Applications of Quantum Theory to Some Simple Systems

Arbitrariness in the value of total energy. We will use classical mechanics, and for simplicity of the discussion, consider a particle of mass *m* moving in 1D (with position variable *x*) under the action of an external force, *F*(*x*). The total energy of the particle is E=T+V. Classically, the kinetic energy is, $T=p^2/2m$. It is an experimentally measurable quantity with possible values ranging from 0 to ∞ (for a macroscopic particle). Hence there is no arbitrariness in the value of T. The potential energy V(*x*) of the particle is related to force by

$$F = -\frac{dV}{dx} \qquad \text{eq 3.1}$$

The magnitude and direction of force can be experimentally measured; i.e. there is no arbitrariness in F, also. However, this is not the case for V. Thus, if V is replaced by V+C, where C is an arbitrary constant, eq 3.1 will give the same force F. The value of C can not be determined experimentally. As a consequence, there is an arbitrariness in the potential energy V(*x*) within an additive constant. This arbitrariness is reflected in the total energy: E=T+V+C. Thus experimentally we can not measure E, but can measure energy differences, ΔE, because then C will cancel out. Since, in the end, we are interested in ΔE values, we assign a convenient value for C, usually zero, in theoretical treatments. Because the arbitrariness comes from V, the situation is the same in quantum theory.

At several places below, it will be enlightening to compare predictions of classical mechanics against those of quantum mechanics for some dynamical properties of a particle (such as its energy, momentum, etc.). In doing so, we will refer to the particle as the “classical particle” if classical theories are employed to deduce its properties, and “quantum particle” if quantum theory is used instead.

***Independent Particles*.** In several model problems to be discussed below, and in finding approximate solutions of atomic and molecular problems, the Hamiltonian operator of a system containing *n* particles has the special form

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \cdots + \hat{h}_n \qquad \text{eq 3.2}$$

where $\hat{h}_j$ is the Hamiltonian operator for the j^{th} particle, and depends on the position variables of the j^{th} particle only. The Hamiltonian operator of eq 3.2 describes a system of *n* noninteracting particles; each particle in the system moves independently of the others. It can be shown that solutions of the Schrödinger equation, $\hat{H}\Psi = E\Psi$, with such a Hamiltonian has the following properties: i) The total energy of the system is a sum of <u>independent</u> contributions from each particle.

$$E=E_1 + E_2 + \ldots + E_n \qquad \text{eq 3.3a}$$

where E_j is the energy of the j^{th} particle. ii) The *n*-particle state function is a <u>product</u> of one-particle state functions

$$\Psi = \psi_1\psi_2 \ldots \psi_n \qquad \text{eq 3.3b}$$

where the factors ψ_j and one-particle energies E_j are found by solving a series of independent one-particle Schrödinger equations

$$\hat{h}_j\psi_j = E_j\psi_j, \quad j = 1, 2, \dots, n \qquad \text{eq 3.3c}$$

In the majority of applications, all *n* particles in the system are identical. In this case, the *n* equations in eq 3.3c are identical in form, and solving just one of them gives all the information needed in eq 3.3a and eq 3.3b. Hence, an *n*-particle problem reduces to a one-particle problem, which is a great simplification.

A Hamiltonian operator that has a mathematical structure as in eq 3.2 is said to be “separable”.

3.1 Particle in a 1D box

The simplest problem in both classical and quantum mechanics is the 1D motion of a “free” particle of mass *m*, trapped between two walls separated by a given distance *a* (Figure 3.1). A free particle is one that is moving in the absence of any forces; i.e. F=0, hence V=C which we take as zero. Since classically, E=T= $p^2/2m$, and the particle’s momentum can be set (in experiments) to any desired value, all values of E between 0 and infinity are possible. E=0 corresponds to the classical particle at rest at some point between 0 and *a*. At higher values of E, it will be executing back and forth motion between the two walls.

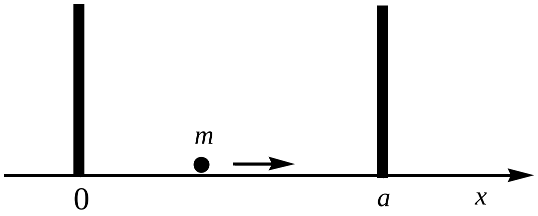

Figure 3.1 A free particle of mass *m* moving between two impenetrable walls.

