Quantum Mechanics

The Hydrogen Like Atom

A two body system | Change of variables

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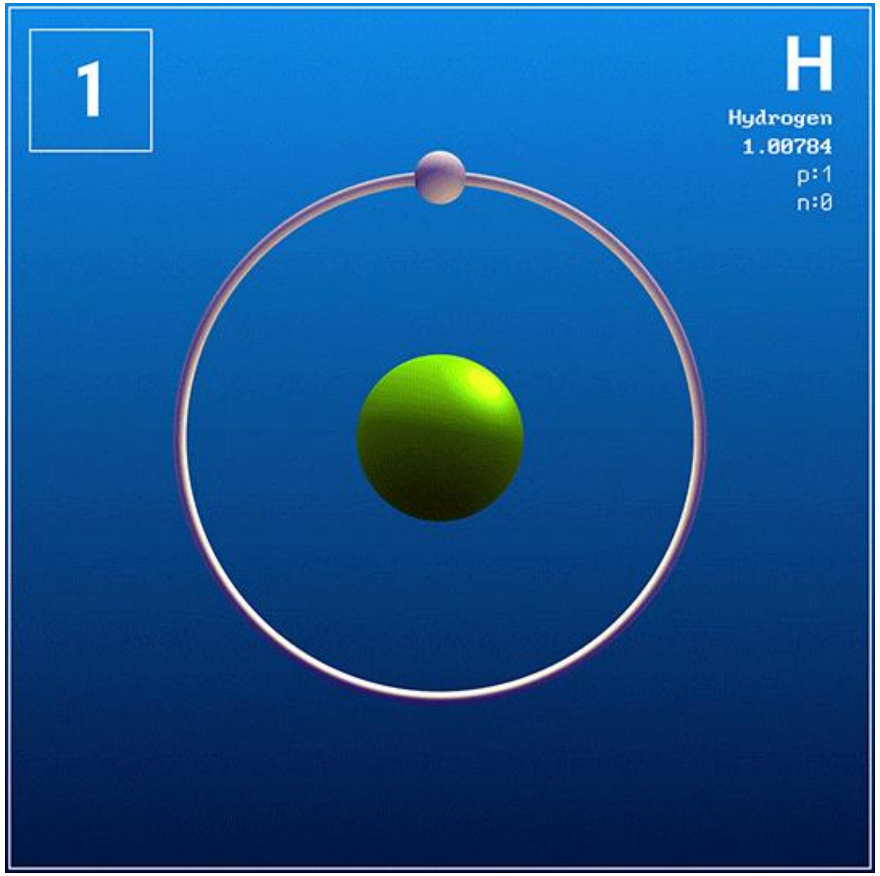
Hydrogen atom



Wikipedia

Particle	Position	Momentum
Electron	$\mathbf{r}_1$	$\mathbf{p}_1$
Proton	$\mathbf{r}_2$	$\mathbf{p}_2$

$$[(\hat{\mathbf{r}}_1)_i,\ (\hat{\mathbf{p}}_1)_j] = i\hbar\delta_{ij}$$
$$[(\hat{\mathbf{r}}_2)_i,\ (\hat{\mathbf{p}}_2)_j] = i\hbar\delta_{ij}$$

The Hydrogenic Atom

A hydrogen atom or a hydrogen like atom (He^+, Li^{2+}, Be^{+3}, etc.) consists of an atomic nucleus of charge Ze and an electron of charge $-e$. Their mutual interaction is given by the Coulomb potential

$$V(|\mathbf{r}_1 - \mathbf{r}_2|) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

where $\mathbf{r}_1 = \mathbf{r}_1(x_1, y_1, z_1)$ and $\mathbf{r}_2 = \mathbf{r}_2(x_2, y_2, z_2)$ are the electron and nucleus position vectors, respectively.

The Schrödinger equation

The time-independent Schrödinger equation for the system is given by

$$\left\{-\frac{\hbar^2}{2m_1}\nabla_1^2-\frac{\hbar^2}{2m_2}\nabla_2^2+V(|\mathbf{r}_1-\mathbf{r}_2|)\right\}\Psi(\mathbf{r}_1,\mathbf{r}_2)=E_{\text{tot}}\Psi(\mathbf{r}_1,\mathbf{r}_2),$$

where m_1 and m_2 are the masses of electron and nucleus.

$$\nabla_i^2=\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}; \qquad i=1,2$$

Wave function

Particle	Position	Momentum
Electron	$\mathbf{r}_1$	$\mathbf{p}_1$
Proton	$\mathbf{r}_2$	$\mathbf{p}_2$

$$\text{Wave function: } \Psi(\mathbf{r}_1,\, \mathbf{r}_2)$$

$$\text{Normalization: } \int \Psi^*(\mathbf{r}_1,\, \mathbf{r}_2)\Psi(\mathbf{r}_1,\, \mathbf{r}_2)\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 = 1$$

Separation of the Center of Mass Motion

The transformation from coordinates ($\mathbf{r}_1$, $\mathbf{r}_2$) to coordinates ($\mathbf{R}$, $\mathbf{r}$) is given by introducing the relative coordinate

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

and the vector

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$$

which determines the position of the centre of mass system.

