Feynman-Hellmann theorem and Kramers method

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Feynman-Hellman theorem
Kramers method
The virial theorem

Here we calculate the average $\langle r^{-s} \rangle$ for the hydrogen-like atom using the Feynman-Hellman theorem and Kramers method.

1. Feynman-Hellmann theorem

$$\frac{dE_\lambda}{d\lambda} = \langle \psi(\lambda) | \frac{dH_\lambda}{d\lambda} | \psi(\lambda) \rangle .$$

The proof of the Feynman-Hellmann theorem requires that the wavefunction be an eigenfunction of the Hamiltonian under consideration; however, one can also prove more generally that the theorem holds for non-eigenfunction wavefunctions which are stationary (partial derivative is zero) for all relevant variables (such as orbital rotations). The Hartree-Fock wavefunction is an important example of an approximate eigenfunction that still satisfies the Feynman-Hellmann theorem. Notable example of where the Feynman-Hellmann theorem is not applicable is for example finite-order Møller–Plesset perturbation theory, which is not variational.

The proof also employs an identity of normalized wavefunctions– that derivatives of the overlap of a wavefunction with itself must be zero. Using Dirac's bra-ket notation these two conditions are written as

$$H_\lambda |\psi(\lambda)\rangle = E_\lambda |\psi(\lambda)\rangle ,$$

with the normalization condition that

$$\langle \psi(\lambda) | \psi(\lambda) \rangle = 1 ,$$

or

$$\langle \psi(\lambda) | H_\lambda | \psi(\lambda) \rangle = E_\lambda .$$

This average value is regarded as a function of λ.

$$
\begin{aligned}
\frac{dE_\lambda}{d\lambda} &= (\frac{d}{d\lambda}\langle\psi(\lambda)|)H_\lambda|\psi(\lambda)\rangle + \langle\psi(\lambda)|\frac{dH_\lambda}{d\lambda}|\psi(\lambda)\rangle + \langle\psi(\lambda)|H_\lambda(\frac{d}{d\lambda}|\psi(\lambda)\rangle) \\
&= E_\lambda[\frac{d}{d\lambda}\langle\psi(\lambda)|)|\psi(\lambda)\rangle + \langle\psi(\lambda)|(\frac{d}{d\lambda}|\psi(\lambda)\rangle] + \langle\psi(\lambda)|\frac{dH_\lambda}{d\lambda}|\psi(\lambda)\rangle \\
&= E_\lambda\frac{d}{d\lambda}\langle\psi(\lambda)|\psi(\lambda)\rangle + \langle\psi(\lambda)|\frac{dH_\lambda}{d\lambda}|\psi(\lambda)\rangle \\
&= \langle\psi(\lambda)|\frac{dH_\lambda}{d\lambda}|\psi(\lambda)\rangle
\end{aligned}
$$

since

$$\frac{d}{d\lambda}\langle\psi(\lambda)|\psi(\lambda)\rangle = \frac{d}{d\lambda}1 = 0 .$$

2. Example of the Feynman-Hellmann in the simple harmonics

The Hamiltonian of the simple harmonics is given by

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{q}^2 ,$$

with the energy eigenvalue as

$$E_n = \hbar\omega(n+\frac{1}{2}) .$$

We apply the Feynman-Hellmann theorem to this system,

$$\left\langle\frac{\partial\hat{H}}{\partial\omega}\right\rangle = \frac{\partial E_n}{\partial\omega}$$

or

$$\langle m\omega\hat{q}^2\rangle = \hbar(n+\frac{1}{2})$$

Then we have

$$\langle V\rangle = \langle K\rangle = \frac{1}{2}E_n$$

which is also derived from the virial theorem.

((**Note**)) The word **virial**:

The word **virial** derives from vis, the Latin word for "force" or "energy", and was given its technical definition by Rudolf Clausius in 1870.

3. **Calculation of the average** $\langle r^{-2}\rangle$ and $\langle r^{-1}\rangle$ using the Feynman-Hellmann theorem

(i)

The Hamiltonian of the hydrogen-like atom is given by

$$H=-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial}{\partial r}(\frac{\partial}{\partial r}r)+\frac{\hbar^2 l(l+1)}{2\mu r^2}-\frac{Ze^2}{r},$$

with

$$n = l + 1 + n_r,$$

where n_r is a positive integer. For $n = 3$, we have $l = 0$ (s) and $n_r = 2$, $l = 1$(p) and $n_r = 1$, $l = 2$ (d) and $n_r = 0$.

