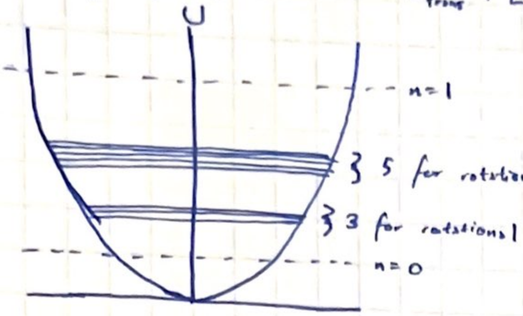
Comparing energies: $\sum E = E_{trans} + E_{rot} + E_{vib}$, where $E_{tr} << E_{rot} << E_{vib}$.



$E_{vibr} = h\nu(n + 1/2)$, $E_{rot} = \frac{\hbar^2}{2I} l(l+1)$

The Hydrogen Atom

The hydrogen atom contains two particles: e^- and p^+ which are not bound to each other.

$m_{e^-} = 9.1 \times 10^{-31}$ kg $\approx \frac{1}{2000}(m_{p^+})$

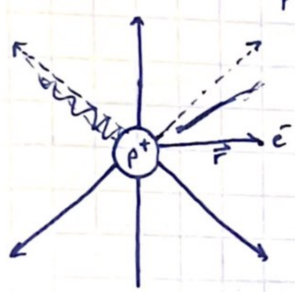
$m_{p^+} = 1.7 \times 10^{-27}$ kg

$$U = -\frac{e^2}{r}\underbrace{\left(\frac{1}{4\pi\varepsilon_0}\right)}_{\text{Permittivity of Free Space (A constant)}}$$

Center of mass calculation: $R_{com} = \frac{\vec{r}_{p^+} m_{p^+} + \vec{r}_{e^-} m_{e^-}}{m_{p^+}} \approx \vec{r}_p$

↳ All of the mass is practically centered on the proton.

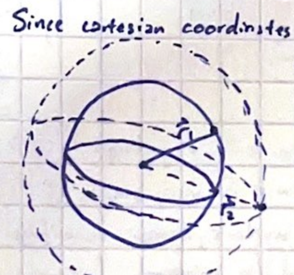
Reduced mass: $\frac{m_{p^+}(m_{e^-})}{m_{p^+} + m_{e^-}} \approx m_{e^-} = \mu = m$



The potential energy of this system does not depend on orientation – "central potential."

$$U = -\frac{1}{4\pi\varepsilon_0}\left(\frac{e^2}{r}\right), \text{ where } r = \sqrt{x^2 + y^2 + z^2}$$

Since cartesian coordinates are not convenient, we swap $\{x, y, z\} \to \{r, \theta, \phi\}$



→ The potential does not change along the sphere, however, movement along layers of a sphere, $\frac{\partial}{\partial r}$, depends on the potential. The total hamiltonian can be expressed as:

$$\hat{\mathcal{H}} = \hat{K} + \hat{U} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}, \text{ where } m = m_{e^-}$$

We can express this more explicitly using $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2}{2mr^2\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)$

Recall that $\hat{K} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}_{\text{equals 0 for particle in a sphere, but cannot = 0 for hydrogen atom model.}} - \frac{\hbar^2}{2mr^2\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)$

We can calculate the energies of the hydrogen atom by using Schrödinger's time independent equation:

$\hat{\mathcal{H}}\Psi = E\Psi$,

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\Psi\right) - \frac{\hbar^2}{2mr^2\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\Psi \cdot \frac{r^2}{4\pi\varepsilon_0}\frac{e^2}{r}\Psi = E\Psi$$

We can use some tricks to make sure only one side depends on r and one side on ϕ, θ.

