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	J K^{-1} mol^{-1}	8.2057×10^{-2}	l atm mol^{-1} K^{-1}
σ_{SB}:	5.6704×10^{-8}	J s^{-1} m^{-2} 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}	C^2 J^{-1} m^{-1}	5.52635×10^{-3}	e^2 $\mathrm{Å}^{-1}$ 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 $a < x < b = \int_a^b \tilde{P}(x)dx$

(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

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

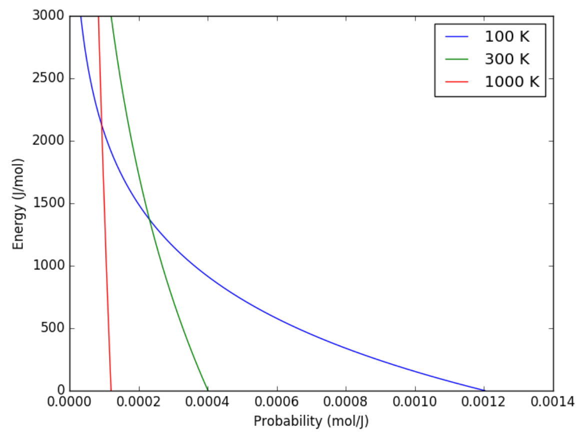


Figure 1: Boltzmann distribution at various temperatures

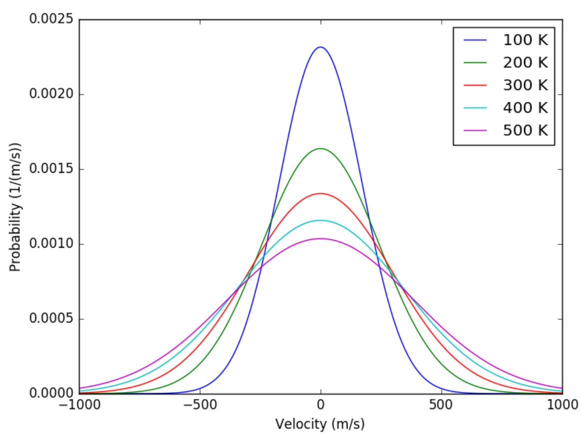


Figure 2: One-dimensional (Gaussian) velocities of N_2 gas

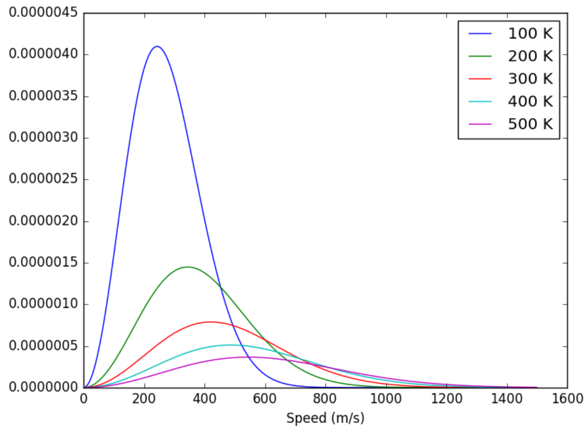


Figure 3: Maxwell-Boltzmann speed distribution of N_2 gas

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 << 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, λ, mean distance between collisions

Table 4: Kinetic theory of gases key equations

Boltzmann distribution ($g(E)$: degeneracy of E)	$P(E) = g(E)e^{-E/k_BT}$
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

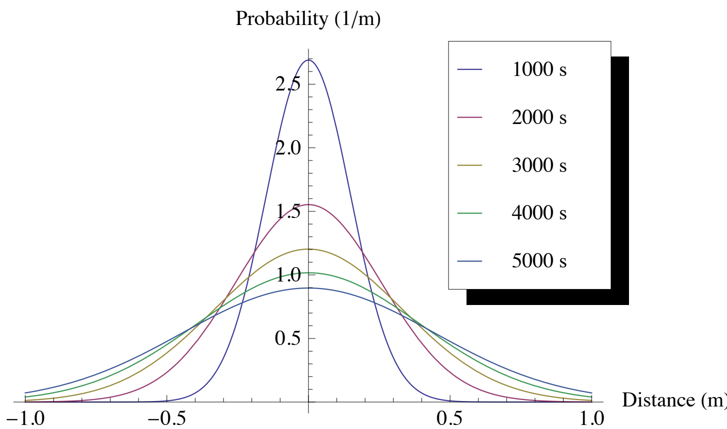


Figure 4: Diffusional spreading, $\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$

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: $\frac{dc}{dt} = D\frac{d^2c}{dx^2}$
   (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

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 ν

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 → ultraviolet catastrophe
3. Planck model
   (a) Energy spectrum of oscillators are *quantized*, $\epsilon_\nu = nh\nu$
   (b) Expected energy of a quantized oscillator, $\langle\epsilon\rangle_\nu = h\nu/\left(e^{h\nu/k_B T} - 1\right)$
   (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, $\epsilon = h\nu, p = h/\lambda$

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))

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

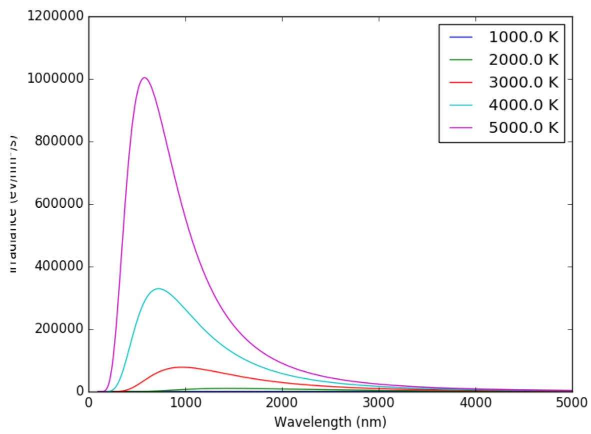


Figure 5: Blackbody irradiance

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*

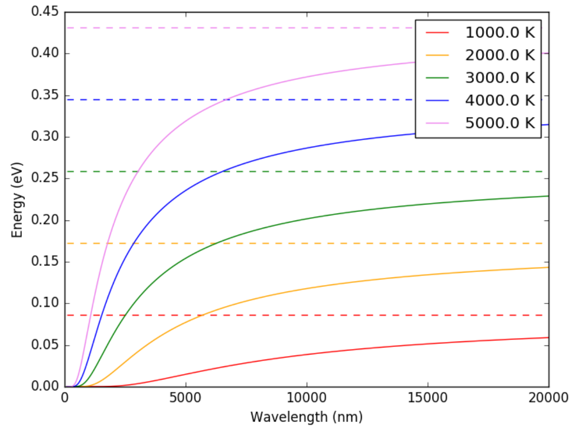


Figure 6: Average energy of a Planck quantized oscillator

Table 6: The new physics

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

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 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

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

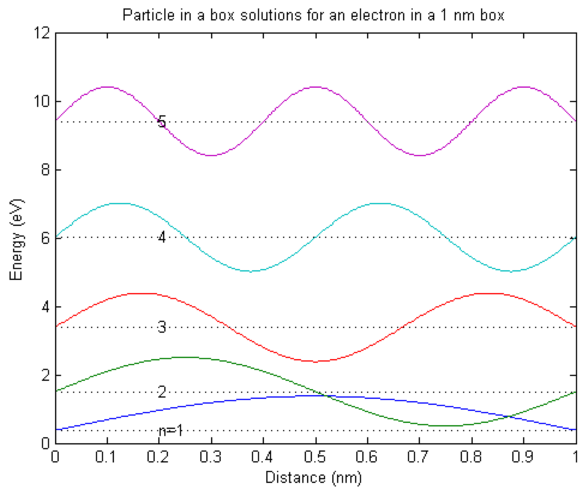
Postulate 5: (The **uncertainty principle**.) Operators that do not commute ($\hat{A}(\hat{B}\Psi) \neq \hat{B}(\hat{A}\Psi)$) are called *conjugate*. Conjugate observables cannot be determined simultaneously to arbitrary accuracy. For example, the standard deviation in the measured positions and momenta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

