Week 3

Vibrational Motion and the Harmonic Oscillator

3.1 Vibrational Motion and the Harmonic Oscillator

10/11:
- Suppose we have an attractive force F proportional to the displacement x from the center of a system
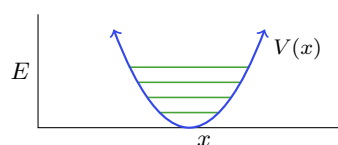
$$F = -kx$$

  - Then we also have an associated potential energy
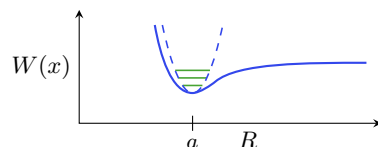
$$V(x) = \frac{1}{2}kx^2$$

  - Recall that $F = -\partial V/\partial x$.

- Thus, we have a harmonic (or parabolic) potential well.

(a) Harmonic (parabolic) well.   (b) Approximating a potential well.

Figure 3.1: Parabolic potential wells.

  - However, because this is a quantum system, the attainable energy levels will be quantized (see Figure 3.1a).
  - We can use a parabolic well to approximate the minimum of the potential well (see Figure 3.1b).

- **Reduced mass**: For two objects of mass m_A, m_B, the quantity

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

  - We can map the two body problem of two atoms being drawn together and pulled apart onto the one body problem of a single harmonic oscillator of reduced mass μ at the center of mass of the diatomic system.

- The Taylor series expansion of the Moiré Potential about $x = a$ where a is the minimum potential:

$$W(x) = W(a) + (x-a)W'(a) + \frac{1}{2!}(x-a)^2 W''(a) + \cdots$$
$$= W(a) + \frac{1}{2}(x-a)^2 W''(a)$$
$$= \frac{1}{2}kx^2$$

  - We reduce by noting that $W'(a) = 0$ at the minimum of the potential well, we can let $W(a) = 0$, we can set $a = 0$ to be the origin of our coordinate system, and we can let $k = W''(a)$.

- The Schrödinger equation describing this system is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) + \frac{1}{2}m\omega^2 x^2 \psi(x) = E\psi(x)$$

  - Note that since $\omega = \sqrt{k/m}$, we substituted $k = m\omega^2$.

- If we let $x = y\sqrt{\hbar/m\omega}$ and $E = \omega\hbar\epsilon/2$, then we can simplify the above to the form

$$\frac{\mathrm{d}^2}{\mathrm{d}y^2}\psi(y) + (\epsilon - y^2)\psi(y) = 0$$

- Asymptotic solution: In the limit of large y, the finite value of ϵ becomes negligible, that is

$$\frac{\mathrm{d}^2}{\mathrm{d}y^2}\psi(y) - y^2\psi(y) = 0$$

- General form solution:

$$\psi(y) = y^p e^{-y^2/2}$$

  - This is the Gaussian exponential.
  - p is any integer.

- Because the sign of the exponential must be negative for the wave function to be bounded, we have the form
$$\psi(y) = e^{-y^2/2}H(y)$$
where $H(y)$ are polynomials.

- Hermite equation:

$$\frac{\mathrm{d}^2}{\mathrm{d}y^2}H(y) - 2y\frac{\mathrm{d}}{\mathrm{d}y}H(y) - (\epsilon - 1)H(y) = 0$$

  - Whenever $H(y)$ solves this equation, it yields a full solution.

- What are the correct polynomials?

  - The polynomials that are even about the origin will give us the even solutions, and vice versa for the odd ones.
  - Even solution: Because the potential has a definite parity (even-ness or odd-ness), we know that the solution to the polynomials must be even or odd.
  - Expanding in an infinite power series:

$$H(y) = \sum_{j=0}^{\infty} c_j y^{2j}$$

- This is the power series solution to differential equations. We have to plug into the differential equation and get a recursion relation.

    - Upon substitution,

$$\sum_{j=0}^{\infty} \left(2j(2j-1)c_j y^{2j-2} + (\epsilon - 1 - 4j)c_j y^{2j}\right) = 0$$

    - The indices are arbitrary, so

$$\sum_{j=0}^{\infty} (2(j+1)(2j+1)c_{j+1} + (\epsilon - 1 - 4j))y^{2j} = 0$$

    - Recursion relation: The whole coefficient above must equal 0 for all j, but that gives us a relationship between c_j and c_{j+1}! Explicitly,

$$c_{j+1} = \frac{4j + 1 - \epsilon}{2(j+1)(2j+1)} c_j$$

- How do we know when to stop?

    - If the recursion never stops, then the ratio is approximately equal to

$$\frac{c_{j+1}}{c_j} = \frac{1}{j}$$

    - But this means that asymptotically, the boundary conditions will be violated because it will keep expanding. The probability of finding the particle will actually diverge (infinite probability at infinite distances). Thus, the expansion procedure *must* terminate.

