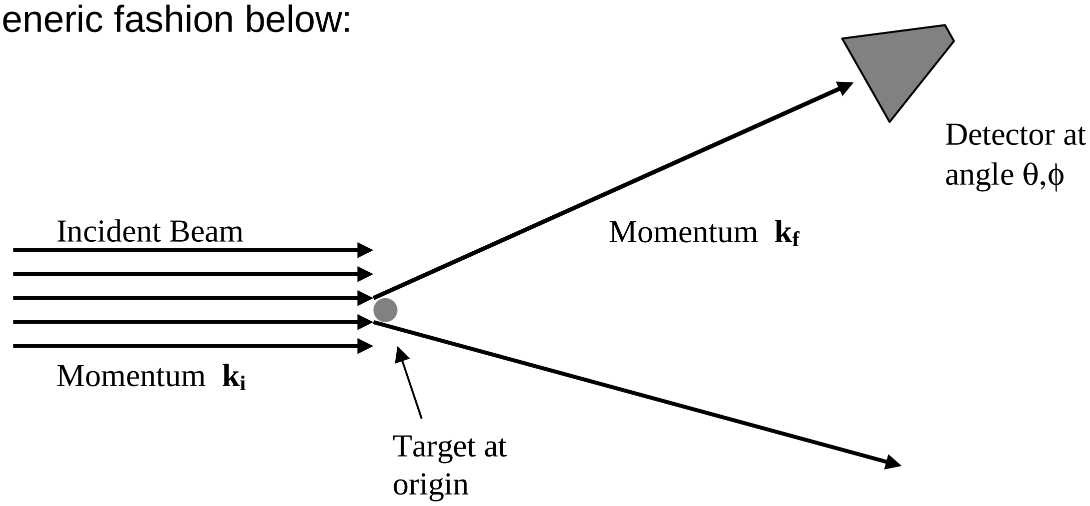
V. Scattering

a. Design of a scattering experiment

Up to now, we have dealt primarily with systems where the goal was essentially to find the eigenvalues and eigenstates of some Hamiltonian. This approach covers a vast amount of chemistry, but is not all-inclusive. In practice, one often probes the character of a molecular system by performing a scattering experiment as depicted in generic fashion below:



Here, there is a beam of particles incident on the “target” we are interested in and we have a detector that is able to sense the arrival of these particles once they have been deflected off the target. It is assumed that the interaction between the particles and the target decays as a function of the distance between them (thus, harmonic interactions are out) and that the detector is far enough away that the interaction can be neglected by this point. Our goal, of course, is to obtain information about the target from the angular distribution of scattered particles. The paradigm is the search for *steady states* instead of the search for *stationary states*. Also, note that the scattering off multiple targets (as might happen in a crystal) can be treated by repeated applications of the formalism we will develop.

b. Elastic Scattering

At this point, most introductory texts neglect any internal structure of the incident particles (e.g. vibrational state, rotational state, spin, etc.). The scattering is therefore *elastic* (i.e. no energy is absorbed by the incident particles). In general, this approximation is ***not at all*** relevant to chemistry! Typically, the incident beam consists of some molecules and the scattered beam consists of different molecules (reactive scattering) and/or the same molecules in different quantum states (inelastic scattering).

Hence, we will be most interested in a formalism that goes beyond the standard treatment. However, there are several aspects of the theory of elastic scattering that carry over to the more general case, and we touch on those now. We will also assume that the particles interact with the target through a potential $V(\mathbf{r})$ to give the equations a concrete form.

1. The Scattering Cross Section

In general the thing we will be most interested in is the number of scattered particles, dn, per unit of incident particle flux, F_i. That is, we are interested in the ratio dn/F_i for a particular detector position. This is the analog of the "reaction probability". Typically, we envision the detector as occupying an infinitesimal span of angles $d\theta$ and $d\phi$. Clearly, the number of particles sensed by the detector will be proportional to this angular area – bigger detectors will detect more particles. Hence, we can write

$$dn/F_i = \sigma(\theta,\phi)\ \sin\theta\, d\theta\, d\phi$$

where the constant of proportionality, $\sigma(\theta,\phi)$, is called the ***differential cross section***, and we have noted explicitly that it depends on θ and ϕ. We can also define the ***total cross section*** by

$$\sigma = \int dn/F = \int\int \sigma(\theta,\phi)\sin\theta\, d\theta\, d\phi$$

The name "cross section" arises from the fact that σ has the dimensions of area and therefore represents the effective size of the target from the point of view of the incident particles – smaller cross sections mean less scattering which means an effectively smaller target.

2. The Integral Equation

In order to solve the scattering problem what we would really like is a way to transform the incoming wave into the scattered wave. It turns out that the ***Green's function*** provides just such a transformation and hence we proceed to discuss it.

It is useful to first define the **Green's operator** for a given $\hat{H}$. Essentially, we want something that takes any initial state and gives us back an eigenstate of energy E. Formally, one might write something like this:

$$\hat{G}(E) = \frac{1}{E - \hat{H}}.$$

This operator gives infinite weight to any state with eigenvalue E and finite weight to all other states. It is thus a "filter" that selects states that have the energy we are interested in. However, the fact that this operator has some infinite eigenvalues poses some technical mathematical difficulties. It turns out that this can be formally fixed by adding or subtracting a small imaginary part from the denominator

$$\hat{G}_{\pm}(E) = \frac{1}{E - \hat{H} \pm i\varepsilon}$$

These two operators are the Green's operators for $\hat{H}$. The small imaginary parts ensure that the Greens operator is never *quite* singular. At the end of the calculation, one always takes the limit $\varepsilon \to 0$ and so this small imaginary part never appears explicitly in any final result.

