

Table 1: Key units in Physical Chemistry

N_{Av} :	6.02214×10^{23}	mol^{-1}		
1 amu:	1.6605×10^{-27}	kg		
k_{B} :	1.38065×10^{-23}	J K^{-1}	8.61734×10^{-5}	eV K^{-1}
R :	8.314472	$\text{J K}^{-1} \text{mol}^{-1}$	8.2057×10^{-2}	$\text{l atm mol}^{-1} \text{K}^{-1}$
σ_{SB} :	5.6704×10^{-8}	$\text{J s}^{-1} \text{m}^{-2} \text{K}^{-4}$		
c :	2.99792458×10^8	m s^{-1}		
h :	6.62607×10^{-34}	J s	4.13566×10^{-15}	eV s
\hbar :	1.05457×10^{-34}	J s	6.58212×10^{-16}	eV s
hc :	1239.8	eV nm		
e :	1.60218×10^{-19}	C		
m_e :	$9.10938215 \times 10^{-31}$	kg	1: 0.5109989	MeV c^{-2}
ϵ_0 :	8.85419×10^{-12}	$\text{C}^2 \text{J}^{-1} \text{m}^{-1}$	5.52635×10^{-3}	$e^2 \text{\AA}^{-1} \text{eV}^{-1}$
$e^2/4\pi\epsilon_0$:	2.30708×10^{-28}	J m	14.39964	eV \AA
a_0 :	0.529177×10^{-10}	m	0.529177	\AA
E_{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 μ , variance σ^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	1×10^{-26} kg
h	1 m	1 m
mgh	9800 J	9.8×10^{-26} J
	6.1×10^{22} eV	6.1×10^{-7} eV
T	298 K	298 K
$k_B T$	0.026 eV	0.026 eV
$mgh/k_B T$	2.4×10^{24}	2.3×10^{-5}
$P(1 \text{ m})/P(0)$	$e^{-2.4 \times 10^{-24}}$	0.99998
$\langle h \rangle$	0 m	42 km
$\langle v_x \rangle^{1/2}$	2×10^{-12} m/s	640 m/s

Table 3: Energy conversions and correspondences

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

```

1  import numpy as np
2  import matplotlib.pyplot as plt
3
4  RO = 8.31441    J/mol K
5  mass = 28. /1000  kg/mol N2
6
7  def Boltzmann(E,T):
8      return np.exp(E/(RO*T))/(RO*T)
9
10 def MB1D(v,T):
11     return np.sqrt(mass/(2*np.pi*RO*T))*np.exp((mass*v*v)/(2*RO*T))
12
13 def MB(c,T):
14     K = 0.5 * mass * c * c
15     degeneracy = 4 * np.pi * c * c
16     normalization = (mass/(2*np.pi*RO*T))**1.5
17     return normalization*Boltzmann(K,T)
18
19 energy = np.linspace(0,3000,1500)
20 velocity = np.linspace(1000,1000,1000)
21 speed = np.linspace(0,1500,1000)
22
23 plt.figure()
24 for Temperature in [100,300,1000]:
25     Probability = Boltzmann(energy,Temperature)
26     plt.plot(Probability,energy,label=0 K.format(Temperature))
27
28 legend = plt.legend()
29
30 plt.ylabel(Energy (J/mol))
31 plt.xlabel(Probability (mol/J))
32 plt.title(Boltzmann distribution at various temperatures)
33 plt.savefig(./Images/Boltzmann.png)
34
35 plt.figure()
36 for Temperature in [100,200,300,400,500]:
37     Probability = MB1D(velocity,Temperature)
38     plt.plot(velocity,Probability,label= K.format(Temperature))
39
40 legend=plt.legend()
41 plt.xlabel(Velocity (m/s))
42 plt.ylabel(Probability (1/(m/s)))
43 plt.title(Boltzmann distribution at various temperatures)
44 plt.savefig(./Images/MB1D.png)
45
46 plt.figure()
47 for Temperature in [100,200,300,400,500]:
48     Probability = MB(speed,Temperature)
49     plt.plot(speed,Probability,label= K.format(Temperature))
50
51 legend=plt.legend()
52 plt.xlabel(Speed (m/s))
53 plt.ylabel(Probability (1/(m/s)))

