \dfrac{1}{i\hbar} \left\langle \Phi_f \left| -2V \sin\left(\omega t\right) \left(\displaystyle\sum_{i=1}^{N} -ex_i + \sum_{\alpha=1}^{P} Z_\alpha eX_i \right) \right| \Phi_i \right\rangle e^{it \frac{(E_f - E_i)}{\hbar}} & t > 0 \end{cases} \tag{5.40}$$

Because $\left(\displaystyle\sum_{i=1}^{N} -ex_i + \sum_{\alpha=1}^{P} Z_\alpha eX_i \right)$ represents the effect of a dipole potential, we introduce the simplifying notation

$$\hat{\mu}_x \left(\{ \mathbf{r}_i \}_{i=1}^{N}, \{ \mathbf{R}_\alpha \}_{\alpha=1}^{P} \right) \equiv \left(\sum_{i=1}^{N} -ex_i + \sum_{\alpha=1}^{P} Z_\alpha eX_i \right). \tag{5.41}$$

Substituting both this result and Eq. (5.39) into Eq. (5.40), we obtain an equation with pleasing simplicity,

$$\frac{\partial c_f^{(1)}}{\partial t} = \begin{cases} 0 & t \leq 0 \\[2ex] \dfrac{-2V \sin\left(\omega t\right)}{i\hbar} e^{i\omega_{fi} t} \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle & t > 0 \end{cases} \tag{5.42}$$

Because we know that the molecule is in the ith excited state up until the time before it is irradiated, we know that, at $t = 0$,

$$c_i^{(1)}(t = 0) = 1$$

$$c_f^{(1)}(t = 0) = 0 \tag{5.43}$$

Using this initial condition, we can solve the differential equation in Eq. (5.40) for $c_f(t)$, as follows:

$$c_f^{(1)}(t) = \frac{\left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle}{i\hbar} \left(\int_0^t -2V \sin(\omega\tau) e^{i\omega_{fi}\tau} d\tau + \text{constant} \right)$$
$$= \frac{\left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle}{i\hbar} \int_0^t -2V \sin(\omega\tau) e^{i\omega_{fi}\tau} d\tau \qquad (5.44)$$

The constant of integration must be zero because otherwise $c_f(0) \neq 0$.

Equation (5.44) is a key result. We will work much further with it later, but note that no transitions occur between the initial state, i, and the final state, f, unless

$$\left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right| > 0. \qquad (5.45)$$

Also note that the integral is likely to be very small unless the frequency of the light approximately matches the energy gap between the states because unless the two waves, $\sin(\omega t)$ and $e^{i\omega_{fi}t} = \cos(\omega_{fi}t) + i \sin(\omega_{fi}t)$ are "coherent" (have similar frequencies), the integral will tend towards zero as $t \to \infty$.

Though we shall not use the result, it is instructive to note what happens in the next order of perturbation theory. One obtains, from Eq. (5.31),[12]

$$\hat{H}_{molecule} \sum_{l=0}^{\infty} c_l^{(2)} \Phi_l e^{-iE_l t/\hbar} + \hat{V} \sum_{k=0}^{\infty} c_k^{(1)} \Phi_k e^{-iE_k t/\hbar} = i\hbar \frac{\partial}{\partial t} \sum_{l=0}^{\infty} c_l^{(2)} \Phi_l e^{-iE_l t/\hbar}$$

$$\sum_{l=0}^{\infty} c_l^{(2)} E_l \Phi_l e^{-iE_l t/\hbar} + \hat{V} \sum_{k=0}^{\infty} c_k^{(1)} \Phi_k e^{-iE_k t/\hbar} = \sum_{l=0}^{\infty} i\hbar \Phi_l e^{-iE_l t/\hbar} \frac{\partial c_l^{(2)}}{\partial t} + \sum_{l=0}^{\infty} c_l^{(2)} E_l \Phi_l e^{-iE_l t/\hbar}$$

$$\hat{V} \sum_{k=0}^{\infty} c_k^{(1)} \Phi_k e^{-iE_k t/\hbar} = \sum_{l=0}^{\infty} i\hbar \Phi_l e^{-iE_l t/\hbar} \frac{\partial c_l^{(2)}}{\partial t}$$

$$\sum_{k=0}^{\infty} c_k^{(1)} \left\langle \Phi_g \left| \hat{V} \right| \Phi_k \right\rangle e^{-iE_k t/\hbar} = \sum_{l=0}^{\infty} i\hbar \left\langle \Phi_g \middle| \Phi_l \right\rangle e^{-iE_l t/\hbar} \qquad (5.46)$$

$$\frac{\partial c_g^{(2)}}{\partial t} = \frac{1}{i\hbar} \sum_{k=0}^{\infty} c_k^{(1)} \left\langle \Phi_g \left| \hat{V} \right| \Phi_k \right\rangle e^{i(E_g - E_k)t/\hbar}$$

$$\frac{\partial c_g^{(2)}}{\partial t} = \frac{1}{i\hbar} \sum_{k=0}^{\infty} c_k^{(1)} \left\langle \Phi_g \left| \hat{V} \right| \Phi_k \right\rangle e^{i\omega_{gk}t}$$

Substituting Eq. (5.44) and the form of the perturbation into Eq. (5.46), we obtain[13]

---

[12] In fact, it is clear from the structure of the perturbation equations, Eqs. (5.31), that the general result is

$$\frac{\partial c_g^{(n)}}{\partial t} = \frac{1}{i\hbar} \sum_{k=0}^{\infty} c_k^{(n-1)} \left\langle \Phi_g \left| \hat{V} \right| \Phi_k \right\rangle e^{i\omega_{gk}t/\hbar}.$$

[13] In this equation we use the relations

$$\cos(\omega t) = \frac{e^{i\omega t} + e^{-i\omega t}}{2}$$

$$\sin(\omega t) = \frac{e^{i\omega t} - e^{-i\omega t}}{2i}$$

Alternatively, we could have used the Euler formula

$$\frac{\partial c_g^{(2)}}{\partial t} = \frac{-1}{\hbar^2} \sum_{k=0}^{\infty} \left\langle \Phi_g \left| \hat{\mu}_x \right| \Phi_k \right\rangle \left\langle \Phi_k \left| \hat{\mu}_x \right| \Phi_i \right\rangle \cdot 2V \sin \omega t e^{i\omega_{gk}t} \int_0^t 2V \sin(\omega\tau) e^{i\omega_{ki}\tau} d\tau$$

$$c_g^{(2)}(t) = \frac{-4V^2}{\hbar^2} \sum_{k=0}^{\infty} \left\langle \Phi_g \left| \hat{\mu}_x \right| \Phi_k \right\rangle \left\langle \Phi_k \left| \hat{\mu}_x \right| \Phi_i \right\rangle \int_0^t \int_0^{\tau_1} \sin \omega\tau_1 \sin(\omega\tau_2) e^{i\omega_{gk}\tau_1 + i\omega_{ki}\tau_2} d\tau_2 d\tau_1$$

$$= \frac{-4V^2}{\hbar^2} \sum_{k=0}^{\infty} \left\langle \Phi_g \left| \hat{\mu}_x \right| \Phi_k \right\rangle \left\langle \Phi_k \left| \hat{\mu}_x \right| \Phi_i \right\rangle \int_0^t \int_0^{\tau_1} \frac{\left(e^{i\omega\tau_1} - e^{-i\omega\tau_1}\right)\left(e^{i\omega\tau_2} - e^{-i\omega\tau_2}\right) e^{i\omega_{gk}\tau_1 + i\omega_{ki}\tau_2}}{2i} d\tau_2 d\tau_1$$

$$= \frac{2iV^2}{\hbar^2} \sum_{k=0}^{\infty} \left\langle \Phi_g \left| \hat{\mu}_x \right| \Phi_k \right\rangle \left\langle \Phi_k \left| \hat{\mu}_x \right| \Phi_i \right\rangle \int_0^t \int_0^{\tau_1} \left(e^{i\omega\tau_1} - e^{-i\omega\tau_1}\right)\left(e^{i\omega\tau_2} - e^{-i\omega\tau_2}\right) e^{i\omega_{gk}\tau_1} e^{i\omega_{ki}\tau_2} d\tau_2 d\tau_1 \qquad (5.47)$$

$$= \frac{2iV^2}{\hbar^2} \sum_{k=0}^{\infty} \left\langle \Phi_g \left| \hat{\mu}_x \right| \Phi_k \right\rangle \left\langle \Phi_k \left| \hat{\mu}_x \right| \Phi_i \right\rangle \int_0^t \int_0^{\tau_1} \begin{bmatrix} \left[e^{i(\omega+\omega_{gk})\tau_1} - e^{-i(\omega-\omega_{gk})\tau_1} \right] \\ \left(e^{i(\omega+\omega_{ki})\tau_2} - e^{-i(\omega-\omega_{ki})\tau_2} \right) \end{bmatrix} d\tau_2 d\tau_1$$

$$= \frac{2iV^2}{\hbar^2} \sum_{k=0}^{\infty} \left\langle \Phi_g \left| \hat{\mu}_x \right| \Phi_k \right\rangle \left\langle \Phi_k \left| \hat{\mu}_x \right| \Phi_i \right\rangle \int_0^t \int_0^{\tau_1} \begin{bmatrix} \left[e^{i\left[(\omega+\omega_{gk})\tau_1 + (\omega+\omega_{ki})\tau_2\right]} + e^{-i\left[(\omega-\omega_{gk})\tau_1 + (\omega-\omega_{ki})\tau_2\right]} \\ -e^{i\left[(\omega-\omega_{gk})\tau_1 - (\omega-\omega_{ki})\tau_2\right]} - e^{-i\left[(\omega-\omega_{gk})\tau_1 - (\omega+\omega_{ki})\tau_2\right]} \right] \end{bmatrix} d\tau_2 d\tau_1$$

Based on general considerations, we can see what sorts of processes are described by second-order perturbation theory. Importantly, whenever

$$\omega_{gk} + \omega_{ki} = 2\omega \qquad (5.48)$$

$$e^{i\omega t} = \cos(\omega t) + i \sin(\omega t)$$

and then the trig. identities

$$\cos(x - y) - \cos(x + y) = \begin{pmatrix} \cos(x)\cos(y) - \sin(x)\sin(-y) \\ -\left(\cos(x)\cos(y) - \sin(x)\sin(y)\right) \end{pmatrix}$$

$$= \begin{pmatrix} \cos(x)\cos(y) + \sin(x)\sin(y) \\ -\cos(x)\cos(y) + \sin(x)\sin(y) \end{pmatrix}$$

$$= 2\sin(x)\sin(y)$$

$$\cos(x - y) + \cos(x + y) = \begin{pmatrix} \cos(x)\cos(y) - \sin(x)\sin(-y) \\ +\cos(x)\cos(y) - \sin(x)\sin(y) \end{pmatrix}$$

$$= \begin{pmatrix} \cos(x)\cos(y) + \sin(x)\sin(y) \\ +\cos(x)\cos(y) - \sin(x)\sin(y) \end{pmatrix}$$

$$= 2\cos(x)\cos(y)$$

$$\sin(x + y) + \sin(x - y) = \begin{pmatrix} \cos(x)\sin(y) + \cos(y)\sin(x) \\ +\cos(x)\sin(-y) + \cos(-y)\sin(x) \end{pmatrix}$$

$$= \begin{pmatrix} \cos(x)\sin(y) + \cos(y)\sin(x) \\ -\cos(x)\sin(y) + \cos(y)\sin(x) \end{pmatrix}$$

$$= 2\cos(y)\sin(x).$$

13

the periodic functions in Eq. (5.47) can be in phase, and so second-order perturbation theory describes so-called "two photon" processes, wherein the energy of the transition is twice the energy of the photon, $\hbar\omega$. Note that in Eq. (5.48), it is possible that $k = i$ or $k = g$. That is, there are two sorts of two-photon processes. The first is described by Eq. (5.48) and the second is described by

$$\omega_{gi} = 2\omega. \tag{5.49}$$

The first process $i \neq k \neq g$ is an important "competing" process with magnetic dipole and electric quadrupole transitions. The second process is behind nonlinear optical materials, which can be used to double the frequency of incident light. The second process is also important in "resonance enhanced" spectroscopic techniques: these multi-photon absorption and ionizations are typically used to selectively measure the spectra of specific reactive intermediates.

4. Fermi's Golden Rule

We've concluded that, in the presence of light, the coefficient of a "final" state, $c_f(t)$, is given by (cf. Eq. (5.44))

$$c_f^{(1)}(t) = \frac{\left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle}{i\hbar} \int_0^t -2V \sin(\omega\tau) e^{i\omega_{fi}\tau} d\tau. \tag{5.50}$$

Now we want to find out the probability that we can stimulate a transition from a state i to a state f in some time, t. That is, we want to derive an expression for the transition rate.

Given that a molecule is in state i at $t = 0$, we can find the probability that the molecule is in state f at time t from Eq. (5.50). Namely,[14]

$$
\begin{aligned}
P_f(t) &\equiv \left| c_f^{(1)}(t) \right|^2 \\
&= \frac{\left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 V^2}{\hbar^2} \left| \int_0^t \frac{2}{i} \sin(\omega\tau) e^{i\omega_{fi}\tau} d\tau \right|^2
\end{aligned}
\tag{5.51}
$$

Now we need to do the time-dependent integral. We start with the definition of the cosine, $2\cos(\omega t) = e^{i\omega t} + e^{-i\omega t}$, and manipulate the integral in the following way:

---

[14] The factor of $\frac{2}{i}$ in Eq. (5.51) is included solely for convenience. Since $\left| \frac{2}{i} \right|^2 = 2^2 \left(\frac{1}{i} \right) \left(\frac{1}{-i} \right) = 4 = |2|^2$

$$\int_0^t \frac{2}{i} \sin(\omega\tau) e^{i\omega_{fi}\tau} d\tau = \int_0^t \frac{2}{i} \frac{e^{i\omega t} - e^{-i\omega t}}{2i} e^{i\omega_{fi}\tau} d\tau$$

$$= -\int_0^t e^{i(\omega_{fi}+\omega)\tau} d\tau + \int_0^t e^{i(\omega_{fi}-\omega)\tau} d\tau$$

$$= \frac{-1}{i(\omega_{fi}+\omega)} \left(e^{i(\omega_{fi}+\omega)t} - 1 \right) + \frac{1}{i(\omega_{fi}-\omega)} \left(e^{i(\omega_{fi}-\omega)t} - 1 \right)$$

$$= i \cdot \frac{e^{i(\omega_{fi}+\omega)\frac{t}{2}}}{(\omega_{fi}+\omega)} \left(e^{i(\omega_{fi}+\omega)\frac{t}{2}} - e^{-i(\omega_{fi}+\omega)\frac{t}{2}} \right)$$

$$- i \frac{e^{i(\omega_{fi}-\omega)\frac{t}{2}}}{(\omega_{fi}-\omega)} \left(e^{i(\omega_{fi}-\omega)\frac{t}{2}} - e^{-i(\omega_{fi}-\omega)\frac{t}{2}} \right)$$

$$= i \cdot \frac{e^{i(\omega_{fi}+\omega)\frac{t}{2}}}{(\omega_{fi}+\omega)} \left[\frac{e^{i(\omega_{fi}+\omega)\frac{t}{2}} - e^{-i(\omega_{fi}+\omega)\frac{t}{2}}}{2i} \right] 2i$$

$$- i \frac{e^{i(\omega_{fi}-\omega)\frac{t}{2}}}{(\omega_{fi}-\omega)} \left[\frac{e^{i(\omega_{fi}-\omega)\frac{t}{2}} - e^{-i(\omega_{fi}-\omega)\frac{t}{2}}}{2i} \right] 2i$$

$$= -2 \cdot \frac{e^{i(\omega_{fi}+\omega)\frac{t}{2}}}{(\omega_{fi}+\omega)} \sin\left((\omega_{fi}+\omega)\frac{t}{2} \right) + 2 \frac{e^{i(\omega_{fi}-\omega)\frac{t}{2}}}{(\omega_{fi}-\omega)} \sin\left((\omega_{fi}-\omega)\frac{t}{2} \right)$$

$$= -2 \cdot \frac{e^{i(\omega_{fi}+\omega)\frac{t}{2}}}{(\omega_{fi}+\omega)} \left(\frac{\frac{t}{2}}{\frac{t}{2}} \right) \sin\left((\omega_{fi}+\omega)\frac{t}{2} \right) + 2 \frac{e^{i(\omega_{fi}-\omega)\frac{t}{2}}}{(\omega_{fi}-\omega)} \left(\frac{\frac{t}{2}}{\frac{t}{2}} \right) \sin\left((\omega_{fi}-\omega)\frac{t}{2} \right)$$

$$= -t e^{i(\omega_{fi}+\omega)\frac{t}{2}} \frac{\sin\left((\omega_{fi}+\omega)\frac{t}{2} \right)}{(\omega_{fi}+\omega)\frac{t}{2}} + t e^{i(\omega_{fi}-\omega)\frac{t}{2}} \frac{\sin\left((\omega_{fi}-\omega)\frac{t}{2} \right)}{(\omega_{fi}-\omega)\frac{t}{2}} \qquad (5.52)$$

$$= -t e^{i(\omega_{fi}+\omega)\frac{t}{2}} \mathrm{sinc}\left((\omega_{fi}+\omega)\frac{t}{2} \right) + t e^{i(\omega_{fi}-\omega)\frac{t}{2}} \mathrm{sinc}\left((\omega_{fi}-\omega)\frac{t}{2} \right)$$

Here the sinc function is defined as

$$\mathrm{sinc}(x) = \frac{\sin(x)}{x}. \qquad (5.53)$$

Note that the value of the integral considered in Eq. (5.52) is large when $\omega \approx \pm\omega_{fi} \equiv \frac{\pm E_f \mp E_i}{\hbar}$, but small otherwise.
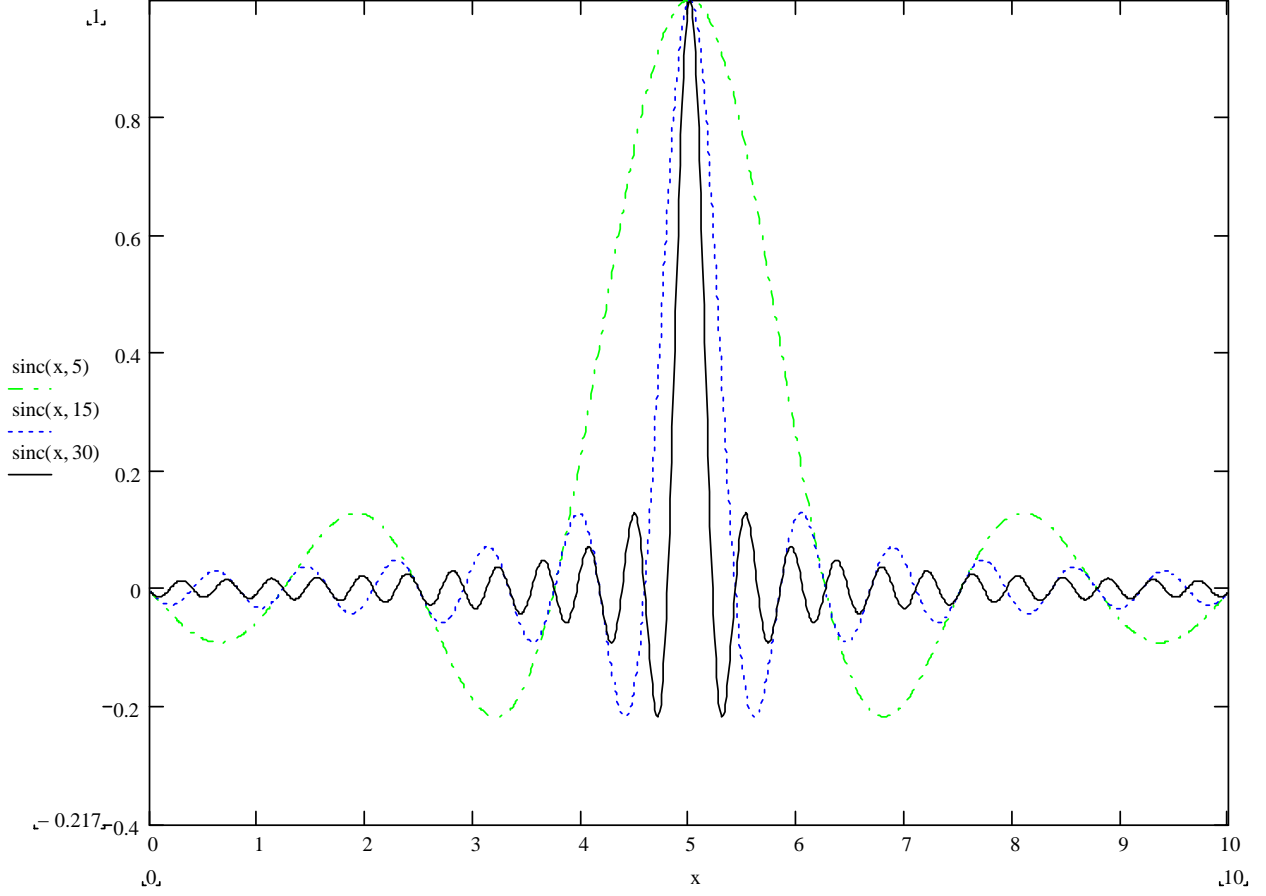
Y-axis labels: 1, 0.8, 0.6, 0.4, 0.2, 0, −0.2, −0.217, −0.4

Legend:
sinc(x, 5)
sinc(x, 15)
sinc(x, 30)

X-axis: 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10   (x)

Figure 5.2. Plot of $\mathrm{sinc}\!\left((\omega - \omega_{fi})\,{}^{t}\!/_{2}\right)$ for $\omega_{fi} = 5$ and different values of t.

