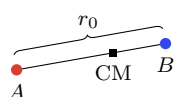


Week 4

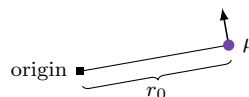
The Hydrogen Atom and Angular Momentum

4.1 Rotational Motion

- 10/18: • Consider the diatomic molecule AB at a distance r_0 apart rotating about its center of mass.



(a) Diatomic.



(b) An equivalent system.

Figure 4.1: Diatomic rotation.

- To simplify the problem, replace the two particles rotating about the center of mass with one particle of reduced mass μ rotating about the center of mass with lever arm r_0 .
- Classically, the kinetic energy of the translational motion is

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

where $I = \mu r_0^2$ and $L = p \times r_0 = pr_0$ (for this kind of rotation; see Figure 4.1b).

- To further talk about this problem, we should introduce **spherical coordinates**.
- **Spherical coordinates:** The coordinate system (r, θ, ϕ) related to the Cartesian coordinates (x, y, z) by

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

- Classically, we will have

$$H = \frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z)$$

in Cartesian coordinates.

- In spherical coordinates, this becomes

$$H = \frac{1}{2\mu} \left(p_r^2 + \frac{L^2}{r^2} \right) + V(r)$$

- Thus, in quantum mechanics, we get

$$\begin{aligned}\hat{H} &= \frac{1}{2\mu}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + V(x, y, z) \\ &= \frac{1}{2\mu} \left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \right) + V(r)\end{aligned}$$

- Thus, we have in spherical coordinates that

$$\hat{T}\psi = -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \psi \right) + \frac{1}{r^2 \sin \theta} \left(\frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \psi \right) \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \psi \right]$$

- 2D rigid rotor:

- Let the system from Figure 4.1b be confined to rotating in two dimensions.
- This simplifies the problem since both the $\partial/\partial r$ and $\partial/\partial \theta$ terms in the kinetic energy operator disappear (since, respectively, the particle is at a fixed distance from the center of mass and it cannot move out of the 2D plane).
- Thus, our Schrödinger equation for this system is

$$-\frac{\hbar^2}{2\mu r_0^2} \frac{\partial^2}{\partial \phi^2} \psi(\phi) = E\psi(\phi)$$

- Solution: Let $\psi(\phi) = e^{im\phi}$; then

$$E_m = \frac{\hbar^2 m^2}{2\mu r_0^2}$$

- $m = 0, 1, 2, \dots$ is a new quantum number.
 - m doesn't go to infinity because $|m|$ is bounded by ℓ (the total angular momentum).
- Remembering our original restriction, we have that this math describes the system from Figure 4.1a but confined to rotate in the xy plane with angular momentum in the z direction.
 - Thus, for example, the energies of the system from Figure 4.1a are dependent on m and $I = \mu r_0^2$.
- Such a system occurs in physical reality when we put the diatomic in an external field, or attach to it a big functional group.
- Zero point energy: $m = 0$ does not violate the UR since we still have $\Delta L \Delta \theta \geq \hbar/2$ (as everything is still rotating in the sense that we have equal probability of the particle being everywhere [as opposed to more localized/normal rotation with higher values of m]).

- 3D rigid rotor:

- Assume that the potential energy is zero on the surface of the sphere (so we basically have a particle on a sphere).
- Then

$$\hat{H} = \frac{\hat{L}^2}{2\mu r_0^2} = \frac{\hat{L}^2}{2I}$$

- Solving $\hat{H}\psi = E\psi$ asserts that the eigenfunctions of the Hamiltonian are the spherical harmonics $Y_{\ell m}(\theta, \phi)$.
- Energy:

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

where $\ell = 0, 1, 2, \dots$

- Recall that m corresponds to the projection of angular momentum onto the z -axis, so that

$$m = -\ell, \dots, +\ell$$

4.2 Hydrogen Atom

10/20:

- Microwaves (for food) excite the rotational motion of water molecules.
- Spherical harmonics: The solution of $\psi_{lm}(\theta, \phi) = Y_{lm}(\theta, \phi)$, where l, m are quantum numbers.
- $E_l = \hbar^2/2I \cdot l(l+1)$ for $l = 0, 1, 2, \dots$

- Form of the spherical harmonics:

$$Y(\theta, \phi) = P_{lm}(\cos \theta) e^{im\phi}$$

where $P_{lm}(\cos \theta)$ is a polynomial.

