**CHM 3411 - Physical Chemistry II**
**Chapter 7 - Supplementary Material**


**1. Review of concepts from physics**

To understand the ways in which quantum mechanics differs from classical (macroscopic) physics it is useful to review some basic results.

Conservation laws - There are various quantities that remain unchanged in closed systems. These include mass, energy, momentum, angular momentum, and charge. Note the following:

1) Since mass can be converted into energy, and energy into mass (as indicated by the relationship $E = mc^2$), it is the total mass + energy that is conserved in a closed system. However, for the processes we will consider it is an extremely good approximation to treat mass and energy as separately conserved quantities.

2) Momentum ($\mathbf{p}$) is a vector quantity, $\mathbf{p} = m\mathbf{v}$ (where boldface is used to indicate vectors). Velocity ($\mathbf{v}$) is also a vector quantity. Vectors have two properties, magnitude and direction. The magnitude of a vector is indicated as follows: $|\mathbf{p}|$ = magnitude of the momentum vector. Quantities that have only magnitude, such as mass, are referred to as scalar quantities.

3) Angular momentum ($\mathbf{L}$) is also a vector. The angular momentum of an object is given by the relationship $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, where "x" indicates the cross product of the vectors $\mathbf{r}$ and $\mathbf{p}$, and $\mathbf{r}$ is a vector representing the position of the center of mass of the object in some coordinate system. Recall that the "right hand rule" applies to cross products.

4) The importance of conservation laws is that they place constraints on the behavior of closed systems. For example, mass and charge conservation (and also conservation of the numbers of atoms of each element in a closed system, which in the absence of nuclear reactions are conserved quantities) are used by chemists in balancing chemical reactions.

Equations of motion - For a one dimensional system

$$F = ma \tag{7.1.1}$$

where F = force and a = acceleration. Acceleration is the time derivative of velocity, that is, $a = dv/dt$. Since velocity is the time derivative of position ($v = dx/dt$) it follows that acceleration is equal to the second time derivative of position, $a = d^2x/dt^2$. Since $p = mv$, eq 7.1.1 may be rewritten as

$$F = m\,(dv/dt) = d(mv)/dt = dp/dt \tag{7.1.2}$$

where p is momentum. For a closed system with no dissipative forces (such as friction), force is also related to potential energy by the expression

$$F = -\,dV(x,t)/dx \tag{7.1.3}$$

where $V(x,t)$ is potential energy. Such systems are termed conservative systems, because the total energy of the system is constant.

Using eq 7.1.2 and 7.1.3 we may show that

$$d^2x/dt^2 = -\,(1/m)\,dV/dx \tag{7.1.4}$$

a differential equation for the motion of an object of mass m in a potential V. Given $V(x,t)$, $x_0$, and $(dx/dt)_0$ (the potential, initial position, and initial velocity) it is possible (in principle) to find an expression for $x(t)$.

There are various ways in which the equations of motion can be written in more general forms that make it easier to find solutions to problems of physical interest. The two most useful forms are the <u>Lagrangian</u> and the <u>Hamiltonian</u> equations of motion. The Hamiltonian for a conservative system is

$$H = T + V = E \qquad\qquad (7.1.5)$$

where T = kinetic energy, V = potential energy, and E, the total energy, is constant.

All of the above equations have analogous forms for systems of n dimensions, which can be found by replacing the appropriate scalar quantities in the one dimensional equations with vectors. For example, for a multidimensional system eq 7.1.1 becomes

$$\mathbf{F} = m\mathbf{a} \qquad\qquad (7.1.6)$$

<u>Equipartition theorem</u> - The equipartition theorem gives an expression for the average energy possessed by a system per degree of freedom. The theorem states that there will be an average energy of ½kT (where k is the Boltzmann constant and T is temperature) for each quadratic term in the expression for the energy of a system. This theorem can be proven using statistical mechanics. For example, for a monatomic ideal gas, where the only type of energy present is the kinetic energy due to the motion of the gas atoms, there will be an average energy of ½kT for motion of each atom in the x, y, and z directions. Therefore, the average total energy is

$$E = 3N(\tfrac{1}{2}kT) = (3NkT)/2 = (3nRT)/2 \qquad\qquad (7.1.7)$$

where $n = N/N_0$ is the number of moles of gas molecules, $N_0$ is Avogadro's number, and R is the gas constant (note that R and k are related by the expression $R = N_0 k$). Eq 7.1.7 agrees with the result derived from the kinetic theory of gases for the translational energy of N molecules of an ideal gas.

