

## CHEM 5314: Advanced Physical Chemistry

### Overall Goals:

- Use quantum mechanics to understand that molecules have quantized translational, rotational, vibrational, and electronic energy levels.
  - In a large sample of molecules ( $\sim N_A$ ), be able to predict how many molecules are in each energy level.
  - From this analysis and the theory of statistical mechanics, learn how to predict thermodynamic properties.
  - Understand the basic principles of spectroscopy using selection rules and the energy levels.
  - Derive Hund's Rule from the symmetrization postulate.
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### Classical Waves

A classical wave is defined as a solution of the classical wave equation:

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x, t)}{\partial t^2} \quad (1)$$

where  $v$  is the speed of wave propagation.

The wave equation is a partial differential equation. Let us try to solve it using separation of variables:  $u(x, t) = X(x)T(t)$ . Specifically, try  $X(x) = \sin ax$  and  $T(t) = \cos bt$  because these are functions whose second derivative is similar to the original function. This works if  $v^2 = b^2/a^2$ . We need  $ax$  and  $bt$  to be dimensionless;  $a$  thus has to be the wavenumber  $= k = 2\pi/\lambda$  and  $b$  the frequency  $= \omega = 2\pi\nu$ . Then we have  $v = \omega/k$ .

Now let us use the separation of variables technique more formally, using the following recipe:

1) substitute the separation of variables form  $u(x, t) = X(x)T(t)$  into the partial differential equation. This gives

$$X''T = \frac{1}{v^2}XT'' \quad (2)$$

2) divide both sides by  $u(x, t) = X(x)T(t)$ , (and rearrange as needed to get the independent variables on either side of the equation) giving

$$\frac{X''}{X} = \frac{1}{v^2} \frac{T''}{T} \quad (3)$$

3) argue that the only way this can work is if both sides are equal to a constant. We will call this constant  $-c^2$ .

4) write two separate equations, which are now ordinary differential equations, namely

$$X'' = -c^2X \quad \text{and} \quad T'' = -c^2v^2T \quad (4)$$

We can use the trigonometric identity  $\sin A \cos B - \cos A \sin B = \sin(A - B)$  to rewrite the wave form as  $\sin(kx - \omega t)$ . Then we can see that the following four functions are all valid (monochromatic) classical waves:

$$\sin(kx - \omega t), \quad \cos(kx - \omega t), \quad e^{i(kx - \omega t)}, \quad e^{-i(kx - \omega t)} \quad (5)$$

In 3 spatial dimensions these classical waves generalize to:

$$\sin(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}, \quad e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (6)$$

where  $\mathbf{k} = (k_x, k_y, k_z)$  is the wave vector which points in the direction of propagation of the wave, and  $\mathbf{r} = (x, y, z)$  is the position vector.  $\mathbf{k}$  has length  $|\mathbf{k}| = 2\pi/\lambda$  with  $\omega$  defined as before.

The 3d wave equation is

$$\nabla^2 u = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \quad (7)$$

where  $\nabla^2$  is the Laplacian operator.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (8)$$

### Classical Particles

Newton's 2nd Law:

$$\mathbf{F} = m\mathbf{a} = m \frac{d\mathbf{v}}{dt} = \frac{d}{dt}(m\mathbf{v}) = \frac{d\mathbf{p}}{dt} \quad (9)$$

We can express this as  $d\mathbf{p} = \mathbf{F} dt$

$$dT = \mathbf{F} \cdot d\mathbf{r} \quad (10)$$

Proof:

$$dT = d\left(\frac{p^2}{2m}\right) = \frac{1}{2m}2\mathbf{p} \cdot d\mathbf{p} = \mathbf{v} \cdot \mathbf{F}dt \quad (11)$$

Then we can use  $\mathbf{v} = d\mathbf{r}/dt \Rightarrow \mathbf{v}dt = d\mathbf{r}$

If  $\mathbf{F} = -\nabla V$  where  $V(x, y, z)$  is the potential energy function, then  $dT = -\nabla V \cdot d\mathbf{r} = -dV$  (total derivative). Hence  $dT + dV = 0 \Rightarrow d(T + V) = dE = 0$  This is the expression for conservation of energy. Note: Energy is not conserved if the forces felt by an object cannot be associated with a potential energy function. Examples: (i) friction  $\rightarrow$  forces depend on velocity, (ii) magnetic forces  $\rightarrow$  forces depend on velocity.

