Atomic Physics' starting point: Time dependent Schrödinger Equation

Erwin Schrödinger
Nobel prize 1933

Time-dependent wave equation

$$i\hbar\frac{\partial\Psi}{\partial t}=H\Psi$$

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t)+V\Psi(\vec{r},t)=i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}$$

Time-independent potential

$$V=V(\vec{r})$$

Search for stationary states

$$\Psi(\vec{r},t)=\psi(\vec{r})e^{-iEt/\hbar}$$

Results in time-independent wave equation

$$H\psi(\vec{r})=E\psi(\vec{r})$$

Time-independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r})+V\psi(\vec{r})=E\psi(\vec{r})$$

Stationary states:

$$|\Psi(\vec{r},t)|^2=|\psi(\vec{r})|^2$$

Schrödinger Equation for a two-particle system → Centre of Mass motion

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(r_e,r_p)-\frac{\hbar^2}{2m_p}\nabla^2\psi(r_e,r_p)$$
$$+V(r_e,r_p)=E\psi(r_e,r_p)$$

Central Force:

$$V(\vec{r})=V(\vec{r}_e-\vec{r}_p)=\frac{-Ze^2}{4\pi\varepsilon_0|\vec{r}_e-\vec{r}_p|}$$

Centre of Mass:

$$M\vec{R}=m_p\vec{r}_p+m_e\vec{r}_e$$
$$\vec{r}=\vec{r}_e-\vec{r}_p$$
$$\vec{P}=\vec{p}_p+\vec{p}_e=-i\hbar\vec{\nabla}_p-i\hbar\vec{\nabla}_e=-i\hbar\vec{\nabla}_R$$
$$\frac{\vec{p}}{\mu}=\frac{\vec{p}_e}{m_e}-\frac{\vec{p}_p}{m_p}=-i\hbar\vec{\nabla}_r$$

with $\mu=\frac{m_e m_p}{m_e+m_p}$ reduced mass of electron

$M=m_e+m_p$ atomic mass

Hamiltonian:

$$H=-\frac{\hbar^2}{2m_p}\nabla_p^2-\frac{\hbar^2}{2m_e}\nabla_e^2+V(\vec{r})$$

$$H=\underbrace{-\frac{\hbar^2}{2M}\nabla_R^2}_{\text{CM motion}}\underbrace{-\frac{\hbar^2}{2\mu}\nabla_r^2-\frac{Ze^2}{4\pi\varepsilon_0 r}}_{\text{Relative motion}}$$

$$H=H_{CM}+H_{rel}=E_{CM}+E_{rel}$$

Separation of varaiables → Centre of Mass and Relative motion

Wave function of the CM:

$$-\frac{\hbar^2}{2M}\nabla_R^2\Phi_{cm}(R)=E_{cm}\Phi_{cm}(R)$$

Solution:

$$\Phi_{cm}(R)=e^{i\vec{P}\cdot\vec{R}}$$

$$E_{cm}=P^2/2M$$

Wave function for the relative motion:

$$-\frac{\hbar^2}{2\mu}\nabla_r^2\Psi(\vec{r})-\frac{Ze^2}{4\pi\varepsilon_0 r}\Psi(\vec{r})=E_{rel}\Psi(\vec{r})$$

This is a 1-particle problem in Quantum Mechanics

Reduction to a one particle problem in centre-of-mass coordinates:

$$\psi(\vec{r}_1,\vec{r}_2)=\Psi_{rel}(x,y,z)\Phi_{cm}(X,Y,Z)$$

Atomic Hydrogen as a one-particle problem

Three-dimensional equation:

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi(\vec{r})-\frac{Ze^2}{4\pi\varepsilon_0 r}=E\Psi(\vec{r})$$

Separation of variables: each coordinate

$$\Psi(r,\theta,\phi)=R(r)\mathrm{Y}(\theta,\phi)$$

Insertion in equation

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\Psi(\vec{r})+\Lambda^2\Psi(\vec{r})\right)+V(r)=E\Psi(\vec{r})$$