An alternative approach for applying the Feynman-Hellmann is to promote a fixed or discrete parameter which appears in a Hamiltonian to be a continuous variable solely for the mathematical purpose of taking a derivative. Possible parameters are physical constants or discrete numbers. In the Hamiltonian for the hydrogen atom, $\lambda = l$ is a parameter in the Feynman-Hellmann theorem,

$$\begin{aligned}
\langle r^{-2}\rangle &= \langle nlm|\frac{1}{r^2}|nlm\rangle \\
&= \frac{2\mu}{\hbar^2}\frac{1}{2l+1}\langle nlm|\frac{\partial H}{\partial l}|nlm\rangle \\
&= \frac{2\mu}{\hbar^2}\frac{1}{2l+1}\frac{\partial E_n}{\partial n}\frac{\partial n}{\partial l} \\
&= \frac{2\mu}{\hbar^2}\frac{1}{2l+1}\frac{\partial E_n}{\partial n} \\
&= \frac{2\mu}{\hbar^2}\frac{1}{2l+1}\left(\frac{Z^2\mu e^4}{\hbar^2 n^3}\right) \\
&= \frac{Z^2\mu^2 e^4}{\hbar^4 n^3(l+1/2)}
\end{aligned}$$

where

$$\frac{\partial H}{\partial l} = \frac{\hbar^2 (2l+1)}{2\mu r^2}, \qquad \text{or} \qquad \frac{1}{r^2} = \frac{2\mu}{\hbar^2}\frac{1}{2l+1}\frac{\partial H}{\partial l},$$

$n = l + 1 + n_r$,

$$E_n = -\frac{Ze^2}{2r_n} = -\frac{Z^2 \mu e^4}{2\hbar^2 n^2}.$$

Then we have

$$\langle r^{-2} \rangle = \langle nlm | \frac{1}{r^2} | nlm \rangle = \frac{Z^2}{a^2 n^3 (l+1/2)}.$$

(ii)

Suppose that the charge e is a parameter $\lambda = e$ in the Feynman-Hellmann theorem. Note that e>0 in this case.

$$\frac{\partial H}{\partial e} = -\frac{2Ze}{r} \qquad \text{or} \qquad \frac{1}{r} = -\frac{1}{2Ze}\frac{\partial H}{\partial e},$$

$$\begin{aligned}
\langle r^{-1} \rangle &= \langle nlm | \frac{1}{r} | nlm \rangle \\
&= -\frac{1}{2Ze}\langle nlm | \frac{\partial H}{\partial e} | nlm \rangle \\
&= -\frac{1}{2Ze}\frac{\partial}{\partial e} E_n \\
&= \frac{1}{2Ze}\frac{\mu Z^2 4e^3}{2\hbar^2 n^2} \\
&= \frac{\mu Z e^2}{\hbar^2 n^2} \\
&= \frac{Z}{a n^2}
\end{aligned}$$

or

$$\langle r^{-1}\rangle = \frac{Z}{an^2}.$$

(iii) Suppose that Z is a parameter $\lambda = Z$ in the Feynman-Hellmann theorem.

$$\frac{\partial H}{\partial Z} = -\frac{e^2}{r} \qquad \text{or} \qquad \frac{1}{r} = -\frac{1}{e^2}\frac{\partial H}{\partial Z}$$

$$\begin{aligned}
\langle r^{-1}\rangle &= -\frac{1}{e^2}\langle nlm|\frac{\partial H}{\partial Z}|nlm\rangle \\
&= -\frac{1}{e^2}\frac{\partial}{\partial Z}\langle nlm|H|nlm\rangle \\
&= -\frac{1}{e^2}\frac{\partial}{\partial Z}E_n \\
&= -\frac{1}{e^2}\frac{\partial}{\partial Z}\left(-\frac{Z^2\mu e^4}{2\hbar^2 n^2}\right) \\
&= \frac{Z\mu e^2}{\hbar^2 n^2} \\
&= \frac{Z}{an^2}
\end{aligned}$$

4. Application to the Coulomb potential

This implies that the average of the potential energy is a half of the total energy

$$\langle V\rangle = \left\langle -\frac{Ze^2}{r}\right\rangle = -Ze^2\left\langle\frac{1}{r}\right\rangle = -\frac{Z^2e^2}{an^2} = 2E_n.$$

Thus the average kinetic energy is also a half of the total energy (virial theorem).

