Problem 5.1

A typical interaction potential depends only on the vector displacement $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$ between the two particles: $V(\mathbf{r}_1, \mathbf{r}_2) \to V(\mathbf{r})$. In that case the Schrödinger equation separates, if we change variables from $\mathbf{r}_1$, $\mathbf{r}_2$ to $\mathbf{r}$ and $\mathbf{R} \equiv (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$ (the center of mass).

(a) Show that $\mathbf{r}_1 = \mathbf{R} + (\mu/m_1)\mathbf{r}$, $\mathbf{r}_2 = \mathbf{R} - (\mu/m_2)\mathbf{r}$, and $\nabla_1 = (\mu/m_2)\nabla_R + \nabla_r$, $\nabla_2 = (\mu/m_1)\nabla_R - \nabla_r$, where

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \tag{5.15}$$

is the **reduced mass** of the system.

(b) Show that the (time-independent) Schrödinger equation (5.7) becomes

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

(c) Separate variables, letting $\psi(\mathbf{R}, \mathbf{r}) = \psi_R(\mathbf{R})\psi_r(\mathbf{r})$. Note that ψ_R satisfies the one-particle Schrödinger equation, with the *total* mass $(m_1 + m_2)$ in place of m, potential zero, and energy E_R, while ψ_r satisfies the one-particle Schrödinger equation with the *reduced* mass in place of m, potential $V(\mathbf{r})$, and energy E_r. The total energy is the sum: $E = E_R + E_r$. What this tells us is that the center of mass moves like a free particle, and the *relative* motion (that is, the motion of particle 2 with respect to particle 1) is the same as if we had a *single* particle with the *reduced* mass, subject to the potential V. Exactly the same decomposition occurs in *classical* mechanics;[2] it reduces the two-body problem to an equivalent one-body problem.

[TYPO: ψ_R and ψ_r satisfy the one-particle time-independent Schrödinger equation (Equation 4.8 on page 132).]

Solution

Part (a)

The two equations for $\mathbf{r}$ and $\mathbf{R}$,

$$\begin{cases} \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \\ \mathbf{R} = \dfrac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \end{cases},$$

form a system for two unknowns, $\mathbf{r}_1$ and $\mathbf{r}_2$, which can be determined by substitution. Solve the first equation for $\mathbf{r}_1$,

$$\mathbf{r}_1 = \mathbf{r} + \mathbf{r}_2,$$

and plug it into the second equation.

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

[2]See, for example, Jerry B. Marion and Stephen T. Thornton, *Classical Dynamics of Particles and Systems*, 4th edn, Saunders, Fort Worth, TX (1995), Section 8.2.

Split up the fraction and introduce the reduced mass μ.

$$\begin{aligned}
\mathbf{R} &= \left(\frac{m_1}{m_1+m_2}\right)\mathbf{r} + \mathbf{r}_2 \\
&= \frac{1}{m_2}\left(\frac{m_1 m_2}{m_1+m_2}\right)\mathbf{r} + \mathbf{r}_2 \\
&= \frac{\mu}{m_2}\mathbf{r} + \mathbf{r}_2
\end{aligned}$$

Therefore, solving for $\mathbf{r}_2$,

$$\boxed{\mathbf{r}_2 = \mathbf{R} - \frac{\mu}{m_2}\mathbf{r}.}$$

This means that

$$\begin{aligned}
\mathbf{r}_1 &= \mathbf{r} + \mathbf{r}_2 \\
&= \mathbf{r} + \left[\mathbf{R} - \left(\frac{m_1}{m_1+m_2}\right)\mathbf{r}\right] \\
&= \mathbf{R} + \frac{(m_1+m_2)\mathbf{r} - m_1\mathbf{r}}{m_1+m_2} \\
&= \mathbf{R} + \frac{m_2\mathbf{r}}{m_1+m_2} \\
&= \mathbf{R} + \frac{1}{m_1}\left(\frac{m_1 m_2}{m_1+m_2}\right)\mathbf{r}
\end{aligned}$$

$$\boxed{\mathbf{r}_1 = \mathbf{R} + \frac{\mu}{m_1}\mathbf{r}.}$$

Making the change of variables from $\mathbf{r}_1 = \langle x_1, y_1, z_1\rangle$ and $\mathbf{r}_2 = \langle x_2, y_2, z_2\rangle$ to

$$\begin{aligned}
\mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \\
&= \langle x_1, y_1, z_1\rangle - \langle x_2, y_2, z_2\rangle \\
&= \langle x_1 - x_2, y_1 - y_2, z_1 - z_2\rangle \\
&= \langle x, y, z\rangle
\end{aligned}$$