Squaring the result of Eq. (5.52), we have

$$\left|\int_{0}^{t} \tfrac{2}{i}\sin(\omega\tau)\,e^{i\omega_{fi}\tau}\,d\tau\right|^{2} = \left|-te^{i(\omega_{fi}+\omega){}^{t}\!/_{2}}\mathrm{sinc}\!\left((\omega_{fi}+\omega)\,{}^{t}\!/_{2}\right) + te^{i(\omega_{fi}-\omega){}^{t}\!/_{2}}\mathrm{sinc}\!\left((\omega_{fi}-\omega)\,{}^{t}\!/_{2}\right)\right|^{2}$$

$$= t^{2}e^{i(\omega_{fi}+\omega){}^{t}\!/_{2}}e^{-i(\omega_{fi}+\omega){}^{t}\!/_{2}}\left(\mathrm{sinc}\!\left((\omega_{fi}+\omega)\,{}^{t}\!/_{2}\right)\right)^{2}$$

$$+\,t^{2}e^{i(\omega_{fi}-\omega){}^{t}\!/_{2}}e^{-i(\omega_{fi}-\omega){}^{t}\!/_{2}}\left(\mathrm{sinc}\!\left((\omega_{fi}-\omega)\,{}^{t}\!/_{2}\right)\right)^{2}$$

$$-\,t^{2}\left(\begin{array}{l}e^{i(\omega_{fi}+\omega){}^{t}\!/_{2}}e^{-i(\omega_{fi}-\omega){}^{t}\!/_{2}}\\[4pt]+\,e^{-i(\omega_{fi}+\omega){}^{t}\!/_{2}}e^{+i(\omega_{fi}-\omega){}^{t}\!/_{2}}\end{array}\right)\mathrm{sinc}\!\left((\omega_{fi}+\omega)\,{}^{t}\!/_{2}\right)\mathrm{sinc}\!\left((\omega_{fi}-\omega)\,{}^{t}\!/_{2}\right) \qquad (5.54)$$

$$= t^{2}\left(\mathrm{sinc}\!\left((\omega_{fi}+\omega)\,{}^{t}\!/_{2}\right)\right)^{2} + t^{2}\left(\mathrm{sinc}\!\left((\omega_{fi}-\omega)\,{}^{t}\!/_{2}\right)\right)^{2}$$

$$-\,t^{2}\mathrm{sinc}\!\left((\omega_{fi}+\omega)\,{}^{t}\!/_{2}\right)\mathrm{sinc}\!\left((\omega_{fi}-\omega)\,{}^{t}\!/_{2}\right)\left(e^{i\omega t}+e^{-i\omega t}\right)$$

$$= t^{2}\left(\mathrm{sinc}\!\left((\omega_{fi}+\omega)\,{}^{t}\!/_{2}\right)\right)^{2} + t^{2}\left(\mathrm{sinc}\!\left((\omega_{fi}-\omega)\,{}^{t}\!/_{2}\right)\right)^{2}$$

$$-\,2t^{2}\cos(\omega\mathrm{t})\,\mathrm{sinc}\!\left((\omega_{fi}+\omega)\,{}^{t}\!/_{2}\right)\mathrm{sinc}\!\left((\omega_{fi}-\omega)\,{}^{t}\!/_{2}\right)$$

16

The last term in this expression is negligible for all but the very shortest times, because any time $\omega + \omega_{fi}$ is small, so that $\text{sinc}\left((\omega + \omega_{fi})\,t\!/\!2\right) \approx 1$, $\omega - \omega_{fi}$ will be large, and so $\text{sinc}\left((\omega - \omega_{fi})\,t\!/\!2\right) \approx 0$. Substituting the first two terms in Eq. (5.54) into Eq. (5.51), we obtain

$$P_f(t) = \frac{\left|\left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle\right|^2 V^2 t^2}{\hbar^2}\left[\text{sinc}^2\left((\omega_{fi} + \omega)\,t\!/\!2\right) + \text{sinc}^2\left((\omega_{fi} - \omega)\,t\!/\!2\right)\right] \tag{5.55}$$

Note that the probability of "up-transitions" and "down transitions" is exactly equal. That is, $P_f(t)$ is large when $\omega_{fi} = \omega$ or when $-\omega_{fi} = \omega$. The former case is absorption, the second case is stimulated emission, wherein a photon at the excitation frequency causes a state to emit radiation, so that the final state has lower energy than the initial state. Stimulated emission reflects the fact that photons are bosons[15] and, unlike fermions, it is favorable for bosons to be in the same state at the same time. Thus, when an excited state encounters a radiation field it can either absorb the photon or, failing that, might be able emit a photon with the same energy, polarization, etc. as the incident light, which gives the favorable "boson pairing" effect.

The number of transitions per unit time, $W_{fi} \equiv \dfrac{P_f(t)}{t}$, can be computed if we know the strength of the radiation. There are two cases. If the radiation is very monochromatic, and can be considered to have a single frequency ω, then Eq. (5.55) is valid. The important case is when the frequency of the light matches the frequency of the transition, and then, because $\text{sinc}(0) = 1$,

$$P_f(t) = \frac{\left|\left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle\right|^2 V^2 t^2}{\hbar^2} \tag{5.56}$$

and

$$W_{fi}^{monochromatic} = \frac{\left|\left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle\right|^2 V^2 t}{\hbar^2}. \tag{5.57}$$

Equation (5.57) is only valid for very short times (typically on the order of femtoseconds)[16].

If, as is typical, the radiation has a spread of frequencies then

---

[15] A photon is a boson because, unlike the electron it has integer spin.

[16] 1 femtosecond $= 10^{-15}$ seconds $=$ one quadrillionth of a second.

$$P_f(t) \equiv \int_0^\infty \tfrac{V^2 t^2}{\hbar^2} \left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 \left[\left(\mathrm{sinc}\left((\omega_{fi} - \omega) \tfrac{t}{2} \right) \right)^2 + \left(\mathrm{sinc}\left((\omega_{fi} + \omega) \tfrac{t}{2} \right) \right)^2 \right] g(\hbar\omega) \, d(\hbar\omega) \qquad (5.58)$$

where $g(\hbar\omega) \, d(\hbar\omega)$ is the probability that a given photon has energy between $\hbar\omega$ and $\hbar(\omega + d\omega)$.[17] If the perturbation is applied for a long time,[18] then we can use the identity:

$$\lim_{t \to \infty} \left[\tfrac{t}{2} \cdot \left(\mathrm{sinc}\left((\omega_{fi} - \omega) \tfrac{t}{2} \right) \right)^2 \right] = \pi \cdot \delta(\omega_{fi} - \omega) \qquad (5.59)$$

---

[17] You should be careful to make sure what type of characterization of the "density of states" of the light source is used. I have opted to use a characterization in terms of the energy (which is common), but it is almost as common for authors to use the frequency profile of the light source, $g_\omega(\omega)$, which gives the (relative) number of photons with energy between ω and $\omega + d\omega$. In either case, the total value of the perturbation depends both on the frequency (or energy) profile of the light source and the total intensity focused on the molecule (V^2). However, when $g_\omega(\omega)$ is used, there an additional factor of $\tfrac{1}{\hbar}$.

[18] What is a long time? Typically, if a molecule sits through many cycles of radiation, we can consider it to have been exposed for a "long time." Since the characteristic period of an oscillation for the light associated with electronic transitions is $T = \tfrac{1}{\nu} = \tfrac{\lambda}{c} \approx \tfrac{300 \, nm}{3 \cdot 10^8 \, m/s} \tfrac{300 \cdot 10^{-9} \, m}{3 \cdot 10^8 \, m/s} = 1 \cdot 10^{-15} \, s$, it is clear that the "long time" assumption is usually justified. For example, the first node in the $\mathrm{sinc}^2\left((\omega - \omega_0) \tfrac{t}{2} \right)$ occurs at $\omega = \pm \tfrac{2\pi}{t} + \omega_0$. If $t = 2\pi \cdot 10^{-n} \, s$, then the spread in angular frequency will be about $10^n \tfrac{1}{s}$, so that the relative spread in angular frequencies is a mere 10^{-13+n} %. This is tiny, as is evidenced by the fact that the induced "impurity" in the wavelength is a mere:

$$\Delta\lambda = 2\pi \left(\tfrac{c}{\omega + 10^n \, s} - \tfrac{c}{\omega} \right) \approx 2\pi \left(\tfrac{c}{\omega}\left(1 - \tfrac{10^n \, s}{\omega}\right) - \tfrac{c}{\omega} \right) = 2\pi \left(\tfrac{3 \cdot 10^8 \, m/s}{2\pi \cdot 3 \cdot 10^{15} \, s} \left(\tfrac{10^n \, s}{2\pi \cdot 3 \cdot 10^{15} \, s} \right) \right) = \tfrac{3 \cdot 10^{8+n}}{5 \cdot 10^{31}} \, m \sim 10^{-23+n} \, m$$

We conclude that, for all but the shortest times, the replacement in Eq. (5.59) will be justified. In addition, we may conclude that for all but the most monochromatic light sources or most rapidly pulsed lasers, the characteristic width of the sinc function will be much less than that of the source.
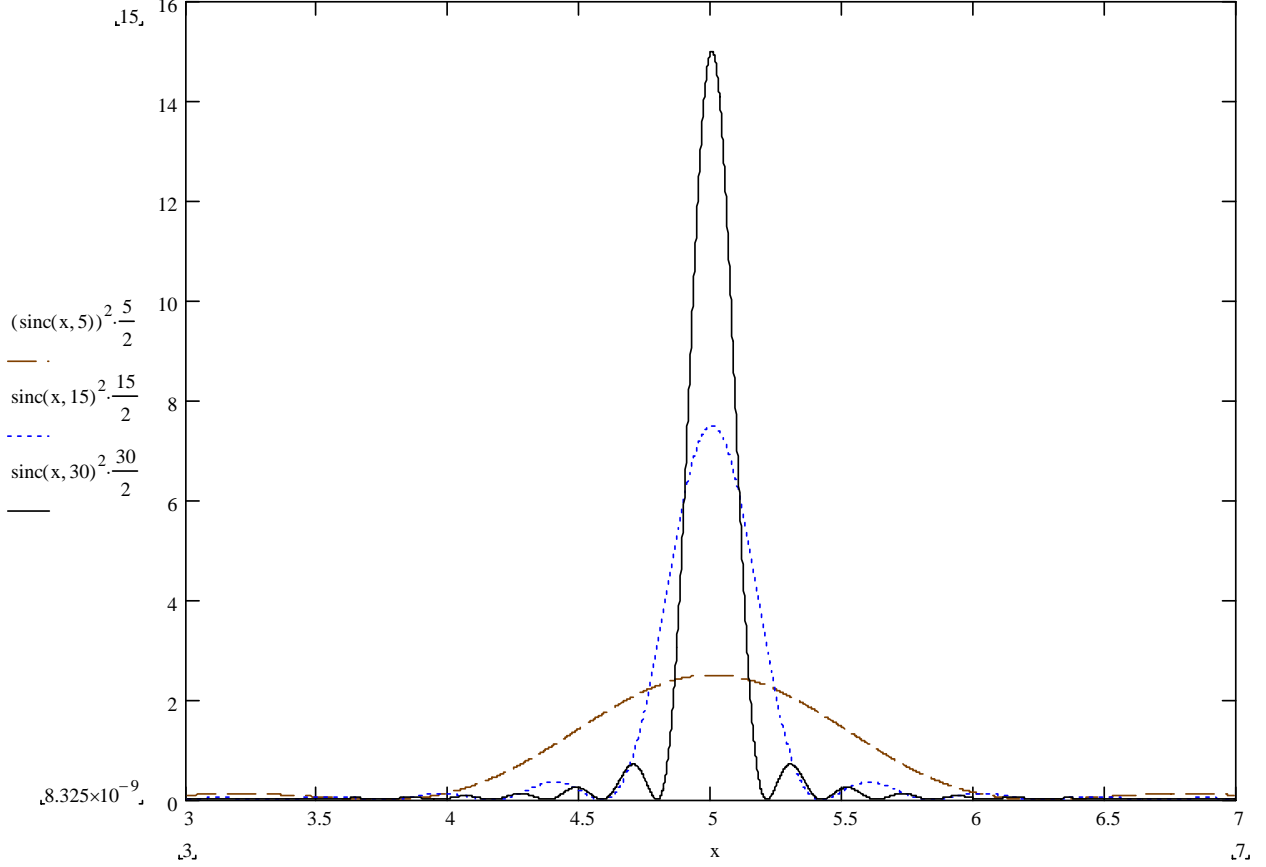
Figure 5.3. Plot of $\frac{\text{sinc}^2\left((\omega-5)t/2\right)}{\left((\omega-5)t/2\right)^2}\left(\dfrac{t}{2}\right)$ for various different values of t.

Using Eq. (5.59) in Eq. (5.58) gives

$$
\begin{aligned}
W_{fi} &= \lim_{t\to\infty}\frac{P_f(t)}{t}\\[4pt]
&= \lim_{t\to\infty}\frac{1}{t}\int_0^\infty \frac{V^2 t^2}{\hbar^2}\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2\left[\left(\text{sinc}\left((\omega_{fi}-\omega)\tfrac{t}{2}\right)\right)^2+\left(\text{sinc}\left((\omega_{fi}+\omega)\tfrac{t}{2}\right)\right)^2\right]g\left(\hbar\omega\right)d\left(\hbar\omega\right)\\[4pt]
&= \int_0^\infty \frac{2V^2}{\hbar^2}\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 g\left(\hbar\omega\right)\left\{\lim_{t\to\infty}\left[\left(\text{sinc}\left((\omega_{fi}-\omega)\tfrac{t}{2}\right)\right)^2+\left(\text{sinc}\left((\omega_{fi}+\omega)\tfrac{t}{2}\right)\right)^2\right]\left(\tfrac{t}{2}\right)\right\}d\left(\hbar\omega\right)\\[4pt]
&= \int_0^\infty \frac{2V^2}{\hbar^2}\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 g\left(\hbar\omega\right)\left\{\pi\delta\left(\omega_{fi}-\omega\right)+\pi\delta\left(\omega_{fi}+\omega\right)\right\}d\left(\hbar\omega\right)\\[4pt]
&= \frac{2\pi V^2\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar}\left(g\left(\hbar\omega_{fi}\right)+g\left(-\hbar\omega_{fi}\right)\right)\\[4pt]
&= \frac{2\pi V^2\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar}\left(g\left(\hbar\omega_{fi}\right)+g\left(\hbar\omega_{if}\right)\right)
\end{aligned}
\tag{5.60}
$$

Equation (5.60) is called Fermi's golden rule or, sometimes, the Fermi-Wentzel rule. It is probably the single most important result in all of spectroscopy, for it reflects the rate of excitation (or relaxation) from an initial state, *f* of higher (or lower) energy. Note that

19

since it is impossible for the frequency of a photon to be negative,[19] $g(\hbar\omega) = 0$ for $\omega < 0$, and so Eq. (5.60) indicates that:

- if $E_f > E_i$, then

$$W_{fi} = \frac{2\pi V^2 g(\hbar\omega_{fi})\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar} \qquad (5.61)$$

- if $E_f < E_i$, then $\omega_{fi} < 0$ and

$$W_{fi} = \frac{2\pi V^2 g(-\hbar\omega_{fi})\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar}. \qquad (5.62)$$

In particular, this says that if $\frac{E_f - E_i}{\hbar} = \omega_{fi} > 0$, then

$$W_{fi} = \frac{2\pi V^2 g(\hbar\omega_{fi})\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar} = \frac{2\pi V^2 g(-\hbar\omega_{if})\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar} = W_{if} \qquad (5.63)$$

and so, in the presence of radiation, the rate of "excitation" (absorption) and "deexcitation" (stimulated emission) are predicted to be exactly equal. We will often consider Eq. (5.61) to be the statement of Fermi's Golden rule; the more correct (and thorough) statement (cf. Eq. (5.60)) is important when both stimulated emission and absorption are being studied at the same time.

5. Higher-Order Perturbation theory, Revisited.

With the preceding analysis, we can now revisit the effects of higher-order perturbation theory. Using Eq. (5.52) in Eq. (5.47) allows us to simplify our expression for the second-order perturbation coefficient. Specifically,

$$
\begin{aligned}
c_g^{(2)}(t) &= \frac{-4V^2}{\hbar^2}\sum_{k=0}^{\infty}\left\langle\Phi_g\left|\hat{\mu}_x\right|\Phi_k\right\rangle\left\langle\Phi_k\left|\hat{\mu}_x\right|\Phi_i\right\rangle\int_0^t\int_0^{\tau_1}\sin\omega\tau_1\sin(\omega\tau_2)e^{i\omega_{gk}\tau_1 + i\omega_{ki}\tau_2}d\tau_2 d\tau_1 \\
&= \frac{-2iV^2}{\hbar^2}\sum_{k=0}^{\infty}\left\langle\Phi_g\left|\hat{\mu}_x\right|\Phi_k\right\rangle\left\langle\Phi_k\left|\hat{\mu}_x\right|\Phi_i\right\rangle\int_0^t e^{i\omega_{gk}\tau_1}\sin\omega\tau_1\int_0^{\tau_1}\frac{2}{i}\sin(\omega\tau_2)e^{i\omega_{ki}\tau_2}d\tau_2 d\tau_1 \qquad (5.64) \\
&= \frac{V^2}{\hbar^2}\sum_{k=0}^{\infty}\left\langle\Phi_g\left|\hat{\mu}_x\right|\Phi_k\right\rangle\left\langle\Phi_k\left|\hat{\mu}_x\right|\Phi_i\right\rangle\int_0^t\frac{2}{i}e^{i\omega_{gk}\tau_1}\sin\omega\tau_1\left[\begin{matrix}-\tau_1 e^{i(\omega_{fi}+\omega)\tau_1/2}\mathrm{sinc}\left((\omega_{fi}+\omega)\tau_1/2\right)\\ +\tau_1 e^{i(\omega_{fi}-\omega)\tau_1/2}\mathrm{sinc}\left((\omega_{fi}-\omega)\tau_1/2\right)\end{matrix}\right]d\tau_1
\end{aligned}
$$

Simplifying the integral, we obtain

---

[19]   But see note 22 to find out that a negative frequency can, in fact, be interpreted.

$$\int_0^t \frac{2}{i} e^{i\omega_{gk}\tau_1} \sin\omega\tau_1 \begin{pmatrix} -\tau_1 e^{i(\omega_{ki}+\omega)^{\tau_1}/2}\text{sinc}\left((\omega_{ki}+\omega)^{\tau_1}/2\right) \\ +\tau_1 e^{i(\omega_{ki}-\omega)^{\tau_1}/2}\text{sinc}\left((\omega_{ki}-\omega)^{\tau_1}/2\right) \end{pmatrix} d\tau_1$$

$$= \int_0^t \frac{2}{i} e^{i\omega_{gk}\tau_1}\left(\frac{e^{i\omega\tau_1}-e^{-i\omega\tau_1}}{2i}\right)\begin{pmatrix} -\tau_1 e^{i(\omega_{ki}+\omega)^{\tau_1}/2}\dfrac{e^{i(\omega_{ki}+\omega)^{\tau_1}/2}-e^{-i(\omega_{ki}+\omega)^{\tau_1}/2}}{2i(\omega_{fi}+\omega)^{\tau_1}/2} \\[2mm] +\tau_1 e^{i(\omega_{ki}-\omega)^{\tau_1}/2}\dfrac{e^{i(\omega_{ki}-\omega)^{\tau_1}/2}-e^{-i(\omega_{ki}-\omega)^{\tau_1}/2}}{2i(\omega_{ki}-\omega)^{\tau_1}/2} \end{pmatrix} d\tau_1$$

$$= \int_0^t \frac{2}{i} e^{i\omega_{gk}\tau_1}\left(\frac{e^{i\omega\tau_1}-e^{-i\omega\tau_1}}{2i}\right)\begin{pmatrix} -e^{i(\omega_{ki}+\omega)^{\tau_1}/2}\dfrac{e^{i(\omega_{ki}+\omega)^{\tau_1}/2}-e^{-i(\omega_{ki}+\omega)^{\tau_1}/2}}{i(\omega_{ki}+\omega)} \\[2mm] +e^{i(\omega_{ki}-\omega)^{\tau_1}/2}\dfrac{e^{i(\omega_{ki}-\omega)^{\tau_1}/2}-e^{-i(\omega_{ki}-\omega)^{\tau_1}/2}}{i(\omega_{ki}-\omega)} \end{pmatrix} d\tau_1$$

$$= -\int_0^t \left(e^{i(\omega_{gk}+\omega)\tau_1}-e^{i(\omega_{gk}-\omega)\tau_1}\right)\left(-\frac{e^{i(\omega_{ki}+\omega)\tau_1}-1}{i(\omega_{ki}+\omega)}+\frac{e^{i(\omega_{ki}-\omega)\tau_1}-1}{i(\omega_{ki}-\omega)}\right) d\tau_1$$

$$= -\int_0^t \begin{pmatrix} -\dfrac{e^{i(\omega_{gk}+\omega_{ki}+2\omega)\tau_1}-e^{i(\omega_{gk}+\omega)\tau_1}}{i(\omega_{ki}+\omega)}+\dfrac{e^{i(\omega_{gk}+\omega_{ki})\tau_1}-e^{i(\omega_{gk}-\omega)\tau_1}}{i(\omega_{ki}+\omega)} \\[3mm] +\dfrac{e^{i(\omega_{ki}+\omega_{gk})\tau_1}-e^{i(\omega_{gk}+\omega)\tau_1}}{i(\omega_{ki}-\omega)}-\dfrac{e^{i(\omega_{ki}+\omega_{gk}-2\omega)\tau_1}-e^{i(\omega_{gk}-\omega)\tau_1}}{i(\omega_{ki}-\omega)} \end{pmatrix} d\tau_1$$

$$= -\begin{pmatrix} -\dfrac{e^{i(\omega_{gk}+\omega_{ki}+2\omega)t}-1}{i(\omega_{gk}+\omega_{ki}+2\omega)i(\omega_{ki}+\omega)}+\dfrac{e^{i(\omega_{gk}+\omega)t}-1}{i(\omega_{gk}+\omega)i(\omega_{ki}+\omega)} \\[3mm] +\dfrac{e^{i(\omega_{gk}+\omega_{ki})t}-1}{i(\omega_{gk}+\omega_{ki})i(\omega_{ki}+\omega)}-\dfrac{e^{i(\omega_{gk}-\omega)t}-1}{i(\omega_{gk}-\omega)i(\omega_{ki}+\omega)} \\[3mm] +\dfrac{e^{i(\omega_{ki}+\omega_{gk})t}-1}{i(\omega_{ki}+\omega_{gk})i(\omega_{ki}-\omega)}-\dfrac{e^{i(\omega_{gk}+\omega)t}-1}{i(\omega_{gk}+\omega)i(\omega_{ki}-\omega)} \\[3mm] -\dfrac{e^{i(\omega_{ki}+\omega_{gk}-2\omega)t}-1}{i(\omega_{ki}+\omega_{gk}-2\omega)i(\omega_{ki}-\omega)}+\dfrac{e^{i(\omega_{gk}-\omega)t}-1}{i(\omega_{gk}-\omega)i(\omega_{ki}-\omega)} \end{pmatrix}$$

$$= \begin{pmatrix} -\dfrac{e^{i(\omega_{gk}+\omega_{ki}+2\omega)t}-1}{(\omega_{gk}+\omega_{ki}+2\omega)(\omega_{ki}+\omega)}-\dfrac{e^{i(\omega_{ki}+\omega_{gk}-2\omega)t}-1}{(\omega_{ki}+\omega_{gk}-2\omega)(\omega_{ki}-\omega)} \\[3mm] +\dfrac{e^{i(\omega_{gk}+\omega)t}-1}{(\omega_{gk}+\omega)(\omega_{ki}+\omega)}-\dfrac{e^{i(\omega_{gk}-\omega)t}-1}{(\omega_{gk}-\omega)(\omega_{ki}+\omega)} \\[3mm] +\dfrac{e^{i(\omega_{gk}-\omega)t}-1}{(\omega_{gk}-\omega)(\omega_{ki}-\omega)}-\dfrac{e^{i(\omega_{gk}+\omega)t}-1}{(\omega_{gk}+\omega)(\omega_{ki}-\omega)} \\[3mm] +\dfrac{e^{i(\omega_{gk}+\omega_{ki})t}-1}{(\omega_{gk}+\omega_{ki})(\omega_{ki}+\omega)}+\dfrac{e^{i(\omega_{ki}+\omega_{gk})t}-1}{(\omega_{ki}+\omega_{gk})(\omega_{ki}-\omega)} \end{pmatrix} \quad (5.65)$$

We could simplify this term further, but this is far enough for us to deduce the effect of higher-order perturbation theory:

- The first two terms in Eq. (5.65) are "two-photon" nonlinear processes. They represent the fact that one can stimulate a change from state i to state g with two photons with frequency $\frac{\omega_{gi}}{2}$, as is clear from the fact that $\omega_{gk} + \omega_{ki} = \omega_{gi}$.