#### Photons

Planck (1900): “blackbody” radiation

Einstein (1905): photoelectric effect

Light (electromagnetic radiation) behaves like a field of particles called “photons,” each with energy  $E = h\nu$

From electromagnetic theory, the momentum should be  $p = E/c$  as verified by Compton (1922) in the scattering of x-rays from electrons. [One way to think about this is to use Einstein’s formula  $E = mc^2$ , which yields  $p = E/c = mc^2/c = mc$  which is of the form “momentum equals mass times velocity” with the velocity being the speed of light.]

Using  $c = \lambda\nu$  we can write  $p = h/\lambda$

#### Wave-Particle Duality

de Broglie (1923): if light (a “wave” phenomenon) can behave like particles, then particles should behave like waves. Wave properties ( $\lambda, \nu$ ) and particle properties ( $p, E$ ) are connected by  $p = h/\lambda, E = h\nu$ , or, in terms of  $k$  and  $\omega, p = \hbar k, E = \hbar\omega$ , where  $\hbar \equiv h/2\pi$ .

#### Schroedinger Equation

“Matter waves” in 1d could have the form

$$\sin(kx - \omega t), \quad \cos(kx - \omega t), \quad e^{i(kx - \omega t)} \quad (12)$$

where  $k$  and  $\omega$  are related by

$$E = \frac{p^2}{2m} \Rightarrow \hbar\omega = \frac{\hbar^2 k^2}{2m} \quad (13)$$

For “ordinary” waves, we had  $\omega = kv$  and therefore matter waves cannot satisfy the “ordinary” wave equation. After considering the effect of  $\partial/\partial x$  and  $\partial/\partial t$  on the three wave forms, we deduce that:

1. a linear wave equation consistent with  $\hbar\omega = \frac{\hbar^2 k^2}{2m}$  cannot be found for  $\sin(kx - \omega t)$  or  $\cos(kx - \omega t)$

2. for  $\psi(x, t) = e^{i(kx - \omega t)}$  the equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \quad \text{works!} \quad (14)$$

Notice that both the wave equation and its solutions  $\psi(x, t)$  are complex. The wave equation is called the Schroedinger Wave Equation (1926). It is valid for particles in free space only (no forces acting). In 3d, it has the form

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi \quad (15)$$

### Schroedinger Equation in a Potential

Consider the simple situation below:

(figure here)

There is a constant potential in both regions (*i.e.* zero force) hence we have a wave of form  $e^{i(kx - \omega t)}$  on both sides of the boundary. For continuity at the boundary,  $\omega$  (*i.e.* the frequency) must be the same on both sides. This suggests that  $\omega$  is related to the total energy  $E$  and not the kinetic energy  $T$  because only the total energy  $E$  is conserved over the boundary. Therefore

$$E \text{ (total)} = \hbar\omega \quad \text{(both sides)} \quad (16)$$

However,  $k$  changes:

In region 1:

$$E = \frac{p_1^2}{2m} \Rightarrow \hbar\omega = \frac{\hbar^2 k_1^2}{2m} \quad (17)$$

In region 2:

$$E = \frac{p_2^2}{2m} + V_{\text{const}} \Rightarrow \hbar\omega = \frac{\hbar^2 k_2^2}{2m} + V_{\text{const}} \quad (18)$$

A wave equation that works in both regions is:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi \quad (19)$$

where

$$V(x) = \begin{cases} 0 & : x < 0 \\ V_{\text{const}} & : x \geq 0 \end{cases}$$

For a general potential  $V(x)$ , think about approximating it in a piecewise manner:  
(figure here)

and imagine the limit of infinitely small steps. We get

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi \quad (20)$$

In 3d, this becomes

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r})\psi \quad (21)$$

and is called the time dependent Schroedinger equation (TDSE). The solutions  $\psi(x, y, z, t) = \psi(\mathbf{r}, t)$  are called wavefunctions.

