

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

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

## 1 The Classical Foundations

### 1.1 Lecture 0: Introduction

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

### 1.2 Lecture 1: Basic statistics

#### 1.2.1 Discrete probability distributions—Coin flip

1. Example of Bernoulli trial,  $2^n$  possible outcomes from  $n$  flips
2. Number of ways to get  $i$  heads in  $n$  flips,  ${}_nC_i = n!/i!(n-i)!$
3. Probability of  $i$  heads  $P_i \propto {}_nC_i$
4. Normalized probability,  $\tilde{P}_i = P_i / \sum_i P_i = {}_nC_i / 2^n$
5. Expectation value  $\langle i \rangle = \sum_i i \tilde{P}_i$

**1.2.2 Continuous distributions—temperature**

1. Probability density  $P(x)$  has units  $1/x$
2. Normalized  $\tilde{P}(x) = P(x) / \int P(x) dx$
3. (Unitless) probability  $a < x < b = \int_a^b \tilde{P}(x) dx$
4. Expectation value  $\langle f(x) \rangle = \int f(x) \tilde{P}(x) dx$
5. Mean  $= \langle x \rangle$
6. Mean squared  $= \langle x^2 \rangle$
7. Variance  $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$
8. Standard deviation  $\Delta x = \sigma$

**1.2.3 Boltzmann distribution**

1.  $P(E) \propto e^{-E/k_B T}$ , in some sense the definition of temperature (Figure 1)
2. Energy and its units
3. Absolute temperature and its units
4.  $k_B T$  as an energy scale, 0.026 eV at 298 K
5. Equipartition – energy freely exchanged within and between all degrees of freedom

**1.2.4 Boltzmann distribution: Gravity example**

1.  $E(h) = mgh$ , linear, continuous energy spectrum
2. Exponential distribution

$$P(h) = \frac{1}{\int_0^\infty \exp(-mgh/k_B T) dh} \exp\left(\frac{-mgh}{k_B T}\right) = \frac{1}{k_B T} \exp\left(\frac{-mgh}{k_B T}\right)$$

3. molecule vs car in a gravitational field (Table 2)
4. Implies exponential decrease in gas density with altitude
5. Barometric law for gases,  $P = P_0 e^{-mgh/k_B T}$

**1.2.5 Boltzmann distribution: Kinetic energy in 1-D example**

1.  $KE = \frac{1}{2} m v_x^2$
2.  $P_{1D}(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m|v_x|^2}{2k_B T}\right)$
3. Gaussian distribution, mean  $\mu$ , variance  $\sigma^2$

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

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

5. Molecule vs car again

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

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

### 1.3 Lecture 2: Kinetic theory of gases

#### 1. Postulates

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

#### 2. Maxwell-Boltzmann distribution of molecular speeds (Figure 3)

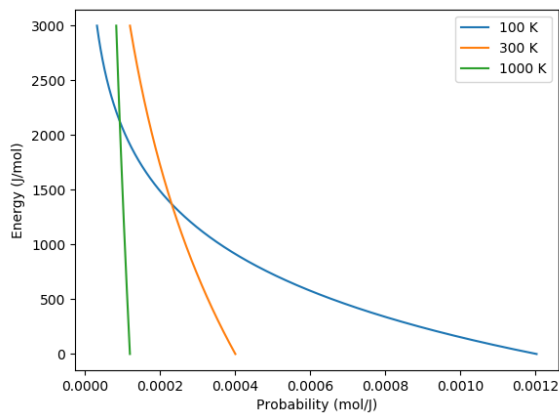
- (a) Speed  $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$
- (b)  $P_{MB}(v)dv = P_{1D}(v_x)P_{1D}(v_y)P_{1D}(v_z) * \text{degeneracy}(v)dv$  (Table 4)
- (c) mean speeds  $\langle v \rangle = \int_{-\infty}^{\infty} v P_{MB}(v)dv \propto \sqrt{T}$
- (d) mean kinetic energy  $\langle U \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}RT$
- (e) heat capacity  $C_v = dU/dT = \frac{3}{2}R$

#### 3. Flux and pressure

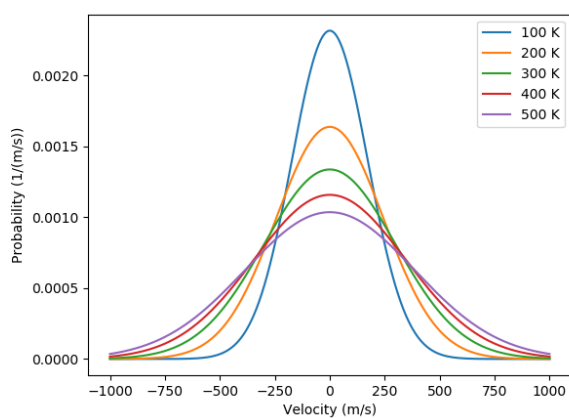
- (a) Velocity flux  $j(v_x)dv_x = v_x \frac{N}{V} P(v_x)dv_x$ , molecules /area /time / $v_x$

**Table 3:** Energy conversions and correspondences

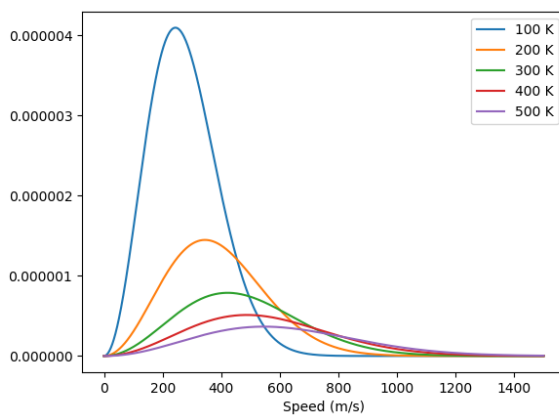
	J	eV	Hartree	$\text{kJ mol}^{-1}$	$\text{cm}^{-1}$
1 J =	1	$6.2415 \times 10^{18}$	$2.2937 \times 10^{17}$	$6.0221 \times 10^{20}$	$5.0340 \times 10^{22}$
1 eV =	$1.6022 \times 10^{-19}$	1	0.036748	96.485	8065.5
1 Ha =	$4.3598 \times 10^{-18}$	27.212	1	2625.6	219474.6
1 $\text{kJ mol}^{-1}$ =	$1.6605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