$$\langle K\rangle = -E_n.$$

since

$$E_n = \langle K\rangle + \langle V\rangle.$$

((**Note**))

$$E_n = -\frac{Ze^2}{2r_n} = -\frac{Z^2\mu e^4}{2\hbar^2 n^2} = -\frac{Z^2 e^2}{2n^2 a} = -\frac{Z^2\Re}{n^2},$$

or

$$\frac{Z^2\mu e^4}{2\hbar^2} = -Z^2\left(\frac{\mu}{m}\right)\frac{\alpha^2 mc^2}{2},$$

$$a = \frac{\hbar^2}{\mu e^2} = \frac{m}{\mu}\left(\frac{\hbar^2}{me^2}\right) = \frac{m}{\mu}a_B,$$

$$\Re = \frac{\mu e^4}{2\hbar^2} = \frac{e^2}{2a} = \frac{\mu}{m}\frac{me^4}{2\hbar^2} = \frac{\mu}{m}\Re_0.$$

where α is the structure fine constant (the definition is given below) and m is the mass of electron.

$a_B = \dfrac{\hbar^2}{me^2}$ =0.52917720859(36) Å. (Bohr radius)

$\Re_0 = \dfrac{me^4}{2\hbar^2}$ =13.6056923(12) eV. (Rydberg)

mc^2 = 0.510997 MeV. (electron rest mass)

$\alpha = \dfrac{e^2}{\hbar c} = \dfrac{1}{137.036}$ (CGS units) $\alpha = \dfrac{e^2}{4\pi\varepsilon_0\hbar c}$ (SI units)

(fine structure constant)

5. Virial theorem

A proof of the virial theorem in quantum mechanics can be given in analogy with the corresponding proof in classical mechanics. In the latter, The starting point is the time average of the operator $\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}$, which is zero for a periodic system. The analogous quantity in quantum mechanics is the time derivative of the expectation value $\langle\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}\rangle$ is also zero.

$$\frac{d}{dt}\langle \hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}\rangle = -\frac{i}{\hbar}\langle [(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}),\hat{H}]\rangle = 0\,,$$

where the commutation relation is given by

$$\begin{aligned}
[(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}),\hat{H}] &= [\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z, \frac{1}{2m}(\hat{p}_x{}^2 + \hat{p}_y{}^2 + \hat{p}_z{}^2) + V(\hat{x},\hat{y},\hat{z})] \\
&= \frac{i\hbar}{m}(\hat{p}_x{}^2 + \hat{p}_y{}^2 + \hat{p}_z{}^2) - i\hbar(\hat{x}\frac{\partial V}{\partial \hat{x}} + \hat{y}\frac{\partial V}{\partial \hat{y}} + \hat{z}\frac{\partial V}{\partial \hat{z}}) \\
&= 2i\hbar\hat{K} - i\hbar(\hat{x}\frac{\partial V}{\partial \hat{x}} + \hat{y}\frac{\partial V}{\partial \hat{y}} + \hat{z}\frac{\partial V}{\partial \hat{z}})
\end{aligned}$$

((**Note**))

$$.\frac{d}{dt}\langle \psi(t)|\hat{A}|\psi(t)\rangle = -\frac{i}{\hbar}\langle \psi(t)|[\hat{A},\hat{H}]|\psi(t)\rangle \qquad \text{(Schrödinger picture)}$$

Then we have the virial theorem as

$$2\langle \hat{K}\rangle = \left\langle \hat{x}\frac{\partial V}{\partial \hat{x}} + \hat{y}\frac{\partial V}{\partial \hat{y}} + \hat{z}\frac{\partial V}{\partial \hat{z}}\right\rangle,$$

or

$$2\langle K\rangle = \langle \boldsymbol{r}\cdot\nabla V\rangle\,.$$

If $V(\boldsymbol{r})$ is of degree *n*, that is

$$V \propto r^n\,,$$

then we get

$$\boldsymbol{r}\cdot\nabla V = r\frac{d}{dr}V = nV\,,$$

and

$$2\langle K\rangle = n\langle V\rangle\,.$$

In conjunction with $E = \langle K \rangle + \langle V \rangle$, then

$$\langle K \rangle = \frac{n}{n+2} E, \qquad \langle V \rangle = \frac{2}{n+2} E.$$