### Interpretation of $\psi$

What is the physical interpretation of  $\psi$ ?

$|\psi|^2 = \psi^* \psi$  is a probability density in space. What this means is that the probability of finding the particle in the volume element  $dx dy dz$  at time  $t$  is  $|\psi(x, y, z, t)|^2 dx dy dz$ . And the probability of finding the particle in the extended region  $A$  is

$$\iiint_A |\psi(x, y, z, t)|^2 dx dy dz \quad (22)$$

For this interpretation to make sense we must have

$$1 = \iiint_{\text{all space}} |\psi(x, y, z, t)|^2 dx dy dz \quad (23)$$

Wavefunctions  $\psi$  satisfying condition (23) are called normalized.

### General Solution for $\psi(x, t)$

Our goal is to solve Eq. (20). This equation is a linear partial differential equation. We will try the separation of variables approach. Namely, we will assume we can express the solution  $\psi(x, t)$  as a product of two one-variable functions,  $\psi(x, t) = \psi_n(x)\theta_n(t)$ . Note that although  $\psi$  and  $\psi_n$  have similar names, they are very different since the former is a function of two variables while the latter is a function of one variable. To begin, note that

$$\frac{\partial \psi}{\partial t} = \psi_n \frac{d\theta_n}{dt} \quad \text{and} \quad \frac{\partial^2 \psi}{\partial x^2} = \frac{d^2 \psi_n}{dx^2} \theta_n \quad (24)$$

Substituting into Eq. (20) yields

$$i\hbar \psi_n \frac{d\theta_n}{dt} = -\frac{\hbar^2}{2m} \frac{d^2 \psi_n}{dx^2} \theta_n + V \psi_n \theta_n \quad (25)$$

Now divide both sides by  $\psi = \psi_n \theta_n$  to give

$$i\hbar \frac{1}{\theta_n} \frac{d\theta_n}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi_n} \frac{d^2\psi_n}{dx^2} + V \quad (26)$$

The left hand side (LHS) is a function of time only, and the right hand side (RHS) is a function of space only. We have separated the two independent variables to either side of the equation. How can this work? Only if both sides are constant. Since the dimensions of the constant are energy, call it  $E_n$

Then,

$$\text{LHS becomes } i\hbar \frac{1}{\theta_n} \frac{d\theta_n}{dt} = E_n \Rightarrow \frac{d\theta_n}{dt} = -\frac{iE_n}{\hbar} \theta_n \quad (27)$$

This ordinary differential equation has the simple solution

$$\theta_n(t) = e^{-iE_n t/\hbar} \quad (28)$$

and,

$$\text{RHS becomes } -\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} + V\psi_n = E_n\psi_n \quad (29)$$

with solutions depending on the potential energy  $V(x)$ . This equation has many solutions for different energy values  $E_n$  (hence the  $n$  subscript, to label the different solutions). This equation is called the time independent Schroedinger equation (TISE).

Putting everything back together, the general solution for  $\psi(x, t)$  is

$$\psi(x, t) = \sum_n c_n \psi_n(x) \theta_n(t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar} \quad (30)$$

with linear combination coefficients  $c_n \in \mathbb{C}$

### Stationary States

Consider the special case where all the coefficients are zero except for  $c_1 = 1$ . Then

$$\psi(x, t) = \psi_1(x) e^{iE_1 t/\hbar} \quad (31)$$

The probability density in this special case is  $|\psi(x, t)|^2 = |\psi_1(x)|^2$ , namely time independent. Hence the probability density is literally “stationary” or static. In electromagnetic theory, a static charge density cannot emit radiation. This suggests that these are the stationary, non-radiating, states imagined by Bohr (1913). To summarize, the stationary (or “allowed”)

states of a particle under the influence of the potential energy  $V$  are given by the time independent Schroedinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} + V\psi_n = E_n\psi_n \quad (32)$$

where the constant  $E_n$  is the energy of the particle in that state (will prove later).

