

# Quantum Mechanics 2

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Hydrogen Atom  
Kramers' Relation



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# 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.

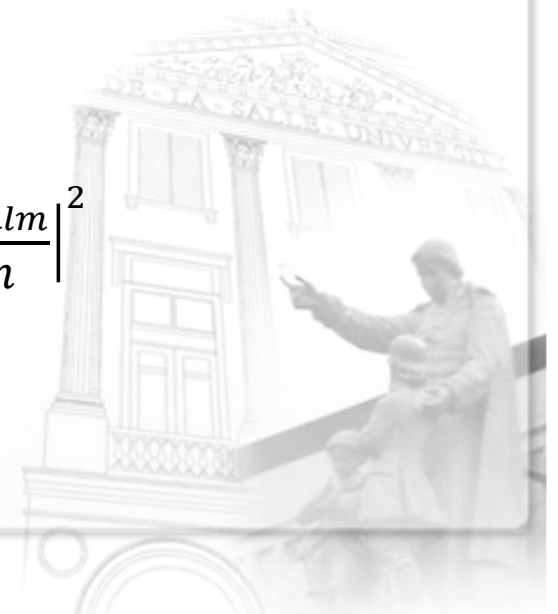
$$\psi(x) = \sum_{nlm} a_{nlm} u_{nlm}$$

Finding the expectation values of energy is straightforward since

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

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

$$\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[ E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right] r^2 R = 0$$

If we consider the function

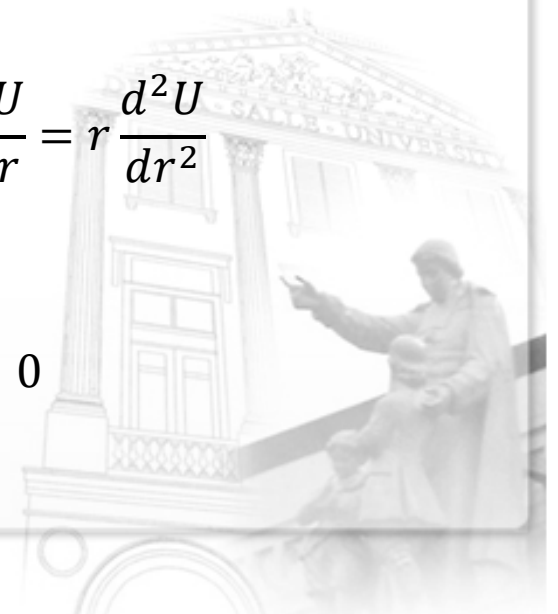
$$U(r) = rR(r)$$

Then

$$\begin{aligned} \frac{dR}{dr} &= \frac{d(U/r)}{dr} = \frac{1}{r} \frac{dU}{dr} - \frac{U}{r^2} \\ \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) &= \frac{d}{dr} \left( r \frac{dU}{dr} - U \right) = r \frac{d^2U}{dr^2} + \frac{dU}{dr} - \frac{dU}{dr} = r \frac{d^2U}{dr^2} \end{aligned}$$

The radial equation can then be recast as

$$\frac{d^2U}{dr^2} + \frac{2m}{\hbar^2} \left[ E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right] U = 0$$



# Effective Hamiltonian

We may then think of an effective radial Hamiltonian

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

such that

$$-\frac{\hbar^2}{2m} \frac{d^2 U}{dr^2} + \left[ \frac{l(l+1)\hbar^2}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right] U = EU$$

The eigenenergies are known [hydrogen 2],

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

Expressing this in terms of the Bohr radius [Bohr]

