A DEEPER LOOK 3 Separation of variables

A number of physical systems can be regarded intuitively as combinations of motion of different kinds, such as motion through space and an internal motion. These intuitive notions can be justified mathematically and typically result in the separate, but sometimes linked, equations for each type of motion.

(a) Particle on a sphere

This section shows how to separate the Schrödinger equation for a particle able to move on the surface of a sphere into separate equations for the azimuth ϕ and the colatitude θ.

The Schrödinger equation for the motion of a particle of mass m on the surface of a sphere is

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

The laplacian is

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\Lambda^2 \tag{1a}$$

and the legendrian is

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

Because r is constant, the part of the laplacian that involves differentiation with respect to r can be discarded, and the equation then becomes

$$-\frac{\hbar^2}{2mr^2}\Lambda^2\psi = E\psi \tag{1b}$$

In terms of the moment of inertia, $I = mr^2$, this expression becomes

$$\Lambda^2\psi = -\varepsilon\psi \qquad \varepsilon = \frac{2IE}{\hbar^2} \tag{1c}$$

Step 1 *Insert the factorized possible solution*

Insert $\psi = \Theta\Phi$ and obtain

$$\Lambda^2\Theta\Phi = \frac{1}{\sin^2\theta}\frac{\partial^2(\Theta\Phi)}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial(\Theta\Phi)}{\partial\theta} = -\varepsilon\Theta\Phi$$

Now use the fact that Θ and Φ are each functions of one variable, so the partial derivatives become complete derivatives:

$$\frac{\Theta}{\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\Phi}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} = -\varepsilon\Theta\Phi$$

Division through by $\Theta\Phi$ and multiplication by $\sin^2\theta$ gives

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} = -\varepsilon\sin^2\theta$$

and, after minor rearrangement,

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} + \varepsilon\sin^2\theta = 0 \tag{2}$$

Step 2 *Verify that the expression is separable*

The first term on the left depends only on ϕ and the remaining two terms depend only on θ. Each term is therefore equal to a constant. Thus, if the first term is set equal to the constant $-m_l^2$, the separated equations are

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m_l^2 \qquad \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} + \varepsilon\sin^2\theta = m_l^2$$

(b) Hydrogenic atoms

The goal of this calculation is to show that the full Schrödinger equation for a hydrogenic atom separates into two equations, one for the motion of the atom as a whole through space and the other for the motion of the electron relative to the nucleus.

Step 1 *Separate the internal motion from the external motion*

Consider a one-dimensional system (which is easily generalized to three dimensions) in which the potential energy depends only on the separation of the two particles. The total energy is

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(x_1 - x_2) \tag{3}$$

where $p_1 = m_1(\mathrm{d}x_1/\mathrm{d}t)$ and $p_2 = m_2(\mathrm{d}x_2/\mathrm{d}t)$. The centre of mass (Fig. 1) is located at

$$X = \frac{m_1}{m}x_1 + \frac{m_2}{m}x_2 \qquad m = m_1 + m_2 \tag{4a}$$

and the separation of the particles is $x = x_1 - x_2$. It follows that

$$x_1 = X + \frac{m_2}{m}x \qquad x_2 = X - \frac{m_1}{m}x \tag{4b}$$

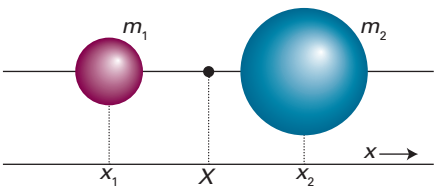

Figure 1 The coordinates used for discussing the separation of the relative motion of two particles from the motion of their centre of mass (the black dot).

