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}	$\mathrm{J\ K}^{-1}$	8.61734×10^{-5}	$\mathrm{eV\ K}^{-1}$
R:	8.314472	$\mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$	8.2057×10^{-2}	$\mathrm{l\ atm\ mol}^{-1}\ \mathrm{K}^{-1}$
σ_{SB}:	5.6704×10^{-8}	$\mathrm{J\ s}^{-1}\ \mathrm{m}^{-2}\ \mathrm{K}^{-4}$		
c:	2.99792458×10^{8}	$\mathrm{m\ s}^{-1}$		
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	$\mathrm{MeV\ c}^{-2}$
ϵ_0:	8.85419×10^{-12}	$\mathrm{C}^2\ \mathrm{J}^{-1}\ \mathrm{m}^{-1}$	5.52635×10^{-3}	$e^2\ \text{Å}^{-1}\ \mathrm{eV}^{-1}$
$e^2/4\pi\epsilon_0$:	2.30708×10^{-28}	J m	14.39964	eV Å
a_0:	0.529177×10^{-10}	m	0.529177	Å
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 $a < x < b = \int_a^b \tilde{P}(x)dx$

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

   (b) Energy and its units

   (c) Absolute temperature and its units

   (d) k_BT 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, $P = P_0 e^{-mgh/k_BT}$

   (f) Kinetic energy in 1-D example

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

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

      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, $\mu = \langle v_x\rangle = 0$, $\sigma^2 = \langle v_x^2\rangle = k_BT/m$

      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_BT	0.026 eV	0.026 eV
mgh/k_BT	2.4×10^{24}	2.3×10^{-5}
$P(1\,\mathrm{m})/P(0)$	$e^{-2.4\times10^{-24}}$	0.99998
$\langle h\rangle$	0 m	42 km
$\langle v_x\rangle^{1/2}$	2×10^{-12} m/s	640 m/s

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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

```python
import numpy as np
import matplotlib.pyplot as plt

R0 = 8.31441   J/mol K
mass = 28. /1000  kg/mol N2

def Boltzmann(E,T):
    return np.exp(E/(R0*T))/(R0*T)

def MB1D(v,T):
    return np.sqrt(mass/(2*np.pi*R0*T))*np.exp((mass*v*v)/(2*R0*T))

def MB(c,T):
    K = 0.5 * mass * c *c
    degeneracy = 4 * np.pi * c * c
    normalization = (mass/(2*np.pi*R0*T))**1.5
    return normalization*degeneracy*Boltzmann(K,T)

energy = np.linspace(0,3000,1500)
velocity = np.linspace(1000,1000,1000)
speed = np.linspace(0,1500,1000)

plt.figure()
for Temperature in [100,300,1000]:
   Probability = Boltzmann(energy,Temperature)
   plt.plot(Probability,energy,label=0 K.format(Temperature))

legend = plt.legend()

plt.ylabel(Energy (J/mol))
plt.xlabel(Probability (mol/J))
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/Boltzmann.png)

plt.figure()
for Temperature in [100,200,300,400,500]:
    Probability = MB1D(velocity,Temperature)
    plt.plot(velocity,Probability,label= K.format(Temperature))

legend=plt.legend()
plt.xlabel(Velocity (m/s))
plt.ylabel(Probability (1/(m/s)))
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/MB1D.png)

plt.figure()
for Temperature in [100,200,300,400,500]:
    Probability = MB(speed,Temperature)
    plt.plot(speed,Probability,label= K.format(Temperature))

legend=plt.legend()
plt.xlabel(Speed (m/s))
plt.ylabel(Probability (1/(m/s)))
```

