Supplement 8-A

A Useful Theorem

The following useful result appears in Pauli's 1930 "Handbuch Article on Quantum Theory":

Consider eigenvalues and eigenfunctions of a Hamiltonian that depends on some parameter—for example, the mass of the electron, or the charge of the electron, or any other parameter that may appear in more complicated problems. The Schrödinger eigenvalue equation may then be written with the parameter α explicitly indicated as,

$$H(\alpha)u_n(\mathbf{r}, \alpha) = E(\alpha)u_n(\mathbf{r}, \alpha) \tag{8A-1}$$

It follows that with the eigenfunctions normalized to unity,

$$\int d^3r u_n^*(\mathbf{r}, \alpha)u_n(\mathbf{r}, \alpha) = 1 \tag{8A-2}$$

that

$$E(\alpha) = \int d^3r u_n^*(\mathbf{r}, \alpha)H(\alpha)u_n(\mathbf{r}, \alpha) \tag{8A-3}$$

Let us now differentiate both sides with respect to α . We get

$$\frac{\partial E(\alpha)}{\partial \alpha} = \int d^3r \frac{\partial u_n^*(\mathbf{r}, \alpha)}{\partial \alpha} H(\alpha)u_n(\mathbf{r}, \alpha) + \int d^3r u_n^*(\mathbf{r}, \alpha)H(\alpha)\frac{\partial u_n(\mathbf{r}, \alpha)}{\partial \alpha} + \int d^3r u_n^*(\mathbf{r}, \alpha)\frac{\partial H(\alpha)}{\partial \alpha} u_n(\mathbf{r}, \alpha)$$

Consider now the first two terms on the right-hand side. Using the eigenvalue equation and its complex conjugate (with hermiticity of H), we see that they add up to

$$E(\alpha)\int d^3r \frac{\partial u_n^*(\mathbf{r}, \alpha)}{\partial \alpha} u_n(\mathbf{r}, \alpha) + E(\alpha)\int d^3r u_n^*(\mathbf{r}, \alpha)\frac{\partial u_n(\mathbf{r}, \alpha)}{\partial \alpha} = E(\alpha)\frac{\partial}{\partial \alpha}\int d^3r u_n^*(\mathbf{r}, \alpha)u_n(\mathbf{r}, \alpha) = 0$$

We are therefore left with

$$\frac{\partial E(\alpha)}{\partial \alpha} = \int d^3r u_n^*(\mathbf{r}, \alpha)\frac{\partial H(\alpha)}{\partial \alpha} u_n(\mathbf{r}, \alpha) = \left\langle \frac{\partial H(\alpha)}{\partial \alpha} \right\rangle \tag{8A-4}$$

The utility of this result is somewhat limited, because it requires knowing the exact eigenvalues and, for the calculation on the right-hand side, the exact eigenfunctions.[1] Nevertheless, the theorem does allow us certain shortcuts in calculations.

[1] The extension of this to certain approximate solutions is due to R. P. Feynman and H. Hellmann. See Problem 10 in Chapter 14.

Consider, for example, the one-dimensional simple harmonic oscillator, for which the Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 \tag{8A-5}$$

The eigenvalues are known to be

$$E_n = \hbar\omega(n + \tfrac{1}{2}) \tag{8A-6}$$

If we differentiate E_n with respect to ω, and if we note that

$$\frac{\partial H}{\partial \omega} = m\omega x^2$$

we can immediately make the identification

$$\hbar(n + \tfrac{1}{2}) = m\omega\langle x^2\rangle_n$$

or

$$\langle x^2\rangle_n = \frac{\hbar}{m\omega}\left(n + \frac{1}{2}\right) = \frac{E_n}{m\omega^2} \tag{8A-7}$$

Examples of relevance to the hydrogen atom are of particular interest. In the Hamiltonian, the factor

$$\frac{-e^2}{4\pi\varepsilon_0 r} = -\frac{\hbar c\alpha}{r}$$

appears. The eigenvalue has the form

$$E_{nl} = -\frac{1}{2}\frac{mc^2\alpha^2}{n^2}$$

If we take as our parameter to be α, then we get

$$-\hbar c\left\langle\frac{1}{r}\right\rangle_{n,l} = \frac{\partial}{\partial\alpha}E_{nl} = -\frac{mc^2\alpha}{n^2} \tag{8A-8}$$

so that

$$\left\langle\frac{1}{r}\right\rangle_{nl} = \frac{mc\alpha}{\hbar n^2} = \frac{1}{a_0 n^2} \tag{8A-9}$$

