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

\[
-\frac{\hbar^2}{2} \sum_{i=1}^{n} \frac{1}{m_i} \nabla_i^2 \Psi(r_1, r_2, \ldots, r_n, t) + V(r_1, r_2, \ldots, r_n, t) \Psi(r_1, r_2, \ldots, r_n, t) = i\hbar \frac{\partial}{\partial t} \Psi(r_1, r_2, \ldots, r_n, t) \tag{2}
\]

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 \( r \equiv r_1 - r_2 \) of the two particles, we can fiddle with it a bit and produce a simpler form.

First, we define the centre of mass

\[
R \equiv \frac{m_1 r_1 + m_2 r_2}{m_1 + m_2} \tag{3}
\]

If we also introduce the reduced mass

\[
\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \tag{4}
\]

then we get

\[
r_1 = R + \frac{\mu}{m_1} r \tag{5}
\]
\[
r_2 = R - \frac{\mu}{m_2} r \tag{6}
\]

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 $\mathbf{r}_1$ and $\mathbf{r}_2$ are independent vectors, each with 3 components, so there is a total of 6 independent position variables):

\[
\frac{\partial f}{\partial r_{1x}} = \frac{\partial f}{\partial r_{x}} \frac{\partial r_{x}}{\partial r_{1x}} + \frac{\partial f}{\partial R_{x}} \frac{\partial R_{x}}{\partial r_{1x}} (7)
\]

\[
= \frac{\partial f}{\partial r_{x}} (1) + \frac{\partial f}{\partial R_{x}} m_1 \frac{\partial r_{1x}}{m_1 + m_2} \tag{8}
\]

\[
= \frac{\partial f}{\partial r_{x}} + \frac{\partial f}{\partial R_{x}} \frac{\mu}{m_1 + m_2} \tag{9}
\]

\[
\frac{\partial f}{\partial r_{2x}} = \frac{\partial f}{\partial r_{x}} (-1) + \frac{\partial f}{\partial R_{x}} m_2 \frac{\partial r_{2x}}{m_1 + m_2} \tag{10}
\]

\[
= - \frac{\partial f}{\partial r_{x}} + \frac{\partial f}{\partial R_{x}} \frac{\mu}{m_1} \tag{11}
\]

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

\[
\nabla_1 = \nabla_r + \frac{\mu}{m_2} \nabla_R \tag{12}
\]

\[
\nabla_2 = -\nabla_r + \frac{\mu}{m_1} \nabla_R \tag{13}
\]

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

\[
\frac{\partial^2 f}{\partial r_{1x}^2} = \left( \frac{\partial}{\partial r_{x}} + \frac{\mu}{m_2} \frac{\partial}{\partial R_{x}} \right) \left( \frac{\partial f}{\partial r_{x}} + \frac{\partial f}{\partial R_{x}} \frac{\mu}{m_2} \right) \tag{14}
\]

\[
= \frac{\partial^2 f}{\partial r_{x}^2} + \frac{\partial f}{\partial r_{x}} \frac{2m_1}{m_1 + m_2} + \frac{\partial^2 f}{\partial R_{x}^2} \left( \frac{\mu}{m_2} \right)^2 \tag{15}
\]

\[
\frac{\partial^2 f}{\partial r_{2x}^2} = - \frac{\partial^2 f}{\partial r_{x}^2} + \frac{\partial f}{\partial r_{x}} \frac{2m_2}{m_1 + m_2} + \frac{\partial^2 f}{\partial R_{x}^2} \left( \frac{\mu}{m_1} \right)^2 \tag{16}
\]

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

\[
- \frac{\hbar^2}{2m_1} \frac{\partial^2 f}{\partial r_{1x}^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2 f}{\partial r_{2x}^2} = - \frac{\hbar^2}{2(m_1 + m_2)} \frac{\partial^2 f}{\partial R_{x}^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2 f}{\partial r_{x}^2} \tag{17}
\]
The calculations for the other two components are similar, so the final result is:

$$-\frac{\hbar^2}{2(m_1 + m_2)} \nabla_R^2 \psi - \frac{\hbar^2}{2\mu} \nabla_r^2 \psi + V(r) \psi = E\psi \quad (18)$$

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

$$\psi = A(r) B(R) \quad (19)$$

We get, after substituting and dividing through by $AB$:

$$-\frac{\hbar^2}{2(m_1 + m_2)B} \nabla_R^2 B - \frac{\hbar^2}{2\mu A} \nabla_r^2 A + V(r) = E \quad (20)$$

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

$$-\frac{\hbar^2}{2(m_1 + m_2)} \nabla_R^2 B = E_R B \quad (21)$$

$$-\frac{\hbar^2}{2\mu} \nabla_r^2 A + AV(r) = E_r A \quad (22)$$

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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