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```
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/MB.png)
```

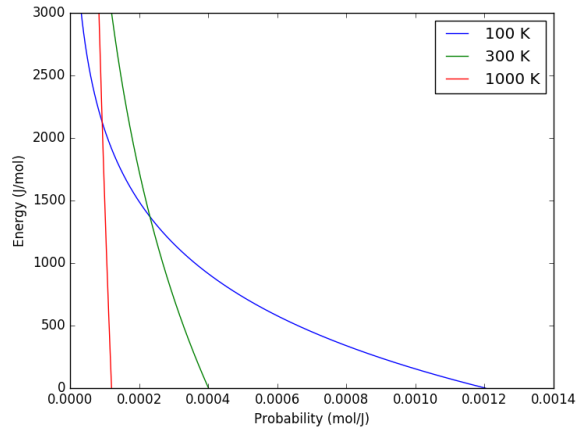

Figure 1: Boltzmann distribution at various temperatures

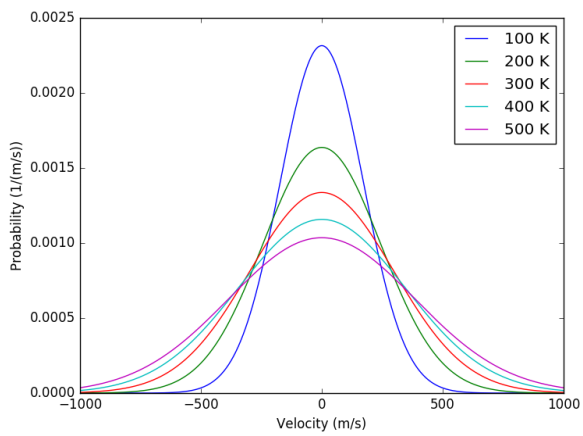

Figure 2: One-dimensional (Gaussian) velocities of N_2 gas

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 << total volume
2. Maxwell-Boltzmann distribution of molecular speeds
   (a) Speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$

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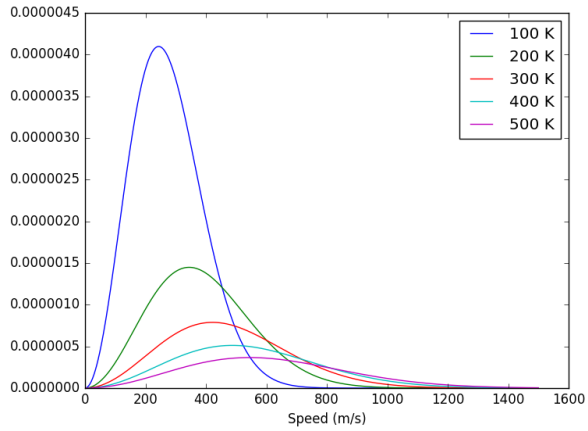

Figure 3: Maxwell-Boltzmann speed distribution of N_2 gas

(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

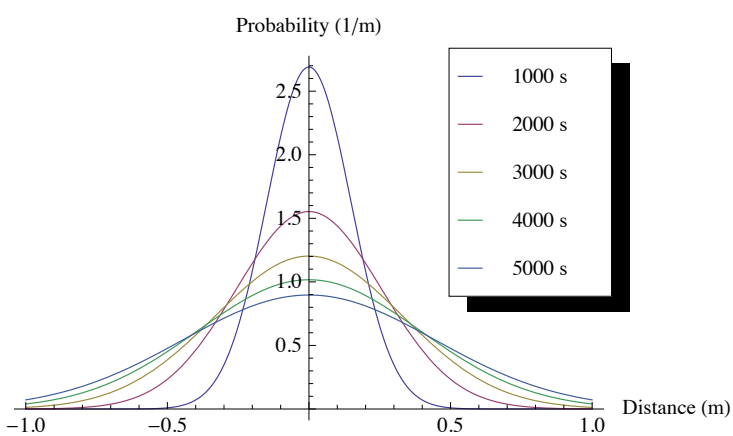

Figure 4: Diffusional spreading, $\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$

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Table 4: Kinetic theory of gases key equations

Boltzmann distribution ($g(E)$: degeneracy of E)	$P(E) = g(E)e^{-E/k_BT}$
Maxwell-Boltzmann distribution	$P_{\mathrm{MB}}(v) = 4\pi v^2 \left(\frac{m}{2\pi k_BT}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_BT}\right)$
Mean and RMS speeds	$\langle v\rangle = \left(\frac{8k_BT}{\pi m}\right)^{1/2} \quad \langle v^2\rangle^{1/2} = \left(\frac{3k_BT}{m}\right)^{1/2}$
Pressure	$\langle P\rangle = \frac{\Delta p}{\Delta t} = m\frac{N}{V}\frac{1}{3}\langle v^2\rangle = \frac{Nk_BT}{V} = \frac{nRT}{V}$
Wall collision frequency	$J_W = \frac{1}{4}\frac{N}{V}\langle v\rangle = \frac{P}{(2\pi mk_BT)^{1/2}}$
Molecular collision frequency	$z = \sqrt{2}\sigma\langle v\rangle\frac{N}{V} = \frac{4\sigma P}{(\pi mk_BT)^{1/2}}$
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	$P = P_0e^{-t/\tau}, \tau = \frac{V}{A}\left(\frac{2\pi m}{k_BT}\right)^{1/2}$
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	$D_{11} = \frac{k_BT}{4\pi\eta r}$ "Slip" boundary
	$D_{\mathrm{Brownian}} = \frac{k_BT}{6\pi\eta r}$ "Stick" boundary

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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: $\frac{dc}{dt} = D\frac{d^2c}{dx^2}$
   (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_BT, 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, $\langle\epsilon\rangle_\nu = k_BT$ for all ν

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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, $\langle\epsilon\rangle_\nu = h\nu/\left(e^{h\nu/k_BT} - 1\right)$
   (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, $\epsilon = h\nu, p = h/\lambda$

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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 formala
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