- The next two terms are "corrections" to the usual "linear" processes. Note that these corrections are relatively small unless $\omega_{gk} = \pm\omega$ and $\omega_{ki} \approx \pm\omega$. This reflects the fact that when many different molecular excitations have similar frequencies, these processes tend to "resonate" with, and thereby influence, one another.

- The last term can be considered an "excite" + "deexcite" process. That is, the photon excites the molecule to the kth state, which then immediately relaxes to the gth excited state, with $\omega_{kg} \approx \omega_{ki} \approx \omega$. To see what this means, suppose we have a system prepared in a state i, which is nearly degenerate with another state g. If one shines a light on the system that can excite the system to the kth state $\omega = \pm\omega_{ki}$, then one will begin to populate the gth state.

In practice, the first effect is sometimes noticeable, since it allows transitions that would not otherwise be observed. The second effect does not serve to "allow" new transitions, but merely causes an adjustment in the intensity of existing transitions—it is usually difficult to perceive this shift, because there are other approximations in this theory. The third effect is difficult to see without measuring the coincidence of the incident and emitted photons (spontaneous decay competes very effectively with the "deexcitation" stage of the process). However, if we measure the incident and the "scattered" (emitted) light, then we say we are observing a resonant Raman spectrum of the molecule. When the incident light has a higher frequency than the scattered light $\left(\omega_{kg} < \omega_{ki}\right)$ we say we are observing Stokes scattering; when the scattered light has higher frequency that the incident light $\left(\omega_{kg} > \omega_{ki}\right)$ we say we are observing Anti-Stokes scattering.
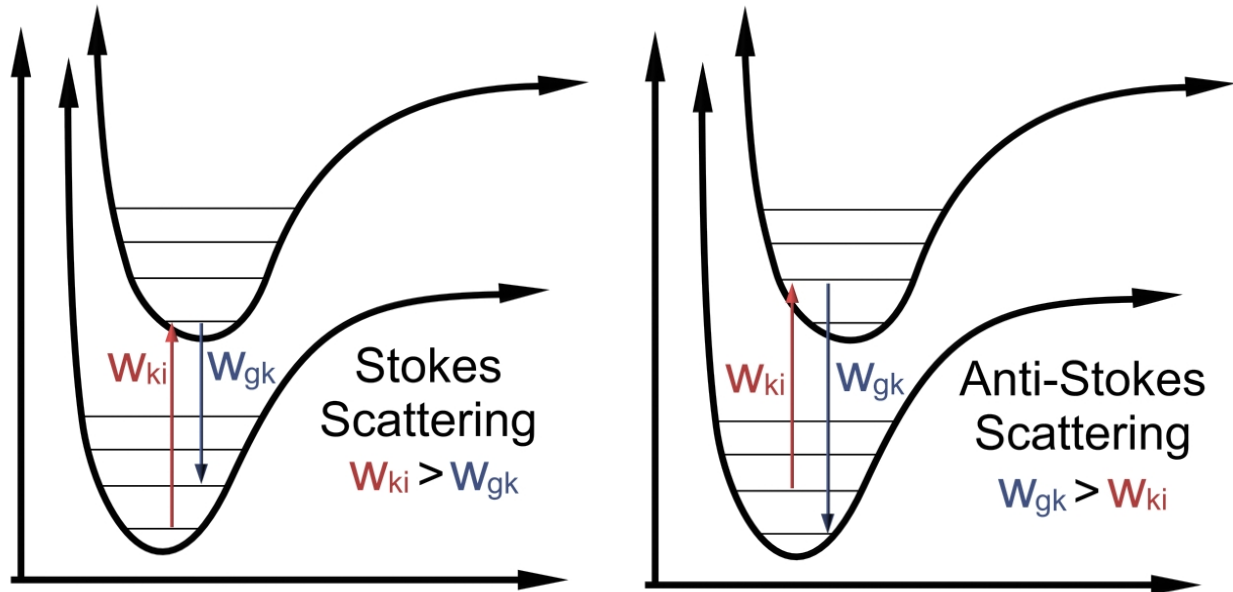
Figure 5.4. Resonance Raman and the Stokes and Anti-Stokes spectral lines

By the same sorts of arguments, we surmise that the primary importance of ever-higher orders of perturbation theory is the fact that we can stimulate transitions with $\omega_{fi} = \pm n\omega$, where n is the order of perturbation theory under consideration. Sometimes three-photon processes are important, but I am not aware of any useful applications of four (or more)-photon transitions.

In the limit where the frequency of the radiation is zero $\omega \to 0$, the change in energy observed becomes the static (dipole) polarizability when the long-wavelength approximation is used, with the leading order "short-wavelength corrections" being be the magnetic (dipole) susceptibility and the electric quadrupole polarizability. Higher-order terms in the perturbation series, unsurprisingly, allow one to compute various hyperpolarizabilities of the molecule.

6. Interpreting Fermi's Golden Rule

Before proceeding any further, we should examine Fermi's Golden rule in more detail. First of all, from

$$W_{fi} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar} \tag{5.66}$$

we see that the transition rate is faster when square magnitude of the incident field, $V^2 g(\hbar\omega)$, is larger. In addition, we conclude that no transitions occur if the dipole matrix element is equal to zero, so observing a high-intensity transition suggests that

$$\left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \equiv \left\langle \Phi_f \left| \sum_{i=1}^{N} -ex_i + \sum_{\alpha=1}^{P} Z_\alpha e X_i \right| \Phi_i \right\rangle \neq 0 \,. \tag{5.67}$$

When Eq. (5.67) is satisfied, we say that a given transition is allowed or, sometimes "dipole-allowed" or "E1-allowed." Sometimes the intensities of spectral lines in terms of their oscillator strengths,

$$f_{if} = \frac{2 m_e \omega_{fi} \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2}{3 e^2 \hbar} \tag{5.68}$$

When $\left\langle \psi_f \left| \hat{\mu}_x \right| \psi_i \right\rangle = 0$, the rate of excitation, W_{fi} is much slower. W_{fi} is not quite zero, however, because there are other terms, though, corresponding to the magnetic dipole,

$$W_{fi}^{\substack{\text{magnetic} \\ \text{dipole}}} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right) k^2 \left| \left\langle \Phi_f \left| \sum_{i=1}^{N} \beta_e \hat{L}_y\left(\boldsymbol{r}_i\right) + \sum_{\alpha=1}^{P} \frac{\beta_e}{M_\alpha} \hat{L}_y\left(\boldsymbol{R}_\alpha\right) \right| \Phi_i \right\rangle \right|^2}{\hbar} \tag{5.69}$$

and electric quadrupole,

$$W_{fi}^{\substack{\text{electric} \\ \text{quadrupole}}} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right) k^2 \left| \left\langle \Phi_f \left| \sum_{i=1}^{N} ex_i z_i + \sum_{\alpha=1}^{P} -Z_\alpha e\left(x_\alpha z_\alpha\right) \right| \Phi_i \right\rangle \right|^2}{\hbar} \tag{5.70}$$

transitions. See the discussion following Eq. (5.14) and, in particular, footnote 6. (I may be missing a factor of two in Eqs. (5.69) and (5.70), but the crucial dependences are there.) For UV-visible spectroscopy, magnetic dipole transitions tend to occur about ten thousand times more slowly than electric dipole transitions, and electric quadrupole transitions tend to occur about a hundred million times more slowly than dipole transitions. Such contributions to the spectra are usually negligible when the dipole transition is allowed. (That is, Eq. (5.67) is true.) In addition, nonlinear processes are sometimes of similar importance to the magnetic dipole and (especially) the electric quadrupole transitions.

Another interesting line of inquiry relates to the mechanism of excitation. That is, before the molecule is irradiated, it is in state i with wave function $\Psi_i = \Phi_i e^{-iE_i t/\hbar}$. After the molecule is irradiated, it will be (with any luck) in the state f, with wave function $\Psi_f = \Phi_f e^{-iE_f t/\hbar}$. What does the molecule look like during the excitation process, that is,

what does the molecule look like when it is "between" the initial and final state, or does it just "jump" discontinuously from one state to another?

Answering this question requires a quantum treatment of light. In particular, during the process of excitation, the molecule is not "isolated", and so to treat the actual process of excitation we must write the wave function for the molecule *and* the exciting photon. Perhaps some of you (or perhaps I am just a bit weird) remember playing with a garden hose when you were little. You can, by flailing the garden hose about, cause the garden hose to make a single sweeping arc between you—say, drenching your unsuspecting sister—and the faucet. Experimenting a bit, you can learn how to make the garden hose make two arcs (a complete wave length), three arcs, etc.. If you let the "number of arcs" represent the "state" of the garden hose, then you can see that, by flailing around on the "action" end of the hose, you can "change the state" of the garden hose. Now, what is the state of the garden hose in the intermediate state? Well, it is complicated—somewhere between the initial and final state—but one thing is certain, a complete description of what is happening to the garden hose during the course of the "transition" cannot be made by merely describing the hose: you must also include the way you are flailing your arms about. Similarly, to describe what happens "during the transition" from one state of a system to another, you must describe both the molecule and the photon that is coupled to it, inducing the transition.

7. Selection Rules

For atoms and small, symmetric, molecules, one can construct "selection rules" to tell one when the rate of a transition is zero. For example, for an atom, the selection rules for a transition from a state with quantum numbers L, S, J, M_J to a state with $L', S', J', M_J{}'$ are

- An electric dipole transition is allowed, that is,

$$\left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 > 0 \tag{5.71}$$

   if

   (a) $L - L' = 0, \pm 1$ but $\Delta l \neq 0$ for the electron that jumps and $L = 0 \to L' = 0$ transitions are forbidden

   (b) $\Delta S = 0$. Once spin-orbit coupling becomes important, these transitions are allowed. In fact, for heavy atoms the spin-forbidden transitions can be quite

important. One of the characteristic UV-spectral lines for Hg is the $^3P_1 \to {}^1S_0$ transition. However, to the best of my knowledge, there are no cases where the spin-forbidden transitions are stronger than the corresponding spin-allowed transition. For example, while the $^3P_1 \to {}^1S_0$ transition in mercury is quite intense, the $^1P_1 \to {}^1S_0$ is even stronger.

(c) $J - J' = 0, \pm 1$ but $J = 0 \to J' = 0$ is forbidden.

The electic-dipole selection rules are often called the "E1" selection rules.

- A magnetic dipole transition is allowed, that is,

$$\left| \left\langle \Phi_f \left| \sum_{i=1}^{N} \beta_e \hat{L}_y(\boldsymbol{r}_i) + \sum_{\alpha=1}^{P} \frac{\beta_e}{M_\alpha} \hat{L}_y(\boldsymbol{R}_\alpha) \right| \Phi_i \right\rangle \right|^2 > 0 , \tag{5.72}$$

if

(a) $J - J' = 0, \pm 1$ but $J = 0 \to J' = 0$ is forbidden.

(b) $\Delta S = 0$. Once spin-orbit coupling becomes important, these transitions are allowed.

The magnetic-dipole selection rules are often called the "M1" selection rules.

- A electric quadrupole transition is allowed, that is,

$$\left| \left\langle \Phi_f \left| \sum_{i=1}^{N} e x_i z_i + \sum_{\alpha=1}^{P} -Z_\alpha e \left(x_\alpha z_\alpha \right) \right| \Phi_i \right\rangle \right|^2 > 0 \tag{5.73}$$

if

(a) $L - L' = 0, \pm 1, \pm 2$.

(b) $\Delta S = 0$. Once spin-orbit coupling becomes important, these transitions are allowed.

(c) $J - J' = 0, \pm 1, \pm 2$.

The electric-quadrupole selection rules are often called the "E2" selection rules.

As already mentioned, the most important case is the electric dipole transition. For an atom, we can think about these transitions by noting that the dipole operator can be written as a sum of the first-order spherical harmonics, $Y_1^M(\theta, \phi)$. Similarly, the total wave function of an atom with good-quantum numbers L, M_L or J, M_J has an angular dependence similar to $Y_L^{M_L}$ or $Y_J^{M_J}$.[20] Thus

---

[20]   These are not "proper" spherical harmonics but the eigenfunctions of $\hat{J}^2$ and $\hat{J}_z$ (or $\hat{L}^2$ and $\hat{L}_z$) for an N-electron atom. However, these are still angular-momentum-type states, and they still follow the same orthonormality rules. This is what is intimated by Eq. (5.74).

$$\left\langle Y_{L'}^{M} \left| Y_{1}^{M} \right| Y_{L}^{M} \right\rangle = 0 \tag{5.74}$$

unless $L - L' = \pm 1$. The $\Delta L = 0$ case is more difficult to explain, but is exemplified by the fact that because promoting an electron from an s-orbital to a p-orbital should be allowed (since $\left\langle Y_{0}^{0} \left| Y_{1}^{m} \right| Y_{1}^{m} \right\rangle = 1$), the transition from the ^{3}P term associated with an $s^{1}p^{1}$ configuration to the ^{3}P term associated with an p^{2} configuration should be allowed.

Of course, most systems are not as easy to picture as an atom, and so it is helpful to develop some general rules of thumb for what constitutes an allowed transition.

- Suppose the orbital-model is valid. Consider exciting two-electrons from the initial state's Slater determinant, $\Phi_{i} = \left| \psi_{1} \psi_{2} \ldots \psi_{N} \right|$, to the final state's Slater determinant, $\Phi_{f} = \left| \psi_{1} \psi_{2} \ldots \psi_{N-2} \psi_{m} \psi_{l} \right|$. This transition will be strongly forbidden, because the orthogonality of the orbitals means that integrals like[21]

$$\begin{aligned}
\left\langle \Phi_{f} \left| \hat{\mu}_{x} \right| \Phi_{i} \right\rangle &= \left\langle \left| \psi_{1} \psi_{2} \ldots \psi_{N-2} \psi_{m} \psi_{l} \right| \left| \hat{\mu}_{x} \right| \left| \psi_{1} \psi_{2} \ldots \psi_{N} \right| \right\rangle \\
&= \left\langle \psi_{m} \left| \psi_{N-1} \right\rangle \left\langle \psi_{1} \psi_{2} \ldots \psi_{N-2} \psi_{m} \left| \hat{\mu}_{x} \right| \psi_{1} \psi_{2} \ldots \psi_{N} \right\rangle + \text{other similar terms} \\
&= 0
\end{aligned} \tag{5.75}$$

are encountered. (This is one of the *Slater-Condon rules* for evaluating the expectation values of operators with Slater determinants.) In practice, we can observe double-excitations (both because of nonlinear effects (from higher-order perturbation theory) and because the Slater determinant is only an approximate model for the excited-state wave function), but ***multi-electron excitations are generally weak compared to single excitations.*** As a good first approximation, then, the electronic spectrum consists of taking an electron from an occupied molecular orbital and putting it in an unoccupied molecular orbital.[22]

- Because of the previous point, a transition tends to be dipole-allowed when

$$\left| \left\langle \psi_{f} \left| \hat{\mu}_{x} \right| \psi_{i} \right\rangle \right| = \left| \left\langle \psi_{f} \left| -ex \right| \psi_{i} \right\rangle \right| > 0 \tag{5.76}$$

---

[21] To derive this, consider the Slater determinant wave function for the Lithium atom. You can show that a single excitation gives a formula like Eq. (5.76) while a double excitation gives a formula like Eq. (5.75). The formulas here are just the generalization of this to systems with more electrons.

[22] It bears repeating that this only applies for *molecular orbitals*. In the valence-bond theory, excitation from an occupied atomic orbital to an unoccupied atomic orbital is usually *not* a good description of molecular excitation.

where $\psi_i(\boldsymbol{r})$ is the initially occupied orbital and $\psi_f(\boldsymbol{r})$ is the orbital to which the electron is excited. The extension to magnetic-dipole allowed transitions and electric quadrupole transitions is obvious, just replace the dipole operator with $\hat{L}_y$ or xz.

- For atoms and molecules in free space, we cannot specify that it is the x-component of the dipole operator that is relevant. That is, the molecules in the sample will be not be aligned, and so the wave vector (the direction the light waves move) will form different angles to the characteristic molecular axis (for a linear molecule) or axes (for a nonlinear molecule) for different molecules. For this reason, the appropriate dipole transition element is the average,

$$\left\langle \psi_f \left| \tfrac{x+y+z}{3} \right| \psi_i \right\rangle \tag{5.77}$$

For magnetic dipole interactions and electric quadrupole interactions, the appropriate generalization is similar,[23]

$$
\begin{aligned}
&\left\langle \psi_f \left| \frac{\hat{L}_x(\boldsymbol{r}) + \hat{L}_y(\boldsymbol{r}) + \hat{L}_z(\boldsymbol{r})}{3} \right| \psi_i \right\rangle && \text{magnetic dipole} \\
&\left\langle \psi_f \left| \frac{\frac{x^2-y^2}{\sqrt{2}} + \frac{2z^2-x^2-y^2}{\sqrt{6}} + xy + xz + yz}{5} \right| \psi_i \right\rangle && \text{electric quadrupole}
\end{aligned}
\tag{5.78}
$$

Sometimes one uses either a molecular beam or a static electric (or magnetic) field to fix the orientation of the molecules. In this case, the angle between the molecular axes and the light waves is fixed, and the original formulae (cf. Eqs. (5.66), (5.69), and (5.70)) are appropriate. In general, for molecules in the gas phase or solution in the absence of any external field except the light, Eqs. (5.77) and (5.78) are more appropriate.

- For the important case of a dipole transition, we can often analyze the situation pictorially. That is, draw the starting orbital and the ending orbital. Can one impose a dipole field and "shove the starting orbital towards the ending orbital"? (There is a group-theoretic way to do this, but in complicated polyatomic molecules, where there is usually no symmetry, this is still a useful approach for discerning whether a transition is "essentially allowed" or "almost forbidden". For example, a transition from an s-orbital to a p-orbital is clearly

---

[23] If I were you, I wouldn't trust this result on the electric quadrupole transition. It seems right, but who knows.

allowed, as is the transition from a *p*-orbital to a *d*-orbital, the transition from a σ-orbital to a π orbital, and the transition from a σ orbital to a σ^* (σ-antibonding) orbital. However, the transition from a σ-orbital to a π^* orbital is forbidden (but quadrupole allowed). In a heteronuclear diatomic, the transition from a σ-orbital to a π^* orbital is allowed, but the associated absorbance is expected to be rather weak.

The basic idea here follows from Eq. (5.77). We will have that

$$\left| \left\langle \psi_f \left| \frac{x+y+z}{3} \right| \psi_i \right\rangle \right| = \left| \int \psi_f^*(\boldsymbol{r}) \psi_i(\boldsymbol{r}) \left(\frac{x+y+z}{3} \right) d\boldsymbol{r} \right| > 0 \qquad (5.79)$$

only if the product of the initial and final orbitals, $\psi_f^*(\boldsymbol{r}) \psi_i(\boldsymbol{r})$, resembles one of the Cartesian coordinates. In group theoretic language, $\psi_f^*(\boldsymbol{r}) \psi_i(\boldsymbol{r})$, must transform as one of the Cartesian coordinates; this means, effectively, that $\psi_f^*(\boldsymbol{r}) \psi_i(\boldsymbol{r})$ must resemble a *p*-orbital (in the sense that it must be "polarized") in some direction, with the positive portions of $\psi_f^*(\boldsymbol{r}) \psi_i(\boldsymbol{r})$ on one side of the system and the negative portions on the other side.

There is a group theoretic way of doing this. Simply take the character of the initial and final states, and multiply them together to find how the product of the orbital transforms. If the product of the orbitals transforms according to one of the Cartesian coordinates, the transition is electric dipole allowed. If it transforms like the rotation about some axis, the transition is magnetic dipole allowed. If it transforms like one of the *d*-orbitals (products of two Cartesian coordinates), then the transitions is electric quadrupole allowed.

The most useful technique, however, is probably the "multiplying orbitals" pictorial technique on the next page. This allows one to evaluate whether a transition is allowed and, based on the magnitude and extent of polarization of the product wave function, the intensity of the transition can also be estimated. Moreover, this technique is applicable even in asymmetric molecules, where there is often "approximate symmetry" (and thus approximately forbidden transitions) but, based on group theory, every transition is allowed. Finally, this method directly reflects the physical significance of what one is doing and ensures that, even if you are stranded on a desert island without your inorganic chemistry textbook, you'll be able to do your quantum mechanics homework.
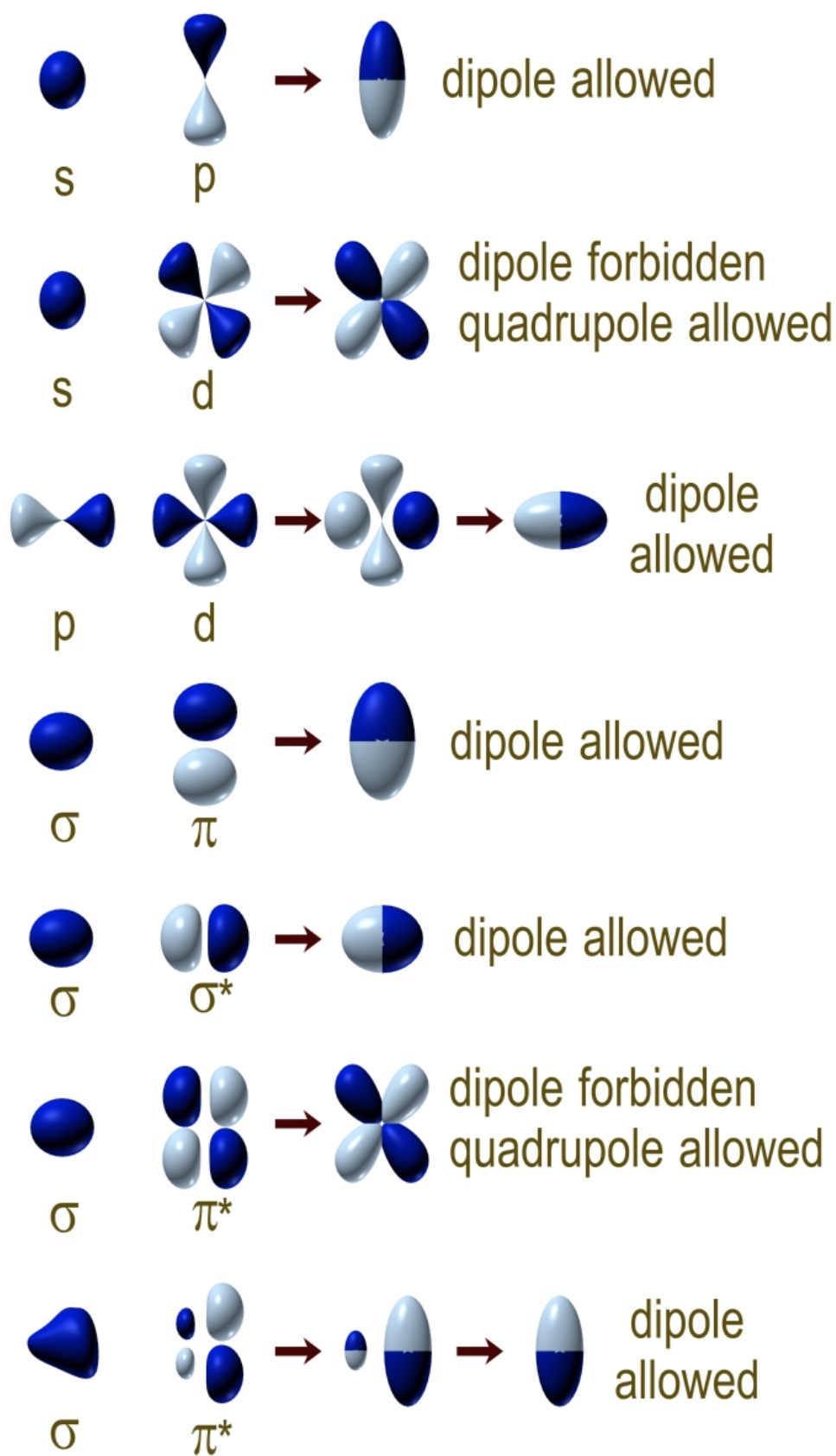
Figure 5.5. How to use "sketches" of orbitals to determine dipole (E1) selection rules.