(i) Simple harmonics, n = 2

$$\langle K \rangle = \langle V \rangle = \frac{1}{2} E$$

(ii) Hydrogen atoms where the Coulomb potential has n = -1,

$$\langle K \rangle = -E, \qquad \langle V \rangle = 2E$$

((**Mathematica**))
Proof of the commutation relation

$$[\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z, \frac{1}{2m}(\hat{p}_x{}^2 + \hat{p}_y{}^2 + \hat{p}_z{}^2) + V(\hat{x}, \hat{y}, \hat{z})]$$
$$= \frac{i\hbar}{m}(\hat{p}_x{}^2 + \hat{p}_y{}^2 + \hat{p}_z{}^2) - i\hbar(\hat{x}\frac{\partial V}{\partial \hat{x}} + \hat{y}\frac{\partial V}{\partial \hat{y}} + \hat{z}\frac{\partial V}{\partial \hat{z}})$$

```
Clear["Global`*"]; px := ℏ/ⅈ D[#, x] &;
py := ℏ/ⅈ D[#, y] &; pz := ℏ/ⅈ D[#, z] &;
RP = (x px[#] + y py[#] + z pz[#]) &;
K1 = 1/(2 m) (px[px[#]] + py[py[#]] + pz[pz[#]]) &;

A1 =
 RP[V[x, y, z] ψ[x, y, z]] -
   V[x, y, z] RP[ψ[x, y, z]] +
   RP[K1[ ψ[x, y, z]]] - K1[ RP[ψ[x, y, z]]] //
  FullSimplify
```

$$-\frac{1}{m} i\hbar \left(m\,\psi[x,y,z]\left(z\,V^{(0,0,1)}[x,y,z] + y\,V^{(0,1,0)}[x,y,z] + x\,V^{(1,0,0)}[x,y,z]\right) + \hbar^2\left(\psi^{(0,0,2)}[x,y,z] + \psi^{(0,2,0)}[x,y,z] + \psi^{(2,0,0)}[x,y,z]\right)\right)$$

```
A2 =
  2 ⅈ ℏ K1[ψ[x, y, z]] -
    ⅈ ℏ ψ[x, y, z]
     (x D[V[x, y, z], x] + y D[V[x, y, z], y] +
       z D[V[x, y, z] , z]) // FullSimplify;

A1 - A2 // Simplify
```

0

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6. Kramers method for the expression of $\langle r^s \rangle$

$r = \dfrac{\rho}{2\kappa}$,

with

$$\kappa = \frac{Z}{na}.$$

The wave function is given by

$$\begin{aligned} R_{nl}(r) &= \sqrt{\frac{4Z^3(n-l-1)!}{a^3n^4(n+l)!}} e^{-\frac{Zr}{na}} (\frac{2Zr}{na})^l L_{n-l-1}^{2l+1}(\frac{2Zr}{na}) \\ &= \sqrt{\frac{4Z^3(n-l-1)!}{a^3n^4(n+l)!}} e^{-\frac{\rho}{2}} \rho^l L_{n-l-1}^{2l+1}(\rho) \\ &= A_{nl} e^{-\frac{\rho}{2}} \rho^l L_{n-l-1}^{2l+1}(\rho) \end{aligned}$$

where

$$A_{nl} = \sqrt{\frac{4Z^3(n-l-1)!}{a^3n^4(n+l)!}}$$

The wave function is given by

$$\begin{aligned} u_{nr}(\rho) &= rR_{nl}(r) \\ &= \frac{Z^{1/2}}{na^{1/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} e^{-\frac{\rho}{2}} \rho^{l+1} L_{n-l-1}^{2l+1}(\rho), \\ &= \frac{Z^{1/2}}{na^{1/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \Phi_{n-l-1}^{2l+1}(\rho) \end{aligned}$$

where

$$\Phi_{n-l-1}^{2l+1}(\rho) = e^{-\frac{\rho}{2}} \rho^{l+1} L_{n-l-1}^{2l+1}(\rho)$$

satisfying the differential equation

$$[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{n}{\rho} - \frac{1}{4}]\Phi_{n-l-1}^{2l+1}(\rho) = 0.$$

Then the average $\langle r^s \rangle$ is defined as

$$\begin{aligned}\langle r^s \rangle &= \int_0^\infty dr r^2 [R_{nl}(r)]^2 r^s \\ &= \int_0^\infty dr r^{s+2} [R_{nl}(r)]^2 \\ &= A_{nl}^2 \left(\frac{na}{2Z}\right)^{s+3} \int_0^\infty d\rho \rho^{2l+s+2} e^{-\rho} [L_{n-l-1}^{2l+1}(\rho)]^2 \\ &= A_{nl}^2 \left(\frac{na}{2Z}\right)^{s+3} \int_0^\infty d\rho \rho^s [\rho^{l+1} e^{-\rho/2} L_{n-l-1}^{2l+1}(\rho)]^2\end{aligned}$$

