

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

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



Proof

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

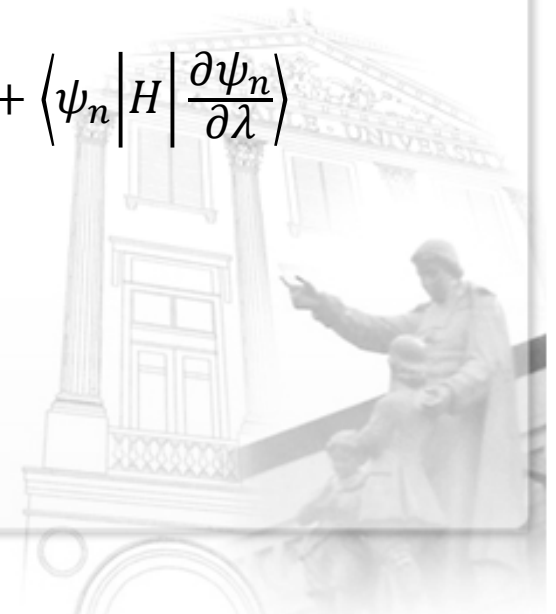
$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

and

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

Now,

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



Proof

We note that

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

But

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

Hence,

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



Application

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

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

and the eigenvalues are

$$E_n = -\frac{m}{2n^2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2$$

Moreover,

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



Application

There are two parameters that we can identify in

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

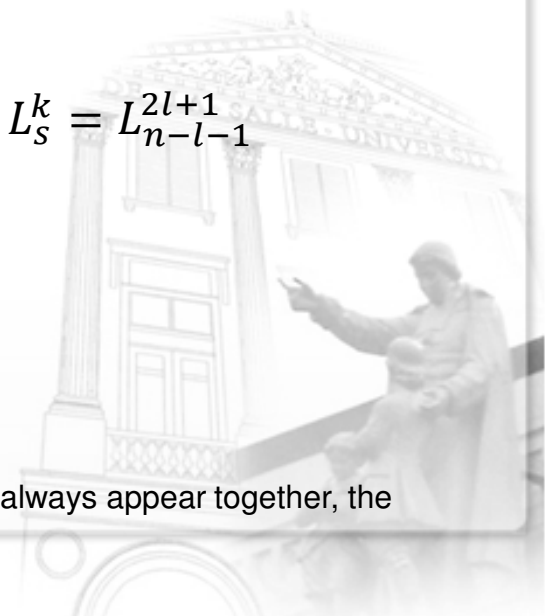
These are the atomic number Z^{**} and the angular momentum quantum number l .

The eigenenergy must therefore be parametrized similarly,

$$E_n = -\frac{m}{2(s+l+1)^2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2$$

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

$$\frac{\partial H}{\partial Z} = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$\frac{\partial E}{\partial Z} = -\frac{2Zm}{2(s+l+1)^2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2$$

The Feynman-Hellman Theorem

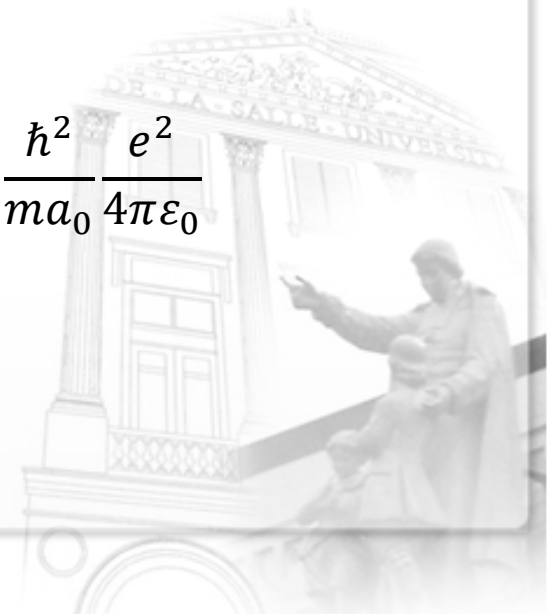
$$\left\langle \psi_n \left| \frac{\partial H}{\partial \lambda} \right| \psi_n \right\rangle = \frac{\partial E_n}{\partial \lambda}$$

yields [\[see Bohr for definition of Bohr radius\]](#)

$$-\frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{2Zm}{2(s+l+1)^2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = -\frac{Zm}{n^2\hbar^2} \frac{\hbar^2}{ma_0} \frac{e^2}{4\pi\epsilon_0}$$

or

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



Parameter l

If we take l as our parameter, then

$$\frac{\partial H}{\partial l} = \frac{(2l + 1)\hbar^2}{2mr^2}$$
$$\frac{\partial E}{\partial l} = \frac{2m}{2(s + l + 1)^3 \hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2$$

The Feynman-Hellman Theorem then yields the expression

$$\frac{\hbar^2(2l + 1)}{2m} \left\langle \frac{1}{r^2} \right\rangle = \frac{2m}{2(s + l + 1)^3 \hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 = \frac{mZ^2}{n^3 \hbar^2} \left(\frac{\hbar^2}{ma_0} \right)^2$$

from which we find

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

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