- The polynomials $P_{lm}(\cos \theta)$ are the associated Legendre polynomials.
- When $m = 0$, we have the Legendre polynomials.

- The differential equation describing these is

$$\frac{d}{dx} \left((1-x^2) \frac{d}{dx} P_l(x) + l(l+1) P_l(x) \right) = 0$$

- The Legendre polynomials converge very quickly to functions on $[-1, 1]$.
- People map these polynomials onto other domains, too, to solve a variety of problems.
- Legendre polynomials have more of their roots at the boundaries — since the boundary conditions are the most important part of solving a differential equation, it makes sense that accurate representations would sample near the boundary more.
- Examples:

$$P_0(x) = 1$$

$$P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$$

$$P_1(x) = x$$

$$P_3(x) = \frac{5}{2}x^3 - \frac{3}{2}x$$

- Consider HCl.

- For it,

$$\frac{\hbar^2}{2I} = 1.3 \times 10^{-3} \text{ eV}$$

- Rotational spectral lines may arise from different values of the quantum number l .
- The molecule vibrates in harmonic oscillation with spacings $\approx 0.1 \text{ eV}$ (it's not strictly rigid).
- Rovibrational spectra includes both forms of movement.
 - Very high precision.
 - Very big in the 90s.
- Electronic spectra: A few electron volts.

- The hydrogen atom.

- Two generalizations of the 3D rigid rotor combine to treat the hydrogen atom:
 1. An addition of the kinetic energy in the radial direction \hat{r} .
 2. An addition of the Coulomb potential.

- Schrödinger equation:

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

where

$$\begin{aligned}\hat{H} &= \frac{1}{2\mu} \left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \right) + V(r) \\ \hat{p}_r^2 &= -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \psi(r) \right) \\ V(r) &= -\frac{e(eZ)}{4\pi\epsilon_0 r}\end{aligned}$$

- Because the particle has spherical symmetry (that it, does not depend on θ or ϕ), the wave function is separable, that is, it may be written as a product

$$\psi(r, \theta, \phi) = R_n(r)Y_{lm}(\theta, \phi)$$

- Note that there is no analytic solution to the Schrödinger equation in Cartesian coordinates — we need spherical coordinates to take advantage of the spherical symmetry.
- Substitution into the Schrödinger equation yields

$$\left(\frac{1}{2\mu} \left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \right) + V(r) \right) R(r)Y(\theta, \phi) = ER(r)Y(\theta, \phi)$$

where μ is the reduced mass of the electron and the nucleus (which is approximately the mass of the electron).

- But since

$$\frac{1}{2\mu r^2} \hat{L}^2 Y_{lm}(\theta, \phi) = \frac{l(l+1)}{2\mu r^2} \hbar^2 Y_{lm}(\theta, \phi)$$

we have that

$$\frac{1}{2\mu} \left(\hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2} + V(r) \right) R_n(r) = E_n R_n(r)$$

- We have reduced the three-dimensional case of the hydrogen atom to a one-dimensional differential equation.

4.3 Hydrogen Atom (cont.)

10/22:

- We want to solve the SE $\hat{H}\psi_n = E\psi_n$ for the hydrogen atom.
- To exploit the spherical symmetry of the hydrogen atom, we use (r, θ, ϕ) .
- Thus, our Hamiltonian is equal to

$$\hat{H} = \frac{1}{2\mu} \left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2} \right) + V(r)$$

- Since V is just a function of r , the wave function is separable: $\psi(r, \theta, \phi) = R_n(r)Y_{lm}(\theta, \phi)$.
- “Whenever you have a separation of variables additively in the Hamiltonian, you have a separation of variables multiplicatively in the wave function.”

