Periodic table, constants, and conversion factors

1A																	8A
1 H 1.01	2A											3A	4A	5A	6A	7A	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc [98]	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]	103 Lr [262]	104 Rf [261]	105 Db [262]	106 Sg [266]												

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm [145]	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
89 Ac [227]	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]

Miscellaneous constants and conversion factors

R = 8.314 J/mol·K   1 atm = 1.01325 bar   1 bar = 10^5 Pa = 10^5 N/m^2
R = 0.08314 L·bar/mol·K   1 atm = 760. torr
R = 0.08206 L·atm/mol·K N_A = 6.022 x 10^{23}

c = 2.998 x 10^8 m/s
h = 6.626 x 10^{-34} J·s $\hbar = h/2\pi$ = 1.055 x 10^{-34} J·s   1 cm^{-1} = 1.986 x 10^{-23} J
k = 1.381 x 10^{-23} J/K   1 eV =1.602 x 10^{-19} J
                                                                       1 amu = 1.661 x 10^{-27} kg
m_e = 9.109 x 10^{-31} kg
m_p = 1.673 x 10^{-27} kg R_H = 109677. cm^{-1} = 1.09677 x 10^5 cm^{-1}
m_n = 1.675 x 10^{-27} kg

CHAPTER 7

Black body radiation (see Chapter 7 handout)

An ideal blackbody is a perfect absorber and emitter of light (electromagnetic radiation)

Note that $c = \lambda\nu$, where λ = wavelength (m), ν = frequency (s^{-1}), and c = speed of light = 2.998 x 10^8 m/s

The relationship between intensity ($M(\lambda,T)$ dλ) and energy density ($\xi(\lambda,T)$ dλ) is

$$M(\lambda,T) \, d\lambda = (c/4) \, \xi(\lambda,T) \, d\lambda$$

The correct equation for $M(\lambda,T)$ dλ must be consistent with Wien's law and the Stefan-Boltzmann law

By assuming vibrational energy is quantized in units of $E = nh\nu$, n = 0, 1, 2, … the Planck distribution law may be derived.

Photoelectric effect (see Chapter 7 handout)

Assume light is quantized as photons, with the energy of a photon $E_\gamma = h\nu = hc/\lambda$

If Φ is the minimum energy required for an electron to escape a metal (the work function), then the critical wavelength for the metal is $\lambda_0 = hc/\Phi$

If $\lambda > \lambda_0$, the light photons do not have sufficient energy to produce electrons from the metal

If $\lambda < \lambda_0$, then the light photons do have sufficient energy to produce electrons, and

$$E_\gamma = \Phi + E_{K,max} \text{ , where } E_{K,max} \text{ is the maximum kinetic energy of the electrons that escape the metal}$$

A plot of $E_{K,max}$ vs ν will have a slope equal to h, the Planck constant. The intercept of the plot can be used to find the vaue for the work function for the metal.

Atomic spectra

Atoms absorb and emit light only at specific wavelengths that are characteristic of the particular element present. This can be explained by assuming that atoms can only have certain values of energy, called energy levels.

For the most simple atom, hydrogen, the location of the energy levels is given by the equation

$$E_n = - R_H/n^2 \qquad n = 1, 2, 3, … \qquad R_H = 109677. \text{ cm}^{-1}$$

Heat capacity of metals

At high temperature, the constant volume molar heat capacity of a metal should be $C_{V,m} \cong C = 3R = 24.9$ J/mol·K . This is observed experimentally for most metals (the Dulong-Petit law), but at low temperature $C \rightarrow 0$. By assuming the vibrations in a metal are quantized in units of hν (similar to Planck's assumption for blackbody radiation), Einstein found a formula for C that qualitatively agreed with experiment, and which approached zero as T $\rightarrow$ 0. K. Debye modified Einstein's approach to find a slightly different relationship that better fit experimental data.

de Broglie wavelength

The de Broglie wavelength of a particle is $\lambda_{dB} = h/mv$, where m is the mass and v is the speed of the particle. The de Broglie relationship predicts that particles will exhibit wavelike properties under some conditions, as is observed in electron and neutron diffraction.

Eigenvalue equations (see Chapter 7 handout)

Postulutes of quantum mechanics (see Chapter 7 handout)

The maximum information that can be found in a quantum mechanical system is contained in the solution to the Schrodinger equation. For time independent systems, the time independent Schrodinger equation (TISE) is an eigenvalue equation, and its solutions give the wavefunctions (eigenfunctions) and possible values for energy (eigenvalues) for the system. Multiplying a wavefunction by a constant (real or complex) does not give a new separate solution to a TISE.