8. Rovibrational Structure and Molecular Electronic Spectra

When high-resolution electronic spectra are taken, one frequently observes not a single line for each transition, but a progression of lines associated with the different rovibration states of the Hamiltonian.
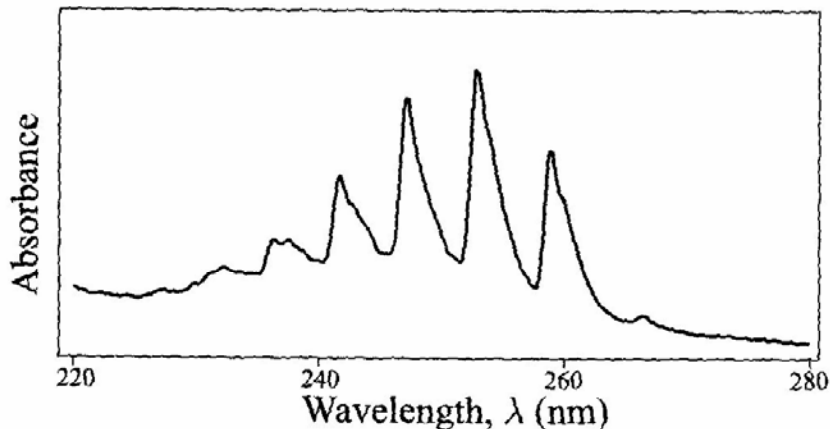

Figure 11.1. Electronic absorption spectrum of benzene in $CHCl_3$ solution, courtesy of Ron Mallery, Department of Chemistry, University of Idaho.

Figure 5.6. From <u>Molecular Spectroscopy</u> by Jeanne L. McHale (Prentice Hall, New Jersey, 1999).

We want to explain the presence and interpretation of the "fine structure" in these spectra.

Unsurprisingly, our starting point is Fermi's Golden Rule,

$$W_{fi} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)\left|\left\langle \Phi_f \left|\hat{\mu}_x\right| \Phi_i \right\rangle\right|^2}{\hbar}$$

$$= \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)\left|\left\langle \Phi_f \left|\sum_{j=1}^{N} -ex_j + \sum_{\alpha=1}^{P} Z_\alpha e X_\alpha\right| \Phi_i \right\rangle\right|^2}{\hbar} \tag{5.80}$$

Recall, from Eq. (5.25), that Φ_i and Φ_f are eigenfunctions of the molecular Hamiltonian. If we approximate these eigenfunctions using the Born-Oppenheimer approximation, we have that

$$\Phi_{\nu i}\left(\boldsymbol{r}_1,...,\boldsymbol{r}_N;\boldsymbol{R}_1,...,\boldsymbol{R}_P\right) = \xi_i\left(\boldsymbol{r}_1,...,\boldsymbol{r}_N;\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)\chi_{\nu i}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right) \tag{5.81}$$

where the electronic wave functions, $\xi_i\left(\boldsymbol{r}_1,...,\boldsymbol{r}_N;\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)$, are obtained by solving the electronic Schrödinger equation for a specific, fixed, position for the atomic nuclei:

$$
\begin{aligned}
&\left(\sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2+\sum_{\alpha=1}^{P}-\frac{Z_\alpha}{\left|\boldsymbol{r}_i-\boldsymbol{R}_\alpha\right|}\right)+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{1}{\left|\boldsymbol{r}_i-\boldsymbol{r}_j\right|}\right.\\
&\left.+\sum_{\alpha=1}^{P}\sum_{\beta=\alpha+1}^{P}\frac{Z_\alpha Z_\beta}{\left|\boldsymbol{R}_\alpha-\boldsymbol{R}_\beta\right|}\right)\xi_i\left(\boldsymbol{r}_1,...,\boldsymbol{r}_N;\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)\\
&\qquad\qquad=U_i^{BO}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)\xi_i\left(\boldsymbol{r}_1,...,\boldsymbol{r}_N;\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)
\end{aligned}
\tag{5.82}
$$

and the different eigenfunctions of Eq. (5.82) are orthogonal in the sense that

$$
\begin{aligned}
\delta_{mn}&=\left\langle\xi_m\left|\xi_n\right.\right\rangle_{r_1...r_N}\\
&\equiv\iiint\cdots\int\xi_m^*\left(\boldsymbol{r}_1,...,\boldsymbol{r}_N;\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)\xi_m\left(\boldsymbol{r}_1,...,\boldsymbol{r}_N;\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)d\boldsymbol{r}_1...d\boldsymbol{r}_N
\end{aligned}
\tag{5.83}
$$

The notation on the bra-ket in the first line of Eq. (5.83) denotes the fact only the electronic coordinates are treated as variables for integration: consistent with the Born-Oppenheimer approximation, for the purposes of the *electronic* wave function, the nuclei are considered to be fixed.

The nuclear wave functions represent the rovibrational states of the molecule, and, in the Born-Oppenheimer approximation, are obtained by solving

$$
\left(\sum_{\alpha=1}^{P}-\frac{1}{2M_\alpha}\nabla_\alpha^2+U_i^{BO}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)\right)\chi_{\nu i}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)=E_{\nu i}^{BO}\chi_{\nu i}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)
\tag{5.84}
$$

Owing to the form of Eq. (5.84), we see that

$$
\delta_{\nu\mu}=\left\langle\chi_{\nu i}\left|\chi_{\mu i}\right.\right\rangle
\tag{5.85}
$$

but that, in general,

$$
\left\langle\chi_{\mu f}\left|\chi_{\nu i}\right.\right\rangle\neq 0
\tag{5.86}
$$

because $\chi_{\mu f}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)$ and $\chi_{\nu i}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)$ are eigenfunctions of differerent Hamiltonians (cf. Eq. (5.84)) because the potential energy surfaces for the initial electronic state, $U_i^{BO}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)$, and final electronic state, $U_f^{BO}\left(\boldsymbol{R}_1,...,\boldsymbol{R}_P\right)$, are different.

Using these results, we now reexamine Fermi's golden rule, examining what transitions will be allowed. We have

$$
\begin{aligned}
W_{\mu f;\nu i} &= \frac{2\pi V^2 g\left(\hbar\omega_{\mu f,\nu i}\right)\left|\left\langle \Phi_{\mu f}\left|\sum_{i=1}^{N}-ex_i + \sum_{\alpha=1}^{P}Z_\alpha eX_i\right|\Phi_{\nu i}\right\rangle\right|^2}{\hbar} \\
&= \frac{2\pi V^2 g\left(\hbar\omega_{\mu f,\nu i}\right)}{\hbar}\left|\left\langle \chi_{\mu f}\xi_f\left|\sum_{i=1}^{N}-ex_i\right|\chi_{\nu i}\xi_i\right\rangle + \left\langle \chi_{\mu f}\xi_f\left|\sum_{\alpha=1}^{P}Z_\alpha eX_i\right|\chi_{\nu i}\xi_i\right\rangle\right|^2 \\
&= \frac{2\pi V^2 g\left(\hbar\omega_{\mu f,\nu i}\right)}{\hbar}\left|\left\langle \chi_{\mu f}\xi_f\left|\sum_{i=1}^{N}-ex_i\right|\chi_{\nu i}\xi_i\right\rangle + \left\langle \xi_f|\xi_i\right\rangle_{r_1\dots r_N}\left\langle \chi_{\mu f}\left|\sum_{\alpha=1}^{P}Z_\alpha eX_i\right|\chi_{\nu i}\right\rangle\right|^2 \\
&= \frac{2\pi V^2 g\left(\hbar\omega_{\mu f,\nu i}\right)}{\hbar}\left|\left\langle \chi_{\mu f}\xi_f\left|\sum_{i=1}^{N}-ex_i\right|\chi_{\nu i}\xi_i\right\rangle + \delta_{if}\left\langle \chi_{\mu f}\left|\sum_{\alpha=1}^{P}Z_\alpha eX_i\right|\chi_{\nu i}\right\rangle\right|^2
\end{aligned}
\tag{5.87}
$$

In particular, the second term vanishes if the initial and final electron states are different. (The case where $i = f$ leads to the dipole selection rules for rotational and vibrational spectra, as here the first term is zero (because the integral of an odd function is always zero).) Restricting ourselves to electronic excitations, we definite the nuclear transition dipole with[24]

$$
\begin{aligned}
\mu_{fi}\left(\boldsymbol{R}_1,\dots,\boldsymbol{R}_P\right) &= \left\langle \xi_f\left|\sum_{i=1}^{N}-ex_i\right|\xi_i\right\rangle_{r_1\dots r_N} \\
&\equiv \iiint\cdots\int \xi_f^*\left(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N;\boldsymbol{R}_1,\dots,\boldsymbol{R}_P\right)\left(\sum_{i=1}^{N}-ex_i\right)\xi_i^*\left(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N;\boldsymbol{R}_1,\dots,\boldsymbol{R}_P\right)d\boldsymbol{r}_1\dots d\boldsymbol{r}_N.
\end{aligned}
\tag{5.88}
$$

The transition rate, then, can be expressed as

$$
W_{\mu f;\nu i} = \frac{2\pi V^2 g\left(\hbar\omega_{\mu f,\nu i}\right)}{\hbar}\left|\left\langle \chi_{\mu f}\left|\mu_{fi}\left(\boldsymbol{R}_1,\dots\boldsymbol{R}_P\right)\right|\chi_{\nu i}\right\rangle\right|^2
\tag{5.89}
$$

Because the electrons move much faster than the nuclei and because electronic excitation occurs rapidly compared to most vibrational motions,[25] the geometry does not change during the process of electronic excitation, for this reason we typically draw the excitation process as follows, with the "vertical line" taking the most probably molecular geometry in the ground state to the potential energy surface appropriate to the excited state. This is often called a "vertical transition".

---

[24]   If, as is common, the molecules are randomly oriented, then

$$
\mu_{fi}\left(\boldsymbol{R}_1,\dots,\boldsymbol{R}_P\right) = \left\langle \xi_f\left|\sum_{i=1}^{N}-e\cdot\frac{x_i+y_i+z_i}{3}\right|\xi_i\right\rangle_{r_1\dots r_N}
$$

See Eq. (5.77).

[25]   As a rule, the time it takes for the electronic transition to occur is about 10-100 times less than a typical vibrational period.
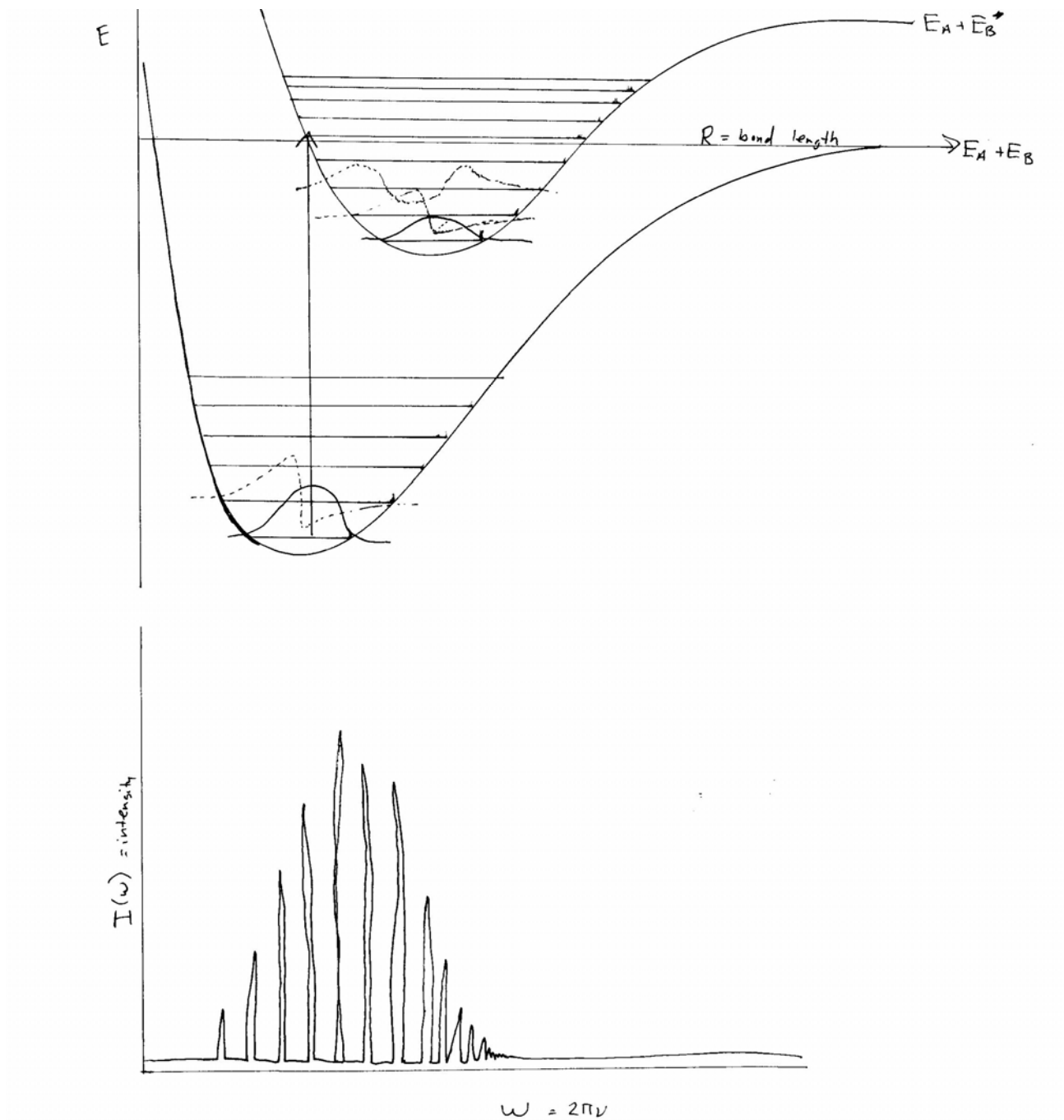
Figure 5.7: Schematic of the process of electronic excitation for a diatomic molecule. The curves denote the potential energy surfaces in the Born-Oppenheimer approximation, and the lines denote vibrational energy levels. A vibrationally resolved "spectrum" is sketched below the curve.

Since the positions of the nuclei will not change much during the process of excitation, we expand the nuclear transition dipole as a Taylor series about the equilibrium configuration of the nuclei in the initial state, $\left(\mathbf{R}_1^{(i)}, \mathbf{R}_2^{(i)}, ..., \mathbf{R}_P^{(i)} \right)$:

$$\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1,\ldots,\boldsymbol{R}_P\right) = \boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right) + \sum_{\alpha=1}^{P}\left(\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{(i)}\right)\cdot\nabla_\alpha\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\ldots\boldsymbol{R}_P^{(i)}\right) + \ldots \tag{5.90}$$

Inserting the Taylor series into Eq. (5.89), we find that

$$
\begin{aligned}
W_{\mu f;\nu i} &= \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)}{\hbar}\left| \begin{array}{l} \left\langle\chi_{\mu f}\left|\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\boldsymbol{R}_2^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right)\right|\chi_{\nu i}\right\rangle \\ +\left\langle\chi_{\mu f}\left|\sum_{\alpha=1}^{P}\left(\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{(i)}\right)\cdot\nabla_\alpha\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\boldsymbol{R}_2^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right)\right|\chi_{\nu i}\right\rangle + \ldots \end{array}\right|^2 \\
&= \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)}{\hbar}\left|\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\boldsymbol{R}_2^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right)\right|^2\left|\left\langle\chi_{\mu f}\left|\chi_{\nu i}\right\rangle\right|^2 \\
&\quad + \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)}{\hbar}\left|\sum_{\alpha=1}^{P}\nabla_\alpha\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\boldsymbol{R}_2^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right)\cdot\left\langle\chi_{\mu f}\left|\left(\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{(i)}\right)\right|\chi_{\nu i}\right\rangle\right|^2 \\
&\quad + \frac{4\pi V^2 g\left(\hbar\omega_{fi}\right)}{\hbar}\left(\begin{array}{l}\left|\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\boldsymbol{R}_2^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right)\right|\left|\left\langle\chi_{\mu f}\left|\chi_{\nu i}\right\rangle\right| \\ \times\left|\sum_{\alpha=1}^{P}\nabla_\alpha\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\boldsymbol{R}_2^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right)\cdot\left\langle\chi_{\mu f}\left|\left(\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{(i)}\right)\right|\chi_{\nu i}\right\rangle\right|\end{array}\right)
\end{aligned}
\tag{5.91}
$$

Truncating the expression after the first term in Eq. (5.91) leads to the *Condon approximation*:

$$W_{\mu f;\nu i} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)}{\hbar}\left|\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\boldsymbol{R}_2^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right)\right|^2\left|\left\langle\chi_{\mu f}\left|\chi_{\nu i}\right\rangle\right|^2 \tag{5.92}$$

and the overlap between the rovibrational wave functions of the ground and excited states,

$$F_{\mu f,\nu i} \equiv \left|\left\langle\chi_{\mu f}\left|\chi_{\nu i}\right\rangle\right|^2 \tag{5.93}$$

is called the *Franck-Condon factor*. Note that $\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1^{(i)},\ldots,\boldsymbol{R}_P^{(i)}\right) = 0$ unless the electronic transition is dipole allowed. Sometimes, however, there is intensity even for a dipole-forbidden transition, and this can arise from the subsequent terms in Eq. (5.91), which are said to represent vibronic coupling: the coupling between the electronic excitation with the motion of the nuclei.

In practice, when the Condon approximation, Eq. (5.92), predicts a transition rate appreciably greater than zero, the second term, called the vibronic coupling term, is usually qualitatively unimportant. However, when the Condon approximation predicts that a transition is forbidden (or very weak), the vibronic coupling terms can play an important role. Because the last term in Eq. (5.91) will be zero (or small) whenever Eq. (5.92) is zero (or small), the rate of transition from vibronic coupling is often simply written as

$$W_{\mu f,\nu i}^{vibronic} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)}{\hbar}\left|\left\langle\chi_{\mu f}\left|\sum_{\alpha=1}^{P}\boldsymbol{R}_\alpha\cdot\nabla_\alpha\boldsymbol{\mu}_{fi}\left(\boldsymbol{R}_1,\ldots\boldsymbol{R}_P\right)\right|\chi_{\nu i}\right\rangle\right|^2 \tag{5.94}$$

When Eq. (5.92) is zero but $W_{\mu f, \nu i}^{vibronic}$, or any of the similar equations arising from higher-order terms in the Taylor series, Eq. (5.90), is nonzero, we say that the transition is allowed by vibronic coupling. Vibronic coupling is an important phenomenon, and is related to the lattice distortion in the BCS theory of superconductivity.