Table 8: Particle-in-a-box model

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

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

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



2.3.6 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

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

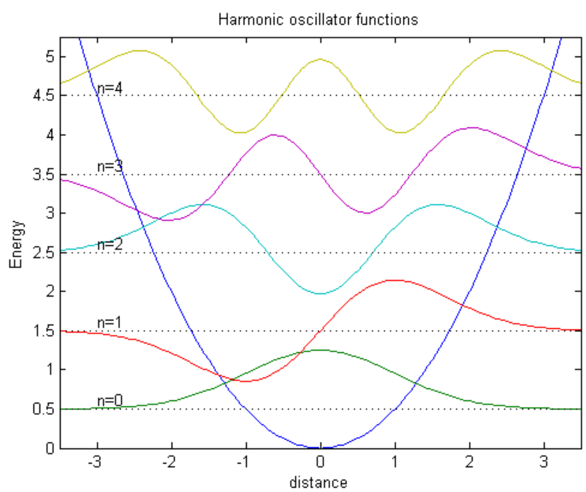
$$\psi_v(x) = N_v H_v(x/\alpha) e^{-x^2/2\alpha^2}, v = 0, 1, 2, \ldots$$

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

<u>Hermite polynomials</u>

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

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



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 mpl_toolkits.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

```

Table 10: 2-D rigid rotor model

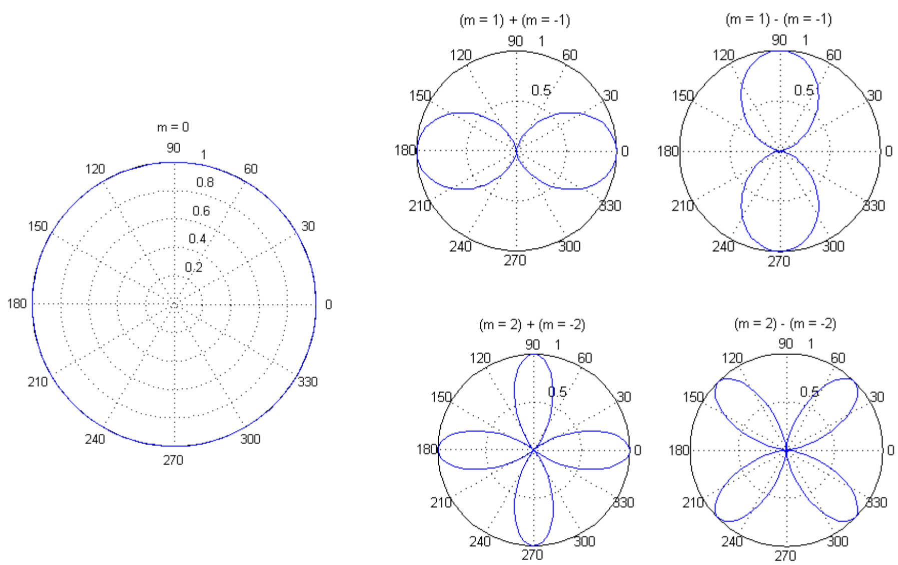
$$V(\phi) = 0, 0 \leq \phi \leq 2\pi$$

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

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

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

$$L_z = m_l \hbar$$




```
 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, $s = 1/2, m_s = \pm 1/2$

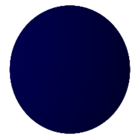


Figure 7: Pythonic s spherical harmonic

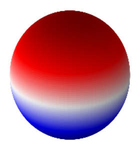


Figure 8: Pythonic p spherical harmonic

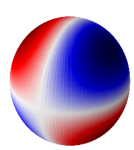


Figure 9: Pythonic d spherical harmonic

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

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

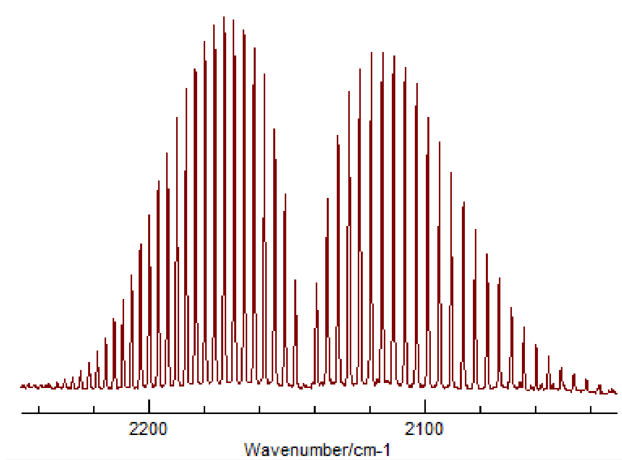


Figure 10: Rovibrational spectrum of carbon monoxide

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

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, … shells
   (b) $n-1$ radial nodes
3. Azimuthal quantum number $l = 0, 1, ..., n-1$
   (a) s, p, d, … 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

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

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 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

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

2.9.5 Electron-electron interactions

1. Coulomb ($\hat{v}_{\mathrm{Coul}}$): classical repulsion between distinguishable electron "clouds"

2. Exchange ($\hat{v}_{\mathrm{ex}}$): accounts for electron indistinguishability (Pauli principle for fermions). Decreases Coulomb repulsion because electrons of like spin intrinsically avoid one another

3. Correlation ($\hat{v}_{\mathrm{corr}}$): 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 $\hat{v}_{\mathrm{Coul}}$

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

$$\hat{h} = -\frac{\hbar^2}{2m_e}\nabla^2 - \sum_\alpha \frac{Z_\alpha e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}-\mathbf{R}_\alpha|} \tag{1}$$

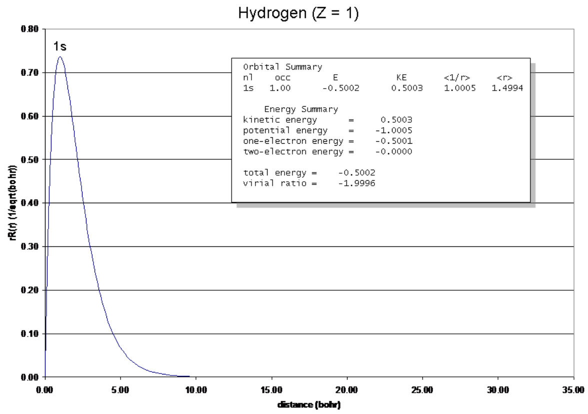
$$\hat{f}\psi = \left\{\hat{h} + \hat{v}_{\mathrm{Coul}}[\psi_i] + \hat{v}_{\mathrm{ex}}[\psi_i] + \hat{v}_{\mathrm{corr}}[\psi_i]\right\}\psi = \epsilon\psi \tag{2}$$

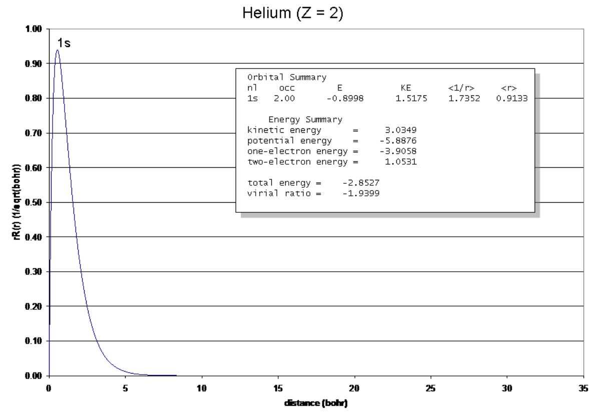
1. Solve as for atoms, using some model for electron-electron interactions