    - The truncation of this expansion requires us to pick a particular energy ϵ (in particular, one such that $\epsilon = 4j + 1$).

- Test on Friday:

    - 5 questions. Each question is approximately 20 points.

    - There will be a formula page in the back with formulas and constants.

    - There will be a periodic table provided.

    - Topics: Everything in problem sets 1-2. BB radiation, Photoelectric effect, SG experiment, particle-wave duality, Heisenberg uncertainty relations, Gaussian wave packets and their role in the Heisenberg uncertainty, de Broglie formula, free particles, particle in a box, potential step, and a bit of the harmonic oscillator.

    - Study for it by going back to the problem sets and seeing which ones might be doable in a 50 minute test.

    - Go back to your notes and review some of the key highlights of each of the topics in the topic list.

    - You're allowed to use a calculator. The test won't be too calculator-heavy though.

    - Deriving vs. understanding and applying: Emphasis on applying and getting answers.

3.2   Harmonic Oscillator (cont.)

10/13:
- Assume that the $(n+1)^{\text{th}}$ coefficient vanishes by the recurrence relation; this causes the energy to be quantized.

    - Therefore, $\epsilon = 4n + 1$.

- For each value of n, there is an even Hermite polynomial[1].

  - Thus, our even solutions include $H_0(y) = 1$, $H_2(y) = 4y^2 - 2$, $H_4(y) = 16y^4 - 48y^2 - 2$, for example.

- Odd solutions:

  - Let

$$H(y) = \sum_{j=0}^{\infty} d_j y^{2j+1}$$

  - Our recurrence relation works out to be

$$d_{j+1} = \frac{4j + 3 - \epsilon}{2(j+1)(2j+3)} d_j$$

  - Again, if it does not terminate, $d_{j+1}/d_j \approx 1/j$, so the solutions will blow up at the edges due to the high powers of y. Therefore, the series must truncate.
  - If the coefficient at n exists but the next one will vanish, it must be true that $4n + 3 = \epsilon$.
  - Example odd solutions: $H_1(y) = 2y$, $H_3(y) = 8y^3 - 12y$, $H_5(y) = 32y^5 - 160y^3 + 120y$.
    - ■ Note that you can make the coefficients pretty much of any scale because they will be normalized later as part of the wave function.

- Energies and wave functions:

  - The energy levels are $\epsilon_n = 2n + 1$ for $n = 0, 1, 2, \dots$ or $E_n = (n + \frac{1}{2})\hbar\omega$ for $n = 0, 1, 2, \dots$.
  - It follows that if $\psi(y) = N_y e^{-y^2/2} H_n(y)$, where

$$N_y = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}}$$

  - In terms of x, we get

$$N_x = \sqrt[4]{\frac{\omega m}{\hbar}} N_y$$

  - Observations:
    1. The energy levels are quantized (discrete).
    2. The energy levels are equally spaced apart where $\Delta E = h\nu$.
    3. The energy levels are non-degenerate.
    4. The zero-point energy is equal to $\hbar\omega/2$. (Recall that the finite energy is there due to the Uncertainty Relation.)
    5. Similar to the levels discovered by Max Planck.

- Classical harmonic oscillator:

  - Position: $x = x_0 \sin(\omega t)$.
  - Velocity: $v = \cos x_0 \sin(\omega t)$.
  - Energy: $E = m\omega^2 x_0^2/2$.
  - Turning point: $x_0 = \sqrt{2E/m\omega^2}$.
  - Probability of the oscillator being at x:

$$P(x)\, dx = \frac{\frac{2dx}{v}}{T} = \frac{dx}{\pi\sqrt{x_0^2 - x^2}}$$

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[1]So named because they were studied by the mathematician Charles Hermite before they were utilized in Quantum Mechanics.

- Thus, classically, the oscillator spends most of its time at the turning points (this makes intuitive sense because a pendulum slows down at the turning points, spending more time there).
- In quantum mechanics, we don't have a hard turning point the way we do classically.
- Classical limit of quantum theory: In higher and higher order Hermite polynomials, the probability gets pushed to the edges.

3.3 Chapter 4: Some Postulates and General Principles of Quantum Mechanics

From McQuarrie and Simon (1997).

10/19:
- **Dynamical variable**: A quantity dealt with by classical mechanics, e.g., position, momentum, angular momentum, and energy.

- **Observable**: A measurable dynamical variable.

- "The classical-mechanical state of a particle at any particular time is specified completely by the three position coordinates (x, y, z) and the three momenta (p_x, p_y, p_z) or velocities (v_x, v_y, v_z) at that time. The time evolution of the system is governed by Netwon's equation" $F = ma$ applied separately in each dimension (McQuarrie & Simon, 1997, p. 115).

