

**Table 1:** Key units in Physical Chemistry

$N_{\text{Av}}$ :	$6.02214 \times 10^{23}$	$\text{mol}^{-1}$		
1 amu:	$1.6605 \times 10^{-27}$	kg		
$k_{\text{B}}$ :	$1.38065 \times 10^{-23}$	$\text{J K}^{-1}$	$8.61734 \times 10^{-5}$	$\text{eV K}^{-1}$
$R$ :	8.314472	$\text{J K}^{-1} \text{mol}^{-1}$	$8.2057 \times 10^{-2}$	$\text{l atm mol}^{-1} \text{K}^{-1}$
$\sigma_{\text{SB}}$ :	$5.6704 \times 10^{-8}$	$\text{J s}^{-1} \text{m}^{-2} \text{K}^{-4}$		
$c$ :	$2.99792458 \times 10^8$	$\text{m s}^{-1}$		
$h$ :	$6.62607 \times 10^{-34}$	$\text{J s}$	$4.13566 \times 10^{-15}$	$\text{eV s}$
$\hbar$ :	$1.05457 \times 10^{-34}$	$\text{J s}$	$6.58212 \times 10^{-16}$	$\text{eV s}$
$hc$ :	1239.8	$\text{eV nm}$		
$e$ :	$1.60218 \times 10^{-19}$	C		
$m_e$ :	$9.10938215 \times 10^{-31}$	kg	1: 0.5109989	$\text{MeV c}^{-2}$
$\epsilon_0$ :	$8.85419 \times 10^{-12}$	$\text{C}^2 \text{J}^{-1} \text{m}^{-1}$	$5.52635 \times 10^{-3}$	$e^2 \text{\AA}^{-1} \text{eV}^{-1}$
$e^2/4\pi\epsilon_0$ :	$2.30708 \times 10^{-28}$	$\text{J m}$	14.39964	$\text{eV \AA}$
$a_0$ :	$0.529177 \times 10^{-10}$	m	0.529177	$\text{\AA}$
$E_{\text{H}}$ :	1	Ha	27.212	eV

## 1 The Classical Foundations

### 1.1 Lecture 0: Introduction

1. Burning lighter
2. Foundations of Physical Chemistry
  - (a) Quantum mechanics
  - (b) Statistical mechanics
  - (c) Thermodynamics, kinetics, spectroscopy
  - (d) Physical and chemical properties of matter

### 1.2 Lecture 1: Basic statistics

1. Discrete probability distributions—Coin flip
  - (a) Example of Bernoulli trial,  $2^n$  possible outcomes from  $n$  flips
  - (b) Number of ways to get  $i$  heads in  $n$  flips,  ${}_nC_i = n!/i!(n-i)!$
  - (c) Probability of  $i$  heads  $P_i \propto {}_nC_i$
  - (d) Normalized probability,  $\tilde{P}_i = P_i / \sum_i P_i = {}_nC_i / 2^n$
  - (e) Expectation value  $\langle i \rangle = \sum_i i \tilde{P}_i$
2. Continuous distributions—temperature
  - (a) Probability density  $P(x)$  has units  $1/x$
  - (b) Normalized  $\tilde{P}(x) = P(x) / \int P(x) dx$
  - (c) (Unitless) probability  $a < x < b = \int_a^b \tilde{P}(x) dx$

(d) Expectation value  $\langle f(x) \rangle = \int f(x) \tilde{P}(x) dx$

(e) Mean =  $\langle x \rangle$

(f) Mean squared =  $\langle x^2 \rangle$

(g) Variance  $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$

(h) Standard deviation  $\Delta x = \sigma$

### 3. Boltzmann distribution

(a)  $P(E) \propto e^{-E/k_B T}$ , in some sense the definition of temperature

(b) Energy and its units

(c) Absolute temperature and its units

(d)  $k_B T$  as an energy scale, 0.026 eV at 298 K

(e) Gravity example

i.  $E(h) = mgh$ , linear, continuous energy spectrum

ii. molecule vs car in a gravitational field (Table 2)

iii. Barometric law for gases,  $P = P_0 e^{-mgh/k_B T}$

(f) Kinetic energy in 1-D example

i.  $KE = \frac{1}{2} m v_x^2$

ii.  $P_{1D}(v_x) = \left( \frac{m}{2\pi k_B T} \right)^{1/2} \exp \left( -\frac{m|v_x|^2}{2k_B T} \right)$

iii. Gaussian distribution, mean  $\mu$ , variance  $\sigma^2$

$$G(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left( -\frac{(x - \mu)^2}{2\sigma^2} \right)$$

iv. By inspection,  $\mu = \langle v_x \rangle = 0$ ,  $\sigma^2 = \langle v_x^2 \rangle = k_B T/m$

v. Molecule vs car again

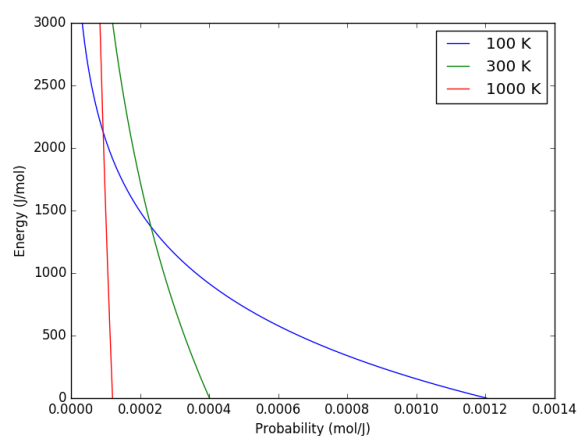
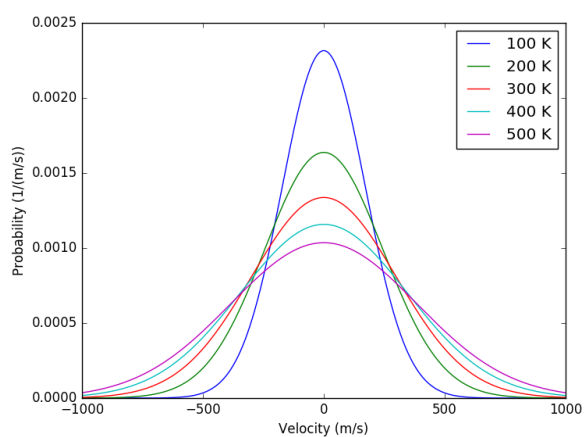
(g) Equipartition – energy freely exchanged between all degrees of freedom

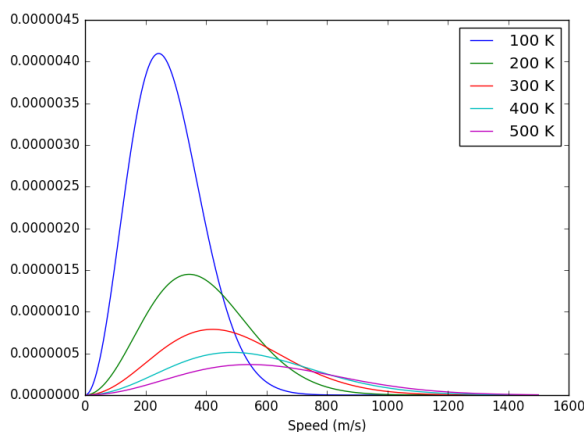
**Table 2:** Car vs gas molecule at the earth's surface

	car	gas molecule
$m$	1000 kg	$1 \times 10^{-26}$ kg
$h$	1 m	1 m
$mgh$	9800 J	$9.8 \times 10^{-26}$ J
	$6.1 \times 10^{22}$ eV	$6.1 \times 10^{-7}$ eV
$T$	298 K	298 K
$k_B T$	0.026 eV	0.026 eV
$mgh/k_B T$	$2.4 \times 10^{24}$	$2.3 \times 10^{-5}$
$P(1 \text{ m})/P(0)$	$e^{-2.4 \times 10^{-24}}$	0.99998
$\langle h \rangle$	0 m	42 km
$\langle v_x \rangle^{1/2}$	$2 \times 10^{-12}$ m/s	640 m/s

**Table 3:** Energy conversions and correspondences

	J	eV	Hartree	$\text{kJ mol}^{-1}$	$\text{cm}^{-1}$
1 J =	1	$6.2415 \times 10^{18}$	$2.2937 \times 10^{17}$	$6.0221 \times 10^{20}$	$5.0340 \times 10^{22}$
1 eV =	$1.6022 \times 10^{-19}$	1	0.036748	96.485	8065.5
1 Ha =	$4.3598 \times 10^{-18}$	27.212	1	2625.6	219474.6
1 $\text{kJ mol}^{-1}$ =	$1.6605 \times 10^{-21}$	0.010364	$3.8087 \times 10^{-4}$	1	83.5935
1 $\text{cm}^{-1}$ =	$1.986410^{-23}$	$1.23984 \times 10^{-4}$	$4.55623 \times 10^{-6}$	0.011963	1