```

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54 plt.title(Boltzmann distribution at various temperatures)
55 plt.savefig('./Images/MB.png')

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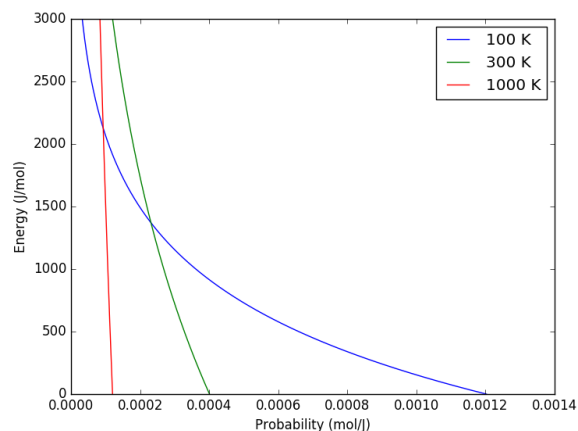


Figure 1: Boltzmann distribution at various temperatures

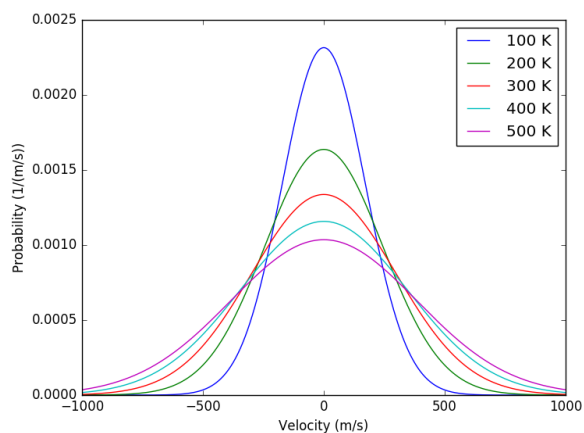


Figure 2: One-dimensional (Gaussian) velocities of N₂ gas

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 $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$

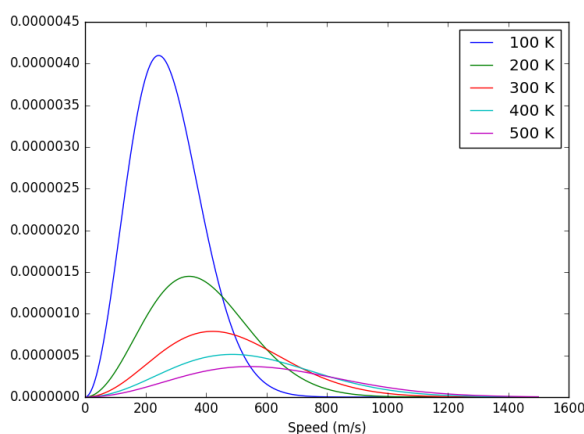


Figure 3: Maxwell-Boltzmann speed distribution of N_2 gas

(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, λ , mean distance between collisions

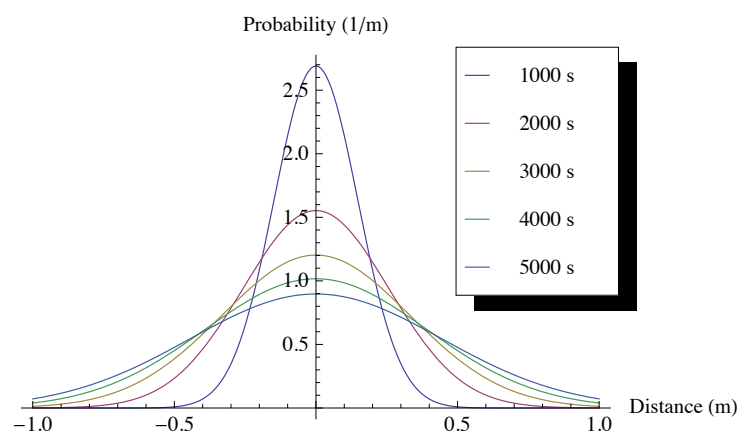


Figure 4: Diffusional spreading, $\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$

