# The hydrogen atom

I. Solving the hydrogen atom problem
II. Informal solution for the relative motion



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# Multiple Particle Systems

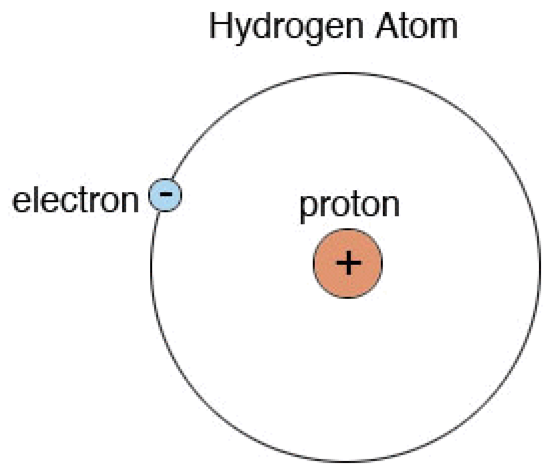
## Schrödinger's equation

$$\hat{H}\psi = E\psi$$

State of the entire system

Hamiltoninan operator for the entire system

Total energy of the entire system




- ✓ Electron coordinates: $x_e$, $y_e$, $z_e$
- ✓ Proton coordinates: $x_p$, $y_p$ , $z_p$

} 6 coordinates for the entire system

$$\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 + V\left(\left|\mathbf{r}_e - \mathbf{r}_p\right|\right)\right]\psi\left(x_e, y_e, z_e, x_p, y_p, z_p\right)$$

$$= E\psi\left(x_e, y_e, z_e, x_p, y_p, z_p\right)$$

$$V\left(\left|\mathbf{r}_e - \mathbf{r}_p\right|\right) = -\frac{e^2}{4\pi\varepsilon_o\left|\mathbf{r}_e - \mathbf{r}_p\right|}$$

# Simplification of Coordinates

## 1. Relative positions coordinates

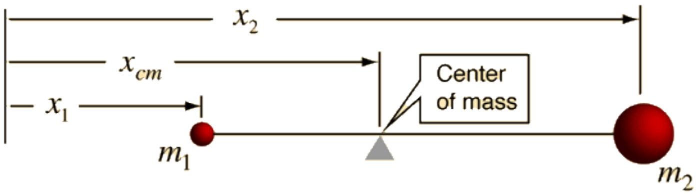
$$x = x_e - x_p \qquad y = y_e - y_p \qquad z = z_e - z_p$$

Relative vector: $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$

$$r = \sqrt{x^2 + y^2 + z^2} = \left|\mathbf{r}_e - \mathbf{r}_p\right|$$

## 2. Center of mass coordinates

$$\mathbf{R} = \frac{m_e\mathbf{r}_e + m_p\mathbf{r}_p}{M} \qquad M = m_e + m_p$$




$$= X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k}$$

$$X = \frac{m_e x_e + m_p x_p}{M}$$

Similar way to Y and Z



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# Second Derivatives Of Coordinates

Schrödinger's equation

$$\left[-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{\hbar^2}{2m_p}\nabla_p^2+V\left(\left|\mathbf{r}_e-\mathbf{r}_p\right|\right)\right]\psi\left(x_e,y_e,z_e,x_p,y_p,z_p\right)$$

Should be substituted!

$$=E\psi\left(x_e,y_e,z_e,x_p,y_p,z_p\right)$$

$$\left.\frac{\partial^2}{\partial x_e^2}\right|_{x_p}=\left.\frac{\partial}{\partial x_e}\right|_{x_p}\left(\left.\frac{\partial}{\partial x_e}\right|_{x_p}\right)=\frac{m_e}{M}\left.\frac{\partial}{\partial x_e}\right|_{x_p}\left.\frac{\partial}{\partial X}\right|_{x}+\left.\frac{\partial}{\partial x_e}\right|_{x_p}\left.\frac{\partial}{\partial x}\right|_{X}$$

$$=\left(\frac{m_e}{M}\right)^2\left.\frac{\partial^2}{\partial X^2}\right|_{x}+\left.\frac{\partial^2}{\partial x^2}\right|_{X}+\frac{m_e}{M}\left(\left.\frac{\partial}{\partial x}\right|_{X}\left.\frac{\partial}{\partial X}\right|_{x}+\left.\frac{\partial}{\partial X}\right|_{x}\left.\frac{\partial}{\partial x}\right|_{X}\right)$$

Similarly,

$$\left.\frac{\partial^2}{\partial x_p^2}\right|_{x_e}=\left(\frac{m_p}{M}\right)^2\left.\frac{\partial^2}{\partial X^2}\right|_{x}+\left.\frac{\partial^2}{\partial x^2}\right|_{X}-\frac{m_p}{M}\left(\left.\frac{\partial}{\partial x}\right|_{X}\left.\frac{\partial}{\partial X}\right|_{x}+\left.\frac{\partial}{\partial X}\right|_{x}\left.\frac{\partial}{\partial x}\right|_{X}\right)$$