**Figure 1:** Boltzmann distribution at various temperatures

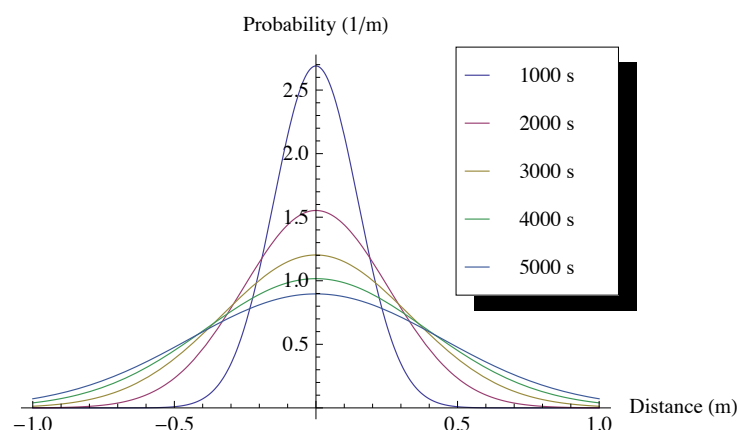


**Figure 2:** One-dimensional (Gaussian) velocities of  $N_2$  gas



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

- (b) Wall collisions,  $J_w$ , total collisions /area /time
- (c) Momentum exchange, pressure, ideal gas law
- 4. Collisions and mean free path
  - (a) Collision cross section  $\sigma = \pi d^2$ , size of molecule
  - (b) Molecular collisions,  $z$  per molecule and  $z_{AA}$  per volume
  - (c) Mean free path,  $\lambda$ , mean distance between collisions
- 5. See Table 4 for important equations



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

### 1.4 Lecture 3: Transport

1. Effusion and Graham's law, effusion rate  $\propto MW^{-1/2}$
2. Fick's first law: net flux proportional to concentration gradient
  - (a)  $j_x = -D \frac{dc}{dx}$
  - (b) Self-diffusion constant,  $D = \frac{1}{3} \lambda \langle v \rangle$
3. Knudsen diffusion,  $D = \frac{1}{3} l \langle v \rangle$
4. Fick's second law: time evolution of concentration gradient
  - (a) Continuity with no advection:  $\frac{\partial c}{\partial t} = -\nabla \cdot \vec{j} + \text{gen}$
  - (b) One-dimension:  $\frac{dc}{dt} = D \frac{d^2 c}{dx^2}$
  - (c) Diffusion has Gaussian probability distribution:  $c(x, t)/c_0 = [2\sqrt{\pi Dt}]^{-1} \exp(-x^2/4Dt)$
5. Seeing is believing—Brownian motion
  - (a) Seemingly random motion of large particles (“dust”) due to “kicks” from invisible molecules
  - (b) Einstein receives Nobel Prize for showing:
    - i. Motion follows same Gaussian diffusion behavior

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

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

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

- ii. From steady-state arguments in a field, diffusion constant is ratio of Boltzmann energy,  $k_B T$ , to mobility
- iii. Mobility inversely related to viscosity
- (c) Stokes-Einstein equation
- (d) Allows measurement of Avogadro's number, final proof of kinetic theory
- (e) Similar model for diffusion of liquid molecules, slip boundary
- 6. Random walk model of diffusion
  - (a) Binomial distribution
  - (b) Large  $N$  and Stirling approximation
  - (c) Einstein-Smoluchowski relation

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

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

#### 2.1.1 Properties of waves

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

#### 2.1.2 Blackbody radiation

1. Hohlraum spectrum (like the sun) empirically observed to obey:
  - (a) Stefan-Boltzmann law, total irradiance
  - (b) Wien's displacement law
2. Rayleigh-Jeans predicts spectrum using classical physics
  - (a) standing waves + classical oscillators  $\rightarrow$  ultraviolet catastrophe

### 3. Planck model

- (a) Energy spectrum of oscillators are *quantized*,  $\epsilon_\nu = nh\nu$
- (b) Expected energy of a quantized oscillator,  $\langle \epsilon \rangle_\nu = h\nu / (e^{h\nu/k_B T} - 1)$
- (c) Correctly reproduces Stefan-Boltzmann and Wien Laws!

### 2.1.3 Heat capacities of solids

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

### 2.1.4 Photoelectric effect

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

### 2.1.5 Compton effect

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

### 2.1.6 Wave-particle duality

### 2.1.7 Rutherford, planetary model of atom

- 1. Inconsistent with Maxwell's equations

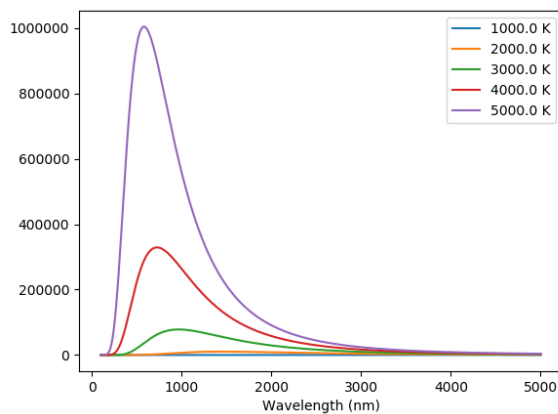
### 2.1.8 Bohr model of H atom

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

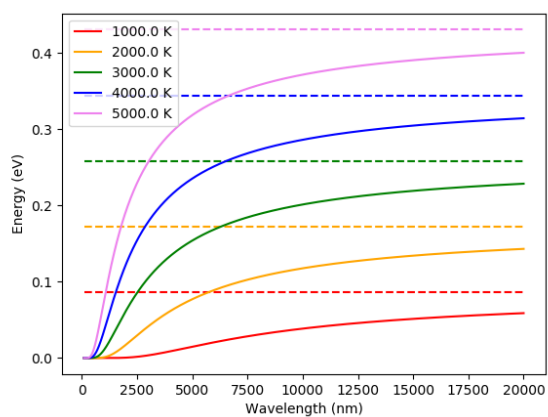
### 2.1.9 de Broglie relation

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





**Figure 5:** Blackbody irradiance



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

**Table 6:** The new physics

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

## 2.2 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*
  - (b) Have eigenvectors and real eigenvalues,  $\hat{O}\psi_i = o\psi_i$
  - (c) Are orthogonal,  $\langle\psi_i|\psi_j\rangle = \delta_{ij}$
  - (d) Always observe an eigenvalue when making an observation
3. Expectation values
4. Energy-invariant wavefunctions given by Schrödinger equation
5. Uncertainty principle