**Figure 1:** Boltzmann distribution at various temperatures**Figure 2:** One-dimensional (Gaussian) velocities of  $\text{N}_2$  gas



**Figure 3:** Maxwell-Boltzmann speed distribution of  $N_2$  gas

### 1.3 Lecture 2: Kinetic theory of gases

#### 1. Postulates

- (a) Gas is composed of molecules in constant random, thermal motion
- (b) Molecules only interact by perfectly elastic collisions
- (c) Volume of molecules is  $\ll$  total volume

#### 2. Maxwell-Boltzmann distribution of molecular speeds

- (a) Speed  $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$
- (b)  $P_{MB}(v)dv = P_{1D}(v_x)P_{1D}(v_y)P_{1D}(v_z) * \text{degeneracy}(v)dv$
- (c) mean speeds  $\propto \sqrt{T}$
- (d) mean energy  $U = \frac{3}{2}RT$  and heat capacity  $C_v = \frac{3}{2}R$

#### 3. Flux and pressure

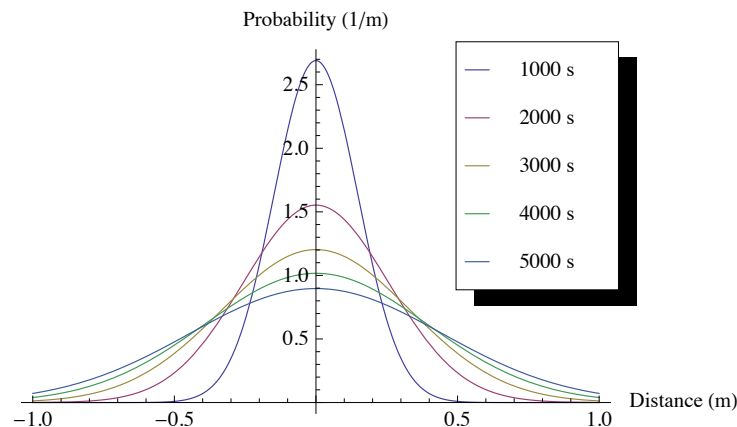
- (a) Velocity flux  $j(v_x)dv_x = v_x \frac{N}{V} P(v_x)dv_x$ , molecules /area /time / $v_x$
- (b) Wall collisions,  $J_w$ , total collisions /area /time
- (c) Momentum exchange, pressure, ideal gas law

#### 4. Collisions and mean free path

- (a) Collision cross section  $\sigma = \pi d^2$ , size of molecule
- (b) Molecular collisions,  $z$  per molecule and  $z_{AA}$  per volume
- (c) Mean free path,  $\lambda$ , mean distance between collisions

**Table 4:** Kinetic theory of gases key equations

Boltzmann distribution ( $g(E)$ : degeneracy of $E$ )	$P(E) = g(E)e^{-E/k_B T}$
Maxwell-Boltzmann distribution	$P_{\text{MB}}(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)$
Mean and RMS speeds	$\langle v \rangle = \left(\frac{8k_B T}{\pi m}\right)^{1/2} \quad \langle v^2 \rangle^{1/2} = \left(\frac{3k_B T}{m}\right)^{1/2}$
Pressure	$\langle P \rangle = \frac{\Delta p}{\Delta t} = m \frac{N}{V} \frac{1}{3} \langle v^2 \rangle = \frac{N k_B T}{V} = \frac{n R T}{V}$
Wall collision frequency	$J_W = \frac{1}{4} \frac{N}{V} \langle v \rangle = \frac{P}{(2\pi m k_B T)^{1/2}}$
Molecular collision frequency	$z = \sqrt{2} \sigma \langle v \rangle \frac{N}{V} = \frac{4\sigma P}{(\pi m k_B T)^{1/2}}$
Total collisions	$z_{AA} = \frac{1}{2} \frac{N}{V} z$
Mean free path	$\lambda = \frac{\langle v \rangle}{z} = \frac{V}{\sqrt{2} \sigma N}$
Graham's effusion law	$\frac{dN}{dt} = \text{Area} \cdot J_w \propto 1/m^{1/2}$
Effusion from a vessel	$P = P_0 e^{-t/\tau}, \tau = \frac{V}{A} \left(\frac{2\pi m}{k_B T}\right)^{1/2}$
Self-diffusion constant	$D_{11} = \frac{1}{3} \langle v \rangle \lambda$
Diffusion rate	$\langle x^2 \rangle^{1/2} = \sqrt{2Dt} \quad \langle r^2 \rangle^{1/2} = \sqrt{6Dt}$
Einstein-Smoluchowski equation	$D_{11} = \frac{\delta^2}{2\tau}$
Stokes-Einstein equation for liquids	$D_{11} = \frac{k_B T}{4\pi\eta r}$ "Slip" boundary
	$D_{\text{Brownian}} = \frac{k_B T}{6\pi\eta r}$ "Stick" boundary



**Figure 4:** Diffusional spreading,  $\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$

### 1.4 Lecture 3: Transport

1. Effusion and Graham's law, effusion rate  $\propto MW^{-1/2}$
2. Fick's first law: net flux proportional to concentration gradient
  - (a)  $j_x = -D \frac{dc}{dx}$
  - (b) Self-diffusion constant,  $D = \frac{1}{3} \lambda \langle v \rangle$
3. Knudsen diffusion,  $D = \frac{1}{3} l \langle v \rangle$
4. Fick's second law: time evolution of concentration gradient
  - (a) Continuity with no advection:  $\frac{\partial c}{\partial t} = -\nabla \cdot \vec{j} + \text{gen}$
  - (b) One-dimension:  $\frac{dc}{dt} = D \frac{d^2 c}{dx^2}$
  - (c) Diffusion has Gaussian probability distribution:  $c(x, t)/c_0 = [2\sqrt{\pi Dt}]^{-1} \exp(-x^2/4Dt)$
5. Seeing is believing—Brownian motion
  - (a) Seemingly random motion of large particles (“dust”) due to “kicks” from invisible molecules
  - (b) Einstein receives Nobel Prize for showing:
    - i. Motion follows same Gaussian diffusion behavior
    - ii. From steady-state arguments in a field, diffusion constant is ratio of Boltzmann energy,  $k_B T$ , to mobility
    - iii. Mobility inversely related to viscosity
  - (c) Stokes-Einstein equation
  - (d) Allows measurement of Avogadro's number, final proof of kinetic theory
  - (e) Similar model for diffusion of liquid molecules, slip boundary
6. Random walk model of diffusion
  - (a) Binomial distribution
  - (b) Large  $N$  and Stirling approximation
  - (c) Einstein-Smoluchowski relation

**Table 5:** Classical waves

The wave equation	$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2}$
General solution	$\Psi(x, t) = A \sin(kx - \omega t)$
Wavelength (distance)	$\lambda = 2\pi/k$
Frequency (/time)	$\nu = \omega/2\pi$
Speed	$v = \lambda\nu$
Amplitude (distance)	$A$
Energy	$E \propto A^2$
Standing wave	$\Psi(x, t) = A \sin(kx) \cos(\omega t), \quad k = n\pi/a$

## 2 Quantum Mechanics: Blurred Lines Between Particles and Waves

### 2.1 Lecture 4: Duality and demise of classical physics

#### 2.1.1 Properties of waves

1. Traveling waves, standing waves
2. interference, diffraction
3. Expected energy of a classical oscillator,  $\langle \epsilon \rangle_\nu = k_B T$  for all  $\nu$

#### 2.1.2 Blackbody radiation

1. Hohlraum spectrum (like the sun) empirically observed to obey:
  - (a) Stefan-Boltzmann law, total irradiance
  - (b) Wien's displacement law
2. Rayleigh-Jeans predicts spectrum using classical physics
  - (a) standing waves + classical oscillators  $\rightarrow$  ultraviolet catastrophe
3. Planck model
  - (a) Energy spectrum of oscillators are *quantized*,  $\epsilon_\nu = nh\nu$
  - (b) Expected energy of a quantized oscillator,  $\langle \epsilon \rangle_\nu = h\nu / (e^{h\nu/k_B T} - 1)$
  - (c) Correctly reproduces Stefan-Boltzmann and Wien Laws!

