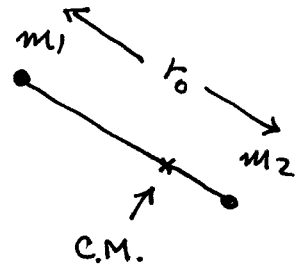
First example of a <u>central force problem</u>: The <u>rigid rotor</u>.

Classically this consists of two masses constrained to be at a fixed distance r_0 from one another:



Reduced mass $\equiv$

$$M = \frac{m_1 m_2}{m_1 + m_2}.$$

Moment of inertia $I = Mr_0^2$. It's an example of central force motion because the constraint $r = r_0$ can be thought of as due to a sharply confining potential centered at $r = r_0$. The classical energy is

$$E = \frac{L^2}{2I} = \frac{L^2}{2Mr_0^2}.$$

It is the same as the centrifugal potential. ~~since the~~ This is logical since the centrif. "potential" is really the angular part of the kinetic energy, which is all there is for a rigid rotor.

The classical configuration (apart from the center of mass degrees of freedom) is just the orientation of the rotor, specific by angles (θ, ϕ). This suggests that the quantum wave fn. should be $\psi(\theta, \phi)$ (with no r-dependence). And since the energy is $L^2/2I$, we guess the quantum Hamiltonian should be

$$H = \frac{L^2}{2I}$$

with eigenvalues $E_\ell = \dfrac{\ell(\ell+1)\hbar^2}{2I} = \dfrac{\ell(\ell+1)\hbar^2}{2Mr_0^2}$.

The eigenfunctions are $Y_{\ell m}(\theta, \phi)$, and are $(2\ell+1)$-fold

degenerate (because of m).

Rigid bodies are an idealization that doesn't exist in nature, but diatomic molecules exsist and have many similar features. Consider for example CO. The masses are $m_C \approx 12 m_H$, $m_O \approx 16 m_H$, m_H = mass of hydrogen $\approx 1800\, m$, m = electron mass. Then

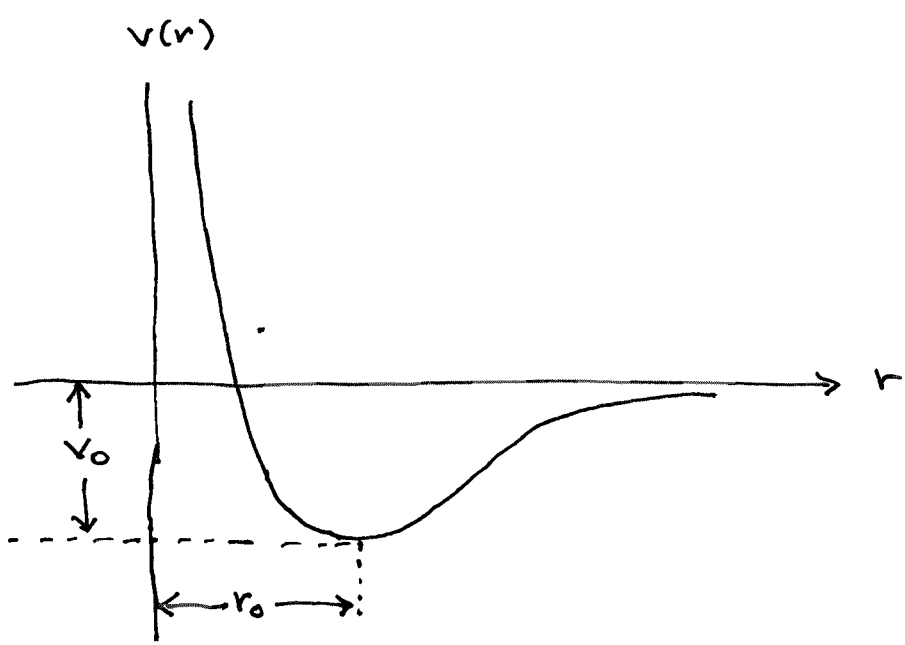
$$M = \text{reduced mass} \approx 7 m_H \approx 10^4\, m,$$

very roughly. This makes some small parameters:

$$\left.\begin{aligned} \frac{m}{M} &= 10^{-4} \\ \sqrt{\frac{m}{M}} &= 10^{-2} \\ \left(\frac{m}{M}\right)^{1/4} &= 10^{-1} \end{aligned}\right\}$$

Very roughly these values apply for most diatomic molecules.

The diatomic molecule is a central force problem because the atoms interact by means of a potential $V(r)$. It has the general shape:



Parameters are the well depth V_0 and radius r_0 at the minimum.

For CO,

$$\left.\begin{aligned} V_0 &= 11\ \text{eV} \\ r_0 &= 1.1\ \text{Å} \end{aligned}\right\}.$$

The force is attractive at large distance because the atoms induce dipole moments in each other and the dipole-dipole force is attractive. It is electrostatic. At short distances the force is repulsive because when you try to force both electron clouds of both atoms into the same region of space, the Pauli principle forces the electrons to go into higher energy states. It is effectively the pressure of a degenerate electron gas that pushes the atoms apart.