- **Trajectory** (of a classical particle): The three-dimensional path of the particle described by the initial conditions and Newton's laws.

    - A particle's trajectory completely describes its state.

- However, since the Uncertainty Principle decrees that we cannot specify the position and momentum of a *microscopic*[2] particle to any desired precision, we have our first postulate of quantum mechanics.

    Postulate 1. *The state of a quantum-mechanical system is completely specified by a function $\psi(x)$ that depends upon the coordinate of the particle. All possible information about the system can be derived from $\psi(x)$. This function, called the wave function or the state function, has the important property that $\psi^*(x)\psi(x)\,\mathrm{d}x$ is the probability that the particle lies in the interval $\mathrm{d}x$, located at the position x.*

    - We will use one-dimensional notation, but note that what is stated in the postulates is equally applicable to two or three dimensions.
    - "If there is more than one particle, say two, then $\psi^*(x_1, x_2)\psi(x_1, x_2)\,\mathrm{d}x_1\,\mathrm{d}x_2$ is the probability that particle 1 lies in the interval $\mathrm{d}x_1$ located at x_1, and that particle 2 lies in the interval $\mathrm{d}x_2$ located at x_2" (McQuarrie & Simon, 1997, p. 116).

- **Normalizable** (function): A function $\psi(x)$ for which the following integral converges.

$$\int_{\text{all space}} \psi^*(x)\psi(x)\,\mathrm{d}x$$

- **Well-behaved** (function): A function $\psi(x)$ such that it and its first derivative are single-valued, continuous, and finite.

- Every state function must be normalizable and well-behaved.

- We now formalize the notion that classical mechanical quantities have analogous linear operators in quantum mechanics.

    Postulate 2. *To every observable in classical mechanics, there corresponds a linear Hermitian operator in quantum mechanics.*

OBSERVABLE		OPERATOR	
Name	Symbol	Symbol	Operation
Position	x	$\hat{X}$	Multiply by x
	$\mathbf{r}$	$\hat{\mathbf{R}}$	Multiply by $\mathbf{r}$
Momentum	p_x	$\hat{P}_x$	$-i\hbar \dfrac{\partial}{\partial x}$
	$\mathbf{p}$	$\hat{\mathbf{P}}$	$-i\hbar \left(\mathbf{i} \dfrac{\partial}{\partial x} + \mathbf{j} \dfrac{\partial}{\partial y} + \mathbf{k} \dfrac{\partial}{\partial z} \right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\dfrac{\hbar^2}{2m} \dfrac{\partial^2}{\partial x^2}$
	K	$\hat{K}$	$-\dfrac{\hbar^2}{2m} \nabla^2$
Potential energy	$V(x)$	$\hat{V}(\hat{x})$	Multiply by $V(x)$
	$V(x,y,z)$	$\hat{V}(\hat{x},\hat{y},\hat{z})$	Multiply by $V(x,y,z)$
Total energy	E	$\hat{H}$	$-\dfrac{\hbar^2}{2m} \nabla^2 + V(x,y,z)$
Angular momentum	$L_x = yp_z - zp_y$	$\hat{L}_x$	$-i\hbar \left(y \dfrac{\partial}{\partial z} - z \dfrac{\partial}{\partial y} \right)$
	$L_y = zp_x - xp_z$	$\hat{L}_y$	$-i\hbar \left(z \dfrac{\partial}{\partial x} - x \dfrac{\partial}{\partial z} \right)$
	$L_z = xp_y - yp_x$	$\hat{L}_z$	$-i\hbar \left(x \dfrac{\partial}{\partial y} - y \dfrac{\partial}{\partial x} \right)$

Table 3.1: Classical-mechanical observables and their corresponding quantum-mechanical operators.

- – Note that we derive the expressions for L_x, L_y, L_z in Table 3.1 from $\mathbf{r} \times \mathbf{p}$.

- If an eigenvalue problem is two-fold degenerate with linearly independent solutions ϕ_1, ϕ_2, then any linear combination of ϕ_1, ϕ_2 is also a solution.

- Although each observable has a corresponding operator by Postulate 2, only eigenvalues of our operators are actually observable.

    Postulate 3. *In any measurement of the observable associated with the operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a_n, which satisfy the eigenvalue equation*

$$\hat{A}\psi_n = a_n\psi_n$$

- We now formally introduce the method for finding the average values of observables.

    Postulate 4. *If a system is in a state described by a normalized wave function ψ, then the average value of the observable corresponding to $\hat{A}$ is given by*

$$\langle a \rangle = \int_{all\ space} \psi^*(x)\hat{A}\psi(x)\,\mathrm{d}x$$

- Note that we can prove from Postulate 4 that σ for any observable is zero, i.e., that we *can* only observe the eigenvalues.