$$a_0 = \frac{\hbar^2}{m} \left( \frac{e^2}{4\pi\epsilon_0} \right)^{-1}$$



# Effective Hamiltonian

With

$$\frac{e^2}{4\pi\epsilon_0} = \frac{\hbar^2}{ma_0}$$

we have

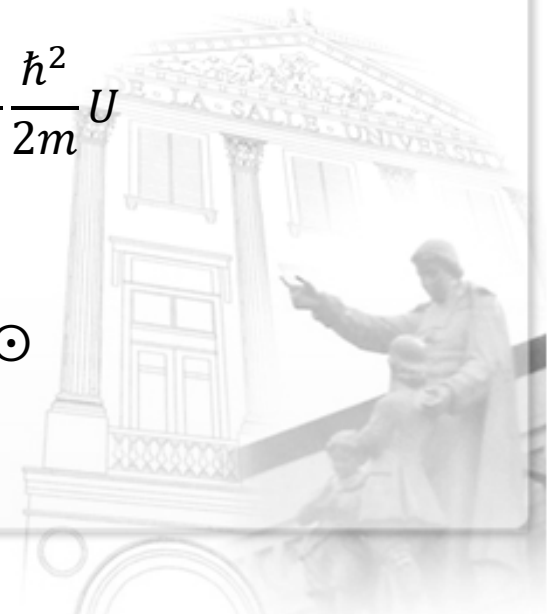
$$E_n = -\frac{m}{2n^2\hbar^2} \frac{\hbar^2}{ma_0} \frac{Z^2 e^2}{4\pi\epsilon_0} = -\frac{Z^2 e^2}{4\pi\epsilon_0} \frac{1}{2n^2 a_0} = -\frac{Z^2}{n^2 a_0^2} \frac{\hbar^2}{2m}$$

The Radial Equation may then be expressed as

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

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

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



# Kramers' Relation

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

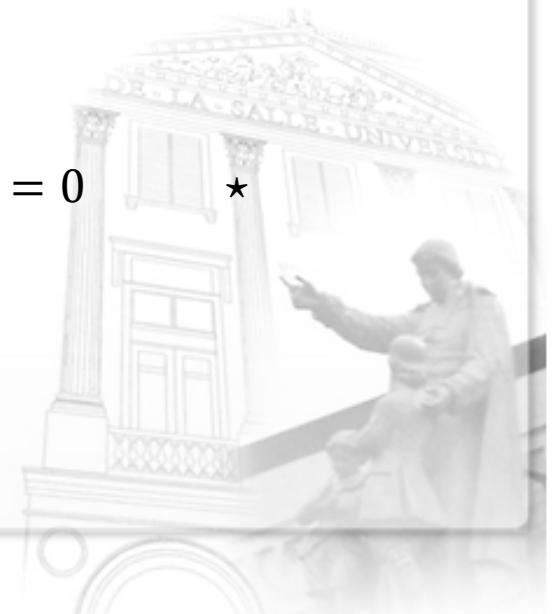
$$\int Ur^s U'' dr - l(l+1) \int Ur^{s-2} U dr + \frac{2Z}{a_0} \int Ur^{s-1} U dr - \frac{Z^2}{n^2 a_0^2} \int Ur^s U dr = 0$$

We now note that since Radial functions are real,

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

Thus,

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



# 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,

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

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

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

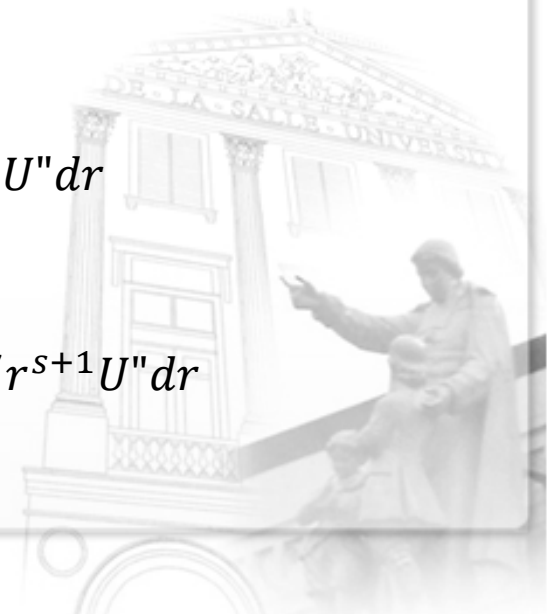
$$I_2 = \int U' r^{s-1} U dr$$

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  $\odot$

$$U'' = \frac{d^2U}{dr^2} = \left[ \frac{l(l+1)}{r^2} - \frac{2Z}{a_0r} + \frac{Z^2}{n^2a_0^2} \right] U$$

We then have

$$\begin{aligned} I_1 &= -\frac{2}{s+1} \int U' r^{s+1} U'' dr = -\frac{2}{s+1} \int U' r^{s+1} \left[ \frac{l(l+1)}{r^2} - \frac{2Z}{a_0r} + \frac{Z^2}{n^2a_0^2} \right] U dr \\ &= -\frac{2}{s+1} \left[ l(l+1) \int U' r^{s-1} U dr - \frac{2Z}{a_0} \int U' r^s U dr + \frac{Z^2}{n^2a_0^2} \int U' r^{s+1} U dr \right] \end{aligned}$$