To gain further insight, we restrict ourselves to the Condon approximation and consider the simple case of a diatomic molecule. In this case, the nuclear wave function can be (approximately) separated into its vibrational and rotational parts,

$$\chi_{\nu i, lm}(\boldsymbol{R}) = \chi_{\nu i}(R) Y_l^m(\Theta, \Phi) \tag{5.95}$$

where we have chosen, for simplicity, the rigid-rotor as a model of the rotational transitions. Here $\chi_{\nu i}(R)$ are a model for the vibrational states and could, for instance, be taken as eigenfunctions of the harmonic oscillator. Neglecting the rotational transitions, as these are often unresolved in electronic spectra,[26] we see that the transition rate can be written as

$$W_{\mu f; \nu i} = \frac{2\pi V^2 g\left(\hbar \omega_{fi}\right)}{\hbar} \left|\mu_{fi}\left(R^{(i)}\right)\right|^2 \left|\left\langle \chi_{\mu f}(R) \middle| \chi_{\nu i}(R) \right\rangle\right|^2 \tag{5.96}$$

That is, the transition probability is proportional to the square of the "overlap" between the vibrational wave functions of the ground and excited states. Some insight is obtained by applying a harmonic oscillator model to both the ground and excited states, in which case we can compute that

$$\left|\left\langle \chi_{\mu f}(R) \middle| \chi_{0i}(R) \right\rangle\right|^2 = \frac{1}{\mu!} \Phi^\mu e^{-\Phi} \tag{5.97}$$

---

[26]   Rotational transitions follow the same selection rules as in the usual rovibrational case, with P, Q, and R bands. The are always P and R bands, and there is a Q band except for so-called $\Sigma \to \Sigma$ transitions, which result when a molecule with no total angular momentum about the internuclear axis is excited to another state with no angular momentum about the internuclear axis. (Matters are complicated further for non-singlet states, and cases where the multiplicity changes during the excitation (spin-forbidden transitions) because then one must account for the spin-angular momentum of the electrons.) Once one moves beyond the rigid-rotor approximation, which is frequently invalid for electronic excited states (where the bond strength tends to be less, and so the centrifugal distortion and the dependence of the moment of inertia on the vibrational state in question tends to be larger), we find that the spectra become quite cluttered, which is why I've opted only to give the general formula (valid in all cases), Eq. (5.92), and treat the specific case of vibrationally resolved electronic spectroscopy for diatomics, merely as a "example" of the sorts of phenomena one sees. For more on rotationally resolved spectra, the reader could start by reading Herzberg's monograph.

where

$$\Phi \equiv \left(\frac{1}{2\hbar} \sqrt{\frac{k_i + k_f}{2} \frac{m_A m_B}{m_A + m_B}} \right) \left(R^{(f)} - R^{(i)} \right)^2 \qquad (5.98)$$

where k_i and k_f are the force constants in the initial and final states, respectively, m_A and m_B are the mass of atoms A and B, respectively, and R_i and R_f are the equilibrium distances for the initial and final states, respectively. Note that this approximation to the Frank-Condon factor computed here only applies to the case where the ground vibrational state is excited to the μth vibrational excited state of the final electronic state. Also note that it is generally difficult to tell from the Franck-Condon factors alone whether the final state has a shorter or longer bond length than the initial state. (In the harmonic oscillator model in Eq. (5.97) it is, in fact, impossible to tell the difference.)
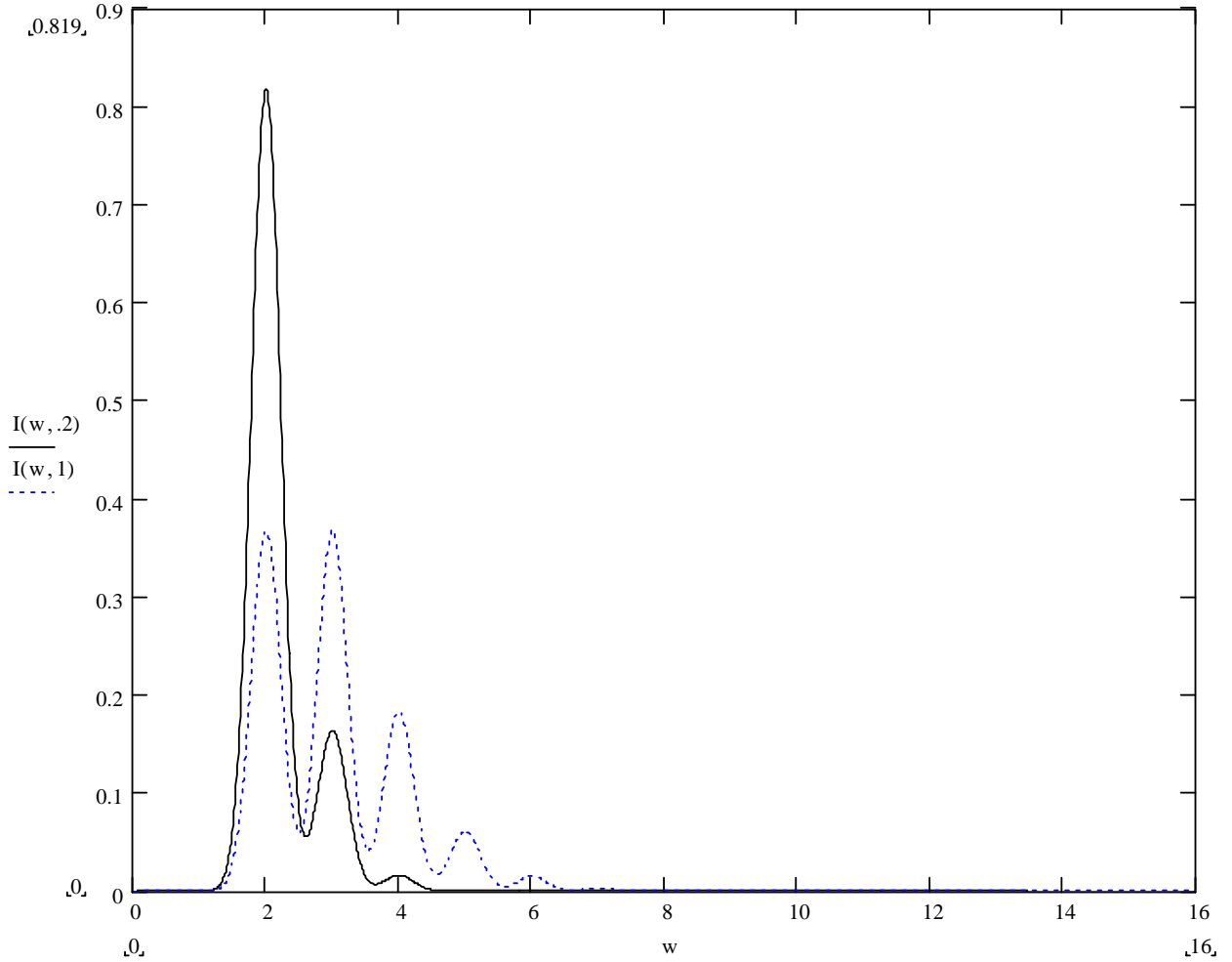

Figure 5.8: Simulated Spectrum (relative absorption vs. frequency) for the case where the bond length in the initial and excited states are very similar (solid line) and less similar (dotted line).
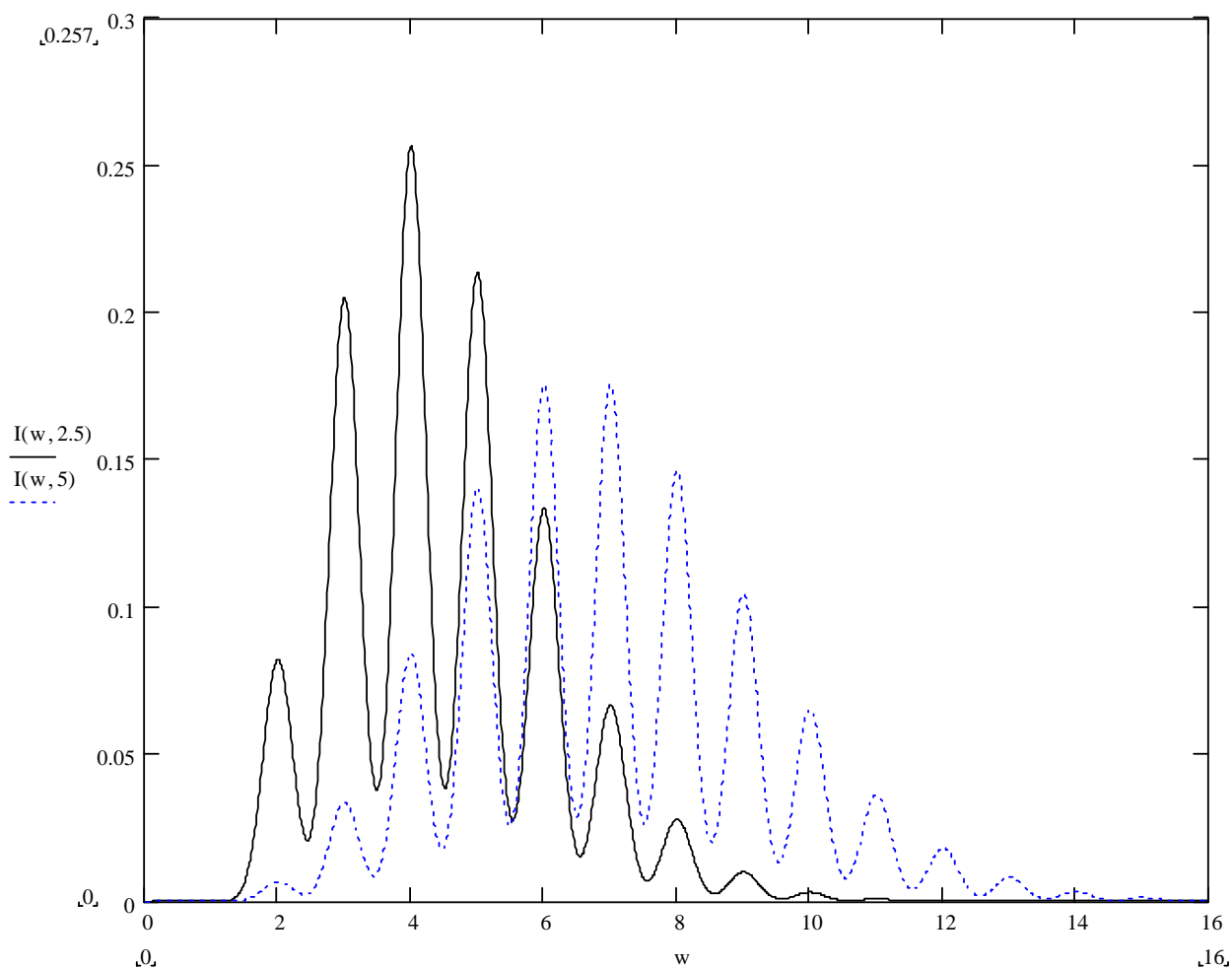
Figure 5.9. Simulated spectrum (relative absorption vs. frequency) for when the diatomic bond length changes moderately (solid line) and also for when it changes quite a bit (dotted line). The dotted line represents (approximately) what happens when the bond length in the excited state is twice that of the ground state. Note that the "intensity" scale here is very different from the preceding figure.

There are several important cases of the Franck-Condon formula that are not revealed in the harmonic-oscillator sort of model. One important situation arises because of the anharmonicity: excitations with more than a certain vibrational energy lead to dissociation of the molecule, and because there are no "stationary" vibration states in this case, no spectral lines are resolved in this region.
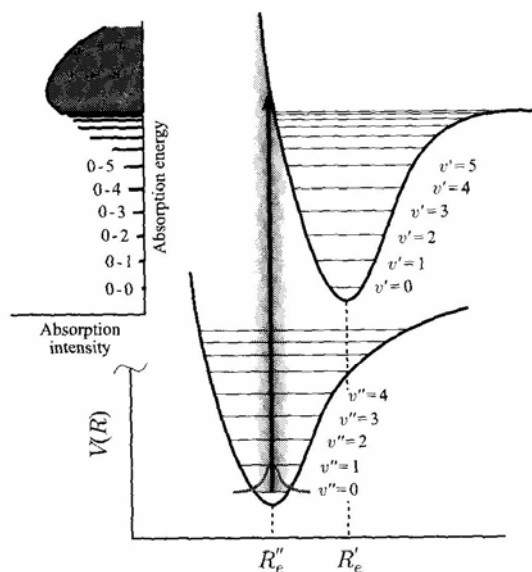
Figure 11.10. Potential energy surfaces leading to dissociation.

Figure 5.10. From <u>Molecular Spectroscopy</u> by Jeanne L. McHale (Prentice Hall, New Jersey, 1999).

A similar, but more complicated effect, occurs when one excites the electron to one state, f, but this state crosses a potential energy surface that is dissociative, d, at some point. Then, there is some probability that the molecule "changes energy states" (this is impossible in the Born-Oppenheimer approximation, but rather likely to occur whenever two potential energy curves cross) with the result that the spectral lines in the "dissociative" region are broadened. (This is lifetime broadening, due to the fleeting existence of the stable state. It is discussed in greater detail later in the notes and also in the homework.) For vibrational energies that are much larger than the energy where the curves cross, the nuclei are moving very quickly near the "curve crossing" value of the bond length, and curve cross is less likely.[27] Thus, one observes that the spectral lines start off narrow, then broaden, and then narrow again in predissociation.

---

[27] Suppose you are driving down one road and then you wish to switch to another road. If you are going slowly, it is easy to turn off onto the different road. If you are going very fast, you will probably miss the intersection. Similarly, when molecules are moving on one potential energy surface, they can switch to a different potential energy surface most easily if the potential energy surfaces cross close to the classical turning point (so that the atoms are moving relatively slowly in the vicinity of the "turnoff"). Conversely, if the potential energy surfaces cross for a molecular conformation where the atoms are moving very quickly, the molecule is unlikely to "turn off" onto the other potential energy surface.
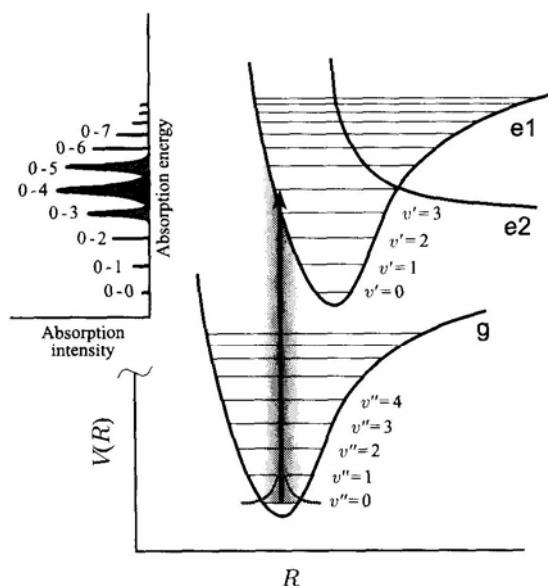
Figure 11.11. Potential energy surfaces leading to predissociation.

Figure 5.11. From <u>Molecular Spectroscopy</u> by Jeanne L. McHale (Prentice Hall, New Jersey, 1999). The initial state is labeled "g", the final state "e1", and the dissociative state "e2." The presence of "broadening" in the 0-3 transition reflects the influence of tunneling.

Finally, it should be noted that the transition rates here discussed work both for excitation and relaxation processes. Consequently, just as excitation to a higher electronic excited state may result in the occupation of higher-energy vibration states, so also relaxation to the ground state potential energy surface—even relaxation from the ground vibrational state—can result in a "Franck-Condon" profile for the emission spectrum.
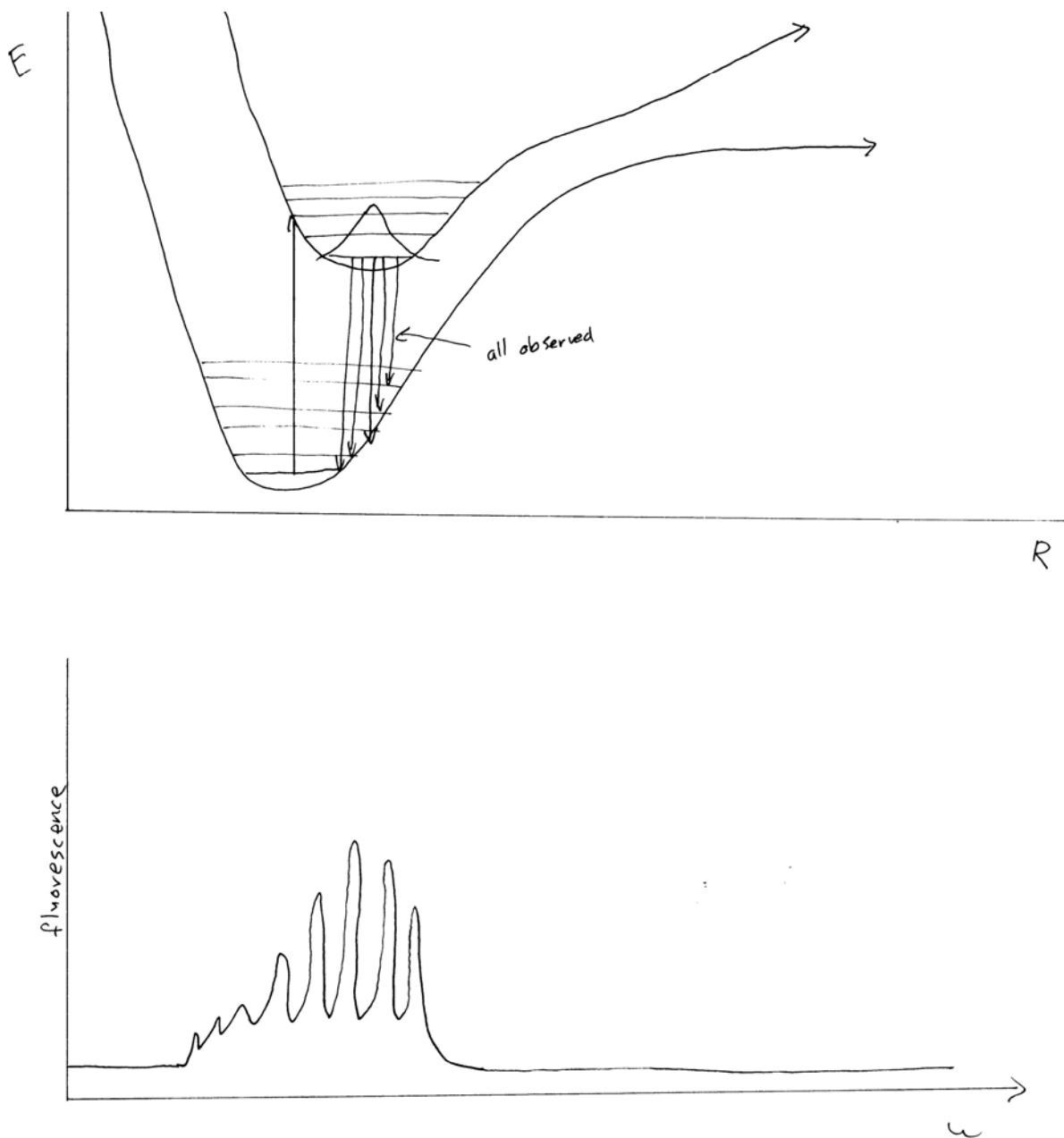
Figure 5.12. Fluorescence spectroscopy showing the Franck-Condon factors effects on emission spectra.

We conclude this section by writing the characteristic frequency for the transition. For this purpose, one often uses the "free rotation" model, and then obtains

$$E_{\mu f} - E_{\nu i} = \varepsilon_{\mu f} - \varepsilon_{\nu i} + \left(U_f^{BO}\left(\left\{\boldsymbol{R}_\alpha^{(f)}\right\}_{\alpha=1}^P\right) - U_i^{BO}\left(\left\{\boldsymbol{R}_\alpha^{(i)}\right\}_{\alpha=1}^P\right)\right) \pm \hbar\omega_J. \qquad (5.99)$$

Here, as in Eq. (5.84), $U_i^{BO}\left(\left\{\boldsymbol{R}_\alpha^{(i)}\right\}_{\alpha=1}^P\right)$ denotes the lowest-energy point on the potential energy surface of the initial electronic state.[28]   Similarly, $U_f^{BO}\left(\left\{\boldsymbol{R}_\alpha^{(f)}\right\}_{\alpha=1}^P\right)$ denotes the lowest-energy point on the potential energy surface of the final electronic state. $\varepsilon_{\mu f}$ denotes the energy of the μth vibrational excited state of the final electronic state and, in the harmonic-oscillator model, can be computed as

$$\varepsilon_{\mu f} \equiv \begin{cases} \hbar\omega_f\left(\mu+\frac{1}{2}\right) & \text{diatomic} \\ \sum_{\alpha=1}^{3P-6} \hbar\omega_{f\alpha}\left(\mu_\alpha+\frac{1}{2}\right) & \text{polyatomic} \end{cases}. \tag{5.100}$$

where ω_f denotes the characteristic vibration frequency (or frequencies) on the final states potential energy surface.   Similarly, $\varepsilon_{\nu i}$, denotes the vibrational energy of the νth vibrational excited state of the initial electronic state and, in the harmonic-oscillator approximation, can be computed using

$$\varepsilon_{\nu i} \equiv \begin{cases} \hbar\omega_i\left(\mu+\frac{1}{2}\right) & \text{diatomic} \\ \sum_{\alpha=1}^{3P-6} \hbar\omega_{i\alpha}\left(\mu_\alpha+\frac{1}{2}\right) & \text{polyatomic} \end{cases}. \tag{5.101}$$

Finally, using a model for unhindered rotation, we obtain

$$\omega_J \equiv \frac{\hbar\left(J\left(J+1\right)\right)}{2I}, \tag{5.102}$$

where I is the moment of inertia for the equilibrium configuration of the nuclei in the initial state.

9. Digression: The Fourier Transform

One of the most important tools in spectroscopy is the Fourier transform, which maps functions of frequency into analogous functions of time, and vice versa. This allows us to related the behavior of molecules in time (in our sample) to the frequency of their absorption and emission (from their spectra), and vice-versa. Particularly relevant to the

---

[28]   At this point, the nuclear positions are mear their most-probable geometry, $\left\{R_\alpha^{(e)}\right\}_{\alpha=1}^P$.   The most-probable geometry, $\left\{R_\alpha^{(e)}\right\}_{\alpha=1}^P$, is only equal to lowest-energy geometry, $\left\{R_\alpha^{(i)}\right\}_{\alpha=1}^P$, when the potential energy surfaces are perfectly harmonic or the nuclei are infinitely heavy. For most systems, though, the minimum of the potential energy curve is close to the equilibrium geometry. In fact, no major changes result if we consider $\left\{R_\alpha^{(e)}\right\}_{\alpha=1}^P$ in Eq. (5.99).

present study is the fact that we can, using knowledge of the molecular motions, determine the way the spectral lines are broadened from the "idealized" infinite-precision spectra we have so far considered. Similarly, given a "real" spectrum, we can then use the width and shape of the spectral lines to characterize the molecular motions in the sample.

The Fourier transform is best introduced with an example. Suppose, for example, you are sitting outside an airport entrance, measuring the "number of people going to the airport" at any given time, $N(t)$. What if you want to know the frequency with which people enter the airport? To compute this, you use the Fourier transform to obtain

$$\hat{N}(\omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} N(t) e^{-i\omega t} dt , \tag{5.103}$$

where $N(\omega)$ characterizes the frequency with which people enter the airport. Similarly, you can transform from the frequency with which people enter the airport to the time-dependence,

$$N(t) = \int\limits_{-\infty}^{\infty} \hat{N}(\omega) e^{i\omega t} d\omega \tag{5.104}$$

What happens if the people enter the airport very regularly—periodically in time with frequency ω_0? Depending on whether there are any persons entering the airport at $t = 0$ or not, $N(t)$ will either be a cosine wave,

$$\hat{N}_{\cos}(\omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} \cos(\omega_0 t) e^{-i\omega t} dt = \frac{1}{2} \delta(\omega - \omega_0) + \frac{1}{2} \delta(\omega + \omega_0) \tag{5.105}$$

or a sine wave,

$$\hat{N}_{\sin}(\omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} \sin(\omega_0 t) e^{-i\omega t} dt = -\frac{i}{2} \cdot \delta(\omega - \omega_0) + \frac{i}{2} \cdot \delta(\omega + \omega_0) , \tag{5.106}$$

respectively. In either case, the picture is clear: because people are entering with a single, "pure" frequency, the Fourier transform of $N(t)$ must be a delta function with frequency $\omega = \pm\omega_0$.[29] From Eqs. (5.105) and (5.106), it is clear that

---

[29] One might object that a negative frequency is unreasonable. But because $\sin(\omega t) = -\sin(-\omega t)$ and $\cos(\omega t) = \cos(-\omega t)$, negative frequencies pose no great problems. Since it is convenient to perform intergrals from $-\infty$ to ∞ than it is to restrict oneself to the range 0 to ∞, we use this technique. However, if we had chosen to (as is our prerogative) use the Fourier Sine or Cosine transform, no such ambiguity would have arisen. We find it convenient, however, to use the complex form of the Fourier Transform.

$$\hat{N}_{\text{exp}}(\omega) = \tfrac{1}{2\pi} \int\limits_{-\infty}^{\infty} \big(\cos(\omega_0 t) + i\sin(\omega_0 t)\big) e^{-i\omega t} dt = \delta(\omega - \omega_0)$$

$$= \tfrac{1}{2\pi} \int\limits_{-\infty}^{\infty} e^{i\omega_0 t} e^{-i\omega t} dt = \delta(\omega - \omega_0) \qquad (5.107)$$

$$= \tfrac{1}{2\pi} \int\limits_{-\infty}^{\infty} e^{-i(\omega - \omega_0)t} dt = \delta(\omega - \omega_0)$$

Of course, anyone who has ever visited an airport know that people don't enter in at an orderly, even rate—they all want to get in the airport and check in at the same time as your esteemed (or loathed) professor. So, let's suppose that I have an important flight to, say, Honolulu at time $t_{vacation}$. Then the time-distribution function for my fellow travelers typically looks something like

$$N_{frustration}(t) = \frac{1}{\sqrt{2\pi}} e^{-\alpha(t - t_{vacation})^2} \qquad (5.108)$$

which gives

$$\hat{N}_{frustration}(\omega) = \tfrac{1}{2\pi} \int\limits_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-\alpha(t - t_{vacation})^2} e^{-i\omega t} dt$$
$$= \frac{1}{2\pi\sqrt{2\alpha}} e^{-\omega^2/4\alpha} \qquad (5.109)$$

Note α is large, reflecting the fact everyone who is flying seems to be trying to check in at the same time I am dreaming of big waves, hula girls, and mahi-mahi (not necessarily in that order), which gives a very large range of frequencies—the frequency of expectant travelers is very high near $t_{vacation}$ and very low at other times. (The frequency of airport enterers is small when $t < t_{vacation}$ because everyone is waiting for me to show up before heading for the entrance, and after the ensuing crush of people as I make my grand entrance, the frequency of expectant travellers is again small ($t > t_{vacation}$) because everyone is waiting in line to check their baggage.) The frequency profile in Eq. (5.109) is called a Gaussian lineshape.