The Green's function is just the position representation of Green's operator

$$G_{\pm}(\mathbf{r}, \mathbf{r}', E) = \langle \mathbf{r} | \frac{1}{E - \hat{H} \pm i\varepsilon} | \mathbf{r}' \rangle.$$

It satisfies the differential equation:

$$\left(E - \hat{H}\right) G_{\pm}(\mathbf{r}, \mathbf{r}', E) = \delta(\mathbf{r} - \mathbf{r}')$$

where one implicitly takes the limit $\varepsilon \to 0$ ***after*** applying $\hat{H}$. These two operations do not commute, and so it is important to do them in the proper order. This equation is just the way of saying, in position space, that $G_{\pm}(\mathbf{r},\mathbf{r}',E)$ is the inverse of $\left(E-\hat{H}\right)$; if we multiply them together, we get the identity ($\delta(\mathbf{r}-\mathbf{r}')$).

There are only a few Green's functions that can be calculated exactly. The most useful Green's function (GF) for scattering is the free particle GF. If we define $\hat{H}_0 \equiv -\tfrac{1}{2}\nabla^2$ and $E \equiv k^2$ then the appropriate GF, $G_{0\pm}(\mathbf{r},\mathbf{r}',E)$, is given by

$$G_{0\pm}(\mathbf{r},\mathbf{r}',E) = -\frac{1}{4\pi}\frac{e^{\pm ik|r-r'|}}{|r-r'|}.$$

We will not derive this result, but it is easy enough to show that (cf. CTDL 916)

$$\left(E-\hat{H}_0\right)G_{0\pm}(\mathbf{r},\mathbf{r}',E) = \delta(\mathbf{r}-\mathbf{r}').$$

This result immediately points out to us the significance of the sign of the small imaginary component; the positive and negative solutions correspond to waves propagating outward and inward, respectively. Only the outward propagating waves are appropriate for our scattering considerations, and so we choose the "+" Green's function and denote it $G_0(\mathbf{r},\mathbf{r}',E)$ from this point on.

We can use the free particle Green's function to transform the incoming wave into the scattered wave. Specifically, we presume the incoming wave is an eigenstate of $\hat{H}_0$ (i.e. a plane wave traveling in the direction $\mathbf{k_i}$). Then the scattered wavefunction is given by

$$\phi(\mathbf{r}) = e^{i\mathbf{k_i}\cdot\mathbf{r}} + \int G_0(\mathbf{r},\mathbf{r}',E)\, V(\mathbf{r}')\phi(\mathbf{r}')d^3r.$$

This is very easy to prove. We want to verify that the above wavefunction is an eigenstate of $\hat{H}_0 + V(\mathbf{r})$. To show this, we operate on the left with $E-\hat{H}_0$:

$$\begin{aligned}
\left(E-\hat{H}_0\right)\phi(\mathbf{r}) &= \cancel{\left(E-\hat{H}_0\right)e^{i\mathbf{k_i}\cdot\mathbf{r}}} + \left(E-\hat{H}_0\right)\int G_0(\mathbf{r},\mathbf{r}',E)\, V(\mathbf{r}')\phi(\mathbf{r}')d^3r \\
&= \quad + \int \left(E-\hat{H}_0\right)G_0(\mathbf{r},\mathbf{r}',E)\, V(\mathbf{r}')\phi(\mathbf{r}')d^3r \\
&= \quad + \int \delta(\mathbf{r}-\mathbf{r}')\, V(\mathbf{r}')\phi(\mathbf{r}')d^3r = -V(\mathbf{r})\phi(\mathbf{r})
\end{aligned}$$

Which shows that the outgoing wavefunction is an eigenstate of $\hat{H}_0 + V(\mathbf{r})$ with eigenvalue E. This equation is more useful than the Schrodinger equation (which can also give an eigenstate of eigenvalue E) because it naturally incorporates the correct boundary conditions (namely that the scattered state comes from a particular incident beam of particles).

We now want to derive an expression for the cross section based on this form for the scattered wavefunction. This involves some rather tedious algebra but there are two key steps

1) One shows that in far away from the target, the scattered wavefunction looks like:

$$\phi(\mathbf{r}) = e^{i\mathbf{k}_\mathbf{i}\cdot\mathbf{r}} - \frac{1}{4\pi}\frac{e^{ikr}}{r}\int e^{-\mathbf{k}_\mathbf{f}\cdot\mathbf{r}'} V(\mathbf{r}')\phi(\mathbf{r}')d^3r'$$

this is clearly the sum of a plane wave and a function proportional to $\frac{e^{ikr}}{r}$ (called a free spherical wave). The latter results only from particles scattering off the target.

2)The cross section can be shown to be just the square modulus of the amplitude of the scattered wave:

$$\sigma(\theta,\phi) = \left| \frac{1}{4\pi}\int e^{-\mathbf{k}_\mathbf{f}\cdot\mathbf{r}'} V(\mathbf{r}')\phi(\mathbf{r}')d^3r' \right|^2$$

This is shown by computing the probability flux (or ***current***) in the θ, ϕ direction:

$$\mathbf{J} = -i\left(\phi^*(\mathbf{r})\nabla\phi(\mathbf{r}) + \phi(\mathbf{r})\nabla\phi^*(\mathbf{r})\right)$$

Note that this is zero if the wavefunctions are real. Also, although the letter $\mathbf{J}$ is used for current and angular momentum, the two are unrelated.

3. The Born Approximation

We return to the integral equation for the scattered wavefunction:

$$\phi(\mathbf{r}) = e^{i\mathbf{k}_\mathbf{i}\cdot\mathbf{r}} + \int G_0(\mathbf{r},\mathbf{r}',E)\, V(\mathbf{r}')\phi(\mathbf{r}')d^3r\,.$$

We have seen how one can obtain the cross section once $\phi(\mathbf{r})$has been determined, but ϕ appears on ***both*** sides of this equation! This complicates the solution of this integral equation significantly.