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) - \frac{\hbar^2}{2mr^2\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\psi \cdot \frac{r^2}{4\pi\varepsilon_0}\frac{e^2}{r}\psi = E\psi$$

$\cdot r^2$

$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right) - \frac{\hbar^2}{2m\sin^2\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\psi \cdot \frac{r^2}{4\pi\varepsilon_0}\frac{e^2}{r}\psi = E\psi r^2$$

Rearrange

$$-\frac{\hbar^2}{2m\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\psi = E\psi r^2 + \frac{\hbar^2}{2m}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\psi + \frac{1}{4\pi\varepsilon_0}\frac{r^2}{r}e^2\psi$$

We see that this statement is essentially, $\psi(r,\theta,\phi) = R(r)\Phi(\theta,\phi)$, therefore $\psi = R\Phi$

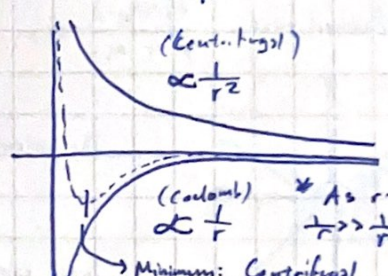
divide both sides by $R\Phi = \psi$

$$\frac{-\frac{\hbar^2}{2m\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right)\Phi}{\Phi} = \frac{ERr^2 + \frac{\hbar^2}{2m}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R + \frac{1}{4\pi\varepsilon_0}\frac{r^2}{r}e^2R}{R} = c$$

The only case when these two statements can be equal is when both sides equal the same constant.

We already have solutions for this, since $\Phi(\theta,\phi) = Y_{l,m_l}(\theta,\phi)$.

* Know that $\frac{1}{r^2} >> \frac{1}{r}$ as $r \to 0$



* As $r\to\infty$, $\frac{1}{r} >> \frac{1}{r^2}$

Minimum: Centrifugal force counteracts attractive forces. Addition of both curves show familiar curve.

$$R\frac{\hbar^2}{2m}l(l+1) = ERr^2 + \frac{\hbar^2}{2m}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R + \frac{1}{4\pi\varepsilon_0}\frac{r^2}{r}e^2R$$

Reorder, divide by r^2 to return to Schrödinger's form.

$$\underbrace{-\frac{\hbar^2}{2mr^2}\frac{d}{dr}r^2\frac{d}{dr}R}_{K_{trans}} + \underbrace{\frac{\hbar^2}{2mr^2}l(l+1)R}_{K_{rot}} - \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}R}_{U} = ER$$

K_{rot}: Centrifugal

$K_{rot} + U$: U_{eff}

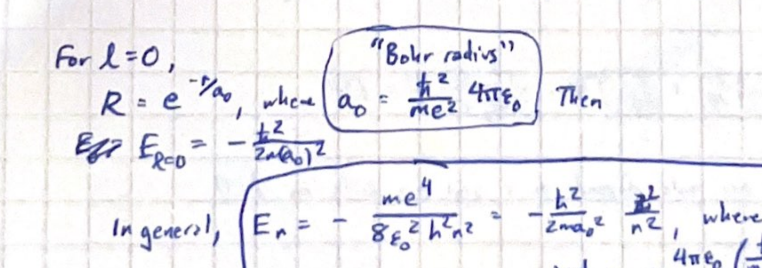
U: Coulomb

- When $l=0$, only K_{trans} and U present
- If $l \neq 0$, there is a rotational force which produces a counter force to the electrostatic interaction.

* When r is very large, $\frac{1}{r} >>> \frac{1}{r^2}$

* When r is very small, $\frac{1}{r^2} >>> \frac{1}{r}$. At distances very close to the nucleus, ~~this~~ is centrifugal force, but ~~but~~ electrostatic interaction dominates will end up ~~losing~~ losing.