and

$$\begin{aligned}
\mathbf{R} &= \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \\
&= \frac{m_1\langle x_1, y_1, z_1\rangle + m_2\langle x_2, y_2, z_2\rangle}{m_1 + m_2} \\
&= \frac{\langle m_1x_1 + m_2x_2, m_1y_1 + m_2y_2, m_1z_1 + m_2z_2\rangle}{m_1 + m_2} \\
&= \left\langle \frac{m_1x_1 + m_2x_2}{m_1 + m_2}, \frac{m_1y_1 + m_2y_2}{m_1 + m_2}, \frac{m_1z_1 + m_2z_2}{m_1 + m_2} \right\rangle \\
&= \langle X, Y, Z\rangle
\end{aligned}$$

affects the gradient operators.

$$\begin{cases} x = x_1 - x_2 \\ y = y_1 - y_2 \\ z = z_1 - z_2 \end{cases} \qquad \begin{cases} X = \dfrac{m_1x_1 + m_2x_2}{m_1 + m_2} \\ Y = \dfrac{m_1y_1 + m_2y_2}{m_1 + m_2} \\ Z = \dfrac{m_1z_1 + m_2z_2}{m_1 + m_2} \end{cases}$$

Use the chain rule to write the old variables of ∇_1 in terms of the new variables. [$x_1 \to (x, X)$, $y_1 \to (y, Y)$, and $z_1 \to (z, Z)$.]

$$\begin{aligned}
\nabla_1 &= \left\langle \frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1} \right\rangle \\
&= \left\langle \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X},\ \frac{\partial y}{\partial y_1}\frac{\partial}{\partial y} + \frac{\partial Y}{\partial y_1}\frac{\partial}{\partial Y},\ \frac{\partial z}{\partial z_1}\frac{\partial}{\partial z} + \frac{\partial Z}{\partial z_1}\frac{\partial}{\partial Z} \right\rangle \\
&= \left\langle (1)\frac{\partial}{\partial x} + \left(\frac{m_1}{m_1 + m_2}\right)\frac{\partial}{\partial X},\ (1)\frac{\partial}{\partial y} + \left(\frac{m_1}{m_1 + m_2}\right)\frac{\partial}{\partial Y},\ (1)\frac{\partial}{\partial z} + \left(\frac{m_1}{m_1 + m_2}\right)\frac{\partial}{\partial Z} \right\rangle \\
&= \left\langle \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right\rangle + \frac{m_1}{m_1 + m_2}\left\langle \frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z} \right\rangle \\
&= \nabla_r + \frac{1}{m_2}\left(\frac{m_1m_2}{m_1 + m_2}\right)\nabla_R
\end{aligned}$$

Therefore,

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

Use the chain rule to write the old variables of ∇_2 in terms of the new variables. [$x_2 \to (x, X)$, $y_2 \to (y, Y)$, and $z_2 \to (z, Z)$.]

$$\begin{aligned}
\nabla_2 &= \left\langle \frac{\partial}{\partial x_2}, \frac{\partial}{\partial y_2}, \frac{\partial}{\partial z_2} \right\rangle \\
&= \left\langle \frac{\partial x}{\partial x_2}\frac{\partial}{\partial x} + \frac{\partial X}{\partial x_2}\frac{\partial}{\partial X},\ \frac{\partial y}{\partial y_2}\frac{\partial}{\partial y} + \frac{\partial Y}{\partial y_2}\frac{\partial}{\partial Y},\ \frac{\partial z}{\partial z_2}\frac{\partial}{\partial z} + \frac{\partial Z}{\partial z_2}\frac{\partial}{\partial Z} \right\rangle \\
&= \left\langle (-1)\frac{\partial}{\partial x} + \left(\frac{m_2}{m_1+m_2}\right)\frac{\partial}{\partial X},\ (-1)\frac{\partial}{\partial y} + \left(\frac{m_2}{m_1+m_2}\right)\frac{\partial}{\partial Y},\ (-1)\frac{\partial}{\partial z} + \left(\frac{m_2}{m_1+m_2}\right)\frac{\partial}{\partial Z} \right\rangle \\
&= -\left\langle \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right\rangle + \frac{m_2}{m_1+m_2}\left\langle \frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z} \right\rangle \\
&= -\nabla_r + \frac{1}{m_1}\left(\frac{m_1 m_2}{m_1+m_2}\right)\nabla_R
\end{aligned}$$

Therefore,

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

Part (b)

Equation 5.7 (on page 198) is the time-independent Schrödinger equation for a system of two particles.

