Quantum Mechanics 2

Robert C. Roleda
Physics Department

Hydrogen Atom

Kramers' Relation

De La Salle University

Energy

Since we now know the energy eigenfunctions of Hydrogen atom, the expansion postulate can be harnessed to ease the calculations of expectation values of observables.

$$\psi(x) = \sum_{nlm} a_{nlm} u_{nlm}$$

Finding the expectation values of energy is straightforward since

$$Hu_{nlm} = \frac{E_1}{n^2} u_{nlm}$$

Hence,

$$\langle E \rangle = \langle \psi | H | \psi \rangle = \sum_{nlm} E_n \, |a_{nlm}|^2 = E_1 \sum_{nlm} \left| \frac{a_{nlm}}{n} \right|^2$$

Position and Momentum

Evaluation of momentum expectation values involves the operator

$$p = -i\hbar\nabla$$

Calculation of derivatives is aided by the recursion relation

$$\rho\frac{dL_s^k(\rho)}{d\rho} = sL_s^k(\rho) - (s+k)L_{s-1}^k(\rho)$$

Thus, momentum expectation values $\langle p^s\rangle$ can ultimately be framed in terms of position expectation values $\langle r^s\rangle$. Much of the work would have been done once we know how to evaluate $\langle r^s\rangle$

Fortunately, expectation values of nearby powers of r are related to each other following a relation developed by Hendrik Anthony (Hans) Kramers

$$\frac{s+1}{n^2}Z^2\langle r^s\rangle - Z(2s+1)a_0\langle r^{s-1}\rangle + \frac{s}{4}[(2l+1)^2 - s^2]a_0^2\langle r^{s-2}\rangle = 0$$

Radial Equation

The starting point of Kramers' relation is the radial equation

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left[E+\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{l(l+1)\hbar^2}{2mr^2}\right]r^2R=0$$

If we consider the function

$$U(r)=rR(r)$$

Then

$$\frac{dR}{dr}=\frac{d(U/r)}{dr}=\frac{1}{r}\frac{dU}{dr}-\frac{U}{r^2}$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)=\frac{d}{dr}\left(r\frac{dU}{dr}-U\right)=r\frac{d^2U}{dr^2}+\frac{dU}{dr}-\frac{dU}{dr}=r\frac{d^2U}{dr^2}$$

The radial equation can then be recast as

$$\frac{d^2U}{dr^2}+\frac{2m}{\hbar^2}\left[E+\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{l(l+1)\hbar^2}{2mr^2}\right]U=0$$

Effective Hamiltonian

We may then think of an effective radial Hamiltonian

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

such that

$$-\frac{\hbar^2}{2m}\frac{d^2U}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]U = EU$$

The eigenenergies are known [hydrogen 2],

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

Expressing this in terms of the Bohr radius [Bohr]

$$a_0 = \frac{\hbar^2}{m}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^{-1}$$

Effective Hamiltonian

With

$$\frac{e^2}{4\pi\varepsilon_0} = \frac{\hbar^2}{ma_0}$$

we have

$$E_n = -\frac{m}{2n^2\hbar^2}\frac{\hbar^2}{ma_0}\frac{Z^2e^2}{4\pi\varepsilon_0} = -\frac{Z^2e^2}{4\pi\varepsilon_0}\frac{1}{2n^2a_0} = -\frac{Z^2}{n^2a_0^2}\frac{\hbar^2}{2m}$$

The Radial Equation may then be expressed as

$$-\frac{\hbar^2}{2m}\frac{d^2U}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2mr^2} - \frac{\hbar^2}{ma_0}\frac{Z}{r}\right]U = -\frac{Z^2}{n^2a_0^2}\frac{\hbar^2}{2m}U$$

Factoring out $-\hbar^2/2m$, we get

$$\frac{d^2U}{dr^2} - \left[\frac{l(l+1)}{r^2} - \frac{2Z}{a_0 r} + \frac{Z^2}{n^2a_0^2}\right]U = 0 \qquad \odot$$