In practice, one follows an iterative route. First, one assumes $\phi(\mathbf{r})=0$. Plugging this in on the right side of the equation gives

$$\phi(\mathbf{r})\approx e^{i\mathbf{k_i}\cdot\mathbf{r}}$$

then, one takes this apprimation to $\phi(\mathbf{r})$, and plugs it in on the right hand side again,

$$\phi(\mathbf{r})\approx e^{\mathbf{ik_i}\cdot\mathbf{r}}+\int G_0(\mathbf{r},\mathbf{r'},E)\,V(\mathbf{r'})e^{\mathbf{ik_i}\cdot\mathbf{r}}d^3r$$

This gives us a slightly better approximation to $\phi(\mathbf{r})$, which we can immediately plug back in to the right hand side of the integral equation to obtain an even better approximation…. Of course, this is something that you never want to do yourself; you want to make a computer do it for you. But it is a direct route to the exact solution of the problem. Note that each successive iteration will involve one higher power of $V(\mathbf{r})$. Hence, this can be thought of as a *perturbative* expansion of the wavefunction in powers of the interaction $V(\mathbf{r})$. Note that it is different than the perturbative expansions we have seen previously. In practice, if one is forced to do such a calculation by hand, one stops at first order, which results in a scattering cross section

$$\sigma(\theta,\phi)=\left|\frac{1}{4\pi}\int e^{-\mathbf{k_f}\cdot\mathbf{r'}}V(r')e^{i\mathbf{k_i}\cdot\mathbf{r'}}d^3r'\right|^2=\left|\frac{1}{4\pi}\int e^{\mathbf{K}\cdot\mathbf{r'}}V(r')d^3r'\right|^2$$

where, on the right hand side, we have defined the scattering wavevector $\mathbf{K}=\mathbf{k_i}-\mathbf{k_f}$. This approximation is called the Born approximation; it is rather simple to apply because all one needs to know is the Fourier transform of the potential. It is not, however, particularly accurate.

c. Inelastic Scattering

For inelastic scattering, we need to consider Hamiltonians of the form:

$$\hat{H}=-\tfrac{1}{2}\nabla^2+\hat{h}_{particle}(\alpha)+\hat{h}_{target}(\beta)+V(\mathbf{r},\alpha,\beta)$$

where α and β denote all the relevant internal degrees of freedom of the incident particle and the target, respectively. These might include tangible variables like the orientation of a molecular dipole moment, but more often we will be interested abstract degrees of freedom like the spin or the vibrational quantum number. Because it is difficult to describe an abstract degree of freedom (like spin) in real space, it is best to work in state space (i.e. the matrix representation) to treat inelastic scattering.

We want to build the Green's function for this Hamiltonian. As was the case for elastic scattering, we do this by identifying the part of $\hat{H}$ that we can solve and then doing a perturbative expansion in the rest. So we define

$$\hat{H} = -\tfrac{1}{2}\nabla^2 + \hat{h}_{particle}(\alpha) + \hat{h}_{target}(\beta) + V(\mathbf{r},\alpha,\beta) = \hat{H}_0 + V(\mathbf{r},\alpha,\beta)$$

with an obvious definition of the zeroth order Hamiltonian and the perturbation. Now, we assume we can obtain all the eigenstates of $\hat{H}_0$:

$$\hat{H}_0\left|\phi_\mu\right\rangle = E_\mu\left|\phi_\mu\right\rangle \Rightarrow H_{\mu\nu} = E_\mu \delta_{\mu\nu}$$

where, in general, the index μ will be discrete in one portion of the spectrum of $\hat{H}_0$ (corresponding to bound states) and another segment that is continuous (corresponding to unbound states). However, in practice, any calculation is done in a large but finite basis, in which case the spectrum is necessarily discrete. It is then a trivial matter to build the Green's operator for $\hat{H}_0$:

$$\hat{G}_{0\pm}(E) \equiv \frac{1}{E - \hat{H}_0 \pm i\varepsilon} = \sum_\mu \frac{\left|\phi_\mu\right\rangle\left\langle\phi_\mu\right|}{E - E_\mu \pm i\varepsilon}.$$

In matrix notation, this is simply

$$\left(G_{0\pm}(E)\right)_{\mu\nu} = \frac{\delta_{\mu\nu}}{E - E_\mu \pm i\varepsilon}.$$

The important point is that the Green's operator ***can be obtained*** if we can solve the Schrodinger equation. On a computer, the limit $\varepsilon \to 0$ can only be taken approximately; too small a value of ε will result give elements of $G_{0\pm}(E)$ that are bigger than the computer can handle. Hence, in practice one chooses this value small enough that the results do not significantly depend on ε and then ignored.

How do we obtain the Green's operator for $\hat{H}$ from the Green's operator for $\hat{H}_0$? Well,

$$\hat{G}_\pm(E) \equiv \frac{1}{E-\hat{H}\pm i\varepsilon} = \frac{1}{E-\hat{H}_0-\hat{V}\pm i\varepsilon} = \frac{1}{\hat{G}_{0\pm}(E)^{-1}-\hat{V}}$$

$$\Rightarrow \hat{G}_{0\pm}(E)\hat{V}\hat{G}_\pm(E) = \frac{\hat{G}_{0\pm}(E)\hat{V}}{\hat{G}_{0\pm}(E)^{-1}-\hat{V}}$$

$$\Rightarrow \hat{G}_{0\pm}(E) + \hat{G}_{0\pm}(E)\hat{V}\hat{G}_\pm(E) = \hat{G}_{0\pm}(E) + \frac{\hat{G}_{0\pm}(E)\hat{V}}{\hat{G}_{0\pm}(E)^{-1}-\hat{V}}$$

$$= \frac{1-\cancel{\hat{G}_{0\pm}(E)}\hat{V}}{\hat{G}_{0\pm}(E)^{-1}-\hat{V}} + \frac{\cancel{\hat{G}_{0\pm}(E)\hat{V}}}{\hat{G}_{0\pm}(E)^{-1}-\hat{V}}$$

$$= \frac{1}{\hat{G}_{0\pm}(E)^{-1}-\hat{V}}$$

This last term, however, is just $\hat{G}_\pm(E)$! This result is no nifty that we will put it in a box:

$$\boxed{\hat{G}_\pm(E) = \hat{G}_{0\pm}(E) + \hat{G}_{0\pm}(E)\hat{V}\hat{G}_\pm(E)}$$