Any physically measurable quantity can be represented in terms of a quantum mechanical operator. The operators are Hermitian, and so average values (for many measurements) or particular values (for a single measurement) will always be real. Wavefunctions that are solutions to a TISE are single valued, continuous, and (except for cases where the potential jumps to $\pm \infty$) have a continuous first derivative. Wavefunctions are normalizable, and there is a general procedure for normalizing a wavefunction. The square of a normalized wavefunction is related to the probability of a particle being located in some region in space.

The solutions to a TISE form a complete orthonormal set of functions (a set of basis function). Other "well behaved" functions can be written in terms of the wavefunctions that are solutions to a TISE. There is a general procedure for finding the average value expected for any observable property of a quantum mechanical system. For a single measurement, the result must (when relevant) be one of the eigenvalues of the operator representing the property being measured.

Finally, the commutator of two operators is defined as [A,B] = AB – BA, where A and B are oertators. The value for a commutator can be found by allowing the commutator to operate on an arbitrary function.

If [A,B] = 0 , then the properties represented by A and B can be measured simultaneously without any inherent error. It is also possible to find a set of functions that are simultaneously eigenfunctions of the operators A and the operator B.

If [A,B] $\neq$ 0 , then there is always a minimum uncertainty when the properties represented by A and B are measured simultaneously. It is also impossible to find a set of functions that are simultaneously eigenfunctions of the operators A and the operator B.

The most important uncertainty relationships are

$$(\Delta x)\,(\Delta p_x) \geq \hbar/2$$

$$(\Delta E)\,(\Delta t) \geq \hbar/2$$

CHAPTER 8

Particle in a 1 dimensional box

The one dimensional particle in a box potential is

$$V(x) = 0 \quad \text{for } 0 \le x \le L \qquad\qquad V(x) = \infty \quad \text{for } x < 0 \text{ or } x > L$$

Because the potential is infinite outside the box, the wavefunction outside the box is equal to zero. Inside the box, the TISE is

$$-\,(\hbar/2m)\,d^2/dx^2\,\psi(x) = E\,\psi(x)$$

The normalized solutions and possible values for energy for this TISE are

$$\psi_n(x) = (2/L)^{1/2} \sin(n\pi x/L) \quad \text{for } 0 \le x \le L \qquad\qquad E_n = n^2 h^2/8mL^2 = n^2 E_0 \quad E_0 = h^2/8mL^2$$

$$\psi_n(x) = 0 \quad \text{for } x < 0 \text{ or } x > L \qquad\qquad n = 1, 2, 3, \ldots$$

The energy of the lowest energy state is E_0. As the quantum number n increases, the spacing between adjacent energy levels increases. The number of nodes in the wavefunction (places where the wavefunction is equal to zero, other that at the boundaries $x = 0$ and $x = L$) is equal to $n - 1$, where n is the quantum number.

Particle in a 3 dimensional box

The three dimensional particle in a box potential is

$$V(x,y,z) = 0 \qquad \text{when} \quad 0 \le x \le L_x \qquad V(x,y,z) = \infty \quad \text{otherwise}$$
$$0 \le y \le L_y$$
$$0 \le z \le L_z$$

This TISE may be solved by separation of variables, saying $\psi(x,y,z) = X(x)\,Y(y)\,Z(z)$ inside the box, and $\psi(x,y,z) = 0$ outside the box. The solution inside the box is therefore the product of three 1-dimensional particle in a box wavefunctions

$$\psi(x,y,z) = (2/L_x)^{1/2} \sin(n_x\pi x/L_x)\,(2/L_y)^{1/2} \sin(n_y\pi y/L_y)\,(2/L_z)^{1/2} \sin(n_z\pi z/L_z)$$

$$= (8/V)^{1/2} \sin(n_x\pi x/L_x) \sin(n_y\pi y/L_y) \sin(n_z\pi z/L_z) \qquad V = L_x L_y L_z = \text{volume of the box}$$

$$E(n_x,n_y,n_z) = (h^2/8m)\,[\,(n_x^2/L_x^2) + (n_y^2/L_y^2) + (n_z^2/L_z^2)\,]$$

$$n_x = 1, 2, 3, \ldots \quad n_y = 1, 2, 3, \ldots \quad n_z = 1, 2, 3, \ldots$$