```
import numpy as np
import matplotlib.pyplot as plt

hc = 1239.8        eV nm
c = 2.9979e8 * 1.e9     nm/s
k = 8.61734e5     eV /K
hck = hc/k         nm K

def Irrad(wl,T):
      return (8. * np.pi * hc * c * wl**5) / (np.exp(hck/(wl*T))1)
def PlanckEnergy(wl,T):
      return (hc/wl) / (np.exp(hck/(wl*T))1)

plt.figure()
wl=np.linspace(100,5000,1000)
for T in [1000.,2000.,3000.,4000.,5000.]:
    Intensity = Irrad(wl,T)
    plt.plot(wl,Intensity,label= K.format(T))

legend=plt.legend()
plt.xlabel(Wavelength (nm))
plt.ylabel(Irradiance (eV/nm3/s))
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/BlackBody.png)

plt.figure()
color=[red,orange,green,blue,violet]
wl=np.linspace(100,20000,1000)
for T in [1000.,2000.,3000.,4000.,5000.]:
    Energy = PlanckEnergy(wl,T)
    plt.plot(wl,Energy,label= K.format(T),color=color[0])
    kT = k*T
    plt.plot([100,max(wl)],[kT,kT],ls=,color=color.pop(0))
```

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```

legend=plt.legend()
plt.xlabel(Wavelength (nm))
plt.ylabel(Energy (eV))
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/Planck.png)
```

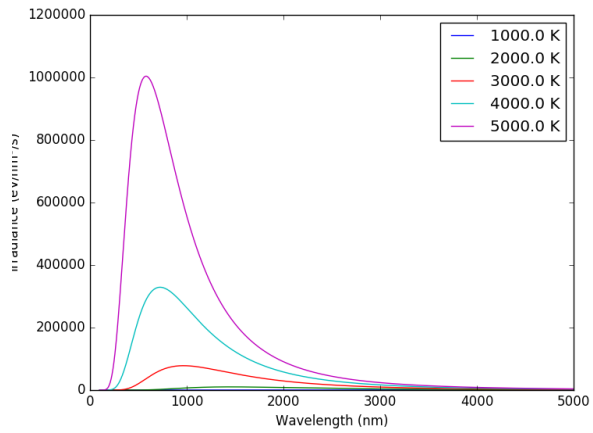

Figure 5: Blackbody irradiance

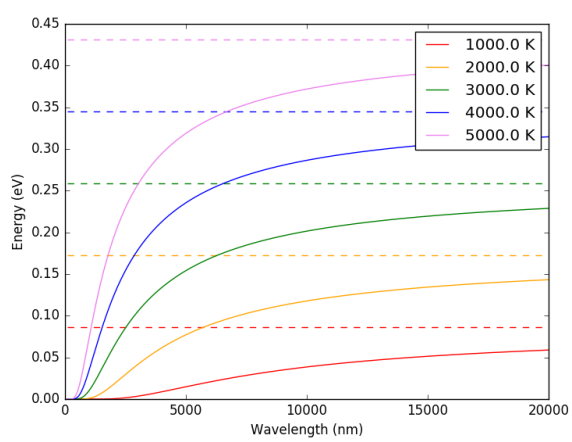

Figure 6: Average energy of a Planck quantized oscillator

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

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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 Schröodinger 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-dimesional QM solutions

1. Schrödinder 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

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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 eignevalues of $\hat{M}$.**

Physical quantity	**Operator**	**Expression**
Position x, y, z	$\hat{x}, \hat{y}, \hat{z}$	$x\cdot, y\cdot, z\cdot$
Linear momentum $p_x, \ldots$	$\hat{p}_x, \ldots$	$-i\hbar\frac{\partial}{\partial x}, \ldots$
Angular momentum $l_x, \ldots$	$\hat{p}_x, \ldots$	$-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \ldots$
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 is a state Ψ, the average resuts with 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 $\Delta x \Delta p_x \geq \hbar/2$.