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

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

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 ν

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	$\Psi(x, t) = A \sin(kx) \cos(\omega t), \quad k = n\pi/a$

2.1.2 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 λ
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

```

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))
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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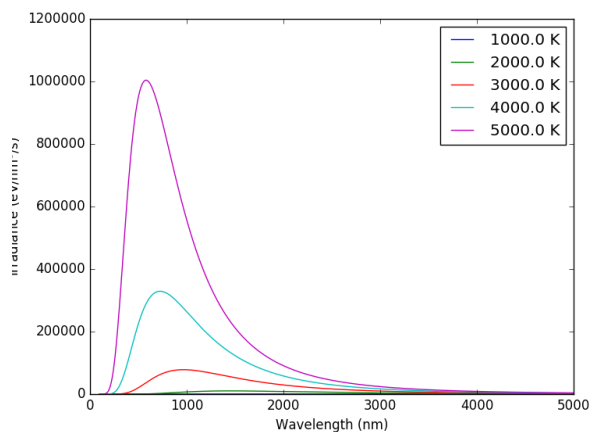


Figure 5: Blackbody irradiance

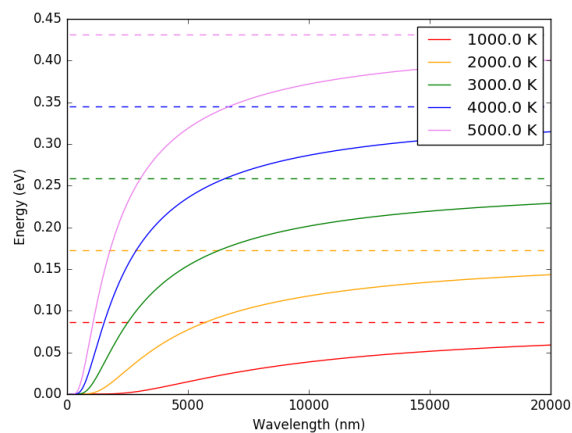


Figure 6: Average energy of a Planck quantized oscillator

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

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	$\lambda = \frac{h}{p}$

2.2.3 Postulates

1. Wavefunction contains all information about a system
2. Operators used to extract that information