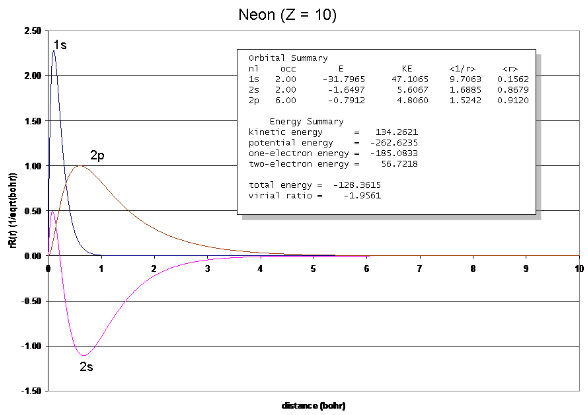
2. Potential energy surface (PES)

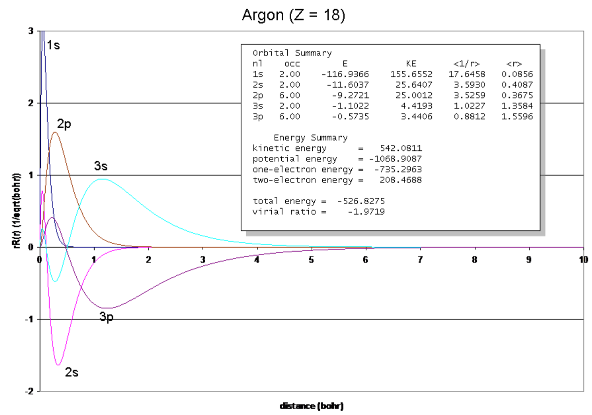
$$E(\mathbf{R}_\alpha, \mathbf{R}_\beta, ...) = E_{\mathrm{elec}} + \frac{e^2}{4\pi\epsilon_0}\sum_\alpha\sum_{\beta>\alpha}\frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}$$

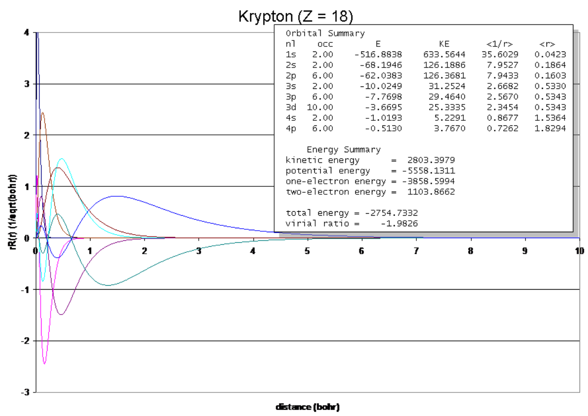
Table 13: Numerical DFT Solutions for Atoms

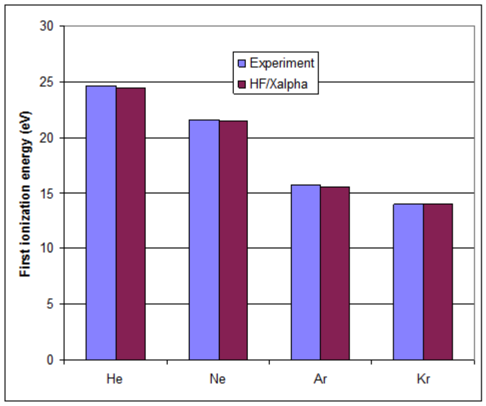












2.10.2 H_2 molecule as perturbation on two H atoms brought from infinite distance

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

2.10.3 Secular equations

1. Expand molecular orbitals in "basis" of atomic-like orbitals

$$\psi_{\mathrm{MO}} = \sum_a c_a \phi_a(\mathbf{r}) \tag{3}$$

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) ϵ 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 ϵs and back-substitute to find correspond c_is

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: $F_{ii} \approx \epsilon_{i,\mathrm{ao}}$
   (b) Off-diagonal elements proportional to overlap and inversely proportional to energy difference:

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

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

2.10.5 H_2 example, again

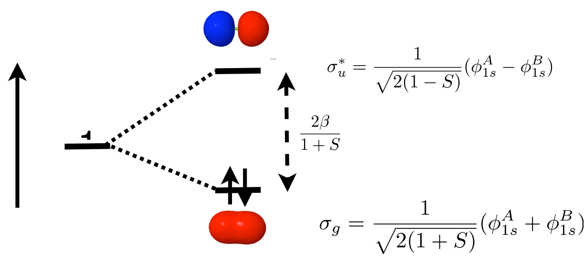
1. Assign one 1s atomic orbital ("basis function") to each atom

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

2. Set-up and solve secular matrix

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

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



3. From Taylor expansion get picture of atomic orbitals destabilized by electron repulsion βS and split by interaction β

$$\begin{aligned} \epsilon_+ &\approx \alpha - \beta S + \beta \\ \epsilon_- &\approx \alpha - \beta S - \beta \end{aligned}$$

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

$$\begin{aligned} \epsilon_+ &\approx \alpha_1 - \beta S - \beta^2/|\alpha_1 - \alpha_2| \\ \epsilon_- &\approx \alpha_2 - \beta S + \beta^2/|\alpha_1 - \alpha_2| \end{aligned}$$

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$_z$ $\rightarrow$ bonding, non-bonding, anti-bonding orbitals

2.10.7 Homonuclear diatomic: O_2

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) $2p_z + 2p_z$ form second bond and anti-bond
   (d) $2p_{x,y} + 2p_{x,y}$ form degenerate π bonds and anti-bonds
   (e) O_2 is a triplet, consistent with experiment!

2.10.8 The Hückel/tight binding model: Roberts, Notes on Molecular Orbital Theory

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

```
from sympy import *
initprinting(useunicode=True)

alpha,beta = symbols(alpha beta)

M = Matrix([[alpha, beta, 0 , 0],[beta, alpha, beta, 0],[0,beta,alpha,beta],[0,0,beta,alpha]])

 M = Matrix([[alpha,beta],[beta,alpha]])

eigs  = M.eigenvects()
print(eigs)
```

[(alpha - beta/2 + sqrt(5)*beta/2, 1, [Matrix([[4/((1 + sqrt(5))*(-sqrt(5) + 1))], [-2/(1 + sqrt(5))], [2/(1 + sqrt(5))], [1]])]), (alpha + beta/2 + sqrt(5)*beta/2, 1, [Matrix([[-4/((1 + sqrt(5))*(-sqrt(5) + 1))], [-2/(-sqrt(5) + 1)], [-2/(-sqrt(5) + 1)], [1]])]), (alpha - sqrt(5)*beta/2 - beta/2, 1, [Matrix([[-4/((-1 + sqrt(5))*(1 + sqrt(5)))], [2/(-1 + sqrt(5))], [-2/(-1 + sqrt(5))], [1]])]), (alpha - sqrt(5)*beta/2 + beta/2, 1, [Matrix([[4/((-1 + sqrt(5))*(1 + sqrt(5)))], [-2/(1 + sqrt(5))], [-2/(1 + sqrt(5))], [1]])])]

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)

