An Atom Coupled to the Continuum - part 1

Up to this point in the course, we have discussed only the situation in which a quantum particle scatters from a fixed potential. We have not discussed cases in which the target is altered by the scattering or in which additional degrees of freedom are excited by the scattering. In this lecture and the next few, I will closely analyze the simplest problem of that type, the excitation of an unstable state of an atom as the result of a collision. This problem can be examined from the point of view of scattering or as a time-dependent situation of a quantum state. The problem can be analyzed in perturbation theory with the coupling of the excited state to the external colliding particle treated as a small parameter, but it is also illuminating to solve this problem exactly. I would like to discuss all of these approaches and to compare them.

The problem of an isolated quantum state coupled to a continuum was first analyzed by Wigner and Weisskopf in 1930. Here is a very simple version of the problem. We first consider an electron satisfying the free-particle Schrödinger equation. We add to the Hilbert space a single quantum state of energy $E_0 > 0$. We allow the electron to make a transition to this state and back again. If $|0\rangle$ is the isolated state and $|\vec{r}\rangle$ are the free-particle electron states, the matrix elements of the Hamiltonian are

$$\langle \vec{r} | H | \vec{r}' \rangle = \langle \vec{r} | -\frac{\nabla^2}{2m} | \vec{r}' \rangle$$

$$\langle \vec{r} | H | 0 \rangle = \lambda \chi(r)$$

$$\langle 0 | H | \vec{r} \rangle = \lambda \chi^*(r)$$

$$\langle 0 | H | 0 \rangle = E_0$$

where, for simplicity, $\chi(r)$ is a spherically symmetric function. The coefficient λ is the *coupling constant.* We will be especially interested in the case where $\lambda \ll 1$. In this limit, the coupling of the state $|0\rangle$ to the continuum is weak and, if the system starts in the state $|0\rangle$, it will stay there a long time. You might also think that, in this limit, the scattering induced by the coupling to $|0\rangle$ is weak, but, as we will see, that is not really correct.

The situation I have described might also be considered as an idealization of the problem in which a photon collides with an atom to produce an excited state which subsequently decays. However, we still have some formalism to develop to treat light and photons in quantum mechanics, whereas we understand nonrelativistic electrons very well already. So I will consider the external particle as an electron to work through this problem.

A general state of this system is a linear combination of a free electron and a state with no electron but with the state $|0\rangle$ populated. The wavefunction of a general state can be written as

$$|\Psi\rangle = \int d^3r \; \psi(\vec{r}) \, |\vec{r}\rangle + \alpha \, |0\rangle$$

The total probability is given by

$$1 = \int d^3r \; |\psi(\vec{r})|^2 + |\alpha|^2$$

I would like to solve for the scattering amplitude of an electron in this model. To do this, we should solve the time-independent Schrödinger equation at an energy

$$E = k^2/2m$$

and look for a solution with outgoing boundary conditions of the form

$$\psi(\vec{r}) = e^{ikz} + \frac{e^{ikr}}{r} f_k(\theta, \phi)$$

The time-independent Schrödinger equation for this model is the pair of equations

$$E\,\psi(r) = -\nabla^2/2m \; \psi(r) + \lambda \, \chi(r) \, \alpha$$

$$E\,\alpha = E_0 \, \alpha + \lambda \int d^3r' \, \chi^*(r') \, \psi(r')$$

To solve these equations, first solve the second equation for α

$$\alpha = \frac{\lambda}{E - E_0} \int d^3r' \, \chi^*(r') \psi(r')$$

and the insert the result in the first equation. This gives the integral equation for $\psi(\vec{r})$

$$\left(E + \frac{\nabla^2}{2m}\right) \psi(r) = \lambda^2 \chi(r) \frac{1}{E - E_0} \int d^3r' \, \chi^*(r') \psi(r')$$

Inserting also

$$\psi(r) = e^{ikz} + F(r)$$

we find

$$\left(E + \frac{\nabla^2}{2m}\right) F(r) = \lambda^2 \chi(r) \frac{1}{(E - E_0)} \int d^3r' \, \chi^*(r') \left[e^{ik\hat{z}\cdot\vec{r}'} + F(r') \right]$$

or

$$(\underset{\sim}{P}^2 - k^2) F(r) = -2m\lambda^2 \frac{\chi(r)}{(E - E_0)} \int d^3r' \, \chi^*(r') \left[e^{ik\hat{z}\cdot\vec{r}'} + F(r') \right]$$