We now turn to the quantum mechanical treatment of this problem, and ask: what are the allowed energy levels of such a particle? The answer will be obtained by solving the Schrödinger equation of the particle

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi \qquad \text{eq 3.4}$$

supplemented by the known circumstances under which the particle is moving. Thus we know that the probability of finding the particle outside of the box is zero. Probability is proportional to $\Psi^*(x)\Psi(x)$, and therefore, all solutions of eq 3.4 must be such that $\Psi(x)$=0 for all values of *x* outside the box. Since $\Psi(x)$ must be a continuous function of *x*, it must also be zero at the exact positions of the walls: $\Psi(0)$=0 and

$\Psi(a)=0$.[1] In mathematical terminology, such physically known conditions about a given system are called "boundary conditions". For a given system, only those solutions of the Schrödinger equation that satisfy the known boundary conditions about the system are physically acceptable.

Eq 3.4 is a second order ordinary differential equation (ODE), and it is known that there are two and only two independent functions that satisfy it. Let us simplify the notation (involving the constants) by rewriting Eq 3.4 in the form

$$\frac{d^2\Psi}{dx^2} = -k^2\Psi \qquad \text{eq 3.5}$$

where

$$k^2 = \frac{2mE}{\hbar^2} \qquad \text{eq 3.6}$$

Because k is a constant, we can easily guess that the two independent functions, $\cos(kx)$ and $\sin(kx)$, satisfy eq 3.5. Therefore, the general solution of eq 3.5 is

$$\Psi(x) = \mathrm{A}\sin(kx) + \mathrm{B}\cos(kx) \qquad \text{for } 0 \le x \le a \qquad \text{eq 3.7}$$

where A and B are arbitrary constants. Note here that this general solution of the Schrödinger equation does not impose any restrictions on the possible values of k, and therefore on E of the particle. We will see that it is because of the boundary conditions (which express the fact that the particle is trapped between the two walls, and therefore not completely free), the allowed values of E will be quantized (i.e. discrete). The condition, $\Psi(0)=0$, requires that B must be zero. Thus,

$$\Psi(x) = \mathrm{A}\sin(kx) \qquad \text{for } 0 \le x \le a \qquad \text{eq 3.8}$$

involving only two constants (A and k) in the physical solution. The constant A is a normalization constant, and will be determined below by the normalization condition. There remains the question of what can be the physically acceptable values of k. The answer to this question is provided by the remaining condition, $\Psi(a)=0$; i.e. $\mathrm{A}\sin(ka) = 0$.[2] This condition is satisfied only for those values of k for which $ka=n\pi$, where $n=0, \pm1, \pm2, \ldots$. However, the choice $n=0$ gives $k=0$, and this value of k causes Ψ of eq 3.8 to be zero for all values of x within the box. The implication is that the probability of finding the particle inside the box is zero, which is contrary to the facts. Therefore, $k=0$ value can not be allowed in eq 3.8. Also, since the sine function has the property, $\sin(-kx) = -\sin(kx)$, replacing a given value of k with $-k$ in eq 3.8 will only change the sign of the normalization constant A. As pointed out before, sign of a normalization constant is not physically significant. Thus the allowed values of k that will give physically acceptable Ψ are:

$$k = \frac{\pi}{a}n, \qquad n = 1, 2, \ldots \qquad \text{eq 3.9}$$

---

[1] Imagine that you approach the walls from outside the walls.

[2] "A" can not be zero because then Ψ would be zero at all positions inside the box.

Having determined the possible values for *k*, the "allowed energy levels" of the particle follow from eq 3.6:

$$E = \frac{\hbar^2}{2m}(n\pi/a)^2 = \frac{h^2}{8ma^2}n^2, \qquad n = 1, 2, \ldots \qquad \text{eq 3.10}$$

For each energy level (i.e. value of *E* obtained for a specified *n*), there is a corresponding state function with the same *n*

$$\Psi(x) = A\, sin(\frac{n\pi}{a}x) \qquad \text{eq 3.11}$$

Let us label the energy levels and the associated state functions by the quantum number *n*, and rewrite the equations above, as

$$E_n = \varepsilon\, n^2, \qquad \Psi_n(x) = A\, sin(\frac{n\pi}{a}x), \qquad n = 1, 2, \ldots \qquad \text{eq 3.12}$$

where

$$\varepsilon = \frac{h^2}{8ma^2} \qquad \text{eq 3.13}$$

The allowed energies of the trapped particle are shown in Figure 3.2.

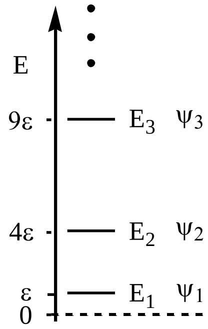

Figure 3.2 Energy level diagram of a particle in a 1D box.

