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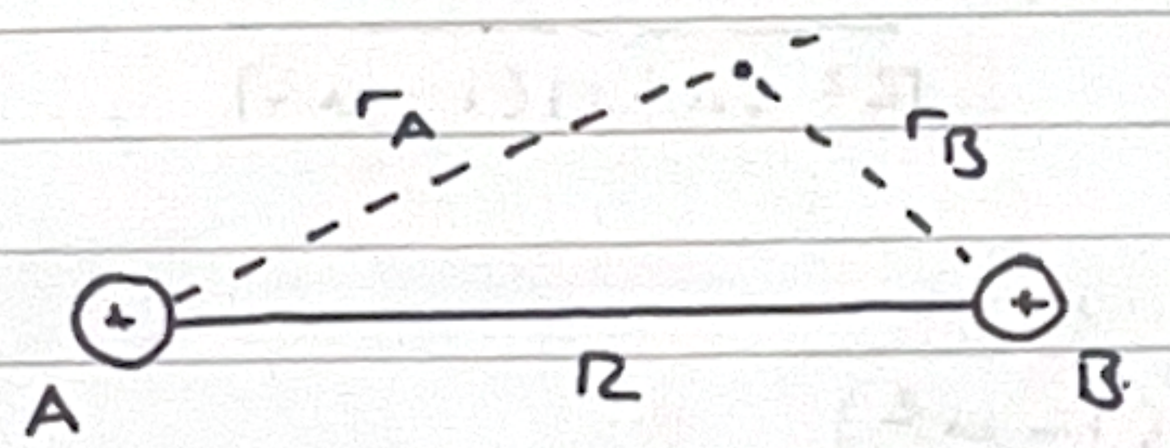
Deriving Diff. Eqns. for ~~Molecule~~ H_2^+.

AMA3020 : Investigations - Pain Project

□ Analogous Equation for new case:



Let A and B be fixed

Previously, potential, $U(\underline{r}) = \frac{+e^2}{r}$

Now, $U(\underline{r}) = \frac{\cancel{+}e^2}{r_A} + \frac{e^2}{r_B}$

$$\Rightarrow \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} \right] \psi(\underline{r}) = E\psi(\underline{r})$$

□ Show differential equation seperates when prolate spheroidal coordinates are used.

$$\lambda \equiv \frac{(r_A + r_B)}{R} \qquad \mu \equiv \frac{(r_A - r_B)}{R}$$

$\phi \leftarrow$ rotation angle about AB

From the Handbook of Mathematical functions:

Let $R = |AB|$

Fix A and B along the x-axis

$$x = \frac{R}{2}\lambda\mu \; ; \; y = \frac{R}{2}\sqrt{(\lambda^2 - 1)(1-\mu^2)}\cos\phi$$

$$z = \frac{R}{2}\sqrt{(\lambda^2-1)(1-\mu^2)}\sin\phi$$

$$\nabla^2 = \frac{1}{h_\lambda h_\mu h_\phi}\left[\frac{\partial}{\partial\lambda}\left(\frac{h_\mu h_\phi}{h_\lambda}\frac{\partial}{\partial\lambda}\right) + \frac{\partial}{\partial\mu}\left(\frac{h_\lambda h_\phi}{h_\mu}\frac{\partial}{\partial\mu}\right) + \frac{\partial}{\partial\phi}\left(\frac{h_\lambda h_\mu}{h_\phi}\frac{\partial}{\partial\phi}\right)\right]$$

$$h_\lambda = \frac{R}{2}\sqrt{\frac{\lambda^2-\mu^2}{\lambda^2-1}} \; ; \; h_\mu = \frac{R}{2}\sqrt{\frac{\lambda^2-\mu^2}{1-\mu^2}} \; ; \; h_\phi = \frac{R}{2}\sqrt{(\lambda^2-1)(1-\mu^2)}$$

We can use these known expressions to express the Laplacian fully

$$h_\lambda h_\mu h_\phi = \frac{R^3}{8}(\lambda^2-\mu^2)$$

$$\Rightarrow \frac{h_\lambda h_\mu}{h_\phi} = \frac{R^3}{8}(\lambda^2-\mu^2) \cdot \frac{4}{R^2(\lambda^2-1)(1-\mu^2)}$$

$$= \frac{R}{2}\frac{(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)}$$

$$\Rightarrow \frac{h_\mu h_\phi}{h_\lambda} = \frac{R^3}{8}(\lambda^2-\mu^2) \cdot \frac{4(\lambda^2-1)}{R^2(\lambda^2-\mu^2)}$$

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

$$\Rightarrow \frac{h_\lambda h_\phi}{h_\mu} = \frac{R^3}{8}(\lambda^2-\mu^2) \cdot \frac{4}{R^2}\frac{(1-\mu^2)}{(\lambda^2-\mu^2)}$$

