SCHRÖDINGER EQUATION FOR 2 PARTICLES - SEPARATION OF VARIABLES

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The Schrödinger equation that we’ve looked at so far involves the wave function for a single particle moving in a potential. To extend this to multi-particle systems, we need to make the wave function and the potential functions of the positions of all the particles and the time. Thus the Schrödinger equation for a system of \( n \) particles becomes

\[
\begin{align*}
-\frac{\hbar^2}{2} & \sum_{i=1}^{n} \frac{1}{m_i} \nabla_i^2 \Psi (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, t) + \\
V (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, t) \Psi (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, t) &= i\hbar \frac{\partial}{\partial t} \Psi (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, t)
\end{align*}
\]

(1)

Needless to say, finding solutions of this equation for even as few as 2 particles is extremely difficult. In one case, however, we can make some progress. In a 2-particle system, if the potential \( V \) is not time-dependent and depends only on the separation \( \mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2 \) of the two particles, we can fiddle with it a bit and produce a simpler form.

First, we define the centre of mass

\[
\mathbf{R} \equiv \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}
\]

(3)

If we also introduce the reduced mass

\[
\mu \equiv \frac{m_1 m_2}{m_1 + m_2}
\]

(4)

then we get

\[
\begin{align*}
\mathbf{r}_1 &= \mathbf{R} + \frac{\mu}{m_1} \mathbf{r} \\
\mathbf{r}_2 &= \mathbf{R} - \frac{\mu}{m_2} \mathbf{r}
\end{align*}
\]

(5)

(6)
In the coordinates $r$ and $R$, we can find the gradient operators. We use a dummy function $f$ to give the gradient something to operate on. We’ll consider the $x$ component and use the chain rule (remember that $r_1$ and $r_2$ are independent vectors, each with 3 components, so there is a total of 6 independent position variables):

$$\frac{\partial f}{\partial r_{1x}} = \frac{\partial f}{\partial r_x} \frac{\partial r_x}{\partial r_{1x}} + \frac{\partial f}{\partial R_x} \frac{\partial R_x}{\partial r_{1x}}$$

(7)

$$= \frac{\partial f}{\partial r_x} (1) + \frac{\partial f}{\partial R_x} \frac{m_1}{m_1 + m_2}$$

(8)

$$= \frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x} \frac{\mu}{m_2}$$

(9)

$$\frac{\partial f}{\partial r_{2x}} = \frac{\partial f}{\partial r_x} (-1) + \frac{\partial f}{\partial R_x} \frac{m_2}{m_1 + m_2}$$

(10)

$$= - \frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x} \frac{\mu}{m_1}$$

(11)

The relations for the other two components are similar, so dropping the test function $f$, we get for the gradients:

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

(12)

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

(13)

To get the Laplacian operators, we differentiate the $x$ component expressions above.

$$\frac{\partial^2 f}{\partial r_{1x}^2} = \left( \frac{\partial}{\partial r_x} + \frac{\mu}{m_2} \frac{\partial}{\partial R_x} \right) \left( \frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x} \frac{\mu}{m_2} \right)$$

(14)

$$= \frac{\partial^2 f}{\partial r_x^2} + \frac{\partial f}{\partial r_x} \frac{2m_1}{m_1 + m_2} + \frac{\partial^2 f}{\partial R_x^2} \left( \frac{\mu}{m_2} \right)^2$$

(15)

$$\frac{\partial^2 f}{\partial r_{2x}^2} = \frac{\partial^2 f}{\partial r_x^2} - \frac{\partial f}{\partial r_x} \frac{2m_2}{m_1 + m_2} + \frac{\partial^2 f}{\partial R_x^2} \left( \frac{\mu}{m_1} \right)^2$$

(16)

The combination of these two expressions that appears in the Schrödinger equation is, after cancelling terms and putting the remaining terms over common denominators:
The Schrödinger equation for 2 particles in the separation of variables form is:

\[ -\frac{\hbar^2}{2m_1} \frac{\partial^2 f}{\partial r_{1x}^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2 f}{\partial r_{2x}^2} = -\frac{\hbar^2}{2(m_1 + m_2)} \frac{\partial^2 f}{\partial R_x^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2 f}{\partial r_x^2} \]  

(17)

The calculations for the other two components are similar, so the final result is:

\[ -\frac{\hbar^2}{2(m_1 + m_2)} \nabla_R^2 \psi - \frac{\hbar^2}{2\mu} \nabla_r^2 \psi + V(r) \psi = E\psi \]  

(18)

We can now try the usual technique of separation of variables, so we try

\[ \psi = A(r) B(R) \]  

(19)

We get, after substituting and dividing through by \(AB\):

\[ -\frac{\hbar^2}{2(m_1 + m_2)B} \nabla_R^2 B - \frac{\hbar^2}{2\mu A} \nabla_r^2 A + V(r) = E \]  

(20)

As usual, the terms involving each of the variables \(r\) and \(R\) must separately be equal to constants, so we get

\[ -\frac{\hbar^2}{2(m_1 + m_2)} \nabla_R^2 B = E_R B \]  

(21)

\[ -\frac{\hbar^2}{2\mu} \nabla_r^2 A + AV(r) = E_r A \]  

(22)

The first equation is that of a free particle with mass \(m_1 + m_2\), while the second is that of a particle with mass \(\mu\) moving in a potential \(V\). Thus the system separates into one equation for a free particle with the total mass and a position at the centre of mass and another for a single particle with the reduced mass \(\mu\). The total energy is \(E = E_R + E_r\).

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