Contents

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, ${}_nC_i = n!/i!(n-i)!$

Table 1: Key units in Physical Chemistry

N_{Av}:	6.02214×10^{23}	mol^{-1}		
1 amu:	1.6605×10^{-27}	kg		
k_{B}:	1.38065×10^{-23}	$\mathrm{J\ K}^{-1}$	8.61734×10^{-5}	$\mathrm{eV\ K}^{-1}$
R:	8.314472	$\mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$	8.2057×10^{-2}	$\mathrm{l\ atm\ mol}^{-1}\ \mathrm{K}^{-1}$
σ_{SB}:	5.6704×10^{-8}	$\mathrm{J\ s}^{-1}\ \mathrm{m}^{-2}\ \mathrm{K}^{-4}$		
c:	2.99792458×10^{8}	$\mathrm{m\ s}^{-1}$		
h:	6.62607×10^{-34}	J s	4.13566×10^{-15}	eV s
$\hbar$:	1.05457×10^{-34}	J s	6.58212×10^{-16}	eV s
hc:	1239.8	eV nm		
e:	1.60218×10^{-19}	C		
m_e :	$9.10938215 \times 10^{-31}$	kg	1: 0.5109989	$\mathrm{MeV\ c}^{-2}$
ϵ_0:	8.85419×10^{-12}	$\mathrm{C}^2\ \mathrm{J}^{-1}\ \mathrm{m}^{-1}$	5.52635×10^{-3}	$e^2\ \text{Å}^{-1}\ \mathrm{eV}^{-1}$
$e^2/4\pi\epsilon_0$:	2.30708×10^{-28}	J m	14.39964	eV Å
a_0:	0.529177×10^{-10}	m	0.529177	Å
E_{H}:	1	Ha	27.212	eV

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 $\phi(x)$ has units $1/x$
2. Normalized $\tilde{\phi}(x) = \phi(x)/\int \phi(x)dx$
3. (Unitless) probability $a < x < b = \int_a^b \tilde{\phi}(x)dx$
4. Expectation value $\langle f(x) \rangle = \int f(x)\tilde{\phi}(x)dx$
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 Temperature example

https://colab.research.google.com/github/wmfschneider/CHE30324/blob/master/Resources/Probability.ipynb

1.2.4 Boltzmann distribution

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

1.2.5 Boltzmann distribution: Gravity example

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

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

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

1.2.6 Boltzmann distribution: Kinetic energy in 1-D example

1. $KE = \frac{1}{2}mv_x^2$, $P(v_x) \propto \exp\left(-mv_x^2/2k_BT\right)$
2. Standard Normalized Gaussian distribution of mean μ and variance σ^2

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

3. By inspection, $\mu = \langle v_x \rangle = 0$, $\sigma^2 = \langle v_x^2 \rangle = k_BT/m$
4. Normalized velocity distribution

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

5. Molecule vs car again (Table 2)

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

	car	gas molecule
m	$1000\,\mathrm{kg}$	$1 \times 10^{-26}\,\mathrm{kg}$
h	$1\,\mathrm{m}$	$1\,\mathrm{m}$
mgh	$9800\,\mathrm{J}$	$9.8 \times 10^{-26}\,\mathrm{J}$
	$6.1 \times 10^{22}\,\mathrm{eV}$	$6.1 \times 10^{-7}\,\mathrm{eV}$
T	$298\,\mathrm{K}$	$298\,\mathrm{K}$
k_BT	$0.026\,\mathrm{eV}$	$0.026\,\mathrm{eV}$
mgh/k_BT	2.4×10^{24}	2.3×10^{-5}
$P(1\,\mathrm{m})/P(0)$	$e^{-2.4\times10^{-24}}$	0.99998
$\langle h \rangle$	$0\,\mathrm{m}$	$42\,\mathrm{km}$
$\langle v_x \rangle^{1/2}$	$2 \times 10^{-12}\,\mathrm{m/s}$	$640\,\mathrm{m/s}$

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

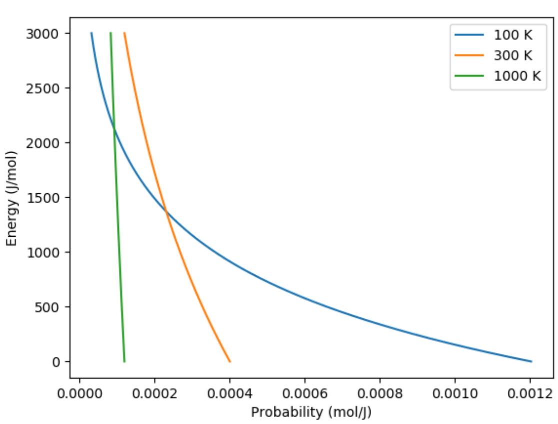


Figure 1: Boltzmann distribution at various temperatures

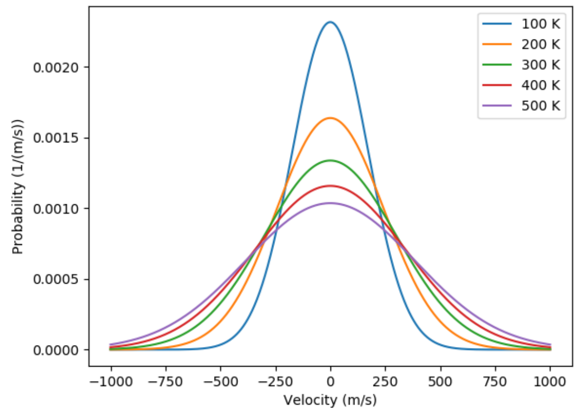


Figure 2: One-dimensional (Gaussian) velocities of N_2 gas

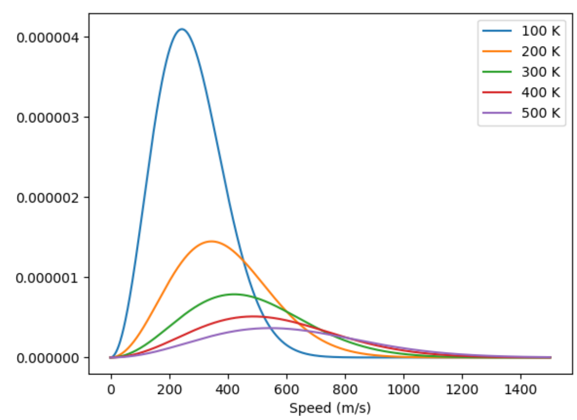


Figure 3: Maxwell-Boltzmann speed distribution of N_2 gas

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 (Figure 3)
   (a) Speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, spherical coordinates

$$\begin{aligned} P_{\text{MB}}(v) &= \int\int P_{1D}(v_x)P_{1D}(v_y)P_{1D}(v_z)v^2\sin(\theta)d\theta d\phi \\ &= 4\pi v^2\left(\frac{m}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{mv^2}{2k_B T}\right) \end{aligned}$$

   (b) mean speeds $\langle v\rangle = \int_0^\infty vP_{MB}(v)dv \propto \sqrt{T}$
   (c) mean kinetic energy $\langle U\rangle = \frac{1}{2}m\langle v^2\rangle = \frac{3}{2}RT$
   (d) 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
   (b) Wall collisions, $J_w = \int j(v_x)dv_x$, total collisions /area /time
   (c) Momentum change with wall collisions (Δ momentum/area/time):

$$P = \int_0^\infty 2mv_x j_x(v_x)dv_x = m(N/V)v_x^2\rangle = Nk_BT/V$$

4. Collisions and mean free path
   (a) Collision cross section $\sigma = \pi d^2$, area swept by molecule
   (b) Molecular collisions per molecule = volume swept * density of targets = $z = \sigma\langle v\rangle(N/V)\sqrt{2}$
   (c) Total collisions per volume = $z_{\text{AA}} = z(N/V)(1/2)$
   (d) Mean free path, $\lambda = \langle v\rangle/z$, mean distance between collisions

Table 4: N_2 at 298 K and 25 L mol^{-1}

$\langle v\rangle$	$475\,\text{m}\,\text{s}^{-1} = 1060\,\text{h}^{-1}$
J_W	$0.48\,\text{mol}\,\text{cm}^{-2}\,\text{s}^{-1}$
P	1 bar
σ	$0.43\,\text{nm}^2$
z	$7\times10^9\,\text{s}^{-1}$
Z_{AA}	$8\times10^{28}\,\text{s}^{-1}\,\text{cm}^{-3}$
λ	$68\,\text{nm} = 183\sigma$
D_{11}	$1.1\times10^{-5}\,\text{m}^2\,\text{s}^{-1}$

Table 5: 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	$\frac{dN}{dt} = \text{Area}\cdot J_w \propto 1/m^{1/2}$
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

1.4 Lecture 3: Transport

1. Transport of energy, momentum, mass across a gradient.
2. Infinite gradient: effusion and Graham's law, effusion rate $\propto MW^{-1/2}$
3. Finite gradient: Fick's first law
   (a) net flux proportional to concentration gradient
   (b) $j_x = -D\frac{dc}{dx}$
   (c) Self-diffusion constant, $D = \frac{1}{3}\lambda\langle v\rangle$
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, point source: $\frac{dc}{dt} = D\frac{d^2c}{dx^2}$, $c(x, t = 0) = c_0$
   (c) Separate variables $c(x, t) = X(x)t(t)$
   (d) Diffusion has Gaussian probability distribution: $c(x, t)/c_0 = [2\sqrt{\pi Dt}]^{-1} \exp(-x^2/4Dt)$
5. Random walk model of diffusion
   (a) N steps, $n = n_r - n_l$ net to the right, $P(n) = \binom{N}{n_r} 2^{-N}$
   (b) Large N and Stirling approximation, $N! \approx (2\pi N)^{1/2} N^N e^{-N}$
   (c) Let $x = \delta(n_r - n_l)$, $N = t/\tau$, Gaussian reappears!