Actual separation

$$\frac{\left[\frac{d}{dr}r^2\frac{dR}{dr}+\frac{2\mu r^2}{\hbar^2}(E-V)R\right]}{R}=-\frac{\Lambda^2\mathrm{Y}}{\mathrm{Y}}$$

radial dependence — angular

Set left and right equal to λ

General: partial differential equation along three coordinates

→ 3 quantization conditions → 3 quantum numberss

Angular part of the one-particle problem

Angular part: $$-\frac{\Lambda^2 \mathrm{Y}}{\mathrm{Y}} = \lambda$$

In full notation:

$$-\frac{\partial^2 \mathrm{Y}}{\partial \phi^2} = \sin\theta \frac{\partial}{\partial\theta} \sin\theta \frac{\partial \mathrm{Y}}{\partial\theta} + \lambda \sin^2\theta \mathrm{Y}$$

Separate angular coordinates

$$\mathrm{Y}(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

Angular equation

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = \frac{1}{\Theta}\left[\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\theta} + \lambda\sin^2\theta\right]$$

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = \text{constant} = \mathrm{m}^2$$

Azimuthal part

$$\frac{\partial^2\Phi(\phi)}{\partial\phi^2} + m^2\Phi(\phi) = 0$$

Solutions: $$\Phi(\phi) = e^{\pm im\phi}$$

For m positive and negative

Boundary conditions imposed: single-valued

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

Insert:

$$e^{im(\phi+2\pi)} = e^{im\phi}e^{2\pi im} = e^{im\phi}$$

$$e^{2\pi im} = 1$$

$$m = \text{integer}$$

m is eigenvalue of L_z

$$L_z\Phi_m(\phi) = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\Phi_m(\phi) = m\hbar\Phi_m(\phi)$$

θ dependence

From ϕ dependence

m is integer

Angular coordinate θ

$$\frac{1}{\sin\theta}\left[\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta}+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\Theta\right]=0$$

Single coordinate differential equation

On $[0,\pi]$, finite and single-valued

Solutions: special class of functions

For; $m=0$ Legendre Polynomials

$$P_\ell(\cos\theta)=\sum_{i=0}^{\ell}a_i(\cos\theta)^i$$

$$\lambda=\ell(\ell+1) \qquad \ell\geq 0$$

$$-m\leq\ell\leq m$$

General solution for $m\neq 0$

Associated Legendre Polynomials:

$$P_{\ell m}(\cos\theta)=\left(1-\cos^2\theta\right)^{m/2}\frac{d^m}{d(\cos\theta)^m}P_\ell(\cos\theta)$$

Structered functions with rules for

m and ℓ

Angular wave functions

Solutions for wave functions angular part

$$\mathrm{Y}_{lm}(\theta,\phi) = \Theta_{lm}(\theta)e^{im\phi} = |l,m\rangle$$

Spherical harmonics
(full set of functions spanning Hilbert space)
Simultaneous eigenfunctions of L^2 and L_z

$$L^2\mathrm{Y}_{lm} = \hbar^2 l(l+1)\mathrm{Y}_{lm}$$
$$L_z\mathrm{Y}_{lm} = \hbar m\mathrm{Y}_{lm}$$

With:

$$l = \text{positive integer}$$
$$-l \le m \le l$$

Orthonormal set:

$$\int_{\Omega(space)} \mathrm{Y}^*_{lm}(\theta,\phi)\mathrm{Y}_{l'm'}(\theta,\phi)d\Omega = \delta_{ll'}\delta_{mm'}$$

Parity property

$$P_{op}\mathrm{Y}_{lm}(\theta,\phi) = \mathrm{Y}(\pi-\theta,\phi+\pi) = (-)^{\ell}\mathrm{Y}_{lm}(\theta,\phi)$$

$\mathrm{Y}_{lm}(\theta,\phi)$ are solutions for any problem with a central potential $V = V(\vec{r})$

Radial part of the Schrödinger equation

Radial equation $\longrightarrow$ quantization of energy

$$\frac{d}{dr} r^2 \frac{dR}{dr} + \frac{2\mu r^2}{\hbar^2}[E - V]R = \lambda R$$

$$\lambda = \ell(\ell + 1)$$

+ set of rules for ℓ, m

Energy does not depend on m:

$(2\ell + 1)$ degeneracy

Effective potential:

$$V_{eff}(r) = V(r) + \frac{\hbar^2}{2\mu r^2}\ell(\ell + 1)$$

In general this equation is an eigenvalue problem solving for E

Eigenvalues $E_{n\ell}$

Eigen functions $R_{n\ell}(r)$

Radial part: special case $l=m=0$

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}r^2\frac{dR}{dr}+\left[V(r)+\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)\right]R=ER$$

Find a solution for $\ell=0, m=0$

$$-\frac{\hbar^2}{2\mu}\left(R''+\frac{2}{r}R'\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}R=ER$$

Physical intuition; no density for $r\to\infty$

trial: $R(r)=Ae^{-r/a}$

$$R'=-\frac{A}{a}e^{-r/a}=-\frac{R}{a}$$

$$R''=\frac{A}{a^2}e^{-r/a}=\frac{R}{a^2}$$

$$\longrightarrow \quad -\frac{\hbar^2}{2\mu}\left(\frac{1}{a^2}-\frac{2}{ar}\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}=E$$

must hold for all values of r

Prefactor for $1/r$: $\frac{\hbar^2}{\mu a}-\frac{Ze^2}{4\pi\varepsilon_0}=0$

$\longrightarrow$ Solution for the length scale paramater $a=\frac{4\pi\varepsilon_0\hbar^2}{Ze^2\mu}$

$\longrightarrow$ $a=\frac{m_e}{Z\mu}a_0$ with $a_0=\frac{4\pi\varepsilon_0\hbar^2}{e^2 m_e}$ Bohr radius

Solutions for the energy

$$E=-\frac{\hbar^2}{2\mu a}=-\frac{\mu}{m_e}Z^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{m_e}{2\hbar^2}$$

$$E=-\frac{\mu}{m_e}Z^2E_0$$

Ground state in the Bohr model ($n=1$)

Radial part: 2nd attempt

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}r^2\frac{dR}{dr}+\left[V(r)+\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)\right]R=ER$$

or:

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}rR-\frac{Ze^2}{4\pi\varepsilon_0 r}R+\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)R=ER$$

start from previous solutions and scaling

$$r=a\rho=\frac{4\pi\varepsilon_0\hbar^2}{Ze^2\mu}\rho$$ radius

$$E=-\frac{\mu}{m_e}Z^2E_0\eta=-\frac{\hbar^2}{2\mu a^2}\eta$$ energy

Insert, this yields:

$$\frac{d}{d\rho^2}\rho R+2R-\frac{\ell(\ell+1)}{\rho}R=\eta\rho R$$

Trial: again exponential damping x polynomial

$$R=e^{-\sqrt{\eta}\rho}\frac{F(\rho)}{\rho}$$

$$F''-2\sqrt{\eta}F'+\left[\frac{2}{\rho}-\frac{\ell(\ell+1)}{\rho^2}\right]F=0$$

Again special case: $\ell=0$

$$F''-2\sqrt{\eta}F'+\frac{2}{\rho}F=0$$

Verify consistency for

$$R=Ae^{-\rho}\qquad\sqrt{\eta}=1$$

Radial part: 2nd attempt, further

Again special case: $\ell = 0$

$$F'' - 2\sqrt{\eta}F' + \frac{2}{\rho}F = 0$$

Polynomial for F

$$F(\rho) = A(\rho + a_2\rho^2 + \cdots + a_n\rho^n)$$

$$F'(\rho) = A(1 + 2a_2\rho + \cdots + na_n\rho^{n-1})$$

$$F''(\rho) = A(2a_2 + \cdots + n(n-1)a_n\rho^{n-2})$$

Fill in and equation should be valid for all ρ

Highest polynomial:

$$-2\sqrt{\eta}Ana_n\rho^{n-1} + \frac{2}{\rho}Aa_n\rho^n = 0$$

Hence: $-2\sqrt{\eta}n + 2 = 0$

$\longrightarrow$ $\eta = \frac{1}{n^2}$

Eigenvalues: $E_{n(\ell=0)} = -\frac{\mu}{m_e}Z^2\frac{E_0}{n^2}$

Again the Bohr energies !

