
Dipole Moments & Intensities

Intensity Expression

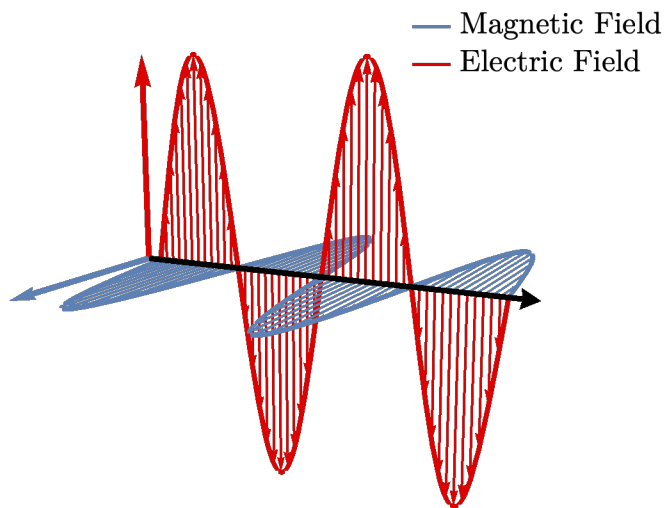
The standard expression for the intensity of a transition from a state $|n\rangle$ to a state $|m\rangle$ is given by

$$I_{n \rightarrow m} \propto \nu_{n \rightarrow m} |\langle n | \boldsymbol{\mu} | m \rangle|^2 \quad (1)$$

where $\nu_{n \rightarrow m}$ is the frequency of the light needed for the transition (given by $E_m - E_n$ and also called the *transition frequency*), and $\langle n | \boldsymbol{\mu} | m \rangle$ is often called the *transition moment*. To have non-zero intensity, this transition moment clearly needs to be non-zero.

Physical Picture

As a very brief sketch of a very hand-wavy justification of why this is reasonable, we'll think about what we're modeling with this. Our intensity is, effectively, a measure of how likely any given photon is to be absorbed. We'll ignore the quantum mechanics for now, and think about light itself, which, per Maxwell, is a paired oscillating electric and magnetic field



To get a light-matter interaction the oscillating electric or magnetic fields need to interact with the electric field of the matter. To justify the transition frequency term, we can note that a higher frequency of oscillation means more chance of the electric field being large as a function of the propagation axis. This means more opportunities for interaction.

Secondly, to justify the transition moment term. The strongest of these types of interactions are going to be dipole-type interactions, looking like $\mathbf{E} \cdot \boldsymbol{\mu}$. In experiments, one assumes that the orientations of the dipoles in the matter are initially uniformly randomly distributed, and so any orientation effects will average out, i.e. we can model our intensity solely based on the norm of the dipole moment, by saying that \mathbf{E} and $\boldsymbol{\mu}$ are oriented in the same direction and so we can say

$$\mathbf{E} \cdot \boldsymbol{\mu} = |\mathbf{E}| |\boldsymbol{\mu}| \quad (2)$$

then assuming, since we're just trying to justify the expression, that our electric field strength is 1, we get

$$\mathbf{E} \cdot \boldsymbol{\mu} = |\boldsymbol{\mu}| \quad (3)$$

Now bringing the quantum mechanics back in, we'll note that given a wavefunction ψ , we can think of ψ^2 as a probability distribution. This is because ψ^2 has three properties that probability distributions need

- The integral of $\psi(\mathbf{r})^2$ over the entirety of its domain is 1, i.e. $\int_{\mathbb{D}} \psi(\mathbf{r})^2 d\mathbf{r} = 1$
- The integral of $\psi(\mathbf{r})^2$ over any subsection of its domain, $\int_{\mathbb{D}} \psi(\mathbf{r})^2 d\mathbf{r}$ is the probability of finding the system in that configuration
- For a function a , the integral $\int_{\mathbb{D}} a(\mathbf{r}) \psi(\mathbf{r})^2$ is the average value of a

We'll now generalize this out to products of wavefunctions, like $\psi_n(\mathbf{r}) \psi_m(\mathbf{r})$. We can think of this as being akin to a joint probability distribution, i.e. one describing the probability of the system being in a configuration allowed by both ψ_n and ψ_m simultaneously. This interpretation is only an analogy, as $\psi_n(\mathbf{r}) \psi_m(\mathbf{r})$ can be negative, but it helps physically justify what we're doing.