### 2.2.4 Particle in a box illustrations

## 2.3 Lecture 6: Particle in a box model

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

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

### 2.3.3 One-dimensional QM solutions

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

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

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

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

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

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

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

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

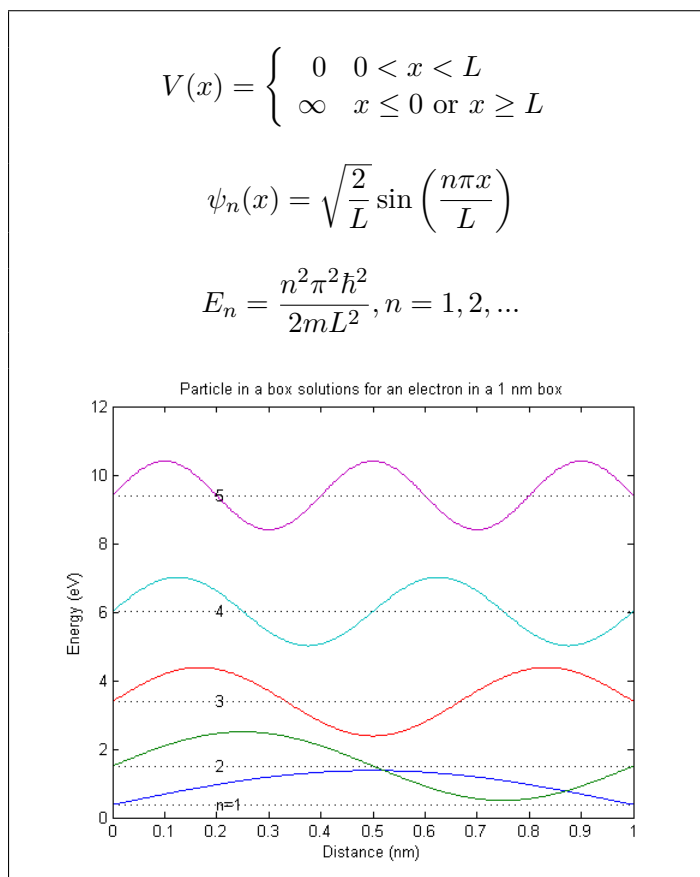
**Postulate 4:** The energy-invariant states of a system are solutions of the equation

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

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

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

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

**Table 8:** Particle-in-a-box model

### 2.3.4 Finite walls and tunneling

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

### 2.3.5 Multiple dimensions

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

**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. Schrödinger equation and boundary conditions
2. Solutions like P-I-A-B + tunneling at boundaries
3. Zero-point energy and uniform energy ladder
4. Parity operator and even/odd symmetry:  $\langle x \rangle = 0$
5. Recursion relations:  $\langle x^2 \rangle = \alpha^2(v + 1/2)$ ,  $\langle V(x) \rangle = \frac{1}{2}h\nu(v + \frac{1}{2})$
6. Virial theorem
7. Classical turning point and tunneling
8. 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

**2.5 Lecture 8: Rigid Rotor****2.5.1 Classical rigid rotor**

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

**Table 9:** Harmonic oscillator model

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

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

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

Hermite polynomials

$$H_0(y) = 1$$

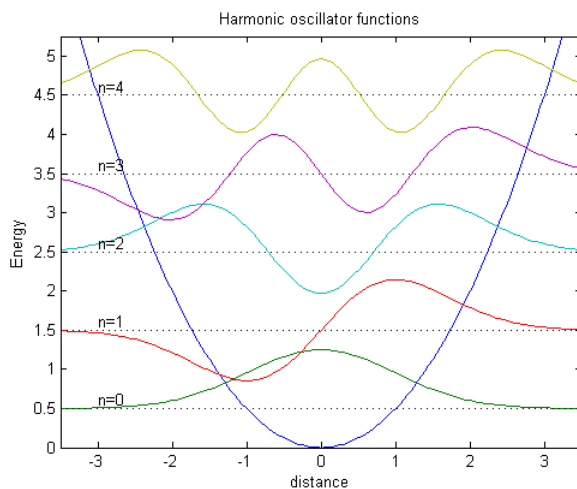
$$H_1(y) = 2y$$

$$H_2(y) = 4y^2 - 2$$

$$H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

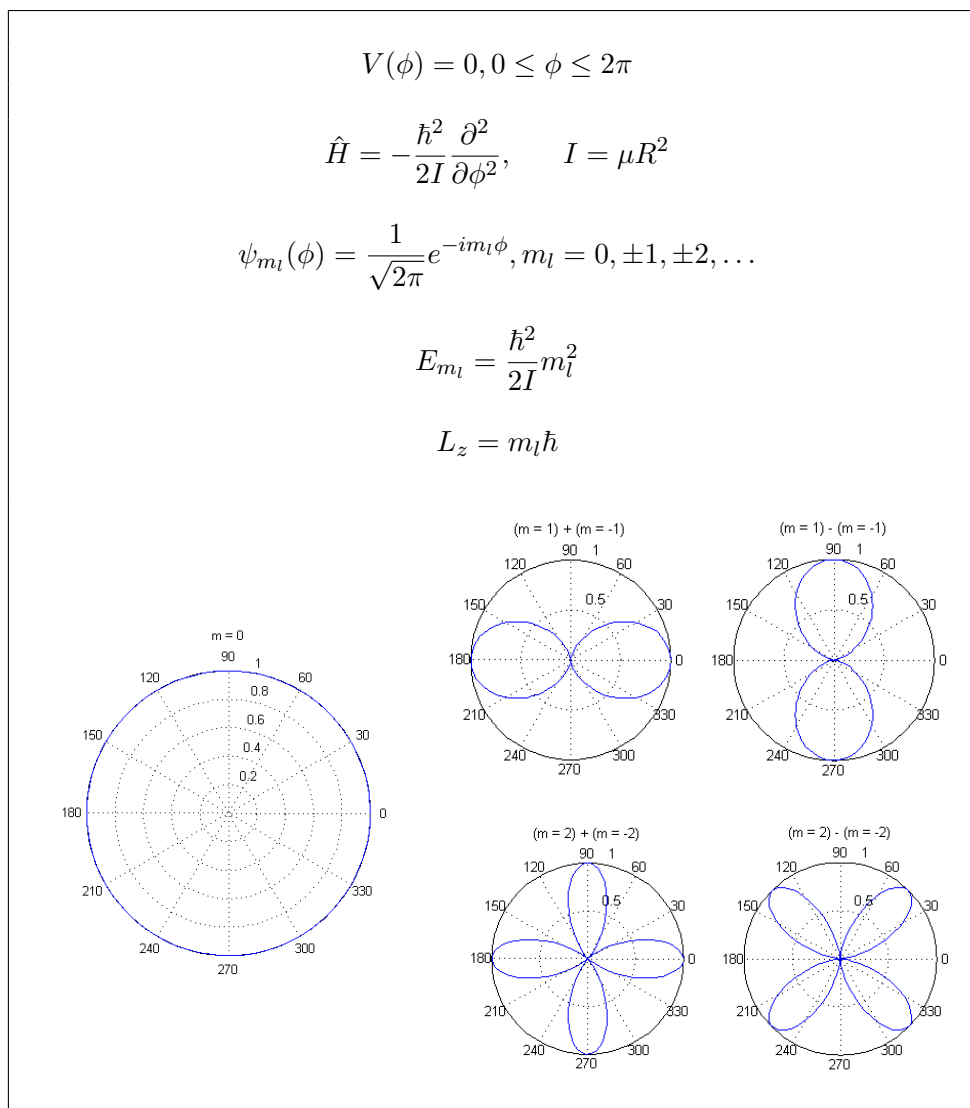
$$E_v = (v + \frac{1}{2})h\nu, v = 0, 1, 2, \dots$$



### 2.5.2 Quantum rotor in a plane

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

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



### 2.5.3 Quantum rotor in 3-D

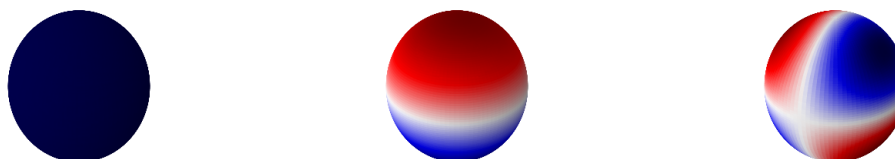
1. Angular momentum and kinetic energy operators in spherical coordinates



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

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

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



**Figure 7:** Pythonic  $s$  ( $l = 0$ ),  $p$  ( $l = 1$ ), and  $d$  ( $l = 2$ ) spherical harmonics. Color scale from red to white to blue corresponds to positive to zero to negative sign of wavefunction.