Radial functions: $R = e^{-\rho/n}\frac{F(\rho)}{\rho}$

Radial part: 3nd attempt

$$F'' - 2\sqrt{\eta}F' + \left[\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]F = 0$$

Now for general case: $\ell \neq 0$

Try now:

$$F(\rho) = A\left(\rho^{1+\ell} + a_2\rho^{2+\ell} + \cdots + a_n\rho^n\right)$$

And follow the proof …

It may be proven that F is a polynomial of order n, with:

$$\sqrt{\eta} = \frac{1}{n}$$

General result:

$$E_{n\ell} = -\frac{\mu}{m_e} Z^2 \frac{E_0}{n^2}$$

This is a general consequence in case of

$$V \propto \frac{1}{r^\alpha} \qquad \text{with} \qquad \alpha = 1$$

For a purely Coulombic potential all angular wave functions are degenerate !

In hydrogen the l,m levels are degenerate

Atomic Hydrogen Radial part

Analysis of radial equation yields:

$$E_{nlm} = -\frac{Z^2}{n^2}(hc)\frac{\mu}{m_e}R_\infty$$

with $$R_\infty = \frac{m_e e^4}{8\varepsilon_0 h^3 c}$$

Wave functions:

$$\Psi_{nlm}(\vec{r},t) = R_{nl}(r)\mathrm{Y}_{lm}(\theta,\phi)e^{-iE_n t/\hbar}$$

$n = 1$	$\ell = 0$	$R_{10} = \frac{2}{\sqrt{a^3}}e^{-\rho}$
$n = 2$	$\ell = 0$	$R_{20} = \frac{1}{\sqrt{2a^3}}\left(1 - \frac{\rho}{2}\right)e^{-\rho/2}$
	$\ell = 1$	$R_{21} = \frac{1}{2\sqrt{6a^3}}\rho e^{-\rho/2}$
$n = 3$	$\ell = 0$	$R_{30} = \frac{2}{3\sqrt{3a^3}}\left(1 - \frac{2}{3}\rho + \frac{2}{27}\rho^2\right)e^{-\rho/3}$
	$\ell = 1$	$R_{31} = \frac{8}{27\sqrt{6a^3}}\rho\left(1 - \frac{\rho}{6}\right)e^{-\rho/3}$
	$\ell = 2$	$R_{32} = \frac{4}{81\sqrt{30a^3}}\rho^2 e^{-\rho/3}$

- *1/n* behaviour

- polynomial functions

For numerical use:

$$u_{n\ell}(\rho) = \sqrt{\frac{2Z}{na_0}}\sqrt{\frac{(n-\ell-1)!}{2n(n+1)!}}e^{-Z\rho/n}\left(\frac{2Z\rho}{n}\right)^{\ell+1}L_{n-\ell-1}^{2\ell+1}\left(\frac{2Z\rho}{n}\right)$$

$$\rho / r = 2Z / na \qquad a = 4\pi\varepsilon_0\hbar^2 / \mu e^2 \qquad R = \frac{u_{n\ell}(r)}{r}$$