→ As l increases, more rotation, and minimum moves right:



The minimum can be calculated as:

$$\frac{d}{dr}\left(\frac{A}{r^2} - \frac{B}{r}\right) = 0$$

$$-\frac{2A}{r^3} + \frac{B}{r^2} = 0$$

$$\frac{-2A + Br}{r^3} = 0, \quad r_{min} = \frac{2A}{B}$$

$$= \frac{2\hbar^2 l(l+1)}{me^2}(4\pi\varepsilon_0)$$

Where $\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} = U$

For $l=0$,

$R = e^{-r/a_0}$, where $\boxed{a_0 = \frac{\hbar^2}{me^2}4\pi\varepsilon_0}$ "Bohr radius" Then

~~E~~ $E_{l=0} = -\frac{\hbar^2}{2m(a_0)^2}$

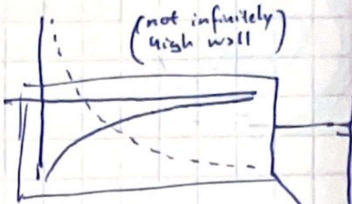
In general, $\boxed{E_n = -\frac{me^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{\hbar^2}{2ma_0^2}\frac{1}{n^2}, \text{ where } n = 1,2,3,\ldots, \text{ and } a_0 = 4\pi\varepsilon_0\left(\frac{\hbar^2}{me^2}\right)}$

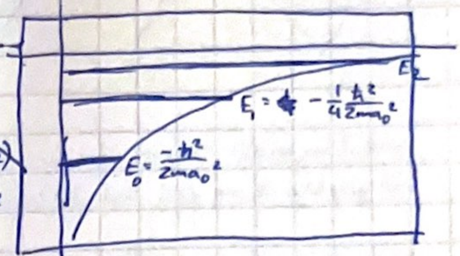
Note that energy only depends on the principal quantum number, n.

$\psi_{n,l,m_l} = \underbrace{R_{n,l}(r)}_{\text{Radial part}} \underbrace{Y_{l,m_l}(\theta,\phi)}_{\text{Spherical harmonics}}$, where $R_{n,l} = A_{n,l} L_{n,l}\left(\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)^{l} e^{-r/na_0}$

- Note that when there is no rotation, $l=0$ and $R_{n,l} = A_{n,l} L_{n,l}\left(\frac{r}{a_0}\right)e^{-\frac{r}{a}}$
- e^{-r/na_0} represents tunneling associated with exponential decay:

$\Delta x = \frac{1}{K}$, e^{-Kx}





For n_1, the energy is not degenerate.
n_2, when $l=0$ or $l=1$, and thus $m_l = 0, \pm 1$, is 4 times degenerate

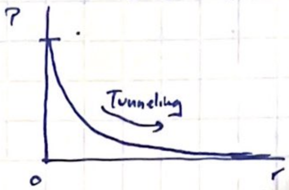
(Since $n = 1, 2, 3, \ldots$ and
$l = 0, 1, \ldots, n-1$
$m_l = -l, \ldots, +l$)

The pattern is already familiar to us:

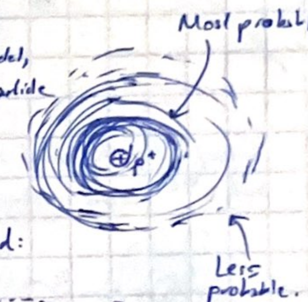
$n\ l$ → 1s	$n=1$, $l=0$
2s	$n=2$, $l=0$
2p	$n=2$, $l=1$
...	

Since $\Delta E = h\nu = -\frac{\hbar^2}{2ma_0}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$ and $n_1 < n_2$, then ΔE must $= \frac{\hbar^2}{2ma_0}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\frac{c}{\lambda}$

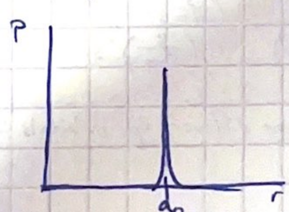
Starting with $n=1$, $l=0$, in the 1s state, we can graph the probability density functions as $(\psi(r))^2 = A^2 e^{-\frac{2r}{a_0}}$.



