

Because the hydrogen atom is a two-particle atom, we previously considered Schrödinger as a single-particle equation for the electron only.

I try to consider the system as two particles and write the Schrödinger in two particle form.

We define the center of mass coordinate \mathbf{R} and the relative coordinate \mathbf{r} as:

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

Expression for \mathbf{r}_1

$$\begin{aligned} (m_1 + m_2)\mathbf{R} &= m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2 \\ &= m_1 \mathbf{r}_1 + m_2 (\mathbf{r}_1 - \mathbf{r}) \\ &= (m_1 + m_2)\mathbf{r}_1 - m_2 \mathbf{r} \end{aligned}$$

Solving for \mathbf{r}_1 :

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

Expression for \mathbf{r}_2

$$\begin{aligned} (m_1 + m_2)\mathbf{R} &= m_1 (\mathbf{r}_2 + \mathbf{r}) + m_2 \mathbf{r}_2 \\ &= (m_1 + m_2)\mathbf{r}_2 + m_1 \mathbf{r} \end{aligned}$$

Solving for \mathbf{r}_2 :

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

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

Then we can also write:

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

In fact, the big \mathbf{R} has been replaced with the big \mathbf{X} and the small \mathbf{R} with the small \mathbf{x} . Note that we did not mean one dimension, just notation. Otherwise, \mathbf{R} is one of the three components X , Y and Z , and we wrote one component for notation.

Let $\mathbf{R} = (X, Y, Z)$, $\mathbf{r} = (x, y, z)$.

Gradient with respect to \mathbf{r}_1

$$(\nabla_1)_x = \frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1} \frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1} \frac{\partial}{\partial x} = \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial X} + \frac{\partial}{\partial x}$$

So the full

$$\nabla_1 = \frac{m_1}{m_1 + m_2} \nabla_R + \nabla_r = \frac{\mu}{m_2} \nabla_R + \nabla_r$$

Gradient with respect to \mathbf{r}_2

$$(\nabla_2)_x = \frac{\partial}{\partial x_2} = \frac{\partial X}{\partial x_2} \frac{\partial}{\partial X} + \frac{\partial x}{\partial x_2} \frac{\partial}{\partial x} = \frac{m_2}{m_1 + m_2} \frac{\partial}{\partial X} - \frac{\partial}{\partial x}$$

So the full gradient:

$$\nabla_2 = \frac{m_2}{m_1 + m_2} \nabla_R - \nabla_r = \frac{\mu}{m_1} \nabla_R - \nabla_r$$

$$\begin{aligned}\nabla_1 &= \frac{\mu}{m_2} \nabla_R + \nabla_r \\ \nabla_2 &= \frac{\mu}{m_1} \nabla_R - \nabla_r\end{aligned}$$

These relations are useful when expressing kinetic energy operators or Laplacians in center-of-mass and relative coordinates. article amsmath

We calculate:

$$\nabla_1^2 \psi = \nabla_1 \cdot (\nabla_1 \psi) = \nabla_1 \cdot \left(\frac{\mu}{m_2} \nabla_R \psi + \nabla_r \psi \right)$$

Applying the divergence operator:

$$= \frac{\mu}{m_2} \nabla_R \cdot \left(\frac{\mu}{m_2} \nabla_R \psi + \nabla_r \psi \right) + \nabla_r \cdot \left(\frac{\mu}{m_2} \nabla_R \psi + \nabla_r \psi \right)$$

Expanding:

$$= \left(\frac{\mu}{m_2} \right)^2 \nabla_R^2 \psi + 2 \frac{\mu}{m_2} (\nabla_r \cdot \nabla_R) \psi + \nabla_r^2 \psi$$

article amsmath

The two-particle Hamiltonian acting on the wavefunction ψ is:

$$H\psi = -\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V(\mathbf{r}_1, \mathbf{r}_2) \psi$$

Using the transformations of $\nabla_1^2 \psi$ and $\nabla_2^2 \psi$:

$$H\psi = -\frac{\hbar^2}{2m_1} \left[\left(\frac{\mu}{m_2} \right)^2 \nabla_R^2 \psi + 2 \frac{\mu}{m_2} (\nabla_r \cdot \nabla_R) \psi + \nabla_r^2 \psi \right] \\ - \frac{\hbar^2}{2m_2} \left[\left(\frac{\mu}{m_1} \right)^2 \nabla_R^2 \psi - 2 \frac{\mu}{m_1} (\nabla_r \cdot \nabla_R) \psi + \nabla_r^2 \psi \right] + V(\mathbf{r})\psi$$

Grouping terms gives:

$$H\psi = -\frac{\hbar^2}{2} \left[\left(\frac{\mu^2}{m_1 m_2^2} + \frac{\mu^2}{m_2 m_1^2} \right) \nabla_R^2 \psi \right. \\ \left. + \left(2 \frac{\mu}{m_1 m_2} - 2 \frac{\mu}{m_1 m_2} \right) (\nabla_r \cdot \nabla_R) \psi \right. \\ \left. + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \nabla_r^2 \psi \right] + V(\mathbf{r})\psi$$

Since the cross terms cancel:

$$2 \frac{\mu}{m_1 m_2} - 2 \frac{\mu}{m_1 m_2} = 0,$$

and using:

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

and

$$\frac{\mu^2}{m_1 m_2^2} + \frac{\mu^2}{m_2 m_1^2} = \frac{\mu^2(m_1 + m_2)}{m_1^2 m_2^2} = \frac{\mu}{m_1 m_2},$$

we get

$$H\psi = -\frac{\hbar^2}{2(m_1 + m_2)} \nabla_R^2 \psi - \frac{\hbar^2}{2\mu} \nabla_r^2 \psi + V(\mathbf{r})\psi = E\psi.$$

—

Separation of variables:

Assume

$$\psi(\mathbf{R}, \mathbf{r}) = \psi_R(\mathbf{R})\psi_r(\mathbf{r}),$$

and divide the Schrödinger equation by $\psi_R\psi_r$:

$$-\frac{\hbar^2}{2(m_1 + m_2)} \frac{1}{\psi_R} \nabla_R^2 \psi_R - \frac{\hbar^2}{2\mu} \frac{1}{\psi_r} \nabla_r^2 \psi_r + V(\mathbf{r}) = E.$$

—