As a better model, if the shuttle-bus from long-term parking gets to the airport every 1 minute, then the rate of people entering the airport is periodic, with period 1 minute. During the crush of people associated with $t_{vacation}$, the number of people getting on and off the shuttle bus peaks, but the "frequency" at which they enter the airport is unchanged. (That is, only the "amplitude" of people entering the airport changes, not the frequency.) If the angular frequency of the shuttle busses is ω_0 and, as seems likely, there are exponentially more people trying to get into the airport when I'm around, we have that

$$N_{\text{w/ shuttle bus}}(t) = e^{i\omega_0 t} e^{-\alpha|t - t_{vacation}|}. \tag{5.110}$$

When we take the Fourier transform, we find that

$$\hat{N}_{\text{w/ shuttle bus}}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega_0 t} e^{-\alpha|t|} e^{-i\omega t} dt$$

$$= \frac{1}{8\pi} \left[\frac{\alpha}{\alpha^2 + (\omega - \omega_0)^2} + \frac{\alpha}{\alpha^2 + (\omega + \omega_0)^2} \right]. \tag{5.111}$$

(For convenience, I set $t_{vacation} = 0$ in Eq. (5.111).) The curve,

$$f(\omega) = \frac{\alpha}{\alpha^2 + (\omega - \omega_0)^2}, \tag{5.112}$$

is called a Lorentzian.

10. Time-Dependent Correlation Functions and Spectral Lines

Let us reexamine Fermi's Golden rule, Eq. (5.66),

$$W_{fi} = \frac{2\pi V^2 g(\hbar\omega_{fi}) \left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2}{\hbar} \tag{5.113}$$

We predict, based on this formula, that light will be absorbed (or emitted) when $\omega = \omega_{fi} = \frac{E_f - E_i}{\hbar}$, and not otherwise. This would predict, for instance, that the spectral lines would be infinitely sharp, with signal observed only for a single frequency. This, of course, is not what we observe, as anyone who has ever measured a spectrum can attest to. In order to address the question of spectral lines, we need to devote some effort to understanding what we see when we measure a spectrum.

First of all, at any given frequency, the spectral intensity is related to every transition that can be driven at that frequency. Thus, if we have a distribution of initial states, wherein there are p_0 molecules in state Φ_0, p_1 molecules in state Φ_1, etc., we will observe transitions from each of these possible initial states to every possible final state. Quite generally, the rate of transition is proportional to the number of molecules in a given state, and so the total rate of transition is the sum of the rate of transition for all possible initial and final states,

$$W = \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i W_{fi} \tag{5.114}$$

In general, the fraction of the total number of molecules in each state depends on the time. However, after the system has been exposed for the radiation for a long time, equilibrium

values of the occupation numbers are achieved.[30] In Eq. (5.114) and what follows, we assume that $\{p_i\}_{i=0}^{\infty}$ denote the equilibrium values for the occupation numbers.

We now do a useful manipulation, inserting Eq. (5.113) into Eq. (5.114) and rewriting this form as an integral over a delta function:

$$
\begin{aligned}
W &= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty} p_i W_{fi} \\
&= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty} p_i \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)\left|\left\langle \Phi_f \left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar} \\
&= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty} p_i \cdot \frac{2\pi}{\hbar} \int V^2 g\left(\hbar\omega\right)\left|\left\langle \Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 \delta\left(\omega - \omega_{fi}\right)d\omega
\end{aligned}
\tag{5.115}
$$

Using Eq. (5.107) to represent the delta function in terms of the Fourier transform, we have

$$
\begin{aligned}
W &= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty} p_i \cdot \frac{2\pi}{\hbar}\int\left[\frac{1}{2\pi}\int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right)\left|\left\langle \Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 e^{-i\left(\omega-\omega_{fi}\right)t}dt\right]d\omega \\
&= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty} \frac{p_i}{\hbar}\int\int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right)\left|\left\langle \Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 e^{-i\left(\omega-\omega_{fi}\right)t}dtd\omega.
\end{aligned}
\tag{5.116}
$$

The next step is to try to write the sum over initial and final states in a more convenient fashion. To do this, we use the Heisenberg picture of quantum mechanics.

Digression: The Heisenberg Picture

There are two ways to look at quantum mechanics. In the *Schrödinger picture*, operators do not have any inherent time dependence, but the wave functions do. Thus, while the Hamiltonian for a system is, in the absence of external fields, time-independent, the wave function, $\Psi \equiv \Phi(\tau)e^{-iEt/\hbar}$ has an inherent periodic time dependence.

In the *Heisenberg picture*, operators are time dependent. (The relationships between the two pictures are summarized in the table on the next page.) To establish the role of these results in simplifying Eq. (5.116), let's evaluate compare the dipole operator in the Heisenberg picture and the Schrödinger picture We have that

$$
\begin{aligned}
\left\langle \Phi_f\left|e^{i\hat{H}t/\hbar}\hat{\mu}_x e^{-i\hat{H}t/\hbar}\right|\Phi_i\right\rangle &= \left\langle e^{-i\hat{H}t/\hbar}\Phi_f\left|\hat{\mu}_x\right|e^{-i\hat{H}t/\hbar}\Phi_i\right\rangle \\
&= \left\langle e^{-iE_f t/\hbar}\Phi_f\left|\hat{\mu}_x\right|e^{-iE_i t/\hbar}\Phi_i\right\rangle \\
&= \left\langle \Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle e^{i\left(E_f - E_i\right)t/\hbar}.
\end{aligned}
\tag{5.117}
$$

---

[30] Remember that a "long time" from the standpoint of electronic spectroscopy is usually very short: equilibrium values for the occupation numbers of the molecular states, $\{p_i\}_{i=0}^{\infty}$, usually are attained in a fraction of a second..

In the going from the second to the third line in Eq. (5.117), we recall that because $e^{-iE_f t/\hbar}$ is in the bra- part of the bra-ket, it is complex conjugated. That is, $\left\langle e^{-iE_f t/\hbar} \Phi_f \right| = e^{iE_f t/\hbar} \left\langle \Phi_f \right|$. To obtain the second line in Eq. (5.117), we use the Taylor series expansion. Thus

$$
\begin{aligned}
e^{-i\hat{H}t/\hbar} \Phi_i &= \left(\sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i\hat{H}t}{\hbar} \right)^n \right) \Phi_i \\
&= \left(\sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-it}{\hbar} \right)^n \hat{H}^n \Phi_i \right) \\
&= \left(\sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-it}{\hbar} \right)^n E_i^n \Phi_i \right) \\
&= \left(\sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-itE_i}{\hbar} \right)^n \right) \Phi_i \\
&= e^{iE_i t/\hbar} \Phi_i
\end{aligned}
\tag{5.118}
$$

It is also useful to note that, at $t = 0$,

$$
e^{-i\hat{H}\cdot 0/\hbar} \Phi_i = e^{iE_i \cdot 0/\hbar} \Phi_i = \Phi_i
\tag{5.119}
$$

Equation (5.118) is a special case of the general result:

> Given a function, $f\left(\hat{H}\right)$, and an eigenfunction of the Hamiltonian, $\hat{H}\Phi_i = E_i \Phi_i$, then[*]

$$
f\left(\hat{H}\right)\Phi_i = f\left(E_i\right)\Phi_i .
\tag{5.120}
$$

When we are referring to the Heisenberg notation, we denote the time-dependence of the operator explicitly so as to avoid confusion. Thus, the Heisenberg picture's operator can be related to the picture of an operator in the Schrödinger picture by the equation:

$$
\hat{A}(t) \equiv e^{iHt/\hbar} \hat{A} e^{-iHt/\hbar}
\tag{5.121}
$$

Entity	Schrödinger	Heisenberg
Wave function	$\Psi(\boldsymbol{\tau}, t) \equiv \Phi(\boldsymbol{\tau}) e^{-iEt/\hbar}$	$\Phi(\boldsymbol{\tau})$
Operator for a time-independent observable	$\hat{A}(\boldsymbol{\tau})$	$\hat{A}(\boldsymbol{\tau}, t) \equiv e^{i\hat{H}t/\hbar} A(\boldsymbol{\tau}) e^{-i\hat{H}t/\hbar}$
"Time-Independent" Hamiltonian	$\hat{H}(\boldsymbol{\tau})$	$\hat{H}(\boldsymbol{\tau}, t) \equiv e^{i\hat{H}t/\hbar} \hat{H}(\boldsymbol{\tau}) e^{-i\hat{H}t/\hbar}$

Table 5.1.   Comparison of the Heisenberg and Schrödinger pictures.

This is the end of our digression on the Heisenberg picture.

---

[*]   This is true whenever the function, $f\left(\hat{H}\right)$ can be approximated arbitrarily closely at any point with a Taylor series. It is possible that different Taylor series expansions will be needed at different places, as, for instance, in the important case where $f(x) = \frac{1}{x-a}$.

We now use Eq. (5.118) in Eq. (5.116):

$$
\begin{aligned}
W &= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty}\frac{p_i}{\hbar}\int\int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right)\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 e^{-i\left(\omega-\omega_{fi}\right)t}\,dt\,d\omega \\
&= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty}\frac{p_i}{\hbar}\int\int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right)\left\langle\Phi_i\left|\hat{\mu}_x\right|\Phi_f\right\rangle\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle e^{-i\left(\omega-\omega_{fi}\right)t}\,dt\,d\omega \\
&= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty}\frac{p_i}{\hbar}\int\int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right)\left\langle\Phi_i\left|\hat{\mu}_x\right|\Phi_f\right\rangle\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle e^{i\omega_{fi}t}e^{-i\omega t}\,dt\,d\omega \qquad (5.122) \\
&= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty}\frac{p_i}{\hbar}\int\int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right)\left\langle\Phi_i\left|e^{i\hat{H}(0)/\hbar}\hat{\mu}_x e^{-i\hat{H}(0)/\hbar}\right|\Phi_f\right\rangle\left\langle\Phi_f\left|e^{i\hat{H}t/\hbar}\hat{\mu}_x e^{-i\hat{H}t/\hbar}\right|\Phi_i\right\rangle e^{-i\omega t}\,dt\,d\omega \\
&= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty}\frac{p_i}{\hbar}\int\int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right)\left\langle\Phi_i\left|\hat{\mu}_x(0)\right|\Phi_f\right\rangle\left\langle\Phi_f\left|\hat{\mu}_x(t)\right|\Phi_i\right\rangle e^{-i\omega t}\,dt\,d\omega
\end{aligned}
$$

The next stage in the derivation recalls that, unless the molecules are aligned, the relative orientation between the dipole field of the light and the molecule will change. Since, at $t=0$, the field will generally not be along the molecules x-axis, we replace $\hat{\mu}_x(0)$ with $\hat{\mu}(0)$,[32] which is the electric dipole operator for whatever orientation our molecule should happen to be in at time $t=0$.[33] Similarly, we replace $\hat{\mu}_x(t)$ with the appropriate dipole direction at time t, $\hat{\mu}(t)$. Next, we write out the integrals over the electronic and nuclear coordinates (which we denoted, collectively, as $\boldsymbol{\tau}$) in Eq. (5.122), and use the fact that

$$
\sum_{f=0}^{\infty}\Phi_f\left(\boldsymbol{\tau}\right)\Phi_f\left(\boldsymbol{\tau}'\right)=\delta\left(\boldsymbol{\tau}-\boldsymbol{\tau}'\right), \qquad (5.123)
$$

to obtain

---

[32]   You may find it helpful to recall the similar extension we made in Eqs. (5.77) and (5.78).

[33]   For example, if the internuclear axis of a diatomic molecule is rotated from the z-axis to the x-axis, then the dipole field (formerly in the x-direction) will now be in the $-z$-direction.

$$W = \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} \frac{p_i}{\hbar} \int \int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right) \left\langle \Phi_i \left| \hat{\mu}_x\left(0\right) \right| \Phi_f \right\rangle \left\langle \Phi_f \left| \hat{\mu}_x\left(t\right) \right| \Phi_i \right\rangle e^{-i\omega t} dt d\omega$$

$$= \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} \frac{p_i}{\hbar} \int \int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right) \int\int \Phi_i^*\left(\boldsymbol{\tau}\right) \hat{\mu}_x\left(\boldsymbol{\tau},0\right) \Phi_f\left(\boldsymbol{\tau}\right) \Phi_f^*\left(\boldsymbol{\tau}'\right) \hat{\mu}_x\left(\boldsymbol{\tau}',t\right) \Phi_i\left(\boldsymbol{\tau}'\right) d\boldsymbol{\tau} d\boldsymbol{\tau}' e^{-i\omega t} dt d\omega$$

$$= \sum_{i=0}^{\infty} \frac{p_i}{\hbar} \int \int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right) \int\int \Phi_i^*\left(\boldsymbol{\tau}\right) \hat{\mu}_x\left(\boldsymbol{\tau},0\right) \left(\sum_{f=0}^{\infty} \Phi_f\left(\boldsymbol{\tau}\right) \Phi_f^*\left(\boldsymbol{\tau}'\right) \right) \hat{\mu}_x\left(\boldsymbol{\tau}',t\right) \Phi_i\left(\boldsymbol{\tau}'\right) d\boldsymbol{\tau} d\boldsymbol{\tau}' e^{-i\omega t} dt d\omega$$

$$= \sum_{i=0}^{\infty} \frac{p_i}{\hbar} \int \int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right) \int\int \Phi_i^*\left(\boldsymbol{\tau}\right) \hat{\mu}_x\left(\boldsymbol{\tau},0\right) \delta\left(\boldsymbol{\tau} - \boldsymbol{\tau}'\right) \hat{\mu}_x\left(\boldsymbol{\tau}',t\right) \Phi_i\left(\boldsymbol{\tau}'\right) d\boldsymbol{\tau} d\boldsymbol{\tau}' e^{-i\omega t} dt d\omega \qquad (5.124)$$

$$= \sum_{i=0}^{\infty} \frac{p_i}{\hbar} \int \int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right) \int \Phi_i^*\left(\boldsymbol{\tau}\right) \hat{\mu}_x\left(\boldsymbol{\tau},0\right) \hat{\mu}_x\left(\boldsymbol{\tau},t\right) \Phi_i\left(\boldsymbol{\tau}\right) d\boldsymbol{\tau} e^{-i\omega t} dt d\omega$$

$$= \sum_{i=0}^{\infty} \frac{p_i}{\hbar} \int \int_{-\infty}^{\infty} V^2 g\left(\hbar\omega\right) \left\langle \Phi_i \left| \hat{\mu}_x\left(0\right) \hat{\mu}_x\left(t\right) \right| \Phi_i \right\rangle e^{-i\omega t} dt d\omega$$

Before we go any further, we should introduce some nomenclature. First of all, the function

$$C\left(t\right) \equiv \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu}_x\left(0\right) \hat{\mu}_x\left(t\right) \right| \Phi_i \right\rangle \qquad (5.125)$$

is called the *time-correlation function*: it measures the "correlation" between the value of the dipole transition moment of the molecule at time t to its initial value $t = 0$. Clearly, when $t \to 0$, we end up with a perfect correlation, and as $t \to 0$ in any system with finite temperature, the correlation vanishes. It is worth mentioning that, in the absence of time-dependent processes external to the molecule itself, $C\left(t\right)$, takes its Fermi-Golden-Rule form,

$$\begin{aligned} C\left(t\right) &\equiv \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu}_x\left(0\right) \hat{\mu}_x\left(t\right) \right| \Phi_i \right\rangle \\ &= \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 e^{i\omega_{fi} t}. \end{aligned} \qquad (5.126)$$

This is clear from the preceding derivation and, in particular, Eq. (5.116). In what follows, we will also use the Fourier transform of the time-correlation function,

$$\hat{C}\left(\omega\right) = \tfrac{1}{2\pi} \int C\left(t\right) e^{-i\omega t} dt , \qquad (5.127)$$

which contains information about the frequencies of dipole correlation in the system.

The important point, however, is that now we have a formula for the intensity of the spectral lines. Recalling that W is the total probability of observing a transition, it is clear that the relative likelihood of observing a transition when light of frequency ω is incident on a molecule can be identified with the frequency-dependent terms in Eq. (5.124). This gives, as an expression for the intensity of the absorption,

$$I\left(\omega\right) \equiv \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu}_x\left(0\right) \hat{\mu}_x\left(t\right) \right| \Phi_i \right\rangle e^{-i\omega t} dt$$

$$= 2\pi \hat{C}\left(\omega\right)$$

(5.128)

Equation (5.128) measures the "inherent" intensity of a transition: note that all the system dependent information (the amplitude of the electric field, the frequency profile of the light source, etc.) has been ignored. Though not as important as Fermi's golden rule, Eq. (5.128) is one of the most important results in spectroscopy.

11. Homogeneous Broadening

Equation (5.128) is the key relationship in describing the actual shape of spectral lines, because it allows us to discern how the time and frequency dependences of the system being studied affect its spectrum.

The first type of broadening we shall consider is homogeneous broadening. Homogeneous effects are those that influence every molecule the same way. For example, let us consider a "cold" sample of molecules at low pressure, P. If we decide to focus on one specific molecule, M, this molecule goes about its business for some time, T, and then it undergoes a collision, which can change the state of the molecule. Thinking in terms of the dipole moment, we say that after the collision the time-correlation function, $C\left(t\right)$, cf. Eq. (5.125), reflects the fact that the dipole moment of the molecule at $t > T$ is less strongly correlated to that from time $t = 0$ than the dipole moment for $t < T$. Suppose that, after $t = T$, the extent of correlation is zero: that is, assume the dipole moments of the molecule before and after the collision are totally uncorrelated. It follows that the integrand in Eq. (5.128) decreases then, as the number of molecules that have undergone a collision increases. In particularly, letting $P_{none}\left(t\right)$ denote the probability that a molecule in state i does not collide with another molecule before time t,[34]

---

[34]   We have assumed that the frequency with which a molecule undergoes collisions does not depend on the state the molecule is in. As a rule, however, molecules are "larger" in their excited states, and thus the collision frequency increases with the level of excitation, i. The following result should be clear at the end of this analysis: because of the enhanced collision rate in excited states, collisional broadening tends to be enhanced for these states. In fact, many line-broadening mechanisms tend to affect highly excited states more than lower states, so the spectral lines associated with excited state absorption spectrum tend to be more diffuse (less sharp) than those associated with excitations from the ground state.

$$I(\omega) \equiv \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i P_{none}(t) \left\langle \Phi_i \left| \hat{\mu}_x(0)\, \hat{\mu}_x(t) \right| \Phi_i \right\rangle e^{-i\omega t} dt \qquad (5.129)$$

because, after the molecule has undergone a collision, the time-correlation of the dipole moments, $\left\langle \Phi_i \left| \hat{\mu}_x(0)\, \hat{\mu}_x(t) \right| \Phi_i \right\rangle$, is assumed to be zero.

What is $P_{none}(t)$? Let z be the collision frequency for the molecules in our sample. Using the kinetic theory of dilute gasses, we have that the collision frequency for molecules is just[35]

$$
\begin{aligned}
z &= (\text{number density}) \cdot \pi\sigma^2 \left\langle v_{12} \right\rangle \\
&= \left(\frac{N}{V} \right) \pi\sigma^2 \left(\sqrt{2}\,\langle v \rangle \right) \\
&= \left(\frac{N}{\left(NkT / P \right)} \right) \pi\sigma^2 \sqrt{2} \sqrt{\frac{8RT}{\pi M}} \\
&= \sigma^2 \left(\frac{P}{kT} \right) \sqrt{\frac{16\pi^2 RT}{\pi M}} \\
&= 4P\sigma^2 \sqrt{\frac{\pi R}{MkT}} \\
&= \left(4P \sqrt{\frac{\pi N_A}{MT}} \right) \sigma^2
\end{aligned}
\qquad (5.130)
$$

where P is the pressure, N_A is Avogadro's number, M is the mass of the molecule, T is the temperature of the system, and σ is the collision diameter of the molecule. Finding the appropriate value of σ is difficult, and so we choose to write the collision frequency as

$$z = \frac{\kappa P}{\sqrt{T}} \qquad (5.131)$$

where κ is a constant to be determined.[36,37]

We now need to compute the fraction of molecules that have yet to collide at time t, $P_{none}(t)$. Between times τ and $\tau + d\tau$, the number of molecules that collide for the first time is equal to the total number of molecular collisions in the time interval $(= z \cdot d\tau)$

[35] Based on Eq. (5.130), you will be unsurprised that the collision frequency for molecules in state i is

$$z_i = \sum_{j=0}^{\infty} p_j \left(4P \sqrt{\frac{\pi N_A}{MT}} \right) \left(\frac{\left(\sigma_i + \sigma_j \right)}{2} \right)^2 = \sum_{j=0}^{\infty} p_j \left(P \sqrt{\frac{\pi N_A}{MT}} \right) \left(\sigma_i + \sigma_j \right)^2 ,$$

where σ_i and σ_j are the collisional diameters of the molecule in states i and j, respectively.