This is called the Lippman-Schwinger (LS) equation. It may look new to you, but let's remember what we found for the real space scattering wavefunction:

$$\phi(\mathbf{r}) = e^{i\mathbf{k_i}\cdot\mathbf{r}} + \int G_0(\mathbf{r},\mathbf{r'},E)\, V(\mathbf{r'})\phi(\mathbf{r'})d^3r$$

if we recall that the Green's function projects out all components of a wavefunction except those with energy E, it becomes clear that this equation is just the LS result applied to an arbitrary wavefunction:

$$\underset{\substack{\big\downarrow \\ \text{Eigenstate of H}}}{\langle\mathbf{r}|\hat{G}_\pm(E)|\psi\rangle} = \underset{\substack{\big\downarrow \\ \text{Eigenstate of H}_0}}{\langle\mathbf{r}|\hat{G}_{0\pm}(E)|\psi\rangle} + \underset{\substack{\big\downarrow \\ \text{Eigenstate of H}}}{\langle\mathbf{r}|\hat{G}_{0\pm}(E)\hat{V}\hat{G}_\pm(E)|\psi\rangle}$$

$$\Rightarrow \langle\mathbf{r}|\phi\rangle = \langle\mathbf{r}|\phi_0\rangle + \langle\mathbf{r}|\hat{G}_{0\pm}(E)\hat{V}|\phi\rangle$$

$$= \langle\mathbf{r}|\phi_0\rangle + \int \langle\mathbf{r}|\hat{G}_{0\pm}(E)|\mathbf{r'}\rangle\langle\mathbf{r'}|\hat{V}|\phi\rangle d^3r'$$

So, the LS equation tells us how to build a perturbative expansion for the full Green's function given an arbitrary zeroth order GF. As we discussed before, it must be solved iteratively. This result is often restated in terms of the transfer matrix, $\hat{T}$,

$$\hat{G}_{\pm}(E)=\hat{G}_{0\pm}(E)+\hat{G}_{0\pm}(E)\hat{T}\hat{G}_{0\pm}(E) \qquad \hat{T}\equiv\hat{V}\hat{G}_{\pm}(E)\hat{G}_{0\pm}(E)^{-1}$$

It is certainly no easier or harder to use this expression than the original, but the $\hat{T}$ matrix has the nice physical role that it ***generates*** the scattering. Hence, $\langle f|\hat{T}|i\rangle$ gives the amplitude for scattering from a given initial state, i, to a given final state, f. Furthermore, the scattering cross section is simply

$$\sigma(\theta,\phi)=\left|\frac{1}{2\pi}\langle f|\hat{T}|i\rangle\right|^2 .$$

This should be compared with our result in real space:

$$\sigma(\theta,\phi)=\left|\frac{1}{4\pi}\int e^{-\mathbf{k_f}\cdot\mathbf{r}'}V(\mathbf{r}')\phi(\mathbf{r}')d^3r'\right|^2 .$$

A few simple manipulations show that the results are equivalent.

d. An Example

To understand all the details of the formalism of scattering, it is good to work out an example of inelastic scattering. We will consider scattering of an electron off of a dipolar diatomic molecule. To complicate matters, the molecule has an important internal degree of freedom: it can vibrate. We will model this vibration with a harmonic oscillator, since that makes the algebra simpler:

$$\hat{h}_{target} = \omega\left(\hat{n}+\tfrac{1}{2}\right)$$

The electron is a free particle, except that it can interact with the dipole moment of the molecule through the standard charge-dipole interaction:

$$V(\mathbf{r},\mu)=\frac{\hat{\mathbf{r}}\cdot\hat{\mu}}{r^3}$$

Where $\hat{\mu}$ is the dipole moment operator for the molecule and we have used atomic units ($\hbar=m_e=e=1$). We will expand the dipole in a power series about its equilibrium value:

$$\hat{\mu} = \vec{\mu}_0 + \vec{\mu}_1\hat{R} + \tfrac{1}{2}\vec{\mu}_2\hat{R}^2 + \ldots$$

$$= \vec{\mu}_0 + \vec{\mu}_1 \frac{\left(\hat{a}^\dagger + \hat{a}\right)}{\sqrt{2/M\omega}} + \vec{\mu}_2 \frac{\left(\hat{a}^\dagger + \hat{a}\right)^2}{2\sqrt{2/M\omega}} + \ldots$$

where $\hat{R}$ is the bond length of our diatomic and in the second line we have just used our expressions for writing $\hat{R}$ in terms of the raising and lowering operators of the Hamiltonian (M is the reduced mass of the diatomic). We will truncate this expansion at first order, so that our interaction potential looks like

$$V(\mathbf{r},\mu) = \frac{\hat{\mathbf{r}}\cdot\vec{\mu}_0}{r^3} + \frac{\hat{\mathbf{r}}\cdot\vec{\mu}_1\left(\hat{a}^\dagger + \hat{a}\right)}{\sqrt{2/M\omega}\,r^3}$$

Hence, our full Hamiltonian is:

$$\hat{H} = -\frac{1}{2}\nabla^2 + \hat{h}_{target} + V(\mathbf{r},\mu) = -\frac{1}{2}\nabla^2 + \omega\left(\hat{n} + \tfrac{1}{2}\right) + \frac{\hat{\mathbf{r}}\cdot\vec{\mu}_0}{r^3} + \frac{\hat{\mathbf{r}}\cdot\vec{\mu}_1\left(\hat{a}^\dagger + \hat{a}\right)}{\sqrt{2/M\omega}\,r^3}.$$

We also note that our zeroth order Hamiltonian is

$$\hat{H}_0 - \frac{1}{2}\nabla^2 + \omega\left(\hat{n} + \tfrac{1}{2}\right).$$

Now, the full LS equation for this problem is very difficult to solve. However, one can extract qualitative results from it much more readily, and this is what we proceed to do.