### 2.5.4 Particle angular momentum

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

## 2.6 Lecture 9: Spectroscopy

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

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

### 2.6.2 Einstein coefficients

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

### 2.6.3 Transition probability

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

## 2.7 Lecture 10: Vibrational and rotational spectroscopy

### 2.7.1 Diatomic rotational spectroscopy

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

### 2.7.2 Diatomic vibrational transitions

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

### 2.7.3 Raman spectroscopy

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

### 2.7.4 Anharmonicity, Morse potential

### 2.7.5 Vibration-rotation spectroscopy

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

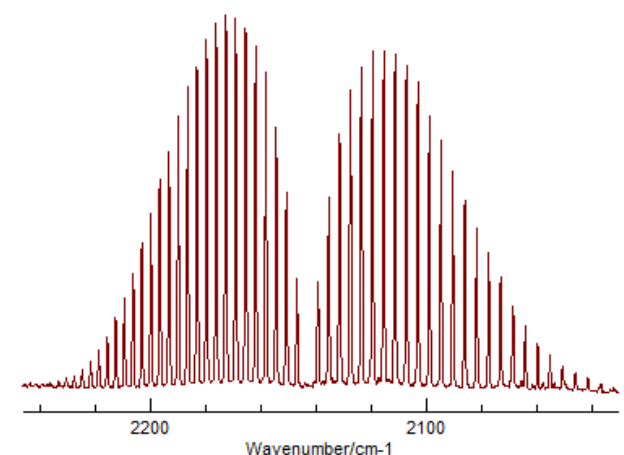


Figure 8: Rovibrational spectrum of carbon monoxide

**2.7.6 Polyatomic vibrational spectroscopy**

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

**2.7.7 Polyatomic rotational spectroscopy**

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

**2.8 Lecture 11: Hydrogen atom****2.8.1 Schrödinger equation**

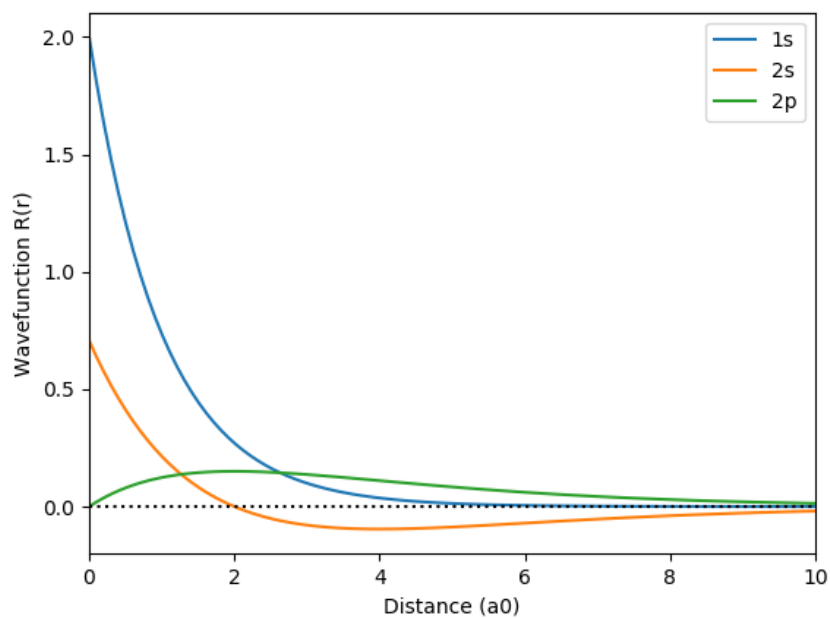
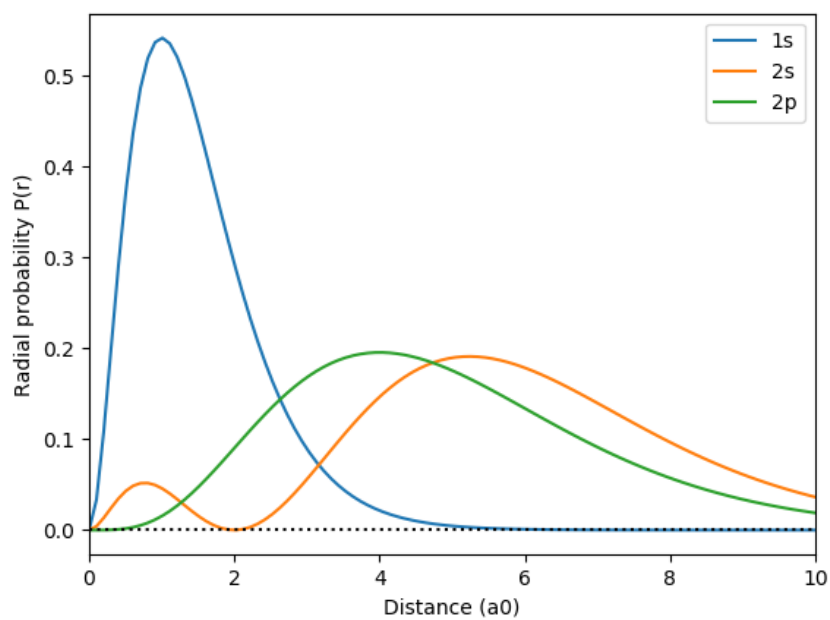
1. Spherical coordinates and separation of variables
2. Coulomb potential  $v_{\text{Coulomb}}(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$
3. Centripetal potential  $v = \hbar^2 \frac{l(l+1)}{2\mu r^2}$

