Quantum Mechanics 2

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Hydrogen Atom

Feynman-Hellmann Theorem

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Feynman-Hellmann Theorem

Suppose the Hamiltonian of a system is parametrized by λ ; Let $E_n(\lambda)$ and $\psi_n(\lambda)$ be the parametrized eigenvalues and eigenfunctions of $H(\lambda)$. Then

$$\frac{\partial E_n}{\partial \lambda} = \left\langle \psi_n \middle| \frac{\partial H}{\partial \lambda} \middle| \psi_n \right\rangle$$

Proof

Let $E_n(\lambda)$ and $\psi_n(\lambda)$ be the parametrized eigenvalues and eigenfunctions of $H(\lambda)$. Then

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

and

$$\langle\psi_n|H|\psi_n\rangle = E_n$$

Now,

$$\frac{\partial E_n}{\partial\lambda} = \frac{\partial}{\partial\lambda}\langle\psi_n|H|\psi_n\rangle = \left\langle\frac{\partial\psi_n}{\partial\lambda}\middle|H\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|\frac{\partial H}{\partial\lambda}\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|H\middle|\frac{\partial\psi_n}{\partial\lambda}\right\rangle$$

Proof

We note that

$$\left\langle\frac{\partial\psi_n}{\partial\lambda}\middle|H\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|H\middle|\frac{\partial\psi_n}{\partial\lambda}\right\rangle = E_n\left\langle\frac{\partial\psi_n}{\partial\lambda}\middle|\psi_n\right\rangle + E_n\left\langle\psi_n\middle|\frac{\partial\psi_n}{\partial\lambda}\right\rangle$$

But

$$\left\langle\frac{\partial\psi_n}{\partial\lambda}\middle|\psi_n\right\rangle + \left\langle\psi_n\middle|\frac{\partial\psi_n}{\partial\lambda}\right\rangle = \int\left[\frac{\partial\psi_n^*}{\partial\lambda}\psi_n + \psi_n^*\frac{\partial\psi_n}{\partial\lambda}\right]dx = \frac{\partial}{\partial\lambda}\int\psi_n^*\psi_n dx = \frac{\partial(1)}{\partial\lambda} = 0$$

Hence,

$$\frac{\partial E_n}{\partial\lambda} = \left\langle\psi_n\middle|\frac{\partial H}{\partial\lambda}\middle|\psi_n\right\rangle \qquad \blacksquare$$

Application

We have seen in [Hydrogen 4] that the effective Hamiltonian of the Radial function $U(r) = rR(r)$ is

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

and the eigenvalues are

$$E_n = -\frac{m}{2n^2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2$$

Moreover,

$$\int Ur^s U\, dr = \langle r^s \rangle$$

Application

There are two parameters that can we can identify in

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

These are the atomic number Z** and the angular momentum quantum number l.

The eigenenergy must therefore be parametrized similarly,

$$E_n = -\frac{m}{2(s+l+1)^2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2$$

where s is the index of the Associated Laguerre polynomials $L_s^k = L_{n-l-1}^{2l+1}$ embedded in the radial function.

** Alternatively, we may choose the electron charge e as our parameter, but since Z and e always appear together, the result will be the same.

Parameter Z

If we take Z as our parameter, then

$$\frac{\partial H}{\partial Z} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$$\frac{\partial E}{\partial Z} = -\frac{2Zm}{2(s+l+1)^2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

The Feynman-Hellman Theorem

$$\left\langle \psi_n \middle| \frac{\partial H}{\partial \lambda} \middle| \psi_n \right\rangle = \frac{\partial E_n}{\partial \lambda}$$

yields [see Bohr for definition of Bohr radius]

$$-\frac{e^2}{4\pi\varepsilon_0}\left\langle\frac{1}{r}\right\rangle = -\frac{2Zm}{2(s+l+1)^2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = -\frac{Zm}{n^2\hbar^2}\frac{\hbar^2}{ma_0}\frac{e^2}{4\pi\varepsilon_0}$$

or

$$\left\langle\frac{1}{r}\right\rangle = \frac{Z}{n^2 a_0}$$

Parameter l

If we take l as our parameter, then

$$\frac{\partial H}{\partial l} = \frac{(2l+1)\hbar^2}{2mr^2}$$

$$\frac{\partial E}{\partial l} = \frac{2m}{2(s+l+1)^3\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2$$

The Feynman-Hellman Theorem then yields the expression

$$\frac{\hbar^2(2l+1)}{2m}\left\langle\frac{1}{r^2}\right\rangle = \frac{2m}{2(s+l+1)^3\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 = \frac{mZ^2}{n^3\hbar^2}\left(\frac{\hbar^2}{ma_0}\right)^2$$

from which we find

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{mZ^2}{n^3\hbar^2}\left(\frac{\hbar^2}{ma_0}\right)^2\frac{2m}{\hbar^2(2l+1)} = \frac{2Z^2}{(2l+1)n^3a_0^2}$$

Since we have found $\langle r^{-2}\rangle$, we can now evaluate all other negative-powered $\langle r^s\rangle$ using Kramers' relation.