Kramers' Relation

Multiplying the new radial equation by Ur^s and integrating, we have

$$\int Ur^s U'' dr - l(l+1)\int Ur^{s-2}U\, dr + \frac{2Z}{a_0}\int Ur^{s-1}U\, dr - \frac{Z^2}{n^2 a_0^2}\int Ur^s U\, dr = 0$$

We now note that since Radial functions are real,

$$\int Ur^s U\, dr = \int rRr^s rR\, dr = \int R^* r^s R\, r^2 dr = \langle r^s \rangle$$

Thus,

$$\int Ur^s U'' dr - l(l+1)\langle r^{s-2}\rangle + \frac{2Z}{a_0}\langle r^{s-1}\rangle - \frac{Z^2}{n^2 a_0^2}\langle r^s \rangle = 0 \qquad \star$$

Kramers' Relation

Let us now consider the integral

$$I = \int U r^s U'' dr$$

Integrating by parts

$$I = \int U r^s U'' dr \;= U r^s U' \Big|_0^\infty - \int U' d(r^s U)$$

Since the eigenfunctions are square-integrable,

$$\lim_{r\to\infty} U(r) = 0$$

Thus the exact term vanishes and

$$I = -\int U' d(r^s U) = -\int U' r^s U' dr - s\int U' r^{s-1} U dr$$

Kramers' Relation

Let

$$I = -I_1 - sI_2$$

where

$$I_1 = \int U' r^s U' dr$$

$$I_2 = \int U' r^{s-1} U dr$$

We now note that

$$d(U' r^{s+1} U') = (s+1)(U' r^s U')dr + 2U' r^{s+1} U'' dr$$

Hence,

$$I_1 = \int U' r^s U' dr = \frac{1}{s+1} U' r^{s+1} U' \Big|_0^\infty - \frac{2}{s+1} \int U' r^{s+1} U'' dr$$

Kramers' Relation

We now expand U'' by using the Radial equation ⊙

$$U" = \frac{d^2U}{dr^2} = \left[\frac{l(l+1)}{r^2} - \frac{2Z}{a_0 r} + \frac{Z^2}{n^2 a_0^2}\right] U$$

We then have

$$I_1 = -\frac{2}{s+1}\int U' r^{s+1} U" dr = -\frac{2}{s+1}\int U' r^{s+1}\left[\frac{l(l+1)}{r^2} - \frac{2Z}{a_0 r} + \frac{Z^2}{n^2 a_0^2}\right] U\, dr$$

$$= -\frac{2}{s+1}\left[l(l+1)\int U' r^{s-1}\, U\, dr - \frac{2Z}{a_0}\int U' r^{s}\, U\, dr + \frac{Z^2}{n^2 a_0^2}\int U' r^{s+1}\, U\, dr\right]$$

All remaining integrals are now of the form

$$I' = \int U' r^{s}\, U\, dr$$

Kramers' Relation

To evaluate integrals like I', we note that

$$d(Ur^sU) = sUr^{s-1}Udr + 2Ur^sU'dr$$

Thus,

$$I' = \int U'r^s\,U\,dr = \frac{1}{2}Ur^sU\Big|_0^\infty - \frac{s}{2}\int Ur^{s-1}U\,dr = -\frac{s}{2}\langle r^{s-1}\rangle$$

Kramers' Relation

Using the

$$I' = \int U' r^s \, U \, dr = -\frac{s}{2}\langle r^{s-1}\rangle$$

we find that

$$I_1 = -\frac{2}{s+1}\left[l(l+1)\int U' r^{s-1}\, U\, dr - \frac{2Z}{a_0}\int U' r^s \, U\, dr + \frac{Z^2}{n^2 a_0^2}\int U' r^{s+1}\, U\, dr\right]$$

becomes

$$I_1 = -\frac{2}{s+1}\left[-l(l+1)\frac{s-1}{2}\langle r^{s-2}\rangle + \frac{2Z}{a_0}\frac{s}{2}\langle r^{s-1}\rangle - \frac{Z^2}{n^2 a_0^2}\frac{s+1}{2}\langle r^s\rangle\right]$$
$$= l(l+1)\frac{(s-1)}{(s+1)}\langle r^{s-2}\rangle - \frac{2Z}{a_0}\frac{s}{s+1}\langle r^{s-1}\rangle + \frac{Z^2}{n^2 a_0^2}\langle r^s\rangle$$