- We now postulate the time-dependent Schrödinger equation[3].

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[2]Note that classical mechanics still describes *macroscopic* bodies perfectly well.
[3]Note that just like Newton's laws, we cannot derive this — we can only show that data is consistent with it.

Postulate 5. *The wave function (or state function) of a system evolves in time according to the time-dependent Schrödinger equation*

$$\hat{H}\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}$$

- Relating the time-dependent and time-independent Schrödinger equations.

    - Consider a system where $\hat{H}$ does not explicitly contain time.
    - In such a case, we may use separation of variables and let

    $$\psi(x,t) = \psi(x)f(t)$$

    - Substituting in the above and dividing by $\psi(x)f(t)$ allows us to fully separate the variables:

    $$\hat{H}\psi(x)f(t) = i\hbar\frac{\mathrm{d}\psi(x)f(t)}{\mathrm{d}t}$$
    $$f(t)\hat{H}\psi(x) = i\hbar\psi(x)\frac{\mathrm{d}f(t)}{\mathrm{d}t}$$
    $$\frac{1}{\psi(x)}\hat{H}\psi(x) = \frac{i\hbar}{f(t)}\frac{\mathrm{d}f(t)}{\mathrm{d}t}$$

    - But if two functions of entirely different variables are equal, the individual functions must both be constant. If we let the constant they are both equal to be E, then we obtain

    $$\frac{1}{\psi(x)}\hat{H}\psi(x) = E \qquad\qquad\qquad \frac{i\hbar}{f(t)}\frac{\mathrm{d}f(t)}{\mathrm{d}t} = E$$
    $$\hat{H}\psi(x) = E\psi(x) \qquad\qquad\qquad \frac{\mathrm{d}f(t)}{\mathrm{d}t} = \frac{1}{-i^{-1}\hbar}Ef(t)$$
    $$= -\frac{i}{\hbar}Ef(t)$$
    $$f(t) = \mathrm{e}^{-iEt/\hbar}$$

    - The left equation above is the time-independent Schrödinger equation, and the right equation allows us to define the general form of a time-dependent wave function as follows.

    $$\psi(x,t) = \psi(x)f(t)$$
    $$= \psi(x)\mathrm{e}^{-iEt/\hbar}$$

- Note, however, that even the time-*dependent* Schrödinger equation gives stationary-state probability densities and averages:

$$\psi_n^*(x,t)\psi_n(x,t)\,\mathrm{d}x = \psi^*(x)\mathrm{e}^{iE_nt/\hbar}\psi_n(x)\mathrm{e}^{-iE_nt/\hbar}\,\mathrm{d}x$$
$$= \psi_n^*(x)\psi_n(x)\,\mathrm{d}x$$

- **Stationary-state** (wave function): The $\psi_n(x)$ in the above equation.

- It follows from postulate 3 that the eigenvalues of quantum mechanical operators must be real (not complex) if they are to, indeed, to be observable.

    - A consequence of this is that any two eigenfunctions $\psi_m(x), \psi_n(x)$ where $m \neq n$ of quantum-mechanical operators are **orthogonal**.

- **Orthogonal** (wave functions): Two wave functions $\psi_m(x), \psi_n(x)$ such that

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x) = 0$$

- **Orthonormal** (set of wave functions): A set of wave functions that are both normalized and mutually orthogonal.

  – In other words, a set $\psi_1, \ldots, \psi_n$ of wave functions is orthonormal iff

  $$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, \mathrm{d}x = \delta_{ij}$$

  for all $1 \leq i, j \leq n$.

- Note that if a quantum-mechanical operator $\hat{A}$ is to have real eigenvalues, it must satisfy the equation

  $$\int_{\text{all space}} f^*(x)\hat{A}g(x) \, \mathrm{d}x = \int_{\text{all space}} g(x)[\hat{A}f]^*(x) \, \mathrm{d}x$$

  where f, g are any two state functions.

  – McQuarrie and Simon (1997) does a worked example of applying the above equation to the momentum operator in the context of the solutions to the one-dimensional harmonic oscillator problem.

- **Hermitian** (operator): An operator that satisfies the previous equation.

- **Commutator** (of $\hat{A}, \hat{B}$): The operator defined as follows. *Denoted by* $[\hat{\boldsymbol{A}}, \hat{\boldsymbol{B}}]$. *Given by*

  $$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

  – We can show that $\hat{A}$ and $\hat{B}$ commute iff the commutator is equal to the zero operator.

- Relating the Uncertainty Principle and the commutator (without proof):

  – Consider two operators $\hat{A}, \hat{B}$ and the standard deviations σ_a, σ_b corresponding to the uncertainties in the observed values of their respective physical quantities.

