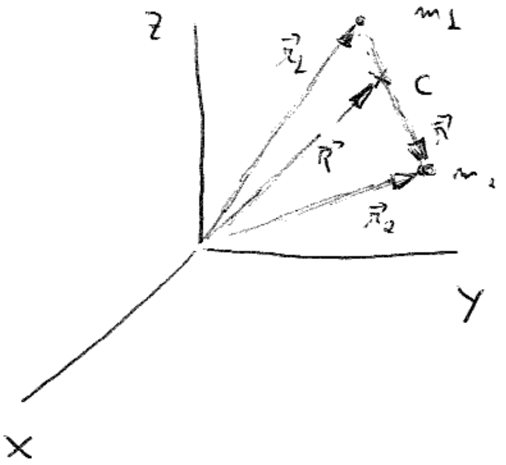
Reduction of the two-particle to the one-particle problem

Consider a system of two interacting particles with masses m_1 and m_2 isolated from the rest of the world. Aiming to quantize this system we look for a suitable Hamiltonian. As usual, first we obtain a classical Hamiltonian.



This system contains six degrees of freedom. And it can be described either by the positions of the two particles $\vec{r}_1$ and $\vec{r}_2$ or by the center of mass $\vec{R}$ and relative position $\vec{r}$.

Two Alternative Descriptions

i) Center of mass and internal coordinates

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

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

ii) Absolute positions of the two particles

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

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

Now the kinetic energy

$$T = \frac{1}{2} m_1 \dot{\vec{r}}_1^{\,2} + \frac{1}{2} m_2 \dot{\vec{r}}_2^{\,2}$$

may be written in terms of $\vec{R}$ and $\vec{r}$ as

$$T = \frac{1}{2} M \dot{\vec{R}}^2 + \frac{1}{2} \mu \dot{\vec{r}}^2$$

where

$$M \equiv m_1 + m_2$$

and

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

while the potential energy depends only on the relative position $\vec{r} = \vec{r}_2 - \vec{r}_1$, that is

$$V = V(\vec{r})$$

Upon quantization we get the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla^2_{\vec{R}} - \frac{\hbar^2}{2\mu} \nabla^2_{\vec{r}} + V(\vec{r})$$

which can be rewritten, in terms of the coordinates x, y, z, X, Y, Z as

$$\hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)$$

where $\vec{R} = X\hat{\imath} + Y\hat{\jmath} + Z\hat{k}$ and $\vec{r} = x\hat{\imath} + y\hat{\jmath} + z\hat{k}$.

The wave function is a function of six coordinates

$$\psi = \psi(x, y, z, X, Y, Z).$$

Now, the Hamiltonian can be written as a sum of two independent terms, one depending only on X, Y, Z and the other on x, y, z.

Therefore the wave function factorizes into

$$\psi(x, y, z, X, Y, Z) = \psi_M(X, Y, Z)\,\psi_\mu(x, y, z)$$

with the factors ψ_M and ψ_μ satisfying

$$-\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_M = E_M\,\psi_M$$

and

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_\mu + V(x,y,z)\,\psi_\mu = E_\mu\,\psi_\mu$$

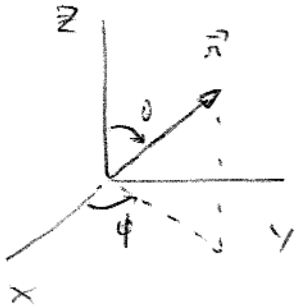
with total energy

$$E = E_M + E_\mu$$

For the first problem we know E_M can assume all non negative ~~r~~real values $E_M \geq 0$ and the solutions ψ_M are plane waves representing a free particle of mass M. We have to solve the second problem for given interaction potential $V(x,y,z)$.

The Two-Particle Rigid Rotor

Regarding the second problem we consider now spherical ~~cartesian~~ coordinates



$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases}$$

and impose the constraint $r = d = \text{const}$.

So we have only two degrees of freedom θ and ϕ while we consider the potential null $V = 0$.