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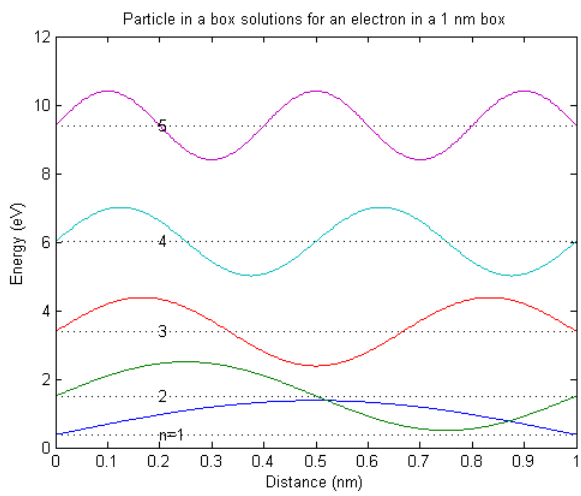
Table 8: Particle-in-a-box model

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x \leq 0 \text{ or } x \geq L \end{cases}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, n = 1, 2, ...$$



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

$$V(x) = \frac{1}{2}kx^2, -\infty < x < \infty$$

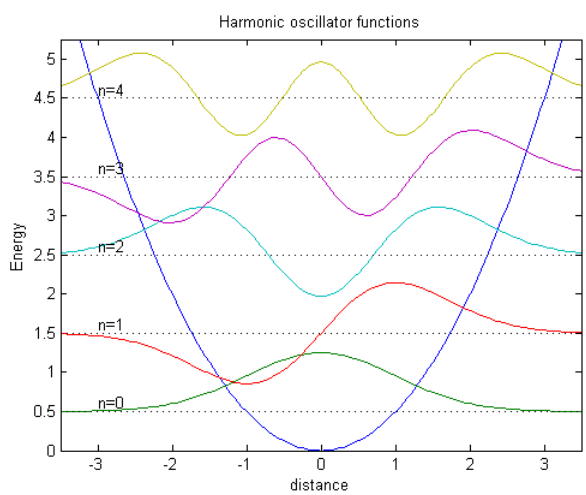
$$\psi_v(x) = N_v H_v(x/\alpha)e^{-x^2/2\alpha^2}, v = 0, 1, 2, \ldots$$

$$\alpha = (\hbar^2/\mu k)^{1/4}, N_v = (2^v v! \alpha\sqrt{\pi})^{-1/2}$$

<u>Hermite polynomials</u>

$$H_0(y) = 1$$
$$H_1(y) = 2y$$
$$H_2(y) = 4y^2 - 2$$
$$H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y)$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$
$$E_v = (v + \frac{1}{2})h\nu, v = 0, 1, 2, ...$$



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2.5 Lecture 8: Rigid Rotor

2.5.1 Classical rigid rotor

1. Compare rotation about an axis vs linear motion
2. Moment of intertia $I = \mu r^2$
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 eignefunctions, $l_z = m_l\hbar$
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 $l = 0, 1, \ldots$
4. Magnetic QN $m_l = -l, -l+1, ..., l$
5. Energy spectrum, $2l + 1$ degeneracy
6. Vector model - can only know total total $|L|$ and L_z
7. Wavefunctions look like atomic orbitals, l nodes

```
import matplotlib.pyplot as plt
from matplotlib import cm, colors
from mpltoolkits.mplot3d import Axes3D
import numpy as np
from scipy.special import sphharm

phi = np.linspace(0, np.pi, 100)
theta = np.linspace(0, 2*np.pi, 100)
phi, theta = np.meshgrid(phi, theta)

 The Cartesian coordinates of the unit sphere
x = np.sin(phi) * np.cos(theta)
y = np.sin(phi) * np.sin(theta)
z = np.cos(phi)

m, l = 0, 0