Atomic orbitals

Interpretation: Born

$$\left|\Psi_{nlm}(\vec{r},t)\right|^2$$

Use $\Psi_{nlm}(\vec{r},t)$ for expectation values

Radial distribution function

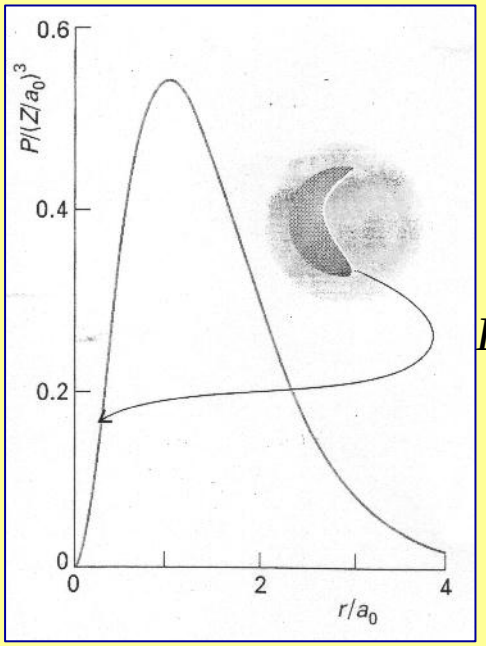
$$P(r)dr = \int_0^{2\pi}\int_0^{\pi} R(r)^2 \left|Y(\theta,\phi)\right|^2 r^2 dr \sin\theta d\theta d\phi$$

$$= r^2 R^2 dr$$

For 1s orbitals: $P(r) = \dfrac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$

Optimum; $\dfrac{dP}{dr} = 0$

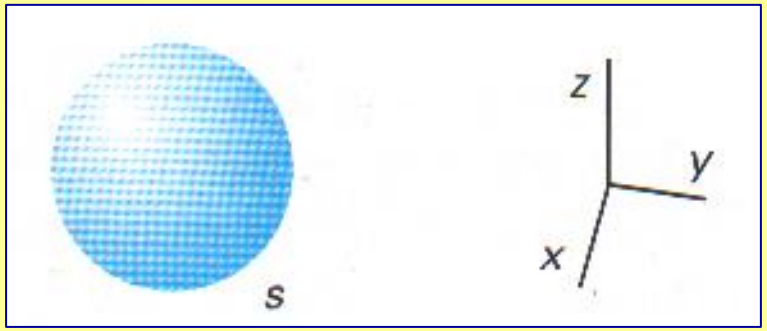
$$r_{opt} = \frac{a_0}{Z}$$



$$\frac{P(r)}{(Z/a_0)^3}$$

function

R_{opt} = 0.53 Å for H
0.26 Å for He^+
0.53 Å for Ne^{9+}



Atomic *p* Orbitals

Orbital with $m_l=0$ has $L_z=0$

No angular momentum around z-axis

np orbital with $m_l=0$

$$p_0 = R_{n1}Y_{10} = r\cos\theta f(r)$$

$$p_z = zf(r)$$

xy is nodal plane

$$p_{\pm 1} = R_{n1}Y_{1,\pm 1} = \mp\frac{1}{\sqrt{2}} r\sin\theta e^{\pm im\phi} f(r)$$

Angular momentum around z-axis

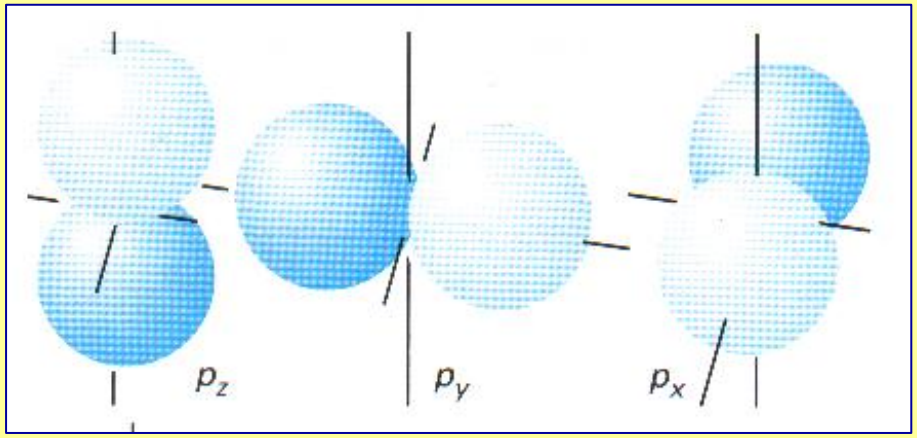
Use real functions

Standing waves without net L_z

$$p_x = \frac{1}{\sqrt{2}}(p_- - p_+) = \sqrt{\frac{3}{4\pi}} R_{n1}\sin\theta\cos\phi = xf(r)$$