The Hamiltonian then should ~~must~~ be written in spherical coordinates

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} +$$

$$+ \frac{1}{r^2}\cot\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

considering r constant and equal to d, we get

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{1}{d^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{d^2}\cot\theta\frac{\partial}{\partial\theta} + \frac{1}{d^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right)$$

By recognizing the total angular momentum operator $\hat{L}^2$, the Hamiltonian can be simply rewritten as

$$\hat{H} = \frac{\hat{L}^2}{2\mu d^2}$$

Since this problem possesses spherical symmetry, we look for simultaneous eigenfunctions $\psi(\theta, \phi)$ of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_3$. Note that $\hat{H}$ and $\hat{L}^2$ are proportional! We have already solved this problem! The solutions were the spherical harmonics $\psi(\theta,\phi) = Y_\ell^m(\theta,\phi)$. Instead of ℓ we shall write $J = 0, 1, 2, \ldots$ for the angular momentum quantum number. So we have

$$\hat{H}\psi_{Jm} = \hat{H}\, Y_J^m = \frac{\hat{L}^2}{2\mu d^2}\, Y_J^m = \frac{J(J+1)\hbar^2}{2\mu d^2}\, Y_J^m$$

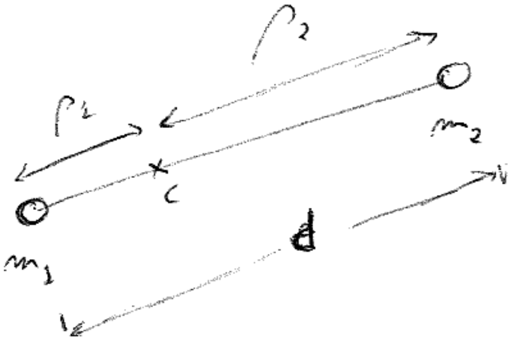
So the possible energies depend only on J and can be written as

$$E_J = \frac{J(J+1)\hbar^2}{2\mu d^2}$$

In terms of the moment of inertia, this can be rewritten as

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

Note that for two point masses m_1 and m_2 we have



$$I = m_1 \rho_1^2 + m_2 \rho_2^2$$

$$\begin{cases} m_1 \rho_1 = m_2 \rho_2 \\ \rho_1 + \rho_2 = d \end{cases}$$

$$\rho_1 = \frac{m_2}{m_1+m_2} d$$

$$\rho_2 = \frac{m_1}{m_1+m_2} d$$

$$\rho_2 = d - \rho_1$$

$$\rho_1 = d - \frac{m_1}{m_2}\rho_1$$

$$\rho_1 = \frac{d}{1 + \frac{m_1}{m_2}}$$

$$\rho_1 = \frac{m_2 d}{m_1+m_2}$$

$$I = \left[\frac{m_1 m_2^2}{(m_1+m_2)^2} + \frac{m_2 m_1^2}{(m_1+m_2)^2}\right] d^2$$

$$I = m_1 m_2 \left[\frac{m_2}{(m_1+m_2)^2} + \frac{m_1}{(m_1+m_2)^2}\right] d^2$$

$$I = \frac{m_1 m_2}{m_1+m_2} d^2 = \mu d^2$$

The rotational spectrum is therefore given by

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

Regarding emission or absorption of electromagnetic radiation, the allowed transitions are

$$\Delta J = \pm 1$$

which leads to frequencies

$$\nu = \frac{E_{J+1} - E_J}{h} = \frac{\left[(J+1)(J+2) - J(J+1)\right] h^2/(2\pi)^2}{h\, 2I}$$

$$\nu = \frac{2(J+1)\,h}{8\pi^2 I}$$

$$\nu = 2(J+1)B$$

where we define

$$B \equiv \frac{h}{8\pi^2 I}$$

as the rotational constant of the molecule.

The Hydrogen Atom

In the following we shall study hydrogenlike atoms. That means atoms/ions with one electron and Z protons. For $Z=1$ we have the hydrogen atom. This is a central-force problem with potential

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

we redefine $e' = e/(4\pi\epsilon_0)^{1/2}$ and rewrite

$$\boxed{V(r) = -\frac{Ze'^2}{r}}$$

To be more precise, our problem amounts to quantum mechanically describe two point particles of masses m_N and m_e with charges respectively Ze and e, interacting through a potential

$$V(r) = -\frac{Ze'^2}{r}$$

where r represents the relative distance between the point particles.

