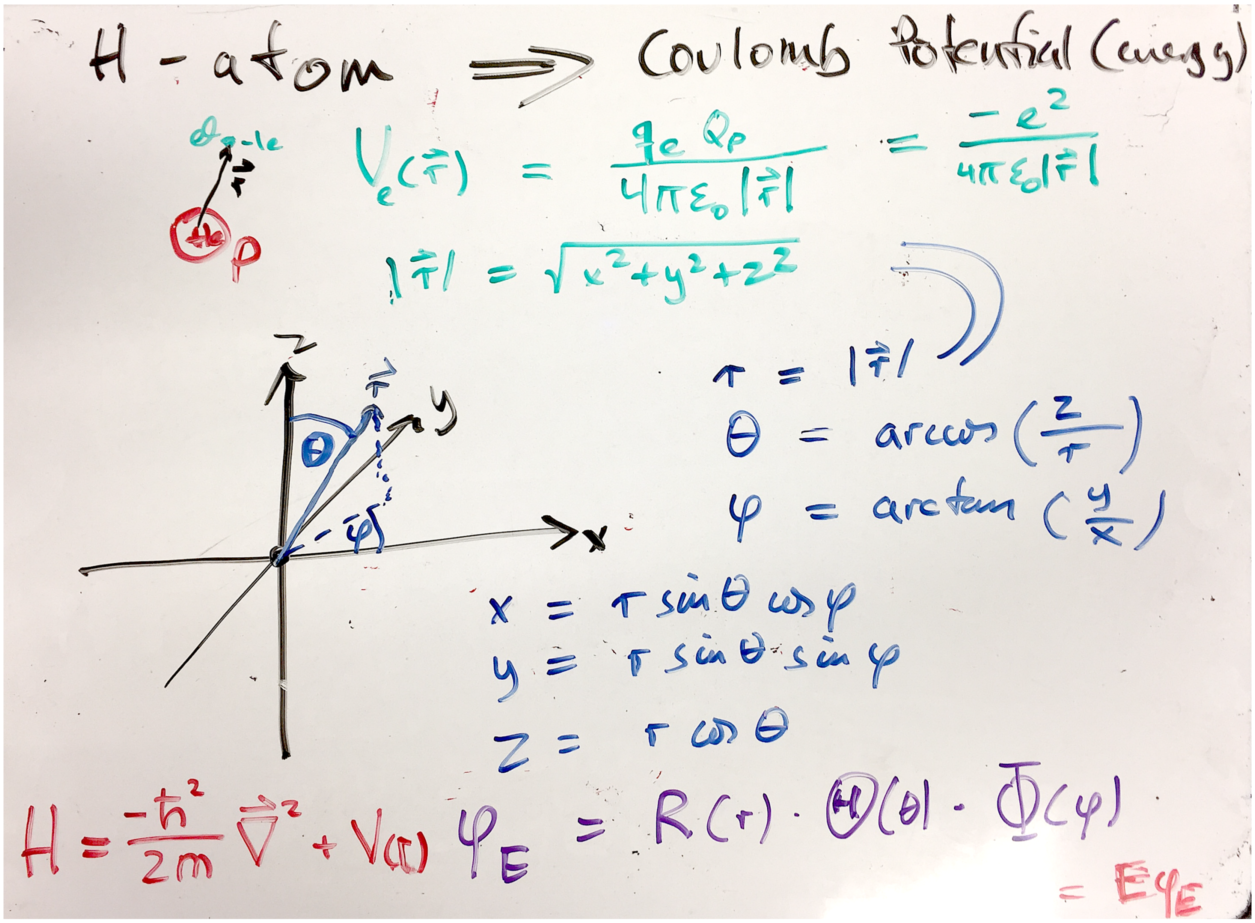
After studying separation of variables in Cartesian coordinates (3D square well with ∞ high walls), we are now trying to solve the Hamiltonian Eigenvalue problem (= “Time-independent Schrödinger equation”) in SPHERICAL coordinates. This is needed for understanding the H atom:



$$H\psi_E = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi_E}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_E}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_E}{\partial\varphi^2}\right]$$

$$- \frac{e^2}{4\pi\varepsilon_0 r}\psi_E = E\psi_E$$

$$\psi_E(r,\theta,\varphi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\varphi)$$

$1 : \psi_E$

$$\rightarrow -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)\cdot\frac{1}{R} - \frac{\hbar^2}{2mr^2}\underbrace{\frac{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta\Phi}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2\Theta\Phi}{\partial\varphi^2}\right]}{\Theta(\theta)\Phi(\varphi)}}_{\text{depends on } \theta,\varphi}$$

$$- \frac{e^2}{4\pi\varepsilon_0 r} = E$$

$\exists!\, C$ such that $\underbrace{\hbar^2\left[\qquad\right]}_{L^2} = C\cdot\Theta(\theta)\cdot\Phi(\varphi)$

Test: What happens if $\theta = 90^\circ = \text{const.}$

heuristic

L_z^2

$-\hbar^2[\quad] \rightarrow -\hbar^2 \dfrac{\partial^2 \cancel{\Theta}\,\Phi(\varphi)}{\partial\varphi^2} = A\cdot\cancel{\Theta}\cdot\Phi(\varphi)$ $\qquad \Phi(\varphi) = e^{i\alpha\varphi}$

$\Rightarrow -\hbar^2(-\alpha^2)e^{i\alpha\varphi} = A\cdot e^{i\alpha\varphi} \Rightarrow A = \hbar^2\alpha^2$

$L_z \rightarrow \dfrac{\hbar}{i}\dfrac{\partial}{\partial\varphi}$ $\qquad L_z e^{i\alpha\varphi} = \hbar\alpha\, e^{i\alpha\varphi}$

MUST have $e^{i\alpha\varphi} = e^{i\alpha(\varphi+2\pi)} \Rightarrow e^{i\alpha 2\pi} = 1$

$\Rightarrow \alpha = m,\ m = 0, \pm1, \pm2, \pm3 \ldots$

$\Rightarrow$ E.V. of L_z $\ 0, \pm\hbar, \pm2\hbar \ldots \pm m\cdot\hbar$

$\varphi(x,y,z)$

n, m, k

$\sin\dfrac{n\pi x}{L_x}\ \sin\dfrac{m\pi y}{L_y}\ \sin\dfrac{k\pi z}{L_z}$

$Y_{\ell,m}(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi)$

$\ell = 0, 1, 2 \ldots$

$\vec{L}^2\, Y_{\ell,m}(\theta,\varphi) = \hbar^2 \ell(\ell+1)\, Y_{\ell m}$

$L_z\, Y_{\ell,m}(\theta,\varphi) = \hbar m\, Y_{\ell m}$

$|m| \le \ell$

$e^{i2\pi} = 1 = e^{i0} = e^{-i2\pi} = e^{i17\cdot 2\pi}$

$P_z = \dfrac{\hbar}{i}\dfrac{\partial}{\partial z}$ $\qquad L_z = \dfrac{\hbar}{i}\dfrac{\partial}{\partial\varphi}$

$\vec{L} = \vec{r}\times\vec{p}$