The linear momenta of the particles can now be expressed in terms of the rates of change of x and X:

$$p_1 = m_1\frac{dx_1}{dt} = m_1\frac{dX}{dt} + \frac{m_1m_2}{m}\frac{dx}{dt}$$
$$p_2 = m_2\frac{dx_2}{dt} = m_2\frac{dX}{dt} - \frac{m_1m_2}{m}\frac{dx}{dt} \quad (5)$$

Then, with

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}, \text{ or } \mu = \frac{m_1m_2}{m_1+m_2} = \frac{m_1m_2}{m} \quad (6)$$

it follows that

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \tfrac{1}{2}m\left(\frac{dX}{dt}\right)^2 + \tfrac{1}{2}\mu\left(\frac{dx}{dt}\right)^2 \quad (7)$$

By writing $P = m(dX/dt)$ for the linear momentum of the system as a whole and $p = \mu(dx/dt)$, it follows that

$$E = \frac{P^2}{2m} + \frac{p^2}{2\mu} + V(x) \quad (8a)$$

The corresponding hamiltonian (generalized to three dimensions) is therefore

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2_{\text{c.m.}} - \frac{\hbar^2}{2\mu}\nabla^2 + V(r) \quad (8b)$$

where the first term differentiates with respect to the centre of mass coordinates and the second with respect to the relative coordinates.

Now write the overall wavefunction as the product $\psi_{\text{total}}(X,x) = \psi_{\text{c.m.}}(X)\psi(x)$, where the first factor is a function of only the centre of mass coordinates and the second is a function of only the relative coordinates. The overall Schrödinger equation, $\hat{H}\psi_{\text{total}} = E_{\text{total}}\psi_{\text{total}}$, then separates, with $E_{\text{total}} = E_{\text{c.m.}} + E$.

Step 2 *Write the Schrödinger equation associated with internal motion*

The Schrödinger equation for the internal motion of a hydrogenic atom is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right)\psi + V\psi = E\psi \quad (9a)$$

Attempt a solution of the form $\psi = RY$, where R depends only on the radius and Y depends only on the angular coordinates. Then

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right)RY + VRY = ERY \quad (9b)$$

and therefore

$$-\frac{\hbar^2}{2\mu}\left(Y\frac{d^2R}{dr^2} + \frac{2Y}{r}\frac{dR}{dr} + \frac{R}{r^2}\Lambda^2Y\right) + VRY = ERY \quad (9c)$$

where the partial derivatives with respect to r have been replaced by complete derivatives because R depends only on r. Multiply through by r^2/RY and obtain

$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{d^2R}{dr^2} + 2r\frac{dR}{dr}\right) + Vr^2 - \frac{\hbar^2}{2\mu Y}\Lambda^2Y = Er^2 \quad (9d)$$

The functions Y satisfy the equation

$$\Lambda^2Y = -l(l+1)Y \quad (10)$$

so eqn 9d becomes

Independent of θ, ϕ because the Ys cancel

$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{d^2R}{dr^2} + 2r\frac{dR}{dr}\right) + Vr^2 + \overbrace{\frac{\hbar^2l(l+1)}{2\mu Y}Y} = Er^2 \quad (9e)$$

Step 3 *Write an expression for the radial contribution*

Continuing the argument from step 2, rewrite eqn 9e by dividing both sides by r^2 and multiplying by R. The result is

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + VR + \frac{\hbar^2l(l+1)}{2\mu r^2}R = ER \quad (11a)$$

Because for a hydrogenic atom $V = -Ze^2/4\pi\varepsilon_0 r$, write

$$V_{\text{eff}} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad (11b)$$

and the equation becomes

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + V_{\text{eff}}R = ER \quad (12)$$

This expression, the **radial wave equation**, has the form of a Schrödinger equation. It describes the motion of a particle of mass μ in the region $0 \le r < \infty$ where the potential energy is V_{eff}. Solving this equation gives the radial wavefunctions R.

(c) Harmonic oscillator

The goal of this calculation is to show that the full Schrödinger equation for the vibration of a diatomic molecule (with a harmonic potential) separates into two equations, one for the motion of the molecule through space and the other for the relative motion of the atoms.