When we look at

$$\langle n | \boldsymbol{\mu} | m \rangle = \int_{\mathbb{D}} \psi_n(\mathbf{r}) \boldsymbol{\mu}(\mathbf{r}) \psi_m(\mathbf{r}) d\mathbf{r} \quad (4)$$

we can think of it as the average dipole coming from the distribution of configurations allowed by ψ_n and ψ_m simultaneously.

Then we put this together with our sense that

$$\mathbf{E} \cdot \boldsymbol{\mu} = |\boldsymbol{\mu}| \quad (5)$$

and this allows us to recover a term like

$$|\langle n | \boldsymbol{\mu} | m \rangle|^2 \quad (6)$$

This is certainly not how one actually shows that

$$I_{n \rightarrow m} \propto \nu_{n \rightarrow m} |\langle n | \boldsymbol{\mu} | m \rangle|^2 \quad (7)$$

but the hope is that it demystifies the expression a bit

Computing the Transition Moment

The difficult part of getting an intensity is generally in computing this integral, so we'll walk through some of the methods for doing this. As with all things quantum mechanics, we don't want to actually have to do an integral, so we'll find approximations to work around it.

Since we tend to study vibrations, we'll focus on the expressions of those integrals that are relevant for vibrational spectroscopy.

Harmonic Oscillator and Hermite Polynomials

We'll start with the harmonic oscillator, whose wavefunctions are given by

$$\psi_n(r) = \frac{1}{\sqrt{N}} H_n(r) e^{-\sqrt{\frac{r^2}{\sigma}}} \quad (8)$$

the term H_n is the n^{th} *Hermite Polynomial*, which is just a family of polynomials that solve the differential equation

$$-r \frac{d}{dr} H_n(r) + \frac{d^2}{dr^2} H_n(r) = n H_n(r) \quad (9)$$

which you can look at as being akin to an eigenequation, i.e.

$$\left(-r \frac{d}{dr} + \frac{d^2}{dr^2} \right) H_n(r) = n H_n(r) \quad (10)$$

this *differential operator*, $(-r \frac{d}{dr} + \frac{d^2}{dr^2})$, doesn't have any particular physical meaning that I can think of (sorry), but similar to a regular eigensystem, this gives us a set of *orthogonal polynomials*. This orthogonality is given by the relationship

$$\int_{-\infty}^{\infty} H_n(r) H_m(r) e^{-\frac{r^2}{\sigma}} dr = \begin{cases} N & n=m \\ 0 & \text{else} \end{cases} = N \delta_{nm} \quad (11)$$

we can see that this will make our wave functions orthogonal. Like many other polynomials that arise through this type of differential eigenequation, these polynomials have one other property that make them incredibly nice to work with, that

$$r H_n(r) = k_n^- H_{n-1}(r) + k_n^+ H_{n+1}(r) \quad (12)$$

I can never remember what k_n^- and k_n^+ are off the top of my head, but the actual forms of them don't really matter. What matters is that we can multiply by r and get a combo of the next higher polynomial and the next lower one.

Finally, we'll look the full expression for the wavefunction

$$\psi_n(r) = \frac{1}{\sqrt{N}} H_n(r) e^{-\sqrt{\frac{r^2}{\sigma}}}$$
(13)

and find that we have two key properties for harmonic oscillator wavefunctions

$$\int_{-\infty}^{\infty} \psi_n(r) \psi_m(r) dr = \delta_{nm}$$

$$r \psi_n(r) = k_n^- \psi_{n-1}(r) + k_n^+ \psi_{n+1}(r)$$
(14)

or in bra-ket notation (simply because we use it more often than the explicit integral forms)

$$\langle n | m \rangle = \delta_{nm}$$

$$r | n \rangle = k_n^- | n-1 \rangle + k_n^+ | n+1 \rangle$$
(15)

Much (like 90%?) of the work in what we do is just figuring out what stuff is non-zero. These two properties make that easy to evaluate for harmonic oscillators, which we'll see by looking at the dipole moment.