<u>Boltzmann distribution law</u> - This is another expression from statistical mechanics. Let i and j represent two <u>energy levels</u> in a system. At equilibrium, the probability of the system being in state j relative to that of being in state i is given by the equation

$$P_j/P_i = \exp[-(E_j-E_i)/kT] \qquad\qquad (7.1.8)$$

where $E_i$ and $E_j$ are the energies of the two states, $P_i$ and $P_j$ are probabilities and k is the Boltzmann constant. This expression can be derived using statistical mechanics.

## 2. Taylor series expansion

The Taylor series expansion of a function f(x) about a point a is given by the expression

$$f(x) = f(a) + (x-a)\,f'(a) + (x-a)^2\,f''(a)/2! + ... \qquad\qquad (7.2.1)$$

where f(a), f'(a), f''(a), ... are the value of the function, the first derivative of the function, the second derivative of the function, and so forth, evaluated at a. For the special case a = 0, the series expansion is called the Maclaurin series.

As an example of a Taylor series expansion of a function consider the following:

$e^x$, about the point a = 0. Since $d^n/dx^n\, e^x = e^x$ (that is, the first, second, third, ... derivative of $e^x$ is $e^x$) it follows that

$$e^x = e^0 + x\,e^0 + x^2\,e^0/2! + x^3\,e^0/3! + ... \qquad\qquad (7.2.2)$$

$$= 1 + x + x^2/2! + x^3/3! + ... \qquad\qquad (7.2.3)$$

Representing functions in terms of their series expansion is often used in calculating numerical values for functions or examining the limiting behavior of expressions or equations containing the functions.

### 3. Blackbody radiation and the Planck distribution law

An <u>ideal blackbody emitter</u> is a perfect absorber (and therefore a perfect emitter) of electromagnetic radiation. An example of such an ideal blackbody is given in Fig 7A.2 of Atkins. There are two related quantities that can be discussed in connection with a blackbody. The <u>energy density</u> of the blackbody, $\xi$, represents the energy per unit volume within the blackbody cavity. The <u>excitance</u>, or <u>intensity</u>, M, is the energy emitted by the blackbody per unit area and unit time. Both of these can be given for a particular wavelength range $\lambda$ to $\lambda + d\lambda$, or the expressions can be integrated over wavelength to give the <u>total energy density</u> or <u>total intensity</u> of the blackbody. Both $\xi$ and M are functions of wavelength and temperature only, with $\xi$ and M related by the expression

$$M(\lambda,T) \, d\lambda = (c/4) \, \xi(\lambda,T) \, d\lambda \tag{7.3.1}$$

where c is the speed of light.

Several observations can be made concerning the light emitted by an ideal blackbody (see Fig 7A.1 of Atkins for examples of such light emission distributions).

1) At any particular wavelength the intensity of emitted light increases monotonically with temperature.

2) The total intensity of emitted light is given by the <u>Stefan-Boltzmann law</u>

$$M(T) = \int_0^\infty M(\lambda,T) \, d\lambda = \sigma T^4 \tag{7.3.2}$$

where $\sigma$, the <u>Stefan-Boltzmann constant</u>, has a numerical value of $5.67 \times 10^{-8}$ W/m$^2\cdot$K$^4$ (where 1 W = 1 watt = 1 J/s, a unit of power).

3) The maximum intensity of emitted light is given by <u>Wien's law</u>

$$\lambda_{max}T = A_W \tag{7.3.3}$$

where $A_W$, the <u>Wien's law constant</u>, has a numerical value of $2.898 \times 10^6$ nm$\cdot$K.

