INTEGRAL FORM OF THE SCHRÖDINGER EQUATION

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 11.8.

As a prelude to the Born approximation in quantum scattering, we need to look at the integral form of the time-independent Schrödinger equation. The equation in its original differential equation form is

$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi \tag{1}$$

which can be written as

$$\left(\nabla^2+k^2\right)\psi = Q \tag{2}$$

$$k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{3}$$

$$Q \equiv \frac{2m}{\hbar^2}V\psi \tag{4}$$

To convert this to an integral equation, we need to define a *Green's function* $G(\mathbf{r})$ which satisfies the differential equation

$$\left(\nabla^2+k^2\right)G(\mathbf{r})=\delta^3(\mathbf{r}) \tag{5}$$

Using this function we can write ψ as an integral equation

$$\psi(\mathbf{r})=\int G(\mathbf{r}-\mathbf{r}_0)\,Q(\mathbf{r}_0)\,d^3\mathbf{r}_0 \tag{6}$$

We can show this works by plugging in G from 5:

$$\left(\nabla^2+k^2\right)\psi(\mathbf{r})=\int\left(\nabla^2+k^2\right)G(\mathbf{r}-\mathbf{r}_0)\,Q(\mathbf{r}_0)\,d^3\mathbf{r}_0 \tag{7}$$

$$=\int\delta(\mathbf{r}-\mathbf{r}_0)\,Q(\mathbf{r}_0)\,d^3\mathbf{r}_0 \tag{8}$$

$$=Q(\mathbf{r}) \tag{9}$$

which gives us back 2.

This isn't a solution of the Schrödinger equation, of course, because Q contains ψ, so we'd need to actually know ψ in advance in order to work out the integral with the Green's function. Rather, it's just a different way of writing the Schrödinger equation which proves useful in scattering theory.

Because 5 doesn't depend on the potential V, we can work out the Green's function which is valid for every potential. The process is rather involved, but Griffiths goes through the details in section 11.4.1, so I won't reproduce them here, apart from noting that the solution uses what is, to me, one of the most beautiful theorems in mathematics: Cauchy's theorem on contour integration. Maybe I'll return to it later.

Anyway, the Green's function turns out to be

$$G(\mathbf{r}) = -\frac{e^{ikr}}{4\pi r} \tag{10}$$

We can verify this is in fact a solution by plugging it back into 5. We need the Laplacian of G which we can get by calculating the divergence of the gradient. Taking the gradient first, we use the product rule for gradients:

$$\nabla(fg) = f\nabla g + g\nabla f \tag{11}$$

We get

$$\nabla G = -\frac{1}{4\pi}\left(\frac{1}{r}\nabla e^{ikr} + e^{ikr}\nabla\frac{1}{r}\right) \tag{12}$$

To calculate the divergence of the gradient, we use the identity for the divergence of the product of a scalar and a vector:

$$\nabla\cdot(f\mathbf{A}) = \mathbf{A}\cdot\nabla f + f\nabla\cdot\mathbf{A} \tag{13}$$

We therefore have

$$\nabla^2 G = -\frac{1}{4\pi}\left[\left(\nabla\frac{1}{r}\right)\cdot\left(\nabla e^{ikr}\right) + \frac{1}{r}\nabla^2 e^{ikr} + \left(\nabla e^{ikr}\right)\cdot\left(\nabla\frac{1}{r}\right) + e^{ikr}\nabla^2\frac{1}{r}\right] \tag{14}$$

The last term turns out to be a delta function:

$$\nabla^2\frac{1}{r} = \nabla\cdot\left(\nabla\frac{1}{r}\right) = -\nabla\cdot\left(\frac{\hat{\mathbf{r}}}{r^2}\right) = -4\pi\delta^3(\mathbf{r}) \tag{15}$$

To work out the second term, we use the formula for the Laplacian in spherical coordinates, for a function that depends only on r:

$$\nabla f(r) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) \tag{16}$$

We get

$$\nabla^2 e^{ikr} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(ikr^2 e^{ikr}\right) \tag{17}$$

$$= \frac{2ik}{r}e^{ikr} - k^2 e^{ikr} \tag{18}$$

Putting this back into 14 we get

$$\nabla^2 G = -\frac{1}{4\pi}\left[2\left(\nabla\frac{1}{r}\right)\cdot\left(\nabla e^{ikr}\right) + \frac{2ik}{r^2}e^{ikr} - \frac{k^2}{r}e^{ikr} - 4\pi\delta^3(\mathbf{r})\,e^{ikr}\right] \tag{19}$$

$$= -\frac{1}{4\pi}\left[-\frac{2ik}{r^2}e^{ikr} + \frac{2ik}{r^2}e^{ikr} - \frac{k^2}{r}e^{ikr} - 4\pi\delta^3(\mathbf{r})\,e^{ikr}\right] \tag{20}$$

$$= -\frac{1}{4\pi}\left[-\frac{k^2}{r}e^{ikr} - 4\pi\delta^3(\mathbf{r})\right] \tag{21}$$

$$= \frac{k^2}{4\pi r}e^{ikr} + \delta^3(\mathbf{r}) \tag{22}$$

$$= -k^2 G(\mathbf{r}) + \delta^3(\mathbf{r}) \tag{23}$$

(24)

$$\left(\nabla^2 + k^2\right) G(\mathbf{r}) = \delta^3(\mathbf{r})$$

where we dropped the e^{ikr} from the last term in the third line since the delta function is zero except when $\mathbf{r} = 0$.

Using this Green's function, the integral form of the Schrödinger equation is

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) - \frac{m}{2\pi\hbar^2}\int \frac{e^{ik|\mathbf{r}-\mathbf{r}_0|}}{|\mathbf{r}-\mathbf{r}_0|}V(\mathbf{r}_0)\,\psi(\mathbf{r}_0)\,d^3\mathbf{r}_0 \tag{25}$$

where ψ_0 is a solution of the free particle Schrödinger equation

$$\left(\nabla^2 + k^2\right)\psi_0(\mathbf{r}) = 0 \tag{26}$$

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