**2.8.2 Solutions**

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

**Table 12:** Hydrogen atom

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

**Figure 9:** H atom radial wavefunctions**Figure 10:** H atom radial probability

### 2.8.3 Variational principle

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

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

1. Optimize wavefunction with respect to variational parameter

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

## 2.9 Lecture 12: Many-electron atoms

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

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

### 2.9.2 Qualitative solutions

1.  $\psi_i$  look like H atom orbitals, labeled by same quantum numbers
2. *Aufbau principle*: “Build-up” electron configuration by adding electrons into H-atom-like orbitals, from bottom up
3. *Pauli exclusion principle*: Every electron in atom must have a unique set of quantum numbers, so only two per orbital (with opposite spin)
4. *Pauli exclusion principle (formally)*: The wavefunction of a multi-particle system must be anti-symmetric to coordinate exchange if the particles are fermions, and symmetric to coordinate exchange if the particles are bosons
5. *Hund’s rule*: Electrons in degenerate orbitals prefer to be spin-aligned. Configuration with highest *spin multiplicity* is the most preferred

### 2.9.3 Structure of the periodic table

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

### 2.9.4 Quantitative solutions

1. Schrödinger equation

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

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

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

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

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

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

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

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

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

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

### 2.9.5 Electron-electron interactions

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

### 2.9.6 Popular models

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



## 2.9.7 DFT calculations on atoms

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

## 2.10 Lecture 13: Molecular orbital theory of molecules

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

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

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

$$\hat{f}\psi = \left\{ \hat{h} + \hat{v}_{\text{Coul}}[\psi_i] + \hat{v}_{\text{ex}}[\psi_i] + \hat{v}_{\text{corr}}[\psi_i] \right\} \psi = \epsilon\psi \quad (2)$$

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

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

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

1. “Bonding” orbital,  $\sigma_g(\mathbf{r}) = 1s_A + 1s_B$
2. “Anti-bonding” orbital,  $\sigma_u(\mathbf{r}) = 1s_A - 1s_B$
3. Interaction scales with “overlap”  $S = \langle 1s_A | 1s_B \rangle$
4. Normalize

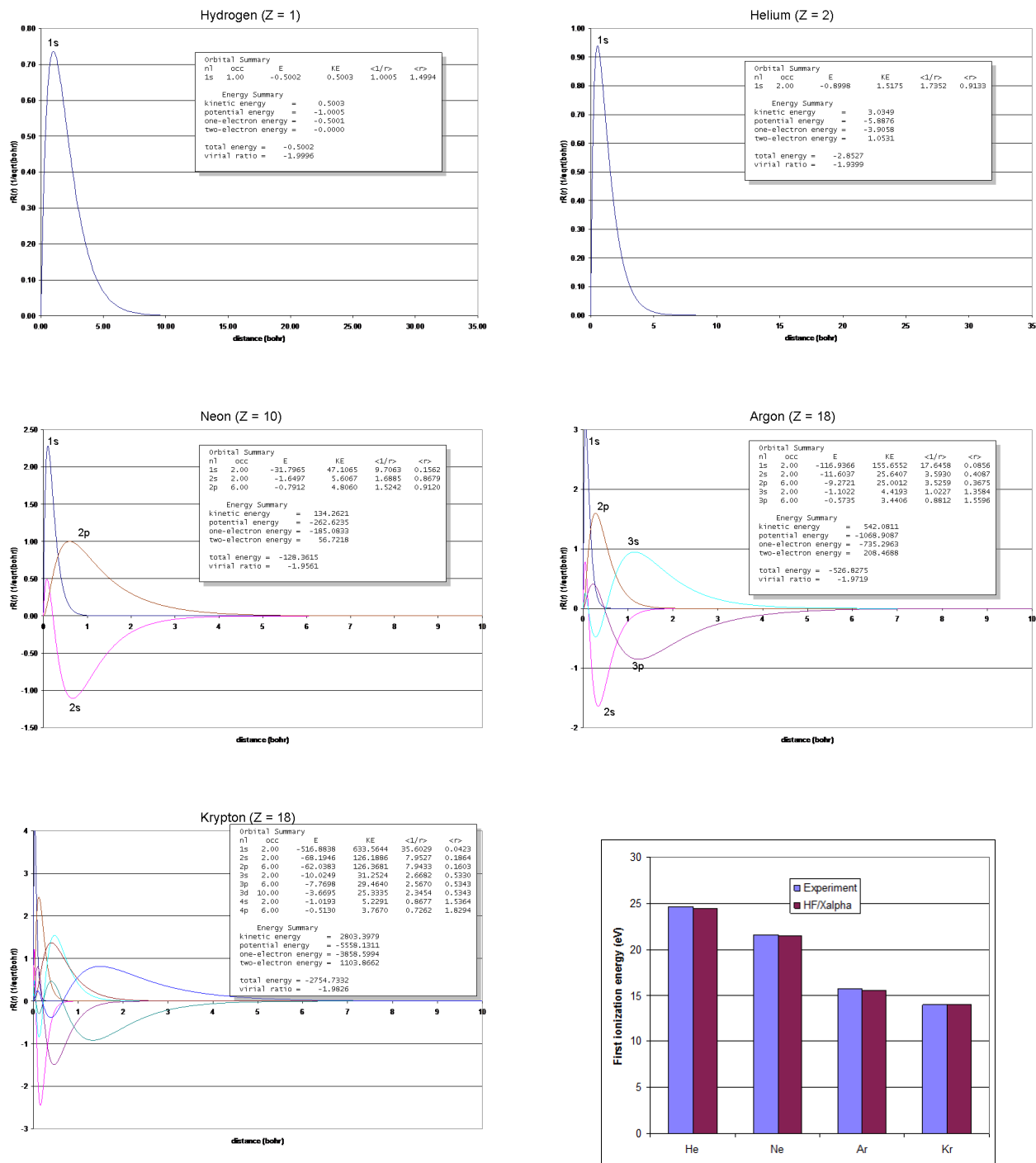
$$\sigma_g = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \quad \sigma_u = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B)$$

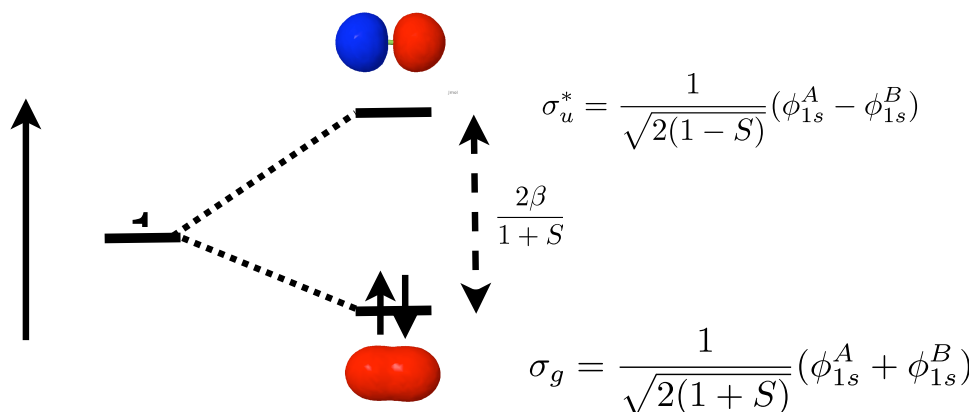
5. Energy expectation value

$$\begin{aligned} \epsilon_g = \langle \sigma_g | \hat{f} | \sigma_g \rangle &= \frac{1}{2(1+S)} \left\{ \langle 1s_A | \hat{f} | 1s_A \rangle + \langle 1s_B | \hat{f} | 1s_B \rangle + 2\langle 1s_A | \hat{f} | 1s_B \rangle \right\} \\ &= \frac{1}{1+S} (F_{AA} + F_{AB}) \\ \epsilon_u = \langle \sigma_u | \hat{f} | \sigma_u \rangle &= \frac{1}{2(1-S)} \left\{ \langle 1s_A | \hat{f} | 1s_A \rangle + \langle 1s_B | \hat{f} | 1s_B \rangle - 2\langle 1s_A | \hat{f} | 1s_B \rangle \right\} \\ &= \frac{1}{1-S} (F_{AA} - F_{AB}) \end{aligned}$$