Linear Dipole

We'll start by a linear approximation of our dipole moment as

$$\mu(r) = \mu(r_e) + \frac{d}{dr} \mu(r_e) (r - r_e)$$
(16)

for convenience we'll say $r_e = 0$. It won't affect our results, but will make them easier to interpret.

I'm also going to make two notation changes for my own convenience

$$\mu(0) = \mu_0$$

$$\frac{d}{dr} \mu(0) = \mu'_0$$
(17)

Now thinking about the transition moment integral we're interested in, we have

$$\begin{aligned} \langle n | \mu | m \rangle &= \langle n | \mu_0 + \mu'_0 r | m \rangle \\ &= \langle n | \mu_0 | m \rangle + \langle n | \mu'_0 r | m \rangle \\ &= \mu_0 \langle n | m \rangle + \mu'_0 k_m^- \langle n | m-1 \rangle + \mu'_0 k_m^+ \langle n | m+1 \rangle \\ &= \mu_0 \delta_{nm} + \mu'_0 k_m^- \delta_{nm-1} + \mu'_0 k_m^+ \delta_{nm+1} \end{aligned}$$
(18)

and since we're absorbing light we're going to assume that $m > n$ and so the *only* way this is non-zero is if $n = m-1$.

For the kind of experimental spectra that we look at, we also always assume than $n=0$, therefore if we had a single vibration in our system and our dipole were linear, we'd expect to see only one peak corresponding to one single-quantum excitation. Even for systems like CH_4 with multiple vibrations, but which are generally quite harmonic, this approximation is actually quite good.

We see two relatively clean peaks, because only two of the normal vibrations give a μ'_0 that's non-zero.

Quadratic Dipole

Obviously we're primarily interested in systems where we have large anharmonicities, but we can still learn something from the harmonic picture when we move beyond a linear dipole approximation. In this case let's look at a quadratic dipole, i.e. one where we have

$$\mu(r) = \mu_0 + \mu'_0 r + \mu''_0 r^2 \quad (19)$$

in this case when we do that integral from before we get even more terms (try to show this for yourself by writing $r^2 = rr$)

$$\langle n | \mu | m \rangle = (\mu_0 + k_m^- k_{m-1}^+ \mu'_0) \delta_{nm} + \mu'_0 k_m^- \delta_{nm-1} + \mu'_0 k_m^+ \delta_{nm+1} + k_{m-1}^- k_m^- \mu''_0 \delta_{nm-2} + k_{m+1}^+ k_m^+ \mu''_0 \delta_{nm+2}$$

and in this case we see both the δ_{nm-1} and δ_{nm-2} terms can be non-zero if $m > n$ (but not simultaneously).

This means our spectrum will now have *two* peaks, for both one-quantum and two-quantum excitations.

This pattern continues as we refine the approximation in our dipole. In general, if we have an order n polynomial, we can up to n -quantum excitations.

Using a Different Basis

As we know, we usually don't have a perfectly harmonic system. Or rather, the systems that are perfectly described by a harmonic approach aren't usually worth studying for us. So a common thing that we do is use a basis that makes the representation of our anharmonic Hamiltonian simple, like a particle on a ring basis.

We don't actually need to specify *what* basis we used, because all basis set approaches are based off of the idea that, given a basis $\{\phi_n\}$, we create a Hamiltonian representation by

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \quad (20)$$

then when we diagonalize we solve for the solutions to

$$H \psi_n = E_n \psi_n \quad (21)$$

and since we expressed our matrix in the $\{\phi_n\}$ basis, ψ_n is expressed as

$$\psi_n = \sum_i c_i^{(n)} \phi_i \quad (22)$$

where the $c_i^{(n)}$ terms come from the diagonalization.