#### 2.1.3 Heat capacities of solids

1. Law of DuLong and Pettite,  $C_v = 3R$ , fails at low  $T$
2. Einstein model
  - (a) Atomic vibrations are *quantized*,  $\epsilon_n = nh\nu$
  - (b) Heat capacity goes to zero at low  $T$

**2.1.4 Photoelectric effect**

1. Stopping potential and work function,  $E_{\text{kinetic}} = h\nu - W$
2. Kinetic energy varies with light frequency, number of electrons varies with light intensity

**2.1.5 Compton effect**

1. light scattering of electrons changes  $\lambda$
2. Photon properties,  $\epsilon = h\nu, p = h/\lambda$

**2.1.6 Wave-particle duality****2.1.7 Rutherford, planetary model of atom**

1. Inconsistent with Maxwell's equations

**2.1.8 Bohr model of H atom**

1. Discrete H energy spectrum and Rydberg formula
2. Bohr model (the old quantum mechanics)
  - (a) Stable electron "orbits," quantized angular momentum
  - (b) Light emission corresponds to orbital jumps,  $\nu = \Delta E/h$
  - (c) Bohr equations
  - (d) Comparison with Rydberg formula
  - (e) Failure for larger atoms

**2.1.9 de Broglie relation**

1.  $\lambda = h/p$  *universally*
2. Relation to Bohr orbits
3. Davison and Germer experiment,  $e^-$  diffraction off Ni