The operator on the left-hand side is familiar to us, so we can rewrite the equation using its Green's function

$$F(\vec{x}) = \int d^3y \; G(\vec{x},\vec{y}) \left(-\frac{2m\lambda^2 \chi(\vec{y})}{E-E_0} \right) \int d^3w \; \chi^*(w) \left[e^{ik\hat{z}\cdot\vec{w}} + F(w) \right]$$

or, explicitly,

$$F(\vec{x}) = \int d^3y \; \frac{e^{ik|\vec{x}-\vec{y}|}}{4\pi|\vec{x}-\vec{y}|} \left(\frac{-2m\lambda^2 \chi(\vec{y})}{(E-E_0)} \right) \int d^3w \; \chi^*(w) \left[e^{ik\hat{z}\cdot\vec{w}} + F(w) \right]$$

It will be instructive to first analyze this equation using the Born approximation. We drop the function $F(\vec{r})$ on the right-hand side and obtain the solution

$$F(\vec{x}) = \int d^3y \; \frac{e^{ik|\vec{x}-\vec{y}|}}{4\pi|\vec{x}-\vec{y}|} \; \frac{-2m\lambda^2 \chi(\vec{y})}{(E-E_0)} \; \tilde{\chi}^*(k\hat{z})$$

I have identified

$$\int d^3w \; \chi^*(w) \, e^{ik\hat{z}\cdot\vec{w}} = \left[\int d^3w \; \chi(w) \, e^{-i(k\hat{z})\cdot\vec{w}} \right]^* = \tilde{\chi}^*(k\hat{z})$$

as the complex conjugate of the Fourier transform of $\chi(r)$. Since $\chi(r)$ is spherically symmetric, its Fourier transform is also, and so $\tilde{\chi}(\vec{k})$ is only a function of $|\vec{k}|$. Now we can take $|\vec{x}|$ to infinity to extract the scattering amplitude. In this limit

$$F(x) = \frac{e^{ik|\vec{x}|}}{x} \int d^3y \left(-\frac{m\lambda^2}{2\pi} \right) e^{-ik\hat{r}\cdot\vec{y}} \, \frac{\chi(\vec{y})}{(E-E_0)} \; \chi^*(k)$$

$$= \frac{e^{ikx}}{x} \left(-\frac{m\lambda^2}{2\pi} \right) \frac{1}{E-E_0} \; \chi(k)\,\chi^*(k)$$

and we find for the scattering amplitude

$$f_k = -\frac{m\lambda^2}{2\pi}\frac{|\chi(k)|^2}{(E - E_0)}$$

The scattering is entirely in the S wave ($\ell = 0$), as we might expect from the fact that the function $\chi(r)$ that couples the new state $|0\rangle$ to the continuum is spherically symmetric.

If λ is small, the scattering is weak – except when the energy is near $E = E_0$. As $E \to E_0$, the Born approximation amplitude goes to infinity no matter how small λ is. This is a *resonance*. The energy of the state $|0\rangle$ acts like the natural frequency of a harmonic oscillator. The frequency of the incoming wave is E (as we set $\hbar = 1$). As $E \to E_0$, the external perturbation comes into resonance with the oscillator, and the excitation of the oscillator increases without bound.

The energy-dependence

$$f_k \sim \frac{1}{E - E_0} \qquad \text{or} \qquad \sigma(E) \sim \frac{1}{(E - E_0)^2}$$

in the vicinity of a resonance is seen throughout atomic, nuclear, and particle physics. An important example is the scattering of light from atoms. Typical atomic excitation energies are in the eV range, that is, in the near ultraviolet. Photons of visible light have energies below the resonances, but photons of blue light have higher energies than photons of red light and thus scatter more. This is why the sky is blue. This process is called *Rayleigh scattering.*

However, there is a problem with the Born approximation formula. In our discussion of partial wave amplitudes, we saw that scattering amplitudes cannot actually go to infinity. In this problem, the scattering is only occurring in the $\ell = 0$ partial wave. Then the scattering amplitude must have the form

$$f_k = \frac{1}{k} e^{i\delta_0(k)} \sin\delta_0(k)$$

This is bounded by unitarity

$$|f_k| < \frac{1}{k}$$

In the harmonic oscillator analogy, the expression for a resonance might not go to infinity if there is some damping in the system. In this quantum mechanics problem, we must find some damping of the resonance in order to conserve probability. Hopefully, we will find this effect if we solve the problem more exactly.