 - (a) QM operators are *Hermitian*
 - (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: NH_3 inversion, H transfer, kinetic isotope effect

Table 7: Postulates of Non-relativistic Quantum Mechanics

Postulate 1: The physical state of a system is completely described by its wavefunction Ψ . In general, Ψ is a complex function of the spatial coordinates and time. Ψ 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, Ψ 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{l}_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 Ψ , the average results will be the expectation value of the operator \hat{M} :

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

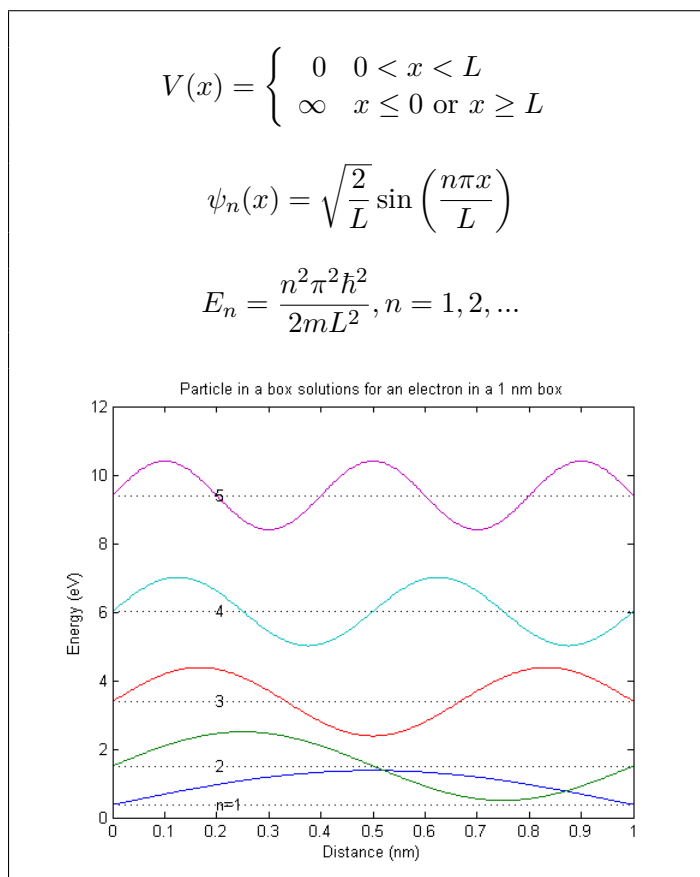
Postulate 4: The energy-invariant states of a system are solutions of the equation

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

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 Ψ must satisfy $\Delta x \Delta p_x \geq \hbar/2$.

Table 8: Particle-in-a-box model