   $$P(x, t) = \left(\frac{2\tau}{\pi t}\right)^{1/2} e^{-x^2\tau/2t\delta^2}$$

   (d) Einstein-Smoluchowski relation $D = \delta^2/2\tau$
6. Knudsen diffusion, $\delta = (3/2)l$, $\delta/\tau = \langle v\rangle$, $D = \frac{1}{3}l\langle v\rangle$
7. Seeing is believing—Brownian motion
   (a) Seemingly random motion of large particles ("dust") due to "kicks" from invisible molecules
   (b) Einstein in one of his four 1905 *Annus Mirabilis* papers shows
      i. Motion of particles suspened in a fluid of molecules must follow same Gaussian diffusion behavior
      ii. From steady-state arguments in a field, diffusion constant is Boltzmann energy, k_BT, times mobility
      iii. Mobility inversely related to viscosity
   (c) Stokes-Einstein equation
   (d) Allows measurement of Avogadro's number, final proof of kinetic theory of matter
   (e) Similar model for diffusion of liquid molecules, slip boundary

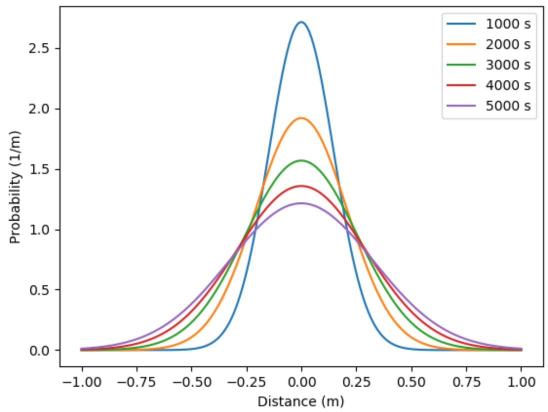


Figure 4: Diffusional spreading, $\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$

Table 6: Classical waves

The free wave equation	$\dfrac{\partial^2 \Psi(x,t)}{\partial x^2} = \dfrac{1}{v^2}\dfrac{\partial^2 \Psi(x,t)}{\partial t^2}$
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. Characterized by frequency, wavelength, amplitude, ...
2. Traveling waves, standing waves
3. Interference, diffraction
4. Characteristic of light, among other thing
5. Expected energy of a classical wave, $\langle \epsilon \rangle_\nu = k_B T$ for all ν

2.1.2 Blackbody radiation - light emitted by all bodies due to their temperature

1. Blackbody/Hohlraum spectrum (like the sun)
   (a) Stefan-Boltzmann law, total irradiance $I(\lambda, T)$

   (b) Wien's displacement law, $\lambda_{\text{text}}T = \text{constant}$

2. Rayleigh-Jeans predicts spectrum using classical physics
   (a) standing waves + classical wave energy → ultraviolet catastrophe
   (b) $I(\lambda, T) = (8\pi/\lambda^4) \cdot k_B T \cdot c$

3. Planck model, 1900
   (a) Energy spectrum of waves are *quantized*, $\epsilon_\nu = nh\nu$, $n = 0, 1, 2, \ldots$
   (b) Expected energy of a quantized wave:

$$\langle\epsilon\rangle_\nu = \sum_{n=0}^{\infty} nh\nu e^{-nh\nu/k_B T} = h\nu/\left(e^{h\nu/k_B T} - 1\right)$$

   (c) Intensity:

$$I(\lambda, T) = \frac{8\pi}{\lambda^4} \cdot \langle\epsilon\rangle_\nu \cdot c$$

   (d) 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) Energy of atomic vibrations ν are *quantized*, $\epsilon_\nu = nh\nu$, $n = 0, 1, 2, \ldots$
   (b) Expected energy of vibration exactly same as Planck's quantized waves
   (c) Heat capacity = derivative of energy wrt temperature goes to zero at low T

2.1.4 Photoelectric effect - electrons emitted when light shined on a metal

1. Energy of most weakly bound electrons to a material defined as work function, W
2. Shine light on metal, observe kinetic energy of electrons $E_{\text{kinetic}} = h\nu - W$
3. Kinetic energy varies with light frequency, number of electrons varies with light intensity
4. Einstein model, 1905 (Nobel prize)
   (a) Light is both wave-like *and* composed of particle-like "photons"
   (b) Photon energy related to frequency: $\epsilon = h\nu \ = hc/\lambda$
   (c) Light intensity related to number of photons

2.1.5 Special theory of relative (Einstein, 1905)

1. speed of light c in a vacuum is a constant for all observes, independent of
2. photons carry momentum $p = h/\lambda$
3. demonstrated by Compton effect, light scattering off electrons changes λ

2.1.6 Rutherford, planetary model of atom

1. Inconsistent with Maxwell's equations

2.1.7 Bohr model of H atom

1. 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. Explains discrete H energy spectrum and Rydberg formala

2.1.8 de Broglie relation

1. $\lambda = h/p$ *universally*
2. Relation to Bohr orbits
3. Davison and Germer experiment, e^- diffraction off Ni
4. Basis of modern electron diffraction to observe structure of materials

2.1.9 Wave-particle duality

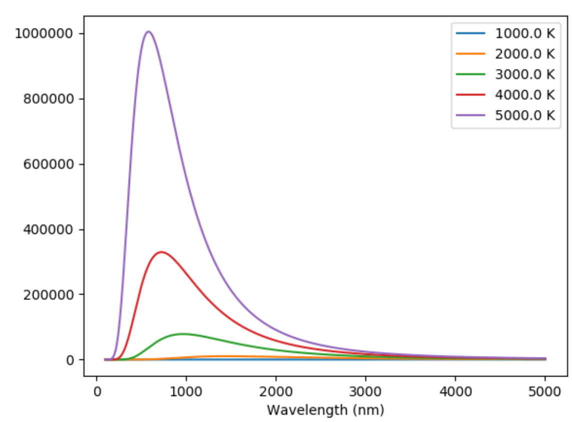


Figure 5: Blackbody irradiance

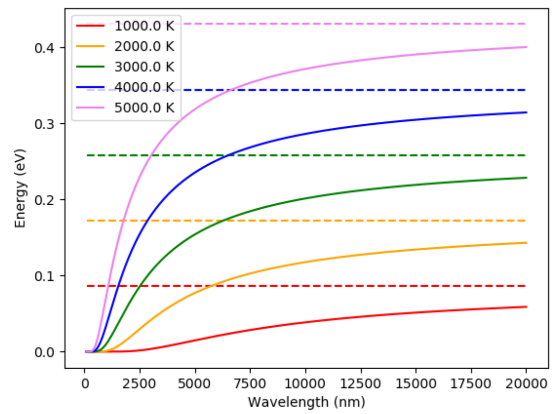


Figure 6: Average energy of a Planck quantized oscillator

Table 7: The new physics

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

2.2 Lecture 5: Postulates of quantum mechanics

2.2.1 Schrödinger equation describes wave-like properties of matter

1. Attempt to mathematically elaborate de'Broglie idea
2. Statement of conservation of energy, kinetic + potential = total
3. One-dimensional, time-independent, single particle Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

4. Second-order differential equation, solutions are steady-states of the system, discrete *eigenvalues* E and *eigenvectors* $\psi(x)$
5. Applied to H atom by Schrödinger to recover Bohr energies

2.2.2 Born interpretation

1. wavefunction $\psi(x)$ is a probability amplitude
2. wavefunction squared $|\psi(x)|^2$ 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 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

1. Classical solution, either stationary or uniform bouncing back and forth

Table 8: 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 $\Delta x \Delta p_x \geq \hbar/2$.

2.3.2 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

2.3.3 Multiple dimensions

1. separation of variables, one quantum number for each dimension
2. $\Psi_{lmn}(x,y,z) = \psi_l(x)\psi_m(y)\psi_n(z)$, 3dbox notebook
3. $E_{lmn} = (l^2+m^2+n^2)\pi^2\hbar^2/2L^2 \longrightarrow$ *degeneracies*

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 Introduce Pauli principle for fermions?