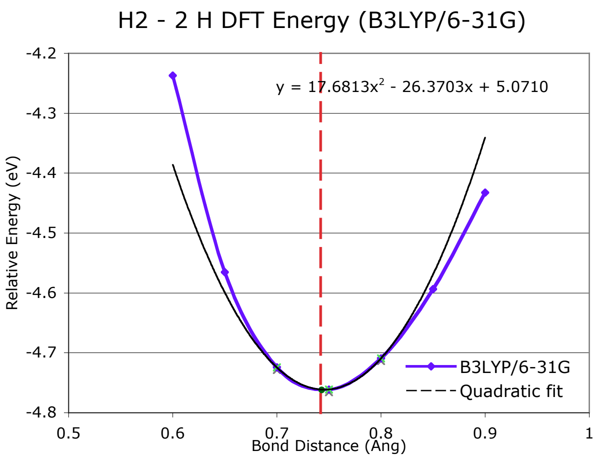
2.11.3 Secular equations solved iteratively until input coefficients = output coefficients

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_2 example

Bond length

H-H exp't:	0.742Å
B3LYP opt:	0.743



Bond energy

H-H exp't	= 4.478 eV
2 H: 2(-0.4969) au	= -27.041 eV
H_2: -1.1687 au	= -31.803 eV
Dissociation E	= 4.762 eV
ZPE corrected	= 4.484 eV

Vibrational frequencies

Experiment:	4401 cm^{-1}
B3LYP harmonic:	4487 cm^{-1}
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

2.13 Lecture 16: Electronic and magnetic properties

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

3.1 Lecture 17: Statistical mechanics

3.1.1 Need machinary to average QM information over macroscopic systems

3.1.2 Equal *a priori* probabilities

3.1.3 Two-state model

1. Box of particles, each of which can have energy 0 or ϵ
2. Thermodynamic state defined by number of elements N, and number of quanta q, $U = q\epsilon$
3. Degeneracy of given N and q given by binomial distribution:

$$\Omega = \frac{N!}{q!(N-q)!}$$

4. Allow energy to flow between two such systems
5. Energy of a closed system is conserved (first law!)
6. Degeneracy of total system is always $\geq$ degeneracy of the starting parts!
7. Boltzmann's tombstone, $S = k_B \ln \Omega$
8. Clausius: entropy of the universe seeks a maximum! Second Law...

3.1.4 Energy flow/thermal equilibrium between two large systems

1. Each subsystem has energy U_i and degeneracy $\Omega_i(U_i)$
2. Bring in thermal contact, $U = U_1 + U_2$, $\Omega = \Omega_1(U_1)\Omega_2(U_2)$
3. If systems are very large, one combination of U_1, U_2 and Ω will be much more probably than all others
4. What value of U_1 and $U_2 = U - U_1$ maximizes Ω?
$$\left(\frac{\partial \ln \Omega_1}{\partial U_1}\right)_N = \left(\frac{\partial \ln \Omega_2}{\partial U_2}\right)_N$$
$$\left(\frac{\partial S_1}{\partial U_1}\right)_N = \left(\frac{\partial S_2}{\partial U_2}\right)_N$$
5. Thermal equilibrium is determined by equal **temperature**!
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$
6. When the temperatures of the two subsystems are equal, the entropy of the combined system is maximized!
7. (Same arguments lead to requirement that equal pressures (P_i) and equal chemical potentials (μ_i) maximize entropy when volumes or particles are exchanged)

3.1.5 Two-state model in limit of large N

1. Large N and Stirling's approximation
2. Fundamental thermodynamic equation of two-state system:
$$S(U) = -k_B\left(x \ln x + (1-x)\ln(1-x)\right), \text{where } x = q/N = U/N\epsilon$$
3. Temperature is derivative of entropy wrt energy yields
$$U(T) = \frac{N\epsilon}{1 + e^{\epsilon/k_B T}}$$
4. $T \to 0, U \to 0, S \to 0$, minimum disorder
5. $T \to \infty, U \to N\epsilon/2, S \to k_B \ln 2$, maximum disorder
6. Differentiate again to get heat capacity

3.1.6 Example of microcanonical ("NVE") ensemble

1. Direct evaluation of $S(U)$ is generally intractable, so seek simpler approach

3.2 Lecture 18: Canonical (NVT) ensemble

3.2.1 Partition function

1. Imagine a system brought into thermal equilibrium with a much larger "reservoir" of constant T, such that the aggregate has a total energy U

2. Degeneracy of a given system microstate j with energy U_j is $\Omega_{res}(U - U_j)$

$$T = \frac{dU_{res}}{k_B d \ln \Omega_{res}}$$
$$\Omega_{res}(U - U_j) \propto e^{-U_j/k_B T}$$

3. Probability for system to be in a microstate with energy U_j given by Boltzmann distribution!

$$P(U_j) \propto e^{-U_j/k_B T} = e^{-U_j \beta}$$

4. Partition function "normalizes" distribution, $Q(T) = \sum_j e^{-U_j \beta}$

5. For system of identical (distinguishable) elements with energy states ϵ_i, can factor probability to show

$$P(\epsilon_i) \propto e^{-\epsilon_i/k_B T} = e^{-\epsilon_i \beta}, \qquad \beta = 1/k_B T$$

3.2.2 Energy factoring (sidebar)

1. If system is large, how to determine it's energy states U_j? There would be many, many of them!

2. One simplification is if we can write energy as sum of energies of individual elements (atoms, molecules) of system:

$$U_j = \epsilon_j(1) + \epsilon_j(2) + ... + \epsilon_j(N) \tag{4}$$
$$Q(N, V, T) = \sum_j e^{-U_j \beta} \tag{5}$$
$$= \sum_j e^{-(\epsilon_j(1)+\epsilon_j(2)+...+\epsilon_j(N))\beta} \tag{6}$$

3. *If* molecules/elements of system can be distinguished from each other (like atoms in a fixed lattice), expression can be factored:

$$Q(N, V, T) = \left(\sum_j e^{-\epsilon_j(1)\beta}\right) \cdots \left(\sum_j e^{-\epsilon_j(N)\beta}\right) \tag{7}$$
$$= q(1) \cdots q(N) \tag{8}$$

Assuming all the elements are the same: (9)

$$= q^N \tag{10}$$
$$q = \sum_j e^{-\epsilon_j \beta} : \text{molecular partition function} \tag{11}$$

4. *If not* distinguishable (like molecules in a liquid or gas, or electrons in a solid), problem is difficult, because identical arrangements of energy amongst elements should only be counted once.

5. Approximate solution, good almost all the time:

$$Q(N, V, T) = q^N/N! \tag{12}$$

6. Sidebar: "Correct" factoring depends on whether individual elements are fermions or bosons, leads to funny things like superconductivity and superfluidity.