6. Matrix elements

$$\begin{aligned} F_{AA} = F_{BB} &\approx \epsilon_{1s} = \alpha \\ F_{AB} = F_{BA} &= \beta \\ \alpha < \beta < 0 &\text{ typically} \end{aligned}$$

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



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

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

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

8. Makes clear that bonding stabilization  $<$  anti-bonding destabilization
9. Ground configuration =  $\sigma_g^2$
10. Bond order =  $\frac{1}{2}(n - n^*)$

### 2.10.3 Secular equations

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

$$\psi_{\text{MO}} = \sum_a c_a \phi_a(\mathbf{r}) \quad (3)$$

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

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

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

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

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

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

1. Set-up and solve secular matrix

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

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

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

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

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

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

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

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

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

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

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

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

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

---

```

1 from sympy import *
2 initprinting(useunicode=True)
3
4 print(6. Cyclobutadiene examplen)
5 alpha,beta = symbols(alpha beta)
6
7 M = Matrix([[alpha, beta, 0 , beta],[beta, alpha, beta, 0],[0,beta,alpha,beta],[beta,0,beta,alpha]])
8
9 print(M)
10 M = Matrix([[alpha,beta],[beta,alpha]])
11
12 eigs = M.eigenvects()
13
14 print(nEnergy state, degeneracy)
15 for state in [0, 1, 2]:
16     print(0    in.format(eigs[state][0],eigs[state][1]))
17
18 print(nEigenvectors)
19 for state in [0, 1, 2]:
20     print(eigs[state][2])

```

---

1. Cyclobutadiene example

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

Energy state, degeneracy

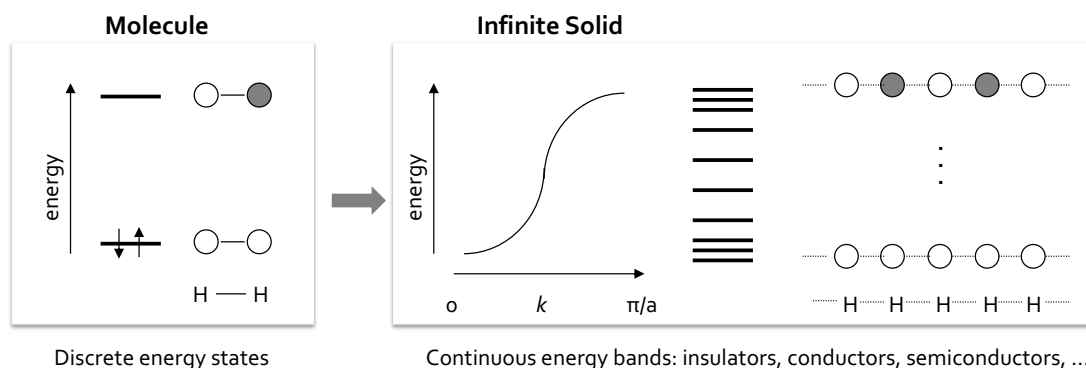
alpha 2

alpha - 2\*beta 1

alpha + 2\*beta 1

### 2.10.9 Band structure of solids

1. Discrete molecular orbitals transform into continuous bands
2. Results in rich range of physical and chemical properties



## 2.11 Lecture 14: Computational chemistry

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

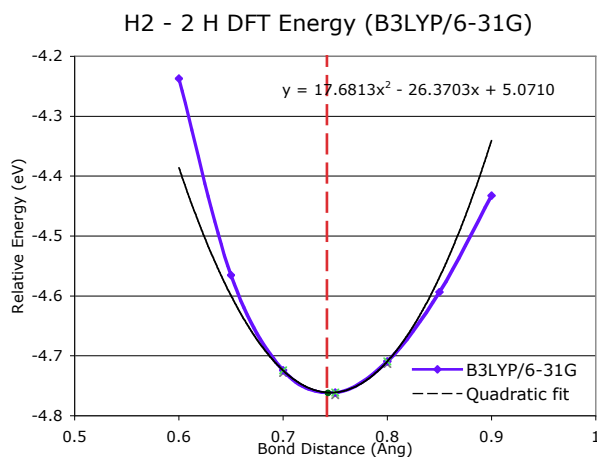
#### 2.11.2 Have to specify:

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

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

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

### 2.11.4 H<sub>2</sub> example



#### Bond length

H-H exp't:	0.742 Å
B3LYP opt:	0.743

#### Bond energy

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

#### Vibrational frequencies

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

### 2.11.5 Polyatomic molecules

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

### 2.12 Lecture 15: Electronic spectroscopy

### 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 machinery 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  $\epsilon$
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
  - (a) Energy of a closed system is conserved (first law!)
  - (b) Degeneracy of total system is always  $\geq$  degeneracy of the starting parts!
  - (c) Boltzmann's tombstone,  $S = k_B \ln \Omega$
  - (d) 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  $\Omega$  will be much more probable than all others
4. What value of  $U_1$  and  $U_2 = U - U_1$  maximizes  $\Omega$ ?

$$\left( \frac{\partial \ln \Omega_1}{\partial U_1} \right)_N = \left( \frac{\partial \ln \Omega_2}{\partial U_2} \right)_N$$

$$\left( \frac{\partial S_1}{\partial U_1} \right)_N = \left( \frac{\partial S_2}{\partial U_2} \right)_N$$

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 ( $\mu_i$ ) 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:

$$S(U) = -k_B (x \ln x + (1-x) \ln(1-x)), \text{ where } x = q/N = U/N\epsilon$$

3. Temperature is derivative of entropy wrt energy yields

$$U(T) = \frac{N\epsilon}{1 + e^{\epsilon/k_B T}}$$

4.  $T \rightarrow 0, U \rightarrow 0, S \rightarrow 0$ , minimum disorder
5.  $T \rightarrow \infty, U \rightarrow N\epsilon/2, S \rightarrow k_B \ln 2$ , 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,  $Q(T, V) = \sum_j e^{-U_j \beta}$

