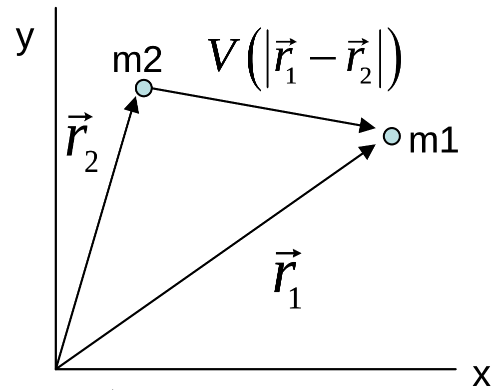
The 2-Particle system:

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V\left(\left|\vec{r}_1 - \vec{r}_2\right|\right)$$

This is difficult to solve.



$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V\left(\left|\vec{r}_1 - \vec{r}_2\right|\right)$$

$\vec{r} = \vec{r}_1 - \vec{r}_2$ relative coordinate of the total momentum

$\hat{\mathcal{P}}_{total} = \hat{p}_1 + \hat{p}_2$ the total momentum

$\hat{p}_r = \frac{m_1\hat{p}_1 - m_2\hat{p}_2}{m_1+m_2}$ and $\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2}$ with $M = m_1 + m_2$

$$\hat{H} = \underbrace{\frac{\hat{\mathcal{P}}^2}{2M}}_{\hat{H}_{CM} = \text{Center of Mass for Particle in free space}} + \underbrace{\frac{\hat{p}_{rel}^2}{2\mu} + V(\vec{r})}_{\hat{H}_{rel} = \text{Relative Hamiltonian}}$$

$$\hat{H} = \hat{H}_{CM} + \hat{H}_{rel}$$

eigenfunction and eigenenergy

$$E = E_{CM} + E_{rel}$$

We learned previously that $\left[x, p_x\right] = i\hbar$

For the transformed system: $[\hat{r}_j, \hat{p}_k] = i\hbar\delta_{jk}$ and $[\hat{R}_j, \hat{\mathcal{P}}_k] = i\hbar\delta_{jk}$

So the Hamiltonian is separated into two independent components.

When the Hamiltonian can be separated into independent components:

The Schrodinger equation has product eigenfunctions:

$$\psi = \psi_{rel}\left(\vec{R}\right)\psi_{rel}(\vec{r})$$

and summation eigenvalues:

$$E = E_{CM} + E_{rel}$$

where

$$\hat{H} = \hat{H}_{CM} + \hat{H}_{rel}$$

$$\hat{H}_{CM}\psi_{CM} = E_{CM}\psi_{CM}$$

$$\hat{H}_{rel}\psi_{rel} = E_{rel}\psi_{rel}$$

First Solve the Free Particle (CM) Part:

$$\hat{H}_{CM}\psi_{CM} = E_{CM}\psi_{CM}$$

$$\psi_k = Ae^{i\vec{k}\cdot\vec{R}}$$

$$E_k = \frac{\hbar^2 k^2}{2M}$$

Now Solve the Relative Hamiltonian with Reduced Mass:

$$\hat{H}_{rel} = \frac{\hat{p}_{rel}^2}{2\mu} + V(\vec{r})$$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ this is the reduced mass

The Schrodinger equation is:

$$\left[\frac{\hat{p}_{rel}^2}{2\mu} + V(\vec{r})\right]\psi_{rel}(\vec{r}) = E_k\psi_k(\vec{r})$$

Using spherical coordinates, we can write it this way:

$$\left[\frac{\hat{p}_{rel}^2}{2\mu} + V(\vec{r})\right]\psi_{rel}(\vec{r}) = E_k\psi_k(\vec{r})$$

$$\left[\frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} + V(\vec{r})\right]\psi_{rel}(\vec{r}) = E_k\psi_k(\vec{r})$$

Here $\frac{\hat{p}_r^2}{2\mu}$ is the radial part of the momentum and $\frac{\hat{L}^2}{2\mu r^2}$ is the rotational part.