```

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Table 10: 2-D rigid rotor model

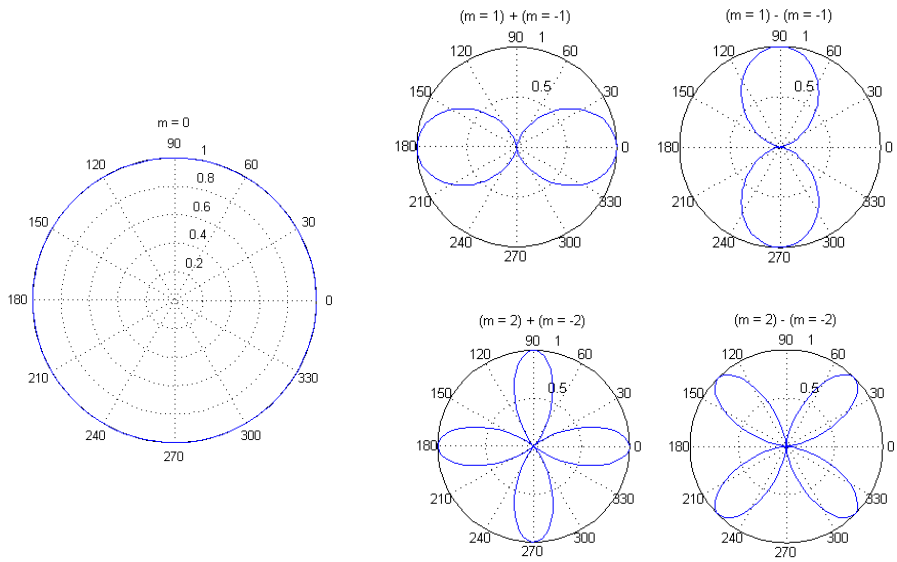
$$V(\phi) = 0, 0 \leq \phi \leq 2\pi$$

$$\hat{H} = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}, \qquad I = \mu R^2$$

$$\psi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}}e^{-im_l\phi}, m_l = 0, \pm1, \pm2, \ldots$$

$$E_{m_l} = \frac{\hbar^2}{2I}m_l^2$$

$$L_z = m_l\hbar$$




```
 Calculate the spherical harmonic Y(l,m) and normalize to [0,1]
fcolors = sphharm(m, l, theta, phi).real
fmax, fmin = fcolors.max(), fcolors.min()
fcolors = (fcolors  fmin)/(fmax  fmin)

 Set the aspect ratio to 1 so our sphere looks spherical
sfig = plt.figure(figsize=plt.figaspect(1.))
s = sfig.addsubplot(111, projection=3d)
s.plotsurface(x, y, z,  rstride=1, cstride=1, facecolors=cm.seismic(fcolors))
 Turn off the axis planes
s.setaxisoff()
plt.savefig(./Images/s.png)

m, l = 0, 1

 Calculate the spherical harmonic Y(l,m) and normalize to [0,1]
fcolors = sphharm(m, l, theta, phi).real
fmax, fmin = fcolors.max(), fcolors.min()
```