The classical theory for blackbody light emission states that the energy density for the blackbody for a small range of wavelengths is the energy density for a single oscillator multiplied by the number density of oscillators in the blackbody, that is

$$\xi(\lambda,T) \, d\lambda = \varepsilon(\lambda,T) \, n(\lambda) \, d\lambda \tag{7.3.4}$$

where $\varepsilon(\lambda,T)$ is the energy density for a single oscillator and $n(\lambda) \, d\lambda$ is the total number of oscillators within the wavelength range $\lambda$ to $\lambda + d\lambda$. The expression for $n(\lambda) \, d\lambda$, derived by James Jeans (and thus called the <u>Jeans number</u>), is

$$n(\lambda) \, d\lambda = (8\pi/\lambda^4) \, d\lambda \tag{7.3.5}$$

If it assumed that the oscillators making up the blackbody are harmonic, then the equipartition theorem predicts that $\varepsilon(\lambda,T) = kT$. Substituting this result and eq 7.3.5 into eq 7.3.4 gives the result

$$\xi(\lambda,T) \, d\lambda = (8\pi kT/\lambda^4) \, d\lambda \tag{7.3.6}$$

the <u>Rayleigh-Jeans equation</u>. This equation is in good agreement with experimental results for large values of $\lambda$, but diverges (becomes infinite) in the limit of small wavelength, the so called "<u>ultraviolet catastrophe</u>".

In 1900 Max Planck derived the correct equation for blackbody radiation. Planck accepted Jeans's result for $n(\lambda) \, d\lambda$. To find an expression for $\varepsilon(\lambda,T)$, Planck assumed that the oscillators making up the blackbody were quantized, with a quantum of energy that is proportional to the frequency of oscillation, that is

$$\varepsilon_n(\nu,T) = nh\nu \; ; n = 0, 1, 2, ... \tag{7.3.7}$$

where, for convenience, we have for the time being written $\varepsilon$ as a function of frequency instead of wavelength, and h is the <u>Planck constant</u>. Using the Boltzmann distribution law (eq 7.1.8) the average energy density of an oscillator at equilibrium at a temperature T can be found. We begin with the expression

$$<\varepsilon(\nu,T)> = (\Sigma_{n=0}^{\infty}\, \varepsilon_n(\nu,T)\, P_n)/(\Sigma_{n=0}^{\infty}\, P_n) = (\Sigma_{n=0}^{\infty}\, nh\nu\, P_n)/(\Sigma_{n=0}^{\infty}\, P_n) \tag{7.3.8}$$

where $P_n$ is the probability of the oscillator having n quanta of excitation, the symbol $< \;>$ is used to indicate an average value for a quantity, and the summations extend from $n = 0$ to $\infty$. From the Boltzmann distribution law, we may say

$$P_n/P_0 = \exp(-nh\nu/kT) \tag{7.3.9}$$

so

$$P_n = P_0 \exp(-nh\nu/kT) \tag{7.3.10}$$

Substitution of this result into eq 7.3.8 gives

$$<\varepsilon(\nu,T)> = [\Sigma_{n=0}^{\infty}\, nh\nu\, P_0 \exp(-nh\nu/kT)]/[\Sigma_{n=0}^{\infty}\, P_0 \exp(-nh\nu/kT)] \tag{7.3.11}$$

$$= (h\nu\, \Sigma_{n=0}^{\infty}\, nr^n)/(\Sigma_{n=0}^{\infty}\, r^n) \tag{7.3.12}$$

where we have canceled a common factor of $P_0$, and defined $r = \exp(-h\nu/kT)$. But expressions for the two sums in eq 7.3.12 are known

$$\Sigma_{n=0}^{\infty} r^n = 1/(1-r) \qquad \Sigma_{n=0}^{\infty} n\, r^n = r/(1-r)^2 \tag{7.3.13}$$

Substituting these two summations into eq 7.3.12, and replacing r with $\exp(-h\nu/kT)$ we get, after a little bit of manipulation, the result

$$<\varepsilon(\nu,T)> = h\nu[\exp(h\nu/kT) - 1]^{-1} \tag{7.3.14}$$

Since $\nu\lambda = c$, then $\nu = c/\lambda$, and so

$$<\varepsilon(\lambda,T)> = (hc/\lambda)[\exp(hc/\lambda kT) - 1]^{-1} \tag{7.3.15}$$