The rotational part is independent of the other two terms

which are functions of r and not θ,ϕ. The solution is spherical harmonics:

$$Y_l^m(\theta,\phi) = |l,m\rangle$$

$$\psi_{rel}(\vec{r}) = R(r)Y_l^m(\theta,\phi) = |n,l,m\rangle$$

$$\left[\frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} + V(\vec{r})\right]R(r)Y_l^m(\theta,\phi) = E_k R(r)Y_l^m(\theta,\phi)$$

$$\hat{p}_r = \frac{-i\hbar}{r}\frac{\partial}{\partial r}r$$

$$Y_l^m(\theta,\phi)\frac{\hat{p}_r^2}{2\mu}R(r) + R(r)\frac{\hbar^2 l(l+1)}{2\mu r^2}Y_l^m(\theta,\phi) + V(\vec{r})R(r)Y_l^m(\theta,\phi) = E_k R(r)Y_l^m(\theta,\phi)$$

The radial component:

$$\left[\frac{\hat{p}_r^2}{2\mu} + \underbrace{\frac{\hbar^2 l(l+1)}{2\mu r^2} + V(\vec{r})}_{\text{effective potential}}\right]R(r) = E_k R(r)$$

So, we have a product of eigenfunctions: a radial part and an angular part. The angular part is solvable without knowing the potential which depends only on r. The angular part are spherical harmonics defined in Table 9.1 on page 373.

The Relative Hamiltonian for a Hydrogenic Atom:

Here: $V(r) = \frac{-Ze^2}{r}$ the Coulomb potential.

Hydrogenic Atoms	Z
H	1
He^{+}	2
Li^{++}	3

Only consider the bound state (lower than free particle energy):

$$\left[\frac{-\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{-\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{r} + |E|\right]R(r) = 0$$

Change the dependent variable to:

$$U(r) = rR(r)$$

$$\left[\frac{-\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{-\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{r} + |E|\right]\frac{U(r)}{r} = 0$$

$$\left[\frac{-\hbar^2}{2\mu}\cancel{\frac{1}{r}}\frac{\partial^2}{\partial r^2}\cancel{r}\frac{U(r)}{\cancel{r}} + \frac{-\hbar^2 l(l+1)}{2\mu r^2}\frac{U(r)}{\cancel{r}} - \frac{Ze^2}{r}\frac{U(r)}{\cancel{r}} + |E|\frac{U(r)}{\cancel{r}}\right] = 0$$

$$-\frac{\partial^2 U(r)}{\partial r^2} + \left[\frac{l(l+1)}{r^2} - \frac{2\mu}{\hbar^2}\frac{Ze^2}{r} + \frac{2\mu|E|}{\hbar^2}\right]U(r) = 0$$

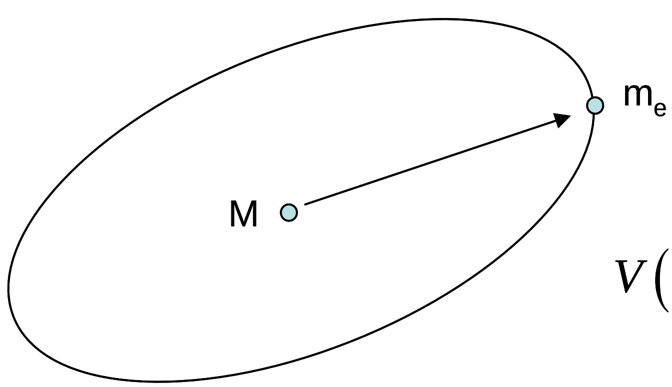
$$\rho \equiv 2\kappa r \quad \text{and} \quad |E| = \frac{\hbar^2\kappa^2}{2\mu}$$

$$\lambda^2 = \left(\frac{Z}{\kappa a_0}\right)^2 = \frac{Z^2}{|E|}□$$

$$□ = \frac{\hbar^2}{2\mu a_0^2} \quad \text{and} \quad a_0 = \frac{\hbar^2}{\mu e^2}$$

where □ is Rydberg constant. Simplify the radial equation:

$$\frac{\partial^2 U}{\partial \rho^2} - \frac{l(l+1)U}{\rho^2} + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)U = 0$$



$$V\left(|\vec{r}_1 - \vec{r}_2|\right) = -\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Look at the solution to the radial relative Hamiltonian equation in the limits, first at ±∞:

$$\frac{\partial^2 U}{\partial \rho^2} - \frac{l(l+1)U}{\rho^2} + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)U = 0$$

$$\rho \to \infty \quad U(\rho) \xrightarrow[\rho\to\infty]{} 0 \text{ (finite)}$$

$$\frac{\partial^2 U}{\partial \rho^2} - \cancelto{0}{\frac{l(l+1)U}{\rho^2}} + \left(\cancelto{0}{\frac{\lambda}{\rho}} - \frac{1}{4}\right)U = 0$$

$$\frac{\partial^2 U}{\partial \rho^2} - \frac{U}{4} = 0$$

$$U \sim Ae^{-\rho/2} + \underbrace{\cancelto{0}{B} e^{\rho/2}}_{\text{B has to be zero because in the limit } \rho\to\infty \text{ this term is infinite}}$$

$$\therefore U \underset{\rho\to\infty}{\sim} Ae^{-\rho/2}$$

Now look at the solution to the radial relative Hamiltonian equation in the limit at 0:

$$\frac{\partial^2 U}{\partial \rho^2} - \frac{l(l+1)U}{\rho^2} + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)U = 0$$

$$\rho \to 0 \quad U(\rho) \xrightarrow[\rho\to 0]{} \text{(finite number)}$$

$$\rho^2 \frac{\partial^2 U}{\partial \rho^2} - \rho^2 \frac{l(l+1)U}{\rho^2} + \rho^2 \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)U = 0$$

$$\frac{\rho^2 \partial^2 U}{\partial \rho^2} - l(l+1)U + \cancelto{0}{\rho\lambda U} - \cancelto{0}{\frac{\rho^2}{4}U} = 0$$

$$\frac{\partial^2 U}{\partial \rho^2} - \frac{l(l+1)U}{\rho^2} = 0$$

Substitute trial solution $U = \rho^q$

$$q(q-1)\rho^{(q-2)} = \frac{l(l+1)\rho^q}{\rho^2}$$

$$q(q-1) = l(l+1)$$

$$\therefore q = l+1 \quad \text{or} \quad q = -l$$

$$U \sim \underbrace{\cancelto{0}{A}\rho^{-l}}_{\text{So that the solution vanishes at the origin}} + B\rho^{l+1}$$

$$U \underset{\rho\to 0}{\sim} B\rho^{l+1} \quad \text{and} \quad U \underset{\rho\to\infty}{\sim} Ae^{-\rho/2}$$

From these results at the limits, we can build the eigenfunction of U(ρ).

$U(\rho) = e^{-\rho/2}\rho^{l+1}F(\rho)$ where $F(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$

Substitute this into the Schrodinger equation and solve.

$$\left[\rho \frac{\partial^2}{\partial\rho^2} + (2l+2-\rho)\frac{\partial}{\partial\rho} - (l+1-\lambda)\right]F(\rho) = 0$$

The solution is:

$$c_{j+1} = \frac{(j+l+1)-\lambda}{(j+1)(j+2l+2)}c_j \equiv \Gamma_{jl}c_j$$

In the limit that $j \to \infty$ $\quad c_{j+1} = \frac{c_j}{j}$

What satisfies this $c_{j+1} = \frac{c_j}{j}$ relation? $F(\rho) = e^{\rho} = \sum_j^{\infty} \frac{\rho^j}{j!}$

Consider total radial solution for Coloumb potential relative Hamiltonian:

$$U(\rho) = e^{-\rho/2}\rho^{l+1}F(\rho) = e^{-\rho/2}\rho^{l+1}\sum_j^{\infty}\frac{\rho^j}{j!} = e^{-\rho/2}\rho^{l+1}e^{\rho} = e^{\rho/2}\rho^{l+1}$$

The problem is that as $j \to \infty$ and $\rho \to \infty$, then $U(\rho) = \infty$.

Therefore $j \not\to \infty$, and j has to have a cut-off or maximum value.

The maximum j is at the point where $\Gamma_{j_{\max},l} = 0$.

$$j_{\max} + l + 1 - \lambda = 0$$

We define a number according to this.

The principle quantum number *n*.