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V(\mathbf{r}_1, \mathbf{r}_2)\psi = E\psi \tag{5.7}$$

Suppose the potential energy function depends only on the vector displacement between the particles.

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V(\mathbf{r}_1 - \mathbf{r}_2)\psi = E\psi \tag{5.7}$$

Make the change of variables from $\mathbf{r}_1$ and $\mathbf{r}_2$ to $\mathbf{r}$ and $\mathbf{R}$.

$$\begin{aligned}
E\psi &= -\frac{\hbar^2}{2m_1}(\nabla_1 \cdot \nabla_1)\psi - \frac{\hbar^2}{2m_2}(\nabla_2 \cdot \nabla_2)\psi + V(\mathbf{r})\psi \\
&= -\frac{\hbar^2}{2m_1}\left[\left(\nabla_r + \frac{\mu}{m_2}\nabla_R\right) \cdot \left(\nabla_r + \frac{\mu}{m_2}\nabla_R\right)\right]\psi - \frac{\hbar^2}{2m_2}\left[\left(-\nabla_r + \frac{\mu}{m_1}\nabla_R\right) \cdot \left(-\nabla_r + \frac{\mu}{m_1}\nabla_R\right)\right]\psi + V(\mathbf{r})\psi \\
&= -\frac{\hbar^2}{2m_1}\left(\nabla_r \cdot \nabla_r + \frac{\mu}{m_2}\nabla_r \cdot \nabla_R + \frac{\mu}{m_2}\nabla_R \cdot \nabla_r + \frac{\mu^2}{m_2^2}\nabla_R \cdot \nabla_R\right)\psi \\
&\quad - \frac{\hbar^2}{2m_2}\left(\nabla_r \cdot \nabla_r - \frac{\mu}{m_1}\nabla_r \cdot \nabla_R - \frac{\mu}{m_1}\nabla_R \cdot \nabla_r + \frac{\mu^2}{m_1^2}\nabla_R \cdot \nabla_R\right)\psi + V(\mathbf{r})\psi
\end{aligned}$$

Notice that the cross-terms cancel out.

$$E\psi = -\frac{\hbar^2}{2m_1}\left(\nabla_r^2 + \cancel{\frac{\mu}{m_2}\nabla_r \cdot \nabla_R} + \cancel{\frac{\mu}{m_2}\nabla_R \cdot \nabla_r} + \frac{\mu^2}{m_2^2}\nabla_R^2\right)\psi$$

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

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

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

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

Therefore,

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

Part (c)

The result of part (b) is a linear and homogeneous partial differential equation, so the method of separation of variables can be applied. Assume a product solution of the form $\psi(\mathbf{r}, \mathbf{R}) = \psi_r(\mathbf{r})\psi_R(\mathbf{R})$ and plug it into the equation.

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

Evaluate the derivatives.

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

Divide both sides by $\psi_r(\mathbf{r})\psi_R(\mathbf{R})$ to separate variables.

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

Let $E = E_r + E_R$.

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

If we set

$$-\frac{\hbar^2}{2(m_1+m_2)}\frac{1}{\psi_R(\mathbf{R})}\nabla_R^2\psi_R = E_R, \tag{2}$$

then equation (1) reduces to

$$-\frac{\hbar^2}{2\mu}\frac{1}{\psi_r(\mathbf{r})}\nabla_r^2\psi_r + V(\mathbf{r}) = E_r. \tag{3}$$

Multiply both sides of equation (2) by $\psi_R(\mathbf{R})$, and multiply both sides of equation (3) by $\psi_r(\mathbf{r})$.

$$\left.\begin{aligned} -\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^2\psi_R + 0\psi_R(\mathbf{R}) = E_R\psi_R(\mathbf{R}) \\ -\frac{\hbar^2}{2\mu}\nabla_r^2\psi_r + V(\mathbf{r})\psi_r(\mathbf{r}) = E_r\psi_r(\mathbf{r}) \end{aligned}\right\}$$

Both ψ_r and ψ_R satisfy the time-independent Schrödinger equation for a single particle (Equation 4.8 on page 132). The particle associated with ψ_r has a mass of μ and a potential energy of $V(\mathbf{r})$ and a total energy of E_r, whereas the particle associated with ψ_R has a mass of $m_1 + m_2$ and a potential energy of zero and a total energy of E_R.