3.2.3 Distinguishable vs. indistinguishable particles

1. Distinguishable (e.g., in a lattice): $Q(N, V, T) = q(V, T)^N$

2. Indistinguishable (e.g., a gas): $Q(N, V, T) \approx q(V, T)^N/N!$

3.2.4 Two-state system again

1. Partition function, $q(T) = 1 + e^{-\epsilon\beta}$

2. State probabilities

3. Internal energy $U(T)$

$$U(T) = -N\left(\frac{\partial \ln(1 + e^{-\epsilon\beta})}{\partial\beta}\right) = \frac{N\epsilon e^{-\epsilon\beta}}{1 + e^{-\epsilon\beta}} \tag{13}$$

4. Heat capacity C_v
   (a) Minimum when change in states with T is small
   (b) Maximize when chagne in states with T is large

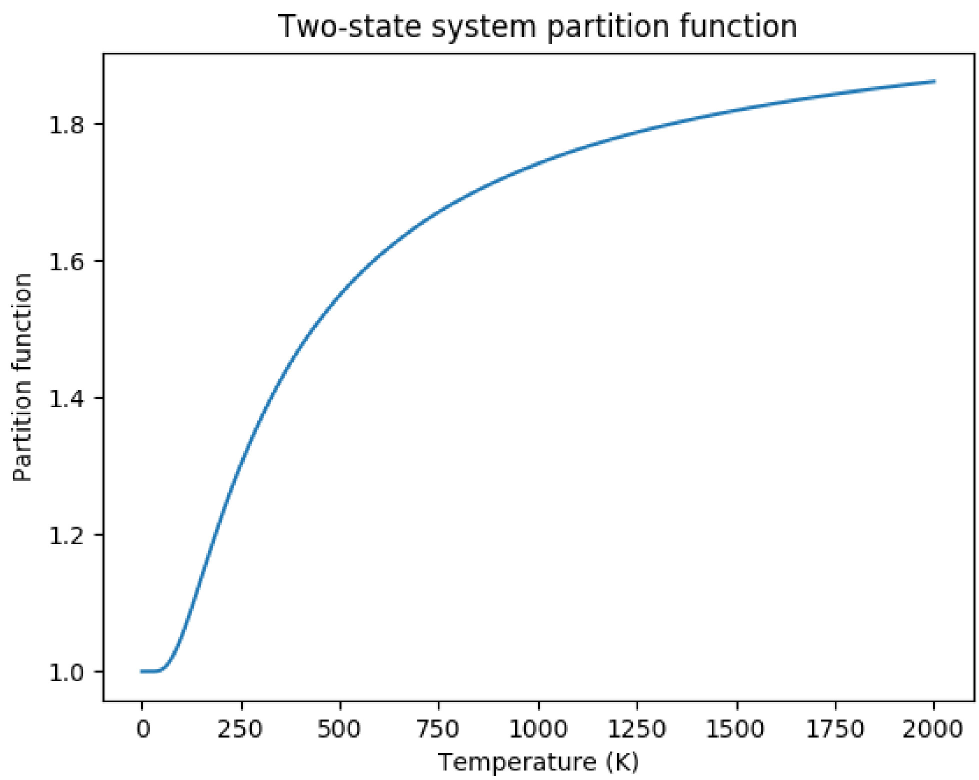
5. Helmholtz energy, $A = -\ln q/\beta$, decreasing function of T

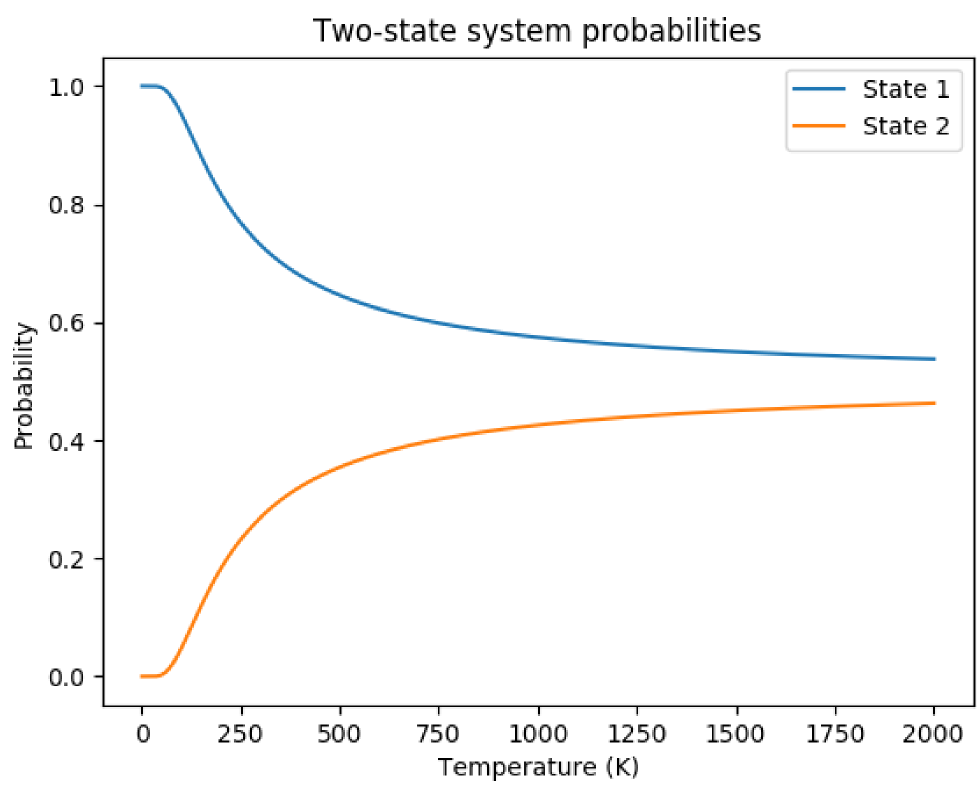
6. Entropy

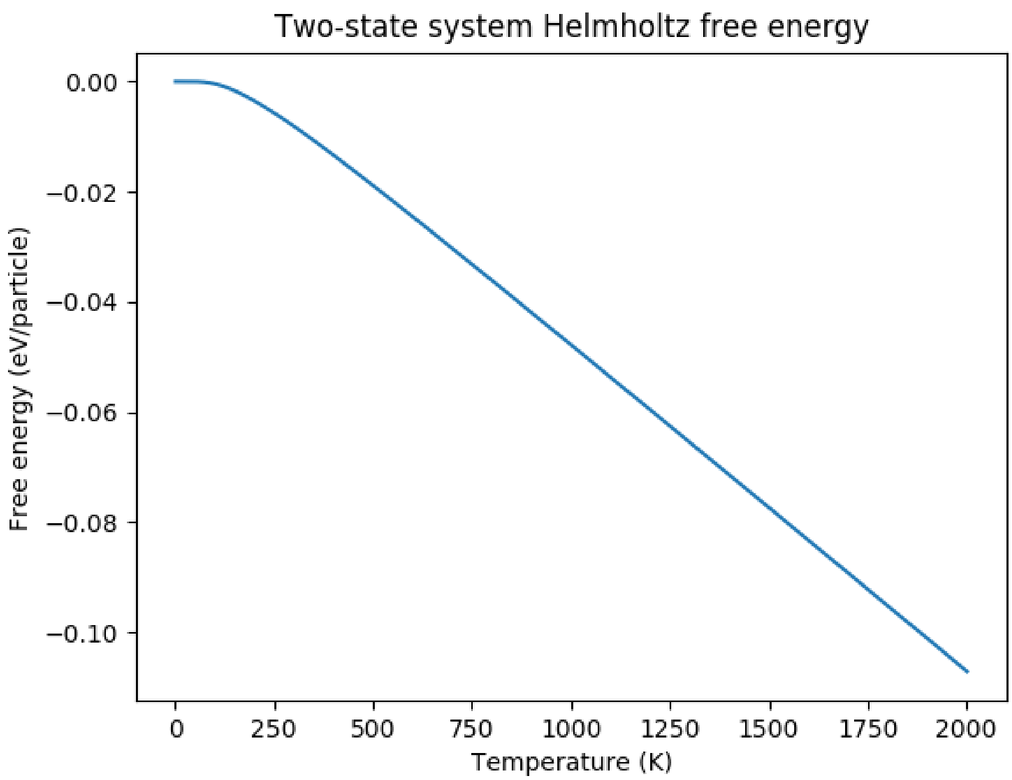
```
import numpy as np
import matplotlib.pyplot as plt

k = 8.61734e5     eV /K
theta = 300.   epsilon/kB


def q(T):
   return 1. + np.exp(theta/T)

def P1(T):
   return 1/q(T)

def P2(T):
   return np.exp(theta/T)/q(T)

def A(T):
   return k*T*np.log(q(T))