The ground state energy of the quantum particle is E_1=ε, a nonzero value. As pointed out above, the lowest energy of the classical particle is zero. The difference, ε, between the quantum and classical predictions for the lowest possible energy of the particle is called "zero-point energy" (ZPE). This concept also occurs in some other types of motion of a particle to be studied below, and we define

$$\text{ZPE} = E_{\text{lowest}}(\text{quantum}) - E_{\text{lowest}}(\text{classical}) \qquad \text{eq 3.14}$$

In the absence of forces, a classical particle moves along a straight line in space. This type of motion is called "translational motion". The ZPE in the "particle in a box" problem is better described as the "translational ZPE" to distinguish it from ZPE of other types of motion (such as rotation and vibration). When ZPE=0 for a certain type of motion, we say that there is no ZPE.

Energy levels of the particle are not equidistant; the spacing between neighboring levels is (2*n*+1) ε, where *n* is the quantum number of the lower level.

“All space” for the trapped particle is, effectively, all *x* values between 0 and *a*, because we know that the particle can not be found outside of the box. The energy parameter ε is inversely proportional to a^2 (eq 3.13), and when $a \to \infty$, then $\varepsilon \to 0$. The latter also becomes very small when the particle has a large mass. In such cases the spacing between energy levels becomes negligible, and the quantization of energy levels disappears: the allowed energies of the quantum particle become the same as those of the classical particle (i.e. <u>continuous</u> from 0 to ∞). Thus quantum effects are significant only when both the box size and the particle mass are small. This is the situation for microscopic particles such as electrons, atoms, molecules, etc.

Normalization constants in quantum mechanics can always be taken as real numbers. Thus the state functions of the particle (eq 3.12) are all real-valued functions. For a real function $\Psi^*=\Psi$, or $\Psi^*\Psi=\Psi^2$. These functions are normalized by using the normalization condition:

$$\int_0^a \Psi_n^2\, dx = 1 = A^2 \int_0^a sin^2\left(\frac{n\pi}{a}x\right) dx = A^2 I$$

Evaluating the integral one finds $I=a/2$, same for all *n*. Thus the normalization constant A has the value

$A=(2/a)^{1/2}$ eq 3.15

Exercise 3.1 Calculate the probability of finding the particle between 0.3*a* and 0.6*a* for the *n*=1, *n*=2, and *n*=3 states. *Answer*: 0.545, 0.178, and 0.319 for *n*=1, 2, 3, respectively.

Exercise 3.2 Show that the functions Ψ_n in eq 3.12 are also eigenfunctions of the operator $\hat{p}_x^2$. What are the eigenvalues?

3.2 Particle in a 2D box

A particle moving in 2D has two degrees of freedom. Therefore, two independent variables (*x*, *y*) are required to locate the position of this particle in the 2D space. We will investigate the allowed energy levels of a free particle of mass *m*, trapped in a rectangular region of space with side lengths *a* and *b* (Figure 3.3)

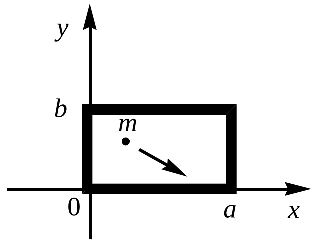

Figure 3.3 A free particle of mass *m* moving in a rectangular box.

The Hamiltonian operator of this particle is

$$\hat{H} = \hat{T} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2) = \left(\frac{1}{2m}\right)\hat{p}_x^2 + \left(\frac{1}{2m}\right)\hat{p}_y^2 \qquad \text{eq 3.16}$$

where $\hat{p}_q^2 = -\hbar^2 \frac{\partial^2}{\partial q^2},\ q = x, y$. Comparison of eq 3.16 with eq 3.2 shows that we can interpret $\hat{H}$ of eq 3.16 as the Hamiltonian for a system of two independent (fictitious) particles, each moving in 1D. The "*x*" particle is confined to move in a 1D box with walls at *x*=0 and *a*, while simultaneously, the "*y*" particle is trapped in another 1D box with walls at *y*=0 and *b*. The motions of these two fictitious particles are completely independent of each other. The energy of the physical particle in Figure 3.3 is a sum of contributions from each of the two fictitious particles (*cf*. eq 3.3a)

$$E = E_x + E_y \qquad \text{eq 3.17a}$$

and, the state function of the physical particle is a product (*cf*. eq 3.3b)

$$\Psi = \psi_x \psi_y \qquad \text{eq 3.17b}$$

The allowed energies of the physical particle follow from those of the "*x*" and "*y*" particles. The energy levels of the latter particles are, from eq 3.12