There is no simple analytic form for $V(r)$, so we will rely on order-of-magnitude estimates that follow from dimensional analysis.

The basic fact we rely on is that the force between the atoms is determined by the dynamics of the electron clouds. There are only three fundamental constants that enter into the electron dynamics: $m, e, \hbar$. The speed of light c is not on the list because the interaction is electrostatic and the motion nonrelativistic.

From $e, m, \hbar$ it is possible to construct a <u>unique</u> distance, energy, time, etc. Denoting these with a 0-subscript, the quantities are:

distance: $a_0 = \dfrac{\hbar^2}{me^2} = 0.5\ \text{Å}$

energy: $K_0 = \dfrac{me^4}{\hbar^2} = 27\ \text{ev}$

velocity: $v_0 = \dfrac{e^2}{\hbar} = \dfrac{e^2}{\hbar c} c = \alpha c = \dfrac{1}{137} c$

frequency: $\omega_0 = \dfrac{me^4}{\hbar^3} = K_0/\hbar$

Time: $T_0 = \hbar^3/me^4 = \dfrac{1}{\omega_0}$

These are exactly the same units of distance, energy etc. that appear in the hydrogen atom, and for the same reason: the only physical constants we have to work with are $e, m, \hbar$. For example, a_0 is the Bohr radius and K_0 is twice the ionization energy of hydrogen (2×13.6 ev). Notice v_0: it is the velocity of the electron in the ground state of hydrogen. Although fast, it is still nonrelativistic ($v_0 < 1\%\, c$). As claimed, the electrons are nonrelativistic.

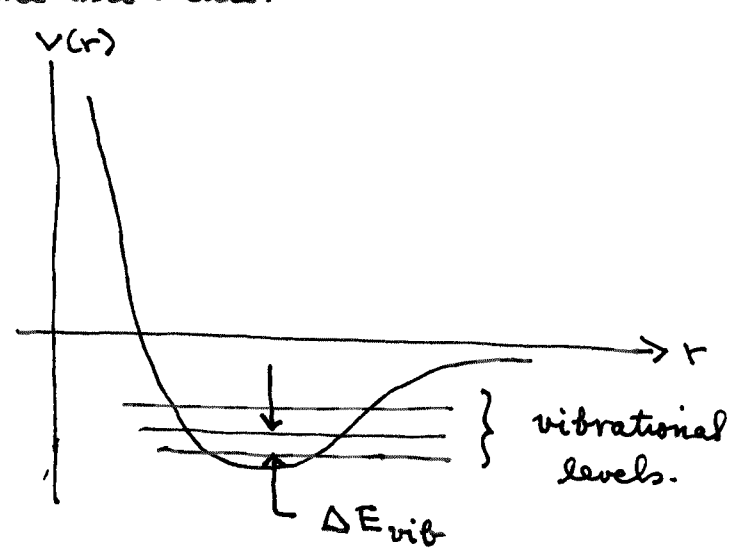
Returning to the CO potential $V(r)$, the well depth V_0 should be of the same order of magnitude as K_0; in fact, it is about 40%. Also, r_0 should be of the same order of magnitude as a_0; in fact, it's a little more than $2\times$ as big. For an order of magnitude estimate, the agreement is not bad.

To return to our potential, the radial Sch. eqn. is

$$-\frac{\hbar^2}{2M}\frac{d^2 f}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2Mr^2} + V(r)\right] f = Ef.$$

At first we take $l=0$, so we get a 1D Sch. eqn with potential $V(r)$. Since this is a well we expect bound states, which physically are the quantized vibrations of the molecule.

The well can be approximated near the bottom by a H.O. potential, presumably only a good approximation for small quantum numbers.



$$V(r) \approx \tfrac{1}{2} M \omega_v^2 (r-r_0)^2$$

where ω_v = freq. of vibrations (M = reduced mass of CO).

We can estimate ω_v by supposing that when $r-r_0 \sim r_0 \sim a_0$, then $\frac{1}{2} M \omega_v^2 (r-r_0)^2 \sim V_0 \sim K_0$. Ignoring all numerical factors, this gives

$$M \omega_v^2 a_0^2 = K_0$$

or $$\omega_v = \frac{1}{a_0}\sqrt{\frac{K_0}{M}} \quad \text{or} \quad \boxed{\omega_v = \sqrt{\frac{m}{M}}\,\omega_0}$$

The vibrational frequency is $\approx 100\times$ smaller than the frequency of electronic motion. Translated into energies $\hbar\omega_0$ and $\hbar\omega_v$, it means that photons emitted or absorbed in vibrational transitions are about $100\times$ lower in energy than those in electronic transitions. The latter are in the optical-UV range, so vibrational transitions take place in the near to mid infrared.