In the *radial* Hamiltonian, there is a term

$$\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

If we treat l as the parameter and recall that $n = n_r + l + 1$, we get

$$\frac{\hbar^2}{2m}\left\langle\frac{2l+1}{r^2}\right\rangle = \frac{1}{2}mc^2\alpha^2\frac{2}{n^3} \tag{8A-10}$$

which is equivalent to

$$\left\langle\frac{1}{r^2}\right\rangle_{nl} = \frac{1}{a_0^2 n^3(l + \frac{1}{2})} \tag{8A-11}$$

Using an observation of J. Schwinger that the average force in a stationary state must vanish, we can proceed from

$$\begin{aligned} F &= -\frac{dV(r)}{dr} = -\frac{d}{dr}\left(-\frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2 l(l+1)}{2mr^2}\right) \\ &= -\frac{e^2}{4\pi\varepsilon_0 r^2} + \frac{\hbar^2 l(l+1)}{mr^3} \end{aligned} \tag{8A-12}$$

to $\langle F(r)\rangle = 0$ and thus obtain

$$\left\langle\frac{1}{r^3}\right\rangle_{nl} = \frac{m}{\hbar^2 l(l+1)}\frac{e^2}{4\pi\varepsilon_0}\left\langle\frac{1}{r^2}\right\rangle_{nl} = \frac{1}{a_0^3 n^3 l(l+\frac{1}{2})(l+1)} \tag{8A-13}$$

Supplement 8-B

The Square Well, Continuum Solutions

We saw in eq. (8-69) that asymptotically the free-particle solution has the form

$$R_l(r) \rightarrow -\frac{1}{2ikr}\,[e^{-i(kr-l\pi/2)} - e^{i(kr-l\pi/2)}]$$

We now assert that the first term is an incoming spherical wave, and the second is an outgoing spherical wave. The description is arrived at in the following way.

Consider the three-dimensional probability flux

$$\mathbf{j} = \frac{\hbar}{2i\mu}\,(\psi^*(\mathbf{r})\nabla\psi(\mathbf{r}) - \nabla\psi^*(\mathbf{r})\psi(\mathbf{r}))$$

We shall see that it is only the radial flux that is of interest for large r. The radial flux, integrated over all angles, is thus

$$\int d\Omega\,\mathbf{i}_r \cdot \mathbf{j}(\mathbf{r}) = \frac{\hbar}{2i\mu}\int d\Omega\left(\psi^*\frac{\partial\psi}{\partial r} - \frac{\partial\psi^*}{\partial r}\psi\right) \tag{8B-1}$$

For a solution of the form

$$\psi(\mathbf{r}) = C\,\frac{e^{\pm ikr}}{r}\,Y_{lm}(\theta, \varphi) \tag{8B-2}$$

with $\int d\Omega|Y_{lm}(\theta, \varphi)|^2 = 1$ the right-hand side of (8B-1) can easily be evaluated, and we find that

$$\int d\Omega j_r = \pm\frac{\hbar k|C|^2}{\mu}\,\frac{1}{r^2} \tag{8B-3}$$

The $\pm$ sign describes outgoing/incoming flux. The factor $1/r^2$ that emerges from our calculation is actually necessary for flux conservation, since the flux going through a spherical surface of radius r is

$$\int r^2\,d\Omega j_r = \pm\frac{\hbar k|C|^2}{\mu}, \qquad \text{independent of } r$$

We therefore see that for the free-particle solution the incoming flux is equal in magnitude to the outgoing flux, which is what it should be, because there are no sources of flux.

We now note that in the presence of a potential flux is still conserved. Any solution will asymptotically consist of an incoming spherical wave and an outgoing spherical wave, with the constraint that the magnitude of the incoming flux and the outgoing flux be equal. Thus if the asymptotic solution has the form

$$R_l(kr) \to -\frac{1}{2ikr}\left(e^{-i(kr-l\pi/2)} - S_l(k)e^{i(kr-l\pi/2)}\right) \tag{8B-4}$$

then it is required that

$$|S_l(k)|^2 = 1 \tag{8B-5}$$

We write $S_l(k)$ in the standard form

$$S_l(k) = e^{2i\delta_l(k)} \tag{8B-6}$$

The real function $\delta_l(k)$ is called the *phase shift*, because the asymptotic form of the radial function (8B-4) may be rewritten in the form

$$R_l(r) \to e^{i\delta_l(k)}\frac{\sin(kr - l\pi/2 + \delta_l(k))}{kr} \tag{8B-7}$$

Aside from the irrelevant phase factor in front, this differs from the asymptotic form of the free-particle solution only by a shift in phase of the argument.