  – It follows from the fact that

  $$\sigma_a^2 = \langle A^2 \rangle - \langle A \rangle^2 = \int \psi^*(x)\hat{A}^2\psi(x) \, \mathrm{d}x - \left[\int \psi^*(x)\hat{A}\psi(x) \, \mathrm{d}x \right]^2$$

  (and similarly for σ_b) that

  $$\sigma_a \sigma_b \geq \frac{1}{2} \left| \int \psi^*(x)[\hat{A}, \hat{B}]\psi(x) \, \mathrm{d}x \right|$$

- Results from the above.

  – If $\hat{A}, \hat{B}$ commute, there is no restriction on the uncertainties in the measurements of a and b.

  – If $\hat{A}, \hat{B}$ do not commute, there will be a restriction on the precision to which we can measure a and b, namely that as our measurements of one get more precise, our measurements of the other necessarily get less precise.

  – In particular, if we consider the case of $\hat{X}, \hat{P}_x$ (the operators corresponding to the standard uncertainty relation), we have that

  $$\hat{P}_x \hat{X}\psi(x) = \left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \right) x\psi(x) \qquad\qquad \hat{X}\hat{P}_x = x\left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \right) \psi(x)$$

  $$= -i\hbar\psi(x) - i\hbar x\frac{\mathrm{d}\psi}{\mathrm{d}x} \qquad\qquad\qquad = -i\hbar x\frac{\mathrm{d}\psi}{\mathrm{d}x}$$

so the corresponding commutator is

$$[\hat{P}_x, \hat{X}] = \hat{P}_x\hat{X} - \hat{X}\hat{P}_x$$
$$= \left[-i\hbar\hat{I} - i\hbar x\frac{\mathrm{d}}{\mathrm{d}x}\right] - \left[-i\hbar x\frac{\mathrm{d}}{\mathrm{d}x}\right]$$
$$= -i\hbar\hat{I}$$

so

$$\sigma_p\sigma_x \geq \frac{1}{2}\left|\int \psi^*(x)(-i\hbar\hat{I})\psi(x)\,\mathrm{d}x\right|$$
$$= \frac{1}{2}\left|-i\hbar\int \psi^*(x)\psi(x)\,\mathrm{d}x\right|$$
$$= \frac{1}{2}\left|-i\hbar \cdot 1\right|$$
$$= \frac{\hbar}{2}$$

which is the typical formulation of the Heisenberg Uncertainty Relation.

3.4   MathChapter D: Spherical Coordinates

From McQuarrie and Simon (1997).

- We can integrate products of multiple variables one at a time and multiply the results instead of taking a traditional triple integral.

- Example:

  - To find the volume of a sphere of radius a with a triple integral, we'd traditionally do the following.

$$V = \int_0^{2\pi}\int_0^{\pi}\int_0^{a} r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$
$$= \int_0^{2\pi}\int_0^{\pi}\frac{a^3}{3}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$
$$= \int_0^{2\pi}\frac{a^3}{3}\cdot 2\,\mathrm{d}\phi$$
$$= \frac{4}{3}\pi a^3$$

  - However, we can alternatively do the following.

$$V = \int_0^{2\pi}\int_0^{\pi}\int_0^{a} r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\phi$$
$$= \frac{a^3}{3}\int_0^{2\pi}\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$
$$= \frac{a^3}{3}\cdot 2\int_0^{2\pi}\mathrm{d}\phi$$
$$= \frac{a^3}{3}\cdot 2\cdot 2\pi$$
$$= \left(\int_0^{a} r^2\,\mathrm{d}r\right)\left(\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\right)\left(\int_0^{2\pi}\mathrm{d}\phi\right)$$

- In fact, to generalize, we can express an integral of the form

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} F(r, \theta, \phi) r^2 \sin\theta \, dr \, d\theta \, d\phi$$

  as an operator

$$I = \int_0^\infty dr \, r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, F(r, \theta, \phi)$$

  where we understand each integral to act on everything that lies to its right, i.e., "we first integrate $F(r, \theta, \phi)$ over ϕ from 0 to 2π, then multiply the result by $\sin\theta$ and integrate over θ from 0 to ϕ, and finally multiply the result by r^2 and integrate over r from 0 to ∞" (McQuarrie & Simon, 1997, p. 150).

- If our integrand is spherically symmetric, i.e., $F(r, \theta, \phi) = f(r)$, then

$$I = \int_0^\infty dr \, r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\theta \, f(r) = \int_0^\infty f(r) 4\pi r^2 \, dr$$

  - In other words, we take a one-dimensional integral, but multiply the integrand by a factor of $4\pi r^2 \, dr$, which is the volume of a spherical shell of radius r and thickness dr.

- On the other hand, we can also hold r constant and integrate over the surface of a sphere of unit radius.

  - In this case, we sum pieces of differential surface area

$$dA = \sin\theta \, d\theta \, d\phi$$

- **Solid angle**: The solid enclosed by the surface that connects the origin and the area dA.