Go back, then, to the integral equation for $F(\vec{r})$ and look for an exact solution. It will help to Fourier transform. Let

$$F(\vec{r}) = \int \frac{d^3p}{(2\pi)^3} e^{i\vec{p}\cdot\vec{r}} \tilde{F}(\vec{p})$$

Then the equation becomes

$$(p^2 - k^2)\tilde{F}(\vec{p}) = -2m\lambda^2 \frac{\tilde{\chi}(p)}{E - E_0} \int d^3r' \, \chi^*(r') \left[e^{ik\hat{z}\cdot\vec{r}'} + F(r') \right]$$

The term involving F on the right-hand side contains the integral

$$\Phi = \int d^3r \; \chi^*(r) F(r)$$

which can be evaluated in terms of the Fourier transform of F

$$\Phi = \int d^3r \; \chi^*(r) \int \frac{d^3q}{(2\pi)^3} e^{i\vec{q}\cdot\vec{r}} \tilde{F}(q) = \int \frac{d^3q}{(2\pi)^3} \tilde{\chi}^*(q) \tilde{F}(q)$$

Then we find

$$(p^2-k^2)\,\tilde{F}(p) = -2m\lambda^2\,\frac{\tilde{\chi}(p)}{E-E_0}\left[\tilde{\chi}^*(k)+\Phi\right]$$

and now we can solve for $\tilde{F}(p)$

$$\tilde{F}(p) = -2m\lambda^2\,\frac{\tilde{\chi}(p)}{(p^2-k^2)}\,\frac{1}{(E-E_0)}\left[\tilde{\chi}^*(k)+\Phi\right]$$

The result implicitly involves Φ on the right-hand side. But we can construct Φ from this solution and solve for it self-consistently. Constructing the Φ integral

$$\Phi = \int\frac{d^3q}{(2\pi)^3}\,\chi^*(q)\tilde{F}(q) = \int\frac{d^3q}{(2\pi)^3}\,\frac{|\chi(q)|^2}{q^2-k^2}\left(\frac{-2m\lambda^2}{E-E_0}\right)\left[\tilde{\chi}^*(k)+\Phi\right]$$

gives a simple algebraic equation for Φ. To write this equation more clearly, define

$$I(k) = \int\frac{d^3q}{(2\pi)^3}\,\frac{|\chi(q)|^2}{q^2-k^2}$$

Then

$$\Phi = I(k)\left(-\frac{2m\lambda^2}{E-E_0}\right)\left[\tilde{\chi}^*(k)+\Phi\right]$$

that is

$$\Phi = -\frac{2m\lambda^2}{(E-E_0)}\,\frac{\tilde{\chi}^*(k)\,I(k)}{\left[1+\frac{2m\lambda^2}{(E-E_0)}\,I(k)\right]}$$

The quantity on the right-hand side of the original equation was

$$\left[\hat{\chi}^*(k) + \Phi \right] = \frac{(E - E_0)\, \chi^*(k)}{E - E_0 + 2m\lambda^2 \Sigma(k)}$$

We can insert this back into the equation for F and find

$$\tilde{F}(p) = \frac{1}{p^2 - k^2} (-2m\lambda^2) \frac{\tilde{\chi}(p) \quad \hat{\chi}^*(k)}{E - E_0 + 2m\lambda^2 \Sigma(k)}.$$

This solution has exactly the same form as the Born approximation, except that we have now replaced

$$(E - E_0) \quad \rightarrow \quad (E - E_0 + 2m\lambda^2 \Sigma(k))$$

Now we can go back to real space and extract the scattering amplitude as before. The result is

$$f_k = -\frac{m}{2\pi} \lambda^2 \frac{|\tilde{\chi}(k)|^2}{E - E_0 + 2m\lambda^2 \Sigma(k)}$$

This is just the same as the Born approximation result, with an extra term in the denominator. Hopefully, this will solve the problems raised above.

