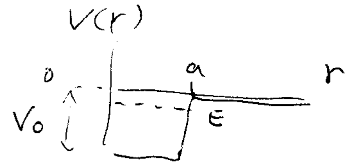
Quantum Mechanics - II. March 1, 2010

- Mid term : 4/19, Final 6/14
- 5/10, 出國
- Today's topics : 3D square well potential; Coulomb potential, Hydrogen atom; O4 symmetry

3D square well potential

$$V(r) = \begin{cases} -V_0 & r<a \\ 0 & r>a \end{cases}$$



define $k_1^2 = \frac{2m(V_0+E)}{\hbar^2}$, $k_2^2 = -\frac{2mE}{\hbar^2}$
(>0) (>0)

The radial WF :

$r<a$ $\quad R'' + \frac{2}{r}R' + \left[k_1^2 - \frac{\ell(\ell+1)}{r^2}\right]R = 0$

$r>a$ $\quad R'' + \frac{2}{r}R' - \left[k_2^2 + \frac{\ell(\ell+1)}{r^2}\right]R = 0$

The solutions to the above Eqs. are spherical Bessel function $j_\ell(kr)$ & linear combinations of $j_\ell(ikr)$ & $n_\ell(ikr)$

We obtained $j_\ell(kr)$ by applying the "creation operator" on $\chi_0(\rho)$

$$j_\ell(\rho) = (-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \left(\frac{\sin\rho}{\rho}\right)$$

$(\because \chi_\ell(\rho) = d_\ell^+ d_{\ell-1}^+ \cdots d_2^+ d_1^+ \chi_0(\rho))$

$(\because -\frac{d^2}{d\rho^2}\chi_0(\rho) = \chi_0(\rho))$, where we have chosen the regular one $\chi_0 = \sin\rho$.

The other independent solution is

$$\underset{\substack{\uparrow \\ \text{by convention}}}{\chi_0' = -\cos\rho}, \quad \& \quad n_\ell(\rho) = (-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \left(-\frac{\cos\rho}{\rho}\right)$$

$$n_0(\rho) = -\frac{\cos\rho}{\rho}$$

$$n_1(\rho) = -\rho\left(\frac{1}{\rho}\frac{d}{d\rho}\right)\left(-\frac{\cos\rho}{\rho}\right) = \frac{d}{d\rho}\left(\frac{\cos\rho}{\rho}\right) = -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho}$$

$$n_2(\rho) = \rho^2\frac{1}{\rho}\frac{d}{d\rho}\left(\frac{1}{\rho}\frac{d}{d\rho}\right)\left(-\frac{\cos\rho}{\rho}\right) = -\rho\frac{d}{d\rho}\left(\frac{1}{\rho}\frac{d}{d\rho}\right)\left(\frac{\cos\rho}{\rho}\right)$$

$$= -\rho\frac{d}{d\rho}\left[\frac{1}{\rho}\left(-\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho}\right)\right] = +\rho\frac{d}{d\rho}\left[+\frac{\cos\rho}{\rho^3} + \frac{\sin\rho}{\rho^2}\right]$$

$$= \rho\left[\frac{-\sin\rho}{\rho^3} - \frac{3\cos\rho}{\rho^4} - \frac{2\sin\rho}{\rho^3} + \frac{\cos\rho}{\rho^2}\right]$$

$$= -\frac{3\cos\rho}{\rho^3} + \frac{\cos\rho}{\rho} - \frac{3\sin\rho}{\rho^2}$$

- - -

The numerical coefficients in the solutions are determined by matching the radial WF & their derivatives at $r=a$.

For $\ell = 0$,

$$\begin{cases} r<a & \chi_i'' + k_1^2\chi_i = 0 \\ r>a & \chi_e'' - k_2^2\chi_e = 0 \end{cases}$$

with B.C.