Now when we evaluate our transition moment we have

$$\begin{aligned}
\langle n | \boldsymbol{\mu} | m \rangle &= \left(\sum_i c_i^{(n)} \langle \phi_i | \right) \left(\boldsymbol{\mu} \sum_j c_j^{(m)} | \phi_j \rangle \right) \\
&= \sum_i \left(c_i^{(n)} \langle \phi_i | \boldsymbol{\mu} \sum_j c_j^{(m)} | \phi_j \rangle \right) \\
&= \sum_i \sum_j c_i^{(n)} c_j^{(m)} \langle \phi_i | \boldsymbol{\mu} | \phi_j \rangle
\end{aligned} \tag{23}$$

for the sake of argument, let's say we've built a matrix representation of our dipole moment in the $\{\phi_n\}$ basis, that means we have the matrix defined by

$$M_{ij} = \langle \phi_i | \boldsymbol{\mu} | \phi_j \rangle \tag{24}$$

now we can substitute that back into our expression to get

$$\langle n | \boldsymbol{\mu} | m \rangle = \sum_i \sum_j c_i^{(n)} c_j^{(m)} M_{ij} \tag{25}$$

some people will be happy to have this in sum form. I've got a personal preference for linear algebra notation because I think it's easier to read, encodes the logic more directly, and when you code things up, the linear algebra version requires fewer lines of code and runs faster. So assuming that we've got the vectors $\mathbf{c}^{(n)}$ and $\mathbf{c}^{(m)}$ this looks like

$$\langle n | \boldsymbol{\mu} | m \rangle = \mathbf{c}^{(n)} \mathbf{M} \mathbf{c}^{(m)} \tag{26}$$

and, even nicer, if we've got the coefficient matrix Ψ from the diagonalization and we want to find the transition dipole moment for *any* transition, we can just get that by

$$\langle n | \boldsymbol{\mu} | m \rangle = \Psi \mathbf{M} \Psi \tag{27}$$

Special Case: a DVR Basis

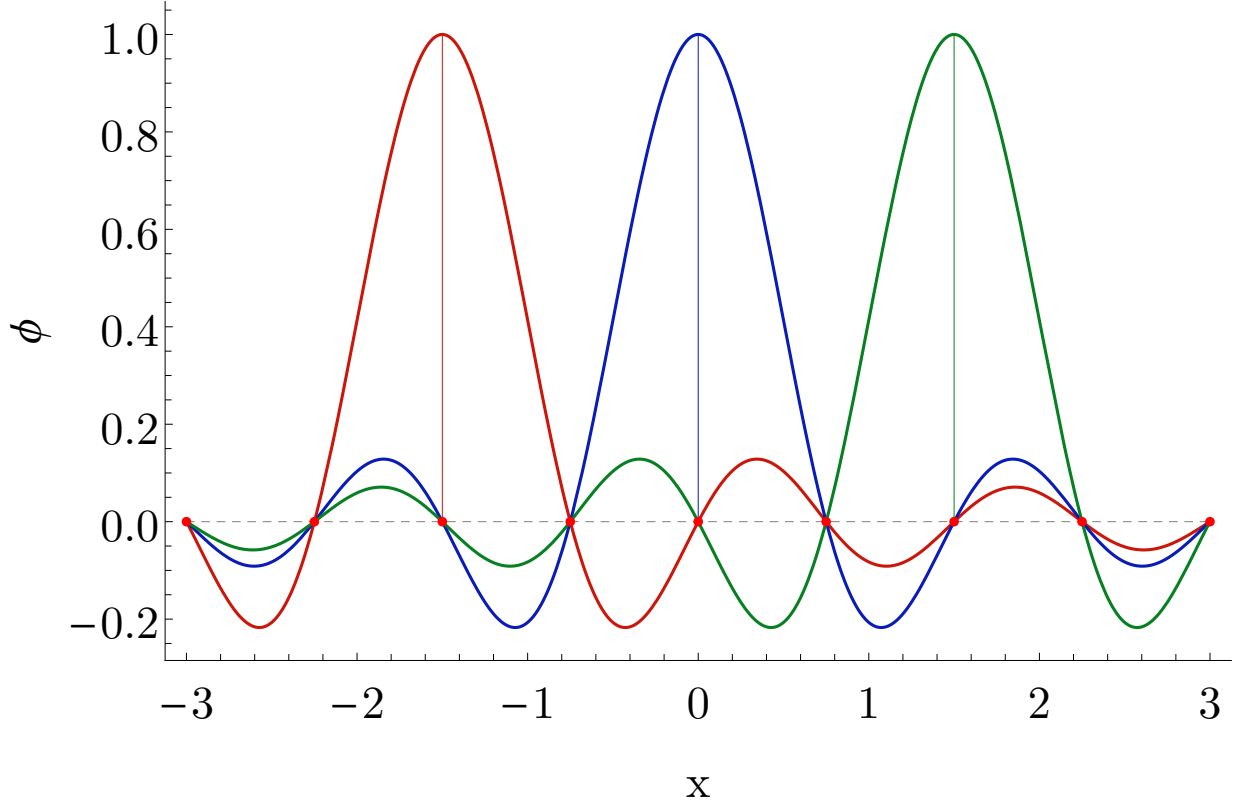
If we're using a *discrete variable representation* (DVR), we've got a basis $\{\phi_i\}$ where each function has a few special properties