$n = j_{\max} + l + 1 = \lambda \qquad n = 1, 2, 3, \cdots$

$\min(j_{\max}) = 0 \qquad \min(l) = 0 \quad \min(n) = 1 \qquad \lambda^2 = n^2$

$l\max = n - 1 \qquad l = 0, 1, 2, ..., n-1 \qquad 0 < j \leq j_{\max}$

$E_n = \frac{-Z^2 \mathcal{R}}{n}$ and $\mathcal{R} = 13.6$ eV

$$U_{nl}(\rho) = e^{-\rho/2}\rho^{l+1}F_{nl}(\rho) = A_{nl}e^{-\rho/2}\rho^{l+1}\sum_{j=0}^{n-l-1}c_j\rho^j$$

$c_{j+1} = \Gamma_{jl}c_j$ and $\rho \equiv 2\kappa_n r$ and $\kappa_n = \frac{Z}{a_0 n}$

Putting together the radial and angular components of the relative Hamiltonian:

$\psi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$ where $R_{nl} = \frac{A_{nl}U_{nl}}{r}$

$E_n = \frac{-Z^2\mathcal{R}}{n^2} = -\frac{\mu(Ze^2)^2}{2\hbar^2 n^2}$ and $\mathcal{R} = \frac{\mu e^4}{2\hbar^2} = 13.6$ eV (Rydberg Constant)

Let's Calculate the Degeneracy of E_n:

$n = j + l + 1$

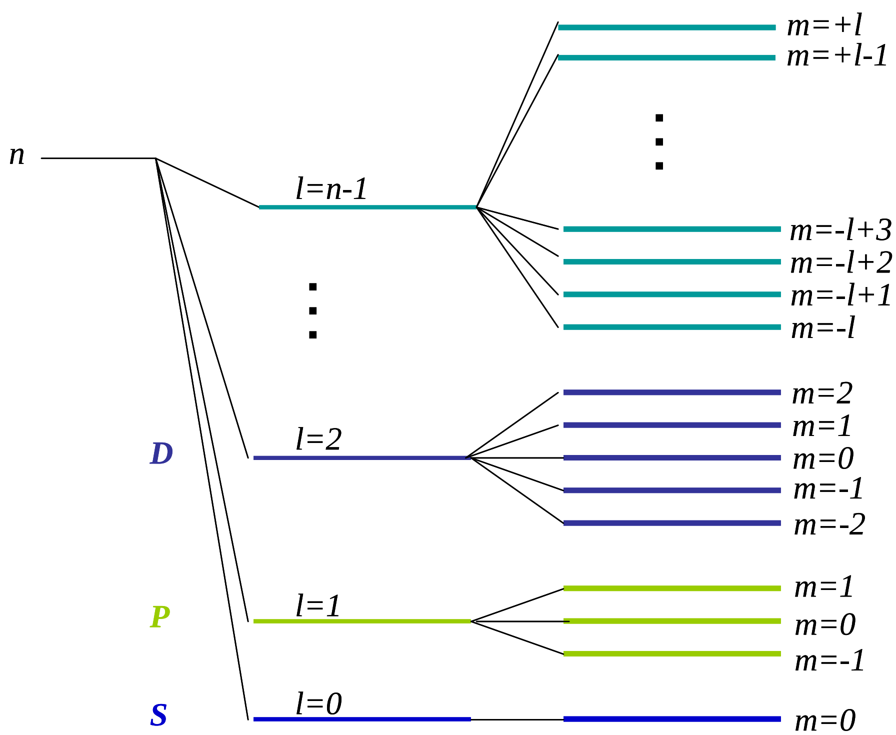
$l_{\max} = n - 1$

$l = 0, 1, 2, ..., n-1$ There are n values of l.

$m = -l, -l+1, ..., 0, ..., l-1, l$ There are $(2l+1)$ values of m.

Degeneracy of $E_n = \sum_{l=0}^{n-1}(2l+1) = 2\sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1 = \frac{2n(n-1)}{2} + n = n^2$

If you consider spin, the degeneracy is double: $D(E_n) = 2n^2$.



When you excite the atom to another state, then it can give light, the light will come out. Next class we will learn about the selection rules – forbidden/allowed, etc.