$\chi(0) = \chi(\infty) = 0$

i: interior e: exterior

also

$$\chi_i'(r=a) = \chi_e'(r=a)$$

$$\chi_i(r=a) = \chi_e(r=a)$$

The solutions are.

$$\begin{cases} r<a & \chi_i = A\sin k_1 r \\ r>a & \chi_e = Be^{-k_2 r} \end{cases} \Rightarrow \tan k_1 a = -\frac{k_1}{k_2}$$

The first bound state appears when

$$k_1 a - \frac{\pi}{2} = 0^+$$

$$\Rightarrow \quad V_0 a^2 > \frac{\pi^2\hbar^2}{8} \quad \text{for a bound state.}$$

B.C. $\chi(0)=0$ makes the lowest solution parity odd in the 1D case.

☆ Hydrogenic atoms. $V = -\frac{Z}{r}$

an electron in the Coulomb field of a nucleus with atomic number Z & mass $M = \infty$.

$$R'' + \frac{2}{r}R' + \frac{2m}{\hbar^2}\left[E + \frac{Z}{r} - \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]R = 0$$

(for simplicity, let's ~~take~~ take $m = \hbar^2 = 1$.)

as $r \to \infty$

$\Rightarrow$ $$R'' + 2ER = 0$$

which has the solutions.

$$R = \exp(\pm\sqrt{-2E}\, r)$$ only (−) is for bound state.

we make the substitution:

$$R = f(r)\exp(-\varepsilon r), \quad \text{where } \varepsilon \equiv \sqrt{-2E} > 0.$$

& f varies very slowly for large r.

then

$$f'' + 2\left(\frac{1}{r} - \varepsilon\right)f' + \left[2\left(\frac{Z-\varepsilon}{r}\right) - \frac{\ell(\ell+1)}{r^2}\right]f = 0$$

We know that $f \sim r^\ell$ for very small r.

Thus we substitute the power series

$$f = r^\ell \sum_{\nu=0}^{\infty} a_\nu r^\nu$$ into the above D.E.

$$= \sum_{\nu=0}^{\infty} a_\nu r^{(\ell+\nu)}$$

$$f' = \sum_{\nu=0}^{\infty} a_\nu(\ell+\nu)\, r^{\ell+\nu-1}$$

$$f'' = \sum_{\nu=0}^{\infty} a_\nu(\ell+\nu)(\ell+\nu-1)\, r^{\ell+\nu-2}$$

$\Rightarrow$

$$\sum_{\nu=0}^{\infty} a_\nu\left\{\left[(\ell+\nu)(\ell+\nu+1) - \ell(\ell+1)\right]r^{\ell+\nu-2} - 2\left[\varepsilon(\ell+\nu+1) - Z\right]r^{\ell+\nu-1}\right\} = 0$$

For arbitrary r it must holds. $\Rightarrow$ for $\nu > 0$

$$\frac{a_\nu}{a_{\nu-1}} = 2\,\frac{\varepsilon(\ell+\nu) - Z}{(\ell+\nu)(\ell+\nu+1) - \ell(\ell+1)}$$

<u>If</u> ν were allowed to be arbitrarily large

$$\Rightarrow \lim_{\nu\to\infty} \quad a_\nu \simeq \frac{2\varepsilon\, a_{\nu-1}}{\ell+\nu+1} \simeq \frac{(2\varepsilon)^2\, a_{\nu-2}}{(\ell+\nu+1)(\ell+\nu)} \cdots$$

$$\simeq c\,\frac{(2\varepsilon)^{\ell+\nu+1}}{(\ell+\nu+1)!}, \quad c: \text{some const.}$$

then this will lead $f \to \sum_{\nu=0}^{\infty} c\,\frac{(2\varepsilon)^{\ell+\nu+1}}{(\ell+\nu+1)!}\, r^{\ell+\nu} \to \exp(2\varepsilon r$

$\Rightarrow \quad R \to \exp(\varepsilon r)$ div at $r\to\infty$.