  - In the same way that a complete angle of the unit circle is 2π, a complete solid angle is 4π.
  - We often denote a complete solid angle by $d\Omega$. Thus, we can write

$$\int_{\text{sphere}} d\Omega = 4\pi$$

- The quantum theory of the hydrogen atom frequently involves angular integrals of the form

$$I = \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, F(\theta, \phi)$$

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

From McQuarrie and Simon (1997).

- **Hooke's law**: The equation describing the motion of a spring whose restoring force is directly proportional to its displacement from equilibrium. *Given by*

$$f = -kx$$

- **Force constant** (of a spring): The positive proportionality constant k in the Hooke's law description of the spring.

- The general solution to $ma = f = -kx$ is

$$x(t) = c_1 \sin\omega t + c_2 \cos\omega t$$

  where $\omega = \sqrt{k/m}$.

– This solution can be rewritten in the form

$$x(t) = A\sin(\omega t + \phi)$$

– Thus, the displacement oscillates sinusoidally, or harmonically, with a natural frequency ω, an amplitude A, and a phase angle ϕ.

- Additionally, since $f = -\,\mathrm{d}V/\mathrm{d}x$ where V is the potential energy of the system, we have that

$$-\frac{\mathrm{d}V}{\mathrm{d}x} = -kx$$

$$V(x) = \frac{1}{2}kx^2 + C$$

where C is an arbitrary constant used to fix the zero energy.

- Kinetic and potential energy:

– If $x(t) = A\cos\omega t$, then

$$K = \frac{1}{2}m\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 \qquad\qquad V = \frac{1}{2}k[x(t)]^2$$

$$= \frac{1}{2}m\omega^2 A^2 \sin^2\omega t \qquad\qquad = \frac{1}{2}kA^2 \cos^2\omega t$$

– It follows that the total energy is

$$E = K + V$$
$$= \frac{1}{2}m\omega^2 A^2 \sin^2\omega t + \frac{1}{2}kA^2 \cos^2\omega t$$
$$= \frac{1}{2}kA^2(\sin^2\omega t + \cos^2\omega t)$$
$$= \frac{1}{2}kA^2$$

– Since the total energy is constant, the system is **conservative**.

- **Conservative system**: A system in which the total energy is conserved.

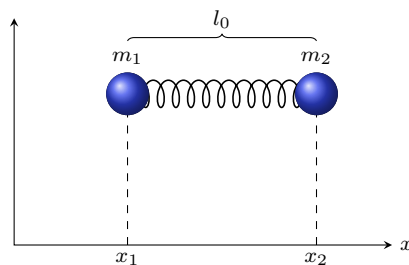- We now analyze a harmonic oscillator classically.

Figure 3.2: Harmonically oscillating diatomic molecule.

– We have two equations of motion, one for each mass.

$$m_1\frac{\mathrm{d}^2 x_1}{\mathrm{d}t^2} = k(x_2 - x_1 - l_0) \qquad\qquad m_2\frac{\mathrm{d}^2 x_2}{\mathrm{d}t^2} = -k(x_2 - x_1 - l_0)$$

– If we add them, we get the equation

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}(m_1 x_1 + m_2 x_2) = 0$$

which tells us that the center of mass of the system is not accelerating.

– Thus, the motion of the two-body system must depend only on the relative separation of the two masses, or on the **relative coordinate**

$$x = x_2 - x_1 - l_0$$

– Indeed, subtracting the initial two equations and substituting for both the relative coordinate and **reduced mass**

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

gives us

$$\frac{\mathrm{d}^2 x_2}{\mathrm{d}t^2} - \frac{\mathrm{d}^2 x_1}{\mathrm{d}t^2} = -\frac{k}{m_2}(x_2 - x_1 - l_0) - \frac{k}{m_1}(x_2 - x_1 - l_0)$$
$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}(x_2 - x_1) = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)(x_2 - x_1 - l_0)$$
$$\mu\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + kx = 0$$

– Conclusion: The kinematics of a diatomic harmonic oscillator are identical to those of a single ball on a spring except with the reduced mass and relative coordinate.

• "Generally, if the potential energy depends upon only the *relative* distances between two bodies, then we can introduce relative coordinates such as $x_2 - x_1$ and reduce a two-body problem to a one-body problem" (McQuarrie & Simon, 1997, p. 163).

• Note that while the harmonic oscillator potential may be a terrible approximation of the exponential curve of bond energy overall, it is a very good approximation in the region of the minimum, which is the physically important region for many molecules at room temperature. In particular, the approximation works well for oscillators of small amplitude.

• **Equilibrium bond length**: The bond length at the minimum potential energy of a molecule.

• McQuarrie and Simon (1997) goes through the Taylor series derivation of Hooke's law for diatomic molecules.