Using the new notation, we have

$$\langle r^s \rangle = A_{nl}^2 \left(\frac{na}{2Z}\right)^{s+3} \int_0^\infty d\rho \rho^s [\Phi_{n-l-1}^{2l+1}(\rho)]^2 \,.$$

6. Derivation of the Kramers' relation

We derive the Kramers' relation. It is the relation between $<r^{s+1}>$, $<r^s>$, and $<r^{s-1}>$.

$$\frac{s+2}{n^2}\langle r^{s+1} \rangle - (2s+3)\frac{a}{Z}\langle r^s \rangle + \frac{s+1}{4}[(2l+1)^2 - (s+1)^2]\left(\frac{a}{Z}\right)^2 \langle r^{s-1} \rangle = 0 \,.$$

For simplicity we use

$$\Phi(\rho) = \Phi_{n-l-1}^{2l+1}(\rho),$$

$$[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{n}{\rho} - \frac{1}{4}]\Phi(\rho) = 0 \,.$$

We now consider the following equation

$$0 = \int_0^\infty d\rho [\frac{d^2\Phi}{d\rho^2} + (-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2})\Phi][\rho^{s+2}\Phi' + c\rho^{s+1}\Phi].$$

where

$$\Phi'(\rho) = \frac{d\Phi(\rho)}{d\rho}, \qquad \Phi''(\rho) = \frac{d^2\Phi(\rho)}{d\rho^2}$$

and c is a constant to be determined (adjust c to cancel terms that do not yield expectation values).

$$0 = \int_0^\infty d\rho[\rho^{s+2}\Phi'\Phi'' + \rho^{s+2}(-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2})\Phi\Phi' + c\rho^{s+1}\Phi\Phi'' + c\rho^{s+1}(-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2})\Phi^2].$$

We calculate four terms separately defined by I_1, I_2, I_3, and I_4.

$$\begin{aligned} I_1 &= \int_0^\infty d\rho\rho^{s+2}\Phi'\Phi'' \\ &= \int_0^\infty d\rho\rho^{s+2}\frac{1}{2}\frac{d}{d\rho}(\Phi')^2 \\ &= -\frac{1}{2}(s+2)\int_0^\infty d\rho\rho^{s+1}(\Phi')^2 \end{aligned}$$

$$\begin{aligned} I_2 &= \int_0^\infty d\rho[\rho^{s+2}(-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2})\Phi\Phi'] \\ &= \int_0^\infty d\rho[-\frac{1}{4}\rho^{s+2} + n\rho^{s+1} - l(l+1)\rho^s)]\frac{1}{2}\frac{d}{d\rho}\Phi^2 \\ &= -\int_0^\infty d\rho\frac{1}{2}\Phi^2[(-\frac{1}{4}(s+2)\rho^{s+1} + n(s+1)\rho^s - sl(l+1)\rho^{s-1})] \end{aligned}$$

$$\begin{aligned} I_3 &= \int_0^\infty d\rho c\rho^{s+1}\Phi\Phi'' \\ &= -c\int_0^\infty d\rho\Phi'\frac{d}{d\rho}(\rho^{s+1}\Phi) \\ &= -c\int_0^\infty d\rho\Phi'[(s+1)\rho^s\Phi + \rho^{s+1}\Phi'] \\ &= -c(s+1)\int_0^\infty d\rho\rho^s(\frac{1}{2}\frac{d}{d\rho}\Phi^2) - c\int_0^\infty d\rho\rho^{s+1}\Phi'^2 \\ &= c\frac{s(s+1)}{2}\int_0^\infty d\rho\rho^{s-1}\Phi^2 - c\int_0^\infty d\rho\rho^{s+1}\Phi'^2 \end{aligned}$$

$$I_4 = c\int_0^\infty d\rho\rho^{s+1}(-\frac{1}{4}+\frac{n}{\rho}-\frac{l(l+1)}{\rho^2})\Phi^2$$