$\Rightarrow$ Thus the series must teminate at $\nu_{max} \equiv n-\ell-1$ and the final term ~~of~~ the series is:

$$a_{n-\ell-1}\, r^{n-1}, \quad \& \quad a_{n-\ell} = 2\,\frac{\varepsilon(\ell+n-\ell) - Z}{(\ell+n-\ell)(\ell+n-\ell+1) - \ell(\ell+1)}\, a_{n-\ell}$$

Therefore, for a given n,

$$= 2\,\frac{n\varepsilon - Z}{n(n+1) - \ell(\ell+1)}$$

$\ell_{max} = n-1$, & $\varepsilon = \frac{Z}{n}$ (~~denominator = 0~~) numerator $= 0$)

(no div from denorminator)

(principle quantum #)

In other words, $\boxed{E_{n\ell} = -\frac{Z^2}{2n^2}}$ $n = 1, 2, 3 \cdots$

$\to$ the well known Balmer formular

indep of ℓ & m (ℓ_z).

$\because$ The $-\frac{Z}{r}$ is spherical symmetric!

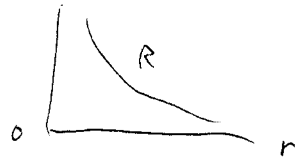
$$\Rightarrow R = -c\,\frac{(2\varepsilon)^{\frac{3}{2}}}{(n+\ell)!^2}\,(2\ell+1)!\,(n-\ell-1)!\; e^{-\frac{\rho}{2}}\,\rho^\ell\, L^{2\ell+1}_{n+\ell}(\rho), \quad c = -\sqrt{\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}$$

where the L^μ_λ are the associated Laguerre polynomials

$$L^\mu_\lambda(\rho) = \frac{d^\mu}{d\rho^\mu}\left[e^\rho \frac{d^\lambda}{d\rho^\lambda}(e^{-\rho}\rho^\lambda)\right] = (-1)^\mu \lambda! \sum_{\alpha=0}^{\lambda-\mu} \binom{\lambda}{\mu+\alpha} \frac{(-\rho)^\alpha}{\alpha!}$$

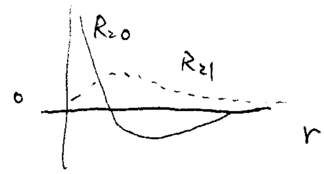
The first few radial functions are: ($R_{n\ell}$)

$$R_{10} = 2 Z^{\frac{3}{2}} e^{-Zr}$$



$$R_{20} = \frac{1}{\sqrt{2}} Z^{\frac{3}{2}} e^{-\frac{Zr}{2}} \left(1 - \frac{Zr}{2}\right)$$

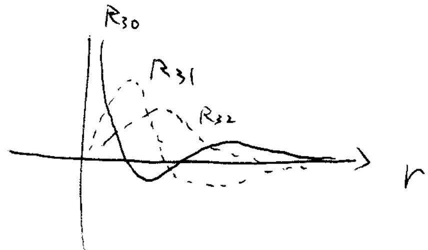
$$R_{21} = \frac{Z^{\frac{5}{2}}}{2\sqrt{6}} r e^{-\frac{Zr}{2}}$$



$$R_{30} = \frac{2}{3\sqrt{3}} Z^{\frac{3}{2}} e^{-\frac{Zr}{3}} \left[1 - \frac{2Zr}{3} + \frac{2Z^2r^2}{27}\right]$$

$$R_{31} = \frac{8}{27\sqrt{6}} Z^{\frac{5}{2}} e^{-\frac{Zr}{3}} r\left[1 - \frac{Zr}{6}\right)$$

$$R_{32} = \frac{4}{81\sqrt{30}} Z^{\frac{7}{2}} r^2 e^{-\frac{Zr}{3}}$$



higher ℓ, less radial nodes

(check Sakurai A.5, A.6 p.453 – 458)