For the special case where $L_x = L_y = L_z = L$ (particle in a cube), then the wavefunction inside the box is

$$\psi(x,y,z) = (8/V)^{1/2} \sin(n_x\pi x/L) \sin(n_y\pi y/L) \sin(n_z\pi z/L) \qquad V = L^3$$

$$E(n_x,n_y,n_z) = (h^2/8mL^2)\,[\,n_x^2 + n_y^2 + n_z^2\,] = [\,n_x^2 + n_y^2 + n_z^2\,]\,E_0 \quad \text{where } E_0 = h^2/8mL^2$$

$$n_x = 1, 2, 3, \ldots \quad n_y = 1, 2, 3, \ldots \quad n_z = 1, 2, 3, \ldots$$

For a cubic box we can have more than one state with the same value for energy. Degeneracy (g) refers to the number of different states with the same value for energy. For example, the states (2,1,1), (1,2,1) and (1,1,2) (where the numbers refer to the values n_x, n_y, n_z) are three different states, all which have an energy $E = 6\ E_0$. The degeneracy of the $E = 6\ E_0$ energy level is therefore $g = 3$.

Qualitative behavior of wavefunctions in 1-dimension

In general, we observe two types of behavior for TISE wavefunctions.

If $E > V$ (classically allowed regions) the wavefunction oscillates (like a sin wave). The larger the value for $E - V$ the more rapid the oscillations in the wavefunction.

If $E < V$ (classically forbidden region, since this would mean $T < 0$) the wavefunction is an exponential decay. The larger the value for $V - E$ the faster the exponential decay.

The wavefunctions have to obey all the other requirements of acceptable wavefunctions (single valued, continuous, continuous first derivative, and so forth).

Harmonic oscillator

The one dimensional harmonic oscillator potential is

$V(x) = kx^2/2$ k = force constant
                        x = displacement of the oscillator from equilibrium

The TISE is

$[- (\hbar/2m)\ d^2/dx^2 + kx^2/2\ ]\ \psi(x) = E\ \psi(x)$

The solutions and possible values for energy for this TISE are

$\psi_v(x) = N_v\ H_v(y)\ \exp(-y^2/2)$ N_v = normalization constant
                                         $H_v(y) = v^{th}$ Hermite polynomial
                                         $y = x/\alpha$ $\alpha = (\hbar^2/mk)^{1/4}$

$E_v = (v + \tfrac{1}{2})\ \hbar\omega$ $\omega = (k/m)^{1/2}$ $v = 0, 1, 2, \ldots$

The energy of the lowest energy state is $E = \tfrac{1}{2}\ \hbar\omega$. This energy is called the zero point energy, and is the difference between the energy of the lowest energy state and an energy of zero. Note that the spacing between adjacent energy levels is constant, and equal to $\hbar\omega$.

The normalization constant, N_v, takes on a different value for different values of v. It is found by the normalization condition

$1 = \int_{-\infty}^{\infty} [\ N_v\ H_v(y)\ \exp(-y^2/2)\ ]^2\ dx$

The wavefunctions that are solutions to the TISE for the harmonic oscillator have a small but finite probability of being in the classically forbidden region of the potential (where $E < V(x)$). The number of nodes in the wavefunction is equal to v, the value for the quantum number. The wavefunctions can be divided into even functions (where $v = 0, 2, 4, \ldots$) and odd functions ($v = 1, 3, 5, \ldots$).

The harmonic oscillator is a good model for vibrations in a diatomic molecule. In this case we usually write energy as $\hat{E}$ (in wavenumbers, or cm^{-1}). In general

$\hat{E}$ (in cm^{-1}) = $\dfrac{E}{hc}$ (in J)

If we rewrite the expression for the energy of a harmonic oscillator in wavenumbers, then the energy levels for a diatomic molecule A-B in the harmonic oscillator approximation are

$$\hat{E}_v = \dfrac{\hbar\omega}{hc}(v + \tfrac{1}{2}) = (v + \tfrac{1}{2})\,\varpi \qquad \varpi = \dfrac{1}{2\pi c}(k/\mu)^{1/2} \qquad \mu = \dfrac{m_A m_B}{(m_A + m_B)}$$

Note that ϖ has units of cm^{-1}. If we find the value for ϖ experimentally we can use the above equation to find the value for k, the force constant. The MKS units for k are kg/s^2, or N/m.