– Additional result: The force constant is equal to the curvature of $V(l)$ at the minimum.

• **Anharmonic term**: A term in the Taylor series expansion of a potential energy curve about the minimum of degree greater than two.

• **Morse potential**: An approximation of an intermolecular potential energy curve. *Given by*

$$V(l) = D(1 - e^{-\beta(l-l_0)})^2$$

– D is the dissociation energy of the molecule measured from the minimum of $V(l)$.

– β is a measure of the curvature of $V(l)$ at its minimum.

– McQuarrie and Simon (1997) derives from the Taylor series expansion of the Morse potential about $V(l_0)$ that the force constant $k = 2D\beta^2$.

• We are now ready to discuss a quantum-mechanical harmonic oscillator.

- Because of our prior simplification of a two-body harmonic oscillator to a single particle of reduced mass μ moving in a potential field described by $V(x) = kx^2/2$, we have that the Schrödinger equation for a one-dimensional harmonic oscillator is

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x)$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi(x) = 0$$

  - This differential equation does not have constant coefficients, so we need a new, custom method to solve it.
  - Indeed, when solved, well-behaved solutions can be obtained only if the energy is restricted to the quantized values

$$E_v = \hbar\omega\left(v + \frac{1}{2}\right) = h\nu\left(v + \frac{1}{2}\right)$$

   where $\omega = \sqrt{k/\mu}$, $\nu = \omega/2\pi$, and $v = 0, 1, 2, \ldots$.
  - Note that these energy levels are equally spaced apart (see Figure 3.1a).
  - Note the nonzero zero-point energy — since $E = p^2/2\mu + kx^2/2$, we cannot have $E = 0$ as this would imply that $0 = 0 \cdot 0 = (\Delta x)(\Delta p) < \hbar/2$, violating the Uncertainty Principle.

- **Selection rule**: A criterion that narrows the states between which a quantum system can move.

- McQuarrie and Simon (1997) will later prove that the harmonic oscillator model allows transitions only between adjacent energy states.

  - Thus, the only frequency absorbed or emitted by a diatomic harmonic oscillator should be

$$\begin{aligned}
\nu_{\mathrm{obs}} &= \frac{\Delta E}{h} \\
&= \frac{E_{v+1} - E_v}{h} \\
&= \frac{h\nu}{h} \\
&= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}
\end{aligned}$$

  - We can convert to wavenumbers by dividing the above by c.

- **Fundamental vibration frequency**: The single frequency absorbed or emitted by a diatomic molecule.

  - We can use the fundamental vibration frequency and the above equation to calculate the force constant of the attraction.

- McQuarrie and Simon (1997) will later prove that the dipole moment of the molecule must change as the molecule vibrates in order for it to absorb infrared radiation.

- As a last note, be aware that although deviations from the prediction do crop up, they can be systematically corrected for.

- Harmonic oscillator wave functions:

$$\psi_v(x) = N_v H_v(\sqrt{\alpha}x)\mathrm{e}^{-\alpha x^2/2}$$

- We have

$$\alpha = \frac{\sqrt{k\mu}}{\hbar} \qquad\qquad N_v = \frac{1}{\sqrt{2^v v!}}\sqrt[4]{\frac{\alpha}{\pi}}$$

where N_v is a normalization constant and $H_v(\sqrt{\alpha}x)$ is the vth-degree **Hermite polynomial** in $\sqrt{\alpha}x$.

- **Hermite polynomials**: A classical orthogonal polynomial sequence. *Examples*

$H_0(\xi) = 1$	$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$	$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$	$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$

Table 3.2: The first few Hermite polynomials.

- The polynomials in Table 3.2 allow us to generate the first few wave functions.

$\psi_0(x) = \sqrt[4]{\dfrac{\alpha}{\pi}}\,e^{-\alpha x^2/2}$	$\psi_1(x) = \sqrt[4]{\dfrac{4\alpha^3}{\pi}}\,xe^{-\alpha x^2/2}$
$\psi_2(x) = \sqrt[4]{\dfrac{\alpha}{4\pi}}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$	$\psi_3(x) = \sqrt[4]{\dfrac{\alpha^3}{9\pi}}(2\alpha x^3 - 3x)e^{-\alpha x^2/2}$

Table 3.3: The first few harmonic-oscillator wave functions.