To understand the significance of the new term in the denominator, we need to evaluate the integral

$$\Sigma(k) = \int \frac{d^3q}{(2\pi)^3} \frac{|\tilde{\chi}(q)|^2}{q^2 - k^2}$$

Although it is not obvious, this integral has both a real and an imaginary part. Write

$$\Xi(k) = \Sigma(k) + i\, H(k)$$

where $\Sigma(k)$ and $H(k)$ are real-valued functions. Then

$$f_k = -\frac{m}{2\pi}\lambda^2 \, |\tilde{\chi}(k)|^2 \; \frac{1}{E - E_0 + 2m\lambda^2\Sigma + i2m\lambda^2 H}$$

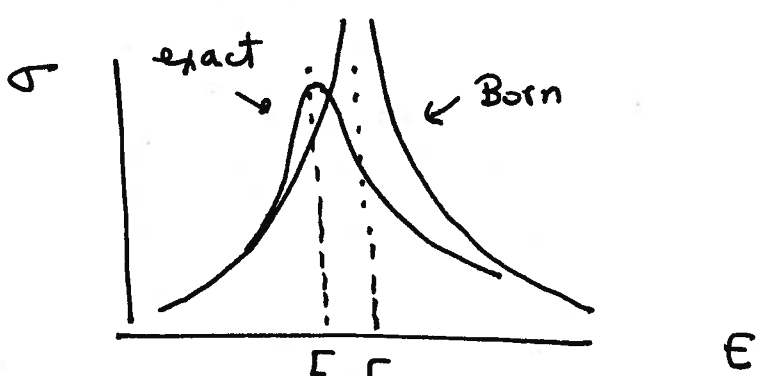
Set

$$E_* = E_0 - 2m\lambda^2\Sigma(k) \qquad \frac{\Gamma}{2} = 2m\lambda^2 H(k)$$

Then the scattering amplitude takes the form

$$f_k = -\frac{m}{2\pi}\,\frac{\lambda^2\,|\tilde{\chi}(k)|^2}{E - E_* + i\,\Gamma/2}$$

The real part $\Sigma(k)$ moves the position of the resonance slightly, by an amount of order λ^2 for small λ. The imaginary part displaces the zero of the denominator into the complex plane. This will have the effect of rounding off the singularity, providing the analog of damping in a harmonic oscillator. This effect is also of order λ^2. If λ is small, these two effects are negligible except very close to the resonance, where they are essential corrections.



It is thus reasonable, for small λ, to evaluate the functions $\Sigma(k)$ and $H(k)$ at the resonance momentum k_*, such that $E_* = k_*^2/2m$

$$E_* \cong E_0 - 2m\lambda^2 \Sigma(k_*) \qquad \frac{\Gamma}{2} \cong 2m\lambda^2 H(k_*)$$

and treat these quantities as constants.

Now we turn to the calculation of Σ and H. The integrand of $X(k)$ is spherically symmetric, and so we can reduce the integral easily to

$$X = \Sigma + iH = \int_0^\infty \frac{dq}{(2\pi)^3} q^2 \cdot 4\pi \, |\chi(q)|^2 \, \frac{1}{q^2 - k^2}$$

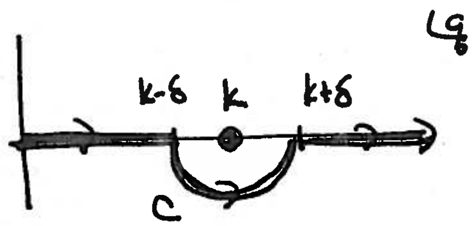
However, here, there is clearly a problem. The denominator of the integrand has a zero on the path of integration, leading to a non-integrable singularity.

This situation, with a zero on the path of integration, is one that we meet often in solving differential equations that arise in physics. Usually, there is a physical reason why the zero is not *exactly* on the integration contour but rather is displaced to one side or the other. In this example, the structure $1/(q^2 - k^2)$ arises from the Green's function for the free particle Schrödinger equation. We know that, to obtain the correct outgoing boundary conditions, this should really be written

$$\frac{1}{q^2 - k^2 - i\epsilon}$$

Then the singularity actually lies at $q = k + i\epsilon$, just slightly above the contour of integration.