We note parenthetically that with a solution that has a $1/r$ behavior, the flux in any direction other than radial goes to zero as $1/r^2$, and we were therefore justified in only considering the radial flux at large values of r.

Let us now consider the special case of a square well. The above argument shows us that we only need to consider the phase shift, since at large distances from the well the only deviation from free particle behavior is the phase shift.

We again consider the well

$$\begin{aligned} V(r) &= -V_0 \qquad \text{for } r \le a \\ &= 0 \qquad\quad\; \text{for } r > a \end{aligned} \tag{8B-8}$$

We again use the notation

$$\kappa^2 = \frac{2\mu(E + V_0)}{\hbar^2} \tag{8B-9}$$

Now the solution for $r \le a$ must be regular at the origin, so that it has the form

$$R_l(r) = Aj_l(\kappa r) \qquad r \le a \tag{8B-10}$$

The solution for $r > a$ will contain an irregular part, so that we have

$$R_l(r) = Bj_l(kr) + Cn_l(kr) \qquad r \ge a \tag{8B-11}$$

The matching of $\frac{1}{R_l(r)}\frac{dR_l(r)}{dr}$ at $r = a$ yields an expression

$$\kappa\left[\frac{dj_l(\rho)/d\rho}{j_l(\rho)}\right]_{\rho=\kappa a} = k\left[\frac{Bdj_l/d\rho + Cdn_l/d\rho}{Bj_l(\rho) + Cn_l(\rho)}\right]_{\rho=ka} \tag{8B-12}$$

from which the ratio C/B can be calculated. The ratio can be related to the phase shift. We do this by looking at the asymptotic form of the larger r solution, which has the form

$$R_l(r) \to B\frac{\sin(kr - l\pi/2)}{kr} - C\frac{\cos(kr - l\pi/2)}{kr}$$

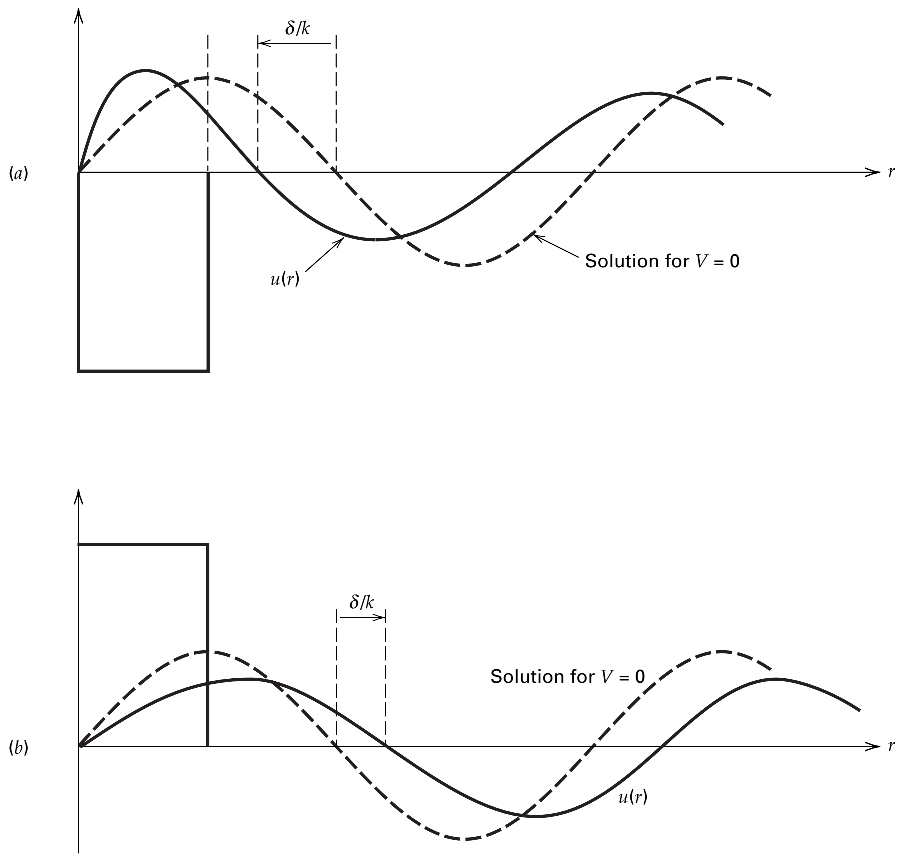

Figure 8B-1 Continuum solution $u(r) = rR(r)$ for $l = 0$ (a) attractive potential; (b) repulsive potential.