1. **Partition function counts the number of states accessible to a system at a given  $T$  and  $V$**

### 3.2.2 Energy factoring (sidebar)

1. If system is large, how to determine its 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:

$$U_j = \epsilon_j(1) + \epsilon_j(2) + \dots + \epsilon_j(N) \quad (4)$$

$$Q(N, V, T) = \sum_j e^{-U_j \beta} \quad (5)$$

$$= \sum_j e^{-(\epsilon_j(1) + \epsilon_j(2) + \dots + \epsilon_j(N))\beta} \quad (6)$$

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

$$Q(N, V, T) = \left( \sum_j e^{-\epsilon_j(1)\beta} \right) \dots \left( \sum_j e^{-\epsilon_j(N)\beta} \right) \quad (7)$$

$$= q(1) \dots q(N) \quad (8)$$

$$\text{Assuming all the elements are the same:} \quad (9)$$

$$= q^N \quad (10)$$

$$q = \sum_j e^{-\epsilon_j \beta} : \text{molecular partition function} \quad (11)$$

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:

$$Q(N, V, T) = q^N / N! \quad (12)$$

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.  $q(V, T)$  counts states available to a single element of a system, like a molecule in a gas or in a solid
2. Distinguishable (e.g., in a solid):  $Q(N, V, T) = q(V, T)^N$
3. 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  $U(T)$

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

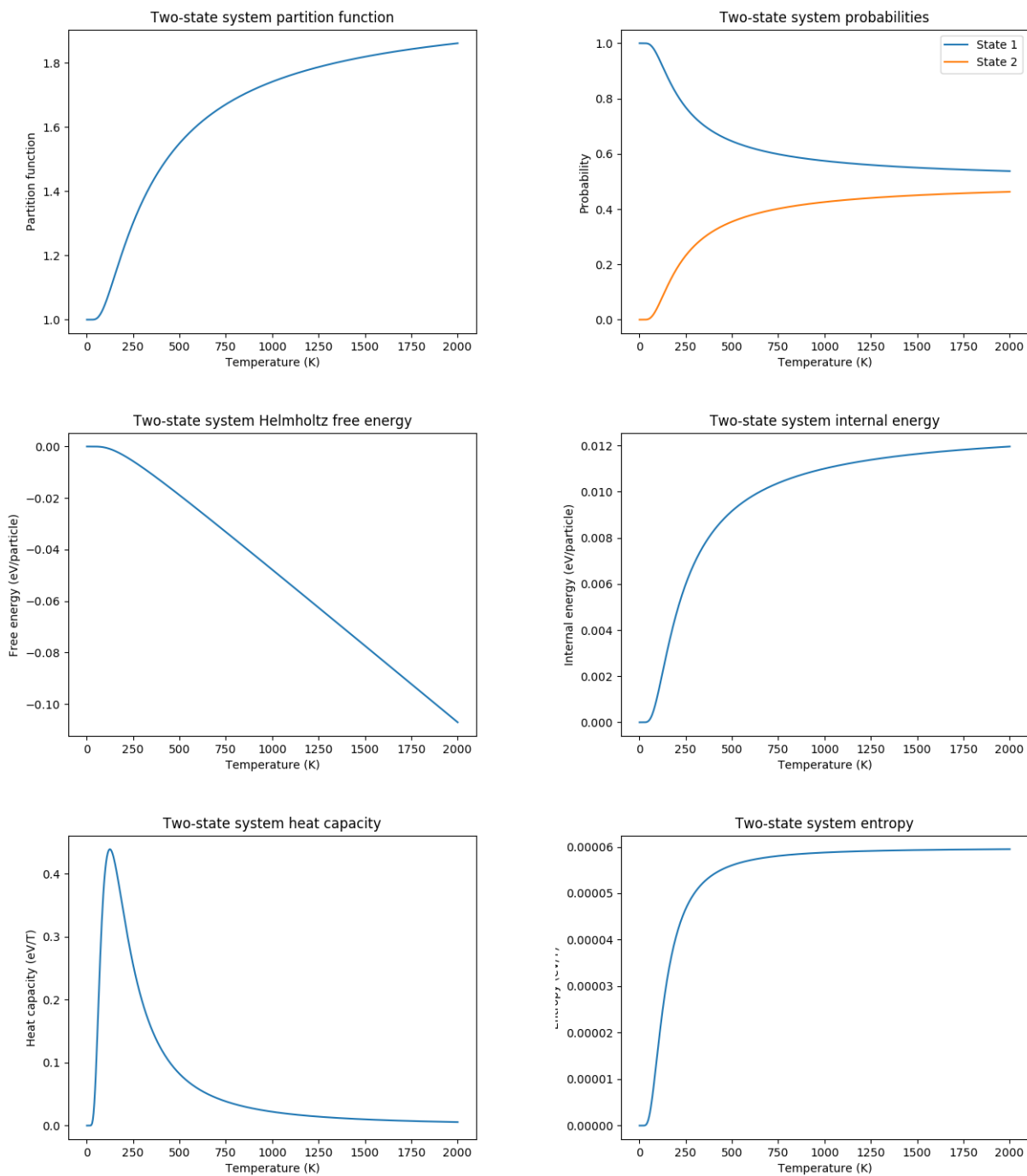
4. Heat capacity  $C_v$ 
  - (a) Minimum when change in states with  $T$  is small
  - (b) Maximize when change in states with  $T$  is large
5. Helmholtz energy,  $A = -\ln q / \beta$ , decreasing function of  $T$
6. Entropy

### 3.2.5 Thermodynamic functions in canonical ensemble

## 3.3 Lecture 19: Molecular Partition Functions

### 3.3.1 Ideal gas of molecules

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

**Table 14:** Two-state system thermodynamics

**Table 15:** Equations of the Canonical ( $NVT$ ) Ensemble

$\beta = 1/k_B T$	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	$\ln Q$	$N \ln q$	$N \ln q - \ln N!$ $\approx N(\ln Q - \ln N + 1)$
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 ( $P$ )	$\frac{1}{\beta} \left( \frac{\partial \ln Q}{\partial V} \right)_{N\beta}$	$\frac{N}{\beta} \left( \frac{\partial \ln q}{\partial V} \right)_\beta$	$\frac{N}{\beta} \left( \frac{\partial \ln q}{\partial V} \right)_\beta$
Entropy ( $S/k_B$ )	$\beta U + \ln Q$	$\beta U + N \ln q$	$\beta U + N (\ln(q/N) + 1)$
Chemical potential ( $\mu$ )	$-\frac{1}{\beta} \left( \frac{\partial \ln Q}{\partial N} \right)_{VT}$	$-\frac{\ln q}{\beta}$	$-\frac{\ln(q/N)}{\beta}$