```



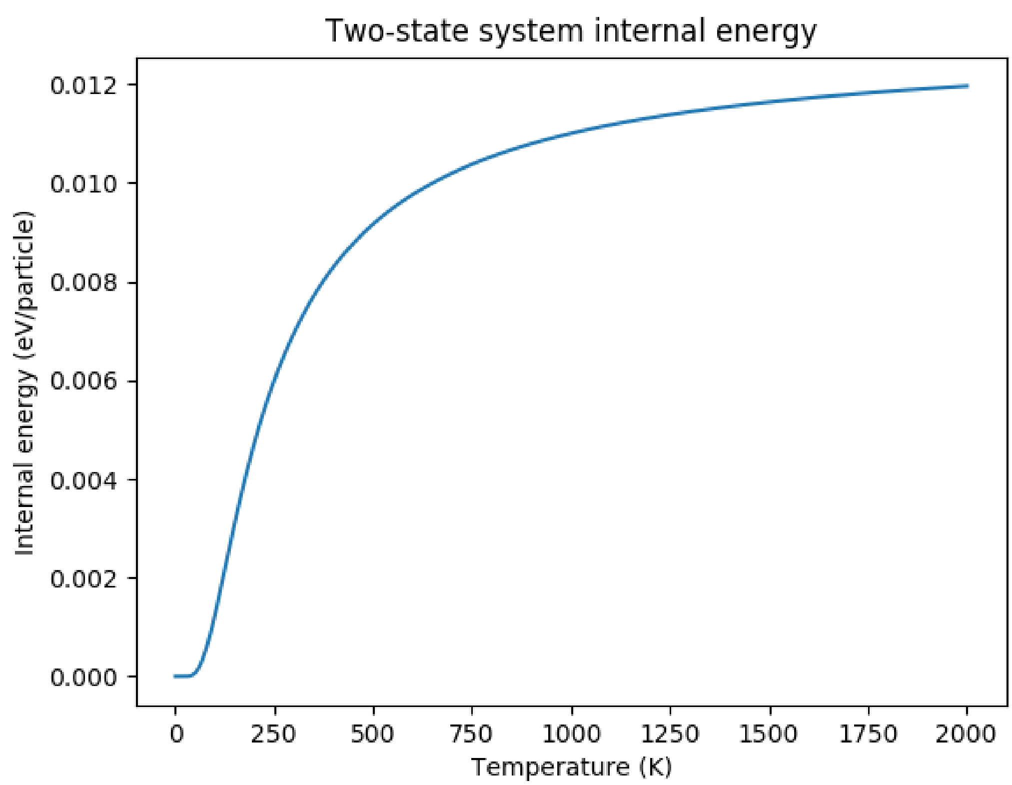
```
def U(T):
   epsilon = theta*k
   return epsilon * np.exp(theta/T) / q(T)

def C(T):
   return (theta/T)**2 * np.exp(theta/T)/(q(T)*q(T))

def S(T):
   return (U(T)  A(T))/T

T = np.linspace(1,2001,500)

plt.figure()
plt.plot(T,q(T))
plt.xlabel(Temperature (K))
plt.ylabel(Partition function)
plt.title(Twostate system partition function)
plt.savefig(./Images/2statepartition.png)

plt.figure()
plt.plot(T,P1(T),label=State 1)
plt.plot(T,P2(T),label=State 2)
plt.xlabel(Temperature (K))
plt.ylabel(Probability)
plt.legend()
plt.title(Twostate system probabilities)
plt.savefig(./Images/2stateprobability.png)

plt.figure()
plt.plot(T,A(T))
plt.xlabel(Temperature (K))
plt.ylabel(Free energy (eV/particle))
plt.title(Twostate system Helmholtz free energy)
plt.savefig(./Images/2statehelmholtz.png)

plt.figure()
plt.plot(T,U(T))
plt.xlabel(Temperature (K))
plt.ylabel(Internal energy (eV/particle))
plt.title(Twostate system internal energy)
plt.savefig(./Images/2stateinternal.png)

plt.figure()
plt.plot(T,C(T))
plt.xlabel(Temperature (K))
plt.ylabel(Heat capacity (eV/T))
plt.title(Twostate system heat capacity)
plt.savefig(./Images/2stateheatcapacity.png)

plt.figure()
plt.plot(T,S(T))
plt.xlabel(Temperature (K))
plt.ylabel(Entropy (eV/T))
plt.title(Twostate system entropy)
plt.savefig(./Images/2stateentropy.png)
```


Two-state system partition function
Partition function
1.0
1.2
1.4
1.6
1.8
0
250
500
750
1000
1250
1500
1750
2000
Temperature (K)

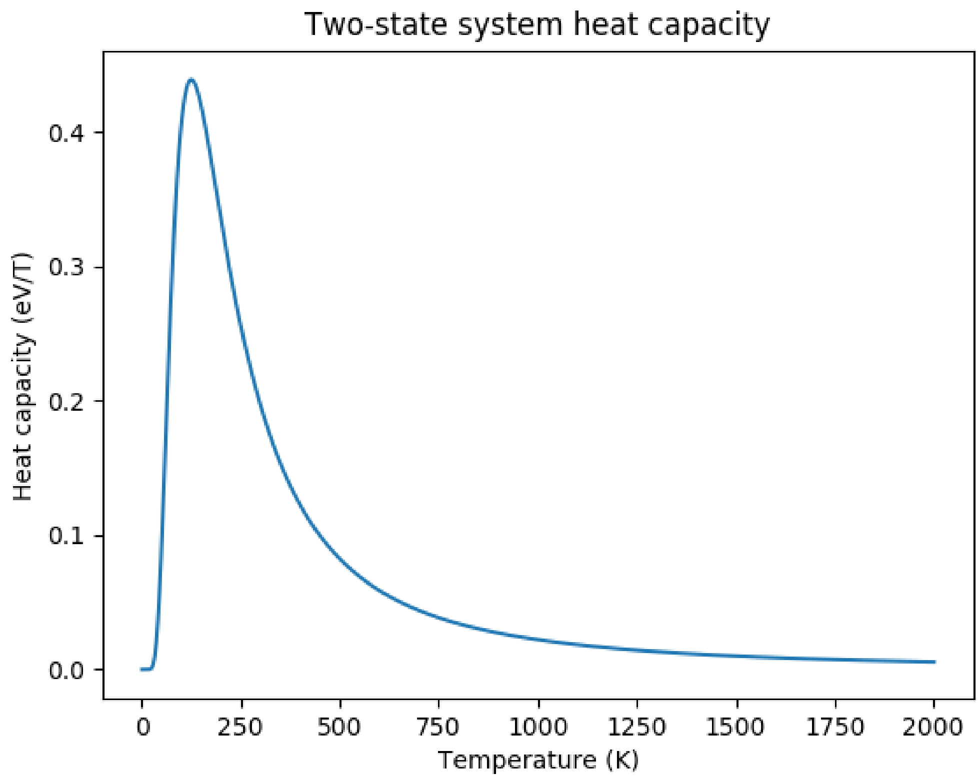

Two-state system probabilities
Probability
0.0
0.2
0.4
0.6
0.8
1.0
State 1
State 2
0
250
500
750
1000
1250
1500
1750
2000
Temperature (K)



Two-state system Helmholtz free energy
Free energy (eV/particle)
0.00
−0.02
−0.04
−0.06
−0.08
−0.10
0
250
500
750
1000
1250
1500
1750
2000
Temperature (K)