[36] Note that because the size of the molecule and the mass of the molecule, M, are roughly proportional, that $\frac{\sigma^2}{\sqrt{M}} \propto \frac{\sigma^2}{\sqrt{size}} \propto \frac{\sigma^2}{\sqrt{\sigma^3}} \propto \sqrt{\sigma}$. κ, then does not depend as strongly on the size of the molecule as you might at first suppose.

[37] Typically κ is determined by fitting the spectrum.

times the fraction of molecules that are colliding for the first time, $P_{none}(\tau)$.[38] Thus, the rate at which $P_{none}(t)$ decreases at time τ is given by

$$dP_{none}(\tau) = -(z \cdot d\tau) \cdot P_{none}(\tau) \tag{5.132}$$

which gives

$$\frac{1}{P_{none}(\tau)} dP_{none}(\tau) = -(z \cdot d\tau)$$

$$\int \frac{1}{P_{none}(\tau)} dP_{none}(\tau) = \int -zd\tau + \text{constant}$$

$$\ln P_{none}(\tau) = -z\tau + \text{constant} \tag{5.133}$$

$$P_{none}(\tau) = e^{-z\tau} e^{(\text{constant})}$$

$$= e^{-z\tau}$$

$$= e^{-\kappa P\tau/\sqrt{T}}$$

The constant of integration must be one, because, at time $t = 0$, $P_{none}(t) = 1$.

Note that, the probability that a molecule underwent no collisions in the time between $t = -\tau$ and $t = 0$ is the same as the probability that the molecule will not collide between time $t = 0$ and time $t = \tau$. Consequently, the appropriate generalization of our formula to the infinite-time interval in Eq. (5.129) is

$$P_{none}(t) = e^{-\kappa P|t|/\sqrt{T}}. \tag{5.134}$$

Substituting Eq. (5.134) into the equation for the spectral intensity, Eq. (5.129), we obtain

$$I(\omega) \equiv \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} p_i e^{-\kappa P|t|/\sqrt{T}} \left\langle \Phi_i \left| \hat{\mu}_x(0) \hat{\mu}_x(t) \right| \Phi_i \right\rangle e^{-i\omega t} dt. \tag{5.135}$$

If, we can capably construct the time correlation function as a product of the exponential damping factor, Eq. (5.134) and the time correlation function for a free molecule, Eq. (5.126), then we have

$$I(\omega) \equiv \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i e^{-\kappa P|t|/\sqrt{T}} \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 e^{i\omega_{fi} t} e^{-i\omega t} dt \tag{5.136}$$

---

[38]   This assumes that the collisions occur totally randomly, so that the fact a molecule collided at time t_1 has no relevance on the possibility it might collide again at time t_2. This approximation is quite poor in solution (where molecules often "collide" several times in quick succession due to "solvent caging"), and so the present treatment must be revised for that case. Even in solution, however, the characteristic exponential decay of Eq. (5.134) is obtained, albeit with a different proportionality constant (proportional to the rotational diffusion constant). More precisely, in Eq. (5.136), $\kappa P|t|/\sqrt{T}$ is replaced by $2D_{rot}|t|$, where D_{rot} is the rotational diffusion constant.

The integral can be evaluated (cf. Eq. (5.111))

$$I(\omega) \equiv \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 \int_{-\infty}^{\infty} e^{-\kappa P|t|/\sqrt{T}} e^{i\omega_{fi} t} e^{-i\omega t} d\omega$$

$$= \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 \frac{1}{8\pi} \left(\frac{\left(\kappa P/\sqrt{T} \right)}{\left(\kappa P/\sqrt{T} \right)^2 + \left(\omega - \omega_{fi} \right)^2} + \frac{\left(\kappa P/\sqrt{T} \right)}{\left(\kappa P/\sqrt{T} \right)^2 + \left(\omega + \omega_{fi} \right)^2} \right). \quad (5.137)$$

The first term (which is large only when $\omega_{fi} > 0$) is relevant to describing the absorption spectrum, while the second term ($\omega_{fi} < 0$) is relevant to the description of stimulated emission. Because of this, if we want $I(\omega)$ to measure the intensity of absorption, we should "correct" equation (5.137) to

$$I(\omega) \equiv \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} \frac{p_i}{8\pi} \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 \left(\frac{\left(\kappa P/\sqrt{T} \right)}{\left(\kappa P/\sqrt{T} \right)^2 + \left(\omega - \omega_{fi} \right)^2} - \frac{\left(\kappa P/\sqrt{T} \right)}{\left(\kappa P/\sqrt{T} \right)^2 + \left(\omega + \omega_{fi} \right)^2} \right). \quad (5.138)$$

The motivation for switching the sign on the second term is that if we stimulate emission by shining light of frequency $\omega_{fi} = -\omega_{if}$ on the system, then more light is detected than was incident on the system, which is a "negative absorption."[39] In practice, when measuring absorption, the second term in Eq. (5.138) is rarely considered. When measuring fluorescence, the first term is almost never considered.

What is the physical interpretation of Eq. (5.138)? The spectrum is a progression of Lorentzian-shaped curves, each peaked at the characteristic frequency of the absorption, $\omega_{fi} = \frac{E_f - E_i}{\hbar}$, and each possessing a characteristic width, determined by the pressure, temperature and molecular size. When there is very little population in the initial state ($p_i \approx 0$) or the electric dipole transition is forbidden ($\left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right| = 0$), the intensity, $I(\omega_{fi})$, will be very small. The lines will be narrower at when the pressure and temperature is low. (From Eq. (5.138), you might suppose that low temperature tends to broaden the lines, but because $P = \frac{nRT}{V}$, at constant volume (the usual situation, since our

---

[39] This equation is an artifact of the fact that we have allowed negative frequencies, ω, with the understanding that the spectrum is symmetric about the origin in frequency space. However, if we restrict ourselves to the physically relevant positive frequencies, this allows us to incorporate the effects of stimulated emission on our spectrum. Such effects can be significant, for instance, when several spectral lines have similar frequency shifts, as then the absorption of one state may compete with the stimulated emission of another state.

samples are usually confined to some "container") increasing the temperature causes the pressure to increase. However, if one does measure a sample at constant pressure, heating the sample will cause the density to decrease, which reduces the number of collisions, which causes the lines to become more narrow.)

High-resolution electronic spectra are usually observed at constant temperature and low pressure (which is usually controlled with a vacuum set-up), and so the broadening pattern observed here is often called "pressure broadening." Sometimes, it is called collisional broadening, which I prefer since it captures the essence of the phenomenon.
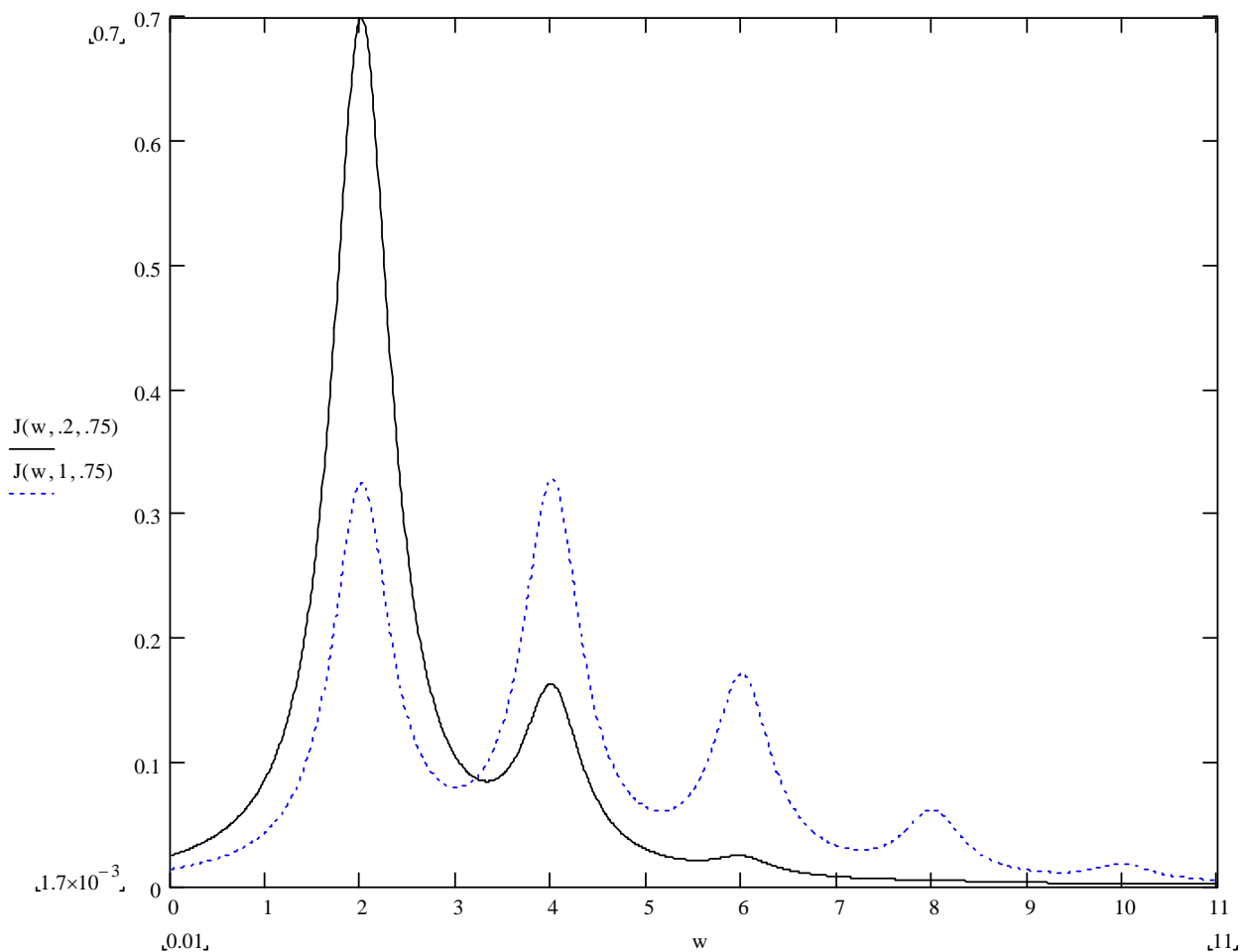
Figure 5.13. Simulated electronic spectrum with Lagrangian line widths, showing vibrational structure

The fact that a mechanism of homogeneous broadening (the pressure is general property of the system, and does not differ from molecule to molecule), gave rise to a Lorentzian line shapes is a general spectroscopic truth:

A mechanism of homogeneous broadening will give Lorentzian line shapes. This is because homogeneous broadening is associated with molecular "relaxation" phenomena.

The "amount" of broadening in a Lorentzian line,[40]

$$L(\omega,\Gamma) = \frac{\frac{\Gamma}{2\pi}}{\left(\frac{\Gamma}{2}\right)^2 + \left(\omega - \omega_{if}\right)^2}, \tag{5.139}$$

is typically measured using the full-width at half maximum, Γ.[41] Referring to Eq. (5.138), we see that the full-width at half-maximum from collisional broadening is

$$\Gamma_{collisional} \equiv \frac{\kappa P}{2\sqrt{T}}. \tag{5.140}$$

More generally, the lifetime of a state is defined using its lifetime, which is defined as the time it takes for the probability to decay to $\frac{1}{e}$ times its value. If the lifetime of the state is τ, then

$$P(t) = P(0)e^{-t/\tau} \tag{5.141}$$

Insertion of this into Eq. (5.129) gives (presuming that the dipole moments subsequent to the decay are totally uncorrelated with those prior to the decay), then we find that the lineshape is

$$L(\omega,\Gamma) = \frac{\frac{1}{2\pi\tau}}{\left(\frac{1}{2\tau}\right)^2 + \left(\omega - \omega_{if}\right)^2} \tag{5.142}$$

and the full-width at half maximum is the inverse lifetime, $\frac{1}{\tau}$. Ergo, states with short lifetimes have broad absorptions and states with long lifetimes have sharp spectra.

The primary effects associated with homogeneous broadening are collisions (pressure broadening and, in liquids, diffusional broadening) and what is called lifetime broadening. Recall that high-energy states decay spontaneously to lower-energy states through a process called spontaneous emission. The rate of spontaneous emission is

$$\begin{pmatrix} \text{rate of spontaneous emission} \\ \text{from state } f \text{ to state } i \end{pmatrix} = A_{fi} \left(\text{number of molecules in the state } f\right) \tag{5.143}$$

where

$$A_{fi} = \frac{2\hbar\omega_{fi}^3}{\pi c^3}\left(\frac{W_{fi}}{g\left(\hbar\omega_{fi}\right)}\right) \tag{5.144}$$

---

[40] Equation (5.139) is normalized to unity.

[41] You might think that a better measure the the "spread" in absorption frequencies would be the standard deviation. The standard deviation of a Lorentzian lineshape is infinite, which is why we use the full width at half-maximum to describe the width of spectral lines.

where W_{fi} is the rate of transition computed from Fermi's golden rule. From Eq. (5.143), it is clear that the number of molecules in an excited state decays as

$$P(t) = P(0) e^{-A_{fi}\tau} \qquad (5.145)$$

with the lifetime of the excited state (relative to emission to the ground state) being given by

$$\tau = \frac{1}{A_{fi}} \qquad (5.146)$$

It is clear that long-lived states will have sharper spectra than short-lived states. Importantly, there is no way to experimentally control the rate of spontaneous emission.[42] Thus, even if we remove every other source of broadening in our spectra, there will always be some residual broadening due to spontaneous emission. For this reason, the lineshape attained when we substitute Eq. (5.145) into Eq. (5.129) is often called the *natural lineshape.*

---

[42] This is not quite true. You may recall from introductory quantum mechanics the "watched pot" paradox, which says that a system under constant observation cannot change its state. Consequently, if a state is observed constantly, we can stop it from emitting and enhance its lifetime accordingly. (In practice, we cannot *constantly* monitor the system, so it is impossible to extend the lifetime of the state indefinitely. However, experiments have shown that the lifetime of the state can be extended in this way. Unfortunately, I don't know of any clever experimentalists who have used this to enhance the resolution of their spectrum. (Presumably this is due to the fact that these experiments are very difficult, and probably the means of "watching" the system perturbs it to the extent that the linewidth is extensively broadened due to interactions with the "observing apparatus.")
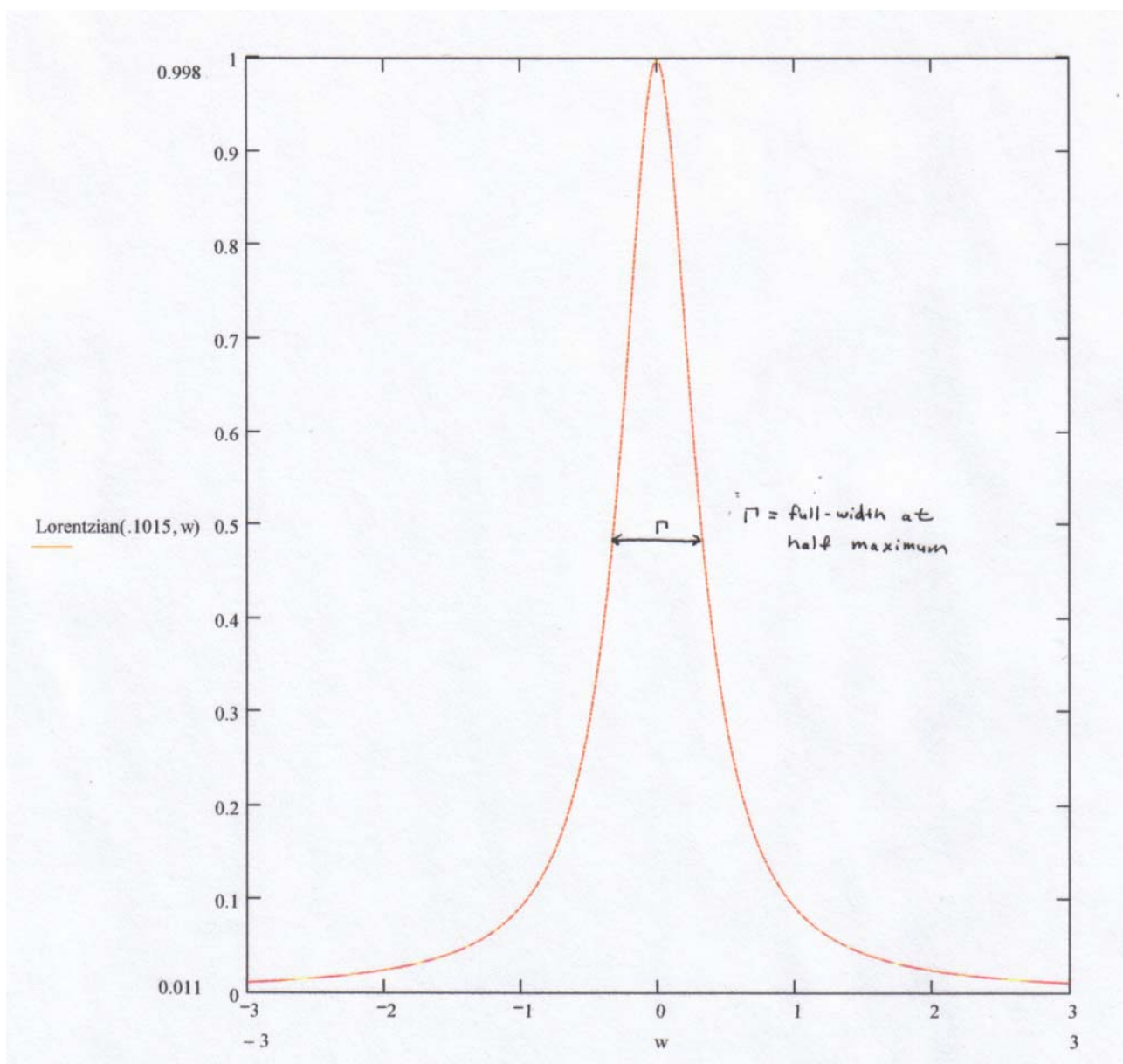
Figure 5.14. The Lorentzian line shape, showing the full-width at half maximum.

12.   Inhomogeneous Broadening

Unlike homogeneous broadening, inhomogeneous broadening is due to different molecules in the sample having different properties. For instance, when measuring the spectrum of a solute, the spectrum is broadened because, at a molecular level, the solvent molecules are arranged in slight different ways around each molecule.

Another case, often of interest, is called Doppler broadening. Suppose we have a sample at temperature T, in a light beam which is propagating in the z-direction. From physics we know that the Doppler effect causes molecules that are moving toward the light

source (against the beam) of the beam to perceive the frequency of the light as being higher than it really is, while molecules moving away from the light source (with the beam) experience a lower frequency. More precisely, a molecule for which the z-component of its velocity is v_z will experience a Doppler shift of

$$
\begin{aligned}
\omega_{observed} &\equiv \frac{\omega_{source}}{1 + \frac{v_z}{c}} \\
&\approx \omega_{source}\left(1 - \frac{v_z}{c}\right),
\end{aligned}
\tag{5.147}
$$

where ω_{source} is the "nominal" frequency of the light source and c is the speed of light.

We need to know what the probability of observing a molecule with a given value of v_z will be. Recalling the Maxwell-Boltzmann velocity distribution function,

$$
P\left(\boldsymbol{v}\right) \equiv \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(\boldsymbol{v}\cdot\boldsymbol{v})/2kT}
\tag{5.148}
$$

we see that the probability of observing a molecule with velocity between v_z and $v_z + dv_z$ is

$$
\begin{aligned}
\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P\left(v_x, v_y, v_z\right) dv_x dv_y dv_z &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m\left(v_x^2 + v_y^2 + v_z^2\right)/2kT} dv_x dv_y dv_z \\
&= \sqrt{\frac{m}{2\pi kT}} e^{-m\left(v_z^2\right)/2kT} \int_{-\infty}^{\infty}\sqrt{\frac{m}{2\pi kT}} e^{-m\left(v_y^2\right)/2kT} dv_y \int_{-\infty}^{\infty}\sqrt{\frac{m}{2\pi kT}} e^{-m\left(v_x^2\right)/2kT} dv_x dv_z \\
&= \sqrt{\frac{m}{2\pi kT}} e^{-m\left(v_z^2\right)/2kT} dv_z
\end{aligned}
\tag{5.149}
$$

We could substituting Eqs. (5.147) and (5.149) into the line-shape equation, Eq. (5.128).[43] However, the final result is clear from the conventional form of Fermi's golden rule,

---

[43]   Using the time-dependent approach requires a more complicated analysis and, in this case, a less accurate answer. If we use Eq. (5.147) in our derivation, we obtain the result

$$
\begin{aligned}
I\left(\omega_{source}\right) &= \sum_{i=0}^{\infty}\sum_{f=0}^{\infty} p_i \left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 \sqrt{\frac{2\pi mc^2}{kT\omega_{source}^2}} e^{-\left(\frac{mc^2}{2\omega_{source}^2 kT}\right)\left(\omega_{source} - \omega_{fi}\right)^2} \\
&\approx \sum_{i=0}^{\infty}\sum_{f=0}^{\infty} p_i \left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 \sqrt{\frac{2\pi mc^2}{kT\omega_{fi}^2}} e^{-\left(\frac{mc^2}{2\omega_{fi}^2 kT}\right)\left(\omega_{source} - \omega_{fi}\right)^2}
\end{aligned}
$$

which is slightly different from what we found before. The fact this is not quite a Gaussian reflects the approximations in the derivation, most probably that from Eq. (5.147). For narrow lines (which is the usual case), the "exact" form of Eq. (5.153) is obtained because $\frac{1}{\omega_{source}^2} = \frac{1}{\omega_{fi}^2 + \left(\omega_{source}^2 - \omega_{fi}^2\right)} \approx \frac{1}{\omega_{fi}^2} - \frac{\omega_{source}^2 - \omega_{fi}^2}{\omega_{fi}^2} + \dots,$ and the higher order terms are entirely negligible when the linewidth is much smaller than the spectral frequency, as is nearly always the case.

$$W_{fi} = \frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar} .$$

(5.150)

A molecule will absorb light at the rate W_{fi} if

$$\omega_{fi} = \frac{\omega_{source}}{1 + \frac{v_z}{c}} .$$

(5.151)

Solving for v_z and putting the result in Eq. (5.149), we see that the transition rate from state i to state f for a molecule in the presence of a photon with wave-length between ω_{source} and $\omega_{source} + d\omega_{source}$ is

$$
\begin{aligned}
W_{fi}\left(\omega_{source}\right) &= \left(\frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar}\right)\left(\sqrt{\frac{m}{2\pi kT}}e^{-m\left(v_z\left(\omega_{source}\right)\right)^2/2kT}\right)\frac{dv_z\left(\omega_{source}\right)}{d\omega_{source}}d\omega_{source} \\
&= \left(\frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar}\right)\left(\sqrt{\frac{m}{2\pi kT}}e^{-m\left(c\left(\frac{\omega_{source}}{\omega_{fi}}-1\right)\right)^2/2kT}\right)\left(\frac{c}{\omega_{fi}}\right)d\omega_{source} \\
&= \left(\frac{2\pi V^2 g\left(\hbar\omega_{fi}\right)\left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2}{\hbar}\right)\left(\sqrt{\frac{mc^2}{2\pi kT\omega_{fi}}}e^{-\frac{mc^2}{2kT\omega_{fi}^2}\left(\omega_{source}-\omega_{fi}\right)^2}\right)d\omega_{source}
\end{aligned}
$$