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

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

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

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

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

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

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. recall energy states and degeneracies of rigid rotor
2.  $\Theta_{\text{rot}} = \hbar^2/2Ik_B$
3. “High” T  $q_{\text{rot}}(T) \approx \sigma\Theta_{\text{rot}}/T$

**3.3.4 Harmonic oscillator (vibrational states of a gas)**

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

**3.3.5 Electronic partition functions  $\rightarrow$  spin multiplicity****3.3.6 Many-particle molecule**

1. partition function is a product of all degrees of freedom

$$q(T, V) = q_{\text{trans}} \left( \prod_{i=1}^3 q_{\text{rot}}^{(i)} \right) \left( \prod_{i=1}^{3N-6} q_{\text{vib}}^{(i)} \right) q_{\text{elec}}$$

2. thermodynamic quantities are sums of all degrees of freedom

**3.3.7 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>

**Table 16:** Statistical Thermodynamics of an Ideal Gas**Translational DOFs** 3-D particle in a box model

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

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

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

**Rotational DOFs** Rigid rotor model

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

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

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

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

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

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

**Vibrational DOFs** Harmonic oscillator model

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

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

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

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

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

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

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

**Table 17:** Contributions to ideal gas thermodynamics

	Characteristic Energy (cm <sup>-1</sup> )	Characteristic Temperature (K)	States @ RT	
translational	$\frac{1}{2} \hbar^2 / 2mL^2 \approx 10^{-21}$	$10^{-21}$	$10^{30}$	classical limit
rotational	$\approx 1$	$\approx 1$	100's	semi-classical
vibrational	$\approx 1000$	$\approx 1000$	1	non-classical
electronic	$\approx 10,000$	$\approx 10,000$	1	non-classical

### 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,  $(N/V)^\circ = c^\circ$
3. Permits functions to be easily computed at other concentrations, e.g.

$$A(T, N/V) = A^\circ(T) + kT \ln((N/V)/(N/V)^\circ) = A^\circ(T) + kT \ln(c/c^\circ)$$

4. For ideal gas, related to pressure by  $P^\circ = c^\circ k_B T$

#### 3.4.2 Chemical reaction $A \rightarrow B$

1. Reaction entropy  $\Delta S^\circ(T) = S_B^\circ(T) - S_A^\circ(T)$
2. Reaction energy must capture difference in 0 K electronic energy

$$\Delta U^\circ(T) = U_B^\circ(T) - U_A^\circ(T) + \Delta E(0)$$

3. Equilibrium condition—equate chemical potentials

$$\begin{aligned} \mu_A(N, V, T) &= \mu_B(N, V, T) \\ E_A(0) - kT \ln(q_A/N_A) &= E_B(0) - kT \ln(q_B/N_B) \\ \frac{N_B}{N_A} = \frac{N_B/V}{N_A/V} &= \frac{q_B(T, V)/V}{q_A(T, V)/V} e^{-\Delta E(0)/kT} \end{aligned}$$

4. Equilibrium constant—specify standard state to eliminate volume dependence

$$\begin{aligned} q_A^\circ(T) &= q_A(T, V)/(Vc^\circ) \\ K_c(T) &= \frac{q_B^\circ(T)}{q_A^\circ(T)} e^{-\Delta E(0)/kT} \end{aligned}$$

#### 3.4.3 Le’Chatelier’s principle

1. Response to temperature: Boltzmann distribution favors higher energy things as  $T$  increases
2. Response to volume change: 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. Functions of  $T$ ,  $P$ , composition  $C_i$
3. differential vs integrated rate laws
4. Arrhenius expression,  $k = Ae^{-E_a/k_BT}$

#### 3.5.3 Reaction mechanisms

1. Elementary steps and molecularity
2. Collision theory
  - (a)  $\{A + B \rightarrow \text{products}\}$
  - (b) rate proportional to A/B collision frequency  $z_{AB}$  weighted by fraction of collisions with energy  $> E_a$

$$r = kC_AC_B, k = \left(\frac{8k_BT}{\pi\mu}\right) \sigma_{AB}N_{av}e^{-E_a/k_BT}$$

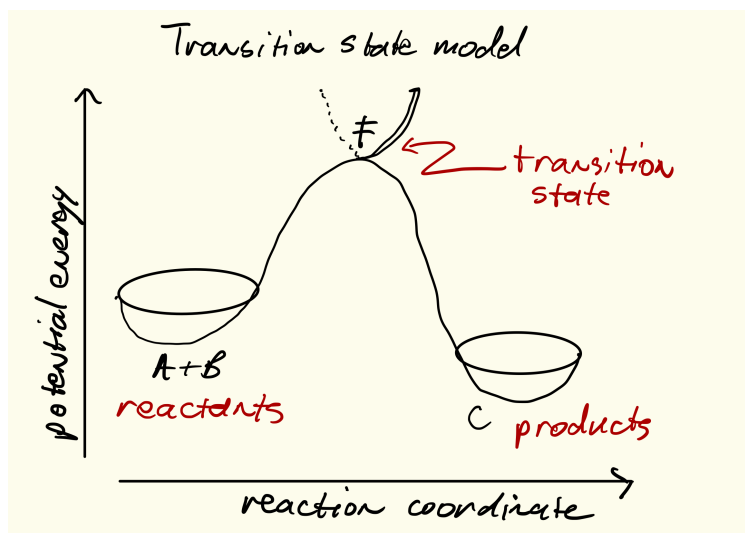
- (a) upper bound on real rates

#### 3.5.4 Transition state theory (TST)

1. Assumptions
  - (a) Existence of reaction coordinate (PES)
  - (b) Existence of dividing surface
  - (c) Equilibrium between reactants and “transition state”
  - (d) Harmonic approximation for transition state
2. rate proportional to concentration of “activated complex” over reactants times crossing frequency

$$r = kC_AC_B, k = \frac{k_BT}{h} \text{frac} q^\ddagger_{AQBE} e^{-\Delta E(0)/k_BT}$$





### 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 18:** Equilibrium and Rate Constants**Equilibrium Constants**  $a \text{ A} + b \text{ B} \rightleftharpoons c \text{ C} + d \text{ D}$ 

$$K_{eq}(T) = e^{\Delta S^\circ(T,V)/k_B} e^{-\Delta H^\circ(T,V)/k_B T}$$

$$K_c(T) = \left(\frac{1}{c^\circ}\right)^{\nu_c + \nu_d - \nu_a - \nu_b} \frac{(q_c/V)^{\nu_c} (q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a} (q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta}$$

$$K_p(T) = \left(\frac{k_B T}{P^\circ}\right)^{\nu_c + \nu_d - \nu_a - \nu_b} \frac{(q_c/V)^{\nu_c} (q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a} (q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta}$$

**Unimolecular Reaction**  $[A] \rightleftharpoons [A]^\ddagger \rightarrow C$ 

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

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

**Bimolecular Reaction**  $A + B \rightleftharpoons [AB]^\ddagger \rightarrow C$ 

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

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