### Particle in a Finite Box: 1d

Consider the following potential energy function:

$$V(x) = \begin{cases} V_0 : x < 0 & \text{region A} \\ 0 : 0 \leq x < L & \text{region B} \\ V_0 : x \geq L & \text{region C} \end{cases}$$

Our goal is to find the stationary (non-radiating, stable, allowed) states for a quantum mechanical particle experiencing  $V(x)$ , whose energy  $E$  satisfies  $0 \leq E < V_0$ . To do this we must solve the TISE which is Eq. (29). We will solve it for each region separately because  $V(x)$  is defined in a piecewise manner, and then we will combine the pieces to assemble the entire solution.

### Regions A and C

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} + V_0\psi_n = E_n\psi_n \quad (33)$$

Rearranging gives

$$\frac{d^2\psi_n}{dx^2} = -\frac{2m}{\hbar^2}(E_n - V_0)\psi_n = \frac{2m}{\hbar^2}(V_0 - E_n)\psi_n \quad (34)$$

The constant prefactor multiplying  $\psi_n$  on the RHS is positive and so we can define  $c^2 = 2m(V_0 - E_n)/\hbar^2$  with  $c \in \mathbb{R}$ . This is a 2nd order linear ordinary differential equation so we are guaranteed to cover all possible solutions if we find two linearly independent solutions and form their linear combinations. Clearly two linearly independent solutions are:

$$\psi_n^+(x) = e^{cx} \quad \text{and} \quad \psi_n^-(x) = e^{-cx} \quad (35)$$

We eliminate the  $\psi_n^-$  solution in region A and the  $\psi_n^+$  solution in region C on physical grounds.

### Region B

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = E_n\psi_n \quad (36)$$

Rearranging gives

$$\frac{d^2\psi_n}{dx^2} = -\frac{2mE_n}{\hbar^2}\psi_n \quad (37)$$

The constant prefactor multiplying  $\psi_n$  on the RHS is negative. We will define  $a^2 = 2mE_n/\hbar^2$  with  $a \in \mathbb{R}$ . Two linearly independent solutions are:

$$\psi_n^{\sin}(x) = \sin(ax) \quad \text{and} \quad \psi_n^{\cos}(x) = \cos(ax) \quad (38)$$

Combine the pieces

Actually, we can multiply the given wavefunctions by an arbitrary constant, so that in fact the solutions we have found can be expressed as:

$$\text{Region A: } \psi_A = Ae^{cx}$$

$$\text{Region B: } \psi_B = B \sin(ax) + C \cos(ax)$$

$$\text{Region C: } \psi_C = De^{-cx}$$

Thus we have 4 unknowns ( $A$ ,  $B$ ,  $C$ , and  $D$ ). To combine the pieces, we must ensure continuity and differentiability across the regions, which gives us 4 equations:

$$\psi_A(x=0) = \psi_B(x=0)$$

$$\psi'_A(x=0) = \psi'_B(x=0)$$

$$\psi_B(x=L) = \psi_C(x=L)$$

$$\psi'_B(x=L) = \psi'_C(x=L)$$

Particle in a Box: 1d

Now consider the limiting case  $V_0 \rightarrow \infty$ . The value of  $c$  in Eq. (35) approaches  $\infty$  which makes the solutions identically zero in regions A and C. Therefore the region B solution  $\psi_B = B \sin(ax) + C \cos(ax)$  is subject to the “boundary conditions”  $\psi_B(x=0) = 0$  and  $\psi_B(x=L) = 0$ . The  $x=0$  boundary condition forces  $C=0$ , so that we are left with  $\psi_B = B \sin(ax)$ . The  $x=L$  boundary condition is then  $B \sin(aL) = 0 = B \sin(\sqrt{2mE_n}L/\hbar)$ . This is satisfied for

$$\sqrt{2mE_n}L/\hbar = n\pi, \quad n \in \mathbb{Z} \quad (39)$$

namely the energy is restricted to a discrete spectrum:

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n \in \mathbb{Z} \quad (40)$$



Another way to say this is that the energy is “quantized”, with  $n$  the quantum number. Note that since the potential energy in region B is zero, the energy we are talking about here is kinetic energy.

