Atom och Molekylfysik - F02
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1 Separation of Center of Mass motion.

$$\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \tag{1}$$

$$\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(r) \tag{2}$$

$$\frac{\hat{p}^2}{2m_1}\frac{(-it\nabla_1)^2}{2m_1} \qquad p = i\hbar\vec{\nabla} \tag{3}$$

The classical momentuym for two particles

$$T = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \frac{P_1^2}{2M} + \frac{p_2^2}{2\mu} \tag{4}$$

$\vec{P}$	total momentum.
M	total mass
$\vec{p}$	relative momentum $\frac{m_2p_1 - m_1p_2}{m_1+m_2}$
μ	reduced mass $\frac{m_1m_2}{m_1+m_2}$

$-\vec{P}$ is the momentum of mass $M = m_1 + m_2$ situated at

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}, \qquad \vec{P} = M\vec{R} \tag{5}$$

The classical hamiltonian

$$H = T + V = \frac{\vec{P}^2}{2M} + \frac{\vec{p}^2}{2\mu} + V(r) \tag{6}$$

Quantum mechanical Hamilton operator

$$\begin{aligned}\vec{P} &\to \hat{P} = -i\hbar\vec{\nabla}_{\vec{R}} \\ \vec{p} &\to \hat{p} = -i\hbar\vec{\nabla}_{\vec{r}}\end{aligned} \tag{7}$$

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2M}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 + V(r) \tag{8}$$

If the potential V is time-independent the Schrödinger equation can be separated, $\Psi(\vec{R}, \vec{r}, t) = \phi(\vec{r})\psi(\vec{r})\theta(t)$

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\phi\psi\theta &= \hat{H}\phi\Psi\theta \\ \psi\phi i\hbar\frac{\partial\theta}{\partial t} &= \theta\hat{H}\phi\psi \\ \frac{1}{\theta}i\hbar\frac{\partial\theta}{\partial t} &= \frac{1}{\psi\phi}\hat{H}\phi\psi = const = E \end{aligned} \tag{9}$$

Now we know the solution for t

$$i\hbar\frac{\partial\theta}{\partial t} = E\theta \quad \Rightarrow \quad \theta(t) = e^{iEt/\hbar} \tag{10}$$

We contine to separate the equation

$$\begin{aligned} &\hat{H}\phi\psi = E\phi\psi \\ &H = -\underbrace{\frac{\hbar^2}{2M}\vec{\nabla}^2_{\vec{R}}}_{H_R} - \underbrace{\frac{\hbar^2}{2\mu}\vec{\nabla}^2_{\vec{r}} + V(r)}_{H_r} \\ &(H_R + H_r)\phi(\vec{R})\psi(\vec{r}) = E\phi(\vec{R})\psi(\vec{r}) \\ &\psi H_R\phi + \phi H_r\psi = E\phi\psi \qquad \cdot\frac{1}{\phi\psi} \\ &\frac{1}{\phi}H_R\phi + \frac{1}{\psi}H_r\psi = E = E_R + E_r \\ &H_R\phi = E_R\phi, \qquad H_r\psi = E_r\psi \end{aligned} \tag{11}$$

Now we have finally arrived at three separated equations. The timedepended equation, a equation describing the Center of mass's motion and finally a equation describing the two particles relative motion.

$$\begin{aligned} &i\hbar\frac{\partial\theta}{\partial t} = E_{tot}\theta \quad \Rightarrow \quad \theta(t) = e^{iE_{tot}t/\hbar}, \qquad E_{tot} = E_R + E_r \\ &-\frac{\hbar^2}{2M}\vec{\nabla}^2_{\vec{R}}\phi(\vec{R}) = E_R\phi(\vec{R}) \qquad \text{(CM motion)} \\ &\left[-\frac{\hbar^2}{2\mu}\vec{\nabla}^2_{\vec{r}} + V(r)\right]\psi(\vec{r}) = E_r\psi(\vec{r}) \qquad \text{(Relative motion)} \end{aligned} \tag{12}$$

This is the stationary Schrödinger equation. A Eigenvalueproblem for a single particle. We solve this by separating the Schrödinger equation.

$$H\psi = E\psi, \qquad H = -\frac{\hbar^2}{2\mu}\vec{\nabla}^2_{\vec{r}} + V(r) \tag{13}$$

Because the potential inte spherically symmetric we will solve the problem in spherical coordinates r, θ, ϕ. We now need the laplacian in spherical coordinates. (look it up)

$$\Delta = \nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2}\underbrace{\left[\sin\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2}\right]}_{-\frac{\hat{l}^2}{\hbar^2}} \tag{14}$$

Where $\hat{l}$ is the operator for angular momentum.The Schrödinger equation in Spherical coordinates

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{\hat{l}^2}{\hbar^2 r^2}\right) + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r}) \tag{15}$$

Because $\hat{H}, l^2, \hat{l}_z$ commute, they have a common set of eigenvectors

$$\psi(r) = R(r)Y(\theta, \phi) \qquad [\hat{H}, l^2] = 0, \quad [\hat{l}, l_z] = 0 \tag{16}$$

Where Y_{lm} are the spherical harmonics, and substitution gives us

$$\begin{aligned} -\frac{\hbar^2}{2\mu}[\frac{1}{r}\frac{\partial^2}{\partial r^2} - \frac{1}{\hbar^2 r^2}\underbrace{l^2] Y_{ml}}_{2} R_{ml} + V(r) Y_{ml} R_{ml} = E R_{ml} Y_{ml} \\ -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{l(l+1)}{r^2}\right] R(r) + V(r)R(r) = E(r) \end{aligned} \tag{17}$$

And finally this gives us

$$\left[\underbrace{-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}}_{T}\underbrace{P(r) + V_{eff}(r)}_{V}\right] P(r) = EP(r), \qquad P(r) = \frac{R(r)}{r} \tag{18}$$