In order to define our initial state, we need to specify ***both*** the state of the electron *and* the state of the molecule. Before the interaction, the oscillator will clearly be in an eigenstate, which can be specified by its value of n. In accordance with the previous results, we will also assume the electron is initially a plane wave with momentum $\mathbf{k_i}$. Hence, we our initial state is $\left|\psi_{\mathbf{k_i}};n\right\rangle$. Similarly, we will be interested in scattering into final states $\left|\psi_{\mathbf{k_f}};n'\right\rangle$. This is because once the electron is "far away" from the molecule, the only states we can observe in an experiment will be eigenstates of the molecular Hamiltonian, and the only electronic states we will observe will be eigenstates of the free particle $\hat{H}$.

We can immediately write down the equation for the scattering wavefunction:

$$\left|\phi(E)\right\rangle = \left|\psi_{\mathbf{k_i}};n\right\rangle + \hat{G}_0\hat{V}\left|\phi(E)\right\rangle$$

Where $\hat{G}_0$ is understood to be the outgoing Green's function for $\hat{H}_0$:

$$\hat{G}_0 = \left(E + \tfrac{1}{2}\nabla^2 - \omega\left(\hat{n} + \tfrac{1}{2}\right) + i\varepsilon\right)^{-1}$$

We can compute the matrix elements of $\hat{G}_0$:

$$\langle \psi';n'|\hat{G}_0|\psi;n\rangle = \langle \psi';n'|\left(E + \tfrac{1}{2}\nabla^2 - \omega\left(\hat{n} + \tfrac{1}{2}\right) + i\varepsilon\right)^{-1}|\psi;n\rangle$$

$$= \langle \psi';n|\left(E - \omega\left(n + \tfrac{1}{2}\right) + \tfrac{1}{2}\nabla^2 + i\varepsilon\right)^{-1}|\psi;n\rangle\delta_{n,n'}$$

where the second line makes use of the fact that the vibrational states are eigenstates of $\hat{n}$, and so $\hat{G}_0$ cannot mix n. This is the first of many selection rules we will find here.

We notice that the operator on the second line only depends on electron variables and, if we define the effective electron energy as $\tilde{E} = E - \omega\left(n + \tfrac{1}{2}\right)$, we see that

$$\langle \psi';n'|\hat{G}_0|\psi;n\rangle = \langle \psi';n|\left(\tilde{E} + \tfrac{1}{2}\nabla^2 + i\varepsilon\right)^{-1}|\psi;n\rangle\delta_{n,n'}$$

which is just the free particle Green's function for an electron with energy $\tilde{E}$. Hence, if we take ψ and ψ' to be position eigenfunctions, we can use our above result for the free particle GF to obtain :

$$\langle \mathbf{r}';n'|\hat{G}_0|\mathbf{r};n\rangle = -\frac{1}{4\pi}\frac{e^{i\tilde{k}|r-r'|}}{|r-r'|}\delta_{n,n'}$$

where $\tilde{k} \equiv \sqrt{2\tilde{E}}$. What about the matrix elements for $\hat{V}$? Well,

$$\langle \psi_j;n'|V(\mathbf{r},\mu)|\psi_i;n\rangle = \langle \psi_j;n'|\frac{\hat{\mathbf{r}}\cdot\vec{\mu}_0}{r^3}|\psi_i;n\rangle + \langle \psi_j;n'|\frac{\hat{\mathbf{r}}\cdot\vec{\mu}_1\left(\hat{a}^\dagger + \hat{a}\right)}{\sqrt{2/M\omega}\,r^3}|\psi_i;n\rangle$$

The first term depends only on electronic operators, so we can write

$$\langle \psi_j;n'|\frac{\hat{\mathbf{r}}\cdot\vec{\mu}_0}{r^3}|\psi_i;n\rangle = \langle \psi_j;n|\frac{\hat{\mathbf{r}}\cdot\vec{\mu}_0}{r^3}|\psi_i;n\rangle\delta_{n,n'} = \delta_{n,n'}\int_{-\infty}^{\infty}\psi_j(\mathbf{r})^*\frac{\hat{\mathbf{r}}\cdot\vec{\mu}_0}{r^3}\psi_i(\mathbf{r})d^3r\,.$$

On the right hand side, we have an integral that, in general, is very difficult to evaluate. In a finite basis, we would simply define the matrix:

$$(V_0)_{ij} = \vec{\mu}_0\cdot\int_{-\infty}^{\infty}\psi_j(\mathbf{r})^*\frac{\hat{\mathbf{r}}}{r^3}\psi_i(\mathbf{r})d^3r\,.$$

However, we can still say something about when this matrix is non-zero. First, we recognize that the operator sandwiched between ψ_i and ψ_j is a spherical tensor of rank 1. This means it has 2k+1=3 elements that can be assigned to the indices q=1,0,-1. To be concrete, these elements look like x+iy, z and x-iy, respectively. Now, if $\left|\psi_i\right\rangle=\left|\alpha,l,m\right\rangle$ and $\psi_j=\left|\alpha',l',m'\right\rangle$ are eigenfunctions of angular momentum, then we can apply the Wigner-Eckart theorem:

$$\left\langle\alpha',l',m'\right|T_k^q\left|\alpha,l,m\right\rangle=\left\langle l,m;k,q\middle|l',m';l,k\right\rangle\left\langle\alpha',l'\right\|T_k\left\|\alpha,l\right\rangle$$

Where we are thinking of the specific cases k=1, q=1,0,-1. This gives us the selection rules

$$m'-m=\pm1{,}0 \quad\text{and}\quad \left|l-l'\right|\le 1\le l+l'$$

which is the same as

$$\Delta m=\pm1{,}0 \quad\text{and}\quad \Delta 1=\pm1{,}0$$

with the particular case $\Delta m=\Delta 1=0$ excluded. So, $(V_0)_{ij}$ obeys these selection rules if we use angular momentum eigenfunctions as a basis.