Clearly this is a two-particle problem. We reduce it to a one-particle problem introducing the reduced mass

$$\mu = \frac{m_N m_e}{m_N + m_e}$$

The Hamiltonian describing the internal motion is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze'^2}{r}$$

We recognize this to be a central force problem and use spherical coordinates. We look for wave functions $\psi(r,\theta,\phi)$ satisfying

$$\hat{H}\psi = E\psi$$

Considering our previous results (7.98) we factor ψ as

$$\psi_{E\ell m}(r,\theta,\phi) = R_{E\ell}(r)\, Y_\ell^m(\theta,\phi)$$

where the radial functions $R_{E\ell}(r)$ should satisfy

$$-\frac{\hbar^2}{2\mu}\left(R'' + \frac{2}{r}R'\right) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}R + \left(-\frac{Ze'^2}{r} - E\right)R = 0$$

Multiplying by $-2\mu/\hbar^2$ we have

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

By defining the quantity

$$a \equiv \frac{\hbar^2}{\mu e'^2}$$

we rewrite

$$R'' + \frac{2}{r}R' + \left[\frac{2E}{a e'^2} + \frac{2Z}{ar} - \frac{\ell(\ell+1)}{r^2}\right]R = 0$$

Note that a has dimensions of length.

For $m_N \to \infty$ and $\mu \to m_e$ we have the Bohr radius

$$a_0 \equiv \frac{\hbar^2}{m_e e'^2} = 0,52918\ \text{Å}$$

It is possible to prove that for all $E \geq 0$ we have allowable solutions to the radial equation corresponding to ionized states.

For $E < 0$, it is possible to prove that we only have nontrivial solutions corresponding to

$$E = -\frac{Z^2}{n^2}\left(\frac{e^2}{2a}\right) = -\frac{Z^2 \mu e^4}{2n^2\hbar^2}$$

with $n = 1, 2, 3, \ldots$ and $n > l$. Note that E does not depend on l and we have further degeneracy. The radial functions depend on E and l. Since for bound states $n \leftrightarrow E$ we write

$$R_{nl} = R_{nl}(r) \quad , \quad \begin{array}{l} n = 1, 2, 3, \ldots \\ l = 0, 1, 2, \ldots, n-1 \end{array}$$

It is also possible to prove that, for $E < 0$, corresponding to bound states the radial wave functions are

$$R_{nl}(r) = r^l e^{-\frac{Zr}{na}} \sum_{j=0}^{n-l-1} b_j r^j$$

with

$$b_{j+1} = \frac{2Z}{na} \frac{j+l+1-n}{(j+1)(j+2l+2)} b_j$$

So the complete hydrogenlike bound-state wave functions read

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi)$$

$$= R_{nl}(r)\, S_{lm}(\theta)\, \frac{1}{\sqrt{2\pi}}\, e^{im\phi}$$

Examples of solutions

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} \qquad (n=1,\ l=0,\ m=0)$$

In chemistry notation we use the notations

	s	p	d	f	g	h	i	k
l	0	1	2	3	4	5	6	7

which comes from spectroscopy (sharp, principal, difuse, fundamental)

So we have $\psi_{1s} = \psi_{100}$

$$\psi_{2s} = \psi_{200} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{2a}\right)^{3/2} \left(1 - \frac{Zr}{2a}\right) e^{-Zr/2a}$$

More examples in pg 145 of Ira Levine

Real Hydrogenlike Functions

In chemistry it is common to work with real hydrogenlike functions which can be obtained as linear combinations from $\psi_{n\ell m}$.

For $n=2$:

$$\left.\begin{aligned} \psi_{2p_{-1}} &= \psi_{21-1} \\ \psi_{2p_0} &= \psi_{210} \\ \psi_{2p_1} &= \psi_{211} \end{aligned}\right\} \longrightarrow \left\{\begin{aligned} \psi_{2p_x} &\equiv \frac{1}{\sqrt{2}}\left(\psi_{2p_{-1}} + \psi_{2p_1}\right) \\ \psi_{2p_y} &= \frac{-i}{\sqrt{2}}\left(\psi_{2p_1} - \psi_{2p_{-1}}\right) \\ \psi_{2p_z} &= \psi_{2p_0} \end{aligned}\right.$$

$$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} r\, e^{-Zr/2a} \sin\theta \cos\phi$$

$$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} e^{-Zr/2a}\, x$$

$$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} r\, e^{-Zr/2a} \sin\theta \sin\phi$$

$$= \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} e^{-Zr/2a}\, y$$