Comparison with the form in (8B-7), which has the form

$$R_l(r) \rightarrow \frac{\sin(kr - l\pi/2)}{kr} \cos \delta_l(k) + \frac{\cos(kr - l\pi/2)}{kr} \sin \delta_l(k)$$

shows that once we know C/B we can find the phase shift from

$$\frac{C}{B} = -\tan \delta_l(k) \tag{8B-13}$$

The actual calculation of C/B is very tedious, except when $l = 0$. In that case, using $u_l(r) = rR_l(r)$, we just have to match $A \sin \kappa r$ to $B \sin kr + C \cos kr$ (and the derivatives) at $r = a$. Figure (8B-1) shows the shape of the wave functions for attractive and repulsive potentials for $l = 0$.

We conclude with the proof of a useful relation

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} (2l + 1)i^l j_l(kr)P_l(\cos \theta) \tag{8B-14}$$

which is of great importance in scattering theory.

The Plane Wave in Terms of Spherical Harmonics

The solution of the free-particle equation

$$\nabla^2\psi(\mathbf{r}) + k^2\psi(\mathbf{r}) = 0 \tag{8B-15}$$

can be written in two ways. One is simply the plane wave solution

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \tag{8B-16}$$

The other way is to write it as a linear superposition of the partial wave solutions—that is,

$$\sum\sum A_{lm}\, j_l(kr)\, Y_{lm}(\theta, \phi) \tag{8B-17}$$

We may therefore find A_{lm} such that $\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$ in (8B-17). Note that the spherical angles (θ, ϕ) are the coordinates of the vector $\mathbf{r}$ relative to some arbitrarily chosen z-axis. If we define the z-axis by the direction of $\mathbf{k}$ (until now an arbitrary direction), then

$$e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ikr\cos\theta} \tag{8B-18}$$

Thus the left side of (8B-18) has no azimuthal angle, ϕ, dependence, and thus on the right side only terms with $m = 0$ can appear; hence, making use of the fact that

$$Y_{l0}(\theta, \phi) = \left(\frac{2l+1}{4\pi}\right)^{1/2} P_l(\cos\theta) \tag{8B-19}$$

where the $P_l(\cos\theta)$ are the Legendre polynomials, we get the relation

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty}\left(\frac{2l+1}{4\pi}\right)^{1/2} A_l j_l(kr)\, P_l(\cos\theta) \tag{8B-20}$$

We may use the relation

$$\frac{1}{2}\int_{-1}^{1} d(\cos\theta)\, P_l(\cos\theta)\, P_{l'}(\cos\theta) = \frac{\delta_{ll'}}{2l+1} \tag{8B-21}$$

which is a direct consequence of the orthonormality relation for the Y_{lm} and (8B-19) to obtain

$$A_l j_l(kr) = \frac{1}{2}[4\pi(2l+1)]^{1/2}\int_{-1}^{1} dz P_l(z)\, e^{ikrz} \tag{8B-22}$$

Compare the two sides of the equation as $kr \to 0$. The first term on the left-hand side is

$$A_l \frac{(kr)^l}{1, 3, 5, \ldots, (2l+1)}$$

and the corresponding power of $(kr)^l$ on the right-hand side has

$$\frac{1}{2}[4\pi(2l+1)]^{1/2}(ikr)^l\int_{-1}^{1} dz\, P_l(z) z^l/l!$$

The integral can be evaluated by noting that $P_l(z)$ is an lth-degree polynomial in z. The coefficient of the leading power, z^l, can be easily obtained from eq. (7-47) as the power of z^l in

$$(-1)^l \frac{1}{2^l l!}\left(\frac{d}{dz}\right)^l (1-z^2)^l = \frac{2l(2l-1)(2l-1)\cdots(l+1)}{2^l l!} z^l + 0(z^{l-1})$$

We can rewrite this in the form

$$z^l = \frac{2^l l!}{2l(2l-1)(2l-2)\cdots(l+1)} P_l(z) + \text{terms involving } P_{l+1}(z) \text{ and higher}$$

With the help of (8B-21) we finally get

$$A_l \frac{(kr)^l}{1, 3, 5, \ldots, (2l+1)} = \frac{1}{2}[4\pi(2l+1)]^{1/2}(ikr)^l \frac{1}{l!} \frac{2^l l!}{2l(2l-1)(2l-2)\cdots(l+1)} \frac{2}{2l+1} \tag{8B-23}$$

What results is the expansion

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} (2l+1)\, i^l j_l(kr)\, P_l(\cos\theta)$$

which we will find exceedingly useful in discussions of collision theory.