Then we have

$$I = I_1 + I_2 + I_3 + I_4 .$$

$$\begin{aligned}
I &= -\frac{1}{2}(s+2)\int_0^\infty d\rho\rho^{s+1}(\Phi')^2 - c\int_0^\infty d\rho\rho^{s+1}\Phi'^2 \\
&\quad + \frac{1}{8}(s+2)\int_0^\infty d\rho\rho^{s+1}\Phi^2 - \frac{n(s+1)}{2}\int_0^\infty d\rho\rho^{s}\Phi^2 + \frac{sl(l+1)}{2}\int_0^\infty d\rho\rho^{s-1}\Phi^2 \\
&\quad + c\frac{s(s+1)}{2}\int_0^\infty d\rho\rho^{s-1}\Phi^2 - \frac{1}{4}c\int_0^\infty d\rho\rho^{s+1}\Phi^2 + nc\int_0^\infty d\rho\rho^{s}\Phi^2 - cl(l+1)\int_0^\infty d\rho\rho^{s-1}\Phi^2 \\
&= 0
\end{aligned}$$

We choose $c = -\frac{1}{2}(s+2)$. Then we get

$$\frac{1}{4}(s+2)\int_0^\infty d\rho\rho^{s+1}\Phi^2 - \frac{n(2s+3)}{2}\int_0^\infty d\rho\rho^{s}\Phi^2 + \frac{(s+1)}{4}[(2l+1)^2-(s+1)^2]\int_0^\infty d\rho\rho^{s-1}\Phi^2 = 0$$

Using

$$\int_0^\infty d\rho\rho^{s}\Phi^2 = \frac{\langle r^s \rangle}{A_{nl}^2(\frac{na}{2Z})^{s+3}},$$

we find the Kramers' relation

$$\frac{s+2}{n^2}\langle r^{s+1}\rangle - (2s+3)\frac{a}{Z}\langle r^{s}\rangle + \frac{s+1}{4}[(2l+1)^2-(s+1)^2]\left(\frac{a}{Z}\right)^2\langle r^{s-1}\rangle = 0.$$

7. Determination of $\langle r^s \rangle$

We note that

$$\langle r^0 \rangle = 1.$$

We apply the Kramers' relation to calculate $\langle r^1 \rangle, \langle r^{-1} \rangle$, $\langle r^{-2} \rangle$, and so on.

(i) The Kramer's relation with s = -1:

$$\frac{1}{n^2}\langle r^0 \rangle - \frac{a}{Z}\langle r^{-1} \rangle = 0 ,$$

or

$$\langle r^{-1} \rangle = \frac{Z}{n^2 a} .$$

(ii) The Kramers' relation with s = 0:

$$\frac{2}{n^2}\langle r^1 \rangle - \frac{3a}{Z}\langle r^0 \rangle + l(l+1)\left(\frac{a}{Z}\right)^2 \langle r^{-1} \rangle = 0 .$$

Then we get

$$\begin{aligned}
\langle r^1 \rangle &= \frac{n^2}{2}[\frac{3a}{Z}\langle r^0 \rangle - l(l+1)\left(\frac{a}{Z}\right)^2 \langle r^{-1} \rangle] \\
&= \frac{n^2}{2}[\frac{3a}{Z} - l(l+1)\left(\frac{a}{Z}\right)^2 \frac{Z}{n^2 a}] \\
&= \frac{a}{2Z}[3n^2 - l(l+1)]
\end{aligned}$$

or

$$\langle r^1 \rangle = \frac{a}{2Z}[3n^2 - l(l+1)] .$$

(iii) The Kramers' relation with s = 1:

$$\frac{3}{n^2}\langle r^2 \rangle - \frac{5a}{Z}\langle r^1 \rangle + \frac{1}{2}[(2l+1)^2 - 4]\left(\frac{a}{Z}\right)^2 \langle r^0 \rangle = 0 ,$$

or

$$\left\langle r^2 \right\rangle = \frac{a^2 n^2}{2Z^2}[5n^2 + 1 - 3l(l+1)].$$

(iv) What happens to the Kramers' relation with *s* = -2.

$$\frac{a}{Z}\left\langle r^{-2} \right\rangle - \frac{a^2}{Z^2} l(l+1)\left\langle r^{-3} \right\rangle = 0.$$

So we cannot determine $\left\langle r^{-2} \right\rangle$ from the Kramers' relation. As is previously described, this can be calculated using the Feynman-Hillman theorem as

$$\left\langle r^{-2} \right\rangle = \frac{Z^2}{n^3 a^2 (l + 1/2)}.$$

Using the Kramers' relation with the expression of $\left\langle r^{-2} \right\rangle$, we get

$$\left\langle r^{-3} \right\rangle = \frac{Z}{al(l+1)}\left\langle r^{-2} \right\rangle = \frac{Z^3}{n^3 a^3 l(l+1/2)(l+1)}.$$