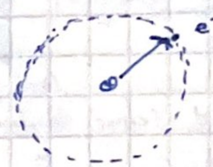
Notice that in this model, the highest probability of the particle is at the nucleus:



Bohr's planetary model would appear like this instead:



translates to



What about for $n=2$, 2s & 2p?

There are 4 possible wave functions for $n=2$, corresponding to $l=0,1$ and $m_l = 0, \pm 1$:

For $n=2, l=0, m_l=0$, $\psi(r) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$

$n=2, l=1, m_l=0$, $\psi(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$

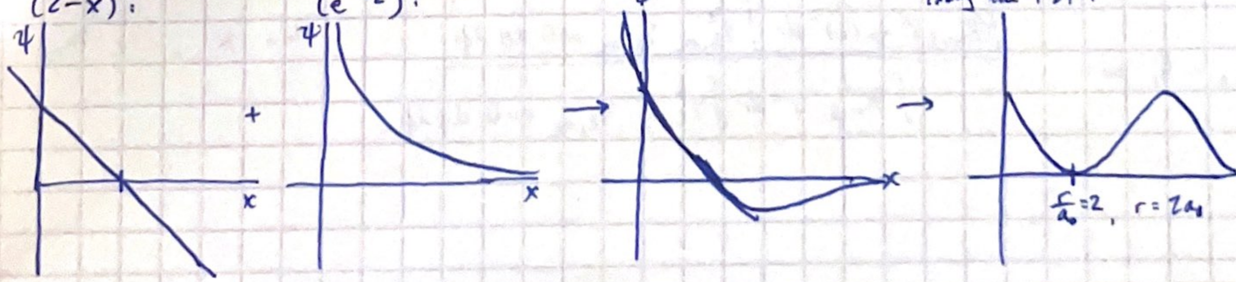
$n=2, l=1, m_l=\pm 1$, $\psi(r,\theta,\phi) = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$

To determine the general shape of the 2s orbital, let us consider exclusively $\psi(r)$, without θ, ϕ dependence:

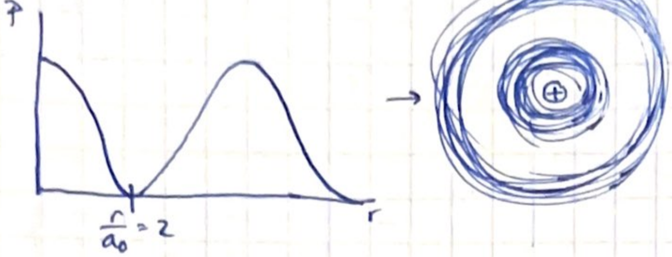
$\psi(r) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$. Let $x = \frac{r}{a_0}$. Then, $\psi(r) = \underbrace{\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}}_{\text{(Constant)}}(2-x)(e^{-\frac{x}{2}})$

Plotting as a function of x, the two parts may be visualized & combined:

$(2-x)$: $\quad (e^{-x/2})$: $\quad$ Taking the PDF:



Now that we have the function combined and converted to probability density, we can begin to visualize the 2s orbital of an electron cloud:

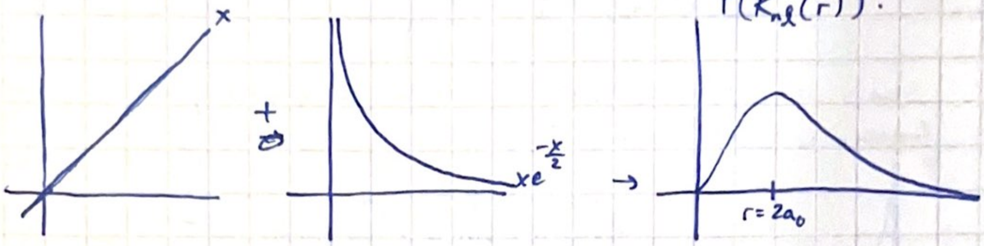


There is a region of 0 probability localized to the central region of the electron cloud, at $\frac{r}{a_0} = 2$. This node is the basis for the electron separation via orbitals.