Multiplication of this result by the Jeans number gives the final result

$$\xi(\lambda,T)\, d\lambda = (8\pi hc/\lambda^5)\, [\exp(hc/\lambda kT) - 1]^{-1}\, d\lambda \tag{7.3.16}$$

<u>the Planck distribution law</u>. The above result is more commonly expressed in terms of the intensity of emitted light, using the relationship between $\xi$ and M, to give

$$M(\lambda,T)\, d\lambda = (2\pi hc^2/\lambda^5)\, [\exp(hc/\lambda kT) - 1]^{-1}\, d\lambda \tag{7.3.17}$$

The Planck distribution law correctly predicts the dependence of the intensity of blackbody radiation on wavelength and temperature, and is in accord with Wien's law, the Stefan-Boltzmann law, and other experimental observations.

## 4. The photoelectric effect

When light strikes a metal surface electrons can be ejected from the metal, a process called the <u>photoelectric effect</u>. Experimentally, it is found that each metal has a characteristic wavelength $\lambda_0$, and that at wavelengths of light larger than this value no electrons are ejected from the metal no matter how intense the light that is used.

In 1905, Einstein proposed an explanation for the photoelectric effect based on the the existance of particles (photons) of light. Borrowing an idea used by Planck to explain blackbody radiation, Einstein assumed that the energy of a light photon was given by the expression

$$E_{photon} = h\nu = hc/\lambda \tag{7.4.1}$$

where $\nu$ is the frequency and $\lambda$ is the wavelength of the light used, and $c = \lambda\nu$. If we define $\Phi$, the <u>work function</u>, as the minimum energy required to remove an electron from a metal, then by conservation of energy it follows that

$$E_{photon} = h\nu = \Phi + E_{K,max} \tag{7.4.2}$$

where $E_{K,max}$ is the maximum kinetic energy of an ejected electron. Since $E_K$, the kinetic energy of the ejected electron, must be positive or zero, Einstein's explanation predicts that existance of a characteristic wavelength for a metal, with

$$\lambda_0 = hc/\Phi \tag{7.4.3}$$

Further, Einstein's explanation predicts that a plot of $E_{K,max}$ vs $\nu$ will (by eq 7.4.2) have a slope equal to h, the Planck constant. Experiments by Philip Lenard and others confirmed this prediction (see Atkins, Fig 7A.11).

## 5. Eigenvalue equations

An <u>eigenvalue equation</u> is an equation of the form

$$\hat{O} f(x) = c\, f(x) \tag{7.5.1}$$

where   $\hat{O}$ = an operator (one or a combination of mathematical operations)
        $f(x)$ = a function
        $c$ = a constant

A function $f(x)$ that satisfies the above equation is termed an <u>eigenfunction</u> of the operator $\hat{O}$, with c, the constant, the corresponding <u>eigenvalue</u>.

For example, consider the operator $\hat{O} = d/dx$. To check whether the function $f(x) = \cos(x)$ is an eigenfunction of this operator we substitute into eq 7.5.1

$$d/dx\,[\cos(ax)] = -\,a\sin(ax) \neq (\text{constant})\cos(ax) \tag{7.5.2}$$

and, therefore, $\cos(ax)$ is not an eigenfunction of the operator $\hat{O} = d/dx$. On the other hand, for the function $f(x) = \exp(ax)$, substitution into eq 7.5.1 gives

$$d/dx\,\exp(ax) = a\exp(ax) = (\text{constant})\exp(ax) \tag{7.5.3}$$

and so $f(x) = \exp(ax)$ is an eigenfunction of the operator $\hat{O} = d/dx$, with corresponding eigenvalue a.