2.3.5 Multiple dimensions

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

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

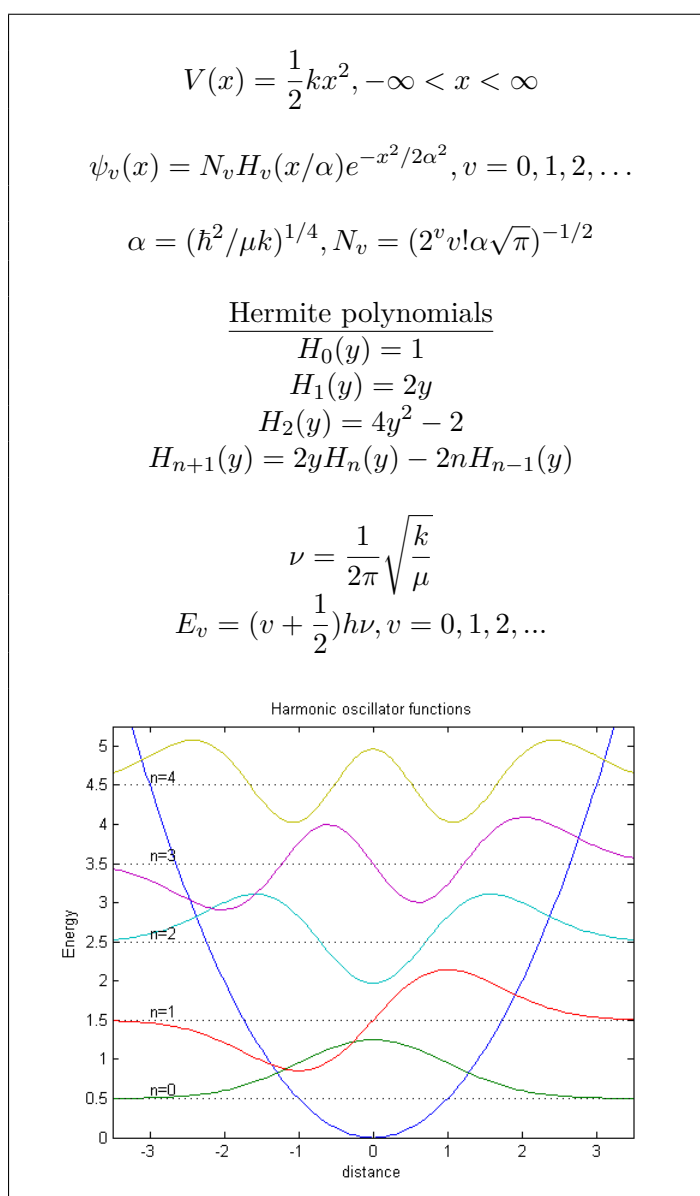
1. Solutions like P-I-A-B, waves, nodes, even/odd symmetry
2. Zero-point energy

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, $\mathbf{l} = I\boldsymbol{\omega} = \mathbf{r} \times \mathbf{p}$, $T = l^2/2I$
 - (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

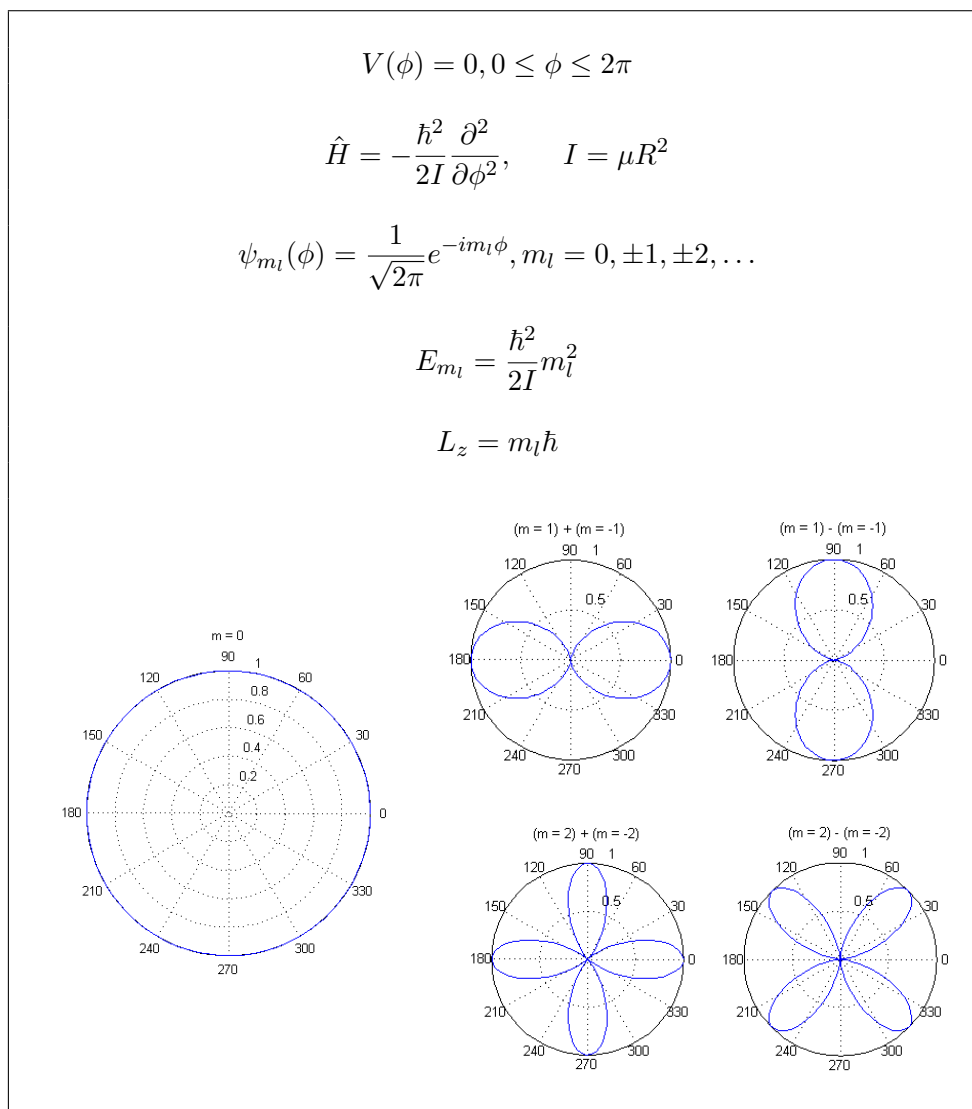
2.5.4 Particle angular momentum

1. Fermions, mass, half-integer spin
 - (a) Electron, $s = 1/2, m_s = \pm 1/2$
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

Table 10: 2-D rigid rotor model

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 $B_{if} = \frac{|\mu_{if}|^2}{6\epsilon_0 \hbar^2}$
2. Classical electric dipole, $\vec{\mu} = q \cdot \vec{r}$, quantum dipole operator $\hat{\mu} = e \cdot \vec{r}$

Table 11: 3-D rigid rotor model