Because such integrals arise often in quantum mechanics, I would like to discuss the evaluation of this integral very carefully. In complex analysis, we can deform the path of integration, and this does not affec the value of the integral as long as we preserve the *topology* of the situation, that the singularity lies above the contour. A useful path to take is the following: We integrate along the real axis until we approach to a distance δ of the singularity, then detour along a semicircular contour C of radius δ, and then proceed along the real axis from $k+\delta$ to infinity.



I will evaluate the integral using this contour, considered in the limit $\delta \to 0$.

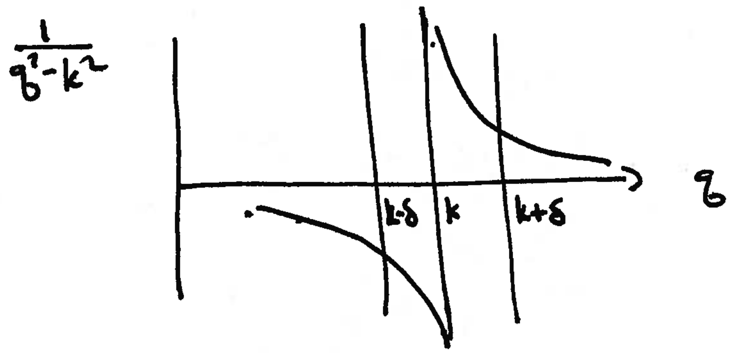
The integral is then given by

$$\mathcal{I} = \frac{1}{2\pi^2}\left(\int_0^{k-\delta} dq + \int_{k+\delta}^{\infty} dq\right) \frac{q^2\,|\tilde{\chi}(q)|^2}{q^2-k^2}$$
$$+ \frac{1}{2\pi^2}\int_C dq\; q^2\,\frac{|\chi(q)|^2}{q^2-k^2}\,.$$

The first line is a manifestly real expression. Notice that each integral separately is divergent, for example,

$$\int_{k+\delta} dq\,\frac{1}{q-k} \sim \log(q-k)\Big|_{k+\delta} \sim -\log\delta$$

However, if the first integral stops a distance δ from the singularity, and the second integral starts, symmetrically, a distance δ from the singularity, the divergent terms cancel and the sum of the integrals gives a finite real value. A way to see this is that the function integrated goes to $-\infty$ below the singularity and returns from $+\infty$,



so the two singular terms are symmetrical, with opposite signs. The finite residue is called the *principal value integral* and is denoted by the symbol $\mathcal{P}$

$$\frac{1}{2\pi^2}\left(\int_0^{k-\delta} dq + \int_{k+\delta}^{\infty} dq\right) \frac{q^2|\tilde{\chi}|^2}{q^2-k^2} = \mathcal{P}\,\frac{1}{2\pi^2}\int_0^{\infty} dq\, \frac{q^2|\tilde{\chi}|^2}{q^2-k^2}$$

The term in the integral X from the semicircular contour C is half of the contribution from integrating around the pole at $q = k$. This contribution then gives

$$(+i\pi)\cdot\frac{1}{2\pi^2}\left[\frac{q^2|\tilde{\chi}(q)|^2}{2q}\right]_{q=k} = i\cdot\frac{1}{4\pi}\,k|\tilde{\chi}(k)|^2$$

Note that it is pure imaginary. The choice of contour that we have made cleanly separates the real and imaginary parts of the integral X.

Often, this analysis is abbreviated in the following way:

$$\int dq\, \frac{f(q)}{q-k-i\varepsilon} = \mathcal{P}\int dq\, \frac{f(q)}{q-k} + i\pi f(k)$$