(v) The Kramers' relation with *s* = -3:

$$-\frac{1}{n^2}\left\langle r^{-2} \right\rangle + \frac{3a}{Z}\left\langle r^{-3} \right\rangle - \frac{a^2}{2Z^2}[(2l+1)^2 - 4]\left\langle r^{-4} \right\rangle = 0.$$

From this we get

$$\left\langle r^{-4} \right\rangle = \frac{Z^4[3n^2 - l(l+1)]}{n^5 a^4 l(l+1/2)(l+1)[2l(l+1) - 3/2]}.$$

8. The uncertainty of the radius

The uncertainty of the radius is defined by

$$(\Delta r)^2 = \langle r^2 \rangle - \langle r \rangle^2$$
$$= \frac{a^2}{2Z^2} n^2[5n^2 + 1 - 3l(l+1)] - \frac{a^2}{4Z^2}[3n^2 - l(l+1)]^2$$
$$= \frac{a^2}{4Z^2}[n^2(n^2+2) - l^2(l+1)^2]$$

and

$$\frac{\Delta r}{\langle r \rangle} = \frac{\sqrt{n^2(n^2+2) - l^2(l+1)^2}}{3n^2 - l(l+1)}$$

The value of $\Delta r / \langle r \rangle$ is calculated for each pair of *n* and *l* and is listed in Table below

Table

n	l	$\frac{\Delta r}{\langle r \rangle}$
1	0 (s)	0.57735
2	0 (s)	0.408248
2	1 (p)	0.447214
3	0 (s)	0.368514
3	1 (p)	0.389872
3	2 (d)	0.377964
4	0 (s)	0.353553
4	1 (p)	0.366354
4	2 (d)	0.377964
4	3 (f)	0.333333

((**Mathematica**))
Here we use *N* instead of *n*.

Kramer' s relation

```
Clear["Global`*"];
```

$$eq1 = \frac{s+2}{N^2} F[s+1] - (2s+3)\frac{a}{Z} F[s] + \frac{s+1}{4}\left((2\ell+1)^2 - (s+1)^2\right)\frac{a^2}{Z^2} F[s-1]$$

```
eq11 = eq1 /. s → n;

eq2 = RSolve[{eq11 == 0, F[0] == a0, F[1] == a1}, F[n], n];
```

$$rule1 = \left\{a0 \to 1,\ a1 \to \frac{a}{2Z}\left(3N^2 - \ell(\ell+1)\right)\right\};$$

```
F[n_] = F[n] /. eq2[[1]] /. rule1;

F[0]
```

1

```
F[1]
```

$$\frac{a\left(3N^2 - \ell(1+\ell)\right)}{2Z}$$

```
F[2] // Simplify
```

$$\frac{a^2 N^2\left(1 + 5N^2 - 3\ell - 3\ell^2\right)}{2Z^2}$$

```
F[3] // Simplify
```

$$\frac{a^3 N^2 \left(35 N^4 - 5 N^2 \left(-5 + 6 \ell + 6 \ell^2\right) + 3 \ell \left(-2 - \ell + 2 \ell^2 + \ell^3\right)\right)}{8 Z^3}$$

```
F[4] // Simplify
```

$$\frac{a^4 N^4 \left(12 + 63 N^4 - 50 \ell - 35 \ell^2 + 30 \ell^3 + 15 \ell^4 - 35 N^2 \left(-3 + 2 \ell + 2 \ell^2\right)\right)}{8 Z^4}$$

```
F[5] // Simplify
```

$$\frac{1}{16 Z^5} a^5 N^4 \left(231 N^6 - 105 N^4 \left(-7 + 3 \ell + 3 \ell^2\right) + 21 N^2 \left(14 - 25 \ell - 20 \ell^2 + 10 \ell^3 + 5 \ell^4\right) - 5 \ell \left(12 + 4 \ell - 15 \ell^2 - 5 \ell^3 + 3 \ell^4 + \ell^5\right)\right)$$

```
F[6] // Simplify
```

$$\frac{1}{16 Z^6} a^6 N^6 \left(180 + 429 N^6 - 882 \ell - 497 \ell^2 + 735 \ell^3 + 280 \ell^4 - 105 \ell^5 - 35 \ell^6 - 231 N^4 \left(-10 + 3 \ell + 3 \ell^2\right) + 21 N^2 \left(101 - 105 \ell - 90 \ell^2 + 30 \ell^3 + 15 \ell^4\right)\right)$$