All remaining integrals are now of the form

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



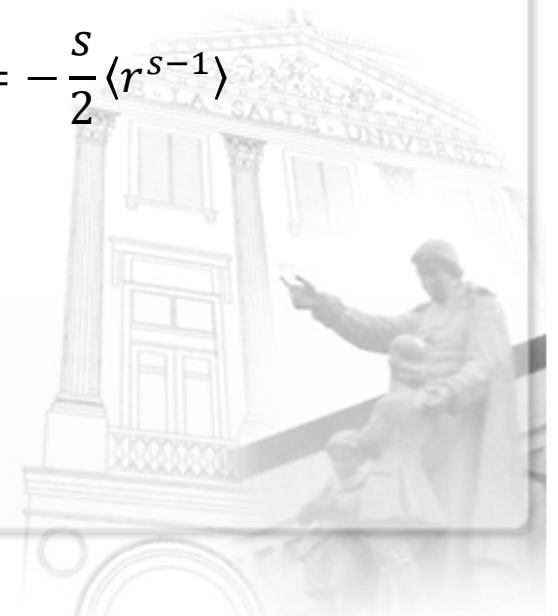
# Kramers' Relation

To evaluate integrals like  $I'$ , we note that

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

Thus,

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



# Kramers' Relation

Using the

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

we find that

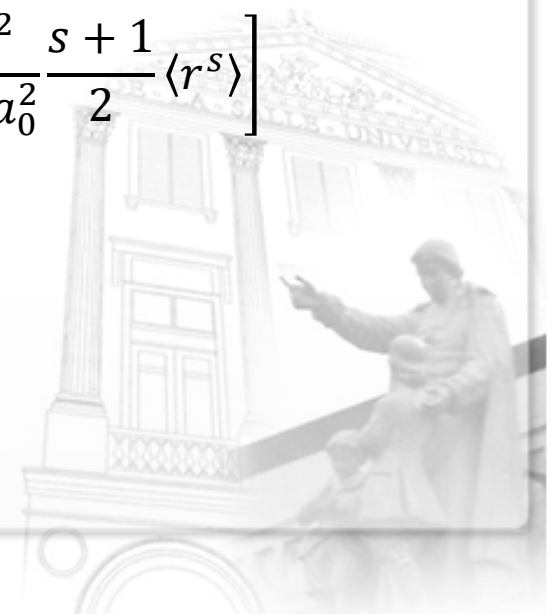
$$I_1 = -\frac{2}{s+1} \left[ l(l+1) \int U' r^{s-1} U dr - \frac{2Z}{a_0} \int U' r^s U dr + \frac{Z^2}{n^2 a_0^2} \int U' r^{s+1} U dr \right]$$

becomes

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

and

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



# Kramers' Relation

Hence,

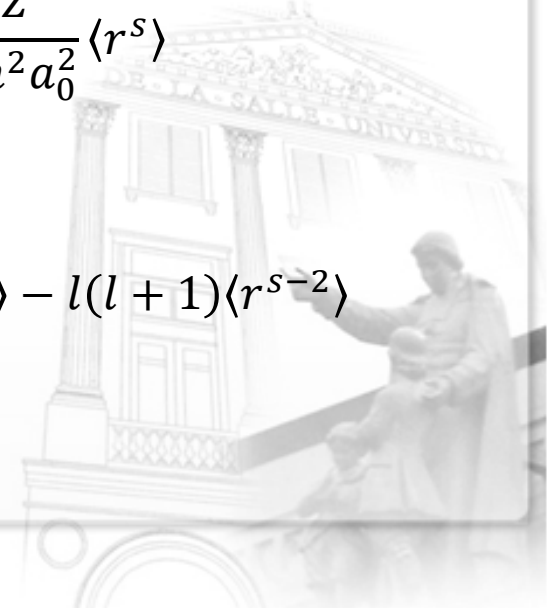
$$\begin{aligned} I &= -I_1 - sI_2 \\ &= -l(l+1) \frac{(s-1)}{(s+1)} \langle r^{s-2} \rangle + \frac{2Z}{a_0} \frac{s}{s+1} \langle r^{s-1} \rangle - \frac{Z^2}{n^2 a_0^2} \langle r^s \rangle + \frac{s(s-1)}{2} \langle r^{s-2} \rangle \\ &= (s-1) \left[ \frac{s}{2} - \frac{l(l+1)}{(s+1)} \right] \langle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

Since  $I$  is also,

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

the two relations combine to give

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



# Kramers' Relation

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

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

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  $\langle r^s \rangle$ ,

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



# Kramers' Relation

We then have

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

or

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