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```

1  import numpy as np
2  import matplotlib.pyplot as plt
3
4  hc = 1239.8          eV nm
5  c = 2.9979e8 * 1.e9  nm/s
6  k = 8.61734e5       eV /K
7  hck = hc/k          nm K
8
9  def Irrad(wl,T):
10     return (8. * np.pi * hc * c * wl**5) / (np.exp(hck/(wl*T))1)
11  def PlanckEnergy(wl,T):
12     return (hc/wl) / (np.exp(hck/(wl*T))1)
13
14  plt.figure()
15  wl=np.linspace(100,5000,1000)
16  for T in [1000.,2000.,3000.,4000.,5000.]:
17     Intensity = Irrad(wl,T)
18     plt.plot(wl,Intensity,label= K.format(T))

```

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```

19
20 legend=plt.legend()
21 plt.xlabel(Wavelength (nm))
22 plt.ylabel(Irradiance (eV/nm3/s))
23 plt.title(Boltzmann distribution at various temperatures)
24 plt.savefig(./Images/BlackBody.png)
25
26 plt.figure()
27 color=[red,orange,green,blue,violet]
28 wl=np.linspace(100,20000,1000)
29 for T in [1000.,2000.,3000.,4000.,5000.]:
30     Energy = PlanckEnergy(wl,T)
31     plt.plot(wl,Energy,label= K.format(T),color=color[0])
32     kT = k*T
33     plt.plot([100,max(wl)], [kT,kT],ls=,color=color.pop(0))
34
35 legend=plt.legend()
36 plt.xlabel(Wavelength (nm))
37 plt.ylabel(Energy (eV))
38 plt.title(Boltzmann distribution at various temperatures)
39 plt.savefig(./Images/Planck.png)

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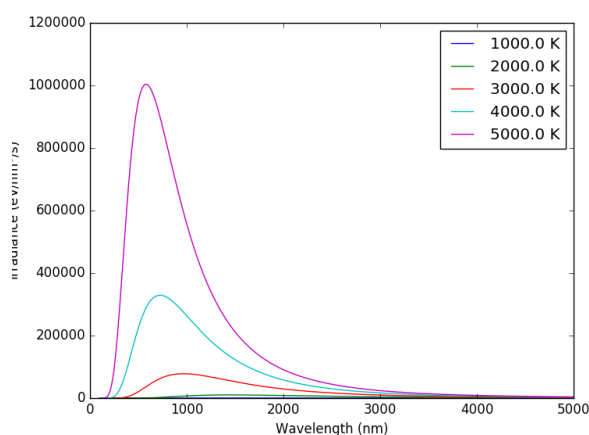


Figure 5: Blackbody irradiance

## 2.2 Lecture 5: Postulates of quantum mechanics

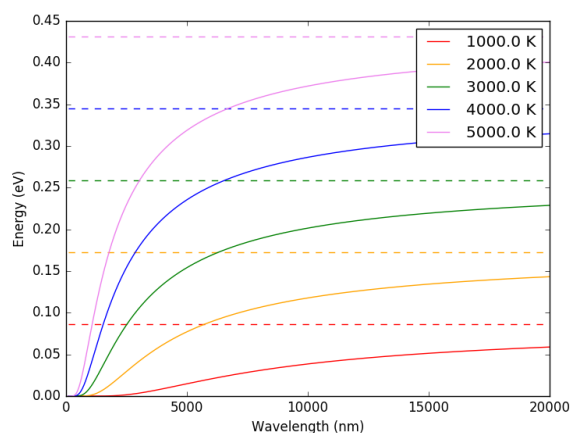
### 2.2.1 Schrödinger equation describes wave-like properties of matter

### 2.2.2 Born interpretation

1. wavefunction is a probability amplitude
2. wavefunction squared is probability density

### 2.2.3 Postulates

1. Wavefunction contains all information about a system
2. Operators used to extract that information
  - (a) QM operators are *Hermitian*



**Figure 6:** Average energy of a Planck quantized oscillator

**Table 6:** The new physics

Stefan-Boltzmann Law	$\int I(\lambda, T) d\lambda = \sigma_{\text{SB}} T^4$
Wien's Law	$\lambda_{\text{max}} T = 2897768 \text{ nm K}$
Rayleigh-Jeans eq	$I(\lambda, T) = \frac{8\pi}{\lambda^4} k_B T c$
Blackbody irradiance	$I(\lambda, T) = \frac{8\pi}{\lambda^5} \frac{hc^2}{e^{hc/\lambda k_B T} - 1}$
Einstein crystal	$C_v = 3R \left( \frac{h\nu}{k_B T} \right)^2 \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2}$
Photon energy	$\epsilon = h\nu = hc/\lambda$
Rydberg equation	$\nu = R_H c \left( 1/n^2 - 1/k^2 \right)$
Bohr equations	$l_n = n\hbar$
$n = 1, 2, \dots$	$r_n = n^2 \left( \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} \right) = n^2 a_0$
	$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -\frac{E_H}{2} \frac{1}{n^2}$
	$p_n = \frac{e^2}{4\pi\epsilon_0} \frac{m_e}{\hbar} \frac{1}{n} = p_0 \frac{1}{n}$
de Broglie equation	$\lambda = \frac{h}{p}$

- (b) Have eigenvectors and real eigenvalues,  $\hat{O}\psi_i = o\psi_i$
  - (c) Are orthogonal,  $\langle\psi_i|\psi_j\rangle = \delta_{ij}$
  - (d) Always observe an eigenvalue when making an observation
3. Expectation values
  4. Energy-invariant wavefunctions given by Schrödinger equation
  5. Uncertainty principle

## 2.2.4 Particle in a box illustrations

## 2.3 Lecture 6: Particle in a box model

### 2.3.1 Particle between infinite walls, electron confined in a wire

### 2.3.2 Classical solution, either stationary or uniform bouncing back and forth

### 2.3.3 One-dimensional QM solutions

1. Schrödinger equation and boundary conditions
2. discrete, quantized solutions
3. standing waves,  $\lambda = 2L/n$ ,  $n - 1$  nodes, non-uniform probability
4. [Ho paper](#), STM of Pd wire
5. zero point energy and uncertainty
6. correspondence principle
7. superpositions

### 2.3.4 Finite walls and tunneling

1. Potential well of finite depth  $V_0$
2. Finite number of bound states
3. Classical region,  $\psi(x) e^{ikx} + e^{-ikx}$ ,  $k = \sqrt{2mE}/\hbar$
4. “Forbidden” region,  $\psi(x) e^{\kappa x} + e^{-\kappa x}$ ,  $\kappa = \sqrt{2m(V_0 - E)}/\hbar$
5. Non-zero probability to “tunnel” into forbidden region
6. Tunneling between two adjacent wells: chemical bonding, STM, nanoelectronics
7. H atom tunneling:  $\text{NH}_3$  inversion, H transfer, kinetic isotope effect

### 2.3.5 Multiple dimensions

1. separation of variables, one quantum number for each dimension