# Hamiltonian Operator With New Coordinates

$$\frac{1}{m_e}\frac{\partial^2}{\partial x_e^2}+\frac{1}{m_p}\frac{\partial^2}{\partial x_p^2}=\frac{m_e+m_h}{M^2}\frac{\partial^2}{\partial X^2}+\left(\frac{1}{m_e}+\frac{1}{m_p}\right)\frac{\partial^2}{\partial x^2}$$

$$=\frac{1}{M}\frac{\partial^2}{\partial X^2}+\frac{1}{\mu}\frac{\partial^2}{\partial x^2}$$

$$\mu=\frac{m_e m_p}{m_e+m_p}$$

Reduced mass

$$\hat{H}=-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2+V(\mathbf{r})$$

$$\nabla_{\mathbf{R}}^2\equiv\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}$$

$$\nabla_{\mathbf{r}}^2\equiv\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

# Solving Schrödinger's Equation

Wave equation can be written as $\psi(\mathbf{R},\mathbf{r}) = S(\mathbf{R})U(\mathbf{r})$

Schrödinger's equation

$$-U(\mathbf{r})\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) + S(\mathbf{R})\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = ES(\mathbf{R})U(\mathbf{r})$$

$$-\frac{1}{S(\mathbf{R})}\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E - \frac{1}{U(\mathbf{r})}\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = \underline{E_{CoM}}$$

Constant

# Solution For Two Particles

$$-\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 S(\mathbf{R}) = E_{CoM} S(\mathbf{R})$$

Center of mass motion

Similar to single particle $S(\mathbf{R}) = \exp(i\mathbf{K}\cdot\mathbf{R})$ $E_{CoM} = \frac{\hbar^2 K^2}{2M}$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{r}}^2 + V(\mathbf{r})\right]U(\mathbf{r}) = E_H U(\mathbf{r})$$

Relative motion

$$E_H = E - E_{CoM}$$

Corresponds to
the “internal” relative motion of the electron and proton


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# Rough Energy Calculation of Relative Motion

## Potential energy

$$\langle E_{potential} \rangle \approx -\frac{e^2}{4\pi\varepsilon_o a_o}$$

$a_0$: Bohr radius

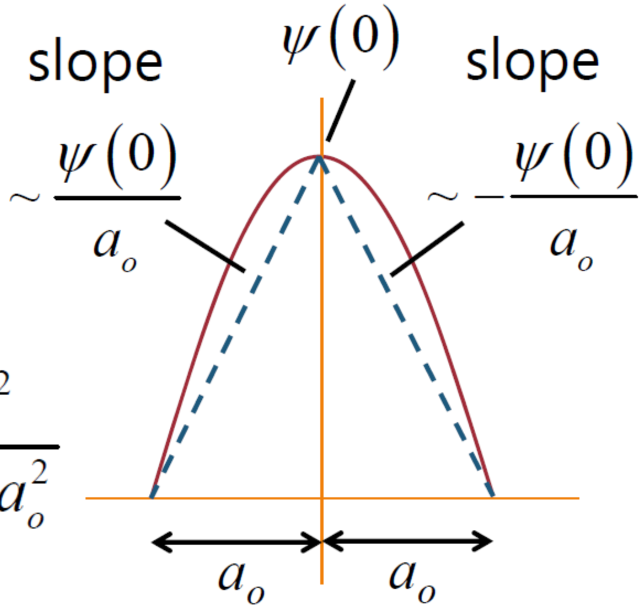
## Kinetic energy

Kinetic energy operator: $-\left(\hbar^2 / 2\mu\right)\nabla^2$

$$\nabla^2 \sim \frac{\left[-\psi(0)/a_o\right]-\left[\psi(0)/a_o\right]}{2a_o}$$

$$\sim -\psi(0)/a_o^2$$

$$\langle E_{kinetic} \rangle \approx \frac{\hbar^2}{2\mu a_o^2}$$




## Total energy

$$\langle E_{total} \rangle = \langle E_{kinetic} \rangle + \langle E_{potential} \rangle \approx \frac{\hbar^2}{2\mu a_o^2} - \frac{e^2}{4\pi\varepsilon_o a_o}$$

# Bohr Radius and Rydberg Energy

$$\langle E_{total} \rangle = \langle E_{kinetic} \rangle + \langle E_{potential} \rangle \approx \frac{\hbar^2}{2\mu a_o^2} - \frac{e^2}{4\pi\varepsilon_o a_o}$$

Minimization of energy with $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2\mu} \sim 0.529\text{Å}$

Minimized energy $\langle E_{total} \rangle = -\frac{\hbar^2}{2\mu a_o^2} = -\frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_o\hbar}\right)^2 \sim -13.6eV$

Rydberg Energy