Particle on a ring

A particle on a ring is a paticle confined to move on a circle with fixed radius r, where $x^2 + y^2 = r^2 =$ constant. To solve this problem we need to work in polar coordinates (see Chapter 8 handout). The TISE in polar coordinates is

$$[\,(-\hbar^2/2mr^2)\,d^2/d\phi^2\,]\,\psi(\phi) = E\,\psi(\phi) \qquad \text{where } 0 \le \phi < 2\pi$$

The normalized solutions and possible values for energy for this TISE are

$$\psi_{m\ell}(\phi) = (1/2\pi)^{1/2}\exp(im_\ell\phi)$$

$$E_{m\ell} = (\hbar^2/2mr^2)\,m_\ell^2 = m_\ell^2\,E_0 \qquad E_0 = (\hbar^2/2mr^2)$$
$$m_\ell = 0, \pm 1, \pm 2, \pm 3, \ldots$$

Notice that the wavefunctions (except for the $m_\ell = 0$ solution) are imaginary functions. It sometimes helps to remember that $\exp(ix) = \cos(x) + i\sin(x)$. All of the energy levels except for the $m_\ell = 0$ level have a degeneracy of 2, since the $\pm m_\ell$ states have the same value for energy. The lowest energy level has an energy of zero, and the spacing between adjacent energy levels increases as $|m_\ell|$ increases.

There is an angular momentum associated with the particle on a ring, in the same direction as the axis perpendicular to the ring (usually taken to be the z axis). The quantum mechanical operator for this angular momentum is $L_z = -i\hbar\,d/d\phi$.

In general, if ψ_a and ψ_b are two solutions to the same TISE corresponding to the same value for energy (that is, if they are degenerate solutions) then any linear combination of these two solutions will also be a solution to the TISE. We can make use of this general property to rewrite the solutions to the TISE for a particle on a ring (which are imaginary functions) in terms of equivalent solutions that are real functions.

Particle on a sphere

A particle on a sphere is a particle confined to move on a sphere with fixed radius r, where $x^2 + y^2 + z^2 = r^2 =$ constant. To solve this problem we need to work in spherical polar coordinates (see Chapter 8 handout). The TISE in spherical polar coordinates is

$$[\,(-\hbar^2/2mr^2)\,\Lambda^2\,]\,\psi(\theta,\phi) = E\,\psi(\theta,\phi) \qquad \text{where} \quad \begin{array}{l} 0 \le \theta < \pi \\ 0 \le \phi < 2\pi \end{array}$$

and the Λ^2 operator is defined in the Chapter 8 handout. Separation of variables (assuming $\psi(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$) can be used to solve this TISE.

The normalized solutions to this TISE are called the spherical harmonics $Y_{\ell,m\ell}(\theta,\phi)$. Normalization for the paeticle on a sphere means

$$1 = \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \; Y^*_{\ell,m\ell}(\theta,\phi) \; Y_{\ell,m\ell}(\theta,\phi)$$

where the term $\sin\theta \, d\theta$ that appears in the integral is an integration factor (see Chapter 8 handout). The expectation (average) value for a physical quantity represented by the quantum mechanical operator $\hat{O}$ is

$$<\hat{O}> = \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \; Y^*_{\ell,m\ell}(\theta,\phi) \; \hat{O} \; Y_{\ell,m\ell}(\theta,\phi)$$

The restrictions on the quantum numbers ℓ and m_ℓ are

$$\ell = 0, 1, 2, \ldots$$

$$m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell$$

The possible values for energy for this system are

$$E_\ell = (\hbar^2/2mr^2) \; \ell \, (\ell + 1) = \ell \, (\ell + 1) \, E_0 \quad \text{where } E_0 = (\hbar^2/2mr^2)$$

Since the energy for a particle on a sphere only depends on the value for the quantum number ℓ, the degeneracy (number of different states with the same energy) for a particular energy level is $g = 2\ell + 1$. The lowest energy state for a particle on a sphere has an energy of zero. As the value for ℓ increases, the spacing between adjacent energy levels also increases.

The particle on a sphere is a good model for rotational motion of a diatomic molecule. As with vibrational motion in a diatomic molecule, we usually work in energy units of cm^{-1}. We also use J and M_J in place of ℓ and m_ℓ for the quantum numbers. In that case, we may say

$$E_J = \frac{h}{8\pi^2 c\mu r_e^2} \; J \, (J + 1) = B \, J \, (J + 1) \quad \text{where } B = \frac{h}{8\pi^2 c\mu r_e^2} \quad \text{is the rotational constant}$$

$$J = 0, 1, 2, \ldots$$
$$M_J = 0, \pm 1, \pm 2, \ldots, \pm J$$

In the above expression r_e is the equilibrium bond distance for the molecule. Note that the restrictions on the quantum numbers J and M_J are the same as on the quantum numbers ℓ and m_ℓ. If the value for B is found from experiment, the above equation for B can be used to find the value for r_e for the diatomic molecule.