The importance of the above lies in the fact that the <u>time independent Schrodinger equation</u> (TISE) is an eigenvalue equation. For a one dimensional system it takes the form

$$H \Psi_n = ( T + V ) \Psi_n = E_n \Psi_n \tag{7.5.4}$$

where H, the <u>Hamiltonian operator</u>, is equal to T + V, the operators for the kinetic and potential energy. These operators are constructed by the procedure discussed below. $\Psi_n$ is the $n^{th}$ solution to the eigenvalue equation, and is called the <u>wavefunction</u> of the system. $E_n$, the constant in the above eigenvalue equation, is the total energy corresponding to a system in a state with wavefunction$\Psi_n$.

One of the main tasks we will have this semester is to find solutions to the TISE for model systems. While the mechanics of finding solutions to the TISE may be complicated, the basic idea will always be that of finding functions that are eigenfunctions of the appropriate TISE, and the corresponding eigenvalues.

## 6. Properties of complex numbers

A <u>complex number</u> is any number that can be written in the form

$$c = a + bi \tag{7.6.1}$$

where a and b are real numbers and $i = (-1)^{1/2}$.

The <u>complex conjugate</u> of a number, written as $c^*$, is found by replacing i with -i everywhere it appears. If $c = a + bi$, then $c^* = a - bi$. Note that for a real number $c^* = c$.

The magnitude of a complex number is

$$|c| = (c^*c)^{1/2} = [(a -bi) (a + bi)]^{1/2} = (a^2 + b^2)^{1/2} \tag{7.6.2}$$

## 7. Postulates of quantum mechanics

The following are some of the main ideas of quantum mechanics. (For the present time we will limit ourselves to statements concerning the TISE (time independent Schrodinger equation), except as noted.)

1) The maximum information that can be known about a quantum mechanical system is contained in the wavefunction for the system.

2) Wavefunctions are found by solving the TISE corresponding to the system. The TISE is

$$H \Psi_n = ( T + V ) \Psi_n = E_n \Psi_n \tag{7.7.1}$$

where H, T and V are operators. The above equation is an <u>eigenvalue equation</u> (see section 4 of this handout for a discussion of eigenvalue equations).

3) The operators in quantum mechanics are found by the following substitution procedure ($\hbar = h/2\pi$).

| Classical quantity | | Quantum mechanical operator |
|---|---|---|
| position | x | $x = x$ |
| momentum | p ( = mv) | $p = - i\hbar \, d/dx$ |
| total energy* | E | $E = i\hbar \, d/dt$ |

\* Applies for the time dependent Schrodinger equation (TDSE) only.

Operators for other quantities may be constructed from the above information. For example, $T = p^2/2m$, so $T = (-\hbar^2/2m)\, d^2/dx^2$.

4) The operators in quantum mechanics corresponding to physically measurable quantities (position, momentum, total energy, and so forth) are <u>Hermitian operators</u>. A Hermitian operator is an operator for which

$$\int \Psi_i^* \, \hat{O} \, \Psi_j \, dx = [\int \Psi_j^* \, \hat{O} \, \Psi_i \, dx]^* \tag{7.7.2}$$

There are important consequences that follow from the fact that quantum mechanical operators are Hermitian operators, as we shall see below.

5) The wavefunctions that are solutions to a TISE have the following properties

a) They are <u>single valued</u>

b) They are <u>continuous functions</u>

c) They have <u>continuous first derivatives</u> (except for "infinite jumps" in V(x))

d) They are <u>normalizable</u> (except for the "free particle" wavefunction). Normalizability implies that

$$0 < \int_{-\infty}^{\infty} \Psi_n^* \, \Psi_n \, dx < \infty \tag{7.7.3}$$

where $\Psi_n^*$ is the <u>complex conjugate</u> of the wavefunction. If $\Psi_n$ is not a normalized wavefunction, it may be normalized by multiplication by a <u>normalization constant</u> N, chosen so that

$$\int_{-\infty}^{\infty} (N\Psi_n)^* \, (N\Psi_n) \, dx = 1 \tag{7.7.4}$$

The new, normalized wavefunction is then $\phi_n = N\Psi_n$.

e) The solutions to a particular TISE can be used to form a <u>complete orthonormal set</u> of functions, (sometimes called a set of <u>basis functions</u>). Orthonormality means that

$$\int_{-\infty}^{\infty} \Psi_i^* \, \Psi_j \, dx = \delta_{ij} \text{ , where } \delta_{ij} \text{ is the } \underline{\text{Kronecker delta function}}, \text{ with } \delta_{ij} = 1 \text{ when } i = j$$
$$= 0 \text{ when } i \neq j$$

This requires that the wavefunctions be normalized, and, for cases where there are <u>degenerate states</u> (different states with the same value for energy), orthonormal combinations of the states are found.