$$E_{n_x} = \varepsilon_x\, n_x^2, \quad n_x = 1,2,\ldots \qquad \varepsilon_x = \frac{h^2}{8ma^2} \qquad \text{eq 3.18a}$$

$$E_{n_y} = \varepsilon_y\, n_y^2, \quad n_y = 1,2,\ldots \qquad \varepsilon_y = \frac{h^2}{8mb^2} \qquad \text{eq 3.18b}$$

and the energy levels of the physical particle are

$$E_{n_x n_y} = E_{n_x} + E_{n_y} \qquad \text{eq 3.19a}$$

with corresponding (normalized) state functions

$$\Psi_{n_x n_y} = \psi_{n_x}\psi_{n_y} = N\, sin(\frac{n_x\pi}{a}x) sin(\frac{n_y\pi}{b}y), \qquad N = \left(\frac{4}{ab}\right)^{1/2} \qquad \text{eq 3.19b}$$

The ground state energy of the physical particle is $E_{11} = \varepsilon_x + \varepsilon_y$. This is also the ZPE of the particle (eq 3.14). The quantum numbers n_x and n_y are independent. If *a*≠*b*, the energy parameters ε_x and ε_y have different values, and a choice for (n_x, n_y), e.g. (1,2) will give a different energy by eq 3.19a than the choice (2,1) in which the two quantum numbers are interchanged; i.e. $E_{12} \neq E_{21}$.

Degeneracy of an energy level. The case of a square box where *a*=*b* deserves some discussion. In this case, $\varepsilon_x = \varepsilon_y \equiv \varepsilon$, and eq 3.19a becomes

$$E_{n_x n_y} = (n_x^2 + n_y^2)\varepsilon, \qquad n_x, n_y = 1,2,\ldots \qquad \text{eq 3.20}$$

This expression is symmetric with respect to the interchange of the two quantum numbers. E.g. E_{12}=E_{21}, so that two <u>different</u> functions Ψ_{12} and Ψ_{21} (see eq 3.19b) are associated with the <u>same energy</u>. We say that this energy level is "degenerate". The "degeneracy" of an energy level is the number of different wavefunctions all having the same energy, and is designated by the standard symbol g. Thus, g=2 for the energy level with energy $E_{12}= E_{21}$, and g=1 for the ground level. An energy level with g=1 is called "nondegenerate". If g=2, the level is called "doubly" degenerate; if g=3, the level is called "triply" degenerate, and so on. Energies of eq 3.20 are shown graphically in Figure 3.4. All levels in the figure are either nondegenerate or doubly degenerate.

Energy levels of a particle with only one degree of freedom are nondegenerate, regardless of the form of its potential energy function, V(x).

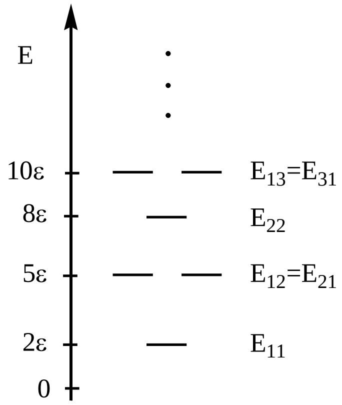

Figure 3.4 Energy levels of a free particle moving in a square box.

Exercise 3.3 *i*) Write the Hamiltonian operator for a free particle of mass m confined in a 3D box of sides a, b, and c. Use arguments similar to those in the 2D case to derive the allowed energies and the associated state functions of the physical particle. *ii*) Consider a cubical box of sides a. Draw an energy level diagram showing the first 10 distinct energy levels of the particle. Find the degeneracy, g, of each level.

3.3 System of *n* identical particles

Let us consider n identical particles moving independently of each other in the 1D box of Figure 3.1.We will refer to the allowed energies of a single particle, shown in Figure 3.2, as the "one-particle" energies. Each particle in this system has the same set of one-particle energies. In general, the total energy, E_{tot}, of a system of independent particles is a sum of contributions from each particle (eq 3.3a). When the particles of a system are identical (and independent), as in this example, we can express E_{tot} in another, more convenient form: We label the one-particle energy levels with an index j=1, 2, … in increasing order of their energies, E_j. Let n_j be the number of particles with energy E_j. Then we can write for the allowed energies of the system

$$E_{tot} = n_1E_1 + n_2E_2 + \cdots \qquad \text{eq 3.21a}$$

under the restriction that the total number, n, of the particles in the system is fixed