Change of variables

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R}, \mathbf{r})$$

$$\frac{\partial \Psi}{\partial x_1} = \frac{\partial X}{\partial x_1} \cdot \frac{\partial \Psi}{\partial X} + \frac{\partial x}{\partial x_1} \cdot \frac{\partial \Psi}{\partial x} = \frac{\mu}{m_2} \frac{\partial \Psi}{\partial X} + \frac{\partial \Psi}{\partial x}$$

where μ is the reduced mass defined as

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1 m_2}.$$

Change of variables in 3D

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R}, \mathbf{r})$$

$$\boxed{\nabla_1 = \frac{\mu}{m_2}\nabla_R + \nabla} \qquad \boxed{\nabla_2 = \frac{\mu}{m_1}\nabla_R - \nabla}$$

The kinetic energy operators

$$\frac{\hbar^2}{2m_1}\nabla_1^2 + \frac{\hbar^2}{2m_2}\nabla_2^2 = \frac{\hbar^2}{2M}\nabla_R^2 + \frac{\hbar^2}{2\mu}\nabla^2$$

where $M = m_1 + m_2$ is the total mass of the system.

The Schrödinger equation in new variables

Since $\mathbf{R}$ and $\mathbf{r}$ are independent to each other the wave function $\Psi(\mathbf{R}, \mathbf{r})$ can be separated into a product of functions of the centre of mass coordinate $\mathbf{R}$ and of relative coordinate $\mathbf{r}$ as $\Psi(\mathbf{R}, \mathbf{r}) = \Phi(\mathbf{R})\psi(\mathbf{r})$. With this the Schrödinger equation can be written as

$$\left\{-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right\}\Phi(\mathbf{R})\psi(\mathbf{r}) = E_{\text{tot}}\Phi(\mathbf{R})\psi(\mathbf{r})$$

Momentum operators corresponding to **r** and **R**

$$\nabla_1 = \frac{\mu}{m_2}\nabla_R + \nabla$$

$$\nabla_2 = \frac{\mu}{m_1}\nabla_R - \nabla$$

$$\hat{\mathbf{p}} = -i\hbar\nabla$$

$$\hat{\mathbf{p}}_1 = \frac{\mu}{m2}\hat{\mathbf{P}} + \hat{\mathbf{p}}$$

$$\hat{\mathbf{p}}_2 = \frac{\mu}{m1}\hat{\mathbf{P}} - \hat{\mathbf{p}}$$

Momentum operators corresponding to **r** and **R**

$$\hat{\mathbf{p}}_1 = \frac{\mu}{m2}\hat{\mathbf{P}} + \hat{\mathbf{p}}$$

$$\hat{\mathbf{p}}_2 = \frac{\mu}{m1}\hat{\mathbf{P}} - \hat{\mathbf{p}}$$

$$\mathbf{p} = \mu\left(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2}\right) = \frac{m_2}{M}\mathbf{p}_1 - \frac{m_1}{M}\mathbf{p}_2,$$

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2.$$

Canonical variables

$$[(\hat{\mathbf{r}}_1)_i,\ (\hat{\mathbf{p}}_1)_j] = i\hbar\delta_{ij}$$
$$[(\hat{\mathbf{r}}_2)_i,\ (\hat{\mathbf{p}}_2)_j] = i\hbar\delta_{ij}$$

$$[\hat{\mathbf{r}}_i,\ \hat{\mathbf{p}}_j] = i\hbar\delta_{ij},$$
$$\left[\hat{\mathbf{R}}_i,\ \hat{\mathbf{P}}_j\right] = i\hbar\delta_{ij}.$$

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$
$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}$$

$$\mathbf{p} = \mu\left(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2}\right)$$
$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2.$$

Change of variables in 3D

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R}, \mathbf{r})$$

$$\nabla_1 = \frac{\mu}{m_2}\nabla_R + \nabla$$

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The kinetic energy operators

$$\frac{\hbar^2}{2m_1}\nabla_1^2 + \frac{\hbar^2}{2m_2}\nabla_2^2 = \frac{\hbar^2}{2M}\nabla_R^2 + \frac{\hbar^2}{2\mu}\nabla^2$$

where $M = m_1 + m_2$ is the total mass of the system.

The Schrödinger equation in new variables

$$\left\{-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right\}\Phi(\mathbf{R})\psi(\mathbf{r}) = E_{\text{tot}}\Phi(\mathbf{R})\psi(\mathbf{r})$$

$$\Psi(\mathbf{R}, \mathbf{r}) = \Phi(\mathbf{R})\psi(\mathbf{r}).$$

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}.$$

Thank you for watching

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