**Table 7:** Postulates of Non-relativistic Quantum Mechanics

**Postulate 1: The physical state of a system is completely described by its wavefunction  $\Psi$ .** In general,  $\Psi$  is a complex function of the spatial coordinates and time.  $\Psi$  is required to be:

- I. Single-valued
- II. continuous and twice differentiable
- III. square-integrable ( $\int \Psi^* \Psi d\tau$  is defined over all finite domains)
- IV. For bound systems,  $\Psi$  can always be normalized such that  $\int \Psi^* \Psi d\tau = 1$

**Postulate 2:** To every physical observable quantity  $M$  there corresponds a Hermitian operator  $\hat{M}$ . **The only observable values of  $M$  are the eigenvalues of  $\hat{M}$ .**

Physical quantity	Operator	Expression
Position $x, y, z$	$\hat{x}, \hat{y}, \hat{z}$	$x, y, z$
Linear momentum $p_x, \dots$	$\hat{p}_x, \dots$	$-i\hbar \frac{\partial}{\partial x}, \dots$
Angular momentum $l_x, \dots$	$\hat{p}_x, \dots$	$-i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \dots$
Kinetic energy $T$	$\hat{T}$	$-\frac{\hbar^2}{2m} \nabla^2$
Potential energy $V$	$\hat{V}$	$V(\mathbf{r}, t)$
Total energy $E$	$\hat{H}$	$-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t)$

**Postulate 3:** If a particular observable  $M$  is measured many times on many identical systems in a state  $\Psi$ , the average results will be the expectation value of the operator  $\hat{M}$ :

$$\langle M \rangle = \int \Psi^* (\hat{M} \Psi) d\tau$$

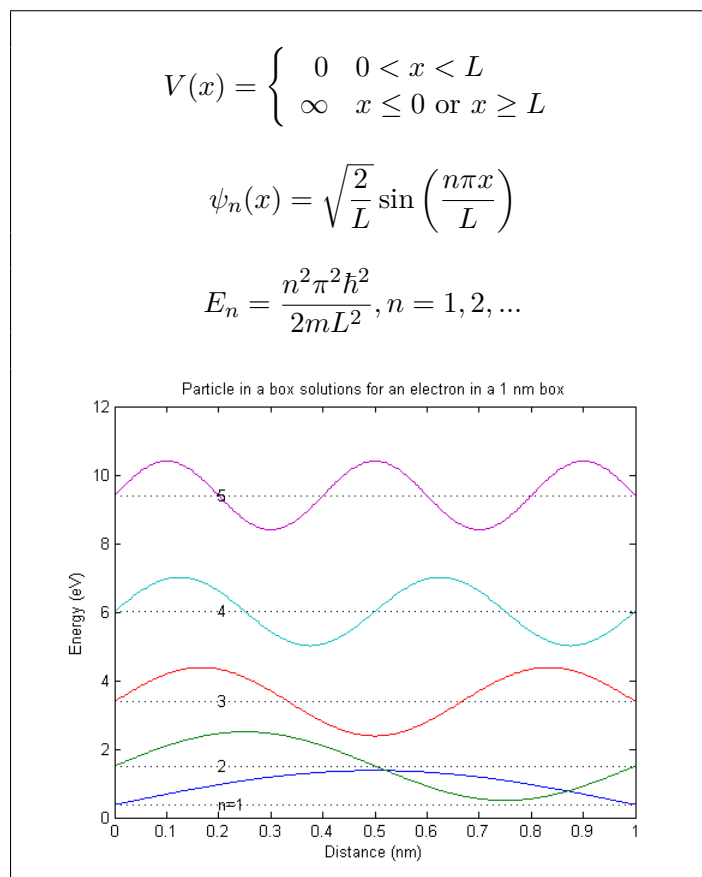
**Postulate 4:** The energy-invariant states of a system are solutions of the equation

$$\begin{aligned} \hat{H} \Psi(\mathbf{r}, t) &= i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) \\ \hat{H} &= \hat{T} + \hat{V} \end{aligned}$$

The time-independent, stationary states of the system are solutions to the equation

$$\hat{H} \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

**Postulate 5:** (The **uncertainty principle**.) Operators that do not commute ( $\hat{A}(\hat{B}\Psi) \neq \hat{B}(\hat{A}\Psi)$ ) are called *conjugate*. Conjugate observables cannot be determined simultaneously to arbitrary accuracy. For example, the standard deviation in the measured positions and momenta of particles all described by the same  $\Psi$  must satisfy  $\Delta x \Delta p_x \geq \hbar/2$ .

**Table 8:** Particle-in-a-box model**2.3.6 Introduce Pauli principle for fermions?****2.4 Lecture 7: Harmonic oscillator****2.4.1 Classical harmonic oscillator**

1. Hooke's law,  $F = -k(x - x_0)$ ,  $k$  spring constant
2. Continuous sinusoidal motion
3.  $x(t) = A \sin(\frac{k}{\mu})^{1/2} t$ ,  $\nu = \frac{1}{2\pi}(\frac{k}{\mu})^{1/2}$ ,  $E = \frac{1}{2}kA^2$
4. Exchanging kinetic and potential energies

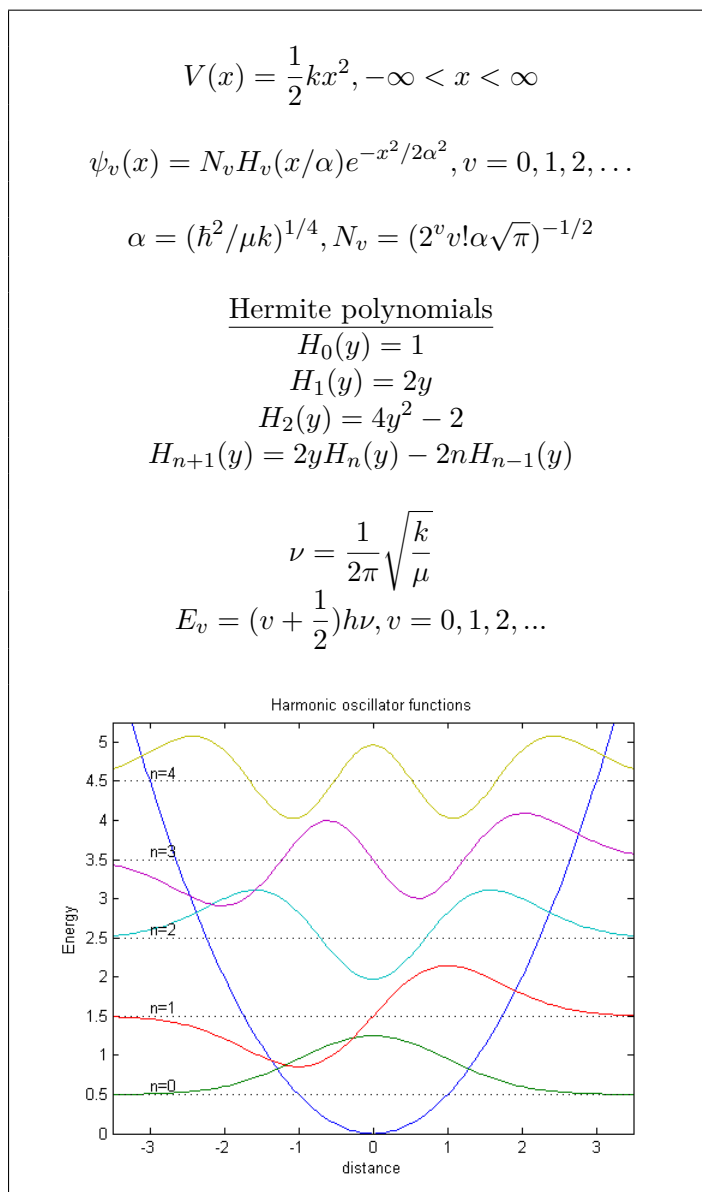
**2.4.2 Quantum harmonic oscillator**

1. Solutions like P-I-A-B, waves, nodes, even/odd symmetry
2. Zero-point energy
3. Expectation values:  $\langle x \rangle = 0$ ,  $\langle x^2 \rangle = \alpha^2(v + 1/2)$ ,  $\langle V(x) \rangle = \frac{1}{2}h\nu(v + \frac{1}{2})$
4. Classical turning point and tunneling

## 5. Classical limiting behavior

## 2.4.3 HCl example

1. Reduced mass,  $\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$
2. ZPE, energy spacing in IR, Boltzmann probabilities

**Table 9:** Harmonic oscillator model

## 2.5 Lecture 8: Rigid Rotor

### 2.5.1 Classical rigid rotor

1. Compare rotation about an axis vs linear motion
2. Moment of inertia  $I = \mu r^2$
3. Angular momentum,  $\mathbf{l} = I\omega = \mathbf{r} \times \mathbf{p}$ ,  $T = l^2/2I$ 
  - (a) Angular momentum and energy continuous variables

### 2.5.2 Quantum rotor in a plane

1. Angular momentum and kinetic energy operators in polar coordinates,  $\hat{l}_z = -i\hbar \frac{d}{d\phi}$
2. Eigenfunctions degenerate, cw and ccw rotation
3. No zero point energy
4. Angular momentum eigenfunctions,  $l_z = m_l \hbar$
5. Energy superpositions and localization

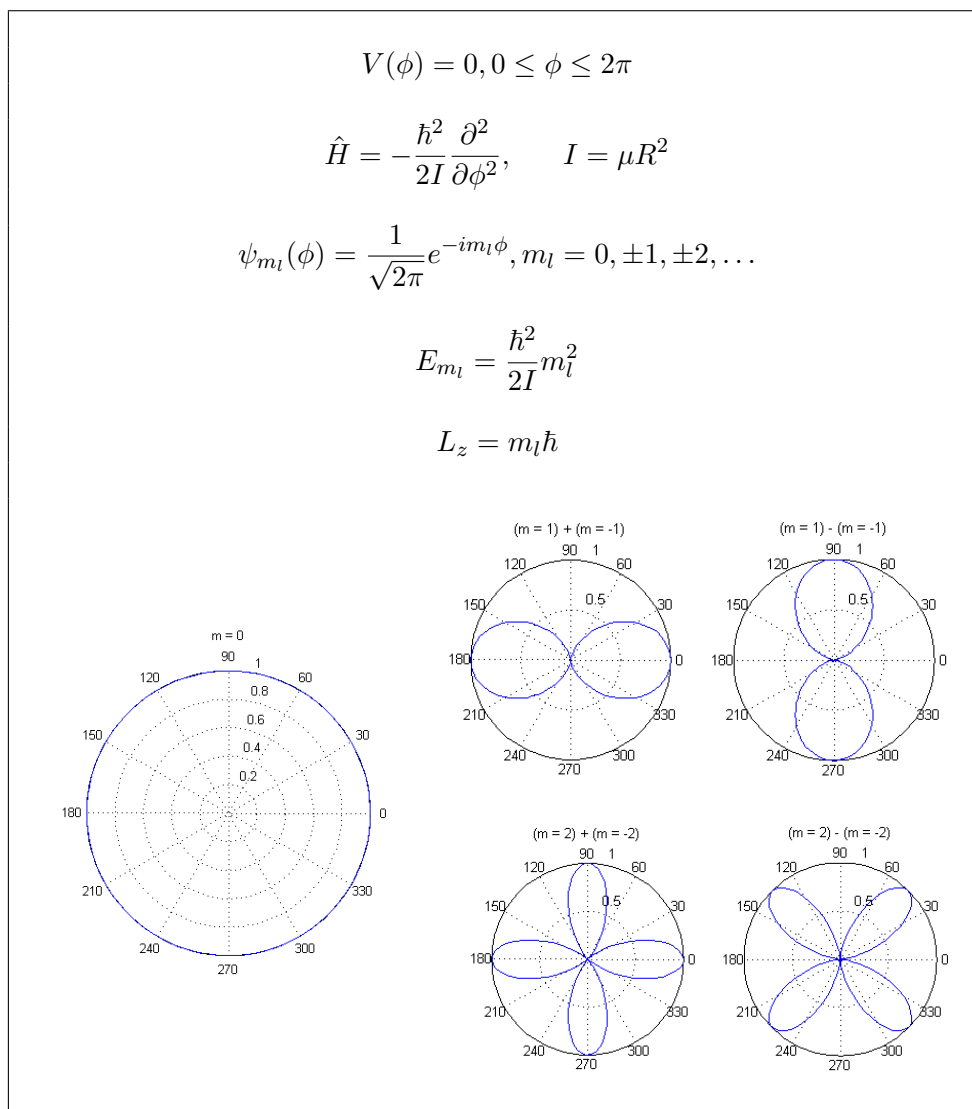
### 2.5.3 Quantum rotor in 3-D

1. Angular momentum and kinetic energy operators in spherical coordinates
2. Spherical harmonic solutions,  $Y_{lm_l}$
3. Azimuthal QN  $l = 0, 1, \dots$
4. Magnetic QN  $m_l = -l, -l+1, \dots, l$
5. Energy spectrum,  $2l+1$  degeneracy
6. Vector model - can only know total  $|L|$  and  $L_z$
7. Wavefunctions look like atomic orbitals,  $l$  nodes

---