$$n_1 + n_2 + \cdots = n \qquad \text{eq 3.21b}$$

The quantity n_j is called the "occupation number" of the j^{th} one-particle energy level. If n_j =0 for a certain level, we say that the level is unoccupied. Any given set of occupation numbers subject to eq 3.21b specifies a possible energy for the system. As an example, let us assume that there are n=5 particles in the 1D box (Figure 3.5). Taking, e.g. n_1=3, n_2=0, and n_3=2, with all other one-particle levels unoccupied, eq 3.21a gives: $E_{tot} = 3E_1 + 2E_3 = 3\varepsilon + 2(9\varepsilon) = 21\varepsilon$. There are, of course, infinitely many different choices for the occupation numbers in combination with one-particle energies. Fortunately, we are usually interested in the lowest few energies of the system.

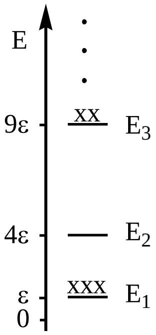

Figure 3.5 Graphical depiction of a particular set of occupation numbers for a system of 5 independent particles in the 1D box. An "x" symbol over a level symbol denotes one particle with an energy equal to that of the level. Here, n_1=3, n_3=2, and all other levels are unoccupied.

Electrons. When the particles under study are electrons, there is a constraint on the occupation numbers, known as the Pauli Exclusion Principle. This principle states that the maximum occupation number of a one-electron energy level is $2g$, where g is the degeneracy of the level. Thus for a nondegenerate level (g=1), the occupation number of the level can only be 0, or 1, or 2, if the particle in question is an electron.

Let us reconsider the previous example of 5 particles in 1D (Figure 3.5), assuming that the particles are electrons. The occupation number n_1=3 is not permitted by the Pauli principle, and therefore E_{tot}=21ε is not an allowed energy of this system.

An electron has a property called "spin", and experiments show that there are only two spin states for an electron. The two spin states are designated by the standard symbols α and β. In energy level diagrams, an electron with α spin is shown by an up arrow (↿), and that with β spin by a down arrow (⇂). The ground state energy of an n-electron system is obtained by choosing the occupation numbers of the one-electron energy levels, consistent with the Pauli principle, to give the minimum total energy. The ground state of "5 electrons in 1D" example is shown in Figure 3.6. The ground state energy is $2E_1 + 2E_2 + E_3 = 19\ \varepsilon$. Excited states of the system are obtained by exciting one or more electrons from the occupied levels to the unoccupied (or partially occupied) ones.

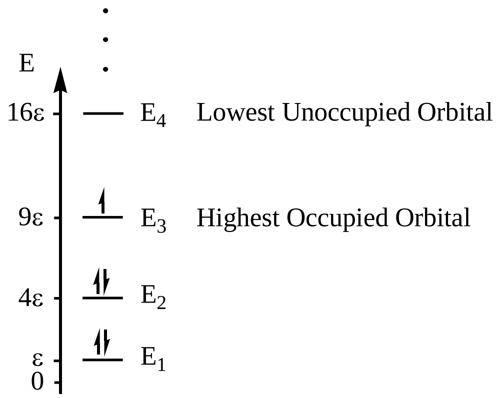

Figure 3.6 Graphical display of the ground state of 5 electrons moving in the 1D box.

In general, a one-electron state function associated with a one-electron energy level is called an "orbital". Thus, an orbital is a function of the spatial variables of a single electron; briefly, an orbital is a one-electron function. This term is used whenever electrons are involved, and at all levels of theory. For example, if the "particle in a 1D box" model is used for this purpose, the orbitals are the functions Ψ_n in eq 3.12, and the associated energies E_n in the same equation are then called "orbital energies". The electrons under investigation might belong either to an atom or a molecule. To distinguish between the two cases, the extended terms: "atomic orbital" (AO) and "molecular orbital" (MO) are used.

Exercise 3.4 The "free electron molecular orbital" method assumes that the π electrons of a linear conjugated polyene such as butadiene and hexatriene can be treated by the particle in a 1D box model. The number of electrons in the box is the number of π electrons in the molecule. The box length, *a*, is taken as the length of the carbon chain in the molecule. Using an average C-C bond length of 150 pm, the length of a chain with n carbon atoms is thus (n-1)x150 pm.

For each of butadiene and hexatriene, what is the excitation energy from the ground to the first excited state? What is the wavelength of light that would be absorbed in the transition? *Hint*: Draw a diagram similar to Figure 3.6 for each molecule.

Answer. Butadiene: 9.286 eV, 134 nm; Hexatriene: 4.680 eV, 265 nm