First example of a central force problem: The rigid rotor.

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

\[
\text{Reduced mass } M = \frac{m_1 m_2}{m_1 + m_2}.
\]

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. This is logical since the centrifugal "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, specified by angles $(\theta, \phi)$. This suggests that the quantum wave function 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 $E_n = \frac{n(n+1)\hbar^2}{2I} = \frac{n(n+1)\hbar^2}{2Mr_0^2}$.

The eigenfunctions are $Y_n(\theta, \phi)$, and are $(2n+1)$-fold.
Rigid bodies are an idealization that doesn't exist in nature, but diatomic molecules exist and have many similar features. Consider for example CO. The masses are \( m_c \approx 12m_H \), \( m_0 \approx 16m_H \), \( m_H = \text{mass of hydrogen} \approx 1800m \), \( m = \text{electron mass} \). Then

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

very roughly. This makes some small parameters:

\[
\begin{align*}
\frac{m}{M} &= 10^{-4} \\
\sqrt{\frac{m}{M}} &= 10^{-2} \\
\left( \frac{m}{M} \right)^{1/4} &= 10^{-1}
\end{align*}
\]

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:

\[
V(r)
\]

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

For CO,

\[
\begin{align*}
V_0 &= 11\text{ eV} \\
r_0 &= 1.1\text{ Å}
\end{align*}
\]
The force is attractive at large distance because the atoms induce dipoles 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 unique distance, energy, time, etc. Denoting these with a 0-subscript, the quantities are:

- Distance: $a_0 = \frac{\hbar^2}{me^2} = 0.5 \text{ Å}$
- Energy: $\kappa_0 = \frac{me^4}{\hbar^2} = 27 \text{ ev}$
- Velocity: $v_0 = \frac{e^2}{\hbar} = \frac{e^2}{\hbar c} = \alpha c = \frac{1}{137} c$
- Frequency: $\omega_0 = \frac{me^4}{\hbar^3} = \kappa_0 / \hbar$
- Time: $T_0 = \frac{\hbar^3}{me^4} = \frac{1}{\omega_0}$
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 $e, \frac{\hbar}{r}, m$. For example, $a_0$ is the Bohr radius and $k_0$ is twice the ionization energy of hydrogen ($2 \times 13.6 \text{ ev}$). 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, $V_0$ should be of the same order of magnitude as $a_0$; in fact, it's a little more than $2 \times a_0$. For an order of magnitude estimate, the agreement is not bad.

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

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

At first we take $\ell = 0$, so we get a 1D Sch. equ. 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.
\[ V(r) \approx \frac{1}{2} M \omega_v^2 (r - r_0)^2 \]

where \( \omega_v \) = freq. of vibrations \( (M = \text{reduced mass of CO}) \).

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

\[
M \omega_v^2 a_0^2 = K_0
\]

or

\[
\omega_v = \frac{1}{a_0} \sqrt{\frac{K_0}{M}} \quad \text{or} \quad \omega_v = \sqrt{\frac{m}{M}} \omega_0
\]

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,

\[
N_{iv} = \frac{K_0}{\hbar \omega_v} = \frac{K_0}{\sqrt{\frac{m}{M} \hbar \omega_0}} = \sqrt{\frac{M}{m}} = 100.
\]

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).

\[
a_{HO} = \sqrt{\frac{\hbar}{M \omega_v}} = \left( \frac{m^{1/2} \hbar}{M} \right)^{1/2} a_0 \approx 10\% a_0.
\]
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 function occupies only a small part of the r-axis near \( r_0 \),
the centrifugal potential is nearly constant over the region where the wave function is nonzero, and we can just replace \( r \) by \( r_0 \) in the centrifugal potential:

\[
\frac{\ell (\ell+1) \hbar^2}{2Mr^2} \rightarrow \frac{\ell (\ell+1) \hbar^2}{2Mr_0^2} = \frac{\ell (\ell+1) \hbar^2}{2I},
\]

where \( I \) is the moment of inertia of the equilibrium point. This approach is not as good when \( n \) and \( \ell \) get large. Thus the Schrödinger equation 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 with shifted origin and a constant term (the centrifugal potential) added. The energy eigenvalues are immediate:

\[
E_{\text{ne}} = (n + \frac{1}{2}) \hbar \omega + \frac{\ell (\ell+1) \hbar^2}{2I}.
\]
They depend on \((nl)\), as expected for generic radial potentials.

Let's examine the spacing between rotational energy levels. Define \(\Delta E_{\text{rot}}\) as spacing between \(l=0\) and \(l=1\) levels:

\[
\Delta E_{\text{rot}} = \frac{\hbar^2}{2I} \sim \frac{\hbar^2}{MA_0^2} = \frac{m}{M} K_0 \sim \frac{1}{10000} K_0.
\]

This is \(1/100\) times smaller than \(\Delta E_{\text{ vib}}\).

So we have 3 energy scales:

\(K_0\): electronic, dissociation

\(\Delta E_{\text{ vib}} \sim \sqrt{\frac{m}{M}} K_0\): vibrations

non-mid IR

\(\Delta E_{\text{ rot}} \sim \frac{m}{M} K_0\): rotations

far IR - \(\mu\)-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 Born-Oppenheimer approximation.