---

9. Summary

$$\langle r^{-4} \rangle = \frac{Z^4[3n^2 - l(l+1)]}{n^5 a^4 l(l+1/2)(l+1)[2l(l+1) - 3/2]},$$

$$\langle r^{-3} \rangle = \frac{Z^3}{n^3 a^3 l(l+1/2)(l+1)},$$

$$\langle r^{-2} \rangle = \frac{Z^2}{n^3 a^2 (l+1/2)},$$

$$\langle r^{-1} \rangle = \frac{Z}{n^2 a},$$

$$\langle r^0 \rangle = 1,$$

$$\langle r \rangle = \frac{a}{2Z}[3n^2 - l(l+1)],$$

$$\left\langle r^2 \right\rangle = \frac{a^2}{2Z^2} n^2[5n^2 + 1 - 3l(l+1)],$$

$$\left\langle r^3 \right\rangle = \frac{a^3}{8Z^3} n^2[35n^4 - 5n^2(6l(l+1) - 5) + 3(l-1)l(l+1)(l+2)],$$

$$\left\langle r^4 \right\rangle = \frac{a^4 n^4}{8Z^4}[63n^4 - 35n^2(2l^2 + 2l - 3) + 15l^4 + 30l^3 - 35l^2 - 50l + 12],$$

$$\left\langle r^5 \right\rangle = \frac{a^5 n^4}{16Z^5}[231n^6 - 105n^4(3l^2 + 3l - 7) + 21n^2(5l^4 + 10l^3 - 20l^2 - 25l + 14)$$
$$- 5l(l^5 + 3l^4 - 5l^3 - 15l^2 + 4l + 12)]$$

10. Quantum mechanical analog of the virial theorem

The average of the kinetic energy is given by

$$< K >= E_n - < V >= -\frac{Z^2 e^2}{2n^2 a} + \frac{Z^2 e^2}{n^2 a} = \frac{Z^2 e^2}{2n^2 a} = -\frac{1}{2}\langle V \rangle,$$

where

$$E_n = -\frac{Ze^2}{2r_n} = -\frac{Z^2 \mu e^4}{2\hbar^2 n^2} = -\frac{Z^2 e^2}{2n^2 a} = -\frac{Z^2 \Re}{n^2},$$

and

$$< V >= -Ze^2 \left\langle \frac{1}{r} \right\rangle = -Ze^2 \frac{Z}{n^2 a} = -\frac{Z^2 e^2}{n^2 a},$$

with

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

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APPENDIX
Wavefunction of hydrogen-like atom

Normalization of the wavefunction;

$$1=\int\left|\psi(\boldsymbol{r})\right|^2 d\boldsymbol{r}\ ,$$

with

$$\psi(\boldsymbol{r})=R_{nl}(r)Y_l^m(\theta,\phi)\,.$$

Then we get

$$1=\int drr^2\left|R_{nl}(r)\right|^2\int d\Omega\left|Y_l^m(\theta,\phi)\right|^2=\int drr^2\left|R_{nl}(r)\right|^2\ .$$

We define $P_r dr$ as

$$P_r dr=r^2\left|R_{nl}(r)\right|^2 dr$$

or

$$P_r=r^2\left|R_{nl}(r)\right|^2\,.$$

We define

$$u_{nl}(r)=rR_{nl}(r)\,.$$

P_r is described as

$$P_r=\left|u_{nl}(r)\right|^2\,.$$

We note that

$$R_{nl}(r) = A_{nl} e^{-\rho/2} \rho^{l} L_{n-l-1}^{2l+1}(\rho),$$

where

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + \left(-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right)\right] R_{nl}(\rho) = 0,$$

with

$$A_{nl} = \frac{2Z^{3/2}}{n^2 a^{3/2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}}.$$

$L_{n-l-1}^{2l+1}(\rho)$: associated Laguerrel polynomial

$\rho = 2\kappa r$ with $\kappa = \dfrac{Z}{na}$.

We define a new function given by

$$\Phi_p^q(\rho) = e^{-\rho/2} \rho^{(q+1)/2} L_p^q(\rho),$$

or

$$L_p^q(\rho) = e^{\rho/2} \rho^{-(q+1)/2} \Phi_p^q(\rho),$$

$$\Phi_{n-l-1}^{2l+1}(\rho) = e^{-\rho/2} \rho^{l+1} L_{n-l-1}^{2l+1}(\rho),$$

$$\left[\frac{d^2}{d\rho^2} - \frac{1}{4} + \frac{2p+q+1}{2\rho} - \frac{q^2-1}{4\rho^2}\right] \Phi_p^q(\rho) = 0.$$