$$p_y = yf(r)$$

p_x, p_y, p_z have same shape, different orientations



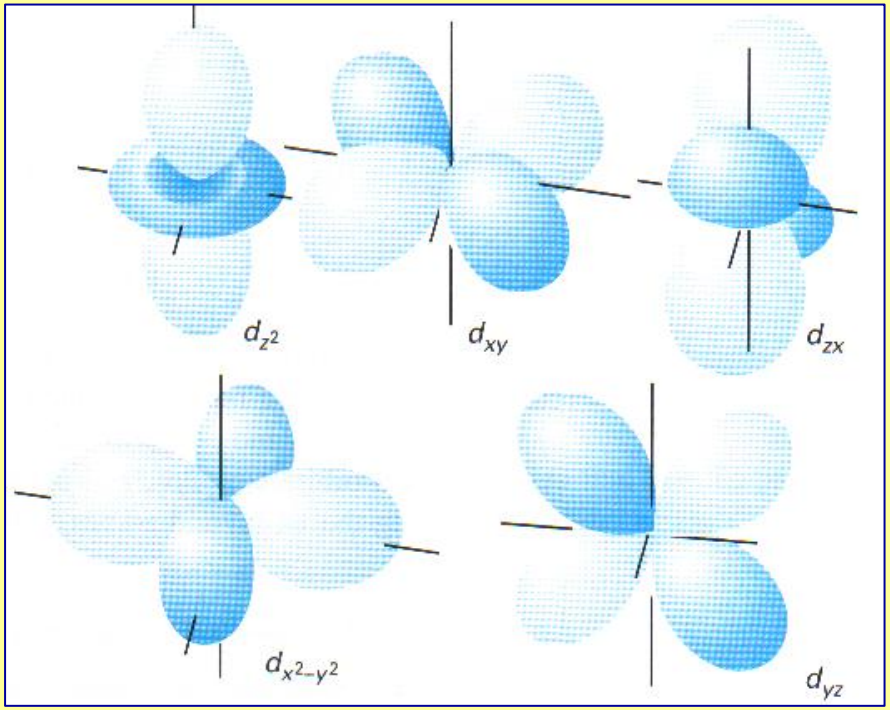
Colors denote positive and negative signs

Atomic *d* Orbitals

5 *d* orbitals with $m_l = 2, 1, 0, -1, -2$

d orbitals can be combined to give standing waves with total $m=0$

$$d_{xy} = xyf(r)$$
$$d_{yz} = yzf(r)$$
$$d_{zx} = zxf(r)$$
$$d_{x^2-y^2} = \frac{1}{2}\left(x^2 - y^2\right)f(r)$$
$$d_{z^2} = \frac{1}{2\sqrt{3}}\left(3z^2 - r^2\right)f(r)$$



Calculation of expectation values in the atom

Now that wave functions are known
expectation values can be computed

Definition $$\langle f(r)\rangle = \int \Psi^*_{nlm} r \Psi_{nlm} d\tau = \int_0^\infty r^3 R_{nl}^2 dr = \int_0^\infty r P_{nl}(r) dr$$

$$\langle r\rangle = an^2\left\{1+\frac{1}{2}\left[1-\frac{\ell(\ell+1)}{n^2}\right]\right\}$$

$$\left\langle \frac{1}{r}\right\rangle = \frac{1}{an^2}$$

$$\left\langle \frac{1}{r^3}\right\rangle = \frac{2}{a^3 n^3 \ell(\ell+1)(2\ell+1)}$$

Use this to proof the quantum virial theorem

$$\langle V\rangle = -\frac{Ze^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r}\right\rangle = \frac{Ze^2}{4\pi\varepsilon_0 an^2} = -Z^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{\mu}{n^2\hbar^2}$$

$$\langle E\rangle = \langle E_n\rangle = -Z^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{\mu}{2n^2\hbar^2}$$

Hence $\langle V\rangle = 2\langle E\rangle$

Kinetic energy;

$$\langle K\rangle = \langle E\rangle - \langle V\rangle = -\langle E\rangle = Z^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{\mu}{2n^2\hbar^2}$$