2.4 Lecture 7: Harmonic oscillator

2.4.1 Classical harmonic oscillator

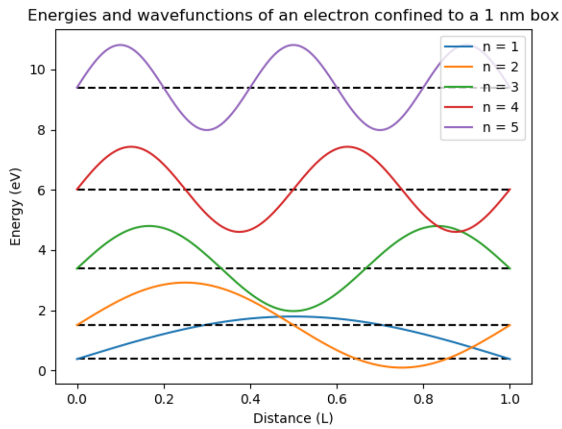
1. Hooke's law, $F = -k(x - x_0)$, k spring constant
2. Continuous sinusoidal motion
3. $x(t) = A\sin(\frac{k}{\mu})^{1/2}t, \nu = \frac{1}{2\pi}(\frac{k}{\mu})^{1/2}, E = \frac{1}{2}kA^2$
4. Exchanging kinetic and potential energies

Table 9: Particle-in-a-box model

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

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

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



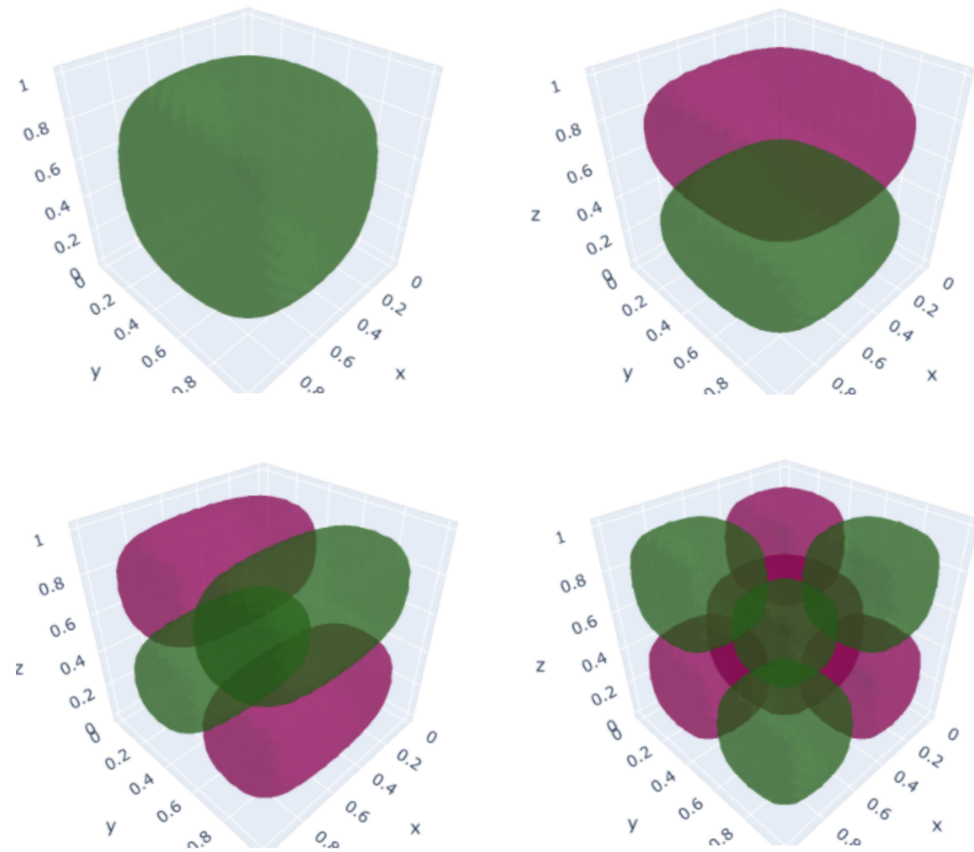
2.4.2 Quantum harmonic oscillator

1. Schrödinger equation and boundary conditions
2. Solutions like P-I-A-B + tunneling at boundaries (see Table 10)
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: $V(x) \propto x^n \rightarrow \langle T \rangle = \frac{n}{2}\langle V \rangle$
7. Classical turning point and `tunneling`
8. Classical limiting behavior: large

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 10: Three-dimensional particle-in-a-box s-like, p-like, d-like, and f-like wavefunctions



2.4.4 Diatomic vibrational spectroscopy

1. Apply harmonic oscillator model
2. Vibrational constant $\tilde{\nu} = (\sqrt{k/\mu}/2\pi)/hc$ cm^{-1}
3. Gross selection rule: dynamic dipole $d\mu/dx$ non-zero (heteronuclear, non homonuclear)
4. Specific selection rule: dipole integral $\langle\psi_v|\hat{\mu}|\psi_{v'}\rangle = 0$ unless $\Delta v = \pm 1$
5. Allowed $\Delta \tilde{E}_v = \tilde{\nu}$ cm^{-1}
6. Boltzmann distribution implies $v = 0$ states dominate at normal T

2.4.5 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

2.5 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

Table 11: Harmonic oscillator model

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

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

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

Hermite polynomials

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

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

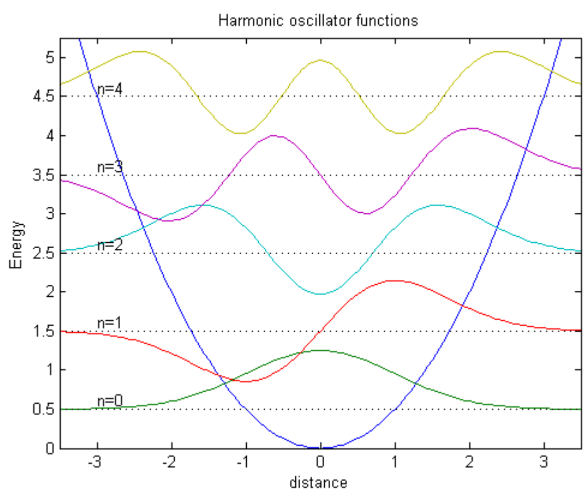


Table 12: 2-D rigid rotor model

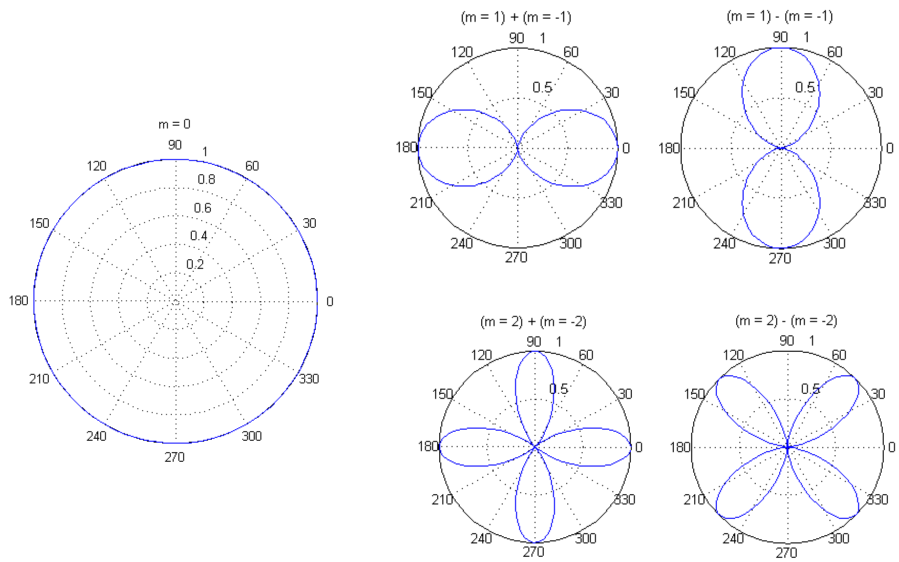
$$V(\phi) = 0, 0 \leq \phi \leq 2\pi$$

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

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

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

$$L_z = m_l \hbar$$



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

Table 13: 3-D rigid rotor model

$V(\theta,\phi) = 0, 0 \le \phi \le 2\pi, 0 \le \theta < \pi$
$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]$
$\hat{H}_{\text{rot}} = \frac{1}{2I}\hat{L}^2$
$Y_{lm_l}(\theta,\phi) = N_l^{\lvert m\rvert} P_l^{\lvert m\rvert}(\cos(\theta)) e^{im_l\phi}$
$l = 0, 1, 2, \ldots, \qquad m_l = 0, \pm 1, \ldots, \pm l$
$E_l = \frac{\hbar^2}{2I} l(l+1)$
$\lvert L\rvert = \hbar\sqrt{l(l+1)}, L_z = m_l\hbar$

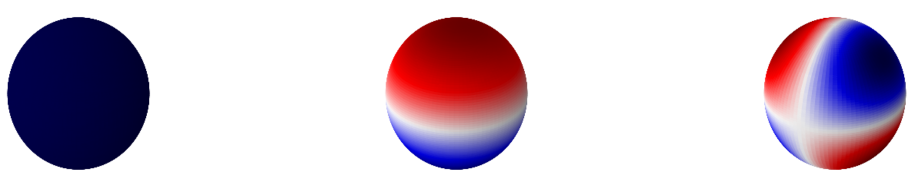


Figure 7: Pythonic s ($l = 0$), p ($l = 1$), and d ($l = 2$) spherical harmonics. Color scale from red to white to blue corresponds to positive to zero to negative sign of wavefunction.