- Substitute the wave function into the Schrödinger equation:

$$\begin{aligned}\left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{\hat{L}^2}{r^2}\right) + V(r)\right) R_n(r) Y_{lm}(\theta, \phi) &= E R_n(r) Y_{lm}(\theta, \phi) \\ \left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2}\right) + V(r)\right) R_n(r) Y_{lm}(\theta, \phi) &= E R_n(r) Y_{lm}(\theta, \phi) \\ \left(\frac{1}{2\mu}\left(\hat{p}_r^2 + \frac{l(l+1)\hbar^2}{r^2}\right) + V(r)\right) R_n(r) &= E_{nl} R_n(r)\end{aligned}$$

- Noting that we only care about the behavior of the differential equation on $[0, \infty)$, specifically at really large distances, we perform an asymptotic analysis.

$$\lim_{r \rightarrow \infty} \left(\frac{1}{2\mu} \hat{p}_r^2\right) R(r) = E R(r)$$

- Plugging in the value of the momentum operator, we have that

$$\begin{aligned}-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} R(r) &= E R(r) \\ R(r) &= e^{-\alpha r}\end{aligned}$$

where $\alpha = i\hbar/\sqrt{2\mu E}$.

- But we want to multiply $e^{-\alpha r}$ by some type of polynomial. Namely, **Laguerre polynomials**.

- These polynomials may be found by expanding a power series.
- Let

$$L\left(\frac{\alpha r}{n}\right) = \sum_{j=0}^{\infty} c_j \left(\frac{\alpha r}{n}\right)^j$$

- A recursion relation may be found.
- The quantization of energy in the hydrogen atom again arises from the truncation of the polynomials.
- Thus, the general solution of $R_{nl}(r)$ is

$$R_{nl}(r) = \left(\frac{\alpha r}{n}\right)^l L_{n+1, 2l+1}\left(\frac{\alpha r}{n}\right) e^{-\alpha r/2n}$$

- Energy levels:

$$E_n = -\frac{\mu}{2\hbar^2} \left(\frac{(Ze)e}{4\pi\epsilon}\right)^2 \frac{1}{n^2}$$

- These are the discrete energies of Bohr!
- But now we also have the electron's probability distributions, i.e., the ground state wave function is

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

- Thus, we can now take a look at the probabilities. *picture*

- The probability is

$$\text{Pr} = |\psi(r, \theta, \phi)|^2 r^2 \sin \theta$$

- The radial probability is

$$\text{Pr}(r) = r^2 |R_{nl}(r)|^2$$

- The radial probability peaks at a_0 , the **Bohr radius**.
 - Thus, the Bohr radius (the radius of the circular orbit of Bohr's hydrogen electron) is just the most probable distance from the nucleus!
- The average distance from the nucleus (the expectation value of r) is

$$\begin{aligned}\langle r \rangle &= \int_0^\infty \text{Pr}(r) r \, dr \\ &= \int_0^\infty \psi^*(r) r \psi(r) \, dr\end{aligned}$$

- Note we also find that $\langle \hat{H} \rangle = E$, so there is no uncertainty in the energy.
- Note that in some ways, quantum mechanics is more certain than classical mechanics since, for instance, in quantum we know the energy exactly.

4.4 Chapter 5: The Harmonic Oscillator and the Rigid Rotator — Two Spectroscopic Models

From McQuarrie and Simon (1997).

- 10/19:
- **Rigid-rotator model:** Two point masses m_1 and m_2 at fixed distances r_1 and r_2 from their center of mass.
 - Since the vibrational amplitude of a rotating molecule is small compared to its amplitude, this is a good model.
 - Kinetic energy of the rigid rotator:

$$\begin{aligned}K &= \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \\ &= \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega^2 \\ &= \frac{1}{2} I \omega^2\end{aligned}$$

- Note that

$$\begin{aligned}I &= m_1 r_1^2 + m_2 r_2^2 \\ &= \mu r^2\end{aligned}$$

(see Problem 5-29).