- When graphed, the above wave functions and their corresponding probabilities look like the following.
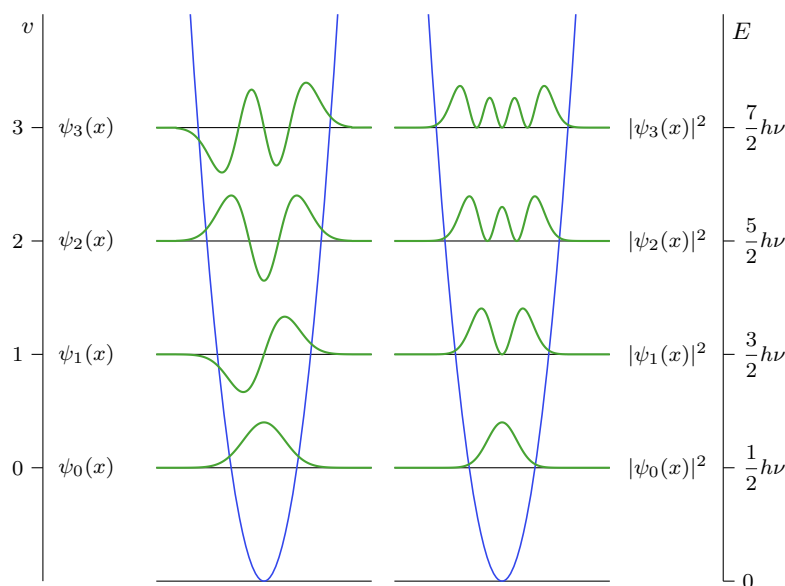

Figure 3.3: Harmonic-oscillator wave functions and probability densities.

- Notice how the probability distributions are slowly converging to the classical limit of a parabola of peaks.

- McQuarrie and Simon (1997) proves that a couple of the given wave functions satisfy the relevant Schrödinger equation, are normalized, and are orthogonal.

- Hermite polynomials are even functions if v is even and odd functions if v is odd.

  - Thus, ψ_v is even when v is even, and odd when v is odd.
  - It follows that ψ_v^2 is even for any v (since the square of either an odd or even function is even).

- Consequently, since $x\psi_v^2(x)$ is odd, we have that

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v(x) x \psi_v(x)\, \mathrm{d}x = 0$$

  for a harmonic operator

- Similarly, since the derivative of an even function is odd and the product of an even and odd function is odd, we have that

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_v(x) \left(-i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \right) \psi_v(x)\, \mathrm{d}x = 0$$

  for a harmonic operator.

Problems

10/26: **3-28.** The Schrödinger equation for a particle of mass m constrained to move on a circle of radius a is

$$-\frac{\hbar^2}{2I} \frac{\mathrm{d}^2\psi}{\mathrm{d}\theta^2} = E\psi(\theta)$$

where $I = ma^2$ is the moment of inertia and $0 \leq \theta \leq 2\pi$ is the angle that describes the position of the particle around the ring. Show by direct substitution that the solutions to this equation are

$$\psi(\theta) = Ae^{in\theta}$$

where $n = \pm\sqrt{2IE}/\hbar$. Argue that the appropriate boundary condition is $\psi(\theta) = \psi(\theta + 2\pi)$ and use this condition to show that

$$E = \frac{n^2\hbar^2}{2I}$$

where $n = 0, \pm 1, \pm 2, \ldots$. Show that the normalization constant A is $1/\sqrt{2\pi}$. Discuss how you might use these results for a free-electron model of benzene.

Answer. We have that

$$
\begin{aligned}
E(Ae^{in\theta}) &= -\frac{\hbar^2}{2I} \frac{\mathrm{d}^2}{\mathrm{d}\theta^2} \left(Ae^{in\theta} \right) \\
&= \frac{An^2\hbar^2}{2I} e^{in\theta} \\
&= \frac{2IEA\hbar^2}{2\hbar^2 I} e^{in\theta} \\
&= EAe^{in\theta}
\end{aligned}
$$

so the given wave wave function is a solution to the given Schrödinger equation, as desired.

Since the free space is a 2D ring into which all wave functions must "fit," i.e., align in phase, it is necessary that $\psi(\theta) = \psi(\theta + 2\pi)$. Substituting in our solutions, we have that

$$
\begin{aligned}
Ae^{in\theta} &= Ae^{in(\theta+2\pi)} \\
&= Ae^{in\theta} e^{2\pi in} \\
e^{2\pi in} &= 1 \\
n &= 0, \pm 1, \pm 2, \ldots
\end{aligned}
$$

as desired.

As for the normalization constant, we have that

$$
\begin{aligned}
1 &= \int_0^{2\pi} \psi^*(\theta)\psi(\theta)\,\mathrm{d}\theta \\
&= \int_0^{2\pi} (A\mathrm{e}^{-in\theta})(A\mathrm{e}^{in\theta})\,\mathrm{d}\theta \\
&= A^2 \int_0^{2\pi} 1\,\mathrm{d}\theta \\
A &= \frac{1}{\sqrt{2\pi}}
\end{aligned}
$$

as desired.

This could potentially be used for a free-electron model of benzene by looking at the energy levels and associated probability densities and overlaying them on the benzene ring. □