Step 1 *Write the Schrödinger equation for the molecule*

The total energy of a two atoms of masses m_1 and m_2 free to move in one dimension and subject to a potential energy that depends on their separation is

$$E_{\text{total}} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(x_1 - x_2) \quad (13)$$

As in Part (b), the linear momenta of the particles are expressed in terms of the rates of change of the separation x and the location of the centre of mass X:

$$p_1 = m_1\frac{\mathrm{d}x_1}{\mathrm{d}t} = m_1\frac{\mathrm{d}X}{\mathrm{d}t} + \frac{m_1m_2}{m}\frac{\mathrm{d}x}{\mathrm{d}t}$$
$$p_2 = m_2\frac{\mathrm{d}x_2}{\mathrm{d}t} = m_2\frac{\mathrm{d}X}{\mathrm{d}t} - \frac{m_1m_2}{m}\frac{\mathrm{d}x}{\mathrm{d}t} \qquad (14)$$

Then, with

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}, \text{ or } \mu = \frac{m_1m_2}{m_1+m_2} = \frac{m_1m_2}{m} \qquad (15)$$

it follows that

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \tfrac{1}{2}m\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)^2 + \tfrac{1}{2}\mu\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 \qquad (16)$$

By writing $P = m(\mathrm{d}X/\mathrm{d}t)$ for the linear momentum of the molecule as a whole and $p = \mu(\mathrm{d}x/\mathrm{d}t)$, the total energy becomes

$$E_{\text{total}} = \frac{P^2}{2m} + \frac{p^2}{2\mu} + V(x) \qquad (17a)$$

For a harmonic oscillator

$$V(x) = \tfrac{1}{2}k_{\text{f}}x^2 \qquad (17b)$$

At this stage, therefore, the hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \tfrac{1}{2}k_{\text{f}}x^2 \qquad (18a)$$

and the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_{\text{total}}(X,x)}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2\psi_{\text{total}}(X,x)}{\partial x^2} + \tfrac{1}{2}k_{\text{f}}x^2\psi_{\text{total}}(X,x) = E_{\text{total}}\psi_{\text{total}}(X,x) \qquad (18b)$$

Step 2 *Show that the equation separates*

Write the overall wavefunction as the product $\psi_{\text{total}}(X,x) = \psi_{\text{c.m.}}(X)\psi(x)$, where $\psi_{\text{c.m.}}(X)$ is a function of only the centre of mass coordinate and $\psi(x)$ is a function of only the separation of the atoms. The overall Schrödinger equation then becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_{\text{c.m.}}(X)\psi(x)}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2\psi_{\text{c.m.}}(X)\psi(x)}{\partial x^2} + \tfrac{1}{2}k_{\text{f}}x^2\psi_{\text{c.m.}}(X)\psi(x) = E_{\text{total}}\psi_{\text{c.m.}}(X)\psi(x) \qquad (19a)$$

and therefore

$$-\frac{\hbar^2}{2m}\psi(x)\frac{\mathrm{d}^2\psi_{\text{c.m.}}(X)}{\mathrm{d}X^2} - \frac{\hbar^2}{2\mu}\psi_{\text{c.m.}}(X)\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \tfrac{1}{2}k_{\text{f}}x^2\psi_{\text{c.m.}}(X)\psi(x) = E_{\text{total}}\psi_{\text{c.m.}}(X)\psi(x) \qquad (19b)$$

After division by $\psi_{\text{total}}(X,x) = \psi_{\text{c.m.}}(X)\psi(x)$, this equation becomes

$$\overbrace{-\frac{\hbar^2}{2m\psi_{\text{c.m.}}(X)}\frac{\mathrm{d}^2\psi_{\text{c.m.}}(X)}{\mathrm{d}X^2}}^{\text{Depends on } X} \overbrace{-\frac{\hbar^2}{2\mu\psi(x)}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \tfrac{1}{2}k_{\text{f}}x^2}^{\text{Depends on } x} = E_{\text{total}} \qquad (19c)$$

Therefore, by the usual separation of variables argument, each term under the braces is equal to a constant, and their sum, $E_{\text{c.m.}} + E$, is the total energy E_{total}. The contribution that depends only on the separation x, after minor rearrangement, is

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \tfrac{1}{2}k_{\text{f}}x^2\psi(x) = E\psi(x) \qquad (20)$$

which is the equation for a particle of effective mass μ in a parabolic potential energy. The separation is independent of whether the potential energy is parabolic: the argument depends only on whether the potential energy depends on the separation of the two atoms; it therefore also applies to anharmonic oscillation.