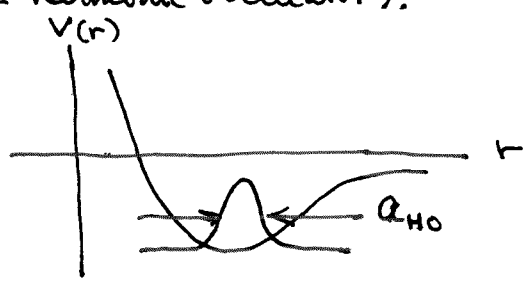
We can estimate the number of vibrational states by taking the ratio,

$$N_{vib} = \frac{K_0}{\hbar\omega_v} = \frac{K_0}{\sqrt{\frac{m}{M}}\,\hbar\omega_0} = \sqrt{\frac{M}{m}} = 100.$$

This is roughly the value for many diatomic molecules.

In the vibrational ground state the wave function is a Gaussian of some width a_{HO} (HO = harmonic oscillator).

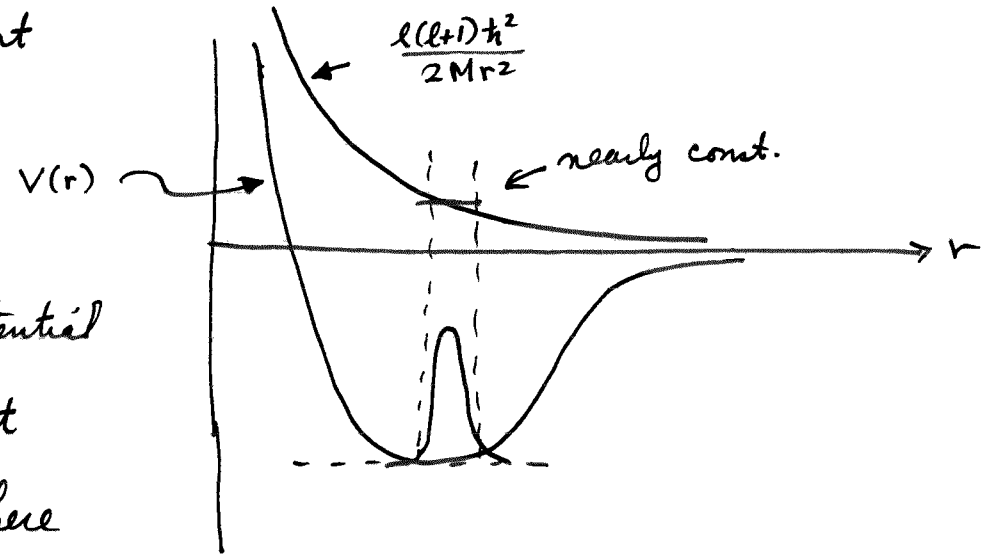
$$a_{HO} = \sqrt{\frac{\hbar}{M\omega_v}} = \left(\frac{m}{M}\right)^{1/4} a_0 \approx 10\%\ a_0.$$



In the ground state, the wave function occupies roughly 10% of a bond length. The molecule does behave like a rigid rotor at least approximately, because the interatomic separation lies in a narrow range near r_0.

To account for the case $l \neq 0$, we must include

the centrifugal potential. But since the wave fn occupies only a small part of the r-axis near r_0, the centrifugal potential is nearly constant over the region where the wave fn. is nonzero, and we can just replace r by r_0 in the centrif. pot:



$$\frac{\ell(\ell+1)\hbar^2}{2Mr^2} \longrightarrow \frac{\ell(\ell+1)\hbar^2}{2Mr_0^2} = \frac{\ell(\ell+1)\hbar^2}{2I},$$

where I is the moment of inertia in the equilibrium posn. This approx. is not as good when n and ℓ get large. Thus the Sch. equ. becomes

$$-\frac{\hbar^2}{2M}\frac{d^2f}{dr^2} + \left[\frac{\ell(\ell+1)\hbar^2}{2I} + \frac{1}{2}M\omega^2(r-r_0)^2\right]f = Ef.$$

It's a H.O. Hamiltonian w. shifted origin and a const. term (the centrif. pot.) added. The energy eigenvalues are immediate:

$$E_{n\ell} = (n+\tfrac{1}{2})\hbar\omega + \frac{\ell(\ell+1)\hbar^2}{2I}.$$

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They depend on (nl), as expected for generic radial potentials.

Let's examine the spacing betw. rotational energy levels. Define ΔE_{rot} as spacing betw. $l=0$ and $l=1$ levels:

$$\Delta E_{rot} = \frac{\hbar^2}{2I} \sim \frac{\hbar^2}{Ma_0^2} = \frac{m}{M} K_0 \sim \frac{1}{10000} K_0 .$$

This is 1/100 times smaller than ΔE_{vib}.

So we have 3 energy scales:

K_0:	electronic, dissociation	optical
$\Delta E_{vib} \sim \sqrt{\frac{m}{M}} K_0$:	vibrations	near-mid IR
$\Delta E_{rot} \sim \frac{m}{M} K_0$	rotations	far IR – μ-wave.

Greenhouse gases absorb IR radiation from the earth by making vibrational transitions. O_2 and N_2 don't do this because being homonuclear they have no dipole moment, hence do not have electric dipole transitions.

The above is the basic set of facts about the spectra of diatomic molecules. The more sophisticated theory is called the <u>Born-Oppenheimer</u> approximation.