$$\langle r^k \rangle = \frac{\int_0^\infty r^k R_{n\ell}^2(r)\, r^2 dr}{\int_0^\infty R_{n\ell}^2(r)\, r^2 dr}$$

can be obtained by brute force

$$\Rightarrow \quad \langle r \rangle = \frac{1}{2Z}\left[3n^2 - \ell(\ell+1)\right]$$

$$\langle r^2 \rangle = \frac{n^2}{2Z^2}\left[5n^2 + 1 - 3\ell(\ell+1)\right]$$

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

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

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

for $\ell = 0$,

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{2Z^2}{n^3}$$

& $$|\psi(0)|_n^2 = \frac{Z^3}{\pi n^3}$$

★ Another track to solve ~~Hydro~~ Hydrogenic atom problem.

Let $R = \frac{\chi}{r}$

$$-\chi'' + 2\left[-\frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2}\right]\chi = 2E\chi$$

or try

$$\left[+\frac{d}{dr} + \left(a+\frac{b}{r}\right)\right]\left[-\frac{d}{dr} + \left(a+\frac{b}{r}\right)\right]$$

$$= -\frac{d^2}{dr^2} - \frac{b}{r^2} + \left(a+\frac{b}{r}\right)^2 = -\frac{d^2}{dr^2} + \frac{b(b-1)}{r^2} + \frac{2ab}{r} + a^2$$

pick $b = \ell+1$, $a = -\frac{Z}{(\ell+1)}$

$$\Rightarrow \underbrace{\left[\frac{d}{dr} + \left(-\frac{Z}{\ell+1} + \frac{\ell+1}{r}\right)\right]}_{= A^+}\underbrace{\left[-\frac{d}{dr} + \left(\frac{-Z}{\ell+1} + \frac{\ell+1}{r}\right)\right]}_{= A}\chi = \left(2E + \frac{Z^2}{(\ell+1)^2}\right)\chi$$

or $H_- = A^+A$ & $H_-\psi_- = E'_-\psi_-$, H_- : Hermitian

$$\Rightarrow \langle\psi_-|H_-|\psi_-\rangle = |A|\psi_-\rangle|^2 \geq 0$$

The only possible ground state is the solution to:

$$0 = A|\psi_-^0\rangle \quad \text{or} \quad \left[-\frac{d}{dr} + \left(\frac{\ell+1}{r} - \frac{Z}{\ell+1}\right)\right]\psi_-^0 = 0$$

$$(\psi_-^0)' = \left(\frac{\ell+1}{r} - \frac{Z}{\ell+1}\right)\psi_-^0$$

$$\frac{d}{dr}\ln(\psi_-^0) = \frac{\ell+1}{r} - \frac{Z}{\ell+1} = (\ell+1)\frac{d}{dr}\ln r - \frac{Z}{\ell+1}$$

$$\Rightarrow d\ln(\psi_-^0) = (\ell+1)\, d\ln r - \frac{Z}{\ell+1}\,dr$$

$$\Rightarrow \psi_-^0 \propto \exp\left(-\frac{Zr}{\ell+1}\right) r^{\ell+1}$$

Therefore $R_0 \propto r^\ell \exp\left[-\frac{Zr}{\ell+1}\right]$

$$\& \; 0 = E_-'^{(0)} = 2E_-^{(0)} + \frac{Z^2}{(\ell+1)^2} \Rightarrow E_-^{(0)} = \frac{-Z^2}{2(\ell+1)^2}$$

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More interestingly,

we can also ~~see that~~ define a new Hamiltonian $H_+ \equiv AA^+$

then
$$H_+ = \left[-\frac{d}{dr} + \left(\frac{-z}{\ell+1} + \frac{\ell+1}{r}\right)\right]\left[\frac{d}{dr} + \left(\frac{-z}{\ell+1} + \frac{\ell+1}{r}\right)\right]$$
$$= \frac{-d^2}{dr^2} + \frac{(\ell+1)(\ell+2)}{r^2} - \frac{2z}{r} + \frac{z^2}{(\ell+1)^2}$$
$$\left(H_- = \frac{-d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} - \frac{2z}{r} + \frac{z^2}{(\ell+1)^2} \right)$$