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

2.5.5 Diatomic rotational spectroscopy

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

2.6 Lecture 11: Hydrogen atom

2.6.1 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 $v = \hbar^2 \frac{l(l+1)}{2\mu r^2}$

2.6.2 Solutions

1. $\psi(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$
2. Principle quantum number $n = 1, 2, \ldots$
   (a) K, L, M, N, $\ldots$ shells
   (b) $n-1$ radial nodes
3. Azimuthal quantum number $l = 0, 1, ..., n-1$
   (a) s, p, d, $\ldots$ orbital sub-shells
   (b) l angular nodes
4. Magnetic quantum number $m_l = -l, -l+1, ..., l$
5. Spin quantum number $m_s = \pm 1/2$
6. Energy spectrum and populations
7. Electronic selection rules

Table 14: Hydrogen atom

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

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

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

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

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

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

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

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

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

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

$$\langle r\rangle = \left\{\frac{3}{2}n^2 - \frac{1}{2}l(l+1)\right\}\frac{a_0}{Z}$$

(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) $\langle r \rangle = \int r P_{nl}(r) dr = \left(\frac{3}{2}n^2 - l(l+1)\right) a_0$

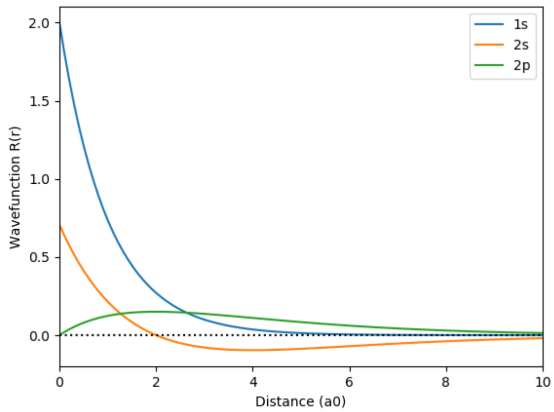


Figure 8: H atom wavefunctions

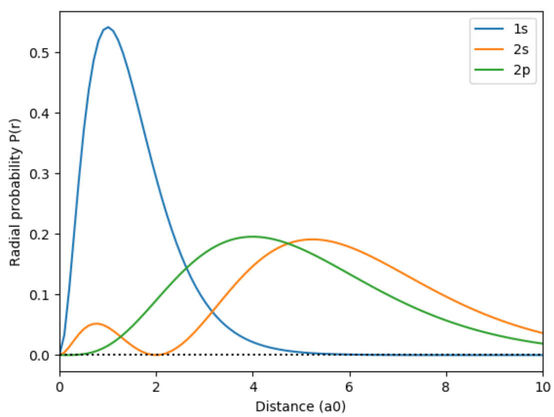


Figure 9: H atom radial probability

2.6.3 *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

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

2.7 Lecture 12: Many-electron atoms

2.7.1 Many-electron problem, Schrödinger equation not exactly solvable (Sad!)

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," ψ_i

2.7.2 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

S	$2S+1$	multiplicity
0	1	singlet
1/2	2	doublet
1	3	triplet
3/2	4	quartet

2.7.3 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

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

2.7.4 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

2.7.5 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

2.7.6 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

2.7.7 Numerical solution

1. All potential terms $\hat{v}$ depend on the solutions, so equations must be solved *iteratively* to *self-consistency*
2. Solved numerically on a grid or by expanding solutions in a basis set

2.7.8 DFT calculations on atoms

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

2.8 Lecture 13: Molecular orbital theory of molecules

2.8.1 Clamped nucleus ("Born-Oppenheimer") approximation

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

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

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

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

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

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

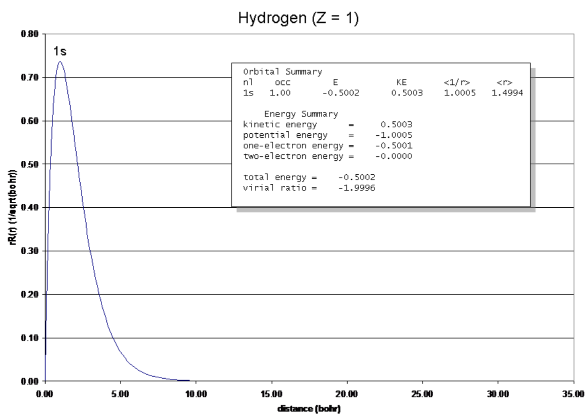
1. "Bonding" orbital, $\sigma_g(\mathbf{r}) = 1s_A + 1s_B$
2. "Anti-bonding" orbital, $\sigma_u(\mathbf{r}) = 1s_A - 1s_B$
3. Interaction scales with "overlap" $S = \langle 1s_A|1s_B\rangle$
4. Normalize

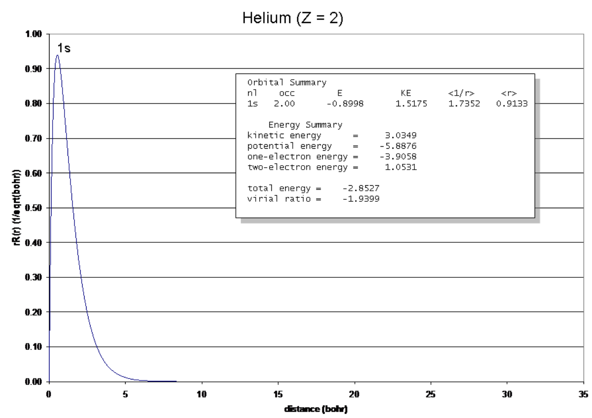
$$\sigma_g = \frac{1}{\sqrt{2(1-S)}}(1s_A + 1s_B) \qquad \sigma_u = \frac{1}{\sqrt{2(1+S)}}(1s_A - 1s_B)$$

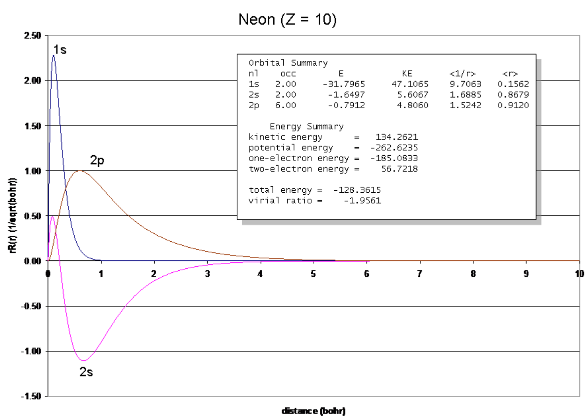
5. Energy expectation value

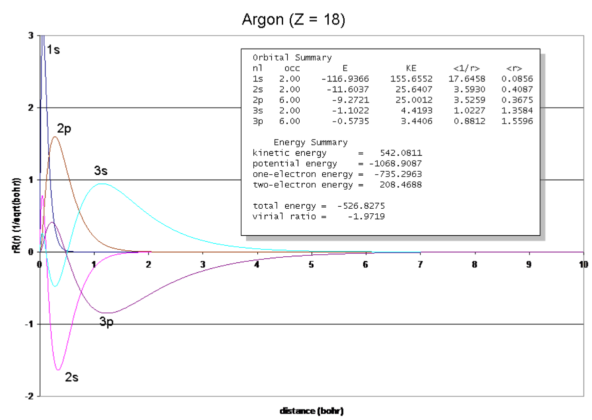
$$\begin{aligned}
\epsilon_g = \langle\sigma_g|\hat{f}|\sigma_g\rangle &= \frac{1}{2(1+S)}\left\{\langle 1s_A|\hat{f}|1s_A\rangle + \langle 1s_B|\hat{f}|1s_B\rangle + 2\langle 1s_A|\hat{f}|1s_B\rangle\right\} \\
&= \frac{1}{1+S}(F_{AA} + F_{AB}) \\
\epsilon_u = \langle\sigma_u|\hat{f}|\sigma_u\rangle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

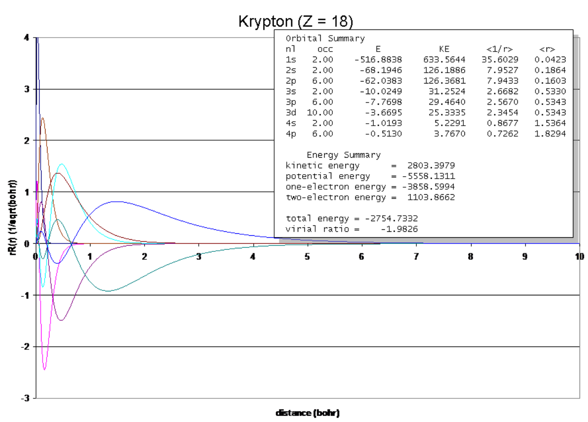
Table 15: Numerical DFT Solutions for Atoms

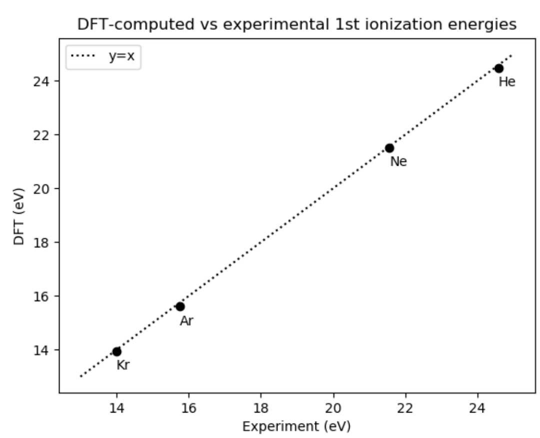






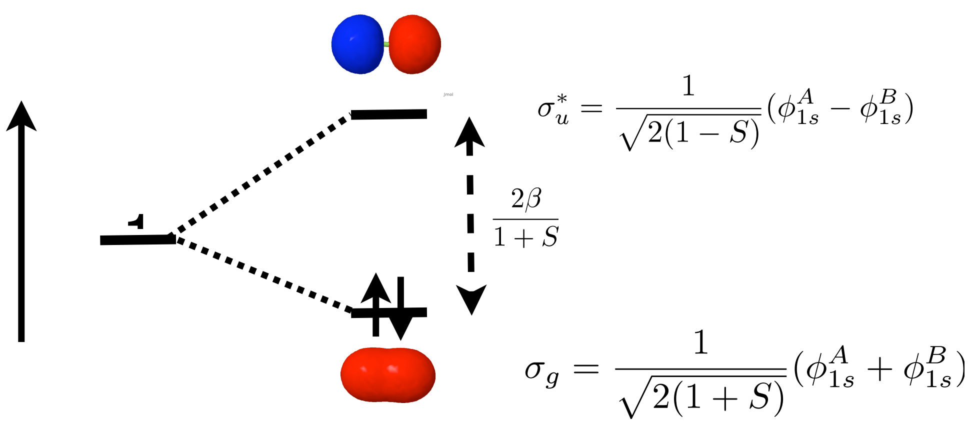






6. Matrix elements

$$F_{\mathrm{AA}} = F_{\mathrm{BB}} \approx \epsilon_{1\mathrm{s}} = \alpha$$
$$F_{\mathrm{AB}} = F_{\mathrm{BA}} = \beta$$
$$\alpha < \beta < 0 \quad \text{typically}$$



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

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

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

9. Ground configuration $= \sigma_g^2$

10. Bond order $= \frac{1}{2}(n - n^*)$

2.8.3 Secular equations

1. Expand wavefunctions ("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 wavefunctions (MOs)

3. Substituting into Schrödinger 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 "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

2.8.4 H_2 example, again

1. Set-up and solve secular matrix

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

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

2.8.5 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 matrix 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 $S_{ij} = 0$

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

2.8.7 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!