Sometimes, one simply sees the formula

$$\frac{1}{q-k-i\varepsilon} = \mathcal{P}\,\frac{1}{q-k} + i\pi\,\delta(q-k)$$

Similarly, for another choice of boundary conditions

$$\frac{1}{q-k+i\epsilon} = \mathcal{P}\,\frac{1}{q-k} - i\pi\,\delta(q-k)$$

We now identify the shift of the resonance position as

$$E_* - E_0 = -2m\lambda^2 \cdot \frac{1}{2\pi^2}\,\mathcal{P}\int_0^\infty dq\,\frac{q^2|\tilde{\chi}(q)|^2}{q^2-k^2}$$

and the imaginary part of the denominator as

$$\frac{\Gamma}{2} = \frac{m}{2\pi}\lambda^2 k\,|\tilde{\chi}(k)|^2$$

The complete scattering amplitude can now be written

$$f_k = \frac{1}{k}\cdot\left(-\frac{m\lambda^2}{2\pi}k\,|\tilde{\chi}(k)|^2\right)\frac{1}{E-E_*+i\,\frac{m\lambda^2}{2\pi}k\,|\tilde{\chi}(k)|^2}$$

or, near $k=k_*$,

$$f_k = -\frac{1}{k}\,\frac{\Gamma/2}{(E-E_*+i\Gamma/2)}$$

It is convenient to make the denominator real,

$$f_k = -\frac{1}{k}\,\frac{(\Gamma/2)(E-E_*-i\Gamma/2)}{(E-E_*)^2+(\Gamma/2)^2}$$

Now it is clear that the maximum value of $|f_k|$ is bounded at $1/k$, as required by unitarity.

We can now define an angle $\delta_0(k)$ through

$$\cos \delta_0(k) = \frac{E_* - E}{\left[(E_* - E)^2 + (\Gamma/2)^2\right]^{1/2}} \qquad \sin \delta_0(k) = \frac{\Gamma/2}{\left[(E_* - E)^2 + (\Gamma/2)^2\right]^{1/2}}$$

In terms of this angle,

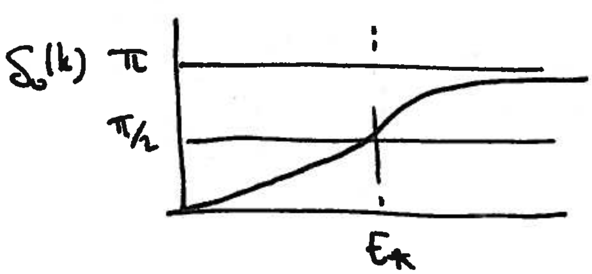
$$f_k = \frac{1}{k}(\sin \delta_0)(\cos \delta_0 + i \sin \delta_0) = \frac{1}{k} e^{i\delta_0} \sin \delta_0$$

Notice that

$$\cos \delta_0 \to 1 \qquad \text{for} \quad E < E_* - \Gamma$$

$$\cos \delta_0 \to -1 \qquad \text{for} \quad E > E_* + \Gamma$$

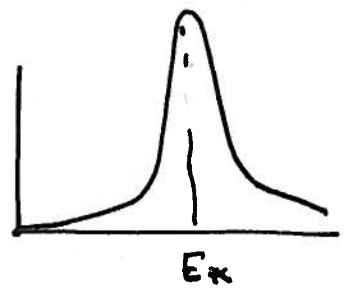
So, as E increases from below to above the resonance at E_*, $\delta_0(k)$ increases from 0 to π.



Since δ_0 increases through $\pi/2$, we have added 1 state to the continuum. This is exactly the original state $|0\rangle$, which is now merged with the continuum electron states in the spectrum of H.

The scattering cross section now has the form

$$\sigma_0 = \frac{4\pi}{k^2} \sin^2 \delta_0$$



The width of the resonance in energy – more precisely, the full width at half maximum – is given by Γ, with

$$\Gamma = \frac{m\lambda^2}{\pi} k_* \left| \hat{\chi}(k_*) \right|^2$$

This quantity is of order λ^2 for small λ, but nevertheless its presence is essential to round off the resonance cross section precisely at the level required by unitarity.

The final formula we have found for the cross section in the vicinity of the resonance is

$$\sigma(k) = \frac{4\pi}{k_*^2} \frac{(\Gamma/2)^2}{(E - E_*)^2 + (\Gamma/2)^2}$$

This formula is called the *Lorentzian line shape* in atomic physics; in nuclear physics, it is called the *Breit-Wigner formula.* It is the natural shape of a narrow resonance in every context from atomic energies to the energies of elementary particle physics. The quantity Γ is the *natural line width* of the resonance. This shape is seen over and over again in quantum mechanical problems.