What about the selection rules for the other half of V? Well, the left-over bit ($\equiv V_1$)is:

$$\left\langle\psi_j;n'\right|\frac{\hat{\mathbf{r}}\cdot\vec{\mu}_1\left(\hat{a}^\dagger+\hat{a}\right)}{\sqrt{2M\omega}r^3}\left|\psi_i;n\right\rangle=\sqrt{n+1}\left(\delta_{n',n+1}+\delta_{n'+1,n}\right)\int_{-\infty}^{\infty}\psi_j(\mathbf{r})^*\,\frac{\hat{\mathbf{r}}\cdot\vec{\mu}_1}{\sqrt{2M\omega}r^3}\psi_i(\mathbf{r})d^3r\,.$$

This operator always changes the state of the oscillator; it either raises or lowers the vibrational energy by 1 quantum. The selection rules for the electronic matrix elements of V_1 are the same as for V_0, because we can pull out the constant terms to get

$$\left\langle\psi_j;n'\right|\frac{\hat{\mathbf{r}}\cdot\vec{\mu}_1\left(\hat{a}^\dagger+\hat{a}\right)}{\sqrt{2M\omega}r^3}\left|\psi_i;n\right\rangle=\sqrt{n+1}\left(\delta_{n',n+1}+\delta_{n'+1,n}\right)\frac{1}{\sqrt{2M\omega}}\vec{\mu}_1\cdot\int_{-\infty}^{\infty}\psi_j(\mathbf{r})^*\,\frac{\hat{\mathbf{r}}}{r^3}\psi_i(\mathbf{r})d^3r$$

Thus, the electronic part not only has the same selection rules, the underlying *integrals* are the same. Note that these integrals are multiplied by different constants and so the relevant magnitude of these two terms will not generally be comparable. However, because the two portions of the potential (the elastic term $V_0$and the inelastic part) are generated by the same operator for the electron, the angular distribution will be ***exactly the same*** for both contributions to the scattering. As a result, just examining the angular distribution for a fixed energy tells us nothing about the inelastic scattering – we can't tell the difference, because the angular distributions are the same.

Let's go order-by-order and see what terms are generated by the scattering potential. To do this, we note that $\hat{G}_0$ is a scalar, and so it is diagonal in the angular momentum basis (to convince yourself of this, notice that the position representation of $\hat{G}_0$ depends only on r and not θ,ϕ). This means that we only need to worry about V. So, writing the LS equation as a power series,

$$\hat{G}(E)=\hat{G}_0(E) \longrightarrow \Delta n=\Delta l=\Delta m=0,$$

$$+\hat{G}_0(E)\hat{V}\hat{G}_0(E) \begin{array}{l} \xrightarrow{V_0} \Delta n=0\ \ \Delta l=\pm1,0\ \ \Delta m=\pm1,0 \\ \xrightarrow[V_1]{} \Delta n=\pm1\ \ \Delta l=\pm1,0\ \ \Delta m=\pm1,0 \end{array}$$

$$+\hat{G}_0(E)\hat{V}\hat{G}_0(E)\hat{V}\hat{G}_0(E) \begin{array}{l} \xrightarrow{V_0\,V_0} \Delta n=0\ \ \Delta l=\pm2,\pm1,0\ \ \Delta m=\pm2,\pm1,0 \\ \xrightarrow[V_1\,V_0]{} \Delta n=\pm1\ \ \Delta l=\pm2,\pm1,0\ \ \Delta m=\pm2,\pm1,0 \\ \xrightarrow[V_1\,V_1]{} \Delta n=\pm2,0\ \ \Delta l=\pm2,\pm1,0\ \ \Delta m=\pm2,\pm1,0 \end{array}$$

$$+\ldots$$

These selection rules would be different for, say a charge-charge interaction (as opposed to the dipole-dipole interactionwe have at the moment) and we would be able to clearly distinguish the two by looking at the angular dependence of $\sigma(\theta,\phi)$. Hence the angular distribution provides detailed information about the form of the interaction between the particle and the target but no information about energy transfer between the two.

One more point should be made about the angular distribution before we find measures of the inelastic scattering. Our Hamiltonian depends on the direction of the dipole moment operator $\hat{\mu}$. Of course, in an experiment, the molecule will be tumbling in space and it becomes necessary to average over the possible orientations of $\hat{\mu}$ in order to get something that corresponds to an experimental cross section. But at what stage? That is, do we average the wavefunctions (which are complex) or the cross sections (which are real)? This depends on whether the scattering is faster or slower than the re-orientation of the dipole; if it is much faster, then an experiment just corresponds to many independent experiments that scatter off of different potentials. Naively, one might expect to have to *integrate* over the angles defining the orientation of the dipole. However, there is a nice rule of thumb that this is equivalent to the average of the cross sections for scattering off a dipole oriented along each of the three axes:

$$\sigma_{av}(E)=\frac{\sigma_x(E)+\sigma_y(E)+\sigma_z(E)}{3}.$$

If the scattering is slower than the re-orientation of the dipole, however, one would average the wavefunctions. This may seem like a small change, but notice that you can get ***destructive interference*** in this case. In fact, if you assume that the dipole is completely free to reorient, the scattering amplitude disappears because you have equal probability of scattering off a +z dipole as a –z dipole and the two wavefunctions have opposite signs. The limit of slow scattering and fast reorientation is only rarely encountered.

