

SCHRÖDINGER EQUATION FOR 2 PARTICLES - SEPARATION OF VARIABLES

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.1.

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

$$-\frac{\hbar^2}{2} \sum_{i=1}^n \frac{1}{m_i} \nabla_i^2 \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, t) + \quad (1)$$

$$V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, t) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, t) \quad (2)$$

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 $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$ of the two particles, we can fiddle with it a bit and produce a simpler form.

First, we define the centre of mass

$$\mathbf{R} \equiv \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2} \quad (3)$$

If we also introduce the reduced mass

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \quad (4)$$

then we get

$$\mathbf{r}_1 = \mathbf{R} + \frac{\mu}{m_1} \mathbf{r} \quad (5)$$

$$\mathbf{r}_2 = \mathbf{R} - \frac{\mu}{m_2} \mathbf{r} \quad (6)$$

In the coordinates \mathbf{r} and \mathbf{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):

$$\frac{\partial f}{\partial r_{1x}} = \frac{\partial f}{\partial r_x} \frac{\partial r_x}{\partial r_{1x}} + \frac{\partial f}{\partial R_x} \frac{\partial R_x}{\partial r_{1x}} \quad (7)$$

$$= \frac{\partial f}{\partial r_x} (1) + \frac{\partial f}{\partial R_x} \frac{m_1}{m_1 + m_2} \quad (8)$$

$$= \frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x} \frac{\mu}{m_2} \quad (9)$$

$$\frac{\partial f}{\partial r_{2x}} = \frac{\partial f}{\partial r_x} (-1) + \frac{\partial f}{\partial R_x} \frac{m_2}{m_1 + m_2} \quad (10)$$

$$= -\frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x} \frac{\mu}{m_1} \quad (11)$$

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

$$\nabla_1 = \nabla_r + \frac{\mu}{m_2} \nabla_R \quad (12)$$

$$\nabla_2 = -\nabla_r + \frac{\mu}{m_1} \nabla_R \quad (13)$$

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

$$\frac{\partial^2 f}{\partial r_{1x}^2} = \left(\frac{\partial}{\partial r_x} + \frac{\mu}{m_2} \frac{\partial}{\partial R_x} \right) \left(\frac{\partial f}{\partial r_x} + \frac{\partial f}{\partial R_x} \frac{\mu}{m_2} \right) \quad (14)$$

$$= \frac{\partial^2 f}{\partial r_x^2} + \frac{\partial f}{\partial r_x} \frac{\partial}{\partial R_x} \frac{2m_1}{m_1 + m_2} + \frac{\partial^2 f}{\partial R_x^2} \left(\frac{\mu}{m_2} \right)^2 \quad (15)$$

$$\frac{\partial^2 f}{\partial r_{2x}^2} = \frac{\partial^2 f}{\partial r_x^2} - \frac{\partial f}{\partial r_x} \frac{\partial}{\partial R_x} \frac{2m_2}{m_1 + m_2} + \frac{\partial^2 f}{\partial R_x^2} \left(\frac{\mu}{m_1} \right)^2 \quad (16)$$

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

$$-\frac{\hbar^2}{2m_1} \frac{\partial^2 f}{\partial r_{1x}^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2 f}{\partial r_{2x}^2} = -\frac{\hbar^2}{2(m_1 + m_2)} \frac{\partial^2 f}{\partial R_x^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2 f}{\partial r_x^2} \quad (17)$$

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

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

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 :

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

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

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

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

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 μ 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 μ . The total energy is $E = E_R + E_r$.

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