Two-state system internal energy
Internal energy (eV/particle)
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
250
500
750
1000
1250
1500
1750
2000
Temperature (K)


Two-state system heat capacity
Heat capacity (eV/T)
0.0
0.1
0.2
0.3
0.4
0
250
500
750
1000
1250
1500
1750
2000
Temperature (K)

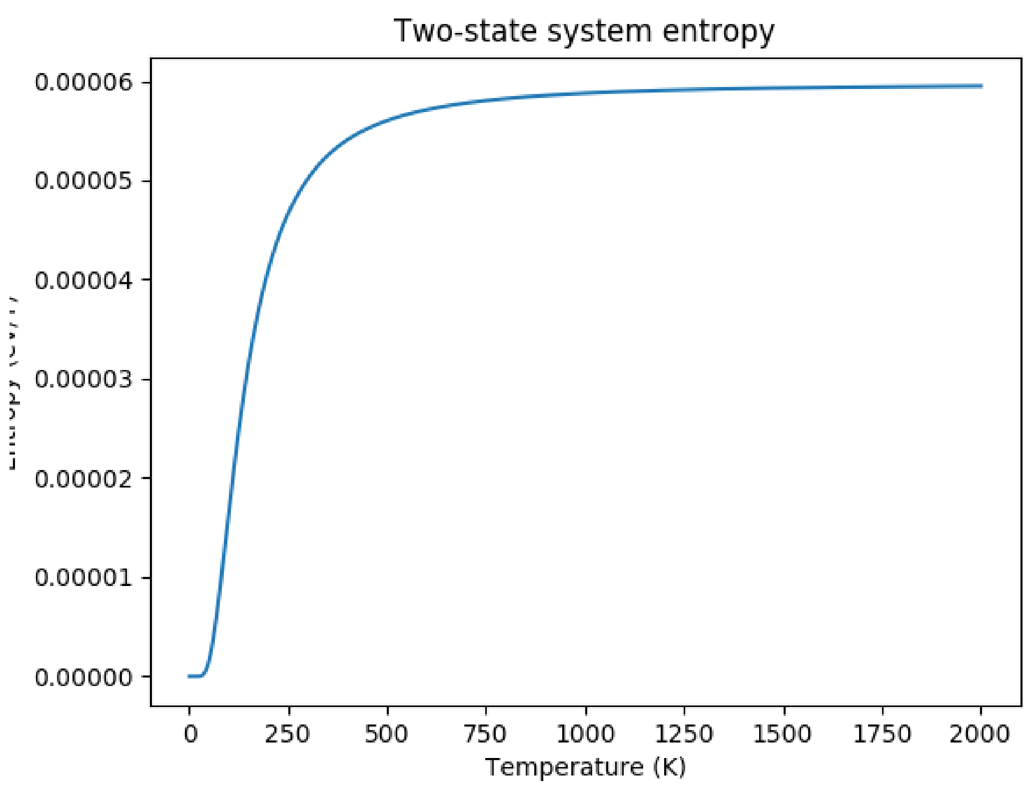

Two-state system entropy
0.00000
0.00001
0.00002
0.00003
0.00004
0.00005
0.00006
0
250
500
750
1000
1250
1500
1750
2000
Temperature (K)

Table 14: Equations of the Canoncial (NVT) Ensemble

$\beta = 1/k_BT$	**Full Ensemble**	**Distinguishable particles** (e.g. atoms in a lattice)	**Indistinguishable particles** (e.g. molecules in a fluid)
Single particle partition function		$q(V,T) = \sum_i e^{-\epsilon_i\beta}$	$q(V,T) = \sum_i e^{-\epsilon_i\beta}$
Full partition function	$Q(N,V,T) = \sum_j e^{-U_j\beta}$	$Q = q(V,T)^N$	$Q = q(V,T)^N/N!$
Log partition function	$\ln Q$	$N \log q$	$N \ln q - \ln N!$ $\approx N(\ln Q - \ln N + 1)$
Helmholtz energy ($A = U - TS$)	$-\frac{\ln Q}{\beta}$	$-\frac{N \ln q}{\beta}$	$-\frac{N}{\beta}\left(\ln \frac{q}{N} + 1\right)$
Internal energy (U)	$-\left(\frac{\partial \ln Q}{\partial \beta}\right)_{NV}$	$-N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$	$-N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$
Pressure (P)	$-\left(\frac{\partial \ln Q}{\partial V}\right)_{N\beta}$	$-N\left(\frac{\partial \ln q}{\partial V}\right)_\beta$	$-N\left(\frac{\partial \ln q}{\partial V}\right)_\beta$
Entropy (S/k_B)	$\beta U + \ln Q$	$\beta U + N \ln q$	$\beta U + N\left(\ln(q/N) + 1\right)$
Chemical potential (μ)	$-\frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial N}\right)_{VT}$	$-\frac{\ln q}{\beta}$	$-\frac{\ln(q/N)}{\beta}$

NOTE! All energies are referenced to their values at 0 K. Enthalpy $H = U + PV$, Gibb's Energy $G = A + PV$.

3.2.5 Thermodynamic functions in canonical ensemble

3.3 Lecture 19: Molecular Partition Functions

3.3.1 Ideal gas of molecules

$$Q_{ig}(N,V,T) = \frac{(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}})^N}{N!}$$

3.3.2 Particle-in-a-box (translational states of a gas)

1. Energy states $\epsilon_n = n^2\epsilon_0, n = 1, 2, \ldots,$ ϵ_0 tiny for macroscopic V
2. $\Theta_{\text{trans}} = \epsilon_0/k_B$ translational temperature
3. $\Theta_{\text{trans}} << T \rightarrow$ many states contribute to $q_{\text{trans}} \rightarrow$ integral approximation

$$q_{\text{trans,1D}} = \int_0^\infty e^{-x^2\beta\epsilon_0} dx = L/\Lambda$$

$$\Lambda = \left(\frac{h^2\beta}{2\pi m}\right)^{1/2} \text{ thermal wavelength}$$

$$q_{\text{trans,3D}} = V/\Lambda^3$$

4. Internal energy
5. Heat capacity
6. Equation of state (!)
7. Entropy: Sackur-Tetrode equation

3.3.3 Rigid rotor (rotational states of a gas)

1. energy states and degeneracies
2. $\Theta_{\mathrm{rot}} = \hbar^2/2Ik_B$
3. "High" T $q_{\mathrm{rot}}(T) \approx \sigma\Theta_{\mathrm{rot}}/T$

3.3.4 Harmonic oscillator (vibrational states of a gas)

1. $\Theta_{\mathrm{vib}} = h\nu/k_B$

3.3.5 Electronic partition functions → spin multiplicity

3.3.6 Non-ideality

1. Real molecules interact through vdW interactions
2. Particle-in-a-box model breaks down, have to work harder but can still get at same ideas
3. See Hill, *J. Chem. Ed.* **1948**, *25*, p. 347 http://dx.doi.org/10.1021/ed025p347

3.4 Lecture 20: Chemical reactions and equilibria

3.4.1 Standard states

1. Translational partition function depends on concentration N/V
2. "Standard state" corresponds to some standard choice for N/V, $c^\
3. For ideal gas, related to pressure by $P^\circ = c^\circ k_B T$

3.4.2 Chemical reaction $A \to B$

1. Reaction entropy $\Delta S^\circ(T) = S^\circ_{\mathrm{B}}(T) - S^\circ_{\mathrm{A}}(T)$
2. Reaction energy $\Delta U^\circ(T) = U^\circ_{\mathrm{B}}(T) - U^\circ_{\mathrm{A}}(T) + \Delta E(0)$
3. Equilibrium condition—equate chemical potentials, $\mu_A(N,V,T) = \mu_B(N,V,T)$
4. Equilibrium constant—evaluate from partition functions directly or indirectly from thermodynamic potentials