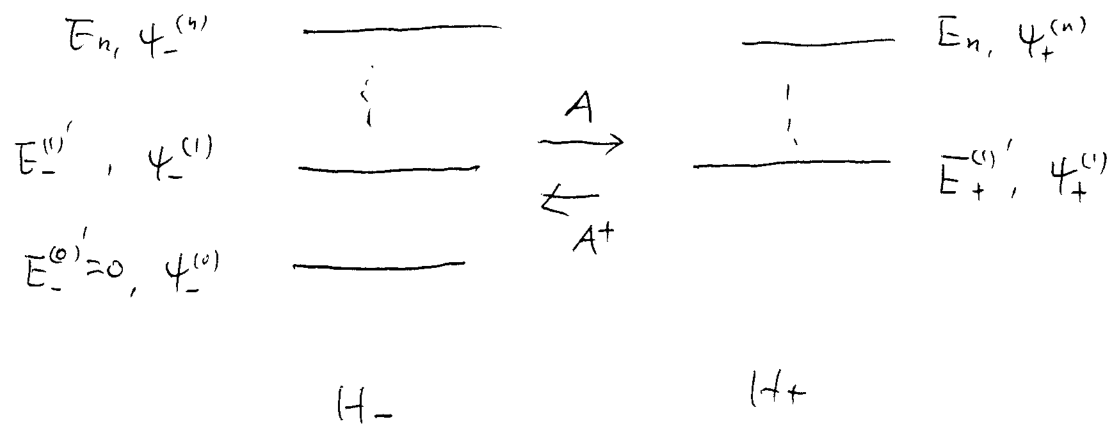
Say, if we already have the solution
$$H_- \psi_-^{(n)} = E_-^{(n)'} \psi_-^{(n)}$$
then
$$A\left(A^+A\,\psi_-^{(n)}\right) = E_-^{(n)'} A\,\psi_-^{(n)} \quad \text{or} \quad H_+\left(A\psi_-^{(n)}\right) = E_-^{(n)'}\left(A\psi_-^{(n)}\right)$$

$\Rightarrow$ H_+ & H_- have degenerate spectrum!

or equivalently $H_+ \psi_+^{(n)} = E_+^{(n)'} \psi_+^{(n)}$

then $A^+(AA^+\psi_+^{(n)}) = E_+^{(n)'} A^+\psi_+^{(n)}$

or $H_-\left(A^+\psi_+^{(n)}\right) = E_+^{(n)'}\left(A^+\psi_+^{(n)}\right)$



☆ Observe that H^+ & H^- have the same form, only difference is $(\ell+1) \rightarrow (\ell+2)$, $H_+^{\ell} = H_-^{\ell+1} + c$

we can also view it a kind of S.H.O Hamiltonian and obtain its ground state energy & solution by requiring
$$\left(\frac{d}{dr} + \frac{-z}{\ell+2} + \frac{\ell+2}{r}\right)\psi_+^{(1)} = 0\,\psi_+^{(1)} \quad \Rightarrow \quad E_+^{(1)} = -\frac{z^2}{2(\ell+2)^2}$$

☆ you can repeat. $\Rightarrow$ $E_n = -\dfrac{z^2}{2n^2}$, $\boxed{n = n_r + \ell + 1}$

$$\Rightarrow \quad \psi_+^{(1)} \propto \exp\left(-\frac{Zr}{\ell+2}\right) r^{\ell+2}$$

and $$\psi_-^{(1)} \propto A_+ \psi_+^{(1)} = \left(\frac{d}{dr} - \frac{Z}{\ell+1} + \frac{\ell+1}{r}\right) r^{\ell+2} \exp\left(-\frac{Zr}{\ell+2}\right)$$

$$= \left[(\ell+2) r^{\ell+1} - \frac{Z}{\ell+2} r^{\ell+2} - \frac{Z}{\ell+1} r^{\ell+2} + (\ell+1) r^{\ell+1}\right] \exp\left(-\frac{Zr}{\ell+2}\right)$$

$$= e^{-\frac{Zr}{\ell+2}} \left[(2\ell+3) r^{\ell+1} - \frac{Z(2\ell+3)}{(\ell+1)(\ell+2)} r^{\ell+2}\right]$$