$$V(\theta, \phi) = 0, 0 \leq \phi \leq 2\pi, 0 \leq \theta < \pi$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \right]$$

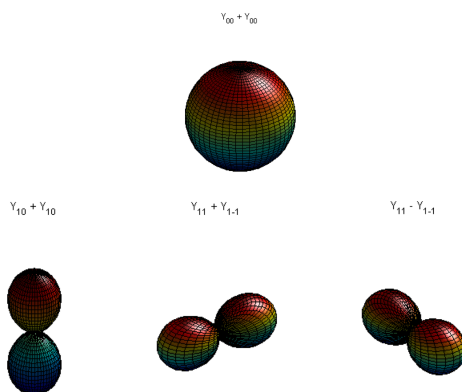
$$\hat{H}_{\text{rot}} = \frac{1}{2I} \hat{L}^2$$

$$Y_{lm_l}(\theta, \phi) = N_l^{|m_l|} P_l^{|m_l|}(\cos(\theta)) e^{im_l \phi}$$

$$l = 0, 1, 2, \dots, \quad m_l = 0, \pm 1, \dots, \pm l$$

$$E_l = \frac{\hbar^2}{2I} l(l+1)$$

$$|L| = \hbar \sqrt{l(l+1)}, L_z = m_l \hbar$$



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 μ_{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: $\Delta \tilde{E} = \tilde{\nu} - 2B(l)$, $\Delta l = -1$

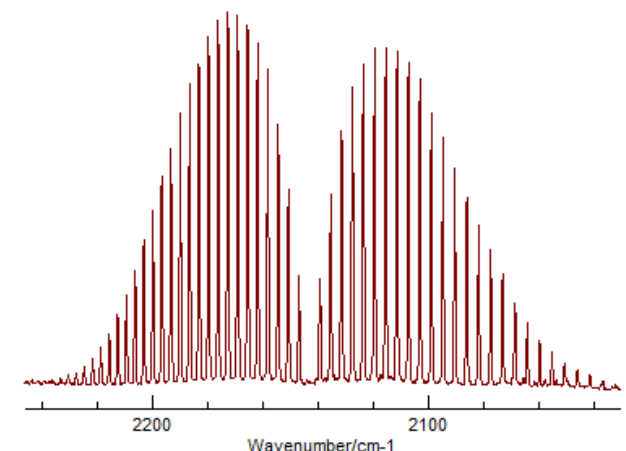


Figure 7: Rovibrational spectrum of carbon monoxide

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. CO₂ 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

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

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. ψ_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

Table 12: Hydrogen atom

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