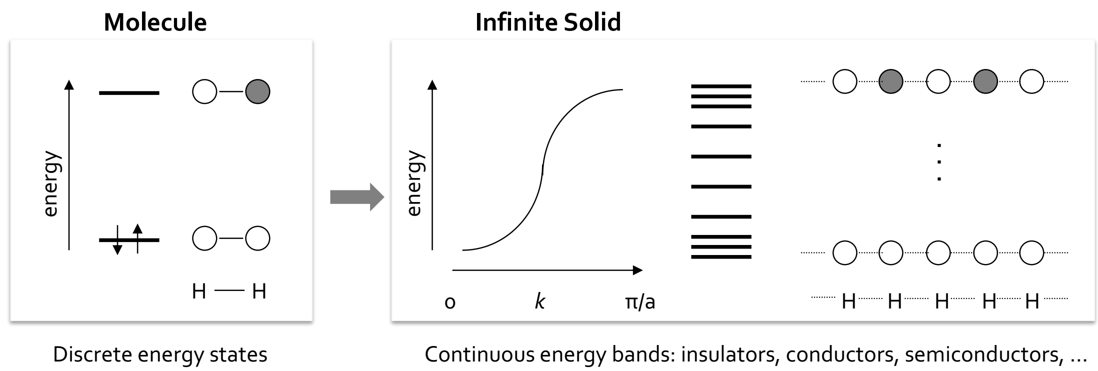
2.8.8 The Hückel/tight binding model: Roberts, Notes on Molecular Orbital Theory

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)

print(6. Cyclobutadiene examplen)
alpha,beta = symbols(alpha beta)

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

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

eigs  = M.eigenvects()

pprint(nEnergy state, degeneracyn)
for state in [0, 1, 2]:
    print(0    1n.format(eigs[state][0],eigs[state][1]))