Table 15: Statistical Thermodynamics of an Ideal Gas

Translational DOFs 3-D particle in a box model

$$\theta_{\text{trans}} = \frac{\pi^2\hbar^2}{2mL^2k_B},\ \Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2}$$

For $T >> \Theta_{\text{trans}}$, $\Lambda << L$, $q_{\text{trans}} = V/\Lambda^3$ (essentially always true)

$$U_{\text{trans}} = \frac{3}{2}RT \quad C_{\text{v,trans}} = \frac{3}{2}R \quad S^\circ_{\text{trans}} = R\ln\left(\frac{e^{5/2}V^\circ}{N^\circ\Lambda^3}\right) = R\ln\left(\frac{e^{5/2}k_BT}{P^\circ\Lambda^3}\right)$$

Rotational DOFs Rigid rotor model

Linear molecule $\theta_{\text{rot}} = hcB/k_B$

$$q_{\text{rot}} = \frac{1}{\sigma}\sum_{l=0}^{\infty}(2l+1)e^{-l(l+1)\theta_{\text{rot}}/T}, \approx \frac{1}{\sigma}\frac{T}{\theta_{\text{rot}}}, \quad T >> \theta_{\text{rot}} \quad \sigma = \begin{cases} 1, & \text{unsymmetric} \\ 2, & \text{symmetric} \end{cases}$$

$$U_{\text{rot}} = RT \quad C_{\text{v,rot}} = R \quad S^\circ_{\text{rot}} = R(1 - \ln(\sigma\theta_{\text{rot}}/T))$$

Non-linear molecule $\theta_{\text{rot},\alpha} = hcB_\alpha/k_B$

$$q_{\text{rot}} \approx \frac{1}{\sigma}\left(\frac{\pi T^3}{\theta_{\text{rot},\alpha}\theta_{\text{rot},\beta}\theta_{\text{rot},\gamma}}\right)^{1/2}, \quad T >> \theta_{\text{rot},\alpha,\beta,\gamma} \quad \sigma = \text{rotational symmetry number}$$

$$U_{\text{rot}} = \frac{3}{2}RT \quad C_{\text{v,rot}} = \frac{3}{2}R \quad S^\circ_{\text{rot}} = \frac{R}{2}\left(3 - \ln\frac{\sigma\theta_{\text{rot},\alpha}\theta_{\text{rot},\beta}\theta_{\text{rot},\gamma}}{\pi T^3}\right)$$

Vibrational DOFs Harmonic oscillator model

Single harmonic mode $\theta_{\text{vib}} = h\nu/k_B$

$$q_{\text{vib}} = \frac{1}{1 - e^{-\theta_{\text{vib}}/T}} \approx \frac{T}{\theta_{\text{vib}}}, \quad T >> \theta_{\text{vib}}$$

$$U_{\text{vib}} = R\frac{\theta_{\text{vib}}}{e^{\theta_{\text{vib}}/T} - 1} \quad C_{\text{v,vib}} = R\left(\frac{\theta_{\text{vib}}}{T}\frac{e^{\theta_{\text{vib}}/2T}}{e^{\theta_{\text{vib}}/T} - 1}\right)^2 \quad S^\circ_{\text{vib},i} = R\left(\frac{\theta_{\text{vib}}/T}{e^{\theta_{\text{vib}}/T} - 1} - \ln(1 - e^{-\theta_{\text{vib}}/T})\right)$$

Multiple harmonic modes $\theta_{\text{vib},i} = h\nu_i/k_B$

$$q_{\text{vib}} = \prod_i \frac{1}{1 - e^{-\theta_{\text{vib},i}/T}}$$

$$U_{\text{vib}} = R\sum_i \frac{\theta_{\text{vib},i}}{e^{\theta_{\text{vib},i}/T} - 1} \quad C_{\text{v,vib}} = R\sum_i\left(\frac{\theta_{\text{vib},i}}{T}\frac{e^{\theta_{\text{vib},i}/2T}}{e^{\theta_{\text{vib},i}/T} - 1}\right)^2 \quad S^\circ_{\text{vib},i} = R\left(\frac{\theta_{\text{vib},i}/T}{e^{\theta_{\text{vib},i}/T} - 1} - \ln(1 - e^{-\theta_{\text{vib},i}/T})\right)$$

Electronic DOFs $q_{\text{elec}} = \text{spin multiplicity}$

3.4.3 Le'Chatlier's principle

1. Response to temperature: Boltzmann distribution favors higher energy things as T increases
2. Response to volume chance: particle-in-a-box states increasingly favor side with more molecules as volume increases

3.5 Lecture 21: Chemical kinetics

3.5.1 Kinetics and reaction rates

1. Rate: number per unit time per unit something

3.5.2 Empirical chemical kinetics

1. Rate laws, rate orders, and rate constants
2. Arrhenius expression, $k = Ae^{-E_a/k_BT}$

3.5.3 Reaction mechanisms

1. Elementary steps and molecularity
2. Collision theory—overpredicts rates

3.5.4 Transition state theory (TST)

1. Existence of reaction coordinate (PES)
2. Existence of dividing surface
3. Equilibrium between reactants and "transition state"
4. Harmonic approximation for transition state

3.5.5 Locating transition states computationally

3.5.6 Thermodynamic connection

3.5.7 Diffusion-controlled reactions

1. Intermediate complex
2. Steady-state approximation
3. Diffusion-controlled limit ($k_D = 4\pi(r_A + r_B)D_{AB}$)
4. Reaction-controlled limit ($k_{app} = (k_D/k_{-D})k_r$)

3.6 Lecture 22: Conclusion

1. Do you think about the burning lighter any differently now?

Table 16: Equilibrium and Rate Constants

Equilibrium Constants $a\ \mathrm{A} + b\ \mathrm{B} \rightleftharpoons c\ \mathrm{C} + d\ \mathrm{D}$

$$\begin{aligned}
K_{eq}(T) &= e^{\Delta S^\circ(T,V)/k_B} e^{-\Delta H^\circ(T,V)/k_B T} \\
K_c(T) &= \left(\frac{1}{c^\circ}\right)^{\nu_c+\nu_d-\nu_a-\nu_b} \frac{(q_c/V)^{\nu_c}(q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a}(q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta} \\
K_p(T) &= \left(\frac{k_B T}{P^\circ}\right)^{\nu_c+\nu_d-\nu_a-\nu_b} \frac{(q_c/V)^{\nu_c}(q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a}(q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta}
\end{aligned}$$

Unimolecular Reaction $[A] \rightleftharpoons [\mathrm{A}]^\ddagger \to C$

$$k(T) = \nu^\ddagger \bar{K}^\ddagger = \frac{k_B T}{h} \frac{\bar{q}_\ddagger(T)/V}{q_A(T)/V} e^{-\Delta E^\ddagger(0)\beta}$$

$$E_a = \Delta H^{\circ\ddagger} + k_B T \quad A = e^1 \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}}$$

Bimolecular Reaction $\mathrm{A} + \mathrm{B} \rightleftharpoons [\mathrm{AB}]^\ddagger \to \mathrm{C}$

$$k(T) = \nu^\ddagger \bar{K}^\ddagger = \frac{k_B T}{h} \frac{q_\ddagger(T)/V}{(q_A(T)/V)(q_B(T)/V)} \left(\frac{1}{c^\circ}\right)^{-1} e^{-\Delta E^\ddagger(0)\beta}$$

$$E_a = \Delta H^{\circ\ddagger} + 2k_B T \quad A = e^2 \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}}$$