Substituting Eq. (40) into  $\psi_B$  yields

$$\psi_n = B \sin\left(\frac{n\pi x}{L}\right) \quad (41)$$

where we have labeled the wavefunction with its quantum number. The constant  $B$  is then determined by requiring normalization:

$$1 = \int_0^L |\psi_n(x)|^2 dx = B^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = B^2(L/2) \Rightarrow B = \sqrt{2/L} \quad (42)$$

### Particle in a Box: 3d

Denote the edge lengths of the box as  $a$ ,  $b$ , and  $c$  in the  $x$ ,  $y$ , and  $z$  directions, respectively. Inside the box we have (since  $V = 0$ )

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi \quad (43)$$

with boundary conditions  $\psi(0, y, z) = 0$ ;  $\psi(a, y, z) = 0$ ;  $\psi(x, 0, z) = 0$ ;  $\psi(x, b, z) = 0$ ;  $\psi(x, y, 0) = 0$ ;  $\psi(x, y, c) = 0$ . This is a linear partial differential equation so we will try the separation of variables technique. We postulate that we can express

$$\psi(x, y, z) = f(x)g(y)h(z) \quad (44)$$

Then  $\nabla^2 \psi = f''(x)g(y)h(z) + f(x)g''(y)h(z) + f(x)g(y)h''(z) = -2mE/\hbar^2 f(x)g(y)h(z)$ . Divide through by  $\psi = f(x)g(y)h(z)$  to get

$$\frac{f''(x)}{f(x)} + \frac{g''(y)}{g(y)} + \frac{h''(z)}{h(z)} = -\frac{2mE}{\hbar^2} \quad (45)$$

For this to work each individual term must be constant. If we call these constants  $-k_x$ ,  $-k_y$ , and  $-k_z$  then we have

$$k_x + k_y + k_z = 2mE/\hbar^2 \quad (46)$$

and

$$f''(x) = -k_x f(x) \quad (47)$$

$$g''(y) = -k_y g(y) \quad (48)$$

$$h''(z) = -k_z h(z) \quad (49)$$

Consider the  $x$ -equation: the solution is  $f(x) = A \sin(\sqrt{k_x}x)$  since the cosine solution is not allowed by the  $x = 0$  boundary condition. To satisfy the boundary condition at  $x = a$  we must have  $\sqrt{k_x}a = n_x\pi$ ,  $n_x \in \mathbb{Z}$ , or  $k_x = n_x^2\pi^2/a^2$ . Similarly,  $k_y = n_y^2\pi^2/b^2$  and  $k_z = n_z^2\pi^2/c^2$ . Put these into Eq. (46) to get

$$\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\pi^2 = \frac{2mE}{\hbar^2} \quad (50)$$

or

$$E = \frac{\pi^2\hbar^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \quad (51)$$

where, for reasons similar to the 1d case,  $n_x$ ,  $n_y$ , and  $n_z \in \mathbb{N} = \{1, 2, 3, \dots\}$ . The normalized stationary states are

$$\psi_{n_x, n_y, n_z}(x, y, z) = \frac{8}{abc}^{1/2} \sin\left(\frac{n_x\pi x}{a}\right) \sin\left(\frac{n_y\pi y}{b}\right) \sin\left(\frac{n_z\pi z}{c}\right) \quad (52)$$

If the box is cubic then  $a = b = c = L$  and  $E$  becomes

$$E_{n_x, n_y, n_z} = (n_x^2 + n_y^2 + n_z^2) \frac{\pi^2\hbar^2}{2mL^2} \quad (53)$$