Based on the above, an arbitrary function f(x) may be written

$$f(x) = \Sigma_{i=1}^{\infty} \, c_i \Psi_i \tag{7.7.5}$$

where $c_i$ are constants, found using the expression

$$c_i = \int_{-\infty}^{\infty} \Psi_i^* \, f(x) \, dx \tag{7.7.6}$$

6) The square of the wavefunction is related to the probability of finding a particle in the region x to x + dx. For a normalized wavefunction this means

$$P_n(x) \, dx = \Psi_n^* \, \Psi_n \, dx \tag{7.7.7}$$

where $P_n(x)$ dx is the probability of finding the particle between x and x + dx. For a macroscopic region of space

$$P_n(a < x < b) = \int_a^b P_n(x) \, dx = \int_a^b \Psi_n^* \, \Psi_n \, dx \tag{7.7.8}$$

7) If $\Psi_n(x)$ is a solution of a particular TISE, then $[\Psi_n(x) \exp(i\theta)]$, where $\theta$ is a constant (a _phase factor_) is a solution to the TISE and $[c \, \Psi_n(x)]$, where c is a constant, is also a solution to the TISE. Solutions that differ only by a phase factor or a multiplicative constant are not considered separate solutions to the TISE.

8) Any physically measurable property (_observable_) of a system has a corresponding quantum mechanical operator $\hat{O}$. When a single measurement of the observable is carried out, the result of the measurement must be one of the eigenvalues of $\hat{O}$. When a large number of measurements are carried out on identical systems, the average, or _expectation value_, for the observable is

$$< O > = \int_{-\infty}^{\infty} \psi^* \, \hat{O} \, \psi \, dx \tag{7.7.9}$$

where O is the observable, $\hat{O}$ is the operator for the observable, and $\psi$ is the normalized wavefunction for the system. For the special case where $\psi$ is an eigenfunction of the operator $\hat{O}$, that is, where

$$\hat{O} \, \psi = c \, \psi \tag{7.7.10}$$

it follows that a measurement of the observable O will always given the value c as a result. Note that as a consequence of the fact that $\hat{O}$ is a Hermitian the eigenvalues of $\hat{O}$ will be real numbers, as one would expect for physically measurable quantities.

9) The _commutator_ of two operators A and B is given by the expression

$$[A,B] = AB - BA \tag{7.7.11}$$

For example,

$$[x,p] = xp - px \tag{7.7.12}$$

The easiest way to determine the value for the commutator of two operators is to have it operate on an arbitrary function f(x). If

$$[A,B] \, f(x) = (\text{term}) \, f(x) \tag{7.7.13}$$

then the term is the value for the commutator.

If the commutator $[A,B] = 0$, then we say that A and B _commute_, and it is in principle possible to simultaneously measure the values for the physically measurable properties corresponding to A and B with no uncertainty. In addition, when two operators commute it is possible to find a complete orthonormal set of basis functions that are simultaneously eigenfunctions of both A and B. Conversely, if the value for the commutator is different than zero, then we say that A and B do not commute. There will then be an _uncertainty relationship_ that applies to simultaneous measurement of the two properties, and it will not be possible to find a set of basis functions that are simultaneously eigenfunctions of both operators. Two important uncertainty relationships are the following

$$(\Delta x) \, (\Delta p_X) \geq \hbar/2 \tag{7.7.14}$$

$$(\Delta E) \, (\Delta t) \geq \hbar/2 \tag{7.7.15}$$

where $(\Delta x)$ is the uncertainty in position, $(\Delta p_x)$ is the uncertainty in momentum along the x-axis, and so forth.