Table 11: 3-D rigid rotor model

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

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

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

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

$$l = 0, 1, 2, \ldots, \qquad m_l = 0, \pm 1, \ldots, \pm l$$

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

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

```
fcolors = (fcolors  fmin)/(fmax  fmin)

 Set the aspect ratio to 1 so our sphere looks spherical
 fig = plt.figure(figsize=plt.figaspect(1.))
pfig = plt.figure(figsize=plt.figaspect(1.))
p = pfig.addsubplot(111, projection=3d)
p.plotsurface(x, y, z,  rstride=1, cstride=1, facecolors=cm.seismic(fcolors))
 Turn off the axis planes
p.setaxisoff()

plt.savefig(./Images/p.png)

m, l = 1, 2

 Calculate the spherical harmonic Y(l,m) and normalize to [0,1]
fcolors = sphharm(m, l, theta, phi).real
fmax, fmin = fcolors.max(), fcolors.min()
fcolors = (fcolors  fmin)/(fmax  fmin)

 Set the aspect ratio to 1 so our sphere looks spherical
 fig = plt.figure(figsize=plt.figaspect(1.))
dfig = plt.figure(figsize=plt.figaspect(1.))
d = dfig.addsubplot(111, projection=3d)
d.plotsurface(x, y, z,  rstride=1, cstride=1, facecolors=cm.seismic(fcolors))
 Turn off the axis planes
d.setaxisoff()

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

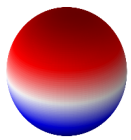


Figure 8: Pythonic p spherical harmonic

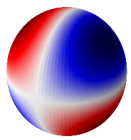


Figure 9: Pythonic d spherical harmonic

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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. $1/A =$ lifetime

2.6.3 Transition probability

1. Einstein coefficient $B_{if} = \frac{|\mu_{if}|^2}{6\epsilon_0 \hbar^2}$
2. Classical electric dipole, $\overrightarrow{\mu} = q \cdot \overrightarrow{l}$, quantum dipole operator $\hat{\mu} = e \cdot \overrightarrow{r}$
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 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 $B = \hbar/4\pi Ic$ 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. $\Delta \tilde{E}_l = 2B(l+1)$ 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

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

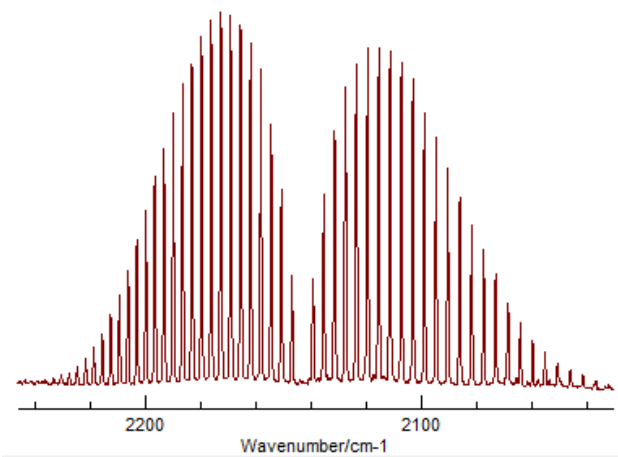

Figure 10: Rovibrational spectrum of carbon monoxide

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_2 example

2.7.7 Polyatomic rotational spectroscopy

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