Therefore $$R_{20} \propto e^{-\frac{Zr}{2}} \left[3 - \frac{3Z}{2} r\right]$$, I will stop here -

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✲ How about the expectation values of $\langle r^n \rangle$?

It's easy to get by using our old friend the Hellmann - Feynman theorem that

$$\frac{\partial E_n}{d\lambda} = \langle \psi_n | \frac{\partial \hat{H}}{\partial \lambda} | \psi_n \rangle$$

$$E_n = -\frac{Z^2}{2(n_r+\ell+1)^2} \qquad \text{principle } n = n_r + \ell + 1$$

& $$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} - \frac{Z}{r}$$

$$\frac{\partial E}{\partial Z} = -\frac{Z}{n^2}, \quad \frac{\partial \hat{H}}{\partial Z} = -\frac{1}{r} \Rightarrow \boxed{\left\langle \frac{1}{r} \right\rangle = \frac{Z}{n^2}}$$

$$\frac{\partial E}{\partial \ell} = \frac{Z^2}{(n_r+\ell+1)^3}, \quad \frac{\partial \hat{H}}{\partial \ell} = \frac{\hbar^2}{2m}\frac{(2\ell+1)}{r^2} \Rightarrow \boxed{\left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{n^3(\ell+\frac{1}{2})}}$$

And again, for any observable.

$$\langle \psi_n | [A, \hat{H}] | \psi_n \rangle = (E_n - E_n) \langle \psi_n | A | \psi_n \rangle = 0$$

$$\left[\frac{d}{dr}, \hat{H}\right] = -\frac{\hbar^2}{2m}\left(\frac{-2}{r^2}\frac{d}{dr}\right) - \frac{2\hbar^2}{2m}\frac{\ell(\ell+1)}{r^3} + \frac{Z}{r^2}$$

so, $$0 = \underbrace{\left\langle \frac{1}{r^2}\frac{d}{dr} \right\rangle}_{\text{must be real too}} \Leftarrow - \ell(\ell+1) \underbrace{\left\langle \frac{1}{r^3} \right\rangle}_{\text{real}} + Z \underbrace{\left\langle \frac{1}{r^2} \right\rangle}_{\text{real}}$$

Since we know that $\langle \frac{1}{r^2}\frac{d}{dr} \rangle$ is real, now

$$\langle \frac{1}{r^2}\frac{d}{dr} \rangle = \int_0^\infty \int d\Omega\, r^2 dr\ \psi^* \frac{1}{r^2}\frac{d}{dr}\psi$$

$$\psi = N\, Y_{\ell m}(\cdots) R_{n\ell}$$

$$= \int_0^\infty dr \int d\Omega\ \psi^* \frac{d}{dr}\psi = \int_0^\infty dr\ R_{n\ell}^* \frac{d}{dr} R_{n\ell}$$

$$= \int_0^\infty dr\ \frac{1}{2}\frac{d}{dr}(R_{n\ell}^* R_{n\ell}) = +\frac{1}{2}\frac{d}{dr}|R_{n\ell}|^2 \Big|_{r=0}^{r=\infty}$$

$$= -\frac{1}{2}|R(0)|^2$$

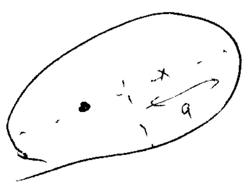
$$\Rightarrow \langle \frac{1}{r^3} \rangle = \frac{1}{\ell(\ell+1)}\left[-\frac{1}{2}|\psi_{n,\ell,m}(0)|^2 + \frac{Z^3}{n^3(\ell+\frac{1}{2})} \right]$$

for $\ell \neq 0$, $|\psi_{n\ell m}(0)|^2 = 0 \Rightarrow \boxed{\langle \frac{1}{r^3} \rangle = \frac{Z^3}{n^3 \ell(\ell+\frac{1}{2})(\ell+1)}}$