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

$$\nabla^2 = \frac{8}{R^3(\lambda^2-\mu^2)}\left[\frac{\partial}{\partial\lambda}\left(\frac{R(\lambda^2-1)}{2}\frac{\partial}{\partial\lambda}\right) + \frac{\partial}{\partial\mu}\left(\frac{R(1-\mu^2)}{2}\frac{\partial}{\partial\mu}\right) + \frac{\partial}{\partial\phi}\left(\frac{R}{2}\frac{(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)}\frac{\partial}{\partial\phi}\right)\right]$$

$$\nabla^2 = \frac{4}{R^2(\lambda^2-\mu^2)}\left[\frac{\partial}{\partial\lambda}\left((\lambda^2-1)\frac{\partial}{\partial\lambda}\right) + \frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial}{\partial\mu}\right) + \frac{(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)}\frac{\partial^2}{\partial\phi^2}\right]$$

We can also transform $U(r) = e^2\left(\frac{1}{r_A} + \frac{1}{r_B}\right)$

$\lambda R = r_A + r_B \qquad \mu R = r_A - r_B$

$\Rightarrow 2r_A = \mu R + \lambda R \qquad 2r_B = \lambda R - \mu R$

$r_A = \frac{R}{2}(\lambda+\mu) \qquad r_B = \frac{R}{2}(\lambda-\mu)$

$$\frac{1}{r_A} + \frac{1}{r_B} = \frac{r_A + r_B}{r_A r_B}$$

$$= \frac{R}{2}\left[\frac{(\lambda+\mu) + (\lambda-\mu)}{\frac{R^2}{4}(\lambda+\mu)(\lambda-\mu)}\right]$$

$$= \frac{2}{R}\left[\frac{2\lambda}{\lambda^2 - \mu^2}\right]$$

$$= \frac{4\lambda}{R(\lambda^2-\mu^2)}$$

Combine and write a Schrödinger equation in prolate spheroidal co-ordinates for this system as :

$$\left[-\frac{\hbar^2}{2m}\cdot\frac{4}{R^2(\lambda^2-\mu^2)}\left[\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial}{\partial\lambda} + \frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial}{\partial\mu}\right) + \frac{(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)}\frac{\partial^2}{\partial\phi^2}\right] - \frac{4\lambda e^2}{R(\lambda^2-\mu^2)}\right]\psi(\lambda,\mu,\phi) = E\psi(\lambda,\mu,\phi)$$

This is consistent with the expression from the Handbook of Mathematical Functions

~~Divide through by 4~~

~~Multiply by $R(\lambda^2-\mu^2)$~~

$$-\frac{2\hbar^2}{mR^2(\lambda^2-\mu^2)}\left[\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial}{\partial\lambda} + \frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial}{\partial\mu}\right) + \frac{(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)}\frac{\partial^2}{\partial\phi^2}\right]\psi(\lambda,\mu,\phi)$$

$$-\left[E + \frac{4\lambda e^2}{R(\lambda^2-\mu^2)}\right]\psi(\lambda,\mu,\phi) = 0$$

Multiply by $(\lambda^2-1)(1-\mu^2)$

$$- \frac{2\hbar^2(\lambda^2-1)(1-\mu^2)}{MR^2(\lambda^2-\mu^2)}\left(\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial\psi(\lambda,\mu,\phi)}{\partial\lambda}\right)$$

$$- \frac{2\hbar^2(\lambda^2-1)(1-\mu^2)}{MR^2(\lambda^2-\mu^2)}\left(\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial\psi(\lambda,\mu,\phi)}{\partial\mu}\right)$$

$$- \frac{2\hbar^2}{MR^2}\frac{\partial^2\psi(\lambda,\mu,\phi)}{\partial\phi^2}$$

$$- (\lambda^2-1)(1-\mu^2)\left[E + \frac{4\lambda e^2}{R(\lambda^2-\mu^2)}\right]\psi(\lambda,\mu,\phi) = 0$$

Let $\psi(\lambda,\mu,\phi) = \Lambda(\lambda)M(\mu)\Phi(\phi)$ and divide through by $\psi(\lambda,\mu,\phi)$. Multiply by -1. Multiply by $\frac{MR^2}{2\hbar^2}$.

$$\frac{1}{\Lambda(\lambda)}\frac{(\lambda^2-1)(1-\mu^2)}{(\lambda^2-\mu^2)}\left(\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial\Lambda(\lambda)}{\partial\lambda}\right)$$

$$+ \frac{1}{M(\mu)}\frac{(\lambda^2-1)(1-\mu^2)}{(\lambda^2-\mu^2)}\left(\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial M(\mu)}{\partial\mu}\right)$$

$$\boxed{+ \frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}}$$

$$+ \frac{MR^2(\lambda^2-1)(1-\mu^2)}{2\hbar^2}\left[E + \frac{4\lambda e^2}{R(\lambda^2-\mu^2)}\right] = 0$$

This is separable.