(5.152)

We can then compute the spectrum, $I\left(\omega\right)$, by removing the terms that are dependent on the specific experimental setup in question[44] and summing over all possible initial and final states, so that

$$I\left(\omega\right) \equiv \sum_{i=0}^{\infty}\sum_{f=0}^{\infty} p_i \left|\left\langle\Phi_f\left|\hat{\mu}_x\right|\Phi_i\right\rangle\right|^2 \left(\sqrt{\frac{2\pi mc^2}{kT\omega_{fi}}}e^{-\frac{mc^2}{2kT\omega_{fi}^2}\left(\omega_{source}-\omega_{fi}\right)^2}\right).$$

(5.153)

---

[44]   As in Eq. (5.126), we remove a factor of $\frac{g\left(\hbar\omega_{fi}\right)V^2}{\hbar}$.
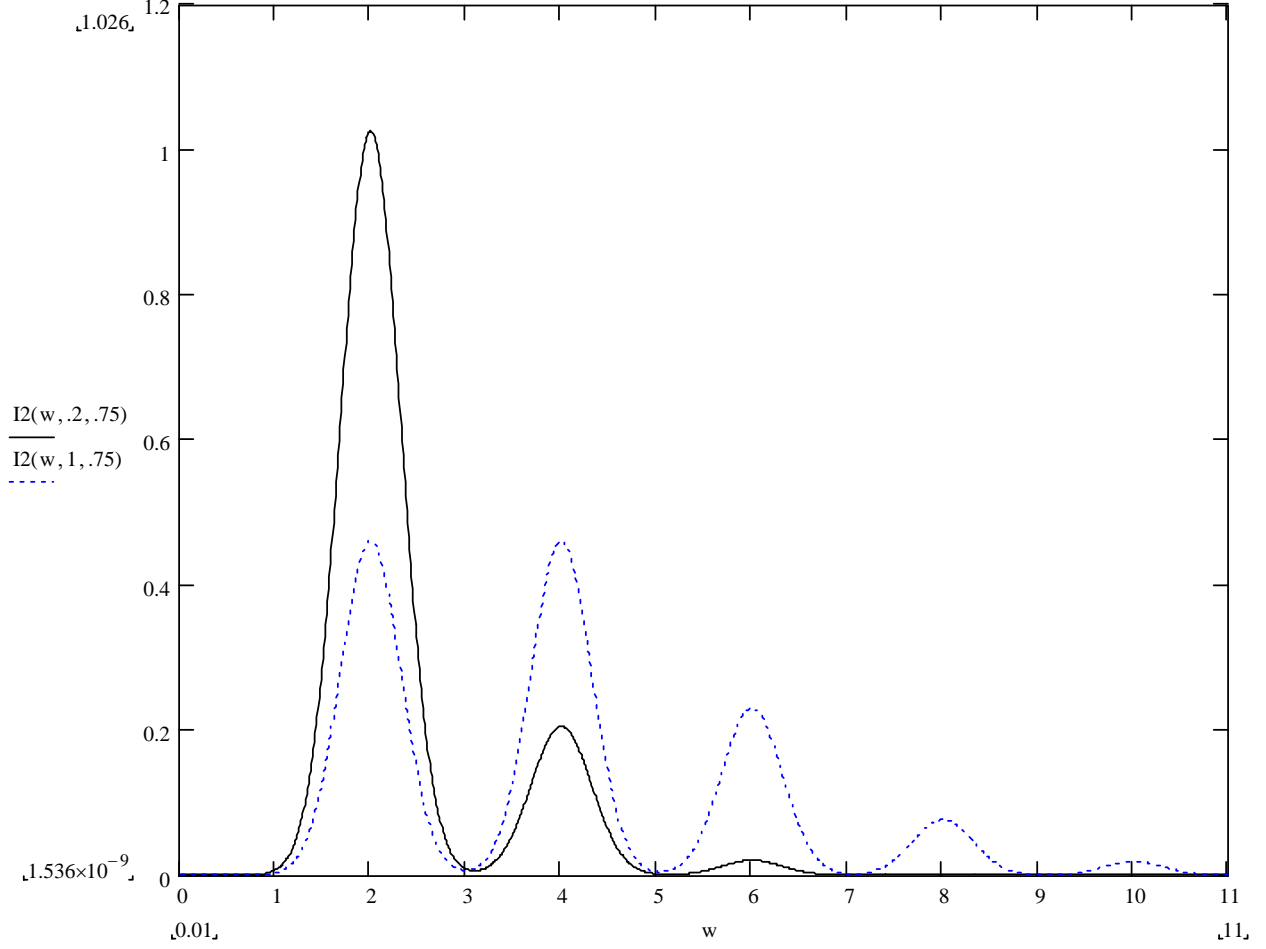
Figure 5.15. Simulated Spectrum with a Gaussian Broadening Function.

Like the Lagrangian, Eq. (5.139), the width of a Gaussian-shaped spectral line,

$$G(\omega) \equiv \frac{2}{\Gamma} \sqrt{\frac{\ln(2)}{\pi}} e^{-4\ln(2)\left(\frac{\omega-\omega_0}{\Gamma}\right)^2}$$

$$= \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\omega-\omega_0}{\sigma}\right)^2} \qquad (5.154)$$

is usually characterized in terms of the full-width at half-maximum, Γ (as opposed to the statistically significant standard deviation, σ). Referring to Eq. (5.154) we see that the full-width at half-maximum for Doppler broadening is given by

$$4\ln(2)\frac{1}{\Gamma_{Doppler}^2} = \left(\frac{mc^2}{2\omega_{fi}^2 kT}\right)$$

$$\Gamma_{Doppler} = 2\frac{\omega_{fi}}{c}\sqrt{2\ln(2)}\sqrt{\frac{kT}{m}} \qquad (5.155)$$

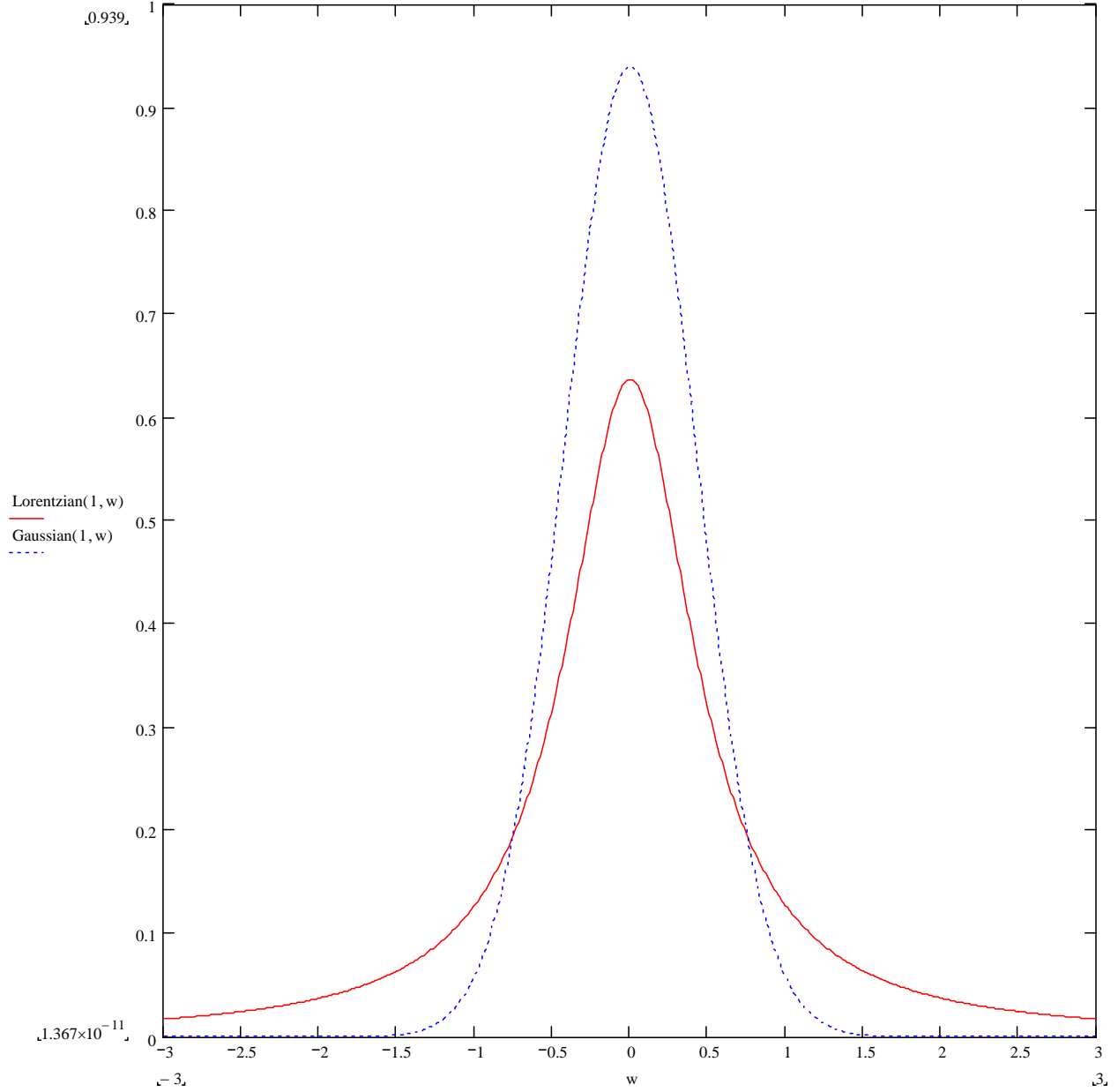$$= 2k_{fi}\sqrt{2\ln(2)}\sqrt{\frac{kT}{m}}.$$

60

Figure 5.16. Comparison of the Gaussian and Lorentzian line shapes. Both curves are normalized and have the same full-width at half-maximum.

where $k_{fi} = \frac{2\pi}{\lambda_{fi}}$ is the characteristic wave number of the transition. As a general rule, spectral lines are broader at higher temperature.

Doppler broadening is an inhomogeneous broadening phenomenon, since the amount of Doppler broadening is related to the presence of molecules in different molecular states (velocities in this case, but more frequently the molecular environment) in our sample. The fact that we observed a Gaussian line-shape is, in fact, an example of the general principle that

Inhomogeneous broadening mechanisms lead to a Gaussian line shape. This is because inhomogeneous broadening is associated with statistical effects governing the distribution of different molecular states.

Inhomogeneous broadening leads to Gaussian lineshapes because inhomogeneous broadening is essentially a statistical phenomenon. The "average" molecule in the system is presumed to absorb at frequency ω_0, but molecules in the system are in a variety of different states, and so there is some spread of frequencies. Due to the law of large numbers, the distribution of different frequencies will usually be a Gaussian, with the probability of any specific molecule having a given frequency, ω, being

$$G(\omega) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2\sigma^2}(\omega-\omega_0)^2}. \tag{5.156}$$

In general, the width of different absorption frequencies is related to σ which, in turn, is related to the statistical-mechanical fluctuation in the energy state. In the gas phase, this was most commonly the translational energy state, and thus we had Doppler broadening. In solution, we instead have "site" broadening, which is due to the fact different molecules are in different environments. Molecules in different environments will have different absorption frequencies, because the surrounding molecules will stabilize the initial and final states to different extents. However, we can still consider the most-probable frequency of absorption and model fluctuations around this value using Eq. (5.156). Additional corrections are sometimes significant.[45]

As long as time-dependent processes related to the transition are small (that is, homogenous broadening is negligible), the lineshape will then be given by the form that we obtain in the absence of other interactions, namely

---

[45] When the simple Gaussian lineshape is no longer sufficient to model the spectrum, we usually consider it to be a sum of two spectral lines. In water, the Cu^{2+} ion usually has coordination number five or six. Rather than considering the ground state of this ion to be a single state, it is better to consider it to be composed of two states: one with coordination number five and one with coordination number six. The most probable frequency of absorption for the two coordination numbers will be different, as will the spread of frequencies. To restate: when molecules in solution exist in a range of *qualitatively* different environments, the absorption/emission spectrum will often have a Gaussian-shaped line characteristic of *each* important solvation environment. Thus, even though we might only be interested in a single transition (say, $3d \rightarrow 4f$) of Cu^{2+}, in aqueous solution it is necessary to consider the "splitting" of the absorption due to different solvation environments.

$$I(\omega) \equiv \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} p_i \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 G(\omega)$$

$$= \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} \begin{pmatrix} \text{number of molecules with} \\ \text{transition frequency } \omega \end{pmatrix} \begin{pmatrix} \text{dipole operator} \\ \text{related to the} \\ \text{"forbiddeness"} \\ \text{of the transition} \end{pmatrix} \quad (5.157)$$

That is, the probability of observing a transition with frequency ω is proportional to the number of molecules with this absorption frequency, $p_i G(\omega)$. The second factor, $\left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2$, just indicates whether the transition is forbidden and, if not, quantifies how "allowed" the transition is. Referring back to Eq. (5.156), it is clear that the Gaussian lineshape is, quite generally, associated with inhomogeneous mechanisms of broadening.

13. Hole-Burning

What happens if both inhomogeneous and homogeneous mechanisms for broadening are effective? In that case, one obtains a Voight lineshape, which is intermediate between a Gaussian and a Lorentzian, and tends to resemble the Gaussian function more closely near resonance but possess long off-resonance tails (similar to the $1/\omega^2$ "tails" of the Lorentzian distribution).

When both homogeneous and inhomogeneous broadening methods are active, but one cannot tell which is most important, one can use the technique of hole-burning. The idea is that one takes a laser and tunes it to a frequency near the center of a broadened spectral line, ω_{burn}. If there is inhomogeneous broadening, the number of molecules in a state with a excitation frequency near ω_{fi} tends to become evenly distributed between the ground and excited state, with the consequence that when one takes another laser with frequency ω_{burn} and shines it on the system, the system is "transparent"—there is no net absorption—near ω_{burn}. It is not that the second laser has no effect. Rather, the second laser stimulates absorption at a rate $W_{fi} = p_i \frac{2\pi V^2 g(\hbar \omega_{fi}) \left| \left\langle \Phi_f | \hat{\mu}_x | \Phi_i \right\rangle \right|^2}{\hbar}$ and stimulates emission at a rate $W_{if} = p_f \frac{2\pi V^2 g(\hbar \omega_{fi}) \left| \left\langle \Phi_f | \hat{\mu}_x | \Phi_i \right\rangle \right|^2}{\hbar}$, but since $p_i = p_f$, there is no net absorption of radiation: for every photon absorbed, another is emitted. For this reason, we say that the transition near ω_{burn} is *saturated*. Now, if the cause of the broadening was not the differences between molecular states in the sample (the homogeneous broadening case), the second laser can be considered to merely increase the intensity of the first laser—there is no

"special" effect since the cause for the broadening was not related to the differences between individual molecular states. Thus, if we take an entire absorption spectrum with the second laser while we keep the first laser locked on ω_{burn}, if inhomogeneous broadening is significant we will see a dip in the middle of the spectrum,[46] as the transitions near ω_{burn} have been "saturated."

This phenomenon may be more clear if we do some accounting. First, we define the so-called Einstein coefficient,

$$B_{fi} = \frac{W_{fi}}{g\left(\hbar\omega_{fi}\right)} \tag{5.158}$$

The energy density of the light is related to the number of photons according to

$$n = \frac{g\left(\hbar\omega_{fi}\right)}{\hbar\omega_{fi}} \tag{5.159}$$

We can then write the rates of absorption and emission as:

State	Number of molecules	Rate of transition (Hz)	Photons in (Hz)	Photons Out (Hz)
initial, i	p_i	$p_i B_{fi} g\left(\hbar\omega_{fi}\right)$ (absorption)	n	$n\left(1 - p_i B_{fi}\left(\hbar\omega_{fi}\right)\right)$
final, f	p_f	$p_f B_{fi} g\left(\hbar\omega_{fi}\right) + p_f A_{fi}$ (emission)	n	$n\left(1 + p_f B_{fi}\hbar\omega_{fi}\right) + p_f A_{fi}$ [47]
total (net absorption rate)		$\left(p_i - p_f\right)W_{fi}$	n	$n + n\left(p_f - p_i\right)B_{fi}\hbar\omega_{fi} + p_f A_{fi}$
total (when $n \to \infty$)		zero	n	$n + \left(\text{corrections of order } n^0\right)$

At time zero, all the molecules will be in the initial state, and $p_f = 0$. Because of this, the rate of absorption is much faster than the rate of stimulated emission, and the value of p_f

---

[46] In practice, hole-burning can only prove that inhomogeneous broadening exists, and the lack of a "hole" could indicate homogeneous broadening, but also could indicate that the rate of absorption for the initial state was too low and so saturation was not achieved. In this case one can, if possible, try to repeat the experiment with a more powerful laser.

[47] The rate of spontaneous emission is given by Eq. (5.144) or, equivalently,

$$A_{fi} = \frac{2\hbar\omega_{fi}^3}{\pi c^3} B_{fi}$$

The rate constants A_{fi} and B_{fi} are known as the *Einstein coefficients*.

will increase. Eventually, we will reach equilibrium; at that point the rate of emission and the rate of absorption will be equal, so that there is no net change in p_i or p_f. Thus At this stage,

$$p_f B_{fi} g\left(\hbar\omega_{fi}\right) + p_f A_{fi} = p_i B_{fi} g\left(\hbar\omega_{fi}\right) \tag{5.160}$$

and so

$$\frac{p_f}{p_i} = \frac{B_{fi} g\left(\hbar\omega_{fi}\right)}{B_{fi} g\left(\hbar\omega_{fi}\right) + A_{fi}}$$
$$\frac{p_f}{p_i} = \frac{B_{fi} n\hbar\omega_{fi}}{B_{fi} n\hbar\omega_{fi} + A_{fi}} \tag{5.161}$$

When the light source is very intense, the rate of spontaneous emission is negligible compared to the rate of stimulated emission. Thus,

$$\lim_{n\to\infty} \frac{p_f}{p_i} = 1 \tag{5.162}$$

If this is true, then, from the last line in the table, the number of photons impinging on the system and the number of photons exiting the system are almost the same; that is, the system appears "transparent" and the transition with frequency ω_{fi} is said to be saturated.

When we shine additional light (from the second laser) on a transition that is saturated, this does not lead to any net absorbance: the number of photons impinging on the system and the number of photons exiting the system will be the same, because for molecules that are in a state that absorbs light with frequency ω_{fi}, $p_f = p_i$. This is not true for homogeneous broadening mechanisms, because homogeneous broadening is not related to different molecules absorbing different frequencies of light, but instead due to time-dependent decay processes that are inherent in the experimental setup. In this case, it is impossible to "saturate" the transition, and so the system still absorbs the light of the second laser.
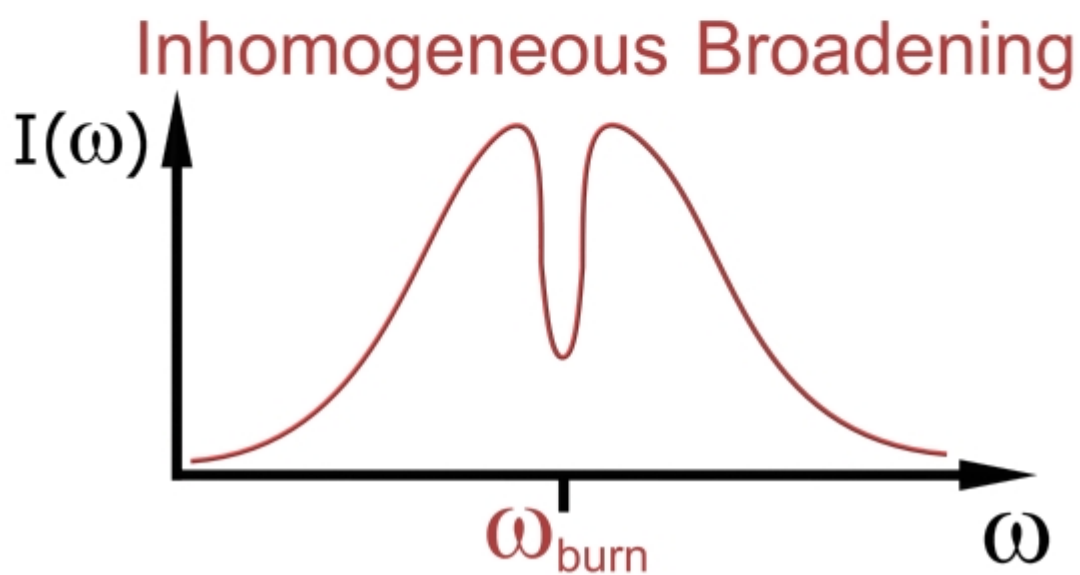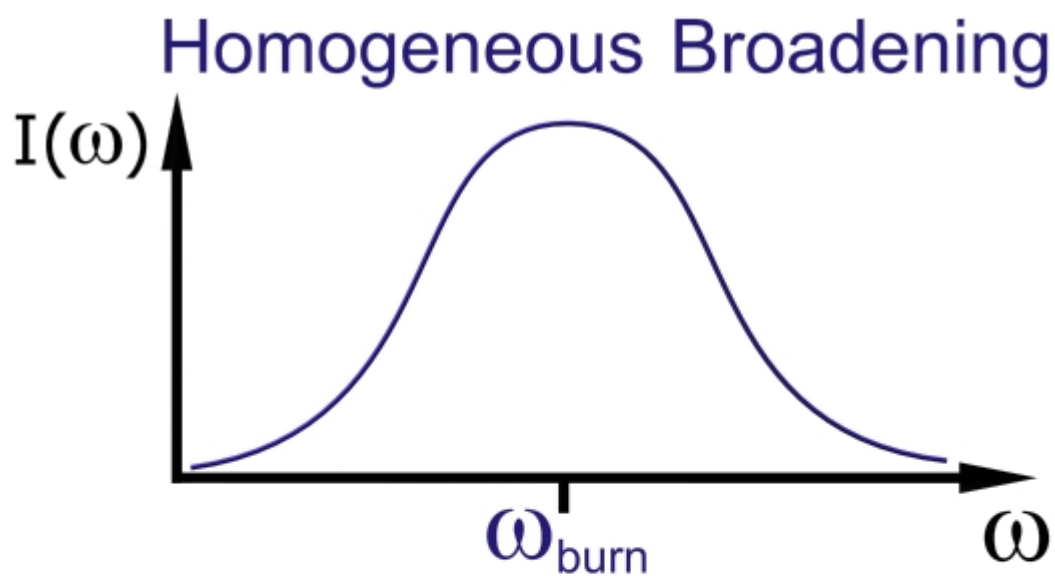
Figure 5.17. Hole burning for a system without significant inhomogeneous broadening and for a system in which inhomogeneous broadening is significant.