CONTENTS

I. SEPARATION OF MOTION: TWO PARTICLES

Consider two particles, with coordinates defined in Fig. 1 We will assume the particles

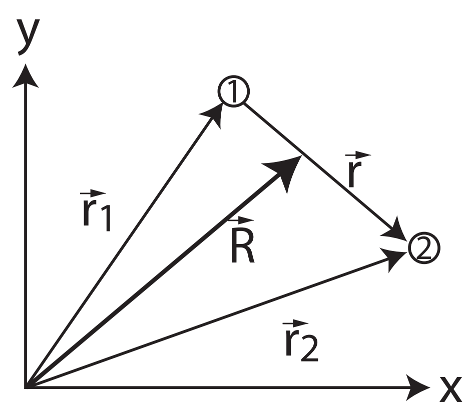

FIG. 1. Coordinate system for two particles of mass m_1 and m_2. For simplicity, we have suppressed the z axis.

interact with a potential $V(r)$ which depends only on the magnitude of the vector which connects them. This is called a "central" force.

A. Classical Treatment

The (scalar) kinetic energy of the two particles is

$$\begin{aligned} T(\vec{r}_1, \vec{r}_2) &= \frac{1}{2}m_1\vec{v}_1^2 + \frac{1}{2}m_2\vec{v}_2^2 = \frac{1}{2}m_1\left(\frac{\partial\vec{r}_1}{\partial t}\right)^2 + \frac{1}{2}m_2\left(\frac{\partial\vec{r}_2}{\partial t}\right)^2 \\ &= \frac{1}{2}m_1\dot{\vec{r}}_1^{\,2} + \frac{1}{2}m_2\dot{\vec{r}}_2^{\,2} \end{aligned} \tag{1}$$

Now, let us define two new coordinates: the position of the center-of-mass

$$\vec{R} = \frac{m_1}{M}\vec{r}_1 + \frac{m_2}{M}\vec{r}_2$$

where $M = m_1 + m_2$ (note that $\vec{R}$ is the mass-weighted average of the positions of the two particles) and the separation between the two particles

$$\vec{r} = \vec{r}_2 - \vec{r}_1$$

You can show that in terms of $\vec{R}$ and $\vec{r}$, the positions of the two particles are

$$\vec{r}_1 = \vec{R} - \frac{m_2}{M}\vec{r}$$

and

$$\vec{r}_2 = \vec{R} + \frac{m_1}{M}\vec{r}$$

Thus, the vector position of the first particle is equal to the vector position of the center-of-mass minus a fraction of the separation vector $\vec{r}$ (and similarly for the vector position of the second particle. Consequently, from Fig. 1 you see that the position of the center of mass (the arrow point of the vector $\vec{R}$) must like between the particles along the separation distance.

Differentiation with respect to time gives

$$\dot{\vec{r}}_1 = \dot{\vec{R}} - \frac{m_2}{M}\dot{\vec{r}}$$

and, similarly for $\dot{\vec{r}}_2$. Thus, the kinetic energy is

$$T = \frac{1}{2}m_1\dot{\vec{R}}^2 + \frac{1}{2}m_1\left[\frac{m_2}{M}\right]^2\dot{\vec{r}}^2 - 2\frac{1}{2}m_1\frac{m_2}{M}\vec{R}\cdot\vec{r}$$

$$+\frac{1}{2}m_2\dot{\vec{R}}^2 + \frac{1}{2}m_2\left[\frac{m_1}{M}\right]^2\dot{\vec{r}}^2 + 2\frac{1}{2}m_2\frac{m_1}{M}\vec{R}\cdot\vec{r}$$

The cross terms vanish, which leaves

$$T = \frac{1}{2}(m_1 + m_2)\dot{\vec{R}}^2 + \frac{1}{2}\frac{m_1 m_2^2 + m_2 m_1^2}{M^2}\dot{\vec{r}}^2 = \frac{1}{2}M\dot{\vec{R}}^2 + \frac{1}{2}\frac{m_1 m_2}{M}\dot{\vec{r}}^2$$
$$= \frac{1}{2}M\dot{\vec{R}}^2 + \frac{1}{2}\mu\dot{\vec{r}}^2 \qquad (2)$$

where $\mu \equiv m_1 m_2/(m_1 + m_2)$ is the "reduced" mass.