Reminder that this is <u>only the case</u> when there is no rotational motion: $l = 0$ and $m_l = 0$

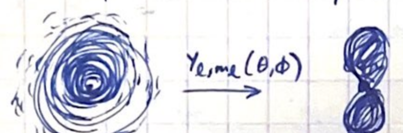
What if we consider the case that $l = 1$? In this case, $\Psi(r, \theta, \phi) \sim A\frac{r}{a_0} e^{-\frac{r}{2a_0}}$. Using the same substitution and graphing it, we find that $\Psi(r, \theta, \phi) \sim x e^{-x/2}$: which corresponds to the 2p orbital:

$P(R_{nl}(r))$:



But remember that this is not the entire picture. $\Psi(r, \theta, \phi)$ should also depend on either $\sin\theta$ or $\cos\theta$ and $e^{\pm i\phi}$.

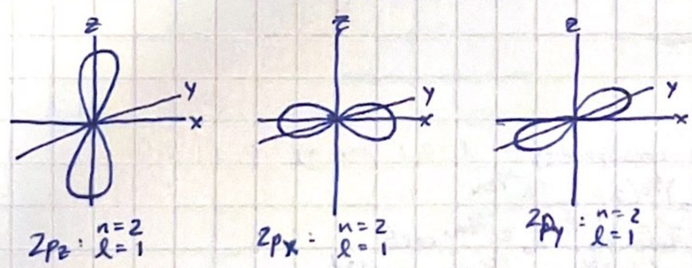
Incorporating the spherical dependence $Y_{l,m_l}(\theta, \phi)$ along side $R_{n,l}(r)$ we see that the terms $\cos\theta, \sin\theta$ and $e^{\pm i\phi}$ further restrict the probability density:



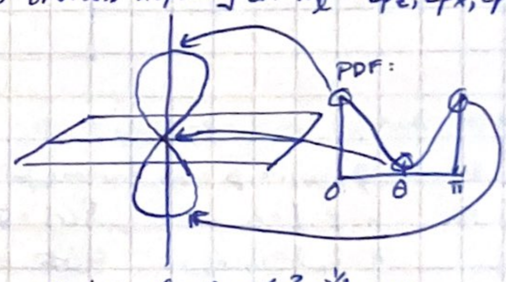
Look familiar?

$$Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$
$$Y_{1,0}(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$
$$Y_{1,\pm1}(\theta, \phi) = \pm\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{\pm i\phi}$$

The θ and ϕ terms therefore correspond to three different 2p orbitals depending on m_l: $2p_z, 2p_x, 2p_y$:



$m_l = 1, 0, -1$
(arbitrary assignment)



For $Y_{1,0}(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$

$Y_{1,\pm1}(\theta, \phi) = \pm\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{\pm i\phi}$

Calculating $\langle U \rangle$:

$U = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$, $\langle U \rangle = \underbrace{-\frac{1}{4\pi\epsilon_0} e^2}^{\text{Constants}} \langle \frac{1}{r} \rangle$, $\langle \frac{1}{r} \rangle = \frac{\int \psi^* \frac{1}{r} \psi \, dV}{\int \psi^* \psi \, dV}$. If we assume the case that $n=1$, $l=0$, $m_l = 0$, then $R_{1,0} = e^{-r/a_0} A$