e. Resonances

How do we recognize inelastic scattering, if not from the angular distribution? Well, it is clear that once the electron is very far from the target, the interaction between the electron and the molecule goes to zero and

$$\hat{H}\xrightarrow[r\to\infty]{}\hat{H}_0=-\tfrac{1}{2}\nabla^2+\omega\left(n+\tfrac{1}{2}\right)$$

Thus, for large separations, the eigenvalue equation becomes

$$\hat{H}\left|\phi(E)\right\rangle=E\left|\phi(E)\right\rangle\xrightarrow[r\to\infty]{}-\tfrac{1}{2}\nabla^2+\omega\left(\hat{n}+\tfrac{1}{2}\right)\left|\phi(E)\right\rangle=E\left|\phi(E)\right\rangle$$

We can immediately identify the eigenfunctions on the right side; they are just plane waves for the electron and vibrational eigenstates for the nuclei, in which case

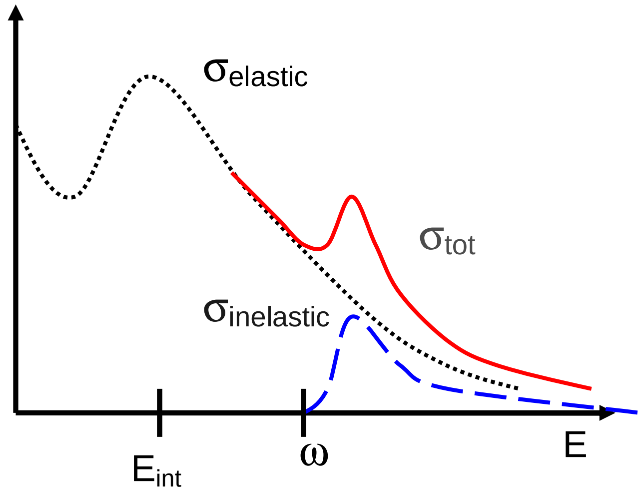
$$E\left|\phi(E)\right\rangle=-\tfrac{1}{2}\nabla^2+\omega\left(\hat{n}+\tfrac{1}{2}\right)\left|\phi(E)\right\rangle=\left(\frac{k^2}{2}+\omega\left(n+\tfrac{1}{2}\right)\right)\left|\phi(E)\right\rangle$$

$$\Rightarrow E=\left(\frac{k^2}{2}+\omega\left(n+\tfrac{1}{2}\right)\right)$$

In order for the energy, E, to be the same for both the incoming and outgoing states, any energy gained (lost) by the nuclear vibrations must be compensated by energy lost (gained) by the electron. Hence if we can measure *either* the energy of the electron at the detector *or* the state of the molecule after the collision, we can separate the scattering into elastic and inelastic parts.

Unfortunately, in many experiments, one cannot do this. Fortunately, there are still ways to extract qualitative information about the inelastic scattering (which tells us about the internal structure of the target) by examining at the qualitative ***energy dependence*** of the total scattering cross section $\sigma(E)$.

First of all, $\sigma_{elastic}(E)$ should generally be a ***decreasing*** function of energy, at least once the energy is above any barriers presented by the interaction with the target ($E > E_{\text{int}}$). This simply results from the fact that as the velocity of our particle increases, it spends less time in the vicinity of the target and is therefore less likely to scatter. Hence, we expect the elastic part to look something like the picture below.



On the other hand, the inelastic part is ***zero*** unless the incoming particle has enough energy to excite the target. In our case, the kinetic energy needs to be at least ω. $\sigma_{inelastic}(E)$ will generally rise rapidly for energies just above this and then tend to zero for higher energies in a similar manner to the elastic part, as shown in the picture above. Just looking qualitatively at the total cross section, then, one expects to see a peak in $\sigma_{tot}(E)$ around the energy where inelastic scattering becomes possible. We will be able to separate out the different contributions if the different inelastic and elastic processes have different energy scales (i.e. assuming E_{int} is not too close to ω).

A peak in the total cross section such as the one above is said to be due to a **resonance**, which can be thought of as a state that is almost an eigenstate of $\hat{H}$, but not quite. The location of the peak gives the energy of the resonance in a straightforward manner. However, one is also typically interested in accounting for the ***width*** of the peak in terms of some microscopic property of the system. We can do this in two different ways:

1) Quantitative Result

In our case, the resonance is the first excited state of the oscillator; in the absence of the interaction with the electrons, this is an eigenstate of the Hamiltonian, but the interaction mixes this state with other states where, for example, the oscillator is in the ground state and the electron kinetic energy is increased by ω. Hence, it is “almost” an eigenstate. To see how this gives rise to a width in the resonance, we should compute the uncertainty in energy for the n=1 state:

$$\begin{aligned}\Delta E^2 &= \langle \mathbf{k}; n=1 | (\hat H_0 + \hat V)^2 | \mathbf{k}; n=1\rangle - \langle \mathbf{k}; n=1 | (\hat H_0 + \hat V) | \mathbf{k}; n=1\rangle^2 \\ &= \langle \mathbf{k}; n=1 | \hat H_0{}^2 + \hat H_0 \hat V + \hat V \hat H_0 + \hat V \hat V | \mathbf{k}; n=1\rangle \\ &\quad - \langle \hat H_0\rangle^2 - 2\langle \hat H_0\rangle\langle \hat V\rangle - \langle \hat V\rangle^2\end{aligned}$$