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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 $n = 1, 2, \ldots$
   (a) K, L, M, N, $\ldots$ shells
   (b) $n-1$ radial nodes
3. Azimuthal quantum number $l = 0, 1, ..., n-1$
   (a) s, p, d, $\ldots$ orbital sub-shells
   (b) l angular nodes
4. Magnetic quantum number $m_l = -l, -l+1, ..., l$
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

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

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Table 12: Hydrogen atom

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}, 0 < r < \infty$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\left[\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \hat{L}^2\right] + V(r)$$

$$\psi(r,\theta,\phi) = R(r)Y_{l,m_l}(\theta,\phi)$$

$$\left\{-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right\}R(r) = ER(r)$$

$$R_{nl}(r) = N_{nl}e^{-x/2}x^l L_{nl}(x), \quad x = \frac{2r}{na_0}$$
$$P_{nl}(r) = r^2 R_{nl}^2$$

$$n = 1, 2, \ldots, \quad l = 0, \ldots, n-1 \quad m_l = 0, \pm 1, \ldots, \pm l$$

$$N_{nl} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}}$$

$$L_{10} = L_{21} = L_{32} = \ldots = 1 \quad L_{20} = 2 - x \quad L_{31} = 4 - x$$

$$E_n = -\frac{1}{2}\frac{\hbar^2}{m_e a_0^2}\frac{1}{n^2} = -\frac{E_H}{2}\frac{1}{n^2}$$

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

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 wave-function, 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

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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

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

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

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

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

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

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

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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

2.11 Lecture 14: Computational chemistry

2.12 Lecture 15: Electronic spectroscopy

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

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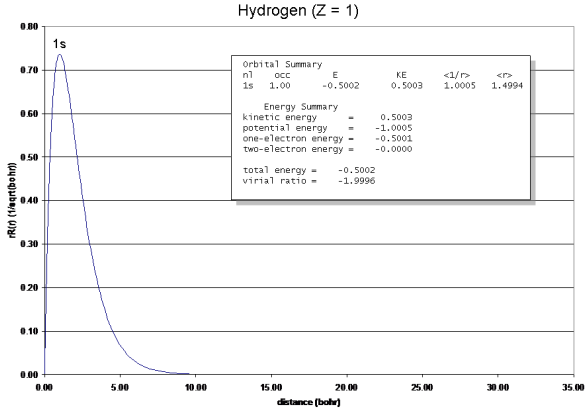
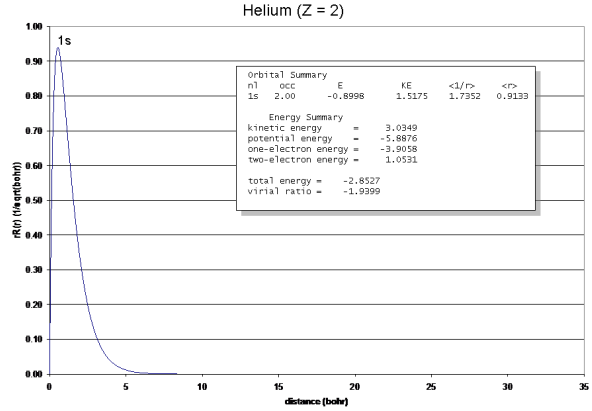
Table 13: Numerical DFT Solutions for Atoms

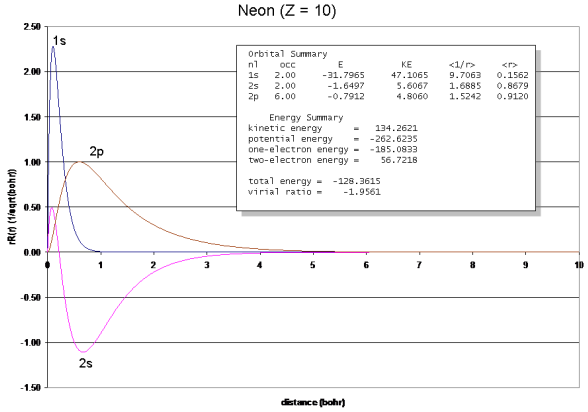
Hydrogen (Z = 1)



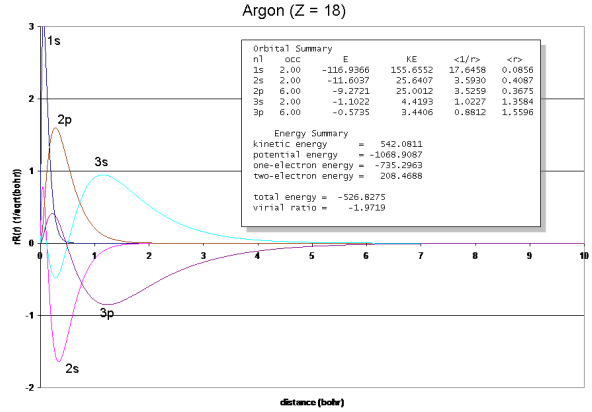
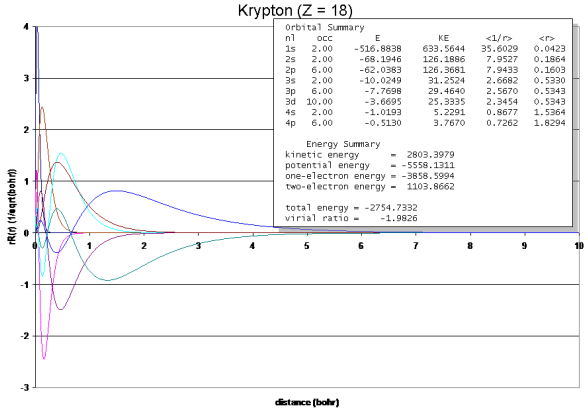
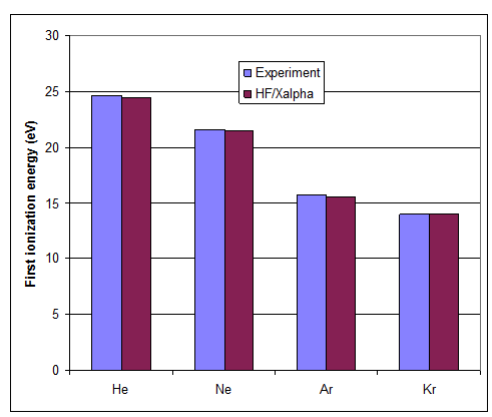
Helium (Z = 2)



Neon (Z = 10)



Argon (Z = 18)



Krypton (Z = 18)