and

$$I_2 = \int U' r^{s-1} U dr = -\frac{s-1}{2}\langle r^{s-2}\rangle$$

Kramers' Relation

Hence,

$$I = -I_1 - sI_2$$
$$= -l(l+1)\frac{(s-1)}{(s+1)}\langle r^{s-2}\rangle + \frac{2Z}{a_0}\frac{s}{s+1}\langle r^{s-1}\rangle - \frac{Z^2}{n^2a_0^2}\langle r^s\rangle + \frac{s(s-1)}{2}\langle r^{s-2}\rangle$$
$$= (s-1)\left[\frac{s}{2} - \frac{l(l+1)}{(s+1)}\right]\langle r^{s-2}\rangle + \frac{2Z}{a_0}\frac{s}{s+1}\langle r^{s-1}\rangle - \frac{Z^2}{n^2a_0^2}\langle r^s\rangle$$

Since I is also,

$$I = \int U r^s U'' dr = l(l+1)\langle r^{s-2}\rangle - \frac{2Z}{a_0}\langle r^{s-1}\rangle + \frac{Z^2}{n^2a_0^2}\langle r^s\rangle$$

the two relations combine to give

$$(s-1)\left[\frac{s}{2} - \frac{l(l+1)}{(s+1)}\right]\langle r^{s-2}\rangle + \frac{2Z}{a_0}\frac{s}{s+1}\langle r^{s-1}\rangle - \frac{Z^2}{n^2a_0^2}\langle r^s\rangle - l(l+1)\langle r^{s-2}\rangle$$
$$+ \frac{2Z}{a_0}\langle r^{s-1}\rangle - \frac{Z^2}{n^2a_0^2}\langle r^s\rangle = 0$$

Kramers' Relation

Combining factors of the same powers, for $\langle r^{s-2}\rangle$

$$(s-1)\left[\frac{s}{2}-\frac{l(l+1)}{(s+1)}\right]-l(l+1)=(s-1)\left[\frac{s}{2}-\frac{l(l+1)}{(s+1)}-\frac{l(l+1)}{(s-1)}\right]$$

$$=\frac{s(s+1)(s-1)-2(s-1)l(l+1)-2(s+1)l(l+1)}{2(s+1)}=\frac{s(s^2-1)-4sl(l+1)}{2(s+1)}$$

$$=\frac{s}{2}\left[\frac{s^2-1-4l^2-4l}{(s+1)}\right]=\frac{s}{2}\left[\frac{s^2-(2l+1)^2}{(s+1)}\right]$$

For $\langle r^{s-1}\rangle$,

$$\frac{2Z}{a_0}\frac{s}{s+1}+\frac{2Z}{a_0}=\frac{2Z}{a_0}\left[\frac{s}{s+1}+1\right]=\frac{2Z}{a_0}\left[\frac{s+s+1}{s+1}\right]=\frac{2Z}{a_0}\left[\frac{2s+1}{s+1}\right]$$

For $\langle r^{s}\rangle$,

$$-\frac{Z^2}{n^2a_0^2}-\frac{Z^2}{n^2a_0^2}=-\frac{2Z^2}{n^2a_0^2}$$

Kramers' Relation

We then have

$$\frac{s}{2}\left[\frac{s^2-(2l+1)^2}{(s+1)}\right]\langle r^{s-2}\rangle+\frac{2Z}{a_0}\left[\frac{2s+1}{s+1}\right]\langle r^{s-1}\rangle-\frac{2Z^2}{n^2a_0^2}\langle r^s\rangle=0$$

or

$$\frac{s+1}{n^2}Z^2\langle r^s\rangle-(2s+1)Za_0\langle r^{s-1}\rangle+\frac{s}{4}[(2l+1)^2-s^2]a_0^2\langle r^{s-2}\rangle=0$$