Thus, since the potential depends only on $|\vec{r}|$, the Hamiltonian separates into a term describing the kinetic energy of the center-of-mass, moving through space with mass M, and the kinetic energy and potential energy of the *relative* motion of particle 2 with respect to particle 1, with the kinetic energy proportional to the reduced mass.

B. Quantum treatment

In quantum mechanics the kinetic energy operator is proportional to the Laplacian so that (in atomic units)

$$\hat{T}(\vec{r}_1, \vec{r}_2) = -\frac{1}{2m_1}\nabla^2_{r_1} - \frac{1}{2m_2}\nabla^2_{r_2}$$

By the chain rule

$$\frac{\partial}{\partial x_1} = \frac{\partial}{\partial X}\frac{\partial X}{\partial x_1} + \frac{\partial}{\partial x}\frac{\partial x}{\partial x_1}$$

$$= \frac{m_1}{M}\frac{\partial}{\partial X} - \frac{\partial}{\partial x} \qquad (3)$$

By squaring this, we find

$$\frac{\partial^2}{\partial x_1^2} = \frac{m_1^2}{M^2}\frac{\partial^2}{\partial X^2} - 2\frac{m_1}{M}\frac{\partial^2}{\partial X \partial x} + \frac{\partial^2}{\partial x^2}$$

and, similarly

$$\frac{\partial^2}{\partial x_2^2} = \frac{m_2^2}{M^2}\frac{\partial^2}{\partial X^2} + 2\frac{m_2}{M}\frac{\partial^2}{\partial X \partial x} + \frac{\partial^2}{\partial x^2}$$

Entirely equivalent relations apply to the y and z components of the Laplacian operator.

Consequently, in terms of $\vec{R}$ and $\vec{r}$, the kinetic energy operator becomes (here we show explicitly only differentiation with respect to x)

$$\hat{T}(\vec{r}_1, \vec{r}_2) = -\frac{m_1 + m_2}{2M^2}\frac{\partial^2}{\partial X^2} - \frac{1-1}{M}\frac{\partial^2}{\partial X \partial x} - \frac{1}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2} + \cdots$$

$$= -\frac{1}{2M}\frac{\partial^2}{\partial X^2} - \frac{1}{2\mu}\frac{\partial^2}{\partial x^2} + \cdots \tag{4}$$

where the dots indicate the corresponding terms in y and z. Thus, in terpms of the coordinates $\vec{R}$ and $\vec{r}$, the kinetic energy operator is

$$\hat{T}(\vec{r}_1, \vec{r}_2) = -\frac{1}{2M}\nabla_R^2 - \frac{1}{2\mu}\nabla_r^2$$

The total Hamiltonian is then

$$\hat{H}(\vec{r}_1, \vec{r}_2) = -\frac{1}{2M}\nabla_R^2 - \frac{1}{2\mu}\nabla_r^2 + V(r)$$

Because the Hamiltonian is separable into terms which depend separately on $\vec{R}$ and on $\vec{r}$, the wave function can be written as a product of a function of $\vec{R}$ and a function of $\vec{r}$, namely

$$\Psi(\vec{R}, \vec{r}) = \Phi(\vec{R})\psi(\vec{r})$$

The wave function for motion of the center of mass satisfies the equation

$$-\frac{1}{2M}\nabla_R^2\Phi(\vec{R}) = E_{cm}\Phi(\vec{R})$$

whereas the wave function for internal motion satisfies the equation

$$\left[-\frac{1}{2\mu}\nabla_r^2 + V(r)\right]\psi(\vec{r}) = \mathcal{E}_{int}\psi(\vec{r})$$

The total energy is the sum of the internal energy $\mathcal{E}_{int}$ plus the energy associated with the motion of the center of mass E_{cm}.