However, recalling that

$$\hat H_0 |\mathbf{k}; n=1\rangle = \left(\frac{k^2}{2} + \frac{\omega}{2}\right)|\mathbf{k}; n=1\rangle \equiv E_0 |\mathbf{k}; n=1\rangle$$

we find

$$\Delta E^2 = \langle \mathbf{k}; n=1 | \cancel{E_0}{}^2 + \cancel{\cancel{E_0}}\hat V + \hat V\cancel{\cancel{E_0}} + \hat V \hat V | \mathbf{k}; n=1\rangle - \cancel{E_0}{}^2 - 2\cancel{\cancel{E_0}}\langle \hat V\rangle - \langle \hat V\rangle^2$$

which means that the only terms that contribute to the width are the terms from the interaction

$$\Delta E^2 = \langle \mathbf{k}; n=1 | \hat V \hat V | \mathbf{k}; n=1\rangle - \langle \hat V\rangle^2 .$$

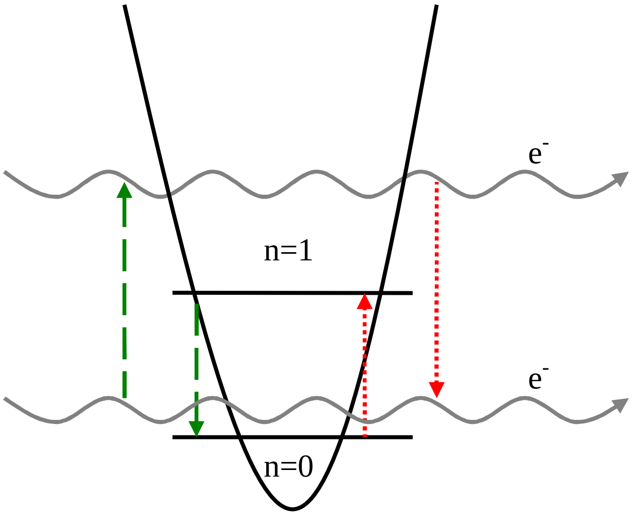
If we expand the right hand side in terms of $\hat V_1$ and $\hat V_0$ and remember that our selection rules were $\Delta n = \pm 1$ for the former and $\Delta n = 0$ for the latter, we get:

$$\Delta E^2 = \langle \mathbf{k}; n=1 | \hat V_1 \hat V_1 + \cancel{\hat V_0 \hat V_1} + \cancel{\hat V_1 \hat V_0} + \hat V_0 \hat V_0 | \mathbf{k}; n=1\rangle - \langle \hat V_0\rangle^2 - 2\langle \hat V_0\rangle\cancel{\langle \hat V_1\rangle} - \cancel{\langle \hat V_1\rangle}^2$$

$$\Rightarrow \Delta E^2 = \langle \hat V_1 \hat V_1\rangle + \langle \hat V_0 \hat V_0\rangle - \langle \hat V_0\rangle^2 = \langle \hat V_1 \hat V_1\rangle + \Delta V_0{}^2$$

Thus the uncertainty arises from two different sources; an inelastic part (the first term) and an elastic part (the second term). The second term clearly corresponds to the contribution from $\sigma_{elastic}(E)$, and so we can neglect it when discussing the width of the inelastic part of the resonance. The second term would be ***zero*** if there was no n=0 state. Thus, it accounts for some additional “smearing out” of the energy due to the possibility of inelastic scattering involving n=0.

2) Qualitative Picture



What is going on physically? Consider scattering off a molecule in the n=1 state. The n=1 state can ***decay*** back to the n=0 state by transferring the excitation energy to the electron, as shown in the picture at right. This describes a loss of probability for being found in the n=1 state. The uncertainty in energy arises from the fact that, after the decay, the molecule can still be re-excited back to the n=1 state by interacting with the electron a second time. This second order term will look like $\hat{V}_1\hat{V}_1$, analogous to the inelastic contribution to the uncertainty in energy. Hence, the width of the resonance must be attributable to these very rapid excitation-decay processes.

In order to model this decay, one might postulate that the time dependence of the n=1 state looks something like:

$$\left|k;n=1;t\right\rangle = e^{-iEt-\Gamma t/2}\left|k;n=1;t=0\right\rangle$$

where the first term in the exponential is the approximate energy of the state (given, perhaps, by the center of the resonance) and Γ is some constant that represents the decay rate of the state. At the very least, this prescription gives a straightforward representation of a state that is clearly decaying, since

$$\left\langle k;n=1;t\middle|k;n=1;t\right\rangle = e^{-\Gamma t}$$

which indicates that the probability of finding the system in this state is a monotonically decreasing function of time.

We notice, however, that the same form could be obtained if we assume that $\hat{H} = \hat{H}_0 - i\Gamma/2$, for then

$$\left|k;n=1;t\right\rangle = e^{-i\hat{H}t}\left|k;n=1;t=0\right\rangle = e^{-iE_0t-\Gamma t/2}\left|k;n=1;t=0\right\rangle .$$

In this case, the energy becomes associated with the edge of the resonance, but this is a small difference if the resonance is narrow.

Given this form for $\hat{H}$, we can easily compute the scattering cross section for scattering in the n=1 state:

$$\sigma \approx \left|\left\langle \mathbf{k};n=1\right|\frac{1}{E-\hat{H}}\left|\mathbf{k};n=1\right\rangle\right|^2 = \left|\left\langle \mathbf{k};n=1\right|\frac{1}{E-E_0+i\Gamma/2}\left|\mathbf{k};n=1\right\rangle\right|^2$$

$$=\frac{1}{(E-E_0)+(\Gamma/2)^2}$$

This form for the shape of the resonance (or linewidth) is usually called the Breit-Wigner form. It shows that the scattering off a resonance with lifetime $1/\Gamma$ is described by a Lorentzian of width $\Gamma/2$. Thus, we see a complete story of the physical origin of the width of the resonance; it arises from the fact that the n=1 state is not an eigenstate of $\hat{H}$, and therefore there is some “smearing out” of the intensity around the approximate energy of the n=1 state. Further, this smearing out can be qualitatively associated with the lifetime of the metastable n=1 state. Because of the simple association of lifetimes with Lorentzian lineshapes, one often sees experimental data fit to this functional form in an effort to extract the lifetime.