$\ell = 0$, div

✻ Accidental degeneracy & O4 symmetry

consider first a classical particle with $m=1$, moving in a closed orbit about a fixed center of force, with potential $V = -\frac{Z}{r}$.



a : semi-major axis

e : eccentricity of the ellipse.

Then the orbital angular momentum is a const vector perpendicular to the orbit plane & of magnitude

$$|\vec{L}| = \sqrt{Za}\sqrt{1-e^2}$$

While the total energy is $E = -\frac{Z}{2a}$ (indep of e!!)

for a given a, many different values of $\vec{L}$ correspond to the same E.

$$(M_0)_i = x_i \dot{x}_j \dot{x}_j - \dot{x}_i x_j \dot{x}_j - Z \frac{x_i}{\sqrt{x_j x_j}}$$

To understand this, define the "Runge-Lenz" vector in CM,

$$\vec{M}_0 = \vec{p} \times \vec{L} - \frac{Z \vec{r}}{r}$$

$\because$ $\vec{L} = \vec{r} \times \vec{p}$ and E.O.M. $\dot{\vec{p}} = \ddot{\vec{r}} = -\frac{Z}{r^3} \vec{r}$

$$\Rightarrow \dot{\vec{M}}_0 = \dot{\vec{p}} \times \vec{L} - \frac{Z \dot{\vec{r}}}{r} + \frac{Z (\vec{r} \cdot \dot{\vec{r}}) \vec{r}}{r^3} = -\frac{Z}{r^3} \vec{r} \times \vec{L} - \frac{Z \dot{\vec{r}}}{r} + \frac{Z (\vec{r} \cdot \dot{\vec{r}}) \vec{r}}{r^3}$$

$$\left(\vec{r} \times \vec{L} = \epsilon_{ijk} r_j \epsilon_{kab} r_a \dot{r}_b = (\delta_{ia}\delta_{jb} - \delta_{ib}\delta_{ja}) r_j r_a \dot{r}_b \Rightarrow \vec{r}(\vec{r} \cdot \dot{\vec{r}}) - r^2 \dot{\vec{r}} \right)$$

$$= 0$$

Thus $\vec{M}_0$ is a <u>conserved vector</u> like $\vec{L}$

but it lies <u>in</u> the plane of the orbit (in fact along the major axis)

$$\Rightarrow \vec{L} \cdot \vec{M}_0 = 0$$

Since $\vec{M}_0$ is a constant vector, we determine its magnitude by the case when r is a maximum (apogee).

$r = a(1+e)$, and $\vec{r} \cdot \vec{p} = 0$

$$\Rightarrow |M_0| = Ze \Leftarrow \text{eccentricity}$$

rescale it $\vec{M} = \sqrt{\frac{a}{Z}}\, \vec{M}_0 = \sqrt{\frac{1}{-2E}}\, \vec{M}_0$

$$\Rightarrow (\vec{L} + \vec{M})^2 = \vec{L}^2 + \vec{M}^2 = Za(1-e^2) + Zae^2 = Za$$

$$\& \quad E = -\frac{Z}{2a} = -\frac{Z^2}{2(\vec{L}+\vec{M})^2} = -\frac{Z^2}{2(\vec{L}^2+\vec{M}^2)}$$

It looks like the Balmer formula, doesn't it?

$$n^2 \Leftrightarrow \vec{L}^2 + \vec{M}^2$$