```

1  import matplotlib.pyplot as plt
2  from matplotlib import cm, colors
3  from mpl_toolkits.mplot3d import Axes3D
4  import numpy as np
5  from scipy.special import sphharm
6
7  phi = np.linspace(0, np.pi, 100)
8  theta = np.linspace(0, 2*np.pi, 100)
9  phi, theta = np.meshgrid(phi, theta)
10
11  The Cartesian coordinates of the unit sphere
12  x = np.sin(phi) * np.cos(theta)
13  y = np.sin(phi) * np.sin(theta)
14  z = np.cos(phi)
15
16  m, l = 0, 0
17
```

**Table 10:** 2-D rigid rotor model

```

18  Calculate the spherical harmonic Y(l,m) and normalize to [0,1]
19  fcolors = sphharm(m, l, theta, phi).real
20  fmax, fmin = fcolors.max(), fcolors.min()
21  fcolors = (fcolors - fmin)/(fmax - fmin)
22
23  Set the aspect ratio to 1 so our sphere looks spherical
24  sfig = plt.figure(figsize=plt.figaspect(1.))
25  s = sfig.add_subplot(111, projection='3d')
26  s.plotsurface(x, y, z, rstride=1, cstride=1, facecolors=cm.seismic(fcolors))
27  Turn off the axis planes
28  s.setaxisoff()
29  plt.savefig('./Images/s.png')
30
31  m, l = 0, 1
32
33  Calculate the spherical harmonic Y(l,m) and normalize to [0,1]
34  fcolors = sphharm(m, l, theta, phi).real
35  fmax, fmin = fcolors.max(), fcolors.min()

```



**Table 11:** 3-D rigid rotor model

$$\begin{aligned}
 V(\theta, \phi) &= 0, 0 \leq \phi \leq 2\pi, 0 \leq \theta < \pi \\
 \hat{L}^2 &= -\hbar^2 \left[ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right] \\
 \hat{H}_{\text{rot}} &= \frac{1}{2I} \hat{L}^2 \\
 Y_{lm_l}(\theta, \phi) &= N_l^{|m_l|} P_l^{|m_l|}(\cos(\theta)) e^{im_l \phi} \\
 l &= 0, 1, 2, \dots, \quad m_l = 0, \pm 1, \dots, \pm l \\
 E_l &= \frac{\hbar^2}{2I} l(l+1) \\
 |L| &= \hbar \sqrt{l(l+1)}, L_z = m_l \hbar
 \end{aligned}$$