2.9.3 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 $d \dots$, 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 Ψ 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 ψ_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 ψ_i

2.9.5 Electron-electron interactions

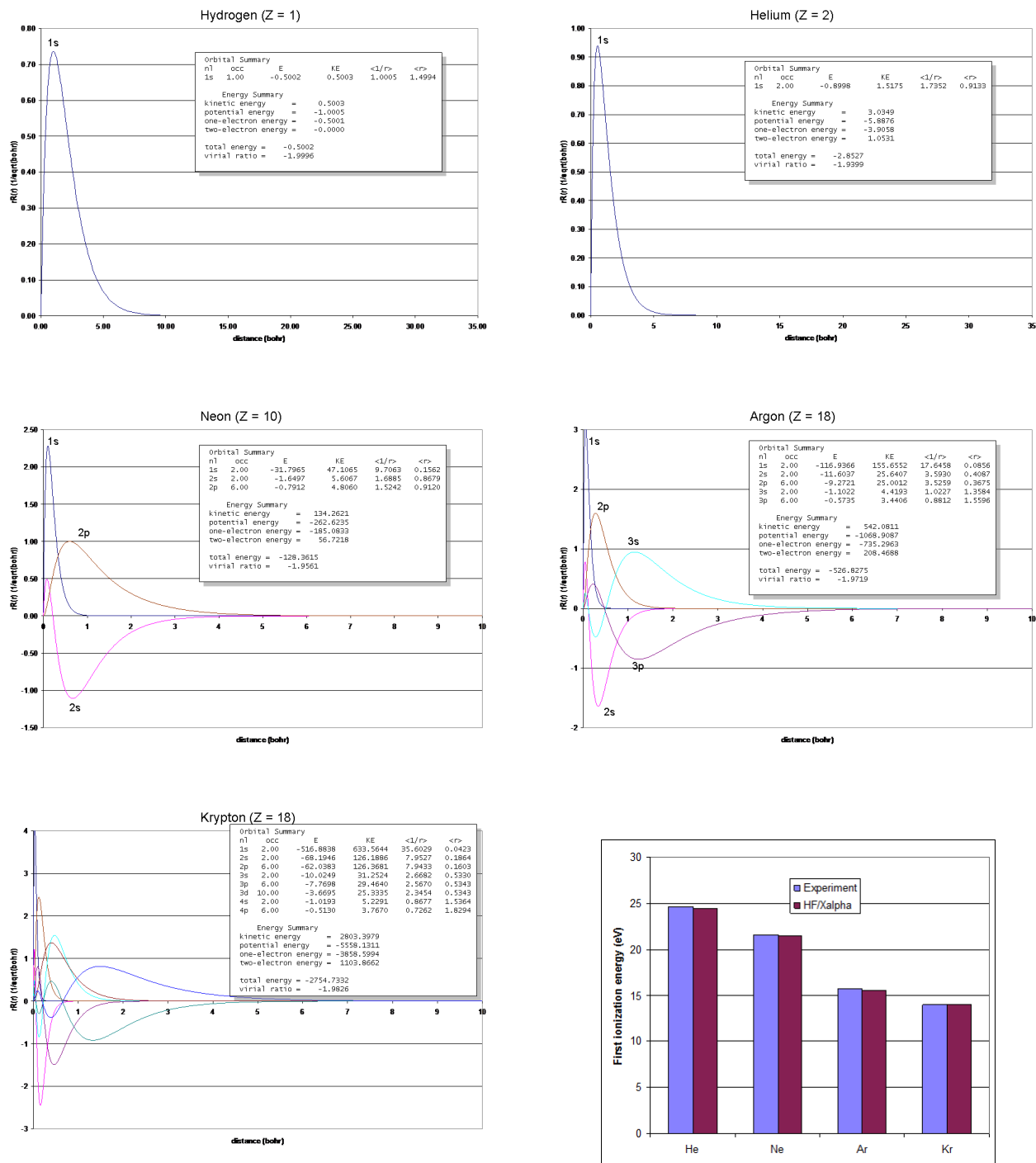
1. Coulomb (\hat{v}_{Coul}): classical repulsion between distinguishable electron “clouds”
2. Exchange (\hat{v}_{ex}): accounts for electron indistinguishability (Pauli principle for fermions). Decreases Coulomb repulsion because electrons of like spin intrinsically avoid one another
3. Correlation (\hat{v}_{corr}): 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}_{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>

Table 13: Numerical DFT Solutions for Atoms

2.10 Lecture 13: Molecular orbital theory of molecules

2.11 Lecture 14: Computational chemistry

2.12 Lecture 15: Electronic spectroscopy

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