The $\boxed{\;}$ only depends on ϕ. Bring to other side. Both sides of equation are independent, so can be let equal to a constant, α.

$$\alpha = -\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2} \Rightarrow \boxed{\frac{\partial^2\Phi(\phi)}{\partial\phi^2} + \alpha\Phi(\phi) = 0}$$

$$\alpha = \frac{1}{\Lambda(\lambda)}\frac{(\lambda^2-1)(1-\mu^2)}{\lambda^2-\mu^2}\left(\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial\Lambda}{\partial\lambda}\right)$$

$$+ \frac{1}{M(\mu)}\frac{(\lambda^2-1)(1-\mu^2)}{(\lambda^2-\mu^2)}\left(\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial M}{\partial\mu}\right)$$

$$+ \frac{MR^2}{2\hbar^2}(\lambda^2-1)(1-\mu^2)\left[E + \frac{4\lambda e^2}{R(\lambda^2-\mu^2)}\right]$$

We want to separate the λ and μ terms.

Multiply by $\dfrac{\lambda^2 - \mu^2}{(\lambda^2 - 1)(1-\mu^2)}$:

$$\frac{1}{\Lambda(\lambda)}\left(\frac{\partial}{\partial\lambda}(\lambda^2 - 1)\frac{\partial\Lambda}{\partial\lambda}\right) + \frac{1}{M(\mu)}\left(\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial M}{\partial\mu}\right)$$

$$+ \frac{mR^2}{2\hbar^2}(\lambda^2-\mu^2)\left[E + \frac{4\lambda e^2}{R(\lambda^2-\mu^2)}\right] - \frac{\alpha(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)} = 0$$

- $$\frac{mR^2}{2\hbar^2}(\lambda^2-\mu^2)\left[E + \frac{4\lambda e^2}{R(\lambda^2-\mu^2)}\right]$$

$$= \frac{mR^2(\lambda^2-\mu^2)E}{2\hbar^2} + \frac{2\lambda mRe^2}{\hbar^2}$$

$$= \underbrace{\frac{EmR^2}{2\hbar^2}\lambda^2 + \frac{2mRe^2}{\hbar^2}\lambda}_{\lambda \text{ terms}} \underbrace{- \frac{EmR^2\mu}{2\hbar^2}}_{\mu \text{ term}}$$

- $$-\frac{\alpha(\lambda^2-\mu^2)}{(\lambda^2-1)(1-\mu^2)} = -\left(\underbrace{\frac{\alpha}{\lambda^2-1}}_{\lambda \text{ term}} + \underbrace{\frac{\alpha}{1-\mu^2}}_{\mu \text{ term}}\right)$$

Hence, the equation is separable.
Let $-\beta$ be a separation constant.

$$\frac{1}{\Lambda(\lambda)}\left(\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial\Lambda}{\partial\lambda}\right) + \frac{EmR^2}{2\hbar^2}\lambda^2 + \frac{2mRe^2}{\hbar^2}\lambda - \frac{\alpha}{\lambda^2-1}$$

$$= -\frac{1}{M(\mu)}\left(\frac{\partial}{\partial\mu}(1-\mu^2)\frac{\partial M}{\partial\mu}\right) + \frac{EmR^2}{2\hbar^2}\mu^2 + \frac{\alpha}{1-\mu^2} = -\beta$$

First, consider the $\Lambda(\lambda)$ equation:

$$\frac{\partial}{\partial\lambda}\left((\lambda^2-1)\frac{\partial\Lambda}{\partial\lambda}\right) + \left[\beta + \frac{EmR^2}{2\hbar^2}\lambda^2 + \frac{2mRe^2}{\hbar^2}\lambda - \frac{\alpha}{\lambda^2-1}\right]\Lambda = 0$$

And the $M(\mu)$ equation:

$$\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial M}{\partial\mu}\right)+\left[-\frac{Em R^2}{2\hbar^2}\mu^2 - \frac{\alpha}{1-\mu^2} - \beta\right]M = 0$$

Let $p^2 = -\frac{m}{2\hbar^2}ER^2$; $q = \frac{me^2}{\hbar^2}$

Hence, $\Lambda(\lambda)$ and $M(\mu)$ satisfy:

$$\frac{\partial}{\partial\lambda}\left((\lambda^2-1)\frac{\partial\Lambda}{\partial\lambda}\right)+\left[\beta - p^2\lambda^2 + 2qR\lambda - \frac{\alpha}{\lambda^2-1}\right]\Lambda = 0$$

$$\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial M}{\partial\mu}\right)+\left[p^2\mu^2 - \frac{\alpha}{1-\mu^2} - \beta\right]M = 0$$

And we also have $\Phi(\phi)$ satisfying:

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