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

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

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

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