- It follows that we the two-body problem of the rigid rotator is equivalent to the one-body problem of a single body of mass μ rotating at a distance r from a fixed center.
- Since there are no external forces on the rigid rotator (we're not applying any electric or magnetic fields), the energy of the molecule is solely kinetic (i.e., there is no potential energy term in the Hamiltonian).
 - Thus, for a rigid rotator,

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2\mu} \nabla^2$$

- Since this particle has a natural center of spherical symmetry, we opt for spherical coordinates. However, this necessitates expressing ∇^2 as the following.

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)_{\theta, \phi} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right)_{r, \phi} + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right)_{r, \theta}$$

– See Problem ?? for a derivation.

- With respect to the rigid rotator, r is constant. Thus,

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ \bar{H} &= -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right] \\ \bar{L}^2 &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right]\end{aligned}$$

– Note that since both θ and ϕ are unitless, the units of angular momentum for quantum system are \hbar .

- Rigid-rotator wave functions are customarily denoted by $Y(\theta, \phi)$.
- In solving $\hat{H}Y(\theta, \phi) = EY(\theta, \phi)$, it will be useful to multiply the original Schrödinger equation by $\sin^2 \theta$ and let $\beta = 2IE/\hbar^2$ to obtain the partial differential equation

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} + (\beta \sin^2 \theta)Y = 0$$

- The solutions to the above equation are intimately linked to those for the hydrogen atom.
- Solving the above equation yields the condition that $\beta = J(J+1)$ for $J = 0, 1, 2, \dots$. Therefore,

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

for $J = 0, 1, 2, \dots$

■ Each energy level has a degeneracy $g_J = 2J + 1$ as well.

- Once again, electromagnetic radiation can cause a rigid rotator to undergo transitions from one state to another subject to the selection rules that only transitions between adjacent states are allowed and the molecule must possess a permanent dipole moment.
- As before, we can calculate

$$\Delta E = \frac{h^2}{4\pi^2 I} (J+1)$$

and the frequencies at which absorption transitions occur are

$$\nu = \frac{h}{4\pi^2 I} (J+1)$$

for $J = 0, 1, 2, \dots$

- It follows from reduced mass, bond length, and moment of inertia data that the frequencies typically lie in the microwave region.
- **Microwave spectroscopy:** The direct study of rotational transitions.
- **Rotational constant** (of a molecule): The following quantity. *Given by*

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

- We often write the absorption frequencies as $\nu = 2B(J + 1)$.
- The spacing of lines in a microwave spectrum is $2B$.
- Like IR spectroscopy can be used to determine the force constants of molecular attractions in diatomics, microwave spectroscopy can be used to determine the bond lengths of diatomics.

Problems

5-29. Show that the moment of inertia for a rigid rotator can be written as $I = \mu r^2$ where $r = r_1 + r_2$ (the fixed separation of the two masses) and μ is the reduced mass.

Answer. First, note that $m_1 r_1 = m_2 r_2$ for such a rotation about the center of mass. Then

$$\begin{aligned} I &= \mu r^2 \\ &= \frac{m_1 m_2}{m_1 + m_2} (r_1 + r_2)^2 \\ &= \frac{m_1 m_2 r_1}{m_1 r_1 + m_2 r_1} (r_1 + r_2)^2 \\ &= \frac{m_1 m_2 r_1}{m_2 r_2 + m_2 r_1} (r_1 + r_2)^2 \\ &= \frac{m_1 r_1}{r_2 + r_1} (r_1 + r_2)^2 \\ &= m_1 r_1 (r_1 + r_2) \\ &= m_1 r_1^2 + m_1 r_1 r_2 \\ &= m_1 r_1^2 + m_2 r_2^2 \end{aligned}$$

as desired. □