Now we have degenerate energy levels, namely different states with the same energy.

$$\begin{array}{cccc} n_x & n_y & n_z & n_x^2 + n_y^2 + n_z^2 \propto E \end{array} \quad (54)$$

$$\begin{array}{cccc} 1 & 1 & 1 & 3 \end{array} \quad (55)$$

$$\text{triple degeneracy} \left\{ \begin{array}{cccc} 2 & 1 & 1 & 6 \\ 1 & 2 & 1 & 6 \\ 1 & 1 & 2 & 6 \end{array} \right. \quad (56)$$

$$\text{triple degeneracy} \left\{ \begin{array}{cccc} 1 & 2 & 2 & 9 \\ 2 & 1 & 2 & 9 \\ 1 & 2 & 2 & 9 \end{array} \right. \quad (57)$$

$$\text{triple degeneracy} \left\{ \begin{array}{cccc} 3 & 1 & 1 & 11 \\ 1 & 3 & 1 & 11 \\ 1 & 1 & 3 & 11 \end{array} \right. \quad (58)$$

$$\begin{array}{cccc} 2 & 2 & 2 & 12 \end{array} \quad (59)$$

$$\begin{array}{cccc} \vdots & \vdots & \vdots & \vdots \end{array} \quad (60)$$

This is the simplest example of a general rule in quantum mechanics: symmetry often implies degeneracy.

Particle on a Ring

Consider a ring of radius  $R$ , with  $V = 0$  on the ring and  $V = \infty$  off the ring. By analogy to the particle in a box problem, the wavefunction is identically zero off the ring. Therefore we only need to find the solution  $\psi_n(x)$  on the ring.

The TISE with  $V = 0$  is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_n(x)}{\partial x^2} = E_n \psi_n(x) \quad (61)$$

where  $x$  is the distance along the circumference of the ring (called arclength). It is more natural to use  $\theta$  for this problem where  $x = R\theta$ . Changing variables gives the TISE as

$$-\frac{\hbar^2}{2mR^2} \frac{\partial^2 \psi_n(\theta)}{\partial \theta^2} = E_n \psi_n(\theta) \quad \text{or} \quad \frac{\partial^2 \psi_n(\theta)}{\partial \theta^2} = -\frac{2mR^2 E_n}{\hbar^2} \psi_n(\theta) \quad (62)$$

The boundary conditions are not obvious for this problem. It turns out they consist of enforcing the periodicity of the angular variable; namely  $\psi_n(\theta = 0) = \psi_n(\theta = 2\pi)$ ,  $\psi'_n(\theta = 0) = \psi'_n(\theta = 2\pi)$ ,  $\psi''_n(\theta = 0) = \psi''_n(\theta = 2\pi)$ ,  $\dots$ . Both real (sin and cos) and complex ( $e^{+i}$  and  $e^{-i}$ ) solutions are possible. We will use the real representation. If we define  $c^2 = 2mR^2 E_n / \hbar^2$  then the sin solution is  $\psi_n^{\text{sin}}(\theta) = A \sin(c\theta)$  with the boundary condition  $2\pi c = 2n\pi$ ,  $n \in \mathbb{Z}$ . Thus

$$\psi_n^{\text{sin}} = A_n \sin(n\theta), \quad n \in \mathbb{Z} > 0 \quad (63)$$

and

$$E_n = \frac{n^2 \hbar^2}{2mR^2} \quad (64)$$

Likewise, the cos solution is  $\psi_n^{\text{cos}}(\theta) = A \cos(c\theta)$  with the boundary condition  $2\pi c = 2n\pi$ ,  $n \in \mathbb{Z}$ . Thus

$$\psi_n^{\text{cos}} = A_n \cos(n\theta), \quad n \in \mathbb{Z} \geq 0 \quad (65)$$

and

$$E_n = \frac{n^2 \hbar^2}{2mR^2} \quad (66)$$

Negative  $n$  values are redundant because only  $|\psi|^2$  has physical meaning. But  $n = 0$  gives a valid solution for cos, so we need to be careful not to miss this.