pprint(nEigenvectors)
for state in [2,1,0]:
    print(Eigenvector(s) of state,state,:,eigs[state][2])
    print( )
```

2.8.9 Band structure of solids

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



2.9 Lecture 14: Computational chemistry

2.9.1 Numerical Schrödinger equation solvers for discrete (molecule) and periodic (solids/liquids/interfaces) readily available today

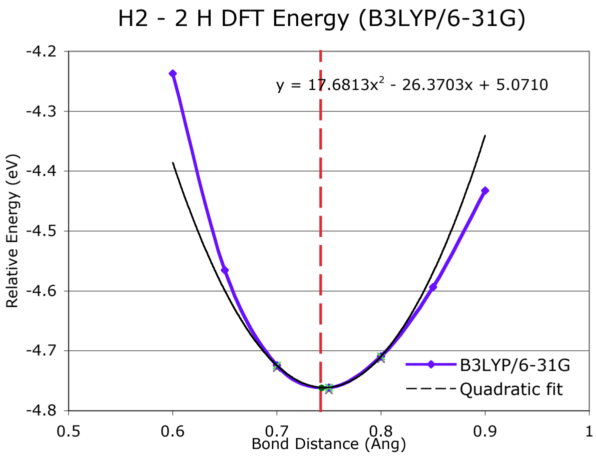
2.9.2 Have to specify:

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)

2.9.3 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

2.9.4 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	= <u>-31.803</u> 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

2.9.5 Polyatomic molecules

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

2.10 Lecture 15: Electronic spectroscopy

2.10.1 Electronic spectroscopy probes electron jumps between energy states, or "orbitals"

1. The electronic structure of each substance is unique, so no general energy expression for electronic transitions
2. Core, valence, virtual, vacuum states
3. Transitions approximately difference between orbital energies (Koopman's theorem)

$$h\nu \approx \epsilon_{\text{final}} - \epsilon_{\text{initial}}$$

4. This "theorem" is an approximation because the orbitals are not static; more correctly, the energy difference is given by a full electronic structure calculation on the initial and final states

2.10.2 Selection Rules

1. $\Delta S = 0$ "allowed"
2. $\Delta S \neq 0$ "forbidden"

2.10.3 Classes of transitions

- UV/visible spectroscopy
  1. electron jumps from valence filled to empty orbital
  2. energies of an eV or so
  3. π to π^* classic example
- UV photoelectron spectroscopy
  1. electron ionized from valence filled orbital
  2. 10's of eVs
- X-ray spectroscopy
  1. electron ionized from core orbital or promoted from core to an empty orbital
  2. 100's-1000's eV energies
  3. many types, from lab scale to massive synchrotrons
  4. information about elemental composition, oxidation state, coordination, ...
- Stimulated absorption
  1. photon causes jump from lower to higher energy electronic state
  2. often convoluted with jumps to different vibrational, rotational states
- Spontaneous emission
  1. electron spontaneously drops to a lower energy state and emits a photon
  2. basis of fluorescence ($\Delta S = 0$)
  3. basis of long-lived phosphorescence ($\Delta S \neq 0$)
  4. long-lived because it breaks the spin selection rule
- Stimulated emission
  1. passing photon causes electron to jump from higher to a lower energy state and to emit another photon
  2. cascade of such stimulated events is the basis of laser action#+BEGINC̃OMMENT

2.11 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:

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

4. Allow energy (heat!) to exchange between two such systems
   (a) Energy of composite system is sum of individual systems (first law, $q_1 + q_2 = q$)
   (b) Degeneracy of composite system is always $\geq$ degeneracy of the starting parts!

$$\Omega(N_1 + N_2, q_1 + q_2) > \Omega(N_1, q_1) \cdot \Omega(N_2, q_2)$$

   (c) Boltzmann's tombstone, $S = k_B \ln \Omega$
   (d) Second Law:

Die Energie der Welt ist constant. Die Entropie der Welt strebt einem Maximum zu. - Clausius

3.1.4 Large two-state system

1. Stirling's approximation:

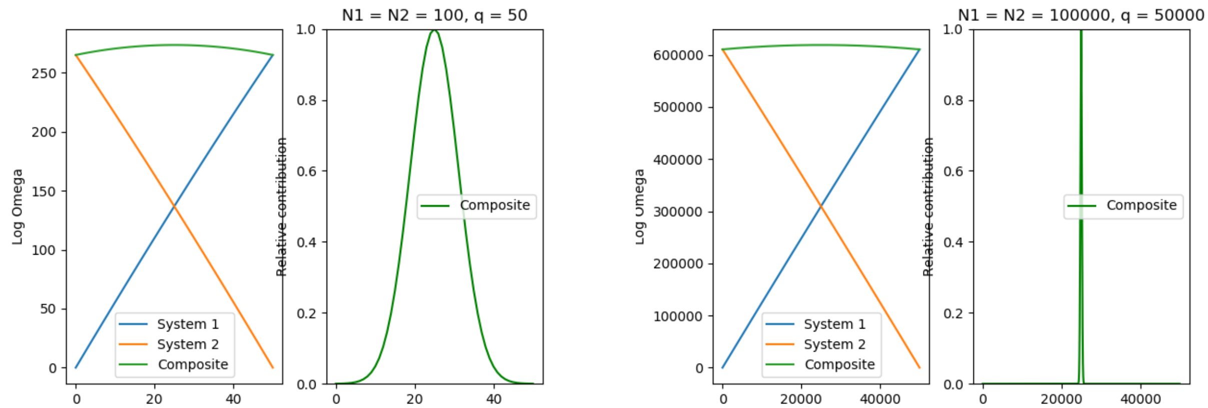
$$\Omega(N, q) \approx N^N/(N-q)^{(N-q)}$$

2. Composite system

$$\Omega(N, q) = \sum_{i \leq q} \Omega(N_1, i) \cdot \Omega(N_2, q-i)$$

3. For large N, one term *overwhelmingly* dominates sum

Table 16: Left: Energy distribution in two small, interacting two-state systems. Right: Energy distribution in two large interacting two-state systems



3.1.5 Consequences of energy flow between two large systems

1. Each subsystem has energy U_i and degeneracy $\Omega_i(U_i)$

2. Bring in thermal contact, $U = U_1 + U_2$, $\Omega = \sum_{U_1} \Omega_1(U_1)\Omega_2(U - U_1)$

3. If systems are very large, one combination of U_1, U_2 will dominate Ω sum. Find largest term.

$$\left(\frac{\partial \Omega}{\partial U_1}\right)_N = 0$$

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

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

4. Thermal equilibrium is determined by equal **temperature**!

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$$

