

Two quantum particles

Finding the probability to have particle 1 in the interval $[x_1, x_1 + dx_1]$ and finding particle 2 in $[x_2, x_2 + dx_2]$

$|\Phi(x_1, x_2)|^2 dx_1 dx_2$ for example in a **diatomic molecule**.

For a fixed total energy E one obtains for

$$\text{fixed } x_2 \quad -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} \Phi(x_1, x_2) + V(x_1 - x_2) \Phi(x_1, x_2) = (E_{pot} + E_{kin1}) \Phi(x_1, x_2)$$

$$\text{fixed } x_1 \quad -\frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} \Phi(x_1, x_2) + V(x_1 - x_2) \Phi(x_1, x_2) = (E_{pot} + E_{kin2}) \Phi(x_1, x_2)$$

Schrödinger equation for two particles $E = E_{pot} + E_{kin1} + E_{kin2}$

$$-\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} \Phi(x_1, x_2) - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} \Phi(x_1, x_2) + V(x_1 - x_2) \Phi(x_1, x_2) = E \Phi(x_1, x_2)$$

- p_1 is now replaced by $-i\hbar \frac{\partial}{\partial x_1}$ and p_2 is replaced by $-i\hbar \frac{\partial}{\partial x_2}$

in the energy equation $\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V = E$

Two quantum particles in the center of mass system

03/02/2005

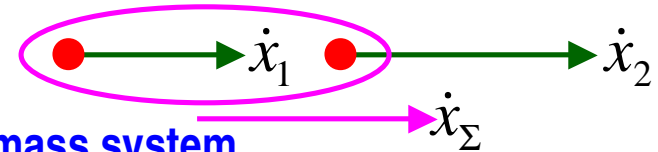
$$-\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} \Phi(x_1, x_2) - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} \Phi(x_1, x_2) + V(x_1 - x_2) \Phi(x_1, x_2) = E \Phi(x_1, x_2)$$

$$x_\Sigma = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}, \quad x_\Delta = x_1 - x_2, \quad \frac{\partial}{\partial x_1} = \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial x_\Sigma} + \frac{\partial}{\partial x_\Delta}, \quad \frac{\partial}{\partial x_2} = \frac{m_2}{m_1 + m_2} \frac{\partial}{\partial x_\Sigma} - \frac{\partial}{\partial x_\Delta}$$

$$\frac{1}{m_1} \frac{\partial}{\partial x_1^2} + \frac{1}{m_2} \frac{\partial}{\partial x_2^2} = \frac{1}{m_1 + m_2} \frac{\partial^2}{\partial x_\Sigma^2} + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial x_\Delta^2}$$

$$-\frac{\hbar^2}{2m_\Sigma} \frac{\partial^2}{\partial x_\Sigma^2} \Phi(x_\Sigma, x_\Delta) - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x_\Delta^2} \Phi(x_\Sigma, x_\Delta) + V(x_\Delta) \Phi(x_\Sigma, x_\Delta) = E \Phi(x_\Sigma, x_\Delta)$$

$$m_\Sigma = m_1 + m_2, \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}, \quad E = E_{\text{kin}} + E_{\text{int}}$$

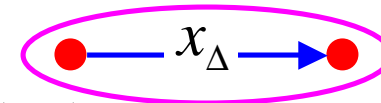


Product solution for a given kinetic energy of the center of mass system

$$\Phi(x_\Sigma, x_\Delta) = \Phi_\Sigma(x_\Sigma) \Phi_\Delta(x_\Delta) \quad \rightarrow \quad -\frac{\hbar^2}{2m_\Sigma} \frac{\partial^2}{\partial x_\Sigma^2} \Phi_\Sigma(x_\Sigma) = E_{\text{kin}} \Phi_\Sigma(x_\Sigma)$$

A diatomic molecule therefore has a de Broglie wavelength that corresponds to the total mass and to the energy of the center of mass system.

Schrödinger equation for the internal coordinate



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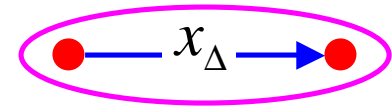
$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x_\Delta^2} \Phi_\Delta(x_\Delta) + V(x_\Delta) \Phi_\Delta(x_\Delta) = E_{\text{int}} \Phi_\Delta(x_\Delta)$$

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Diatomic molecules

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For **small oscillation** energies around the equilibrium distance the potential can be expanded to second order and then expresses a **harmonic oscillator** $V = \frac{1}{2} Cx^2$



Schrödinger equation for the internal coordinate:

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x_\Delta^2} \Phi(x_\Delta) + \frac{1}{2} \mu \omega_0^2 \Phi(x_\Delta) = E_{\text{int}} \Phi(x_\Delta) \quad \rightarrow \quad E_{\text{int}} = \hbar \omega_0 \left(n + \frac{1}{2} \right)$$

Measuring the regular distance between energy levels of the emission or absorption spectrum is sufficient to compute the linearized force **Cx** between the atoms.