```

36 fcolors = (fcolors - fmin)/(fmax - fmin)
37
38 Set the aspect ratio to 1 so our sphere looks spherical
39 fig = plt.figure(figsize=plt.figaspect(1.))
40 pfig = plt.figure(figsize=plt.figaspect(1.))
41 p = pfig.add_subplot(111, projection='3d')
42 p.plot_surface(x, y, z, rstride=1, cstride=1, facecolors=cm.seismic(fcolors))
43 Turn off the axis planes
44 p.setaxisoff()
45
46 plt.savefig('./Images/p.png')
47
48 m, l = 1, 2
49
50 Calculate the spherical harmonic Y(l,m) and normalize to [0,1]
51 fcolors = sphharm(m, l, theta, phi).real
52 fmax, fmin = fcolors.max(), fcolors.min()
53 fcolors = (fcolors - fmin)/(fmax - fmin)
54
55 Set the aspect ratio to 1 so our sphere looks spherical
56 fig = plt.figure(figsize=plt.figaspect(1.))
57 dfig = plt.figure(figsize=plt.figaspect(1.))
58 d = dfig.add_subplot(111, projection='3d')
59 d.plot_surface(x, y, z, rstride=1, cstride=1, facecolors=cm.seismic(fcolors))
60 Turn off the axis planes
61 d.setaxisoff()
62
63 plt.savefig('./Images/d.png')

```

## 2.5.4 Particle angular momentum

### 1. Fermions, mass, half-integer spin

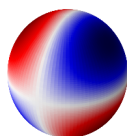
(a) Electron,  $s = 1/2, m_s = \pm 1/2$



**Figure 7:** Pythonic s spherical harmonic



**Figure 8:** Pythonic p spherical harmonic



**Figure 9:** Pythonic d spherical harmonic

2. Bosons, force-carrying, integer spin

## 2.6 Lecture 9: Spectroscopy

### 2.6.1 Spectroscopy is quantitative measurement of interaction of light with matter

1. Observed  $I(\nu)/I(\nu_0)$
2. Bohr condition,  $|E_f - E_i|/h = \nu = c\tilde{\nu} = c/\lambda$
3. Intensities determined by state populations and transition probabilities

### 2.6.2 Einstein coefficients

1. Stimulated absorption,  $dn_1/dt = -n_1 B \rho(\nu)$
2. Stimulated emission,  $dn_2/dt = -n_2 B \rho(\nu)$
3. Spontaneous emission,  $dn_2/dt = -n_2 A$ ,  $A = \left(\frac{8\pi h \nu^3}{c^3}\right) B$
4.  $1/A = \text{lifetime}$

### 2.6.3 Transition probability

1. Einstein coefficient  $B_{if} = \frac{|\mu_{if}|^2}{6\epsilon_0 h^2}$
2. Classical electric dipole,  $\vec{\mu} = q \cdot \vec{r}$ , quantum dipole operator  $\hat{\mu} = e \cdot \vec{r}$
3. Transition dipole moment,  $\mu_{if} = \left(\frac{d\mu}{dx}\right) \langle \psi_i | \hat{\mu} | \psi_f \rangle$
4. Selection rules—conditions that make  $\mu_{if}$  non-zero, “allowed” vs “forbidden” transitions

## 2.7 Lecture 10: Vibrational and rotational spectroscopy

### 2.7.1 Diatomic rotational spectroscopy

1. Rotational constant  $B = \hbar/4\pi I c \text{ cm}^{-1}$ ,  $I = \mu R^2$
2. Gross selection rule: dynamic dipole moment non-zero (heteronuclear, not homonuclear)
3. Specific selection rule:  $\Delta l = \pm 1$ ,  $\Delta m_l = 0, \pm 1$
4.  $\Delta \tilde{E}_l = 2B(l+1) \text{ cm}^{-1}$
5. Rotational state populations

### 2.7.2 Diatomic vibrational transitions

1. Gross selection rule: dynamic dipole  $d\mu/dx$  non-zero
2. Homo- vs. heteronuclear
3. Specific selection rule: dipole integral  $\langle \psi_v | \hat{\mu} | \psi_{v'} \rangle = 0$  unless  $\Delta v = \pm 1$
4. Allowed  $\Delta E = h\nu$
5. Boltzmann distribution implies  $v = 1$  states dominate at normal  $T$

### 2.7.3 Raman spectroscopy

1. Shine in light of arbitrary frequency  $\tilde{\nu}_0$ , mostly get out the same
2. Some light comes out at  $\tilde{\nu}_0 - \tilde{\nu}$  (Stoke's line)
3. Some light comes out at  $\tilde{\nu}_0 + \tilde{\nu}$  (anti-Stoke's line)
4. Gross selection rule: dynamic polarizability non-zero (homonuclear, not heteronuclear)

### 2.7.4 Anharmonicity, Morse potential

### 2.7.5 Vibration-rotation spectroscopy

1. Harmonic oscillator + rigid rotor
2. Selection rules:  $\Delta v = \pm 1, \Delta l = \pm 1$
3. *R* branch:  $\Delta \tilde{E} = \tilde{\nu} + 2B(l+1), \Delta l = 1$
4. *P* branch:  $\Delta \tilde{E} = \tilde{\nu} - 2B(l), \Delta l = -1$

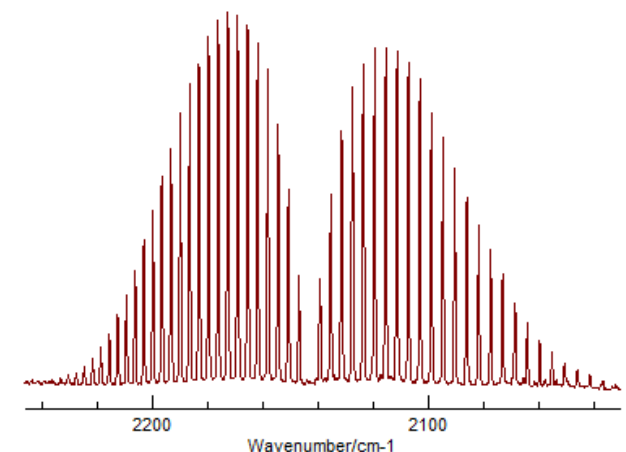


Figure 10: Rovibrational spectrum of carbon monoxide

### 2.7.6 Polyatomic vibrational spectroscopy

1. Polyatomics,  $3n - 6$  ( $3n - 5$  for linear polyatomic) vibrational modes
2. Selection rules and degeneracies affect number of observed features
3. CO<sub>2</sub> example

### 2.7.7 Polyatomic rotational spectroscopy

1. Three distinct moments of inertia ( $I_x, I_y, I_z$ )
2. Spectra more complex

## 2.8 Lecture 11: Hydrogen atom

### 2.8.1 Schrödinger equation

1. Spherical coordinates and separation of variables
2. Coulomb potential  $v_{\text{Coulomb}}(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$
3. Centripetal potential  $v = \hbar^2 \frac{l(l+1)}{2\mu r^2}$

### 2.8.2 Solutions

1.  $\psi(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$
2. Principle quantum number  $n = 1, 2, \dots$ 
  - (a)  $K, L, M, N, \dots$  shells
  - (b)  $n - 1$  radial nodes
3. Azimuthal quantum number  $l = 0, 1, \dots, n - 1$ 
  - (a)  $s, p, d, \dots$  orbital sub-shells
  - (b)  $l$  angular nodes
4. Magnetic quantum number  $m_l = -l, -l + 1, \dots, l$
5. Spin quantum number  $m_s = \pm 1/2$
6. Energy spectrum and populations
7. Electronic selection rules
  - (a)  $\Delta l = \pm 1 \quad \Delta m_s = 0 \quad \Delta m_l = 0, \pm 1$
8. Wavefunctions = “orbitals”
9. Radial probability function  $P_{nl}(r) = r^2 R_{nl}^2(r)$ 
  - (a)  $\langle r \rangle = \int r P_{nl}(r) dr = \left( \frac{3}{2} n^2 - l(l+1) \right) a_0$

### 2.8.3 Variational principle

1. Solutions of Schrödinger equation always form a complete set
2. True wavefunction energy is therefore lower bound on energy of any trial wavefunction

$$\langle \psi_{\text{trial}}^\lambda | \hat{H} | \psi_{\text{trial}}^\lambda \rangle = E_{\text{trial}}^\lambda \geq E_0$$

1. Optimize wavefunction with respect to variational parameter

$$\left( \frac{\partial \langle \psi_{\text{trial}}^\lambda | \hat{H} | \psi_{\text{trial}}^\lambda \rangle}{\partial \lambda} \right) = 0 \rightarrow \lambda_{\text{opt}}$$

**Table 12:** Hydrogen atom

$$\begin{aligned}
 V(r) &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}, 0 < r < \infty \\
 \hat{H} &= -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \left[ \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \hat{L}^2 \right] + V(r) \\
 \psi(r, \theta, \phi) &= R(r) Y_{l, m_l}(\theta, \phi) \\
 \left\{ -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \right\} R(r) &= E R(r) \\
 R_{nl}(r) &= N_{nl} e^{-x/2} x^l L_{nl}(x), \quad x = \frac{2r}{na_0} \\
 P_{nl}(r) &= r^2 R_{nl}^2 \\
 n &= 1, 2, \dots, \quad l = 0, \dots, n-1 \quad m_l = 0, \pm 1, \dots, \pm l \\
 N_{nl} &= \sqrt{\left( \frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \\
 L_{10} = L_{21} = L_{32} = \dots &= 1 \quad L_{20} = 2 - x \quad L_{31} = 4 - x \\
 E_n &= -\frac{1}{2} \frac{\hbar^2}{m_e a_0^2} \frac{1}{n^2} = -\frac{E_H}{2} \frac{1}{n^2} \\
 |L| &= \hbar \sqrt{l(l+1)}, L_z = m_l \hbar
 \end{aligned}$$

## 2.9 Lecture 12: Many-electron atoms

### 2.9.1 Many-electron problem, Schrödinger equation not exactly solvable

1.  $e^- - e^-$  interaction terms prevent separation of variables
2. Independent electron model basis of all solutions, describes each electron by its own wavefunction, or “orbital”

### 2.9.2 Qualitative solutions

1.  $\psi_i$  look like H atom orbitals, labeled by same quantum numbers
2. *Aufbau principle*: “Build-up” electron configuration by adding electrons into H-atom-like orbitals, from bottom up

3. *Pauli exclusion principle*: Every electron in atom must have a unique set of quantum numbers, so only two per orbital (with opposite spin)
4. *Pauli exclusion principle (formally)*: The wavefunction of a multi-particle system must be anti-symmetric to coordinate exchange if the particles are fermions, and symmetric to coordinate exchange if the particles are bosons
5. *Hund's rule*: Electrons in degenerate orbitals prefer to be spin-aligned. Configuration with highest *spin multiplicity* is the most preferred

### 2.9.3 Structure of the periodic table

1. Electrons in different subshells experience different effective nuclear charge  $Z_{\text{eff}} = Z - \sigma_{nl}$
2. Inner (“core”) shells not shielded well at
3. Inner shell electrons “shield” outer electrons well
4. Within a shell, *s* shielded less than *p* less than *d* ..., causes degeneracy to break down
5. Electrons in same subshell shield each other poorly, causing ionization energy to increase across the subshell

### 2.9.4 Quantitative solutions

1. Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$$

$$\hat{H} = \sum_i \hat{h}_i + \frac{e^2}{4\pi\epsilon_0} \sum_i \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{h}_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i|}$$

2. Construct candidate many-electron wavefunction  $\Psi$  from one electron wavefunctions (mathematical details vary with exact approach)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) \approx \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\dots\psi_n(\mathbf{r}_n)$$

