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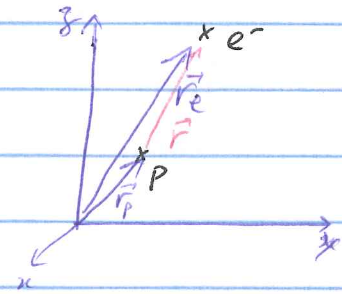
Hydrogen Atom Review



1 – Hamiltonian for a proton + electron

classical Lagrangian:

$$\mathcal{L} = T - V = \frac{1}{2} m_p \dot{\vec{r}}_p^{\,2} + \frac{1}{2} m_e \dot{\vec{r}}_e^{\,2} - V(|\vec{r}_p - \vec{r}_e|)$$

define: center of mass coordinate: $\vec{r}_M = \dfrac{m_p \vec{r}_p + m_e \vec{r}_e}{m_p + m_e}$, $M = m_p + m_e$ = total mass

relative coordinate: $\vec{r}_\mu = \vec{r} = \vec{r}_e - \vec{r}_p$

note: $\vec{r}_e = \vec{r}_M + \dfrac{m_p}{m_e + m_p} \vec{r}$

$$\vec{r}_p = \vec{r}_M - \frac{m_e}{m_e + m_p} \vec{r}$$

The Lagrangian can be rewritten:

$$\mathcal{L} = \frac{1}{2} M \dot{\vec{r}}_M^{\,2} + \frac{1}{2} \mu \dot{\vec{r}}^{\,2} - V(r)$$

where $\mu = \dfrac{m_e m_p}{m_e + m_p}$ = reduced mass $\simeq m_e$

the canonical momenta ~~are~~ are then

$$\vec{p}_M = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_M} = \nabla_{\dot{r}_M} \mathcal{L} = M \dot{\vec{r}}_M$$

= center-of-mass momentum

$$\vec{p} = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}} = \nabla_{\dot{r}} \mathcal{L} = \mu \dot{\vec{r}}$$

= "relative" momentum of proton and e^-

$\simeq$ momentum of e^-

the Hamiltonian is then

$$H = \sum_{i=1}^{3} \left(\dot{r}_i p_i + \dot{r}_{M_i} p_{M_i} \right) - \mathcal{L}$$

$$= \frac{p_M^2}{2M} + \frac{p^2}{2\mu} + V(r) = H_M + H_r$$

neglect

If we consider a hydrogen atom at rest then $\vec{p}_M = 0$ and we consider only the relative ~~coo~~ coordinates $\vec{r}, \vec{p}$.

When we quantize the system : $\left.\begin{array}{l} \vec{r} \longrightarrow \vec{R} \\ \vec{p} \longrightarrow \vec{P} \end{array}\right\}$ operators

with $[R_i, P_j] = i\hbar \delta_{ij}$

the quantum Hamiltonian becomes

$$H = \underbrace{\frac{P_M^2}{2M}}_{H_M} + \underbrace{\frac{P^2}{2\mu} + V(R)}_{H_r} = \frac{P_p^2}{2m_p} + \frac{P_e^2}{2m_e} + V(\vec{R}_e, \vec{R}_p)$$

note: $[H_M, H_r] = 0$

$[H_M, H] = 0$

$[H_r, H] = 0$

we note that if $H_M |\psi_M\rangle = E_M |\psi_M\rangle$

$H_r |\psi_r\rangle = E_r |\psi_r\rangle$

if $|\psi\rangle = |\psi_M\rangle |\psi_r\rangle$

then $H |\psi\rangle = (H_M + H_r) |\psi_M\rangle |\psi_r\rangle$

$= (E_M + E_r) |\psi\rangle$

H_M and H_r operate on different subspaces

2. Hydrogen atom : internal states $\quad V(r) = -\frac{q^2}{4\pi\varepsilon_0} \frac{1}{r} = -\frac{e^2}{r}$

e^2

we want to solve $H_r |\psi_r\rangle = E_r |\psi_r\rangle$ (Schrodinger equation)

classically

$$H_0 \equiv H_r = \frac{\cancel{p}\vec{P}^2}{2\mu} - \frac{e^2}{r} = \frac{1}{2}\mu \vec{v}^2 - \frac{e^2}{r}$$

$$= \frac{1}{2}\mu v_r^2 + \frac{1}{2}\mu v_\perp^2 - \frac{e^2}{r}$$

$$= \frac{1}{2}\mu v_r^2 + \frac{1}{2}\frac{\mu^2 (r v_\perp)^2}{\mu r^2} - \frac{e^2}{r}$$

(L = angular momentum $= \mu \vec{r} \times \vec{v} = \mu r v_\perp$)

$$= \frac{1}{2}\mu v_r^2 + \frac{L^2}{2\mu r^2} - \frac{e^2}{r}$$

$$= \frac{P_{radial}^2}{2\mu} + \frac{L^2}{2\mu r^2} - \frac{e^2}{r}$$

thus H_0 can be rewritten (some algebra)

$$H_0 = \frac{P_{radial}^2}{2\mu} + \frac{L^2}{2\mu R^2} - \frac{e^2}{R}$$

In the ~~(r|~~ $|r\rangle$ representation, ~~———~~ the Schrodinger equation becomes

$$\langle r | H_0 | \psi_r \rangle = \langle r | E_r | \psi_r \rangle$$

drop the "r" subscript

$$\iff \left[-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{2\mu r^2} L^2 - \frac{e^2}{r} \right] \psi(r,\theta,\phi) = E \psi(r,\theta,\phi)$$

with $L^2 = -\hbar^2 \frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan\theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2}$

It turns out ~~clearly~~ $[H, \vec{L}] = 0$ ~~so~~

$[H, L^2] = 0$ so $|\psi\rangle$ is an eigenstate of L^2

$$L^2 |\psi\rangle = l(l+1)\hbar^2 |\psi\rangle$$

since L^2 acts only on the angular parts, we can employ separation of variables

$$\psi(r,\theta,\varphi) = R_l(r) \underbrace{Y_l^m(\theta,\phi)}_{\text{spherical harmonics}}$$

eigenbasis of the L^2 operator and the L_z operator

$[L_z Y_l^m = \hbar m Y_l^m]$

~~$\Rightarrow R$~~

Thus the Schrodinger equation reduces to (Y_l^m's drop out)

$$\left[\frac{-\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \underbrace{\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{e^2}{r}}_{\text{effective potential}} \right] R_l(r) = E_l R_l(r)$$

"m" not necessary since not in Hamiltonian

$$\left[\frac{-\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hbar^2 \, l(l+1)}{2\mu r^2} - \frac{e^2}{r} \right] R_{nl}(r) = E_{nl} R_{nl}(r)$$

upon solving this equation one finds $n = 1, 2, 3 \ldots$

(lengthy solution) $l = 0, 1, \ldots, n-1$

$$n=1, l=0 : R_{10} = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

$$n=2, l=0 ; R_{20} = \frac{2 - r/a_0}{(2a_0)^{3/2}} e^{-r/2a_0}$$

$$n=2, l=1 : R_{21} = \frac{1}{(2a_0)^{3/2}} \frac{r}{\sqrt{3}\, a_0} e^{-r/2a_0}$$

Eigen energies:

$$E_n = \frac{-e^2}{2n^2 a_0}$$

with $a_0 = \frac{\hbar^2}{\mu e^2}$

~~note:~~ $\cancel{\int_0^\infty R_{nl}^* R_n}$ Also:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_1^{\pm 1} = \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi}$$

thus $|\psi\rangle = |n, l, m_l\rangle = R_{nl}(r) \, Y_l^{m_l}(\theta, \phi)$