5. Equal temperatures $\rightarrow$ most probable distribution of energy between subsystems.

6. (Same arguments lead to requirement that equal pressures (P_i) and equal chemical potentials (μ_i) maximize entropy when volumes or particles are exchanged)

3.1.6 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

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

5. Partition function counts the number of states accessible to a system at a given V and in equilibrium with a reservoir at T

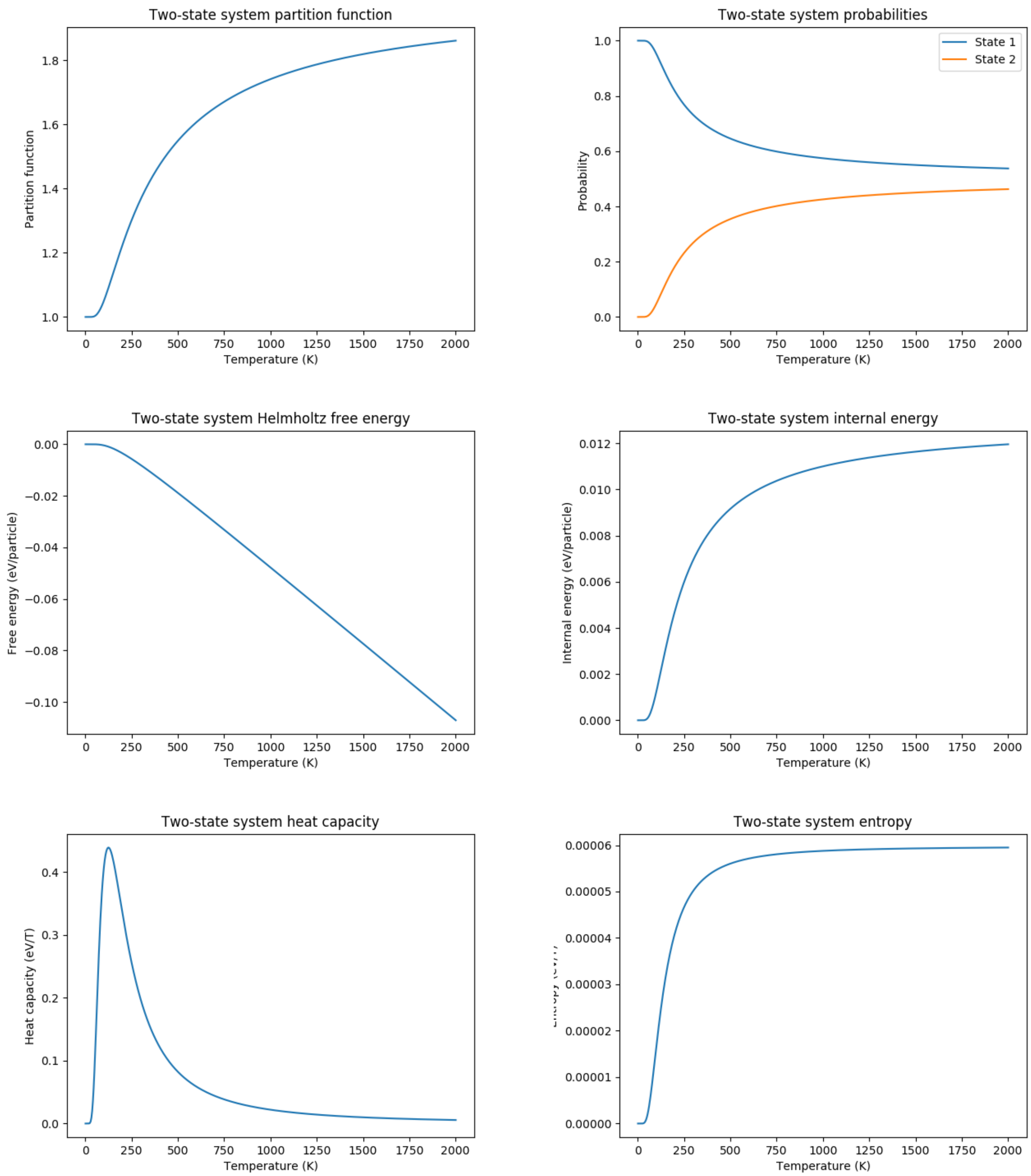
3.2.2 Energy factoring (sidebar)

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, degrees of freedom) of system:

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

Table 17: Two-state system thermodynamics



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. $q(V,T)$ 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 $U(T)$

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

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

Table 18: 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	$\ln Q$	$N \ln q$	$N \ln q - \ln N!$ $\approx N(\ln q - \ln N + 1)$
Helmholtz energy ($A = U - TS$)	$-\dfrac{\ln Q}{\beta}$	$-\dfrac{N \ln q}{\beta}$	$-\dfrac{N}{\beta}\left(\ln \dfrac{q}{N} + 1\right)$
Internal energy (U)	$-\left(\dfrac{\partial \ln Q}{\partial \beta}\right)_{NV}$	$-N\left(\dfrac{\partial \ln q}{\partial \beta}\right)_V$	$-N\left(\dfrac{\partial \ln q}{\partial \beta}\right)_V$
Pressure (P)	$\dfrac{1}{\beta}\left(\dfrac{\partial \ln Q}{\partial V}\right)_{N\beta}$	$\dfrac{N}{\beta}\left(\dfrac{\partial \ln q}{\partial V}\right)_\beta$	$\dfrac{N}{\beta}\left(\dfrac{\partial \ln q}{\partial V}\right)_\beta$
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)	$-\dfrac{1}{\beta}\left(\dfrac{\partial \ln Q}{\partial N}\right)_{VT}$	$-\dfrac{\ln q}{\beta}$	$-\dfrac{\ln(q/N)}{\beta}$

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

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

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

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

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. sum over rigid energy states and degeneracies of rigid rotor
2. $\Theta_{\text{rot}} = \hbar^2/2Ik_B$
3. "High" T $q_{\text{rot}}(T) \approx \sigma\Theta_{\text{rot}}/T$, most often true

3.3.4 Harmonic oscillator (vibrational states of a gas)

1. sum over harmonic oscillator energy states
2. $\Theta_{\text{vib}} = h\nu/k_B$, typically 100's to 1000's K
3. introduce strong non-linear T dependence to thermodynamic properties

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 is a start, have to elaborate to get at properties of liquids, solutions, ...
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 Isothermal, isbaric separation for ideal gas mixture

$$\mathrm{A/B}(N_A, N_B, V, T) \rightarrow \mathrm{A}(N_A, x_A V, T) + \mathrm{B}(N_B, x_B, V, T)$$

1. Apply ideal gas expressions to all parts and compute a difference!
2. Internal energy, $\Delta U(T) = 0$
3. Entropy, $\Delta S(T)/(N_A + N_B) = k_B(x_A \ln(_A) + x_B \ln(x_B))$
4. Minimum work of separation, $\Delta A(T) = \Delta U - T\Delta S > 0$

3.4.2 Chemical reaction

1. General chemical reaction $\sum_i \nu_i A_i = 0$, ν_i stoichiometric coefficients
2. Thermodynamic change $\Delta W^\circ(T) = \sum_i \nu_i W_i^\circ(T)$, where $W = A, U, S, G, \ldots$
3. "Standard state" derives from concentration dependence of entropy
4. "Standard state" corresponds to some standard choice, $(N/V)^\circ = c^\circ$, e.g. 1 mol/l (T-independent), or $(N/V)^\circ = P^\circ/RT$, e.g. 1 bar (T-dependent)
5. Permits functions to be easily computed at other concentrations, e.g.

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

6. Example: ethane dehydrogenation, $C_2H_6 \longrightarrow C_2H_4 + H_2$, 1 bar standard state
7. Reaction entropy captures contributions of all degrees of freedom
8. Reaction energy (internal, Helmholtz, ...) must *also* capture difference in 0 K electronic energy

$$\Delta U^\circ(T) = U^\circ_\mathrm{B}(T) - U^\circ_\mathrm{A}(T) + \Delta E(0)$$

Table 19: 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_{elec} = spin multiplicity

Table 20: Contributions to ideal gas thermodynamics

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

Table 21: Ethane thermodynamics

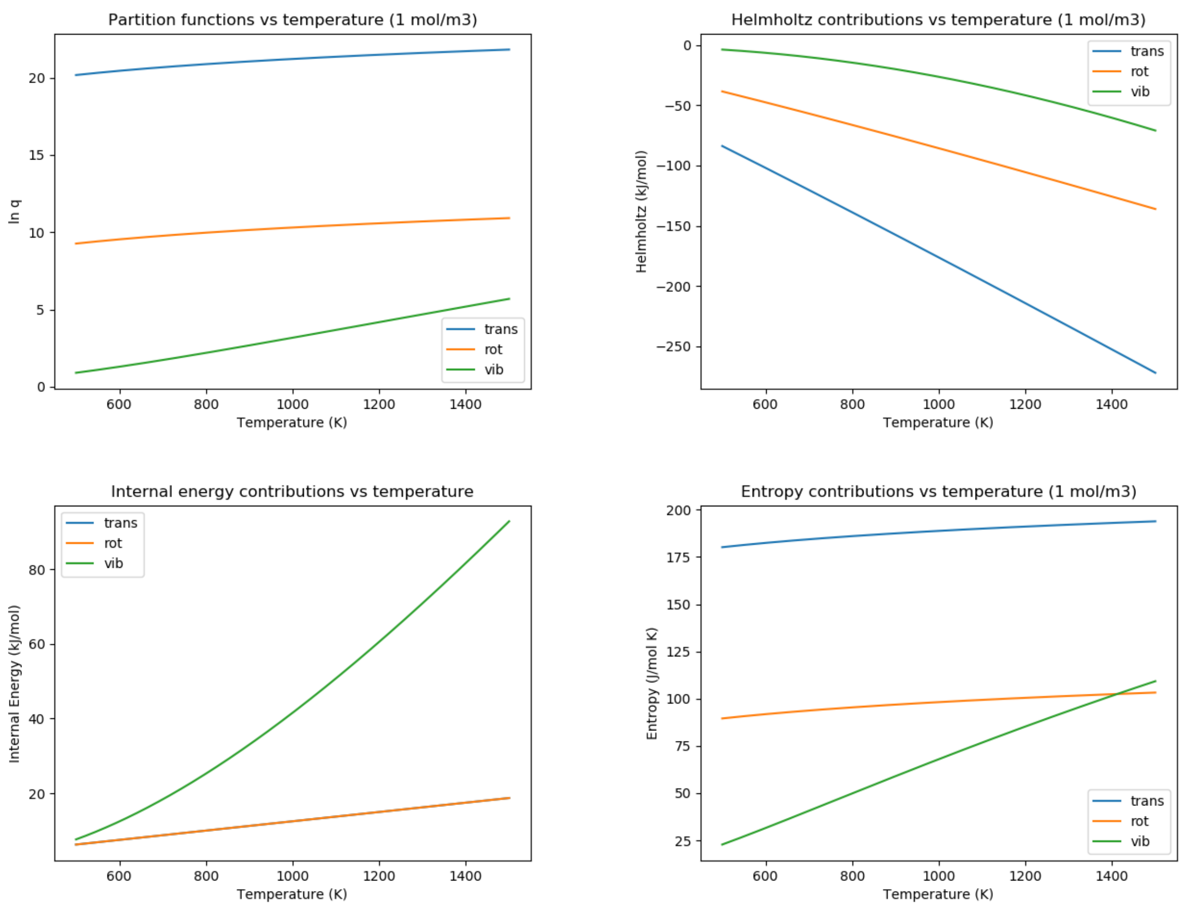
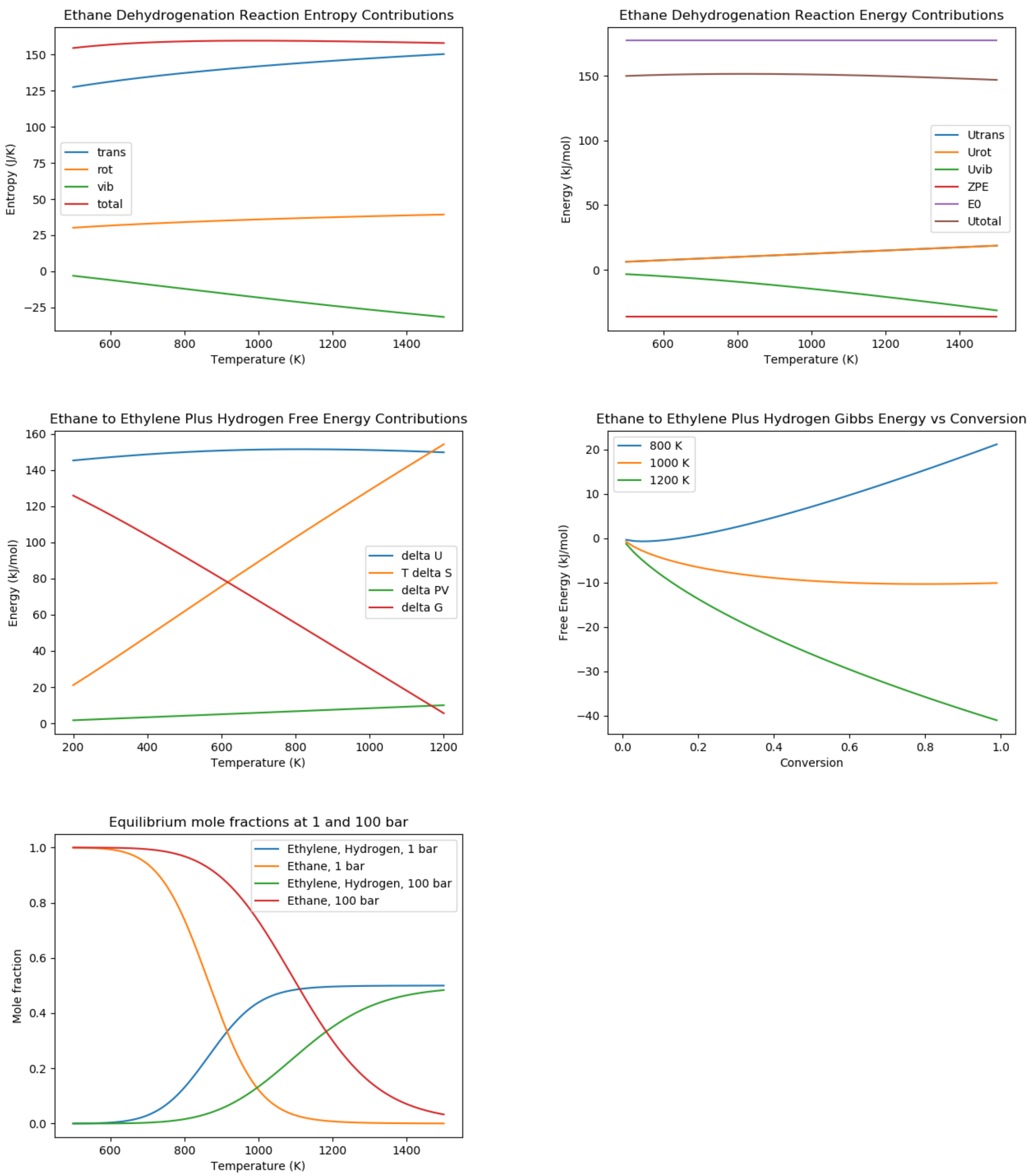