- for each ϕ_i , there's a point x_i such that $\phi_i(x_i) = \kappa$ and ϕ_i is maximized at that point. In this, κ is just a normalization factor to be defined later.
- given any x_j , the special point for basis function ϕ_j , $\phi_i(x_j) = 0$ if $i \neq j$

usually we call these x_i the grid points for the representation, since they "discretize" our domain.

That's all a bit technical, so here's a plot of what this looks like

Out[367]=



I labeled the x_i points in red and you can see that the functions are zero at every point except for their “own” one. The normalization will in general not be to 1, but it made it easier to plot.

This has ramifications for how we evaluate integrals and especially for the expression of the dipole moment from before. When we look at

$$M_{ij} = \langle \phi_i | \mu | \phi_j \rangle = \int_D \phi_i(r) \mu(r) \phi_j(r) dr \quad (28)$$

we can approximate this by a Riemann sum over the grid points where

$$\int_D \phi_i(r) \mu(r) \phi_j(r) dr \approx \sum_{k=1}^N \phi_i(x_k) \mu(x_k) \phi_j(x_k) \Delta x \quad (29)$$

at this point we’ll use the second property of our basis to get (try working through this to convince yourself of it)

$$\sum_{k=1}^N \phi_i(x_k) \mu(x_k) \phi_j(x_k) \Delta x = \begin{cases} \mu(x_i) \kappa^2 \Delta x_i & i=j \\ 0 & \text{else} \end{cases} \quad (30)$$

at this point we’ll let $\kappa = \frac{1}{\sqrt{\Delta x}}$ and that means we have

$$M_{ij} = \mu(x_i) \delta_{ij} = \begin{cases} \mu(x_i) & i=j \\ 0 & \text{else} \end{cases}$$

When we think about our total \mathbf{M} matrix, this means it’ll be diagonal, so then when we do

$$\langle n | \boldsymbol{\mu} | m \rangle = \mathbf{c}^{(n)} \mathbf{M} \mathbf{c}^{(m)}$$

we end up getting

$$\begin{aligned} \langle n | \boldsymbol{\mu} | m \rangle &= \sum_{i=1}^N \left(\mathbf{c}^{(n)}_i \right) \mu(x_i) \left(\mathbf{c}^{(m)}_i \right) \\ &= \mathbf{c}^{(n)} \cdot (\boldsymbol{\mu} * \mathbf{c}^{(m)}) \\ &= \boldsymbol{\mu} \cdot (\mathbf{c}^{(n)} * \mathbf{c}^{(m)}) \\ &= (\boldsymbol{\mu} * \mathbf{c}^{(n)}) \cdot \mathbf{c}^{(m)} \end{aligned}$$

where $\boldsymbol{\mu}$ is the vector of dipole moment values at all of the x_i grid points