3. Calculate expectation value of  $E$  of approximate model and apply *variational principle* to find equations that describe “best” (lowest total energy) set of  $\psi_i$

$$\frac{\partial E}{\partial \psi_i} = 0 \quad \forall i$$

$$\hat{f}\psi = \left\{ \hat{h} + \hat{v}_{\text{Coul}}[\psi_i] + \hat{v}_{\text{ex}}[\psi_i] + \hat{v}_{\text{corr}}[\psi_i] \right\} \psi = \epsilon\psi$$

$$E = \sum_i \epsilon_i - \frac{1}{2} \langle \Psi | \hat{v}_{\text{Coul}}[\psi_i] + \hat{v}_{\text{ex}}[\psi_i] + \hat{v}_{\text{corr}}[\psi_i] | \Psi \rangle$$

4. Motivate as equation for an electron moving in a “field” of other electrons, adding an electron to a known set of  $\psi_i$

### 2.9.5 Electron-electron interactions

1. Coulomb ( $\hat{v}_{\text{Coul}}$ ): classical repulsion between distinguishable electron “clouds”
2. Exchange ( $\hat{v}_{\text{ex}}$ ): accounts for electron indistinguishability (Pauli principle for fermions). Decreases Coulomb repulsion because electrons of like spin intrinsically avoid one another
3. Correlation ( $\hat{v}_{\text{corr}}$ ): decrease in Coulomb repulsion due to dynamic ability of electrons to avoid one another; “fixes” orbital approximation
4. General form of exchange potential is expensive to calculate; general form of correlation potential is unknown

### 2.9.6 Popular models

1. *Hartree model*: Include only classical Coulomb repulsion  $\hat{v}_{\text{Coul}}$
2. *Hartree-Fock model*: Include Coulomb and exchange
3. *Density-functional theory* (DFT): Include Coulomb and approximate expressions for exchange and correlation
4. All the potential terms  $\hat{v}$  depend on the solutions, so equations must be solved *iteratively* to *self-consistency*

### 2.9.7 DFT calculations on atoms

1. See <http://www.chemsoft.ch/qc/fda.htm>

## 2.10 Lecture 13: Molecular orbital theory of molecules

### 2.10.1 Clamped nucleus (“Born-Oppenheimer”) approximation

1. Write one-electron equations parametrically in terms of positions of all atoms

$$\hat{h}_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha} e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} \quad (1)$$

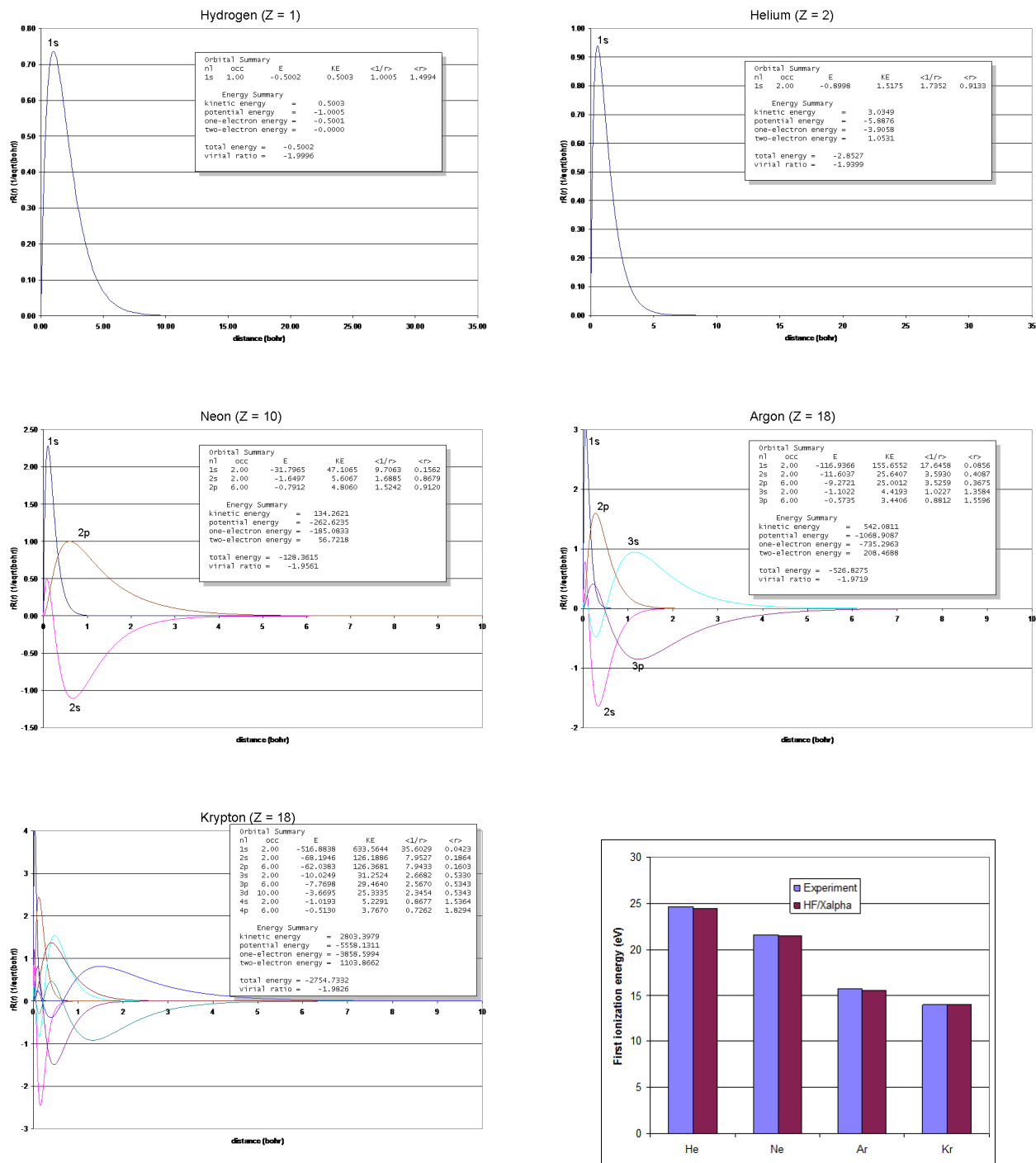
1. Solve as for atoms, using some model for electron-electron interactions
2. Potential energy surface (PES)

$$E(\mathbf{R}_{\alpha}, \mathbf{R}_{\beta}, \dots) = E_{\text{elec}} + \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}$$

### 2.10.2 H<sub>2</sub> molecule as perturbation on two H atoms brought from infinite distance

1. “Bonding” orbital,  $\sigma_g(\mathbf{r}) = 1s_A + 1s_B$
2. “Anti-bonding” orbital,  $\sigma_u(\mathbf{r}) = 1s_A - 1s_B$
3. Interaction scales with “overlap”  $\langle 1s_A | 1s_B \rangle$
4. Ground configuration =  $\sigma_g^2$
5. Bond order =  $\frac{1}{2}(n - n^*)$



**Table 13:** Numerical DFT Solutions for Atoms

### 2.10.3 Secular equations

1. Expand molecular orbitals in “basis” of atomic-like orbitals

$$\psi_{\text{MO}} = \sum_a c_a \phi_a(\mathbf{r}) \quad (2)$$

2. Problem reduces to finding set of  $c_a$  that give best molecular orbitals (MOs)
3. Substituting into Fock equation and integrating yields set of linear equations for the  $c_a$  for each MO

$$\begin{pmatrix} F_{11} - \epsilon S_{11} & F_{12} - \epsilon S_{12} & \dots \\ F_{21} - \epsilon S_{21} & F_{22} - \epsilon S_{22} & \dots \\ \vdots & \vdots & \vdots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} = 0$$

- (a)  $F_{ij} = F_{ji} = \langle \phi_i | \hat{f} | \phi_j \rangle$  are Fock “matrix elements”
  - (b)  $S_{ij} = S_{ji} = \langle \phi_i | \phi_j \rangle$  are overlaps
  - (c) Typically basis functions normalized such that  $S_{ii} = 1$
  - (d)  $\epsilon$  are molecular orbital energies (to be solved for, as many as there are equations)
4. From linear algebra, only possible solutions are those that make the determinant vanish

$$\begin{vmatrix} F_{11} - \epsilon S_{11} & F_{12} - \epsilon S_{12} & \dots \\ F_{21} - \epsilon S_{21} & F_{22} - \epsilon S_{22} & \dots \\ \vdots & \vdots & \vdots \end{vmatrix} = 0$$

5. Solve for  $\epsilon$ s and back-substitute to find correspond  $c_i$ s

### 2.10.4 Qualitative solutions of secular equations

1. Lot's of insight into chemical bonding can be obtained from approximate solutions to secular equations, basis of “molecular orbital theory”
2. Two general assumptions
  - (a) Diagonal Fock elements are approximately equal to energies of corresponding atomic orbitals:  $F_{ii} \approx \epsilon_{i,\text{ao}}$
  - (b) Off-diagonal elements proportional to overlap and inversely proportional to energy difference:

$$F_{ij} \propto \frac{S_{ij}}{\epsilon_{i,\text{ao}} - \epsilon_{j,\text{ao}}}$$

- (c) (Often) set differential overlap  $S_{ij} = 0$

### 2.10.5 H<sub>2</sub> example, again

1. Assign one 1s atomic orbital (“basis function”) to each atom

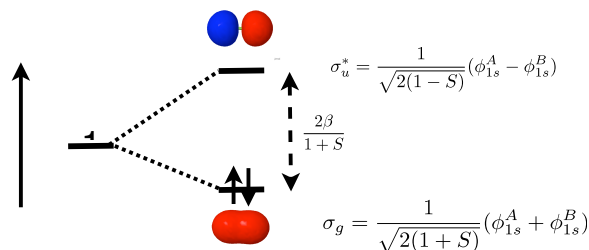
$$\begin{aligned} F_{11} &= F_{22} = \epsilon_{1s} = \alpha \\ F_{12} &= F_{21} = \beta \\ \alpha &< \beta < 0 \quad \text{typically} \end{aligned}$$

2. Set-up and solve secular matrix

$$\begin{vmatrix} \alpha - \epsilon & \beta - \epsilon S \\ \beta - \epsilon S & \alpha - \epsilon \end{vmatrix} = 0$$

$$\epsilon_+ = \frac{\alpha + \beta}{1 + S}, \quad c_1 = c_2 = \frac{1}{\sqrt{2(1 + S)}}$$

$$\epsilon_- = \frac{\alpha - \beta}{1 - S}, \quad c_1 = -c_2 = \frac{1}{\sqrt{2(1 - S)}}$$



3. From Taylor expansion get picture of atomic orbitals destabilized by electron repulsion  $\beta S$  and split by interaction  $\beta$

$$\epsilon_+ \approx \alpha - \beta S + \beta$$

$$\epsilon_- \approx \alpha - \beta S - \beta$$

4. Makes clear that bonding stabilization < anti-bonding destabilization

### 2.10.6 Heteronuclear diatomic: LiH, HF, BH example

1. Only AOs of appropriate symmetry, overlap, and energy match can combine to form MOs

$$\epsilon_+ \approx \alpha_1 - \beta S - \beta^2/|\alpha_1 - \alpha_2|$$

$$\epsilon_- \approx \alpha_2 - \beta S + \beta^2/|\alpha_1 - \alpha_2|$$

2. LiH: H 1s + Li 2s, bond polarized towards H
3. HF: H 1s + F 2p, bond polarized towards F, lots of non-bonding orbitals
4. BH: H 1s, B 2s and 2p<sub>z</sub> → bonding, non-bonding, anti-bonding orbitals

### 2.10.7 Homonuclear diatomic: O<sub>2</sub>

1. Assign aos, 1s, 2s, 2p for each atom (10 total)
2. In principle, solve 10 × 10 secular matrix
3. In practice, matrix elements rules mean only a few off-diagonal elements survive
  - (a) 1s + 1s do nothing
  - (b) 2s + 2s form σ bond and anti-bond
  - (c) 2p<sub>z</sub> + 2p<sub>z</sub> form second bond and anti-bond
  - (d) 2p<sub>x,y</sub> + 2p<sub>x,y</sub> form degenerate π bonds and anti-bonds
  - (e) O<sub>2</sub> is a triplet, consistent with experiment!

### 2.10.8 The Hückel/tight binding model

1.  $F_{ii} = \alpha, S_{ij} = \delta_{ij}, F_{ij} = \beta$  iff  $i$  adjacent to  $j$
2. Ethylene example
3. Butadiene example
4. Benzene example
5. Infinite chain example

### 2.10.9 Band structure of solids

## 2.11 Lecture 14: Computational chemistry

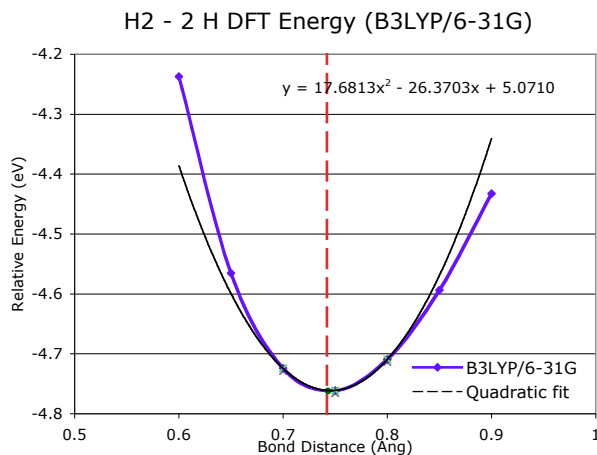
### 2.11.1 Numerical solvers of Schrödinger equation for molecules readily available today

#### 2.11.2 Have to specify:

1. Identity of atoms
2. Positions of atoms (distances, angles, ...)
3. (spin multiplicity)
4. exact theoretical model (how are Coulomb, exchange, and correlation described?)
  - (a) Hartree, Hartree-Fock, DFT (various flavors), ...
5. basis set to express wavefunctions in terms of
6. initial guess of wavefunction coefficients (often guessed for you)

### 2.11.3 Secular equations solved iteratively until input coefficients = output coefficients

1. “self-consistent field”
2. Output
  - (a) energies of molecular orbitals
  - (b) occupancies of molecular orbitals
  - (c) coefficients describing molecular orbitals
  - (d) total electron wavefunction, total electron density, dipole moment, ...
  - (e) total molecular energy
  - (f) derivatives (“gradients”) of total energy w.r.t. atom positions
3. Plot total energy vs. \ internal coordinates: potential energy surface (PES)
4. Search iteratively for minimum point on PES (by hand or using gradient-driven search): equilibrium geometry
5. Find second derivative of energy at minimum point on PES: harmonic vibrational frequency
6. Find energy at minimum relative to atoms (or other molecules): reaction energy

2.11.4 H<sub>2</sub> example

## Bond length

H-H exp't:	0.742 Å
B3LYP opt:	0.743

## Bond energy

H-H exp't	= 4.478 eV
2 H: 2(-0.4969) au = -27.041 eV	
H <sub>2</sub> : -1.1687 au = -31.803 eV	
Dissociation E	= 4.762 eV
ZPE corrected	= 4.484 eV

## Vibrational frequencies

Experiment:	4401 cm <sup>-1</sup>
B3LYP harmonic:	4487 cm <sup>-1</sup>
ZPE:	0.278 eV

## 2.11.5 Polyatomic molecules

1. Gradient-driven optimizations,  $3n - 6$  degrees of freedom
2. Hessian matrix for frequencies

## 2.12 Lecture 15: Electronic spectroscopy

## 3 Statistical Mechanics: The Bridge from the Tiny to the Many