Table 22: Ethane to ethylene plus hydrogen standard state (1 bar) thermodynamcs



3.4.3 Chemical equilibrium

1. At chemical equilbrium, total free energy minimized with respect to reaction advancement ξ
$$G(T,\xi) = \xi(\Delta G^\circ + kT\sum_i \nu_i \ln P_i/P^\circ)$$
2. Convolution of energy and entropy effects
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. $q/V = 1/\Lambda^3$ has units of number/volume, or concentration
5. Equilibrium constant—convert units to some standard concentration c° or pressure P°
$$\begin{aligned} q_A^\circ(T) &= (q_A(T,V)/V)(1/c^\circ) \\ q_A^\circ(T) &= (q_A(T,V)/V)(RT/P^\circ) \\ K_{eq}(T) &= \frac{q_B^\circ(T)}{q_A^\circ(T)} e^{-\Delta E(0)/kT} = e^{-\Delta G^\circ(T)/kT} \end{aligned}$$

3.4.4 Le'Chatlier's principle

1. Example: ethane dehydrogenation, $C_2H_6 \longrightarrow C_2H_4 + H_2$, endothermic, positive entropy
2. Equilibrium composition starting from C_2H_6, at constant pressure
$$K_p(T) = \frac{q^\circ_{C_2H_4}(T) q^\circ_{H_2}(T)}{q^\circ_{C_2H_6}(T)} e^{-\Delta E(0)/k_BT} = \frac{P_{C_2H_4}P_{H_2}}{P_{C_2H_6}}\frac{1}{P^\circ} = \frac{P}{P^\circ}\frac{x^2}{(1-x)}$$
3. Response to temperature: Boltzmann distribution favors higher energy things as T increases
4. Response to pressure change: translational DOFs increasingly favor side with more molecules as volume increases/pressure decreases

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, $k = Ae^{-E_a/k_BT}$
    (a) Arrhenius plot, $\ln k$ vs $1/T$

Table 23: Basic kinetic rate laws

	differential rate	integrated rate	half-life
First order	$r = kC_A$	$C_A = C_{A0}e^{-k\tau}$	$\ln 2/k$
Second order	$r = kC_A^2$	$1/C_A = 1/C_{A0} + k\tau$	$1/kC_{A0}$

3.5.3 Reaction mechanisms

1. Elementary steps and molecularity

2. Ozone decomposition, rate second-order at high P_{O_2}, first-order at low P_{O_2}

$$\begin{array}{l} 2O_3 \longrightarrow 3O_2 \\ \hline O_3 \xrightarrow{k_1} O_2 + O \\ O_2 + O \xrightarrow{k_{-1}} O_3 \\ O + O_3 \xrightarrow{k_2} 2O_2 \end{array}$$

3. Collision theory

   (a) A + B $\rightarrow$ products

   (b) rate proportional to A/B collision frequency z_{AB} weighted by fraction of collisions with energy $> E_a$

$$r = kC_AC_B, k = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}N_{av}e^{-E_a/k_BT}$$

   (c) 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"

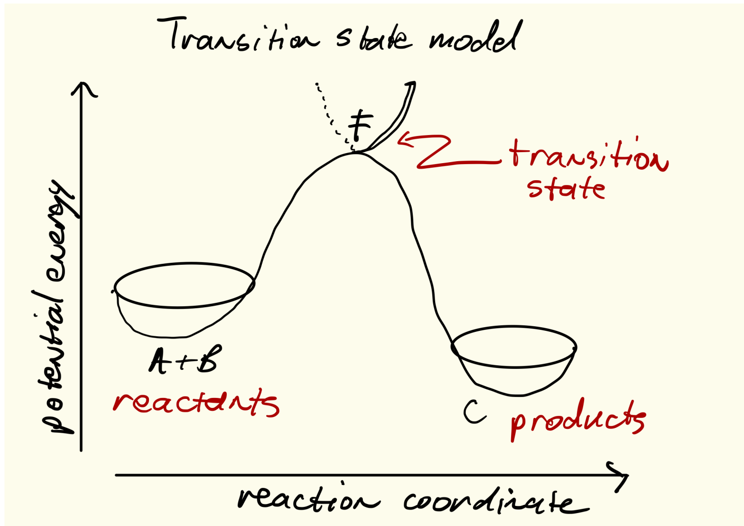
   (d) Harmonic approximation for transition state

2. rate proportional to concentration of "activated complex" over reactants times crossing frequency

$$\begin{aligned} r &= kC_AC_B \\ &= k^\ddagger C_{AB}^\ddagger \\ &= \nu^\ddagger K^\ddagger C_AC_B \\ &= \nu^\ddagger \frac{k_BT}{h\nu^\ddagger}\bar{K}^\ddagger(T)C_AC_B \\ &= \frac{k_BT}{h}\frac{q^\ddagger(T)}{q_A(T)q_B(T)}e^{-\Delta E(0)/k_BT}C_AC_B \end{aligned}$$

3. application to atom - atom collision

4. application to two molecules - vinyl alcohol to acetaldehyde
5. microscopic reversibility
6. equilibrium requirement $K_{eq}(T) = k_f(T)/k_r(T)$



3.5.5 Locating transition states computationally

3.5.6 Thermodynamic connection

1. Relate activated complex equilibrium constant to activation free energy

$$\bar{K}^{\ddagger}(T) = e^{-\Delta G^{\circ\ddagger}(T)/kT} = e^{-\Delta H^{\circ\ddagger}(T)/k_BT} e^{\Delta S^{\circ\ddagger}(T)/k_B}$$

2. Compare to Arrhenius expression

$$E_a = \Delta H^{\circ\ddagger}(T) + kT, A = \frac{k_BT}{h} e^1 e^{\Delta S^{\circ\ddagger}(T)/k_B}$$

3.5.7 Heterogeneous reactions and catalysis

1. molecule-surface collisions
2. surface reactions

./Images/TS-Ethylene.gif

3.5.8 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 ($k_{app} = (k_D/k_{-D})k_r$)

Table 24: Vinyl alcohol to acetaldehyde

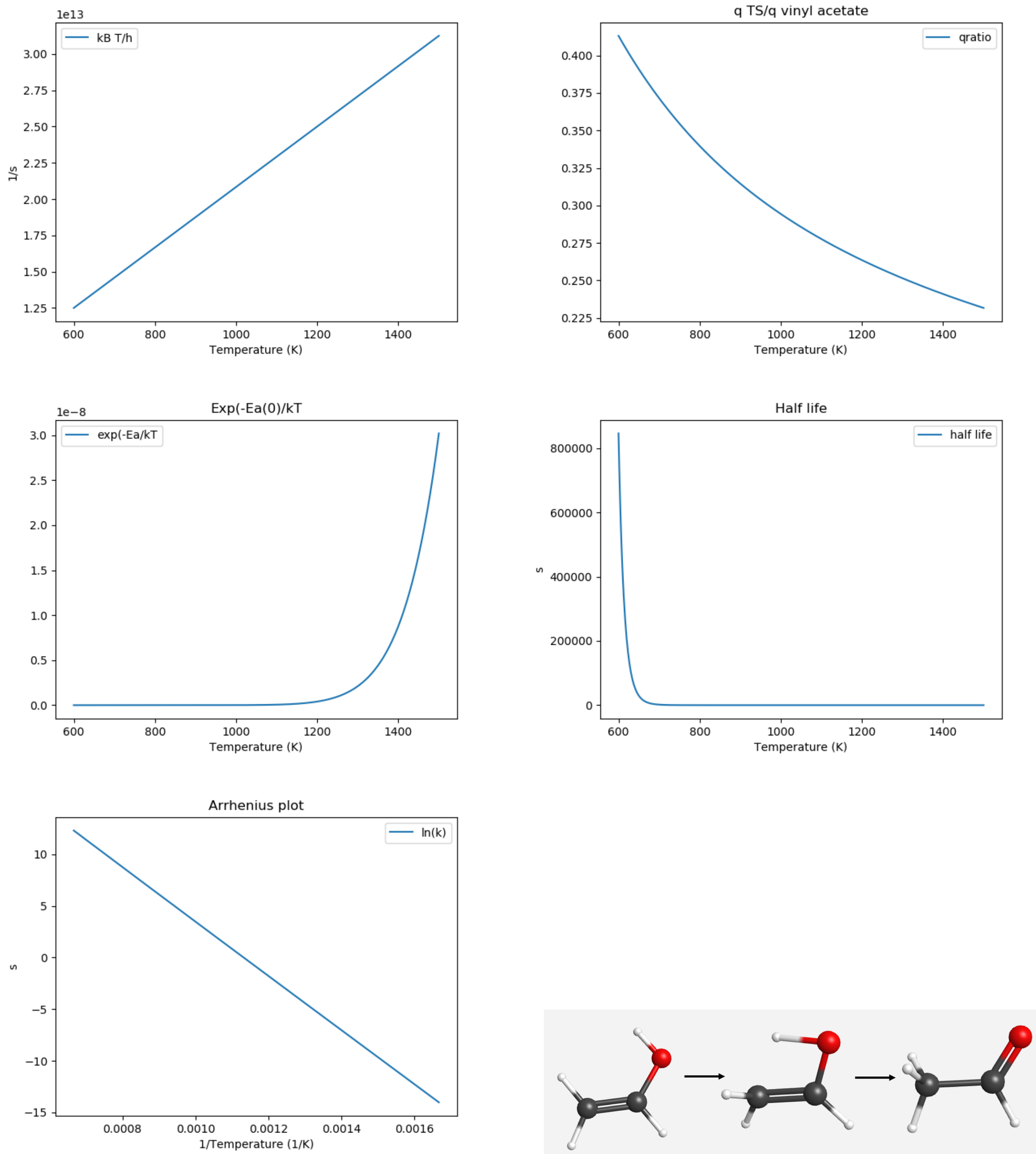


Table 25: DFT PES for ethylene dissociation on Ni2P

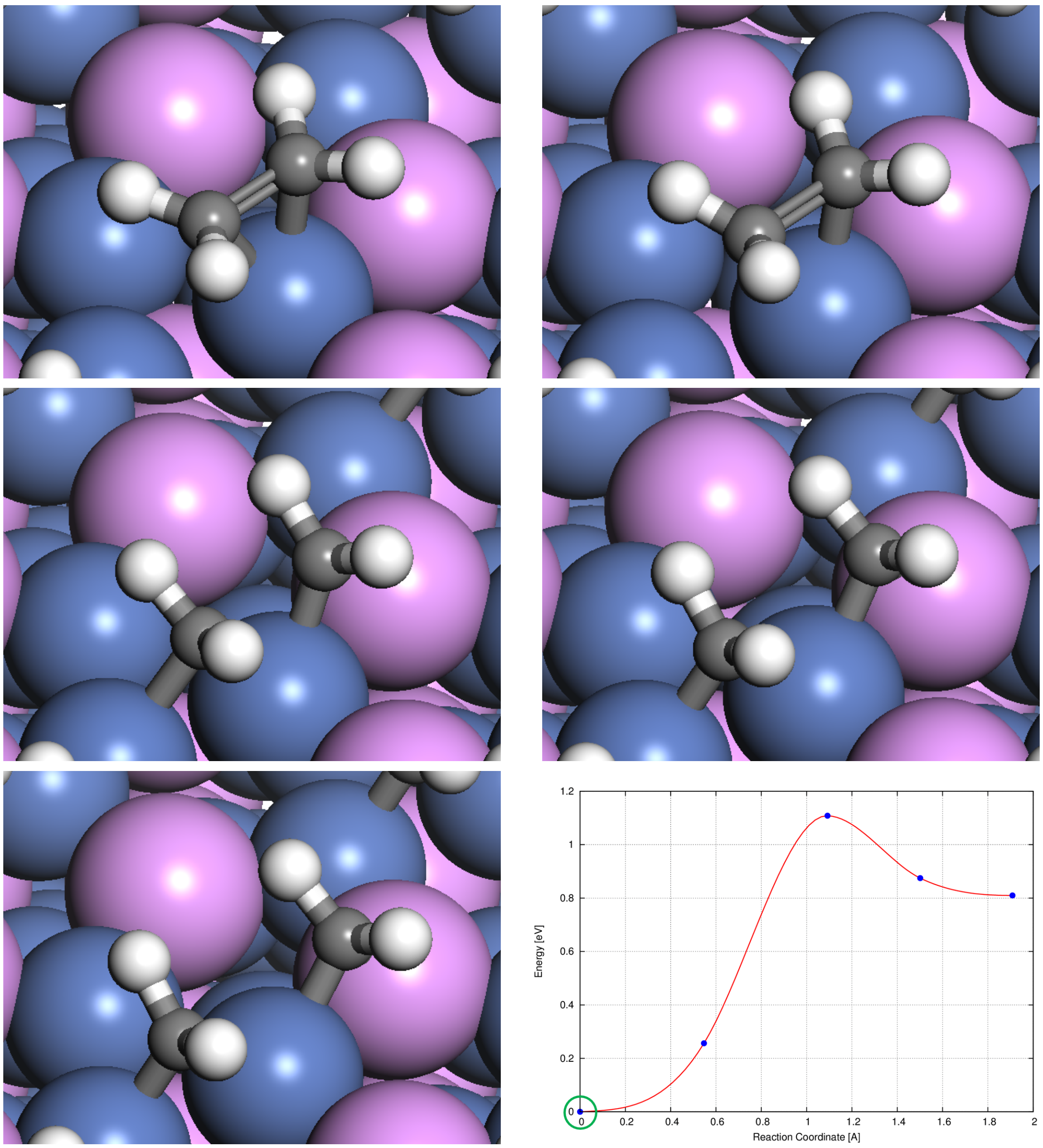


Table 26: Equilibrium and Rate Constants

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

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

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

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

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

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

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

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

3.6 Lecture 22: Conclusion

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