Summary: The ground state is just  $\psi_0^{\cos} = 1$  with  $E_0 = 0$ . The excited states have energies

$$E_n = \frac{n^2 \hbar^2}{2mR^2} \quad (n \in \mathbb{Z} > 0) \quad (67)$$

and are doubly degenerate with pairs of states,  $\psi_n^{\sin} = \sin(n\theta)$  and  $\psi_n^{\cos} = \cos(n\theta)$  for each energy level (ignoring the normalization constants). This is a useful conceptual model for cyclic  $\pi$ -electron systems.

### Harmonic Oscillator

Consider the TISE with  $V(x) = \frac{1}{2}kx^2$ .  $k$  is called the force constant because in Newtonian mechanics the force is given by  $F = -kx$  (Hooke's Law spring). The classical oscillation frequency is  $\omega = \sqrt{k/m}$  where  $\omega = 2\pi\nu$ . In terms of  $\omega$ , the potential energy is  $V(x) = \frac{1}{2}m\omega^2x^2$ . Expressed in this form, the Schroedinger equation to solve is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_n}{\partial x^2} + \frac{1}{2}m\omega^2x^2\psi_n = E_n\psi_n \quad (68)$$

$$\Rightarrow \frac{\partial^2 \psi_n}{\partial x^2} = \left( \frac{m^2\omega^2x^2}{\hbar^2} - \frac{2mE_n}{\hbar^2} \right) \psi_n \quad (69)$$

Let us try  $\psi_0(x) = e^{-\alpha x^2}$  for the ground state. Taking two derivatives, we obtain  $(4\alpha^2x^2 - 2\alpha)e^{-\alpha x^2}$ . Comparing with the RHS of Eq. (69) we see that this guess can work if we make sure that

$$4\alpha^2 = \frac{m^2\omega^2}{\hbar^2} \quad \text{and} \quad 2\alpha = \frac{2mE_0}{\hbar^2} \quad (70)$$

which means that

$$\alpha = \frac{m\omega}{2\hbar} \quad (71)$$

and  $E_0 = \hbar^2\alpha/m$  or

$$E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}h\nu \quad (72)$$

This result is significant because of the zero point energy. The ground state has zero nodes. We know that we must add nodes for the excited states. One way to introduce more nodes is to decrease the wavelength of sin and cos functions. But we don't have a trigonometric solution here. Another common way to introduce more nodes is to use the fact that an  $n^{\text{th}}$

degree polynomial has  $n$  roots. We can think of the ground state as including the zeroth degree polynomial  $x^0 = 1$ . Along these lines, we can guess that the first excited state looks like  $\psi_1(x) = xe^{-\alpha x^2}$ . Taking two derivatives, we obtain  $(4\alpha^2 x^2 - 6\alpha)xe^{-\alpha x^2}$ . Comparing with the RHS of Eq. (69) we see that this guess can work if we make sure that

$$4\alpha^2 = \frac{m^2\omega^2}{\hbar^2} \quad \text{and} \quad 6\alpha = \frac{2mE_1}{\hbar^2} \quad (73)$$

which means that

$$\alpha = \frac{m\omega}{2\hbar} \quad (74)$$

$$E_1 = \frac{3}{2}\hbar\omega \quad (75)$$

In general, the  $n^{\text{th}}$  harmonic oscillator stationary state has energy

$$E_n = (n + 1/2)\hbar\omega, \quad n \in \mathbb{Z} \geq 0 \quad (76)$$

and wavefunction

$$\psi_n(x) = (x^n + Ax^{n-2} + Bx^{n-4} + \dots)e^{-\alpha x^2} \quad (77)$$

with the final term in the polynomial being  $x^1 = x$  or  $x^0 = 1$  depending on whether  $n$  is odd or even, and with  $\alpha = m\omega/2\hbar$ .