$R_{1,0} = \psi_1$ so

$$\frac{\int (R_{n,l})^2 \frac{1}{r} (r)^2 dr \int Y^*_{l,m_l} Y_{l,m_l} \sin\theta \, d\theta \, d\phi}{\int R^2_{n,l} \, r^2 dr \int Y^*_{l,m_l} Y_{l,m_l} \sin\theta \, d\theta \, d\phi}.$$

$$\langle U\rangle = -\frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r}\right\rangle,\quad \left\langle \frac{1}{r}\right\rangle = \frac{\int R_{n,l}^2\,\frac{1}{r}\,r^2\,dr\;\cancel{\int Y^*_{l,m_l}Y_{l,m_l}\sin\theta\,d\theta\,d\phi}}{\int R_{n,l}^2\,r^2\,dr\;\cancel{\int Y^*_{l,m_l}Y_{l,m_l}\sin\theta\,d\theta\,d\phi}} = \frac{\int (R_{n,l})^2\frac{1}{r}r^2\,dr}{\int (R_{n,l})^2 r^2\,dr}$$

(This term is from the Jacobian)

Recall that $R_{n,l}$ for $n=1, l=0, m_l=0$ is $R_{1,0} = Ae^{-\frac{r}{a_0}}$. Then

$$\left\langle \frac{1}{r}\right\rangle = \frac{A^2\int_0^\infty e^{-\frac{2r}{a_0}}\,r\,dr}{A^2\int_0^\infty e^{-\frac{2r}{a_0}}\,r^2\,dr}.$$

The table integral, $\int_0^\infty x^m e^{-ax}\,dx = \frac{m!}{a^{m+1}}$ is used, where $a = \frac{2}{a_0}$, $\left\langle \frac{1}{r}\right\rangle = \frac{1!}{\left(\frac{2}{a_0}\right)^2}\,\frac{\left(\frac{2}{a_0}\right)^3}{2!} = \frac{1}{a_0}.$

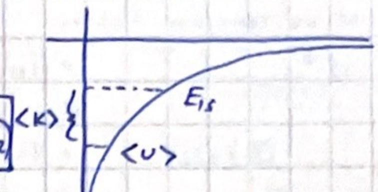
Therefore, $\langle U\rangle = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{a_0}\right) = -\frac{\hbar^2}{ma_0^2}$. This result does not represent a cloud, however. This result appears to tell us that e^- move on a defined orbit for the 1s orbital:

We find that $E_{1s} = -\frac{\hbar^2}{2ma_0^2}\frac{1}{n^2}$, where $a_0 = \frac{4\pi\varepsilon_0}{e^2}\left(\frac{\hbar^2}{m}\right)$

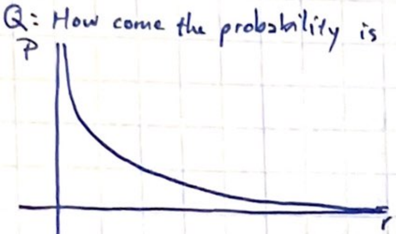
$E_{1s} = \langle K\rangle + \langle U\rangle$, $\therefore$ $\langle K\rangle = -E_{1s}$.

$-E_{tot}$ $\quad$ $2E_{tot}$

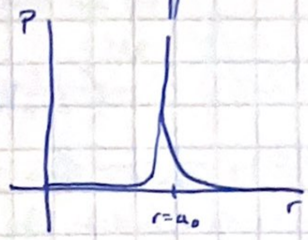
$$\boxed{E = -\frac{e^2}{8\pi\varepsilon_0 a_0}\left(\frac{1}{n^2}\right)}$$



Q: How come the probability is



but the $\langle U\rangle = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{a_0} = -\frac{\hbar^2}{ma_0^2}$ PDF appears like:



A: All points in space will contribute equally to the probability. As radius decreases, the probability of finding the particle will increase. However, think about what else a decreasing radius would imply. The smaller the radius, the less surface area, since $SA = 4\pi r^2$.

$\frac{1}{r}(r^2)e^{-\frac{2r}{a_0}} = P$

surface area of the sphere

For the 1s orbital, $r^2e^{-\frac{2r}{a_0}}$ can be graphed: