

TMP Chem Notebook

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1 Math

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1.1 Introduction

Math Review for PChem

- | | | |
|---|---|---|
| <ul style="list-style-type: none">• Algebra<ul style="list-style-type: none">- polynomial properties- polynomial roots- exponent rules- logarithm rules- complex numbers• Trigonometry<ul style="list-style-type: none">- functions- graphs- unit circle- identities- coordinate systems- Euler's formula | <ul style="list-style-type: none">• Calculus<ul style="list-style-type: none">- derivatives / integrals<ul style="list-style-type: none">* definitions* basic rules* special rules- repeated differentiation- critical points- Taylor series- partial derivatives- multi-dimensional integrals | <ul style="list-style-type: none">• Linear Algebra<ul style="list-style-type: none">- vectors- matrices- determinant- matrix properties- eigenvalues / eigenvectors- Dirac notation- operators- unitary / Hermitian matrices- commutators- diagonalization- functions |
|---|---|---|

1.2 Polynomial Properties

Polynomial Properties

Any function which can be represented as:

$$f(x) = \sum_{n=0}^{F_{\max}} a_n x^n \quad \{n\} \in \mathbb{N} \quad \{a_n\} \in \mathbb{R}$$

positive integers

$$g(x) = \sum_{n=0}^{G_{\max}} b_n x^n \quad \text{real numbers}$$

$N_{\max} \rightarrow \text{"degree"} \rightarrow \text{largest } n \text{ w/ } a_n \neq 0$

$$h(x) = f(x) + g(x) = \sum_{n=0}^{H_{\max}} (a_n + b_n) x^n$$

$$p(x) = f(x) g(x) = \sum_{n=0}^{P_{\max}} \left(\sum_{m=0}^n a_m b_{n-m} \right) x^n$$

$$H_{\max} = \max(F_{\max}, G_{\max}) \quad P_{\max} = F_{\max} + G_{\max}$$

Function	Order
4	0
$2x$	1
x^3	3
$2x^2 - 4$	2
$x^4 - x^3 + x$	4
0	$-\infty$

$$(x^2 + 4) + (x^3 + 3x^2 - 2x - 1) = x^3 + 4x^2 - 2x + 3$$

$$(2x+1)(x^2 - x) = 2x^3 - x - 2x^2 + x^2$$

$$= 2x^3 - x^2 - x$$

1.3 Polynomial Roots

Polynomial Roots

Values at which a polynomial evaluates to zero

even degree $\rightarrow 0 \leq n_{\text{roots}} \leq |\text{degree}|$

odd degree $\rightarrow 1 \leq n_{\text{roots}} \leq |\text{degree}|$

$$f(x) = a_0 \begin{cases} 0 \text{ roots if } a_0 \neq 0 \\ \infty \text{ roots if } a_0 = 0 \end{cases}$$

$$f(x) = a_1x + a_0 \rightarrow 1 \text{ root @ } x = -\frac{a_0}{a_1}$$

$$f(x) = a_2x^2 + a_1x + a_0 \rightarrow 0-2 \text{ real roots}$$

$$x = \frac{-a_1 \pm \sqrt{a_1^2 - 4a_2a_0}}{2a_2}$$

$$\begin{array}{ll} \text{real roots at} & \begin{cases} 0 & \text{if } a_1^2 < 4a_2a_0 \\ 1 & \text{if } a_1^2 = 4a_2a_0 \\ 2 & \text{if } a_1^2 > 4a_2a_0 \end{cases} \end{array}$$

complicated analytic formula
for 3rd and 4th degree

solve numerically for 5th degree
and beyond (Newton-Raphson, etc.)

1.4 Exponent and Logarithm Properties

Exponent / Logarithm Properties

$$e = 2.71828\dots = \lim_{n \rightarrow \infty} (1 + \frac{1}{n})^n = \sum_{n=0}^{\infty} \frac{1}{n!}$$

$e^x \rightarrow "e \text{ to the } x"$

$$e \cdot e = e^2 \quad e \cdot e \cdot e = e^3 \quad \prod_{i=1}^n e = e^n$$

$$e^n \cdot e^m = e^{n+m} \quad (e^n)^m = e^{n \cdot m}$$

$$\frac{1}{e^n} = e^{-n} \quad \frac{e^n}{e^m} = e^{n-m}$$

$$\sqrt[n]{e} = e^{\frac{1}{n}} \quad \sqrt[m]{e} = e^{\frac{1}{m}} \quad \sqrt[n]{e^m} = e^{\frac{m}{n}}$$

$$x^0 = 1 \quad 1^x = 1 \quad 0^x = 0$$

$$10^2 = 100 \quad 5^{-2} = \frac{1}{25} \quad a^x = y$$

$$\log_{10}(100) = 2 \quad \log_5(\frac{1}{25}) = -2 \quad \log_a(y) = x$$

$\log_e(x) = \ln(x) \rightarrow \text{"natural log of } x\text{"}$

$$\ln(a \cdot b) = \ln(a) + \ln(b)$$

$$\ln(\frac{a}{b}) = \ln(a) - \ln(b)$$

$$\ln(a^b) = b \ln(a)$$

$$\ln(\frac{1}{a}) = -\ln(a)$$

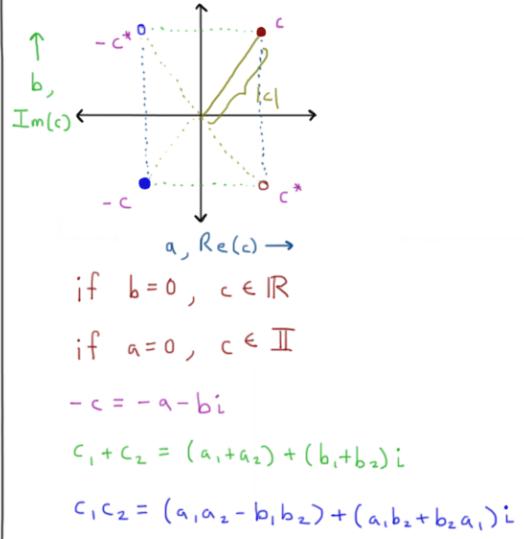
$$\ln(1) = 0 \quad \ln(e^x) = x$$

$$\ln(0) = -\infty \quad e^{\ln(x)} = x$$

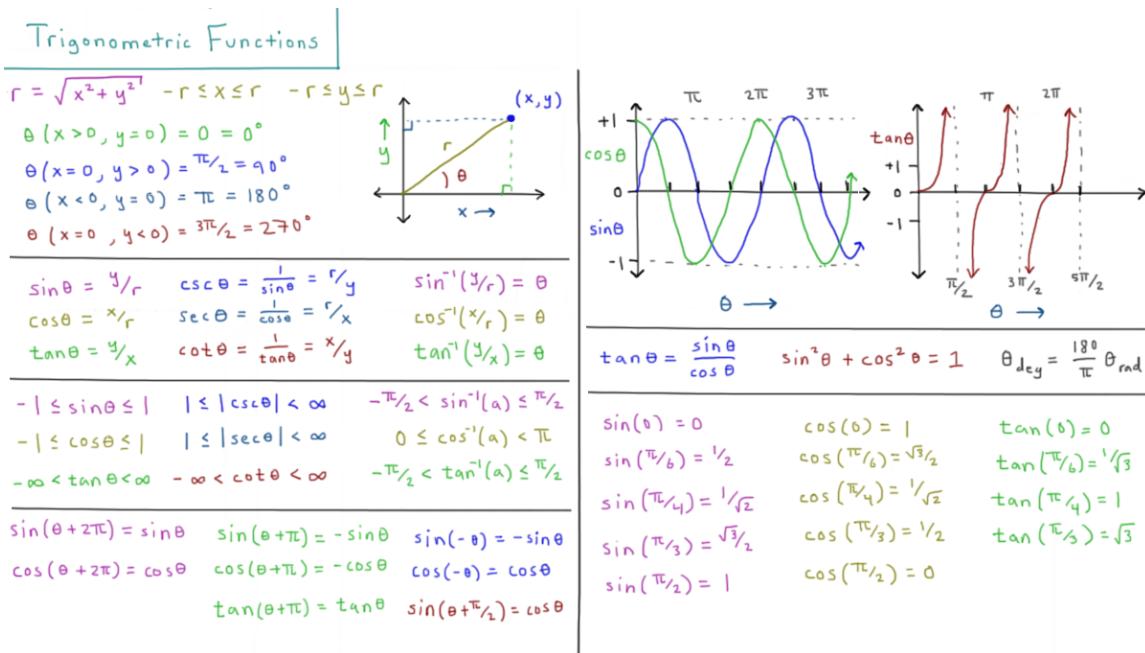
1.5 Complex Numbers

Complex Numbers

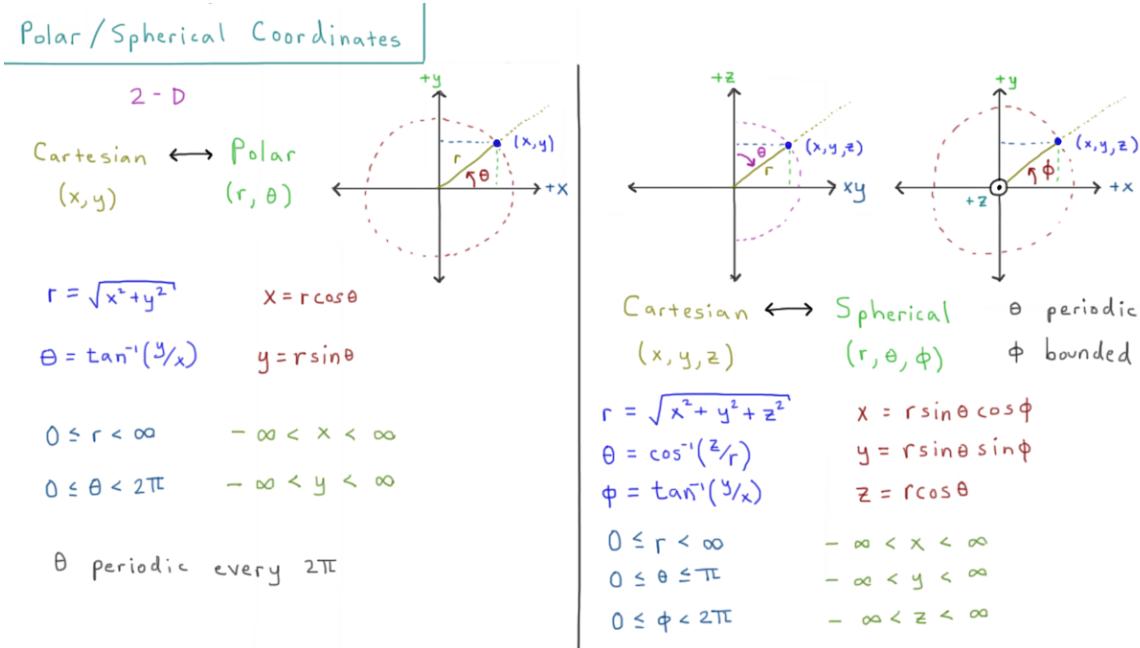
$$\begin{aligned}
 i &= \sqrt{-1} & c &= a + bi & i^2 &= -1 & i^4 &= 1 \\
 i \in \mathbb{I} && \text{"imaginary"} & & -\infty &< a < \infty & \\
 a, b \in \mathbb{R} && \text{"real"} & & -\infty &< b < \infty & \\
 c \in \mathbb{C} && \text{"complex"} & & & & \\
 a &= \operatorname{Re}(c) = \frac{1}{2}(c + c^*) & & & & & \\
 b &= \operatorname{Im}(c) = \frac{1}{2i}(c - c^*) & & & & & \\
 c^* &= a - bi & & & & & \\
 \text{"magnitude of } c \text{"} \rightarrow |c| &= \sqrt{a^2 + b^2} & & & & & \\
 |c|^2 &= a^2 + b^2 = (a + bi)(a - bi) = c^*c & & & & & \\
 x^2 + y^2 &= (x + iy)(x - iy) & & & & &
 \end{aligned}$$



1.6 Trigonometric Functions



1.7 Spherical and Polar Coordinates



1.8 Derivative Definition

Derivative Definition

$$y = f(x)$$

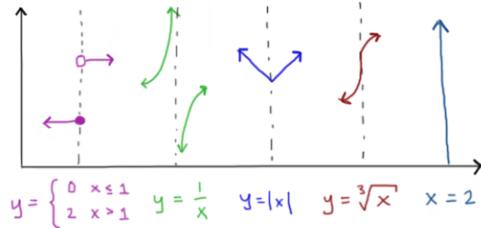
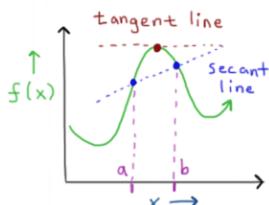
$$\Delta y = f(b) - f(a)$$

$$\Delta x = b - a = h$$

$$\left(\begin{array}{l} \text{average rate} \\ \text{of change} \end{array} \right) = \frac{\Delta y}{\Delta x} = \frac{f(b) - f(a)}{b - a}$$

$$\left(\begin{array}{l} \text{instantaneous} \\ \text{rate of change} \end{array} \right) = \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta y}{\Delta x} \right)$$

$$\frac{dy}{dx} = \frac{df(x)}{dx} = f'(x) = \lim_{h \rightarrow 0} \left(\frac{f(x+h) - f(x)}{h} \right)$$



$dx, dy \rightarrow$ "infinitesimal changes"

$f'(x) \rightarrow$ slope of $f(x)$ at x

$f'(x)$ does not exist at a if $f'(a)$ is

discontinuous undefined sharp
vertical multivalued

1.9 Basic Derivatives

Basic Derivatives

$$\frac{dy}{dx} = \frac{d}{dx} f(x) = f'(x) = \lim_{h \rightarrow 0} \left(\frac{f(x+h) - f(x)}{h} \right)$$

$$f(x) = 3x^2$$

$$f'(x) = \lim_{h \rightarrow 0} \left(\frac{3(x+h)^2 - 3x^2}{h} \right)$$

$$= \lim_{h \rightarrow 0} \left(\frac{3x^2 + 6xh + 3h^2 - 3x^2}{h} \right)$$

$$= \lim_{h \rightarrow 0} (6x + 3h) = 6x$$

$$\frac{d}{dx} (3x^2) = 6x$$

Constant $\frac{d}{dx} (a) = 0 \quad a \in \mathbb{R}$

Polynomial $\frac{d}{dx} (x^n) = nx^{n-1} \quad n \in \mathbb{Z}$

Exponential $\frac{d}{dx} (e^x) = e^x$

Logarithmic $\frac{d}{dx} (\ln(x)) = \frac{1}{x}$

Trigonometric $\frac{d}{dx} (\sin(x)) = \cos(x)$

$$\frac{d}{dx} (\cos(x)) = -\sin(x)$$

1.10 Derivative Rules

Derivative Rules

Scalar Multiple Rule

$$\frac{d}{dx} (a f(x)) = a \frac{d}{dx} f(x)$$

Sum Rule

$$\frac{d}{dx} (f(x) + g(x)) = \frac{d}{dx} f(x) + \frac{d}{dx} g(x)$$

Product Rule

$$\frac{d}{dx} (f(x)g(x)) = f(x) \frac{d}{dx} g(x) + g(x) \frac{d}{dx} f(x)$$

Quotient Rule

$$\frac{d}{dx} \left(\frac{f(x)}{g(x)} \right) = \frac{1}{(g(x))^2} \left(g(x) \frac{d}{dx} f(x) - f(x) \frac{d}{dx} g(x) \right)$$

Chain Rule

$$\frac{d}{dx} (f(g(x))) = \left(\frac{d}{dx} f(g) \right) \frac{d}{dx} g(x)$$

$$\frac{d}{dx} (5x^2) = 10x \quad \frac{d}{dx} (8 \sin(x)) = 8 \cos(x)$$

$$\frac{d}{dx} (2x^3 + 3x^4) = 6x^2 + 12x^3 \quad \frac{d}{dx} (e^x - 1) = e^x$$

$$\frac{d}{dx} (xe^x) = e^x + xe^x$$

$$\frac{d}{dx} (x^2 \cos(x)) = 2x \cos(x) - x^2 \sin(x)$$

$$\frac{d}{dx} \left(\frac{2x}{x^2 - 1} \right) = \frac{2(x^2 - 1) - 2x(2x)}{(x^2 - 1)^2}$$

$$\frac{d}{dx} (\sin(2x^3)) = (6x^2) \cos(2x^3)$$

$$\frac{d}{dx} (e^{-kx^2}) = -2kx e^{-kx^2}$$

1.11 Repeated Derivatives

Repeated Differentiation

$f(x) \rightarrow$ value

$$f'(x) = \frac{d f(x)}{dx} = \frac{d}{dx} f(x) \rightarrow \text{slope}$$

$$f''(x) = \frac{d^2 f(x)}{dx^2} = \frac{d}{dx} f'(x) \rightarrow \text{curvature}$$

$\frac{d^2}{dx^2} \rightarrow$ apply derivative rules twice

$$\frac{d^2}{dx^2}(x^n) = \frac{d}{dx}(nx^{n-1}) = n(n-1)x^{n-2}$$

$$\frac{d^2}{dx^2}(e^x) = \frac{d}{dx}(e^x) = e^x$$

$$\frac{d^2}{dx^2}(\sin(kx)) = \frac{d}{dx}(\cos(kx)) = -k^2 \sin(kx)$$

$$\frac{d^2}{dx^2}(e^{-x^2}) = \frac{d}{dx}(-2xe^{-x^2}) = -2e^{-x^2} + 4x^2e^{-x^2}$$

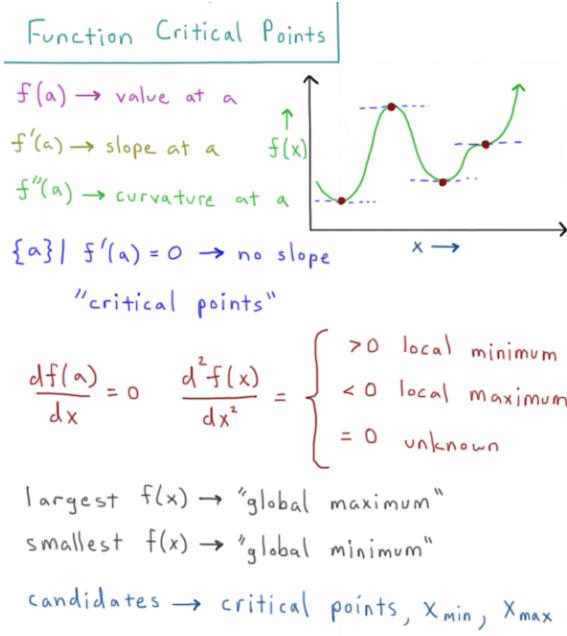
$$a(t) = \frac{d}{dt} v(t) = \frac{d^2}{dt^2} x(t) \quad v(t) = \frac{d}{dt} x(t)$$

$x(t) \rightarrow$ position

$v(t) \rightarrow$ velocity

$a(t) \rightarrow$ acceleration

1.12 Function Critical Points



$$f(x) = 3x^4 + 4x^3 - 12x^2 + 6$$

find min and max from $-3 \leq x \leq 2$

$$\frac{df(x)}{dx} = 12x^3 + 12x^2 - 24x = 0$$

$$12x(x-1)(x+2) = 0 \rightarrow x = -2, 0, 1$$

$$f''(x) = 36x^2 + 24x - 24$$

a	$f(a)$	$f''(a)$	point type
-3	33	228	boundary
-2	-26	72	global minimum
0	6	-24	local maximum
1	1	36	local minimum
2	38	168	global maximum

1.13 Taylor Series

Taylor Series

$f(x)$ can be complicated
 polynomials are simple
 want to approximate $f(x)$ near a
 $f(x) = k_0 + k_1 x + k_2 x^2 + k_3 x^3 + \dots$
 how to find $\{k_n\}$? \rightarrow derivatives

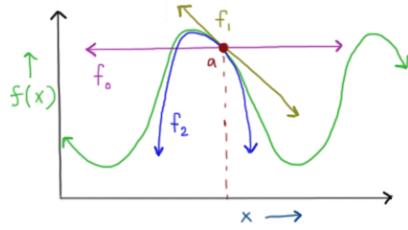
$$f(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{d^n}{dx^n} f(a) \right) (x-a)^n$$

$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2} f''(a)(x-a)^2 + \dots$$

$$f(x) = e^{-x} @ a=0 \rightarrow f(x) = -x + \frac{1}{2}x^2 - \frac{1}{6}x^3 + \dots$$

$$f(x) = 1 - x + O(x^2)$$

$$\begin{pmatrix} \text{Taylor series} \\ @ a=0 \end{pmatrix} = \begin{pmatrix} \text{MacLaurin series} \\ \end{pmatrix}$$



function	MacLaurin Series coefficients
e^x	$1/0!, 1/1!, 1/2!, 1/3!, 1/4!, 1/5!, \dots$
$\cos(x)$	$1, 0, -1/2!, 0, +1/4!, 0, \dots$
$\sin(x)$	$0, 1, 0, -1/3!, 0, +1/5!, \dots$
$\ln(1+x)$	$0, 1, -1/2, +1/3, -1/4, +1/5, \dots$
$\frac{1}{1-x}$	$1, 1, 1, 1, 1, 1, \dots$
$\tan^{-1}(x)$	$0, 1, 0, -1/3, 0, +1/5, \dots$

1.14 Integral Definition

Integral Definition

$$f(x) = \frac{dF(x)}{dx}$$

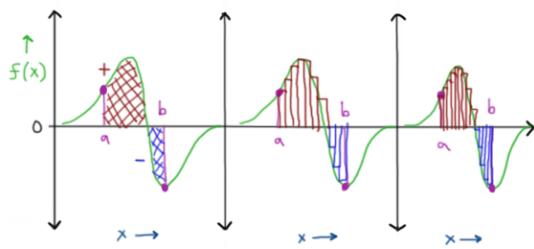
$$F(x) = \int f(x) dx \quad \text{indefinite integral}$$

$$F(b) - F(a) = \int_a^b f(x) dx \quad \text{definite integral}$$

$\int_a^b f(x) dx = \left(\begin{array}{l} \text{area under the} \\ \text{curve from } a \text{ to } b \end{array} \right)$

$$\int_a^b f(x) dx \approx \sum_{i=1}^n f(x_i) \Delta x \quad x_i = a + i \Delta x \quad \Delta x = \frac{b-a}{n}$$

$$\int_a^b f(x) dx = \lim_{n \rightarrow \infty} \left(\sum_{i=1}^n f(x_i) \Delta x \right)$$



$$\int_0^3 x^2 dx = 9$$

$$1 \cdot (0 + 1 + 4) = 5$$

$$1/4 \cdot (0 + 1/4 + 1 + 9/4 + 4 + 25/4) = 6.88$$

$$1/4 \cdot (0 + 1/16 + 1/4 + 9/16 + 1 + 25/16 + 9/4 + 49/16 + 41/16 + 81/16 + 25/4 + 121/16) = 7.91$$

1.15 Basic Integrals

Basic Integrals

$$f(x) = \frac{dF(x)}{dx} \quad F(x) = \int f(x) dx \quad \text{indefinite}$$

$$F(b) - F(a) = \int_a^b f(x) dx \quad \text{definite}$$

$$f(x) = x^2 \quad \frac{d}{dx}(x^3) = 3x^2 \quad \frac{d}{dx}\left(\frac{1}{3}x^3\right) = x^2$$

$\therefore \int x^2 dx = \frac{1}{3}x^3$

$$\int_1^2 x^2 dx = \left(\frac{1}{3}x^3\right|_1^2) = \left(\frac{1}{3}(2)^3\right) - \left(\frac{1}{3}(1)^3\right)$$

$$= \frac{1}{3}(8 - 1) = \frac{7}{3}$$

Constant $\int a dx = ax \quad a \in \mathbb{R}$

Polynomial $\int x^n dx = \frac{1}{n+1} x^{n+1} \quad n \in \mathbb{Z}$
 $n \neq -1$

Exponential $\int e^x dx = e^x$

Inverse $\int \frac{1}{x} dx = \ln(x)$

Trigonometric $\int \sin(x) dx = -\cos(x)$
 $\int \cos(x) dx = \sin(x)$

1.16 Integral Rules

Integral Rules

Scalar Multiple Rule

$$\int a f(x) dx = a \int f(x) dx \quad a \in \mathbb{R}$$

Sum Rule

$$\int (f(x) + g(x)) dx = \int f(x) dx + \int g(x) dx$$

Integration by Substitution

$$\int f'(g) g'(x) dx = f(g(x))$$

Integration by Parts

$$\int u(x) v'(x) dx = u(x) v(x) - \int v(x) u'(x) dx$$

$$\int 12x^3 dx = 3x^4 \quad \int \frac{4}{x} dx = 4 \ln(x)$$

$$\int (\cos(x) + 2e^x) dx = \sin(x) + 2e^x$$

$$\int 2x e^x dx = \int 2x e^u \left(\frac{du}{dx} \right) = e^u = e^{x^2}$$

$$u = x^2 \quad du = 2x dx \quad dx = \frac{du}{2x}$$

$$\begin{aligned} \int x \sin(x) dx &= -x \cos(x) + \int \cos(x) dx \\ &= -x \cos(x) + \sin(x) \end{aligned}$$

$$u = x \quad v = -\cos(x)$$

$$du = dx \quad dv = \sin(x) dx$$

1.17 Partial Derivatives

Partial Derivatives

$$z = f(x, y)$$

$$\Delta z = f(b, y) - f(a, y)$$

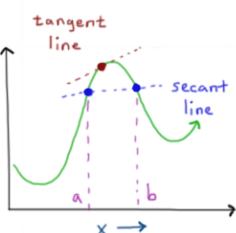
$$\Delta x = b - a = h$$

$$\left(\begin{array}{l} \text{average rate} \\ \text{of change} \end{array} \right)_y = \frac{\Delta z}{\Delta x} = \frac{f(b, y) - f(a, y)}{b - a}$$

$$\left(\begin{array}{l} \text{instantaneous} \\ \text{rate of change} \end{array} \right)_y = \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta w}{\Delta x} \right)$$

$$\frac{\partial w}{\partial x} = \frac{\partial f(x, y)}{\partial x} = \frac{\partial}{\partial x} f(x, y) = \lim_{h \rightarrow 0} \left(\frac{f(x+h, y) - f(x, y)}{h} \right)$$

same rules for $\frac{\partial}{\partial x}$ as $\frac{d}{dx}$



$$\frac{\partial}{\partial x} (2xy + 3x^2z^2) = 2y + 6xz^2$$

$$\frac{\partial}{\partial y} (2xy + 3x^2z^2) = 2x$$

$$\frac{\partial}{\partial z} (2xy + 3x^2z^2) = 6x^2z$$

$$\frac{\partial}{\partial y} (y^2 \ln(z)) = 2y \ln(z)$$

$$\frac{\partial}{\partial z} (y^2 \ln(z)) = \frac{y^2}{z}$$

$$\frac{\partial}{\partial x} (xye^{-zy^2}) = ye^{-zy^2}$$

$$\frac{\partial}{\partial y} (xye^{-zy^2}) = xe^{-zy^2} - 2xy^2ze^{-zy^2}$$

$$\frac{\partial}{\partial z} (xye^{-zy^2}) = -xy^3e^{-zy^2}$$

1.18 Repeated Partial Derivatives

Repeated Partial Differentiation

$$f(x) \rightarrow \frac{d^2 f(x)}{dx^2} = \frac{d}{dx} \left(\frac{df(x)}{dx} \right) = \frac{d}{dx} f'(x) = f''(x)$$

$$f(x, y, z) \rightarrow \frac{\partial^2 f(x, y, z)}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial f(x, y, z)}{\partial x} \right)$$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right) \quad \text{"mixed second partial derivatives"}$$

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y} \quad \text{"equality of mixed partial derivatives"}$$

$$\frac{\partial^2}{\partial x^2} (\sin(2xyz)) = \frac{\partial}{\partial x} (2yz \cos(2xyz)) = -4y^2 z^2 \sin(2xyz)$$

$$\frac{\partial^2}{\partial z^2} (4x^3 y^3 z^3) = \frac{\partial}{\partial z} (12x^3 y^3 z^2) = 24x^3 y^3 z$$

$$\frac{\partial}{\partial x \partial y} (x^2 \ln(y)) = \frac{\partial}{\partial x} \left(\frac{x^2}{y} \right) = \frac{2x}{y}$$

$$\frac{\partial}{\partial y \partial x} (x^2 \ln(y)) = \frac{\partial}{\partial y} (2x \ln(y)) = \frac{2x}{y} \quad \checkmark$$

1.19 Multi-Dimensional Integrals

Multi-Dimensional Integrals

$$f(x) = 6 \sin(3x)$$

$$\int_0^{\pi/3} 6 \sin(3x) dx = (-2 \cos(3x)) \Big|_0^{\pi/3}$$

$$= (-2 \cos(\pi/3)) - (-2 \cos(0))$$

$$= -2(\cos(\pi) - \cos(0)) = -2(-1 - 1) = 4$$

$$f(x, y) = 7x^3y^2$$

"volume under the surface"



$$\int_{-1}^1 dy \int_0^3 dx (7x^3y^2) = \int_{-1}^1 \int_0^3 7x^3y^2 dx dy$$

$$= 7 \left(\int_{-1}^1 y^2 dy \right) \left(\int_0^3 x^3 dx \right) = 7 \left(\frac{1}{3} y^3 \Big|_{-1}^1 \right) \left(\frac{1}{4} x^4 \Big|_0^3 \right)$$

$$= 7 \left(\frac{1}{3} \right) \left(\frac{1}{4} \right) ((1)^3 - (-1)^3) ((3)^4 - (0)^4)$$

$$= 7 \left(\frac{1}{3} \right) \left(\frac{1}{4} \right) (2)(81) = 189/2$$

$$\begin{aligned} & \int_0^\pi \int_0^\pi \sin(x) \sin(y) dx dy \\ &= \int_0^\pi \sin(y) \left(\int_0^\pi \sin(x) dx \right) dy \\ &= \int_0^\pi \sin(y) \left(-\cos(x) \Big|_0^\pi \right) dy \\ &= \int_0^\pi \sin(y) ((1) - (-1)) dy \\ &= 2 \int_0^\pi \sin(y) dy = 2(2) = 4 \end{aligned}$$

1.20 Volume Elements

Volume Elements

$$\underbrace{\int_{-\infty}^{\infty} f(x) dx}_{\text{"all-space integral"}} = \underbrace{\int_{\mathbb{R}} f(x) dx}_{\text{over all real numbers}}$$

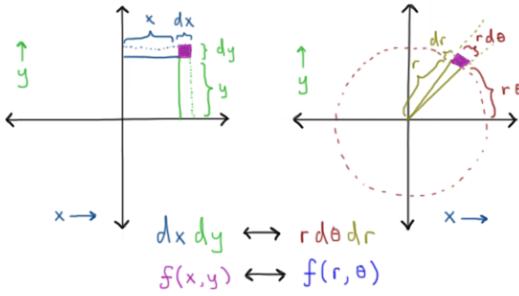
infinitesimal change in x

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy f(x, y) = \int_{\mathbb{R}^2} dx dy f(x, y)$$

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz f(x, y, z) = \int_{\mathbb{R}^3} d^3 r f(x, y, z)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y) dx dy = \int_0^{2\pi} \int_0^{\infty} f(r, \theta) r dr d\theta$$

$$\int_{\mathbb{R}^3} f(x, y, z) dx dy dz = \int_0^{\pi} \int_0^{\pi} \int_0^{\infty} f(r, \theta, \phi) r^2 \sin \theta dr d\theta d\phi$$



$$dx dy dz \leftrightarrow r^2 \sin \theta dr d\theta d\phi$$

$$f(x, y, z) \leftrightarrow f(r, \theta, \phi)$$

Below these equations are two small 3D cube diagrams. The first cube has dimensions dx , dy , and dz . The second cube has dimensions dr , $r d\phi$, and $r \sin \theta d\theta$.

1.21 Euler's Formula

Euler's Formula

$$e^{\pm ikx} = \cos(kx) \pm i \sin(kx)$$

$$\operatorname{Re}(e^{ikx}) = \cos(kx)$$

$$\operatorname{Im}(e^{ikx}) = \sin(kx)$$

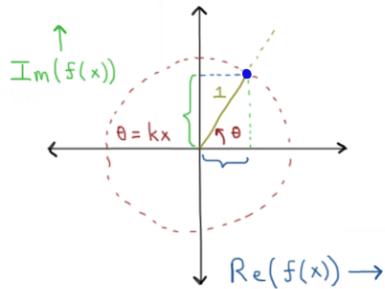
$$e^{i(kx+2\pi)} = e^{ikx}$$

$$|e^{ikx}| = 1$$

$$\cos(kx) = \frac{1}{2}(e^{ikx} + e^{-ikx})$$

$$\sin(kx) = \frac{1}{2i}(e^{ikx} - e^{-ikx})$$

$$(e^{ikx})^* = e^{-ikx} \quad (e^{ikx})^*(e^{ikx}) = 1$$



$$e^{i0} = 1$$

$$e^{i\pi/2} = i \quad \text{"Euler's identity"}$$

$$e^{i\pi} = -1 \rightarrow e^{i\pi} + 1 = 0$$

$$e^{i3\pi/2} = -i$$

$$e^{i2\pi} = 1$$

1.22 Vectors

Vectors

Scalar: quantity w/ only magnitude

Vector: quantity w/ magnitude & direction

$$\vec{a} = \underline{a} = a = a_x \hat{x} + a_y \hat{y} + a_z \hat{z} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$$

$\hat{x}, \hat{y}, \hat{z}$ → basis vectors, unit length, orthogonal

in general $\vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$ n elements $\{a_i\} \in \mathbb{C}$

$$\vec{a} \cdot \vec{b} = \sum_{i=1}^n a_i b_i \quad \text{"dot product"}$$

if $\vec{a} \cdot \vec{b} = 0$, \vec{a} and \vec{b} are "orthogonal"

$$\vec{a} \cdot \vec{a} = \sum_{i=1}^n a_i a_i = |\vec{a}|^2$$

$$|\vec{a}| = \left(\sum_{i=1}^n a_i^2 \right)^{1/2} \quad \text{"magnitude"}$$

$\{\hat{e}_i\} \rightarrow \text{"basis vectors"}$

$$\vec{a} = \sum_{i=1}^n a_i \hat{e}_i \quad \vec{b} = \sum_{i=1}^n b_i \hat{e}_i$$

$$\vec{a} \cdot \vec{b} = \sum_{i=1}^n \sum_{j=1}^n a_i b_j (\hat{e}_i \cdot \hat{e}_j)$$

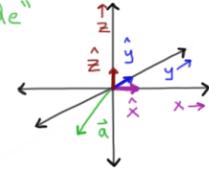
$$\hat{e}_i \cdot \hat{e}_j = \delta_{ij} \quad \delta_{ij} = \begin{cases} 1 & \text{if } i=j \\ 0 & \text{if } i \neq j \end{cases}$$

orthogonal, normalized → "orthonormal"

$$\vec{a} \cdot \hat{e}_i = a_i \quad (\vec{a} + \vec{b})_i = a_i + b_i \quad (\alpha \vec{a})_i = \alpha a_i$$

$$\underline{a}^T = (a_1, a_2, \dots, a_n) \quad \underline{a}^\dagger = (\underline{a}^T)^* = (a_1^*, a_2^*, \dots, a_n^*)$$

$$\vec{a} \cdot \vec{b} = \underline{a}^T \underline{b} \quad \vec{a}^* \cdot \vec{b} = \underline{a}^\dagger \underline{b}$$



1.23 Matrices

Matrices

2-dimensional rectangular array of values

$$\underline{\underline{A}} = \underline{\underline{A}} = \left(\begin{array}{cccc} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{m1} & a_{m2} & \dots & a_{mn} \end{array} \right) \quad \left\{ \begin{array}{l} n \text{ columns} \\ m \text{ rows} \\ \{a_{mn}\} \in \mathbb{C} \end{array} \right.$$

$m \times n$ matrix \rightarrow m rows, n columns, nm elements
 $a_{mn} \rightarrow$ element in row m , column n

$$(\underline{\underline{A}} + \underline{\underline{B}})_{ij} = a_{ij} + b_{ij} \quad \text{must have } n_A = n_B, m_A = m_B$$

$$\underline{\underline{A}} + \underline{\underline{B}} = \left(\begin{array}{cccc} a_{11} + b_{11} & a_{12} + b_{12} & \dots & a_{1n} + b_{1n} \\ a_{21} + b_{21} & a_{22} + b_{22} & \dots & a_{2n} + b_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{m1} + b_{m1} & a_{m2} + b_{m2} & \dots & a_{mn} + b_{mn} \end{array} \right)$$

$$(\alpha \underline{\underline{A}})_{ij} = \alpha a_{ij} \quad \alpha \underline{\underline{A}} = \left(\begin{array}{cccc} \alpha a_{11} & \alpha a_{12} & \dots & \alpha a_{1n} \\ \alpha a_{21} & \alpha a_{22} & \dots & \alpha a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ \alpha a_{m1} & \alpha a_{m2} & \dots & \alpha a_{mn} \end{array} \right)$$

$$(\underline{\underline{A}} \underline{\underline{b}})_{i \cdot} = \sum_{j=1}^{n_A} A_{ij} b_j \quad \text{must have } n_A = m_b$$

$$\left(\begin{array}{c|c} \hline & | \\ \hline \end{array} \right) \left(\begin{array}{c} | \\ \vdots \\ | \end{array} \right) = \left(\begin{array}{c} | \\ \vdots \\ | \end{array} \right) \quad \underline{\underline{A}} \underline{\underline{b}} = \underline{\underline{c}} \quad m_c = m_A$$

$$(\underline{\underline{A}} \underline{\underline{B}})_{ij} = \sum_{k=1}^{n_A} A_{ik} B_{kj} \quad \text{must have } n_A = m_B$$

$$\left(\begin{array}{c|c|c} \hline & | & | \\ \hline \end{array} \right) \left(\begin{array}{c|c|c} | & | & | \\ \vdots & \vdots & \vdots \\ | & | & | \end{array} \right) = \left(\begin{array}{c|c|c} | & | & | \\ \vdots & \vdots & \vdots \\ | & | & | \end{array} \right) \quad m_c = m_A \quad n_c = n_B$$

1.24 Determinants

Determinants	
$\underline{\underline{A}} = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix}$	$n \times n$ matrix $\det(\underline{\underline{A}}) = \underline{\underline{A}} $
$ \underline{\underline{A}} = \sum_{i=1}^{n!} (-1)^{i+1} \underbrace{\partial_i}_{\text{flipping sign}} \prod_{j=1}^n a_{ij}$ $n!$ terms, n products per term	exchange operator diagonal elements
$ a_{11} = a_{11}$ $\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}$	$ \underline{\underline{A}}^T = \underline{\underline{A}} $ $ \alpha \underline{\underline{A}} = \alpha^n \underline{\underline{A}} $ $ \underline{\underline{D}} = \prod_{i=1}^n D_{ii}$ $ \underline{\underline{H}} = \prod_{i=1}^n w_i$
$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$ $= a_{11}a_{22}a_{33} - a_{11}a_{23}a_{32} + a_{12}a_{23}a_{31} - a_{12}a_{21}a_{33} + a_{13}a_{21}a_{32} - a_{13}a_{22}a_{31}$	

1.25 Matrix Properties

Matrix Properties	
$\underline{\underline{A}} = \begin{pmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{pmatrix}$	$\underline{\underline{A}} \rightarrow n \times n$ square matrix
$\underline{\underline{I}} = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 1 \end{pmatrix} = \begin{pmatrix} 1 & & & 0 \\ 0 & 1 & & \vdots \\ 0 & 0 & \ddots & 1 \end{pmatrix}$	"identity matrix" $I_{ij} = \delta_{ij}$
$\underline{\underline{A}}^{-1} \underline{\underline{A}} = \underline{\underline{I}} = \underline{\underline{A}} \underline{\underline{A}}^{-1}$	"inverse matrix"
$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}^{-1} = \frac{1}{ \underline{\underline{A}} } \begin{pmatrix} a_{22} - a_{12} \\ -a_{21} & a_{11} \end{pmatrix}$	$(\underline{\underline{A}} \underline{\underline{B}})^{-1} = \underline{\underline{B}}^{-1} \underline{\underline{A}}^{-1}$
$\text{tr}(\underline{\underline{A}}) = \sum_{i=1}^n a_{ii}$	"trace of $\underline{\underline{A}}$ "
$\text{tr}(\underline{\underline{I}}) = n$	$\text{tr}(\underline{\underline{H}}) = \sum_{i=1}^n \omega_i$ $\{\omega_i\} \rightarrow$ "eigenvalues"
$\underline{\underline{A}}^T \rightarrow$ "transpose" $\underline{\underline{A}}^T_{ij} = \underline{\underline{A}}_{ji}$	
$\underline{\underline{A}}^* = (\underline{\underline{A}}^T)^* \rightarrow$ "adjoint" $\underline{\underline{A}}^*_{ij} = \underline{\underline{A}}_{ji}^*$	
if $\underline{\underline{A}} = \underline{\underline{A}}^T \rightarrow$ "symmetric" $\{a_{ij}\} \in \mathbb{R}$	
if $\underline{\underline{A}} = \underline{\underline{A}}^* \rightarrow$ "Hermitian" $\{a_{ij}\} \in \mathbb{C}$	
if $\underline{\underline{A}}^T = \underline{\underline{A}}^{-1} \rightarrow$ "orthogonal" $\{a_{ij}\} \in \mathbb{R}$	
if $\underline{\underline{A}}^* = \underline{\underline{A}}^{-1} \rightarrow$ "unitary" $\{a_{ij}\} \in \mathbb{C}$	
$\underline{\underline{U}}^* \underline{\underline{U}} = \underline{\underline{I}} = \underline{\underline{U}} \underline{\underline{U}}^* \quad \underline{\underline{U}} = 1 \quad \{(\omega_i)_v\} = 1$	
2x2 $\underline{\underline{U}} = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \quad \theta \in \mathbb{R}$	

1.26 Matrix Eigenvalues and Eigenvectors

Matrix Eigenvectors & Eigenvalues

\underline{A} → $n \times n$ square matrix

\underline{x} → n -dimensional column vector

ω_α → scalar value $\in \mathbb{C}$

if $\underline{A}\underline{x} = \omega_\alpha \underline{x}$, then \underline{x} is an eigenvector of \underline{A} and ω_α is its eigenvalue

\underline{A} has n eigenvectors and n eigenvalues

$$\sum_{j=1}^n A_{ij}x_j = \omega_i x_i \quad \text{for all } i \text{ 1 through } n$$

$$\underline{A}\underline{x} - \omega_\alpha \underline{x} = \underline{0} \quad \underline{0} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$|\underline{A} - \omega_\alpha \underline{I}| = 0$ "secular determinant"

$$(\underline{A} - \omega_\alpha \underline{I})_{ij} = a_{ij} - \omega_\alpha \delta_{ij}$$

solve for $\{\omega_\alpha\}$, then solve for $\{\underline{x}\}$

1.27 Discrete Dirac Notation

Discrete Dirac Notation

$\{\hat{e}_i\} \rightarrow n$ basis vectors in n dimensions

$|i\rangle = \hat{e}_i \rightarrow$ "ket vector", "ket" $1 \leq i \leq n$

$$|\alpha\rangle = \sum_{i=1}^n a_i |i\rangle \quad \{a_i\} \in \mathbb{C}$$

$|\alpha\rangle \rightarrow$ any vector in n dimensions

$\{|i\rangle\}$ "complete" in n dimensions

$$|\alpha\rangle = \vec{\alpha} = \underline{\alpha} = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{pmatrix} \quad \langle \alpha | = \vec{\alpha}^* = \underline{\alpha}^\dagger = \underline{\alpha}^\dagger = (\alpha_1^*, \alpha_2^*, \dots, \alpha_n^*)$$

$\langle \alpha | \rightarrow$ "bra vector", "bra"

$\langle \alpha | \alpha \rangle \rightarrow$ "bra-ket notation"

$$\langle \alpha | b \rangle = \vec{\alpha}^* \cdot \vec{b} = \sum_{i=1}^n \alpha_i^* b_i = (\alpha_1^*, \alpha_2^*, \dots) \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix}$$

$\langle \alpha | b \rangle \rightarrow$ scalar product, inner product, dot product

$$\langle \alpha | \alpha \rangle = \sum_{i=1}^n \alpha_i^* \alpha_i = \sum_i |\alpha_i|^2 = |\alpha|^2$$

$$\langle a | = \sum_{i=1}^n a_i^* \langle i | \quad |b\rangle = \sum_{j=1}^n b_j |j\rangle$$

$$\langle a | b \rangle = \sum_{i=1}^n \sum_{j=1}^n a_i^* b_j \langle i | j \rangle = \sum_{i=1}^n a_i^* b_i$$

$$\sum_{j=1}^n b_j \langle i | j \rangle = b_i = \sum_{j=1}^n b_j \delta_{ij}$$

$\langle i | j \rangle = \delta_{ij} \rightarrow$ "orthonormal basis set"

$$\langle j | a \rangle = \sum_{i=1}^n \langle j | i \rangle a_i = \sum_i \delta_{ij} a_i = a_j$$

$$a_j = \langle j | a \rangle \quad a_j^* = \langle a | j \rangle \quad \langle a | b \rangle^* = \langle b | a \rangle$$

$$|a\rangle = \sum_{i=1}^n a_i |i\rangle = \sum_{i=1}^n |i\rangle \langle i | a \rangle$$

$$\boxed{\hat{1} = \sum_{i=1}^n |i\rangle \langle i |} \quad \text{"Resolution of the Identity"}$$

"Change of Basis"

1.28 Matrix Operators

Matrix Operators

$$\mathcal{O}|\alpha\rangle = |\beta\rangle$$

\mathcal{O} → "operator": transforms a vector into another vector

$$\mathcal{O}|i\rangle = \sum_{j=1}^n O_{ij}|j\rangle \quad \{|i\rangle, |j\rangle\} \rightarrow \text{basis vectors}$$

$\underline{\underline{O}}$ → $n \times n$ matrix representation of \mathcal{O}

$$\langle i|\mathcal{O}|j\rangle = \langle i| \left(\sum_{j=1}^n O_{ij}|j\rangle \right) = \sum_j O_{ij} \langle i|j\rangle = \sum_j O_{ij} \delta_{ij} = O_{ii}$$

$$O_{ij} = \langle i|\mathcal{O}|j\rangle$$

$$\begin{aligned} \langle \alpha | \mathcal{O} | \beta \rangle &= \left(\sum_{i=1}^n \alpha_i^* \langle i | \right) \mathcal{O} \left(\sum_{j=1}^n \beta_j | j \rangle \right) \\ &= \sum_{i=1}^n \sum_{j=1}^n \alpha_i^* \beta_j \langle i | \mathcal{O} | j \rangle \end{aligned}$$

$$\boxed{\langle \alpha | \mathcal{O} | \beta \rangle = \sum_{i=1}^n \sum_{j=1}^n \alpha_i^* O_{ij} \beta_j}$$

$$\langle \alpha | \beta \rangle = \alpha^\dagger \beta = \underline{\alpha^\dagger} \underline{\beta}$$

$$\langle \alpha | \mathcal{O} | \beta \rangle = \alpha^\dagger \mathcal{O} \beta = \underline{\alpha^\dagger} \underline{\mathcal{O}} \underline{\beta}$$

1.29 Unitary Transformation

Unitary Transformation

$$\langle i|i\rangle = \delta_{ij} \quad \sum_{i=1}^n |i\rangle\langle i| = 1 \quad \text{basis 1}$$

$$\langle \alpha|\beta\rangle = \delta_{\alpha\beta} \quad \sum_{\alpha=1}^n |\alpha\rangle\langle \alpha| = 1 \quad \text{basis 2}$$

orthonormal basis sets, complete in n-dimensions

$$|\alpha\rangle = \underline{\underline{U}}|\kappa\rangle = \sum_{i=1}^n |i\rangle\langle i|\alpha\rangle = \sum_{i=1}^n U_{i\alpha}|i\rangle$$

$\underline{\underline{U}}$ → unitary transformation matrix

$U_{i\alpha} = \langle i|\alpha\rangle$ "overlap" of basis vectors $|i\rangle$ & $|\alpha\rangle$

$$|i\rangle = \underline{\underline{U}}|\kappa\rangle = \sum_{\alpha=1}^n |\alpha\rangle\langle \alpha|i\rangle = \sum_{\alpha=1}^n U_{\alpha i}^*|\alpha\rangle = \sum_{\alpha=1}^n (\underline{\underline{U}}^\dagger)_{\alpha i}|\alpha\rangle$$

$$\delta_{ij} = \langle i|j\rangle = \sum_{\alpha=1}^n \langle i|\alpha\rangle\langle \alpha|j\rangle = \sum_{\alpha=1}^n U_{i\alpha}(U^\dagger)_{\alpha j} = (\underline{\underline{U}}\underline{\underline{U}}^\dagger)_{ij}$$

$$\underline{\underline{U}}\underline{\underline{U}}^\dagger = \underline{\underline{I}} \rightarrow \underline{\underline{U}}^\dagger = \underline{\underline{U}}^{-1} \quad \text{unitary definition}$$

$$\underline{\underline{O}}|i\rangle = \sum_j |j\rangle\langle j|\underline{\underline{O}}|i\rangle = \sum_j O_{ji}|i\rangle$$

$$\underline{\underline{O}}|\alpha\rangle = \sum_\beta |\beta\rangle\langle \beta|\underline{\underline{O}}|\alpha\rangle = \sum_\beta O_{\alpha\beta}|\beta\rangle$$

$\underline{\underline{O}}$ → representation of $\underline{\underline{O}}$ in basis $\{|i\rangle\}$

$\underline{\underline{U}}\underline{\underline{O}}$ → representation of $\underline{\underline{O}}$ in basis $\{|\alpha\rangle\}$

$$\underline{\underline{U}}\underline{\underline{O}}|\alpha\rangle = \langle \alpha|\underline{\underline{O}}|\beta\rangle = \langle \alpha| \underline{\underline{U}}\underline{\underline{O}}|\beta\rangle$$

$$= \sum_{ij} \langle \alpha|i\rangle\langle i|\underline{\underline{O}}|j\rangle\langle j|\beta\rangle = \sum_{ij} (\underline{\underline{U}}^\dagger)_{\alpha i} O_{ij} U_{j\beta}$$

$$\underline{\underline{U}}\underline{\underline{O}} = \underline{\underline{U}}^\dagger \underline{\underline{O}} \underline{\underline{U}}$$

unitary transformation

$$\underline{\underline{O}} = \underline{\underline{U}} \underline{\underline{U}}^\dagger \underline{\underline{O}} \underline{\underline{U}}^\dagger$$

change of basis set

back transformation

$$\underline{\underline{O}} = \underline{\underline{U}} \underline{\underline{U}}^\dagger \underline{\underline{O}} \underline{\underline{U}}^\dagger = \underbrace{\underline{\underline{U}} \underline{\underline{U}}^\dagger}_{\underline{\underline{I}}} \underline{\underline{O}} \underbrace{\underline{\underline{U}} \underline{\underline{U}}^\dagger}_{\underline{\underline{I}}} = \underline{\underline{O}}$$

1.30 Hermitian Matrices

Hermitian Matrices

$$\underline{\underline{A}}^T = \underline{\underline{A}} \quad (\underline{\underline{A}}^T)_{ij} = (\underline{\underline{A}})_{ji}^*$$

1) n eigenvalues are real

$$\begin{array}{l} \underline{\underline{O}} \underline{\alpha} = \omega_\alpha \underline{\alpha} \\ \downarrow \\ \underline{\alpha}^T \underline{\underline{O}} \underline{\alpha} = \omega_\alpha \underline{\alpha}^T \underline{\alpha} \\ \downarrow \\ \omega_\alpha \underline{\alpha}^T \underline{\alpha} = \omega_\alpha^* \underline{\alpha}^T \underline{\alpha} \\ \downarrow \\ \underline{\alpha}^T \underline{\underline{O}}^T \underline{\alpha} = \omega_\alpha^* \underline{\alpha}^T \underline{\alpha} \end{array} \quad \begin{array}{l} \underline{\alpha}^T \underline{\underline{O}}^T = \omega_\alpha^* \underline{\alpha}^T \\ \downarrow \\ \underline{\alpha}^T \underline{\underline{O}} \underline{\alpha} = \omega_\alpha^* \underline{\alpha}^T \underline{\alpha} \\ \downarrow \\ \omega_\alpha^* \underline{\alpha}^T \underline{\alpha} = \omega_\alpha \underline{\alpha}^T \underline{\alpha} \end{array}$$

$\therefore \{\omega_\alpha\} \in \mathbb{R}$ Q.E.D.

2) n eigenvectors are orthogonal

$$\begin{array}{l} \underline{\underline{O}} \underline{\alpha} = \omega_\alpha \underline{\alpha} \\ \downarrow \\ \underline{\beta}^T \underline{\underline{O}} \underline{\alpha} = \omega_\alpha \underline{\beta}^T \underline{\alpha} \\ \downarrow \\ \omega_\alpha \underline{\beta}^T \underline{\alpha} = \omega_\beta \underline{\beta}^T \underline{\alpha} \end{array} \quad \begin{array}{l} \underline{\beta}^T \underline{\underline{O}}^T = \omega_\beta \underline{\beta}^T \\ \downarrow \\ \underline{\beta}^T \underline{\underline{O}} \underline{\alpha} = \omega_\beta \underline{\beta}^T \underline{\alpha} \\ \downarrow \\ (\omega_\alpha - \omega_\beta) \underline{\beta}^T \underline{\alpha} = 0 \end{array}$$

$$(\omega_\alpha - \omega_\beta) \underline{\beta}^T \underline{\alpha} = 0$$

if $\omega_\alpha \neq \omega_\beta$ then $\underline{\beta}^T \underline{\alpha} = 0$

$\underbrace{\underline{\alpha}^T \underline{\alpha} = 1}_{\text{normalized}}$ $\underbrace{\underline{\beta}^T \underline{\alpha} = 0}_{\text{orthogonal}}$

$\underbrace{\omega_\alpha = \omega_\beta}_{\text{orthonormal}}$

$$A_{ii} = A_{ii}^* \rightarrow \{A_{ii}\} \in \mathbb{R}$$

all diagonal elements are real

$$\begin{pmatrix} a_{11} + b_{11}i & a_{12} + b_{12}i & \dots & a_{1n} + b_{1n}i \\ a_{12} - b_{12}i & a_{22} + b_{22}i & \dots & a_{2n} + b_{2n}i \\ \vdots & \vdots & \ddots & \vdots \\ a_{1n} - b_{1n}i & a_{2n} - b_{2n}i & \dots & a_{nn} + b_{nn}i \end{pmatrix}$$

1.31 Matrix Diagonalization

Matrix Diagonalization

$$\underline{\underline{A}} = \underline{\underline{U}}^T \underline{\underline{\Lambda}} \underline{\underline{U}} \quad \underline{\underline{U}}^T = \underline{\underline{U}}^{-1}$$

$$\underline{\underline{\Lambda}} = \underline{\underline{U}} \underline{\underline{A}} \underline{\underline{U}}^T \quad \underline{\underline{U}}^T \underline{\underline{U}} = \underline{\underline{I}}$$

unitary transformation \leftrightarrow change of basis
 $\underline{\underline{A}} \rightarrow n \times n$ Hermitian matrix

$\underline{\underline{A}} \rightarrow \underline{\underline{A}}$ in diagonal basis set

$\underline{\underline{A}} = \underline{\underline{U}}^T \underline{\underline{A}} \underline{\underline{U}}$ $\underline{\underline{U}} \rightarrow$ unique unitary matrix which diagonalizes $\underline{\underline{A}}$

$$a_{ij} = \omega_i \delta_{ij}$$

$\{\omega_i\} \rightarrow$ n eigenvalues of $\underline{\underline{A}}$

$$\underline{\underline{\Lambda}} = \begin{pmatrix} \omega_1 & & & \\ & \omega_2 & & \\ & & \ddots & \\ & & & \omega_n \end{pmatrix}$$

$$|\alpha_i\rangle = \sum_{j=1}^n c_{ij} |j\rangle$$

$\{|j\rangle\} \rightarrow$ orthonormal basis vectors

$\{|\alpha\rangle\} \rightarrow$ orthonormal eigenvectors

$$c_{ij} = |\alpha_i\rangle_j = U_{ij}$$

$$\underline{\underline{U}} = (\underline{\underline{\alpha}}_1 \underline{\underline{\alpha}}_2 \dots \underline{\underline{\alpha}}_n)$$

$\underline{\underline{U}} \rightarrow$ matrix of eigenvectors of $\underline{\underline{A}}$

to find $\{\omega_i\}$, find $\underline{\underline{A}}$

to find $\underline{\underline{A}}$, find $\underline{\underline{U}}$

1.32 Matrix Commutators

Matrix Commutators

$\underline{A}, \underline{B} \rightarrow n \times n$ Hermitian matrices

$$[\underline{A}, \underline{B}] = \underline{A}\underline{B} - \underline{B}\underline{A} \quad \text{"commutator"}$$

$$\{\underline{A}, \underline{B}\} = \underline{A}\underline{B} + \underline{B}\underline{A} \quad \text{"anti-commutator"}$$

if $[\underline{A}, \underline{B}] = \underline{0}$, then \underline{A} and \underline{B} commute

and with same \underline{U} :

$$\begin{aligned} \underline{U}^\dagger \underline{A} \underline{U} &= \underline{a} \\ \underline{U}^\dagger \underline{B} \underline{U} &= \underline{b} \end{aligned} \quad \underline{a}, \underline{b} \rightarrow \text{diagonal}$$

can know $\{w_\alpha\}$ and $\{w_\beta\}$ both
exactly simultaneously

$\{| \alpha \rangle\}$ and $\{| \beta \rangle\}$ are the same

if $[\underline{A}, \underline{B}] \neq \underline{0}$ then "uncertainty"
between \underline{A} and \underline{B}

1.33 Matrix Functions

Matrix Functions

$\underline{A} \rightarrow n \times n$ Hermitian matrix

$\underline{U} \rightarrow n \times n$ unitary matrix which diagonalizes \underline{A}

$$\underline{A} = \underline{U}^{\dagger} \underline{A} \underline{U} \quad \underline{A} = \begin{pmatrix} \omega_1 & & & \\ & \omega_2 & & 0 \\ & & \ddots & \\ 0 & & & \omega_n \end{pmatrix}$$

$$\underline{A}^2 = \underline{A}\underline{A} \quad \underline{A}^3 = \underline{A}\underline{A}\underline{A} \quad \underline{A}^n = \prod_{i=1}^n \underline{A}$$

$$\underline{A} \underline{A}^{-1} = \underline{I} \quad \underline{A}^{\frac{1}{2}} \underline{A}^{\frac{1}{2}} = \underline{A} \quad \underline{A}^{\frac{n}{n}} = \underline{I}$$

$$\exp(\underline{A}) = \underline{I} + \underline{A} + \frac{1}{2} \underline{A}^2 + \frac{1}{6} \underline{A}^3 + \dots$$

$$\underline{f}(\underline{A}) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{d^n}{dx^n} f(0) \right) \underline{A}^n \quad \text{Taylor series approach}$$

$$(\underline{a}^n)_{ii} = a_{ii}^n$$

$$(\underline{f}(\underline{a}))_{ii} = f(a_{ii}) \quad \underline{f}(\underline{a}) = \begin{pmatrix} f(a_{11}) & & & \\ & \ddots & & 0 \\ & & f(a_{22}) & \\ 0 & & & \ddots \end{pmatrix}$$

$$\underline{f}(\underline{A}) = \underline{U} \underline{f}(\underline{a}) \underline{U}^{\dagger}$$

$$\underline{f}(\underline{A}) = \underline{U} \underline{f}(\underline{U}^{\dagger} \underline{A} \underline{U}) \underline{U}^{\dagger} \quad \text{diagonalization approach}$$

2 Quantum Chemistry

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2.1 Introduction

Introduction to Quantum Chemistry

Classical Mechanics - everyday-sized objects

Quantum Mechanics - very, very small objects

Classical

large
heavy

continuous

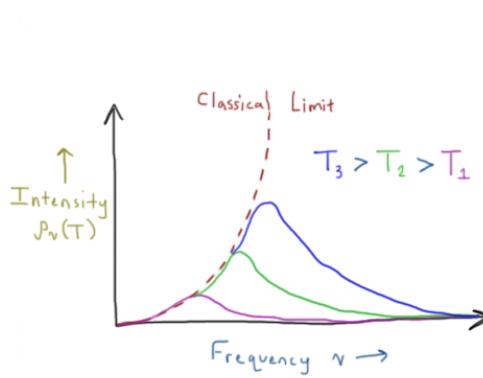
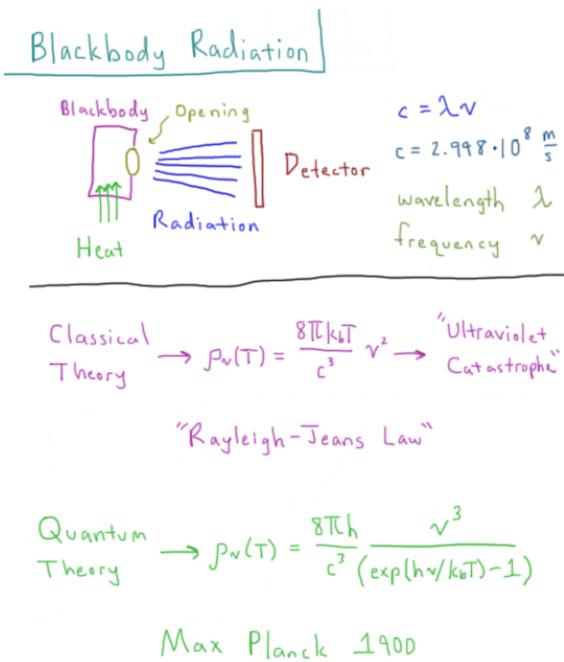
Newton's Eq.
trajectory
deterministic
intuitive

Quantum

small
light

discrete / quantized
Schrodinger Eq.
wavefunction
probabilistic
non-intuitive

2.2 Blackbody Radiation

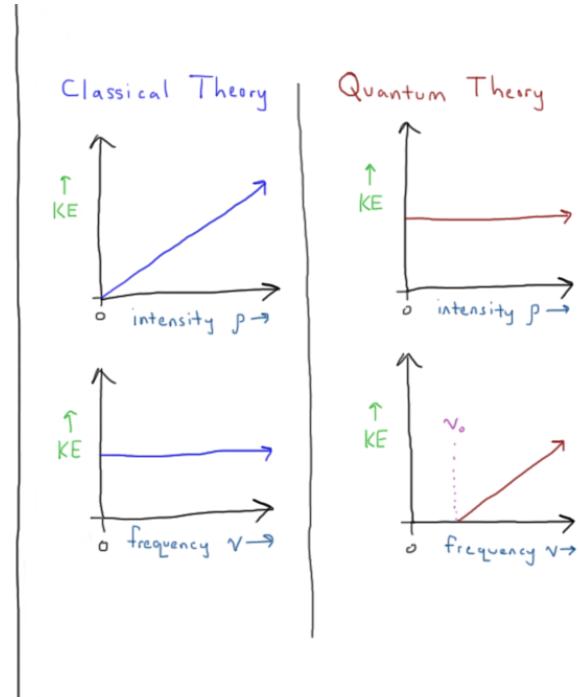
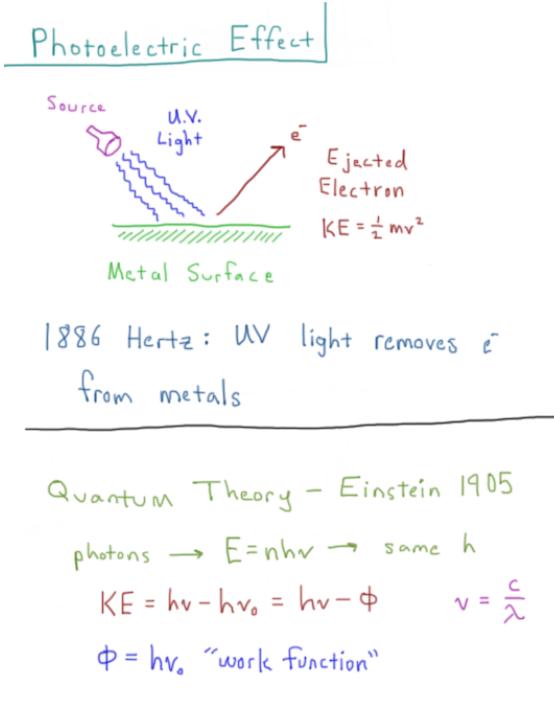


Match exp't when $h = 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$
"Planck's constant"

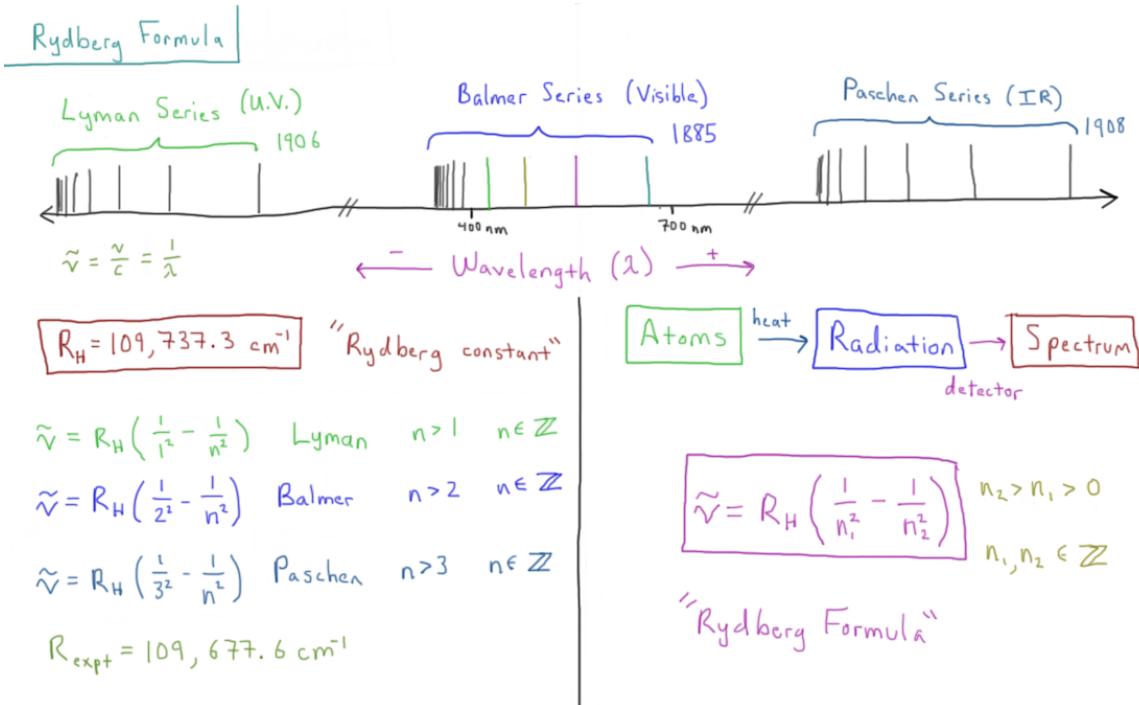
Assumed energy of particles is quantized

$$E = nh\nu \quad n \in \mathbb{Z}$$

2.3 Photoelectric Effect



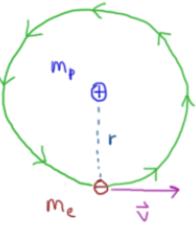
2.4 Rydberg Formula



2.5 Bohr Hydrogen Model 1: Radius

Bohr Hydrogen Model - Radius

Angular vs.	Linear Motion
$m \leftrightarrow I$	$I = mr^2$
$v \leftrightarrow \omega$	$v = rw = 2\pi r\nu$
$p \leftrightarrow l$	$p = mv \quad l = I\omega$
$T \leftrightarrow T$	$T = \frac{1}{2}mv^2 = \frac{1}{2}\frac{p^2}{m}$ $T = \frac{1}{2}I\omega^2 = \frac{1}{2}\frac{l^2}{I}$



$\oplus \leftarrow \ominus \rightarrow$

$$\begin{pmatrix} \text{Coulomb} \\ \text{Force} \end{pmatrix} = \begin{pmatrix} \text{Centrifugal} \\ \text{Force} \end{pmatrix}$$

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r} \quad \text{Two Unknowns} \rightarrow v, r$$

Bohr 1911 → Assume angular momentum is quantized

$$l = m_e v r = nh \quad \text{Two Equations} \rightarrow \text{Two Unknowns}$$

"h-bar" $\hbar = \frac{h}{2\pi} \quad n \geq 1, n \in \mathbb{Z}$

$$v = \frac{nh}{m_e r} \quad \frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e}{r} \left(\frac{nh}{m_e r} \right)^2 = \frac{m_e n^2 \hbar^2}{r^3 m_e^2}$$

$$r m_e c^2 = 4\pi\epsilon_0 n^2 \hbar^2$$

$$r = \frac{4\pi\epsilon_0 \hbar^2 n^2}{m_e c^2} = 5.29 \cdot 10^{-11} \text{ m} = 52.9 \text{ pm}$$

$r = 0.529 \text{ \AA}$

$$1 \text{ \AA} = 100 \text{ pm} = 10^{-10} \text{ m}$$

"Bohr radius" → a_0

2.6 Bohr Hydrogen Model 2: Energy

Bohr Hydrogen Model - Energy

$$\text{Coulomb Force} = \text{Centrifugal Force}$$

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r}$$

$$l = m_e v r = n\hbar \quad n \in \mathbb{Z}$$

$$r = \frac{4\pi\epsilon_0 \hbar^2 n^2}{m_e e^2} = 0.529 \text{ \AA} \quad \text{"Bohr radius"}$$

$$E = T + V = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$\frac{e^2}{8\pi\epsilon_0 r^2} = \frac{m_e v^2}{2r} \quad \frac{1}{2} m_e v^2 = \frac{e^2}{8\pi\epsilon_0 r}$$

$$E = \frac{-e^2}{8\pi\epsilon_0 r} = \frac{-e^2}{8\pi\epsilon_0 r} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2 n^2} \right)$$

$$E = \frac{-m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n^2} \right)$$

$$\Delta E = E_{n_2} - E_{n_1} = h\nu = hc\tilde{\nu} = \frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$\nu = \frac{c}{\lambda} \quad \tilde{\nu} = \frac{1}{\lambda}$$

$$\tilde{\nu} = R_H \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad n_2 > n_1 \quad n_1, n_2 \in \mathbb{Z}$$

$$R_H = \frac{m_e e^4}{8\pi^2 \epsilon_0^2 c \hbar^3} \quad R_H = 109,737.3 \text{ cm}^{-1}$$

accurate w/in 0.05% of experiment

$$m_p \neq \infty \quad m_e \rightarrow \mu = \left(\frac{1}{m_e} + \frac{1}{m_p} \right)^{-1} = \frac{m_e m_p}{m_e + m_p}$$

$$m_p = 1.672 \cdot 10^{-27} \text{ kg} \quad \mu = 0.9995 m_e$$

$$m_e = 9.109 \cdot 10^{-31} \text{ kg}$$

$$m_e \rightarrow \mu \quad R_1 = 109,676 \text{ cm}^{-1}$$

$$R_H \rightarrow R_1 \quad \text{w/in 0.001% error } (109677.6 \text{ cm}^{-1})$$

2.7 Wave-Particle Duality

Wave-Particle Duality

Einstein 1906 → Light is a particle and a wave

De Broglie 1924 → Matter is too!

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \lambda \rightarrow \text{wavelength}$$

$p \rightarrow \text{momentum}$

if large $m \rightarrow \lambda \approx 0$

if small $m \rightarrow \lambda > 0$

$$\lambda_{\text{electron}} \sim \lambda_{\text{x-ray}}$$

de Broglie waves for electron interference

$$2\pi r = n\lambda$$

(Circumference)

n (Wavelength)

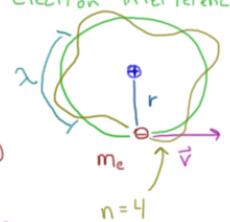
$$2\pi r = n\lambda = \frac{nh}{p} = \frac{nh}{mv}$$

$$mv r = \frac{nh}{2\pi}$$

$$l = mv r \quad h = \frac{h}{2\pi}$$

$l = nh$

Bohr
Quantization
Condition



2.8 Uncertainty Principle in Measurement

Heisenberg Uncertainty Principle

$\Delta x \approx \lambda_{\text{photon}}$

$p = \frac{h}{\lambda} \rightarrow \lambda \downarrow = p \uparrow \quad \Delta x \downarrow = \Delta p \uparrow$

$$\boxed{\Delta x \Delta p \geq \frac{\hbar}{2}}$$

1920's

Heisenberg
Uncertainty
Principle

Macroscopic → Not Important

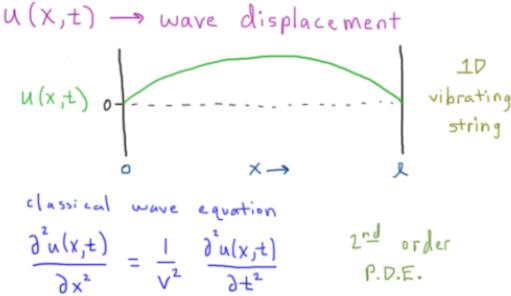
Microscopic → Important!

Bohr Model → $\Delta x = \Delta p = 0 \rightarrow$ bad!

Need more general theory

2.9 Classical Wave Equation

Classical Wave Equation



Assume $u(x,t) = X(x) T(t)$ Separation of Variables

$$\frac{\partial^2 (X(x) T(t))}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 (X(x) T(t))}{\partial t^2}$$

$$T(t) \frac{d^2 X(x)}{dx^2} = \frac{X(x)}{v^2} \frac{d^2 T(t)}{dt^2}$$

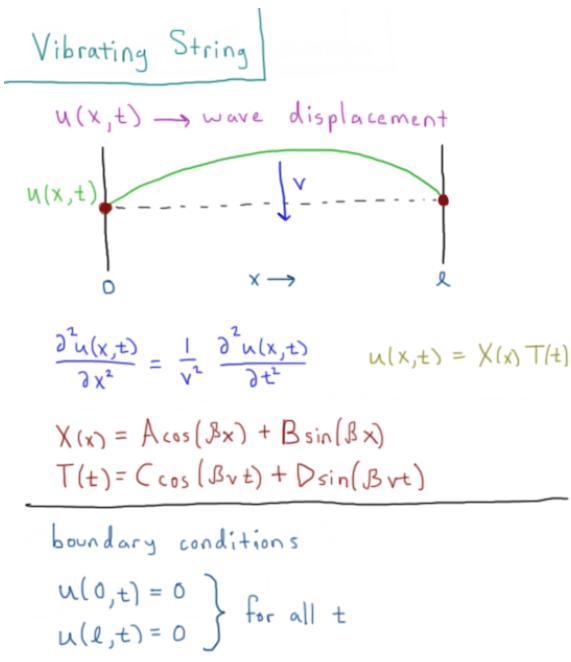
$$\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} = \frac{1}{v^2 T(t)} \frac{d^2 T(t)}{dt^2} = k = -\beta^2$$

$$\frac{d^2 X(x)}{dx^2} = -\beta^2 X(x) \quad \frac{d^2 T(t)}{dt^2} = -\beta^2 v^2 T(t)$$

$$X(x) = A \cos(\beta x) + B \sin(\beta x)$$

$$T(t) = C \cos(\beta v t) + D \sin(\beta v t)$$

2.10 Vibrating String



$$X(0) = 0 = A \cos(\beta \cdot 0) + B \sin(\beta \cdot 0)$$

$$X(l) = 0 = B \sin(\beta l) \quad \beta l = \sin^{-1}(0) = n\pi$$

$$X(x) = B \sin\left(\frac{n\pi x}{l}\right) \quad \beta = \frac{n\pi}{l} \quad n \in \mathbb{Z}$$

$$T(t) = C \cos\left(\frac{n\pi v t}{l}\right) + D \sin\left(\frac{n\pi v t}{l}\right)$$

$$= E \cos\left(\frac{n\pi v t}{l} + \phi\right) \quad \phi \rightarrow \text{phase factor}$$

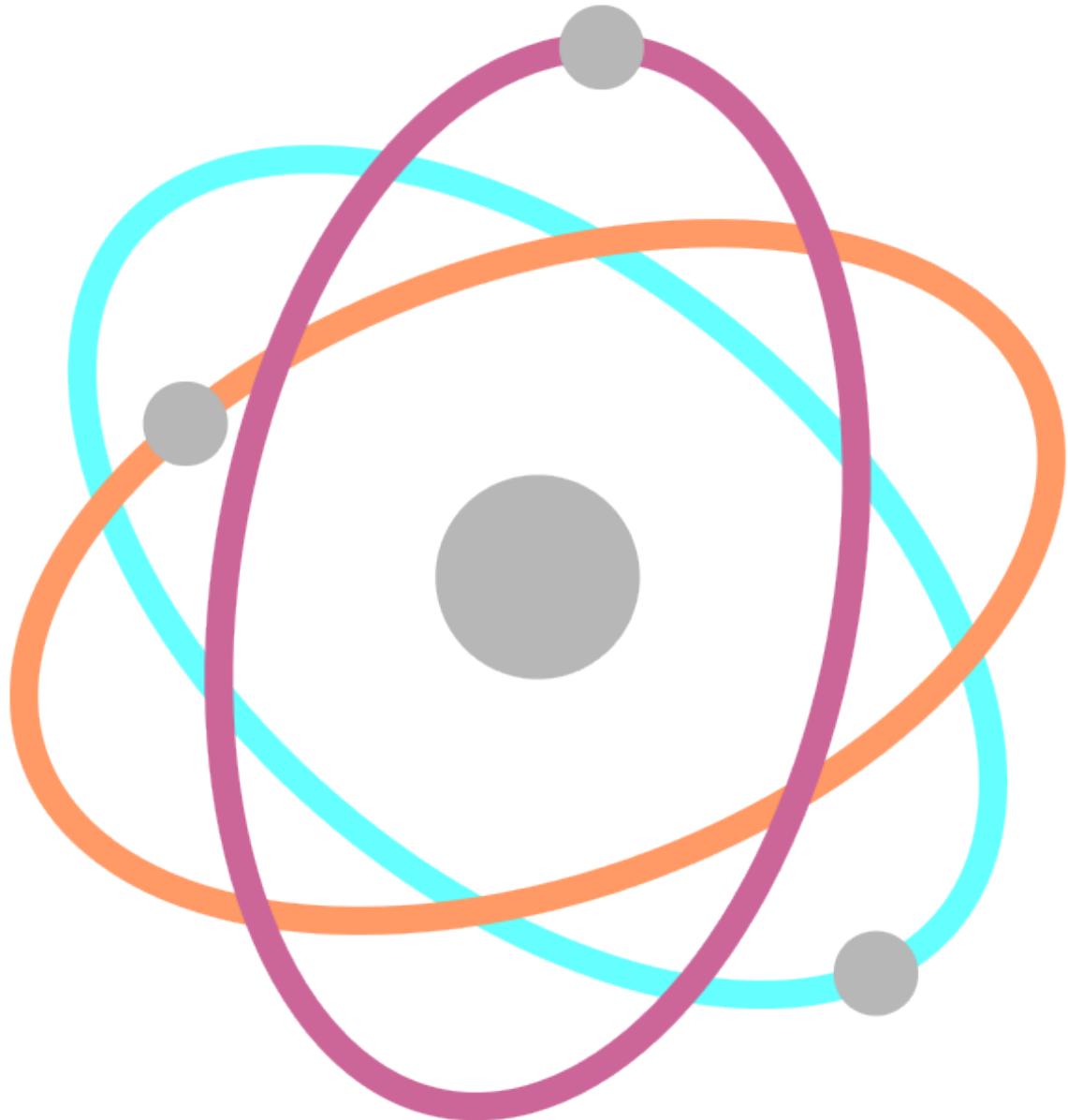
$$u(x,t) = A \cos\left(\frac{n\pi v t}{l} + \phi\right) \sin\left(\frac{n\pi x}{l}\right)$$

$$u(x,t) = \sum_{n=1}^{\infty} A_n \cos\left(\frac{n\pi v t}{l} + \phi_n\right) \sin\left(\frac{n\pi x}{l}\right)$$

$$u(x,t) = \sum_{n=1}^{\infty} A_n u_n(x,t) \quad \text{can represent any function w/ } \{A_n, \phi_n\}$$

$\{u_n(x,t)\} \rightarrow$ "normal modes" "standing waves"

2.11 Vibrating String Animation



2.12 Schrodinger Equation "Derivation"

Schrodinger Equation "Derivation"

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x,t)}{\partial t^2} \Rightarrow u(x,t) = \underbrace{\psi(x) \cos(\omega t)}_{\text{spatial amplitude}}$$

$$\cos(\omega t) \frac{d^2 \psi(x)}{dx^2} = -\frac{\omega^2}{v^2} \psi(x) \cos(\omega t)$$

$$\frac{d^2 \psi(x)}{dx^2} + \frac{\omega^2}{v^2} \psi(x) = 0 \quad \omega = 2\pi\nu \quad v\lambda = v$$

$$\frac{\omega^2}{v^2} = \frac{4\pi^2 \cancel{\lambda^2}}{\cancel{\nu^2} \lambda^2} = \frac{4\pi^2}{\lambda^2}$$

$$\frac{d^2 \psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2} \psi(x) = 0$$

$$E = \underbrace{\frac{p^2}{2m}}_{\text{kinetic}} + \underbrace{V(x)}_{\text{potential}} \quad \text{Total Energy}$$

$$p = \sqrt{2m(E - V(x))}$$

$$\lambda = \frac{h}{p} \quad \text{de Broglie waves} \quad \hbar = \frac{h}{2\pi c}$$

$$\frac{4\pi^2}{\lambda^2} = \frac{4\pi^2 p^2}{h^2} = \frac{p^2}{\hbar^2} = \frac{2m(E - V(x))}{\hbar^2}$$

$$\frac{d^2 \psi(x)}{dx^2} + \frac{2m(E - V(x))}{\hbar^2} = 0$$

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

"Time-Independent Schrödinger Equation"

$\psi(x) \rightarrow \text{"wavefunction"}$

2.13 Operators

Operators

Do something
to object → Create
new object

$$\hat{O} f(x) = g(x)$$

examples of operators

$\frac{d}{dx} f(x)$	$\int f(x) dx$
$\sqrt{f(x)}$	$2f(x)$
	$(f(x))^n$

Linear Operators

$$\hat{O} [c_1 f_1(x) + c_2 f_2(x) + \dots] = c_1 \hat{O} f_1(x) + c_2 \hat{O} f_2(x) + \dots$$

$$\hat{O} \left(\sum_{i=1}^n c_i f_i(x) \right) = \sum_{i=1}^n c_i \hat{O} f_i(x)$$

$$\{c_i\} \in \mathbb{C}$$

$$\frac{d}{dx} (2x^2 + 3x) = 2 \frac{d}{dx}(x^2) + 3 \frac{d}{dx}(x) \quad \checkmark$$

$$\sqrt{2x^2 + 3x} \neq 2\sqrt{x^2} + 3\sqrt{x} \quad \times$$

$(\text{Classical}) \rightarrow (\text{Linear, Quantum})$
 $(\text{Properties}) \rightarrow (\text{Mechanical Operator})$

$\hat{p} \rightarrow \text{momentum}$

$\hat{x} \rightarrow \text{position}$

$\hat{T} \rightarrow \text{kinetic energy}$

$\hat{V} \rightarrow \text{potential energy}$

$\hat{H} \rightarrow \text{total energy "Hamiltonian"}$

2.14 Eigenvalues and Eigenfunctions

Eigenvalues

Operator (function) = constant (^{same} function)

$$\hat{O} \underbrace{f(x)}_{\text{function}} = \omega \underbrace{(f(x))}_{\text{constant}}$$

"Eigenfunction" "Eigenvalue"

"The Eigenvalue problem": Given \hat{O} ,
find the set of $f(x)$ and w

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \Psi(x) = E \Psi(x)$$

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

$$\boxed{\hat{H} \Psi(x) = E \Psi(x)}$$

"Hamiltonian Operator"

$$E, \quad \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad \text{total energy}$$

$$T, \quad \hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad \text{kinetic energy}$$

$$V, \quad \hat{V} = V(x) \quad \text{potential energy}$$

$$p_x, \quad \hat{p}_x = -i\hbar \frac{d}{dx} \quad \text{momentum in } x\text{-direction}$$

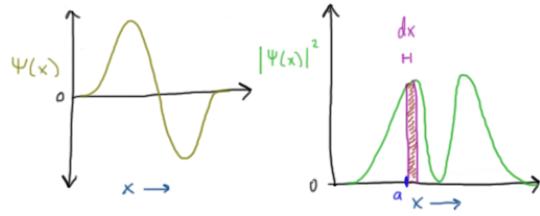
$$x, \quad \hat{x} = x \quad x\text{-position}$$

$$\hat{p}_x^2 = -\hbar^2 \frac{d^2}{dx^2} \quad \text{momentum squared}$$

$$x^2, \quad \hat{x}^2 = x^2 \quad \text{position squared}$$

2.15 Interpreting the Wavefunction

Interpreting the Wavefunction



$\Psi(x) \rightarrow$ wavefunction

$|\Psi(x)|^2 = \Psi^*(x)\Psi(x) \rightarrow$ probability density

$\Psi(x) \in \mathbb{C}$ in general $i = \sqrt{-1}$

$$\Psi(x) = \text{Re}(x) + i\text{Im}(x)$$

$$\Psi^*(x) = \text{Re}(x) - i\text{Im}(x)$$

$$|\Psi(x)|^2 = |\Psi^*(x)\Psi(x)|^2 = |\text{Re}^2(x) + \text{Im}^2(x)|$$

"Born Interpretation"

$\Psi^*(x)\Psi(x)dx =$ (Probability Particle is Between x and $x+dx$)

for small dx

$$\int_{-\infty}^{\infty} dx \Psi^*(x)\Psi(x) = 1$$

"Normalization"

2.16 Particle in a Box

Particle in a Box

Need to specify $V(x)$ for \hat{H}

$$V(x) = \begin{cases} 0 & \text{if } 0 < x < l \\ \infty & \text{otherwise} \end{cases}$$

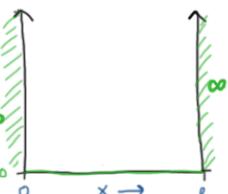
$$\hat{H}\Psi(x) = E\Psi(x)$$

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

$$\frac{d^2\Psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \Psi(x)$$

$$\Psi(x) = A\cos(kx) + B\sin(kx) \quad k = \frac{\sqrt{2mE}}{\hbar}$$

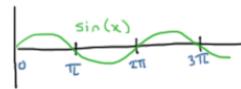
$$\left. \begin{array}{l} \Psi(x \leq 0) = 0 \rightarrow \Psi(0) = 0 \\ \Psi(x \geq l) = 0 \rightarrow \Psi(l) = 0 \end{array} \right\} \begin{array}{l} \text{boundary} \\ \text{conditions} \end{array}$$



$$\Psi(0) = A\cos(k \cdot 0) + B\sin(k \cdot 0) = A \rightarrow A = 0$$

$$\Psi(l) = B\sin(kl) = 0 \quad kl = \sin^{-1}(0) = n\pi$$

$$k = \frac{n\pi}{l} \quad n \in \mathbb{Z}$$



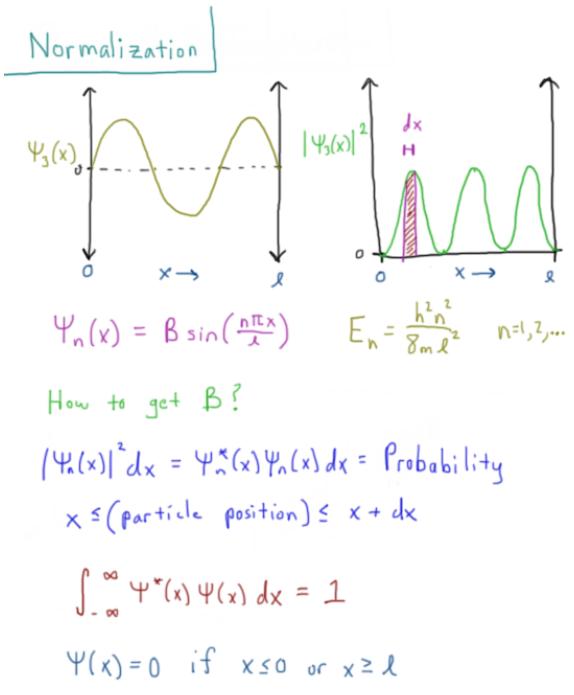
$$\boxed{\Psi_n(x) = B\sin\left(\frac{n\pi x}{l}\right)} \quad n = 1, 2, \dots$$

$$\frac{n\pi}{l} = \frac{\sqrt{2mE}}{\hbar} \quad \frac{n^2\hbar^2\pi^2}{l^2} = 2mE$$

$$\boxed{E_n = \frac{\hbar^2 n^2}{8m l^2}} \quad n = 1, 2, \dots$$

$n \rightarrow$ quantum number

2.17 Normalization



$$1 = \int_0^l [B \sin(n\pi x/l)]^* [B \sin(n\pi x/l)] dx$$

$$1 = B^2 \int_0^l \sin^2(n\pi x/l) dx$$

$$\sin^2(kx) = \frac{1}{2}(1 - \cos(2kx))$$

$$1 = B^2/2 \int_0^l (1 - \cos(2n\pi x/l)) dx$$

$$\frac{2}{B^2} = \left(x - \frac{l}{2\pi n} \sin\left(\frac{2n\pi x}{l}\right) \Big|_0^l \right)$$

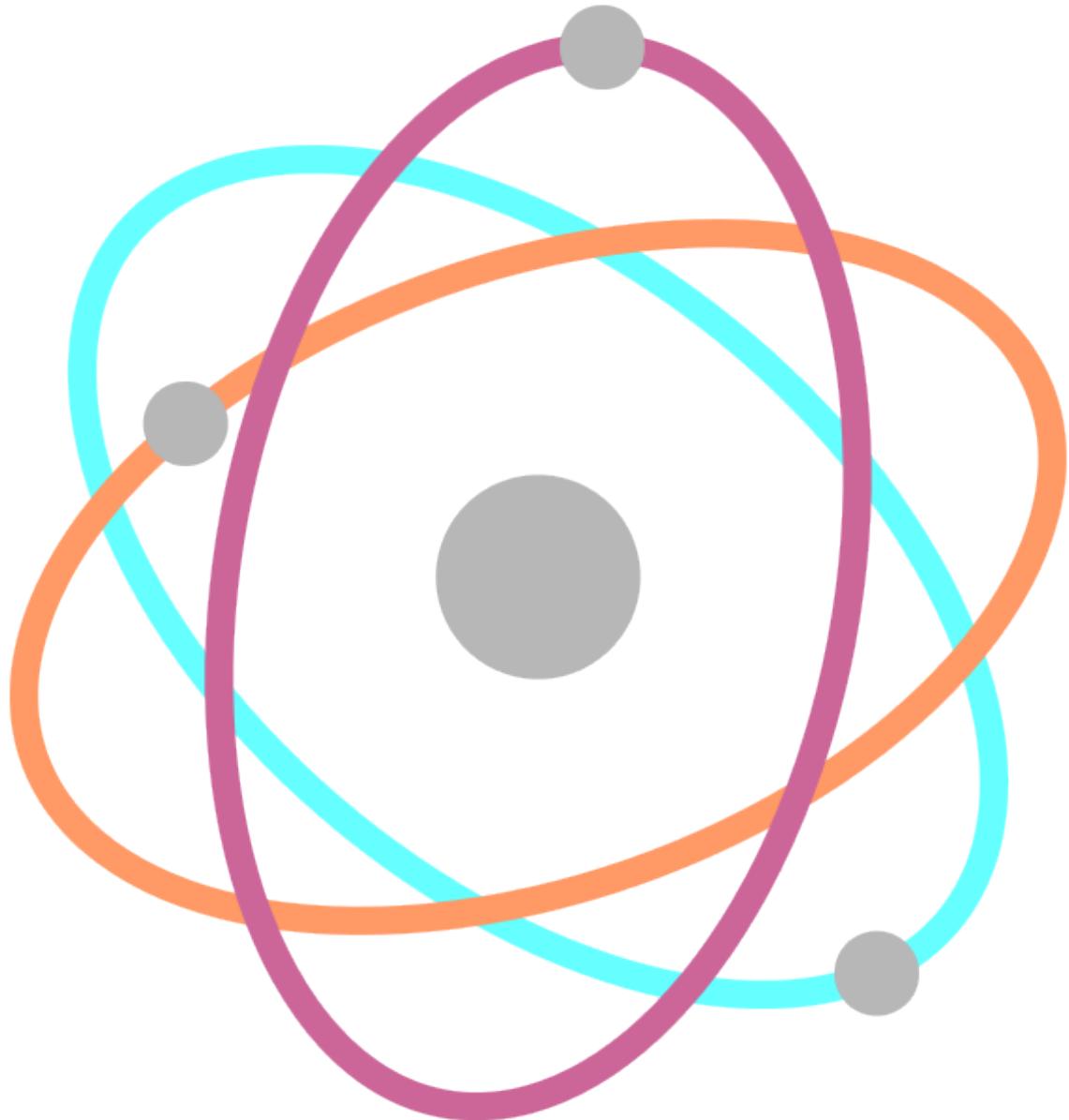
$$\frac{2}{B^2} = \left[l - \frac{l}{2\pi n} \sin(2\pi n) \right] - \left[0 - \frac{l}{2\pi n} \sin(0) \right]$$

$$\frac{2}{B^2} = l \quad B = \sqrt{\frac{2}{l}}$$

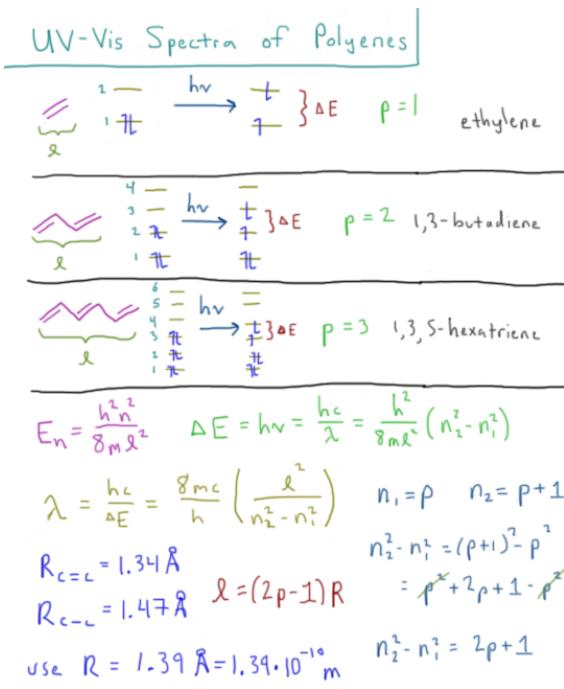
$$\boxed{\Psi_n(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)}$$

$B \rightarrow$ "normalization constant"

2.18 Particle in a Box Wavefunction Plots



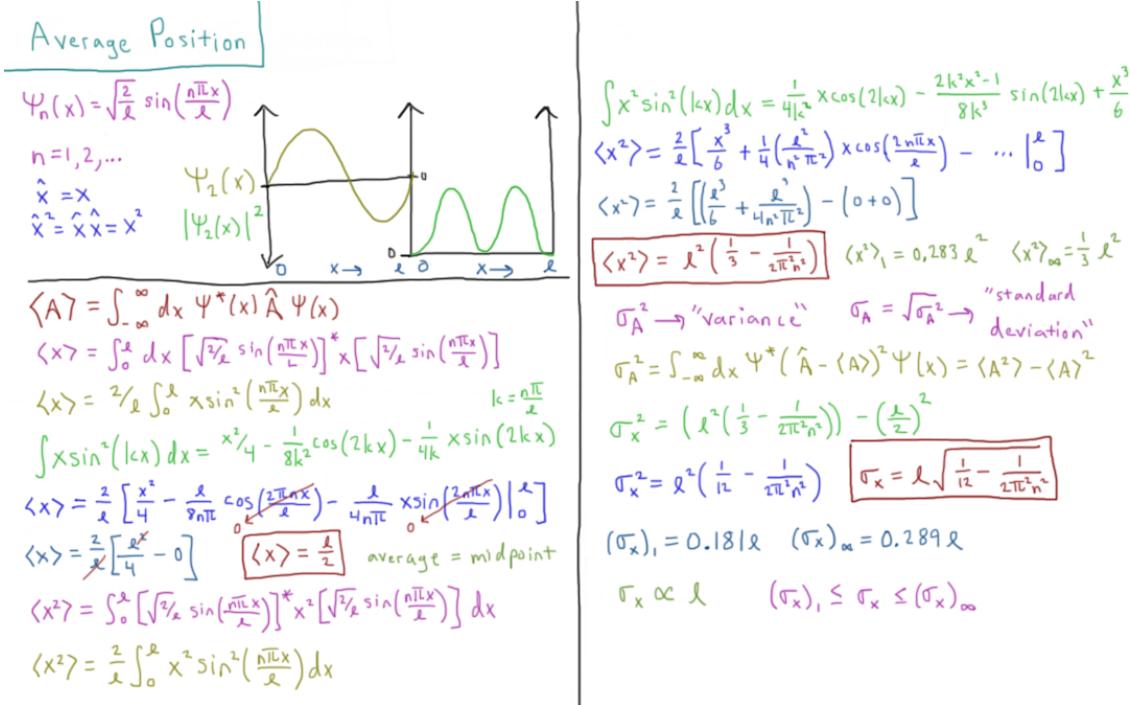
2.19 UV-Vis Spectra of Polyenes



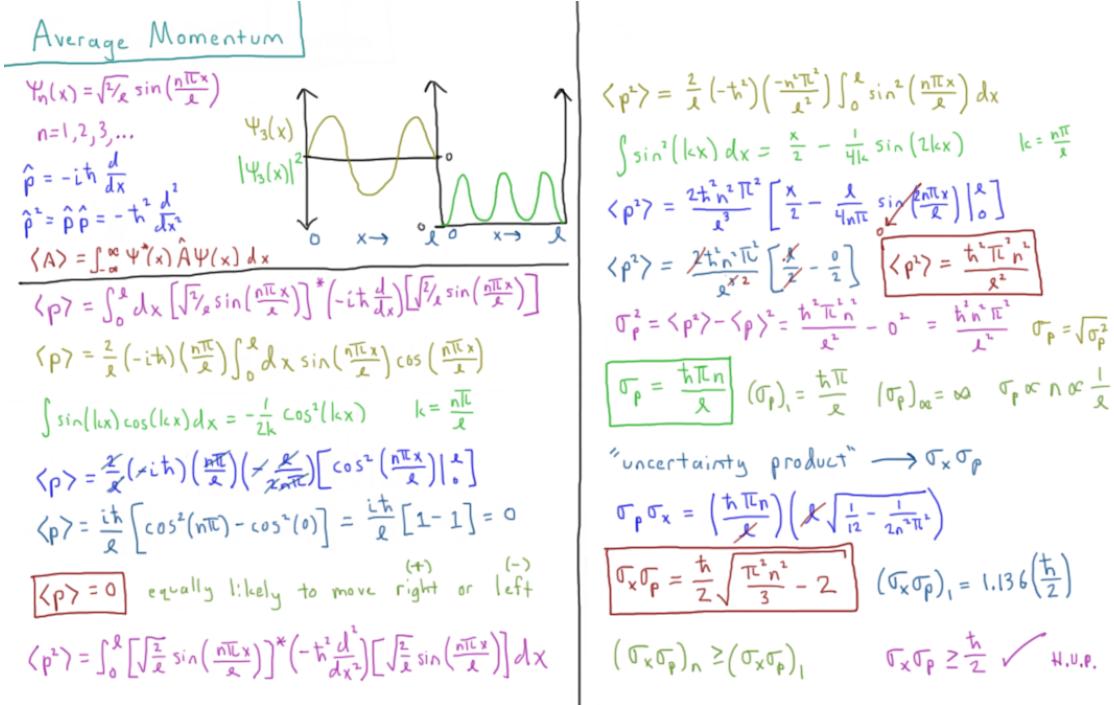
$$\lambda = \frac{8mc}{h} \left(\frac{R^2 (2\rho - 1)^2}{2\rho + 1} \right)$$

ρ	$\lambda_{\text{calc}} (\text{nm})$	$\lambda_{\text{expt}} (\text{nm})$
1	21	171
2	115	217
3	228	258
4	347	304
5	469	334

2.20 Average Position



2.21 Average Momentum



2.22 3-D Particle in a Box

3D Particle in a Box

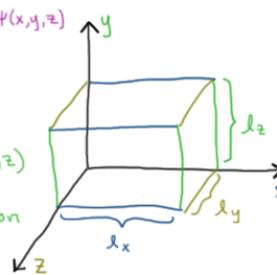
$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) = E \Psi(x, y, z)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(x, y, z) = E \Psi(x, y, z)$$

3-D Schrödinger Equation

$$0 \leq i \leq l_i ; i = x, y, z$$



$$\Psi(0, y, z) = \Psi(l_x, y, z) = 0 ; (y, z) \in \mathbb{R}$$

$$\Psi(x, 0, z) = \Psi(x, l_y, z) = 0 ; (x, z) \in \mathbb{R}$$

$$\Psi(x, y, 0) = \Psi(x, y, l_z) = 0 ; (x, y) \in \mathbb{R}$$

$$\Psi(x, y, z) = X(x) Y(y) Z(z)$$

$$E = E_x + E_y + E_z \quad \text{"separation of variables"}$$

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X(x) \rightarrow X_{n_x}(x) = A_x \sin\left(\frac{n_x \pi x}{l_x}\right)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y(y) \rightarrow Y_{n_y}(y) = A_y \sin\left(\frac{n_y \pi y}{l_y}\right)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} = E_z Z(z) \rightarrow Z_{n_z}(z) = A_z \sin\left(\frac{n_z \pi z}{l_z}\right)$$

$$\int_0^{l_x} dx \int_0^{l_y} dy \int_0^{l_z} dz \Psi^*(x, y, z) \Psi(x, y, z) = 1$$

$$A = A_x A_y A_z = \left(\sqrt{\frac{2}{l_x}}\right) \left(\sqrt{\frac{2}{l_y}}\right) \left(\sqrt{\frac{2}{l_z}}\right) = \sqrt{\frac{8}{l_x l_y l_z}}$$

$$\Psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi x}{l_x}\right) \sin\left(\frac{n_y \pi y}{l_y}\right) \sin\left(\frac{n_z \pi z}{l_z}\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2}{8m} \left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right]$$

2.23 Degeneracy

Degeneracy

$$\Psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin\left(\frac{n_x \pi x}{\ell_x}\right) \sin\left(\frac{n_y \pi y}{\ell_y}\right) \sin\left(\frac{n_z \pi z}{\ell_z}\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{\ell_x^2} + \frac{n_y^2}{\ell_y^2} + \frac{n_z^2}{\ell_z^2} \right)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

$$\hat{H} \Psi_{n_x n_y n_z}(x, y, z) = E_{n_x n_y n_z} \Psi_{n_x n_y n_z}(x, y, z)$$

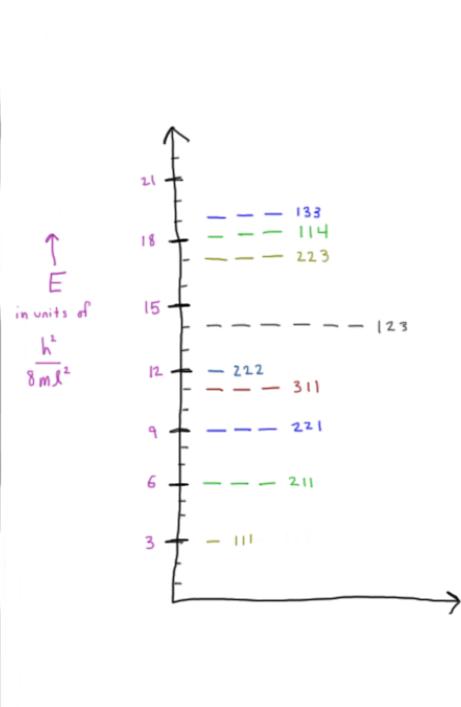
$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

if $\ell_x = \ell_y = \ell_z \rightarrow$ cube!

$$E_{n_x n_y n_z} = \frac{\hbar^2}{8m \ell^2} (n_x^2 + n_y^2 + n_z^2)$$

$E_{112} = E_{121} = E_{211} \rightarrow$ triply degenerate!
(3-fold)

Symmetry \rightarrow Degeneracy



2.24 Postulates of Quantum Mechanics 1: Wavefunction

Postulates of Quantum Mechanics 1

The state of the system is completely specified by $\Psi(\vec{r}, t)$

$$\Psi^*(\vec{r}, t)\Psi(\vec{r}, t) dxdydz = \begin{cases} \text{probability particle} \\ \text{is in volume element} \\ dx dy dz \text{ at } \vec{r} \text{ at } t \end{cases}$$

(Measurable Properties) \rightarrow Observables

If we know $\Psi(\vec{r}, t) \rightarrow$ we know all observables Q.M.

If we know \vec{r}_0, \vec{p}_0 and $F(\vec{r}, t)$ \rightarrow we know $\vec{r}(t)$ C.M.

$$\iiint_{\text{space}} \Psi^*(\vec{r}, t)\Psi(\vec{r}, t) dxdydz = 1$$

$$\int_{\mathbb{R}^3} d\tau \Psi^*(\vec{r}, t)\Psi(\vec{r}, t) dxdydz = 1$$

$$d\tau = dxdydz \quad \int_{\mathbb{R}^n} \rightarrow \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty}$$

$\Psi(\vec{r}, t)$ must be "normalizable" \rightarrow "square integrable"

$$\int_{\mathbb{R}} [f(x)]^2 dx = C$$

$$|C| < \infty$$

2.25 Postulates of Quantum Mechanics 2: Operators

Postulates of Quantum Mechanics 2

For every classical observable, there corresponds a linear, Hermitian, quantum mechanical operator

Linear: $\hat{O}\left(\sum_{i=1}^n c_i \psi_i\right) = \sum_{i=1}^n c_i \hat{\psi}_i \quad \{c_i\} \in \mathbb{C}$

$$x^n \checkmark \quad \frac{d^n}{dx^n} \checkmark \quad \int (\) dx \checkmark \quad \sqrt{X} (\)^2 X$$

Hermitian \rightarrow explained later

Observable	Symbol	Operator
Total Energy	E	$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$
Potential Energy	V	$\hat{V} = V(x, y, z)$
Kinetic Energy	T	$\hat{T} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Position	\vec{x}	$\hat{\vec{x}} = \vec{x}$ $\hat{\vec{r}} = \hat{x}\hat{i} + \hat{y}\hat{j} + \hat{z}\hat{k}$
Momentum	\vec{p}_x	$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ $\hat{p} = -i\hbar \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right)$

2.26 Postulates of Quantum Mechanics 3: Measurement

Postulates of Quantum Mechanics 3

Any measurement of observable A
will only yield eigenvalues of \hat{A}

$$\hat{A}\Psi_n = a_n \Psi_n \quad \{a_n\} \in \mathbb{R}$$

$\{\Psi_n\} \rightarrow$ "eigenfunctions"

$\{a_n\} \rightarrow$ "eigenvalues"

can only measure $a \in \{a_n\}$

if $\Psi = \Psi_i$, can only measure a_i

if $\Psi = \sum_{i=1}^n c_i \Psi_i$, can only measure

$$\{a_i\} \mid c_i \neq 0$$

2.27 Postulates of Quantum Mechanics 4: Expectation Values

Postulates of Quantum Mechanics 4

If a system is described by a wavefunction Ψ , then the average value of A is given by:

$$\langle A \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau}{\int_{-\infty}^{\infty} \Psi^* \Psi d\tau}$$

if normalized, $\int_{-\infty}^{\infty} \Psi^* \Psi d\tau = 1$

then $\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau$

$$\hat{A}\Psi_n = a_n \Psi_n \quad \{\Psi_n\} \rightarrow \text{eigenfunctions}$$

$$\text{if } \Psi = \Psi_i \quad \langle A \rangle = \int d\tau \Psi_i^* \hat{A} \Psi_i = a_i \int d\tau \Psi_i \Psi_i$$

then $\langle A \rangle = a_i$

$$\text{if } \Psi = \Psi_i \quad \langle A \rangle = a_i \quad \langle A^2 \rangle = a_i^2$$

$$\sigma_A = \langle A^2 \rangle - \langle A \rangle^2 = (a_i^2) - (a_i)^2 = 0$$

then $\sigma_A = 0$

2.28 Postulates of Quantum Mechanics 5: Schrodinger Equation

Postulates of Quantum Mechanics 5

The wavefunction evolves in time according to the Time-Dependent

Schrödinger Equation

$$\hat{H}\Psi(\vec{r},t) = i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t} \quad \text{T.D.S.E.}$$

$$\Psi(\vec{r},t) = \psi(\vec{r})\phi(t) \quad \text{"separation of variables"}$$

$$\hat{H}\Psi(\vec{r})\phi(t) = i\hbar \frac{\partial \psi(\vec{r})\phi(t)}{\partial t}$$

$$\phi(t)\hat{H}\Psi(\vec{r}) = i\hbar\psi(\vec{r})\frac{d\phi(t)}{dt} \quad \hat{H} \rightarrow \begin{matrix} \text{time} \\ \text{independent} \end{matrix}$$

$$\frac{\hat{H}\Psi(\vec{r})}{\Psi(\vec{r})} = \frac{i\hbar \frac{d}{dt}\phi(t)}{\phi(t)} = E \rightarrow \text{constant}$$

$$\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \quad \text{T.I.S.E.}$$

$$\frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = \frac{-iE}{\hbar}$$

$$\int \frac{d\phi(t)}{\phi(t)} = \int \frac{-iE dt}{\hbar}$$

$$\ln[\phi(t)] = \frac{-iEt}{\hbar}$$

$$\phi(t) = e^{-iEt/\hbar}$$

$$\Psi(\vec{r},t) = \psi(\vec{r})e^{-iEt/\hbar}$$

2.29 Commutators

Commutators

$$\hat{A}\hat{B}f(x) = \hat{A}(\hat{B}f(x)) \quad \text{operators act right to left}$$

if $\hat{A} + \hat{B}$ "commute" then $\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x)$

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad \text{"commutator"}$$

if $\hat{A} + \hat{B}$ commute, then $[\hat{A}, \hat{B}] = 0$

if $[\hat{A}, \hat{B}] \neq 0$, "uncertainty" exists

$$\sigma_A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \quad \sigma_B = \sqrt{\langle B^2 \rangle - \langle B \rangle^2}$$

$$\boxed{\sigma_A \sigma_B \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle|} = \frac{1}{2} \left| \int \psi^* [\hat{A}, \hat{B}] \psi d\tau \right|$$

$$\hat{p}_x = -i\hbar \frac{d}{dx} \quad \hat{x} = x$$

$$\begin{aligned} [\hat{p}_x, \hat{x}] f(x) &= (\hat{p}_x \hat{x} - \hat{x} \hat{p}_x) f(x) \\ &= (-i\hbar \frac{d}{dx})(x) f(x) - (x)(-i\hbar \frac{d}{dx}) f(x) \\ &= -i\hbar \left(f(x) + x \frac{df(x)}{dx} \right) + i\hbar x \frac{df(x)}{dx} \\ &= -i\hbar \left(f(x) + x \cancel{\frac{df(x)}{dx}} - x \cancel{\frac{df(x)}{dx}} \right) \\ &= -i\hbar f(x) \end{aligned}$$

$$\boxed{[\hat{p}_x, \hat{x}] = -i\hbar}$$

$$\sigma_{p_x} \sigma_x \geq \frac{1}{2} \left| \int \psi^* [\hat{p}_x, \hat{x}] \psi d\tau \right|$$

$$\geq \frac{1}{2} \left| \int \psi^* (-i\hbar) \psi d\tau \right|$$

$$\geq \frac{1}{2} |(-i\hbar) \int \psi^* \psi d\tau| = \frac{1}{2} |-i\hbar| = \frac{\hbar}{2}$$

$$\boxed{\sigma_{p_x} \sigma_x \geq \frac{\hbar}{2}} \quad \text{Heisenberg Uncertainty Principle}$$

2.30 Hermitian Operators

Hermitian Operators

Measured properties must be eigenvalues

$$\hat{A}\Psi_n = a_n \Psi_n$$

$$\langle A \rangle = \int \Psi^* \hat{A} \Psi d\tau = \int \Psi^* a \Psi d\tau = a \int \Psi^* \Psi d\tau = a$$

Physical observables must be real

$$\{a_n\} \subset \mathbb{R} \rightarrow a_n = a_n^*$$

$$\hat{A}^* \Psi_n^* = a_n^* \Psi_n^*$$

$$\langle A \rangle^* = \int \Psi \hat{A}^* \Psi^* d\tau = \int \Psi a_n^* \Psi^* d\tau = a_n^* \int \Psi \Psi^* d\tau = a_n^* = a$$

if Hermitian: $\int \Psi^* \hat{A} \Psi d\tau = \int \Psi \hat{A}^* \Psi^* d\tau$

$$\boxed{\langle A \rangle^* = \langle A \rangle}$$

$$\int \Psi_n^* \hat{A} \Psi_n d\tau = \int \Psi_n \hat{A}^* \Psi_n^* d\tau$$

Eigenfunctions

$$\int_{\mathbb{R}} f^*(x) \hat{A} f(x) dx = \int_{\mathbb{R}} f(x) \hat{A}^* f^*(x) dx$$

General

$$\int_{\mathbb{R}} f_m^*(x) \hat{A} f_n(x) dx = \int_{\mathbb{R}} f_n(x) \hat{A}^* f_m^*(x) dx$$

Most general

2.31 Dirac Notation

Dirac Notation

$$|n\rangle = \Psi_n(x) \quad \text{"ket"}$$

$$\langle m| = \Psi_m^*(x) \quad \text{"bra"}$$

$$\langle m|n\rangle = \int_{-\infty}^{\infty} \Psi_m^*(x) \Psi_n(x) dx \quad \text{"bra-ket"}$$

$$\langle m|\hat{A}|n\rangle = \int_{-\infty}^{\infty} \Psi_m^*(x) \hat{A} \Psi_n(x) dx$$

"matrix element"

$$\langle n|n\rangle = \int_{-\infty}^{\infty} \Psi_n^*(x) \Psi_n(x) dx$$

normalization integral

$$\langle n|\hat{A}|n\rangle = \int_{-\infty}^{\infty} \Psi_n^*(x) \hat{A} \Psi_n(x) dx$$

expectation value integral

$$\langle A \rangle = \frac{\langle n|\hat{A}|n\rangle}{\langle n|n\rangle} \quad \begin{matrix} \text{expectation} \\ \text{value} \end{matrix}$$

$$\langle m|A|n\rangle = \langle n|A|m\rangle^* \quad \begin{matrix} \text{Hermitian} \\ \text{definition} \end{matrix}$$

2.32 Orthogonality

Orthogonality

if $\int_{-\infty}^{\infty} dx \Psi_m^*(x) \Psi_n(x) = \langle m|n \rangle = 0$

then Ψ_m and Ψ_n are "orthogonal"

$$|n\rangle = f_n(x) \quad \langle m| = f_m^*(x)$$

$$\langle m|\hat{A}|n\rangle = \int_{-\infty}^{\infty} dx \Psi_m^*(x) \hat{A} \Psi_n(x)$$

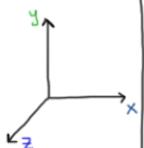
\hat{A} → linear, Hermitian operator

$|m\rangle, |n\rangle$ → eigenfunctions of \hat{A}

$$\begin{aligned} \hat{A}|n\rangle &= a_n|n\rangle & \{a_n, a_m\} \in \mathbb{R} \\ \hat{A}|m\rangle &= a_m|m\rangle \end{aligned}$$

$$\langle m|\hat{A}|n\rangle = \langle m|a_n|n\rangle = a_n\langle m|n\rangle$$

$$\langle m|\hat{A}|n\rangle = \langle n|\hat{A}|m\rangle^* = \langle n|a_m^*|m\rangle = a_m^*\langle n|m\rangle$$



$$a_n\langle m|n\rangle = a_m^*\langle n|m\rangle = a_m\langle m|n\rangle$$

$$(a_n - a_m)\langle m|n\rangle = 0$$

$$\text{if } a_n \neq a_m \quad \langle m|n\rangle = 0$$

$|m\rangle$ and $|n\rangle$ are orthogonal

Eigenfunctions of Hermitian operators are orthogonal
(if non-degenerate)

2.33 Superposition Principle 1: Basis Sets

Superposition Principle - Basis Set

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sum_{n=1}^{\infty} c_n |n\rangle = |f\rangle$$

$\{|n\rangle\}$ → "basis set"

$|n\rangle$ → "basis function"

$\{c_n\} \in \mathbb{C}$ → coefficients

$f(x)$ → any function in the space of $\{|n\rangle\}$

$$\langle m|n\rangle = \int_{-\infty}^{\infty} dx \psi_m^* \psi_n = \delta_{mn}$$

$$\delta_{mn} = \begin{cases} 1 & \text{if } m=n \\ 0 & \text{if } m \neq n \end{cases} \quad \text{"Kronecker delta"}$$

$$\langle m|f\rangle = \sum_{n=1}^{\infty} c_n \langle m|n\rangle = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m$$

$$|f\rangle = \sum_{n=1}^{\infty} c_n |n\rangle = \sum_{n=1}^{\infty} |n\rangle \langle n|f\rangle = \left(\sum_{n=1}^{\infty} |n\rangle \langle n| \right) |f\rangle$$

$$\boxed{\sum_{n=1}^{\infty} |n\rangle \langle n| = 1}$$

"Resolution of the Identity"

statement of "completeness" of basis set

2.34 Superposition Principle 2: Expectation Values

Superposition Principle - Expectation Values

$$f(x) = |f\rangle \quad |n\rangle = \psi_n(x) \quad \langle m| = \psi_m^*(x)$$

$$\langle m|n\rangle = \int_R \psi_m^*(x) \psi_n(x) dx \quad \hat{H}|n\rangle = E_n|n\rangle$$

$$\langle m|A|n\rangle = \int_R \psi_m^*(x) \hat{A} \psi_n(x) dx \quad \{|n\rangle\}$$

$$|f\rangle = \sum_{n=1}^{\infty} c_n |n\rangle$$

$$\langle E \rangle = \langle f | H | f \rangle = \left(\sum_{m=1}^{\infty} c_m^* \langle m| \right) \hat{H} \left(\sum_{n=1}^{\infty} c_n |n\rangle \right)$$

$$\langle E \rangle = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \underbrace{\langle m | \hat{H} | n \rangle}_{\langle m | \hat{H} | n \rangle = \langle m | E_n | n \rangle = E_n \langle m | n \rangle = E_n \delta_{mn}}$$

$$\langle E \rangle = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n E_n \delta_{mn} = \sum_{m=1}^{\infty} c_m^* c_m E_m$$

$$\boxed{\langle E \rangle = \sum_{m=1}^{\infty} |c_m|^2 E_m}$$

$$E_{\text{expt}} \in \{E_n\}$$

$$\langle E \rangle = \underbrace{\sum_{n=1}^{\infty} |c_n|^2 E_n}_{\text{weighted average}} = \sum_{n=1}^{\infty} p_n E_n$$

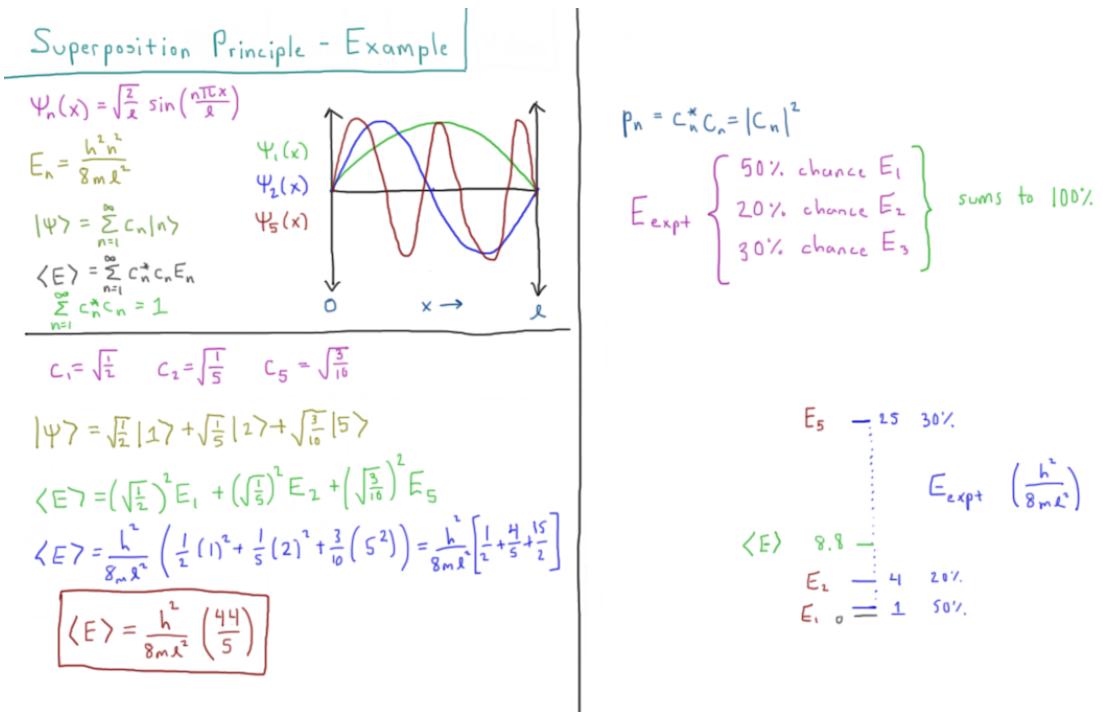
probability of measuring E_n

$$\boxed{p_n = c_n^* c_n = |c_n|^2}$$

$$1 = \sum_{n=1}^{\infty} p_n = \sum_{n=1}^{\infty} c_n^* c_n \quad \text{if } \langle m|n \rangle = \delta_{mn}$$

normalization orthonormal basis set

2.35 Superposition Principle 3: Example



2.36 Commuting Operators

Commuting Operators

If \hat{A} and \hat{B} have the same $\{|n\rangle\}$,
then $[\hat{A}, \hat{B}] = 0$

$$\hat{A}|n\rangle = a_n|n\rangle \quad \hat{B}|n\rangle = b_n|n\rangle$$

$$|\psi\rangle = \sum_n c_n|n\rangle$$

$$[\hat{A}, \hat{B}]|\psi\rangle = \sum_n [\hat{A}, \hat{B}]|n\rangle = \sum_n (\hat{A}\hat{B} - \hat{B}\hat{A})|n\rangle$$

$$= \sum_n (\hat{A}\hat{B}|n\rangle - \hat{B}\hat{A}|n\rangle)$$

$$= \sum_n (b_n\hat{A}|n\rangle - a_n\hat{B}|n\rangle)$$

$$= \sum_n (b_n a_n|n\rangle - a_n b_n|n\rangle)$$

$$= \sum_n (a_n b_n - a_n b_n)|n\rangle$$

$\underset{0}{\cancel{a_n b_n}}$ for all n

$$= \sum_n (0)|n\rangle = 0 \quad \therefore [\hat{A}, \hat{B}] = 0$$

$$[\hat{p}_x, \hat{x}] \neq 0$$

different eigenfunctions

cannot measure exactly, simultaneously

2.37 Time Dependence

Time Dependence

$\Psi_n(\vec{r}, t) \rightarrow$ eigenfunction of \hat{H}

$$\Psi_n(\vec{r}, t) = \psi_n(\vec{r}) e^{-iE_nt/\hbar}$$

$$|\Psi(\vec{r}, t)|^2 = (\psi_n^*(\vec{r}) e^{+iE_nt/\hbar})(\psi_n(\vec{r}) e^{-iE_nt/\hbar}) \\ = \psi_n^*(\vec{r}) \psi_n(\vec{r}) e^{+iE_nt/\hbar - iE_nt/\hbar} \\ = \psi_n^*(\vec{r}) \psi_n(\vec{r})$$

$$|\Psi_n(\vec{r}, t)|^2 = |\psi_n(\vec{r})|^2$$

"stationary states"

$$\Psi(\vec{r}, t) = \sum_{n=1}^{\infty} c_n \psi_n(\vec{r}) e^{-iE_nt/\hbar}$$

$$|\Psi(\vec{r}, t)|^2 = \left(\sum_{m=1}^{\infty} c_m^* \psi_m^*(\vec{r}) e^{+iE_mt/\hbar} \right) \cdot \\ \left(\sum_{n=1}^{\infty} c_n \psi_n(\vec{r}) e^{-iE_nt/\hbar} \right)$$

$$|\Psi(\vec{r}, t)|^2 = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_m^* c_n \psi_m^*(\vec{r}) \psi_n(\vec{r}) e^{-i(E_m - E_n)t/\hbar}$$

$$= \sum_{n=1}^{\infty} c_n^* c_n |\psi_n(\vec{r})|^2 + \sum_{m=1}^{\infty} \sum_{n=m+1}^{\infty} c_m^* c_n \psi_m^*(\vec{r}) \psi_n(\vec{r})$$

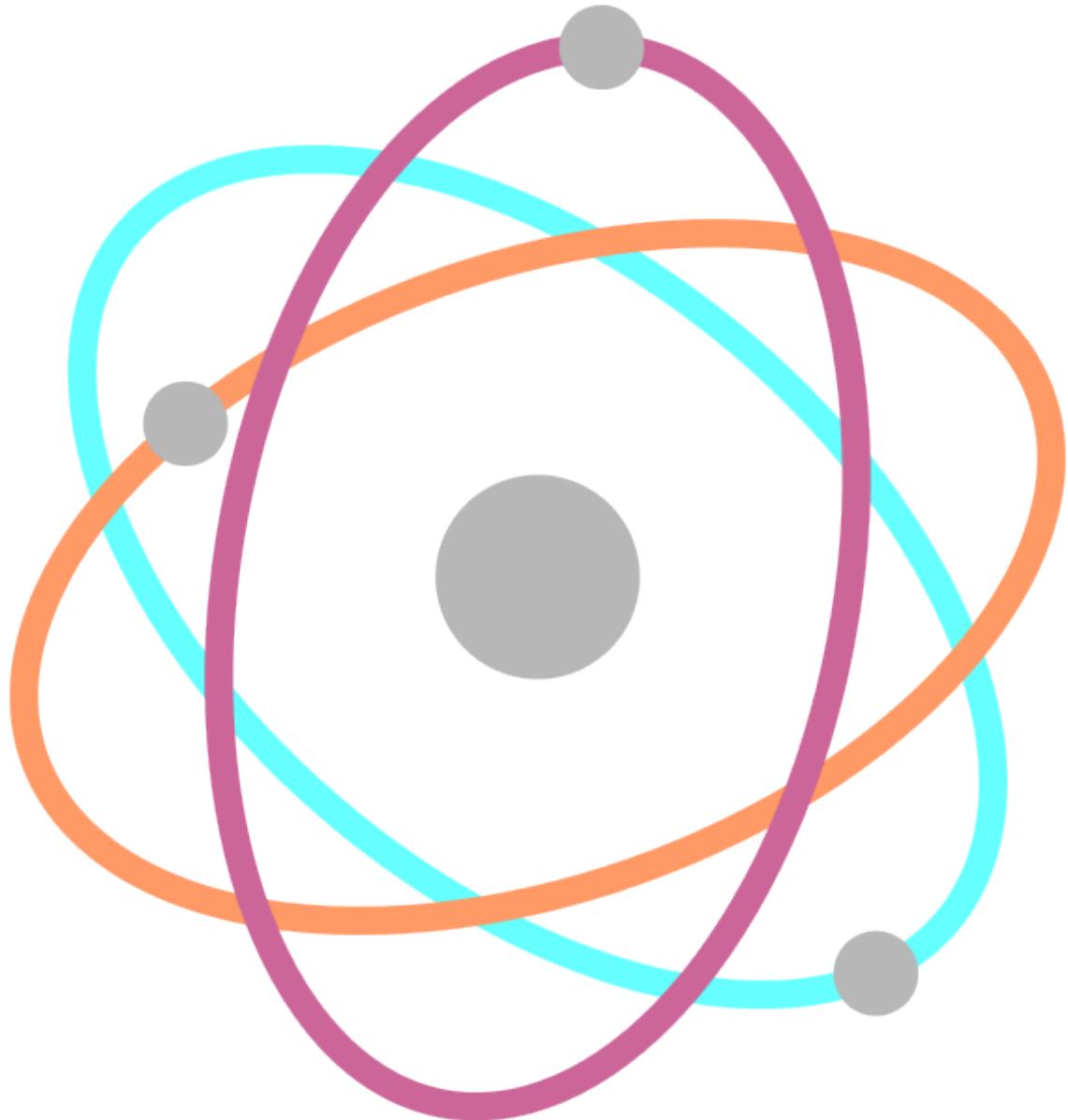
$$\Delta E_{mn} = E_m - E_n \quad 2(e^{i\Delta E_{mn}t/\hbar} + e^{-i\Delta E_{mn}t/\hbar})$$

$$\cos(\Delta Et) = \frac{1}{2}(e^{i\Delta Et} + e^{-i\Delta Et}) \quad 4\cos(\Delta E_{mn}t/\hbar)$$

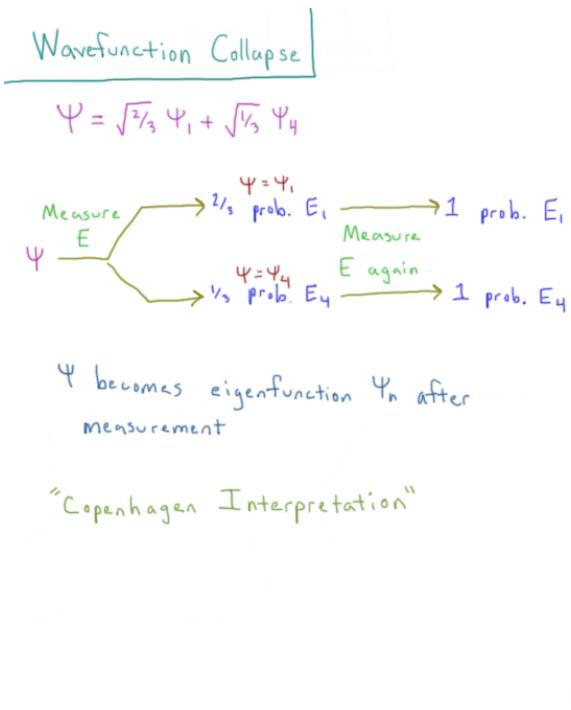
oscillation over time

$\Delta E_{mn} \rightarrow$ greater ΔE gives faster oscillation

2.38 Time Dependence Animation



2.39 Wavefunction Collapse



2.40 Schrodinger's Cat

Schrodinger's Cat

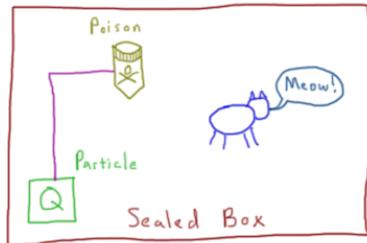
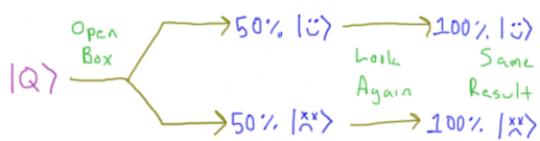
1935 Schrödinger

Quantum particle in binary state

$|Y\rangle = |\psi\rangle = \text{Alive}$

$|N\rangle = |\bar{\psi}\rangle = \text{Dead}$

$$|Q\rangle = \sqrt{\frac{1}{2}} |Y\rangle + \sqrt{\frac{1}{2}} |N\rangle$$



Cat is both alive and dead
until measurement

2.41 Correspondence Principle

Correspondence Principle

Quantum Mechanics $\xrightarrow{\text{Certain Limits}}$ Classical Mechanics

Limit of: $E_n = \frac{\hbar^2 n^2}{8m\ell^2}$ P.I.B.

- High Energy $E_n = (n + \frac{1}{2})\hbar\sqrt{\frac{k}{m}}$ H.O.
- Large Mass $E_J = \frac{\hbar^2}{2mR^2} J(J+1)$ R.R.
- Large Length

$$\lim_{\ell \rightarrow \infty} (E_n) = 0 \quad \lim_{m \rightarrow \infty} (E_n) = 0$$

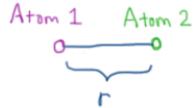
$$\lim_{n \rightarrow \infty} \left(\frac{E_n}{E_{n-1}} \right) = 0$$

if $m = 1 \text{ kg}$
 $\ell = 1 \text{ m}$
 $k = 1 \text{ N/m}$

$$\left. \begin{array}{l} E_1 \approx 10^{-70} \text{ J} \quad \text{P.I.B.} \\ E_1 \approx 10^{-35} \text{ J} \quad \text{H.O.} \\ E_1 \approx 10^{-68} \text{ J} \quad \text{R.R.} \end{array} \right\} \begin{array}{l} \text{QM is} \\ \text{inconsequential} \\ \text{at macroscopic} \\ \text{scales} \end{array}$$

2.42 Harmonic Oscillator Model

Harmonic Oscillator Model

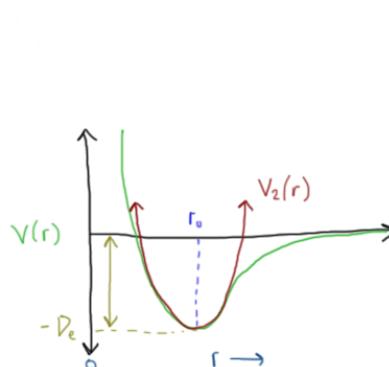
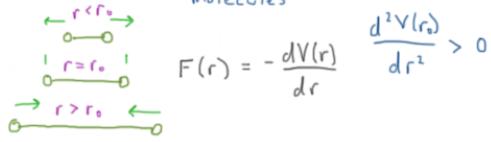


Want model for $V(r)$ $0 < r \leq \infty$

High energy \rightarrow dissociation $\rightarrow V(\infty) = 0$

Condensed phases \rightarrow resists compression $\rightarrow V(0) = \infty$

Gas phase \rightarrow finite size molecules $\rightarrow \frac{dV(r_0)}{dr} = 0$



$V(r) \rightarrow$ complicated

$V_2(r) \rightarrow$ quadratic polynomial

$$V_2(r) = -D_e + \frac{1}{2}k(r-r_0)^2$$

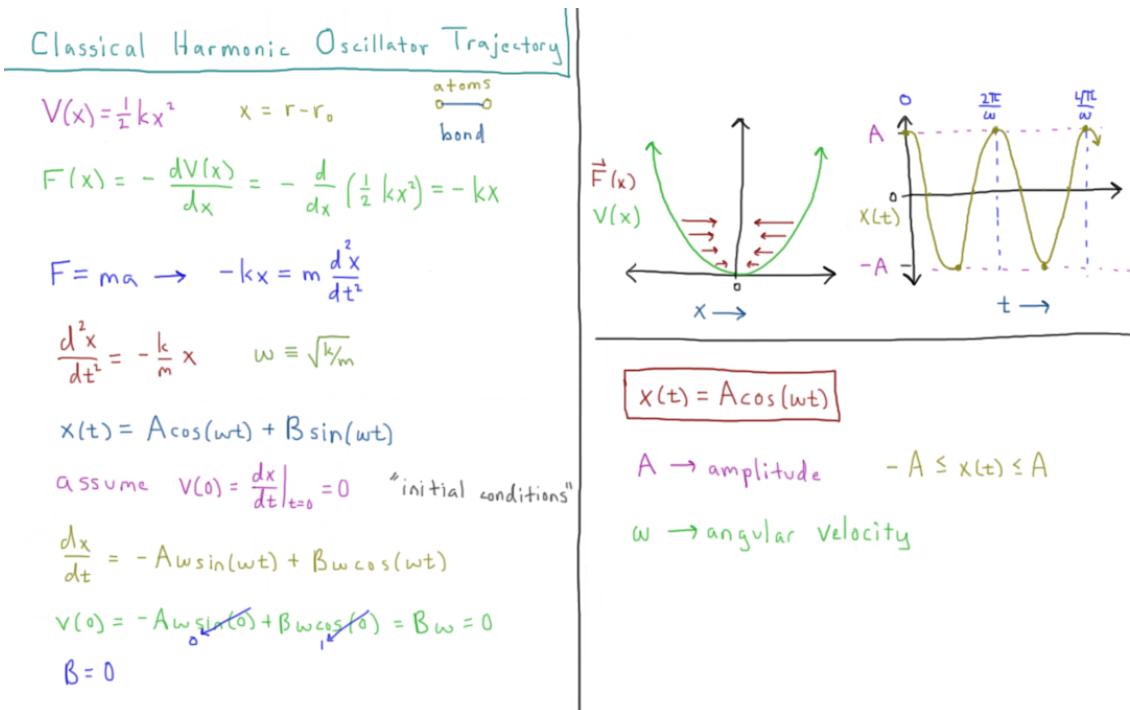
$$x = r - r_0$$

$$V(x) = V_2(r) + D_e$$

$$V(x) = \frac{1}{2}kx^2$$

$$k = \left. \frac{d^2V(r)}{dr^2} \right|_{r=r_0}$$

2.43 Classical Harmonic Oscillator 1: Trajectory

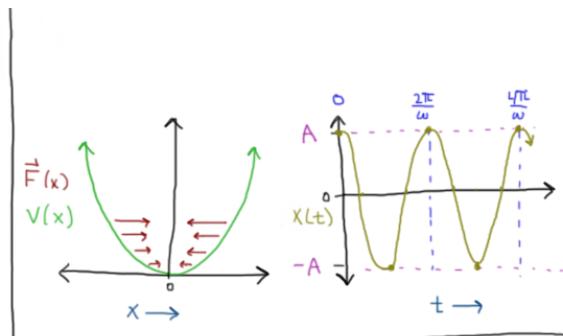


2.44 Classical Harmonic Oscillator 2: Energy

Classical Harmonic Oscillator Energy

$V(x) = \frac{1}{2} kx^2$ $x = r - r_0$ atoms

 $x(t) = A \cos(\omega t)$ $\omega = \sqrt{\frac{k}{m}}$
 $E = T + V$
 $E = \frac{1}{2} mv^2 + \frac{1}{2} kx^2$
 $v(t) = \frac{dx(t)}{dt} = \frac{d}{dt}(A \cos(\omega t)) = -A\omega \sin(\omega t)$
 $E = \frac{1}{2} m(-A\omega \sin(\omega t))^2 + \frac{1}{2} k(A \cos(\omega t))^2$
 $E = \frac{1}{2} m A^2 \omega^2 \sin^2(\omega t) + \frac{1}{2} k A^2 \cos^2(\omega t)$
 $m A^2 \omega^2 = m A^2 \left(\sqrt{\frac{k}{m}}\right)^2 = m A^2 \left(\frac{k}{m}\right) = k A^2$
 $E = \frac{1}{2} k A^2 (\sin^2(\omega t) + \cos^2(\omega t))$



$E(t) = \frac{1}{2} k A^2$

Energy is conserved

Converted between T and V

2.45 Reduced Mass

Reduced Mass

$$m_1 \begin{matrix} & k \\ & \text{---} \\ \text{x}_1 & \text{x}_2 \\ \underbrace{\quad}_{r = |x_2 - x_1|} \end{matrix} m_2$$

$x = r - r_0$

$V(x) = \frac{1}{2} k x^2$

$\frac{dV(x)}{dx} = F = m_a = m \frac{d^2 x}{dt^2}$

$m_1 \frac{d^2 x_1}{dt^2} = -k(x_2 - x_1 - r_0) = -kx$

$m_2 \frac{d^2 x_2}{dt^2} = -k(x_2 - x_1 - r_0) = -kx$

$m_1 \frac{d^2 x_1}{dt^2} + m_2 \frac{d^2 x_2}{dt^2} = 0$

$(m_1 + m_2) \frac{d^2}{dt^2} \left(\frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \right) = 0$

$x(t) = A \cos(\omega t)$

$\omega = \sqrt{\frac{k}{m}}$

$M = m_1 + m_2$ total mass

$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$ center of mass

$M \frac{d^2 X}{dt^2} = 0$ c.o.m. doesn't move

$\frac{d^2 x_2}{dt^2} - \frac{d^2 x_1}{dt^2} = -\frac{k}{m_2} x - \frac{k}{m_1} x$

$\frac{d^2}{dt^2} (x_2 - x_1) = -k \left(\frac{1}{m_1} + \frac{1}{m_2} \right) x$

$\frac{1}{m_1} + \frac{1}{m_2} = \frac{1}{M}$

$M \equiv \left(\frac{1}{m_1} + \frac{1}{m_2} \right)^{-1} = \frac{m_1 m_2}{m_1 + m_2}$

$\underbrace{M \frac{d^2 x}{dt^2}}_{m_a} = -kx$

$\boxed{\omega = \sqrt{\frac{k}{M}}}$

2.46 Harmonic Oscillator Energy Levels

Quantum H.O. Energy Levels

$$\hat{H}\Psi_n(x) = E_n \Psi_n(x)$$

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

$$V(x) = \frac{1}{2} k x^2 \quad |k \rightarrow \text{"spring constant"}$$

$$m = \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{"reduced mass"}$$

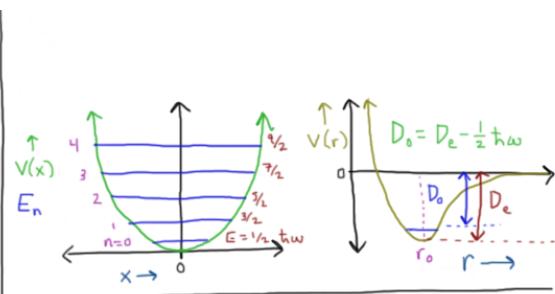
$$\frac{d^2\Psi_n(x)}{dx^2} = -\frac{2\mu}{\hbar^2} \left(E_n - \frac{1}{2} k x^2 \right) \Psi_n(x)$$

$$E_n = \hbar\nu \left(n + \frac{1}{2}\right)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad n=0, 1, 2, \dots$$

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right)$$

$$\omega = \sqrt{\frac{k}{\mu}}$$



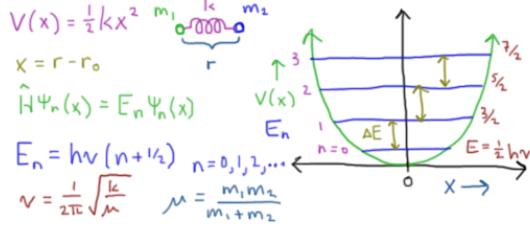
$$\text{Ground State Energy} \quad E_0 = \frac{1}{2} \hbar\omega$$

Z.P.V.E.

Zero Point Vibrational Energy

2.47 Diatomic Infrared Spectra

I.R. Spectra of Diatomic Molecules



$\Delta n = \pm 1$ "Selection Rule"

$+1 \rightarrow$ absorption

$-1 \rightarrow$ emission

most molecules in $n=0$ at 298 K

$$\Delta E = h\nu_{abs} = E_{n+1} - E_n = h\nu(n+1 + 1/2) - h\nu(n + 1/2)$$

$$h\nu_{abs} = h\nu \quad \boxed{v_{obs} = \frac{1}{2\pi c}\sqrt{\frac{k}{M}} \text{ (Hz)}} \quad \begin{aligned} c &= \lambda\nu & \nu &= c/\lambda \\ \tilde{\omega} &= v/c = 1/\lambda & & \end{aligned}$$

$$\tilde{\omega} = \frac{1}{2\pi c}\sqrt{\frac{k}{M}} \text{ (cm}^{-1}\text{)} \quad (\text{c in cm/s})$$

For F_2 ($^{19}F^{19}F$) $\tilde{\omega}_{obs} = 916.6 \text{ cm}^{-1}$ (infrared)

$$\tilde{\omega}_{obs} = \frac{1}{2\pi c}\sqrt{\frac{k}{M}} \quad |c| = 4\pi^2 c^2 M \tilde{\omega}_{obs}^2$$

$$M = \left(\frac{19 \cdot 19}{19 + 19} \right) = \frac{19}{2} \text{ amu} = 1.5775 \cdot 10^{-26} \text{ kg}$$

$$(1 \text{ amu} = 1.66054 \cdot 10^{-27} \text{ kg})$$

$$|c| = 4\pi^2 (2.9979 \cdot 10^10 \text{ cm/s})^2 (1.5775 \cdot 10^{-26} \text{ kg}) (916.6 \text{ cm}^{-1})$$

$$|c| = 470.2 \text{ N/m}$$

$$\left(\frac{\text{cm}}{\text{s}} \right)^2 \text{ kg} \left(\frac{1}{\text{cm}} \right)^2 = \frac{\text{cm}^2 \text{ kg}}{\text{s}^2 \text{ cm}^4} = \frac{\text{kg}}{\text{s}^2} = \left(\frac{\text{kg} \cdot \text{m}}{\text{s}^2} \right) \frac{1}{\text{m}} = \frac{\text{N}}{\text{m}}$$

$$N = \frac{\text{kg} \cdot \text{m}}{\text{s}^2}$$

2.48 Anharmonicity and Overtones

Anharmonicity and Overtones

$$f(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{d^n f(x)}{dx^n} \right|_{x=a} (x-a)^n$$

Taylor Series

$$\begin{aligned} V(r) &= -D_e + 0 + \frac{1}{2} k (r - r_e)^2 \\ &\quad + \frac{1}{6} \gamma_3 (r - r_e)^3 + \frac{1}{24} \gamma_4 (r - r_e)^4 + \dots \end{aligned}$$

$$V(x) = \frac{1}{2} k x^2 + \frac{1}{6} \gamma_3 x^3 + \frac{1}{24} \gamma_4 x^4 + \dots$$

E_n how? \rightarrow perturbation theory

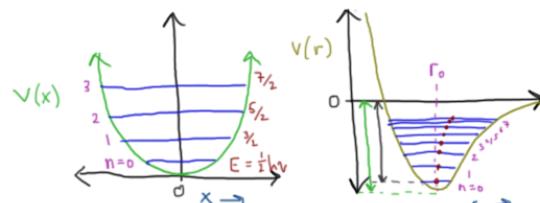
$$\tilde{\omega}_n = \frac{E_n}{\hbar c} = \tilde{\omega}_e \left(n + \frac{1}{2} \right) - \tilde{\chi}_e \tilde{\omega}_e \left(n + \frac{1}{2} \right)^2 + \dots \quad n=0, 1, 2, \dots$$

$\tilde{\omega}_e \rightarrow$ "harmonic frequency"

$\tilde{\chi}_e \rightarrow$ "anharmonicity constant"

$$|\tilde{\chi}_e| \ll 1 \quad (\text{hopefully})$$

$$\begin{aligned} &\text{Diagram: Two masses } m_1 \text{ and } m_2 \text{ connected by a spring of stiffness } k \text{ at position } r. \\ &V(x) = \frac{1}{2} k x^2 \\ &E_n = \frac{1}{2} \hbar \nu \left(n + \frac{1}{2} \right) \\ &\nu = \frac{1}{2\pi} \sqrt{\frac{k}{M}} \\ &M = \frac{m_1 m_2}{m_1 + m_2} \end{aligned}$$



$$\Delta n = \pm 1, \pm 2, \pm 3, \dots \quad \text{selection rule}$$

fundamental overtones

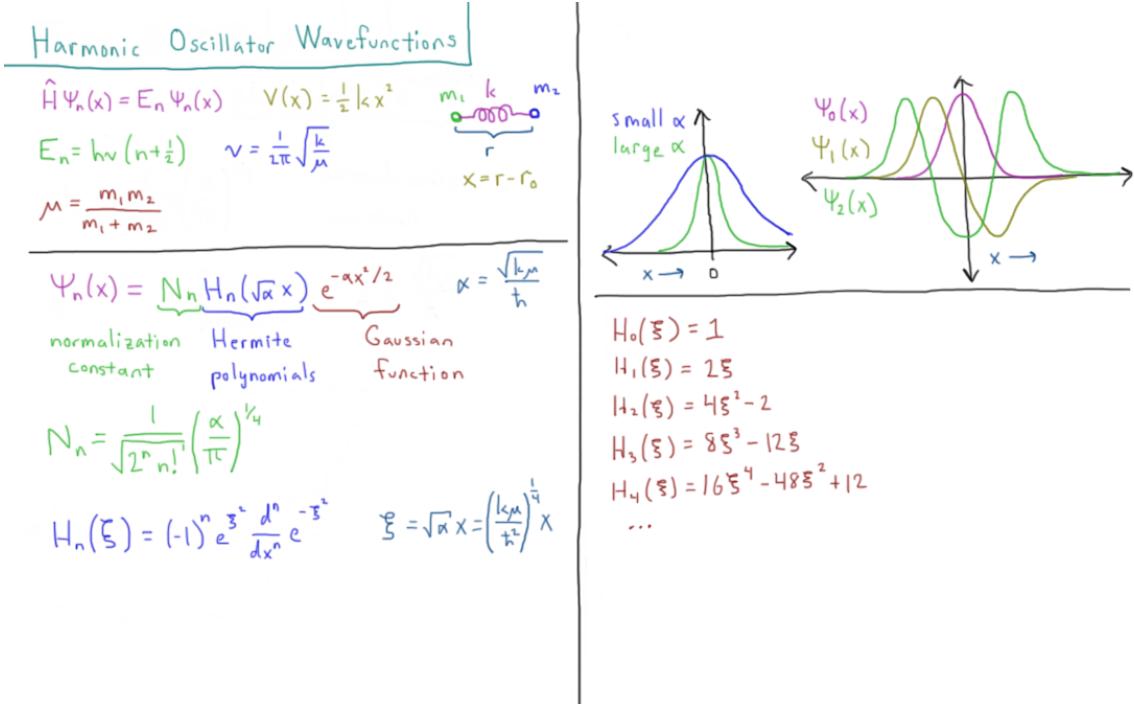
transition from $\Psi_0 \rightarrow \Psi_n$

$$\begin{aligned} \tilde{\omega}_{\text{obs}} &= \tilde{\omega}_n - \tilde{\omega}_0 = \left[n \tilde{\omega}_e + \cancel{\frac{1}{2} \tilde{\omega}_e} - \tilde{\chi}_e \tilde{\omega}_e \left(n + n \cancel{\frac{1}{4}} \right) \right] \\ n + n &= n(n+1) \quad - \left[\cancel{\frac{1}{2} \tilde{\omega}_e} - \cancel{\frac{1}{4} \tilde{\chi}_e \tilde{\omega}_e} \right] \end{aligned}$$

$$\boxed{\tilde{\omega}_{\text{obs}} = n \tilde{\omega}_e - \tilde{\chi}_e \tilde{\omega}_e n(n+1)}$$

$$\tilde{\omega}_{\text{obs}} = n \tilde{\omega}_e [1 - \tilde{\chi}_e (n+1)]$$

2.49 Harmonic Oscillator Wavefunctions



2.50 Even and Odd Functions

Even and Odd Functions	
<p>Even</p> $f(x) = f(-x)$ $(x, y) \rightarrow (-x, y)$ <p>Reflected Across Y-axis</p> $f_e(x) = \frac{f(x) + f(-x)}{2}$	<p>Odd</p> $f(x) = -f(-x)$ $(x, y) \rightarrow (-x, -y)$ <p>Inverted Through Origin</p> $f_o(x) = \frac{f(x) - f(-x)}{2}$
$\begin{array}{ll} 2 & \cos(\alpha x) \\ x^2 & e^{-\alpha x^2} \\ 4x^4 & x \\ x^6 - x^2 & 1/x^2 \end{array}$	$\begin{array}{ll} x & x^5 - 3x^3 + bx \\ 5x^3 & \tan(x) \\ \sin(kx) & 1/2x^2 \\ 1/x & \end{array}$
$\int_{-\infty}^{\infty} f_e(x) dx = 2 \int_0^{\infty} f_e(x) dx$	$\int_{-\infty}^{\infty} f_o(x) dx = 0$
$E + E = E \quad x^2 - 2$ $O + O = O \quad x^3 + x$ $E \cdot E = E \quad 3x^2 \quad x^2 \cdot x^4 = x^6$ $E \cdot O = O \quad -4x \quad x^4 \cdot x = x^3$ $O \cdot O = E \quad x \cdot x^3 = x^4$ $\frac{d}{dx} E = O \quad \frac{d}{dx} (4x^6) = 24x^5$ $\frac{d}{dx} O = E \quad \frac{d}{dx} (\cos(\alpha x)) = - \alpha \sin(\alpha x)$	

2.51 Harmonic Oscillator Even and Odd Functions

H.O. Even/Odd Functions

$$\Psi_n(x) = N_n H_n(\alpha^{\nu_2} x) e^{-\alpha x^2/2}$$

E $E \text{ or } 0$ E

$$\begin{aligned} H_0(\xi) &= 1 \rightarrow E \quad \xi = \alpha^{\nu_2} x \\ H_1(\xi) &= 2\xi \rightarrow 0 \quad \xi = \alpha^{\nu_2} x \\ H_2(\xi) &= 4\xi^2 - 2 \rightarrow E \quad \xi = \alpha^{\nu_2} x \\ H_3(\xi) &= 8\xi^3 - 12\xi \rightarrow 0 \quad \xi = \alpha^{\nu_2} x \\ H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12 \rightarrow E \end{aligned}$$

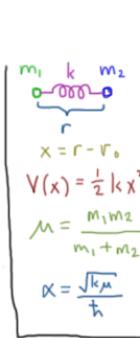
...

$$n_{\text{even}} \rightarrow E \cdot E \cdot E = E$$

$$n_{\text{odd}} \rightarrow E \cdot 0 \cdot E = 0$$

$$\Psi_n^*(x) \Psi_n(x) = |\Psi_n(x)|^2 = \begin{cases} E \cdot E = E & n_{\text{even}} \\ 0 \cdot 0 = 0 & n_{\text{odd}} \end{cases} = E$$

$$\langle n | n \rangle = \int_{-\infty}^{\infty} \Psi_n^*(x) \Psi_n(x) dx = 2 \int_0^{\infty} \Psi_n^*(x) \Psi_n(x) dx$$



$$\hat{x} = x \quad \hat{p} = -i\hbar \frac{d}{dx}$$

$E \cdot 0 = 0$

$$\hat{x}^2 = x^2 \quad \hat{p}^2 = -\hbar^2 \frac{d^2}{dx^2}$$

$E \cdot E = E$

$$\langle x \rangle = \langle n | \hat{x} | n \rangle = \int_{-\infty}^{\infty} \underbrace{\Psi_n^*(x)}_{E \cdot 0 \cdot E = 0} \underbrace{\hat{x} \Psi_n(x)}_{0 \cdot 0 \cdot 0 = 0} dx = 0$$

$$\langle p \rangle = \langle n | \hat{p} | n \rangle = \int_{-\infty}^{\infty} \underbrace{\Psi_n^*(x)}_{E \cdot 0 \cdot E = 0} \underbrace{(-i\hbar \frac{d}{dx}) \Psi_n(x)}_{0 \cdot 0 \cdot 0 = 0} dx = 0$$

∴ for all n

$$\boxed{\langle x \rangle = 0}$$

$$\boxed{\langle p \rangle = 0}$$

2.52 3-D Harmonic Oscillator

3D Harmonic Oscillator

$$V(x, y, z) = \underbrace{\frac{1}{2}k_x x^2}_{V_x} + \underbrace{\frac{1}{2}k_y y^2}_{V_y} + \underbrace{\frac{1}{2}k_z z^2}_{V_z}$$

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) \right] \Psi(x, y, z) = E \Psi(x, y, z)$$

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z \quad \text{"Separable"}$$

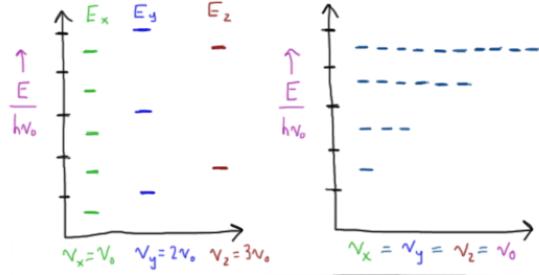
$$\hat{H}_i = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z_i^2} + V_i(z_i) \quad i \in \{x, y, z\}$$

$$\hat{H}_i \Psi_{n_i}(z_i) = E_{n_i} \Psi_{n_i}(z_i)$$

$$E_{n_i} = \hbar \nu_i (n_i + \frac{1}{2}) \quad \nu_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{m}}$$

$$E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} \quad n_x, n_y, n_z = 0, 1, 2, \dots$$

$$\Psi_{n_x n_y n_z}(x, y, z) = \Psi_{n_x}(x) \Psi_{n_y}(y) \Psi_{n_z}(z)$$



if $|k_x| = |k_y| = |k_z| = k$, then

$$E = \hbar \nu (n_x + n_y + n_z + \frac{3}{2})$$

Symmetry \Rightarrow Degeneracy

2.53 Polyatomic Molecular Vibrations

Polyatomic Molecular Vibrations

$$\vec{r}_o = (x_o, y_o, z_o)$$

$$\vec{r}_{H_1} = (x_{H_1}, y_{H_1}, z_{H_1})$$

$$\vec{r}_{H_2} = (x_{H_2}, y_{H_2}, z_{H_2})$$

$\vec{r} = (\vec{r}_o, \vec{r}_{H_1}, \vec{r}_{H_2})$

$\vec{r} = (x_o, y_1, \dots, z_{H_2})$

N nuclei $\rightarrow 3N$ coordinates

$V(\vec{r}) \rightarrow 3N$ -dimensional Potential Energy Surface (P.E.S.)

$$\nabla V(\vec{r}) = \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial x_i} \right) \hat{x}_i \rightarrow \text{gradient}$$

if $\nabla V(\vec{r}) = 0$, $\vec{r} \rightarrow \text{"stationary point"}$

$$V(\vec{r}) \approx V(\vec{r}_o) + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial x_i} \right)_{x_i=x_{i0}} (x_i - x_{i0}) + \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{x_i=x_{i0}, x_j=x_{j0}} (x_i - x_{i0})(x_j - x_{j0}).$$

$$\text{Set } \frac{\partial V}{\partial x_i} = 0 \text{ at S.P.}$$

$$h_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{x_i=x_{i0}, x_j=x_{j0}}$$

$\underline{H} \rightarrow 3N \times 3N \text{ "Hessian Matrix"}$

Eigenvectors of Hessian \rightarrow "Normal modes"

$3N$ normal modes $\begin{cases} 3 \text{ translations} \\ 3(2) \text{ rotations} \\ 3N-6 (5) \text{ vibrations} \end{cases} \{Q_i\}$

non-linear (linear)

Eigenvalues of Hessian \rightarrow Force Constants $\{H_i\}$

$$\hat{H}_{vib} = \sum_{i=1}^{3N-6} \left(-\frac{\hbar^2}{2M_i} \frac{d^2}{dQ_i^2} + \frac{1}{2} H_i Q_i^2 \right)$$

$$E_{vib} = \sum_{i=1}^{3N-6} \hbar v_i (n_i + \frac{1}{2})$$

$$\{n_i\} = 0, 1, 2, \dots$$

$$v_i = \frac{1}{2\pi} \sqrt{\frac{H_i}{M_i}}$$

2.54 Rigid Rotor Model

Rigid Rotor Model

$$T = \frac{1}{2} M_1 V_1^2 + \frac{1}{2} M_2 V_2^2$$

$\nu = \nu_{\text{rot}}$ frequency of rotation

$\omega = 2\pi\nu$ $\omega \rightarrow$ angular velocity

$$V = 2\pi l \nu = l\omega$$

$$T = \frac{1}{2} m_1 l_1^2 \omega^2 + \frac{1}{2} m_2 l_2^2 \omega^2$$

$$T = \frac{1}{2} \omega^2 (m_1 l_1^2 + m_2 l_2^2) \quad M = \frac{m_1 m_2}{m_1 + m_2}$$

$$I = m_1 l_1^2 + m_2 l_2^2 = \mu l^2 \quad I \rightarrow \text{moment of inertia}$$

$$T = \frac{1}{2} I \omega^2$$

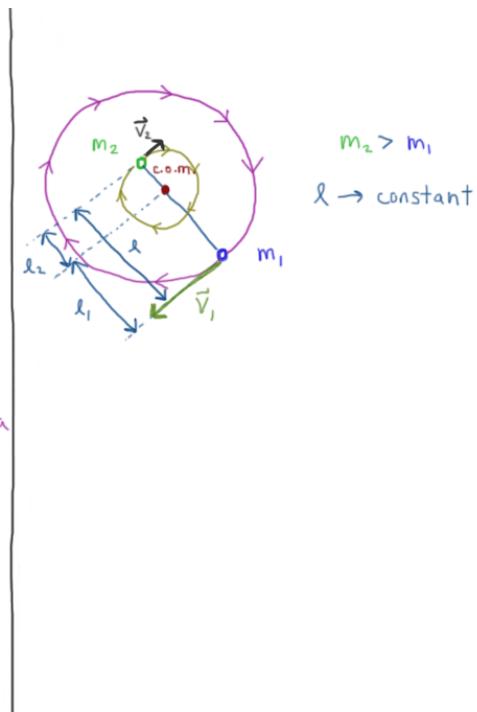
$$L = I \omega \quad L \rightarrow \text{angular momentum}$$

$$T = \frac{1}{2} I \omega^2 = \frac{1}{2} \frac{I^2 \omega^2}{I} = \frac{1}{2} \frac{L^2}{I}$$

$$T = \frac{L^2}{2I}$$

$$V = 0$$

$$l \rightarrow \text{fixed}$$



2.55 Rotation Operators

Rotation Operators

$$\nabla = \frac{\vec{v}_1}{2\pi\lambda_1} = \frac{\vec{v}_2}{2\pi\lambda_2}$$

$$\omega = 2\pi\nu$$

$$L = I\omega$$

$$I = \mu\lambda^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$T = \frac{1}{2}mv^2 = \frac{\vec{p}^2}{2m} = \frac{L^2}{2I}$$

$$V = 0$$

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2\mu} \nabla^2$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\Psi = \Psi(\theta, \phi) \quad (x, y, z) \rightarrow (r, \theta, \phi)$$

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)_{\theta, \phi} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right)_{r, \phi} + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right)_{r, \theta}$$

$$\nabla^2 = \frac{1}{r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \right)$$

$r = \lambda$

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 = \frac{\hat{L}^2}{2I} = \frac{\hat{L}^2}{2\mu\lambda^2}$$

$$\hat{L}^2 = -\hbar\lambda^2 \nabla^2$$

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

$$\hat{L}_z = -i\hbar \frac{d}{d\phi}$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$\hat{H}\Psi(\theta, \phi) = E\Psi(\theta, \phi)$$

2.56 Rigid Rotor Energy Levels

Rigid Rotor Energy Levels

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

$$\hat{H} = \frac{\hat{L}^2}{2I} \quad \hat{H} \Psi(\theta, \phi) = E \Psi(\theta, \phi)$$

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad J=0, 1, 2, \dots$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

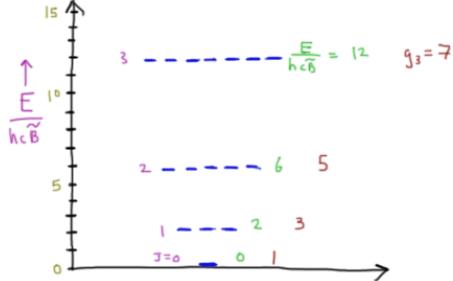
$$I = \mu r^2$$

$$B = \frac{\hbar}{8\pi^2 I} \quad (\text{Hz}) \quad \text{"Rotational Constant"}$$

$$\tilde{B} = \frac{\hbar}{8\pi^2 c I} \quad (\text{cm}^{-1}) \quad c = \lambda v \quad v = \frac{c}{\lambda} \quad \tilde{\omega} = \frac{J}{\lambda}$$

$$E_J = \frac{\hbar^2}{2I} J(J+1) = \hbar B J(J+1) = \hbar c \tilde{B} J(J+1)$$

$$g_J = 2J+1 \quad \text{"degeneracy"}$$



2.57 Diatomic Microwave Spectra

Microwave Spectra

$$E_J = \frac{\hbar^2}{2I} J(J+1) = \hbar\tilde{B}J(J+1) = \hbar c \tilde{B} J(J+1)$$

$\Delta J = \pm 1$ selection rule

$$\Delta E = E_{J+1} - E_J = \hbar c \tilde{B} [(J+1)(J+2) - J(J+1)]$$

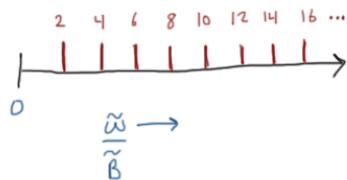
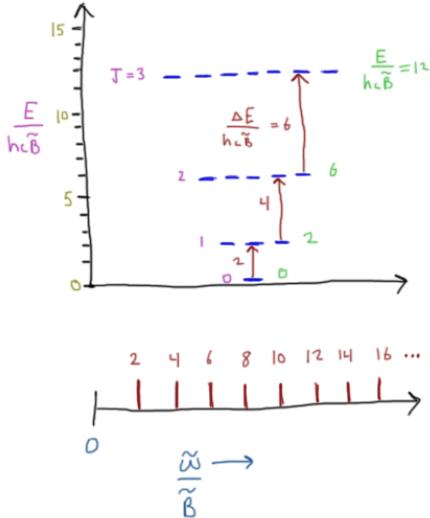
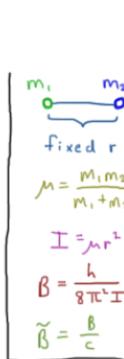
$$\Delta E = \hbar c \tilde{B} [J + 3J + 2 - J - J]$$

$$\Delta E = 2\hbar c \tilde{B} (J+1)$$

$$\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\omega}$$

$$\tilde{\omega} = 2\tilde{B}(J+1) \quad (\text{cm}^{-1})$$

$\tilde{B} \approx 1-10 \text{ cm}^{-1} \rightarrow$ microwave



2.58 Rovibrational Energy Levels

Rovibrational Energy Levels

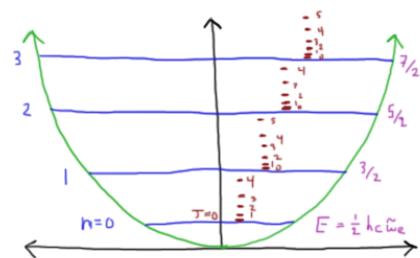
$$E_n = \hbar c \tilde{\omega}_e (n + \frac{1}{2}) \quad n = 0, 1, 2, \dots$$

$$E_T = \hbar c \tilde{B} T (T+1) \quad T = 0, 1, 2, \dots$$

$$\tilde{\omega}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \tilde{B} = \frac{\hbar}{8\pi^2 c \mu r^2}$$

$$E_{n,T} = \hbar c [\tilde{\omega}_e (n + \frac{1}{2}) + \tilde{B} T (T+1)]$$

$m_1 \quad k \quad m_2$
 r
 $\mu = \frac{m_1 m_2}{m_1 + m_2}$
 $I = \mu r^2$



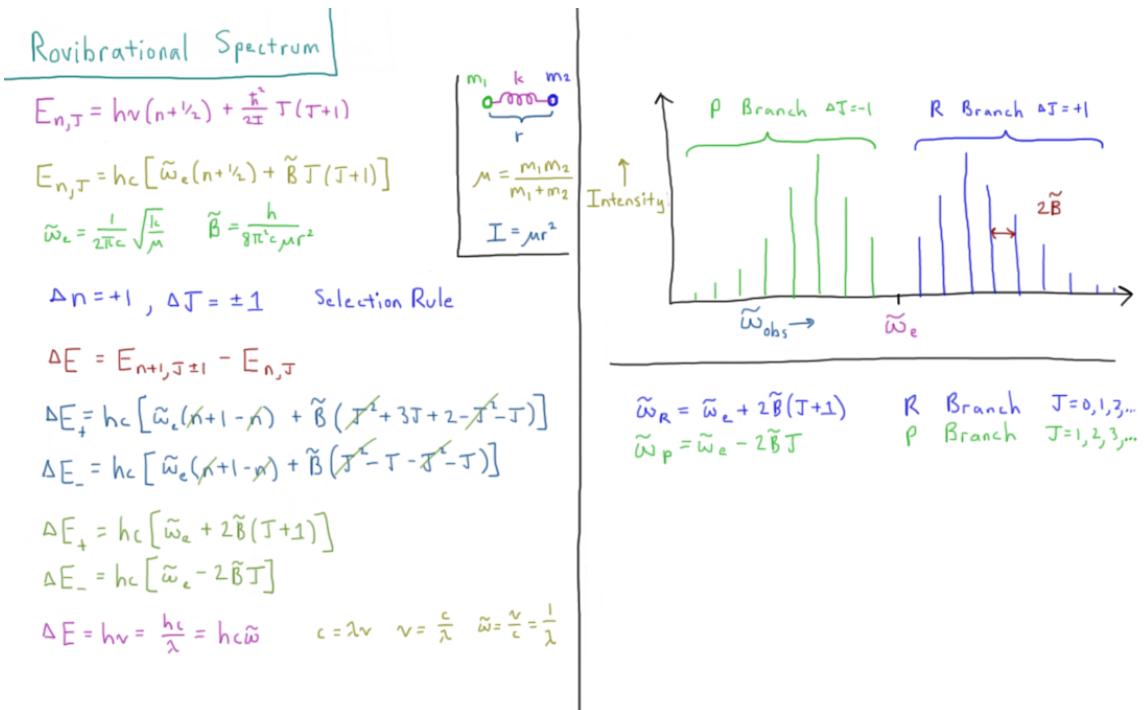
$$E_n = \hbar \nu (n + \frac{1}{2}) = \hbar \omega (n + \frac{1}{2}) = \hbar c \tilde{\omega}_e (n + \frac{1}{2})$$

$$E_T = \frac{\hbar^2}{2I} T(T+1) = \hbar \tilde{B} T(T+1) = \hbar c \tilde{B} T(T+1)$$

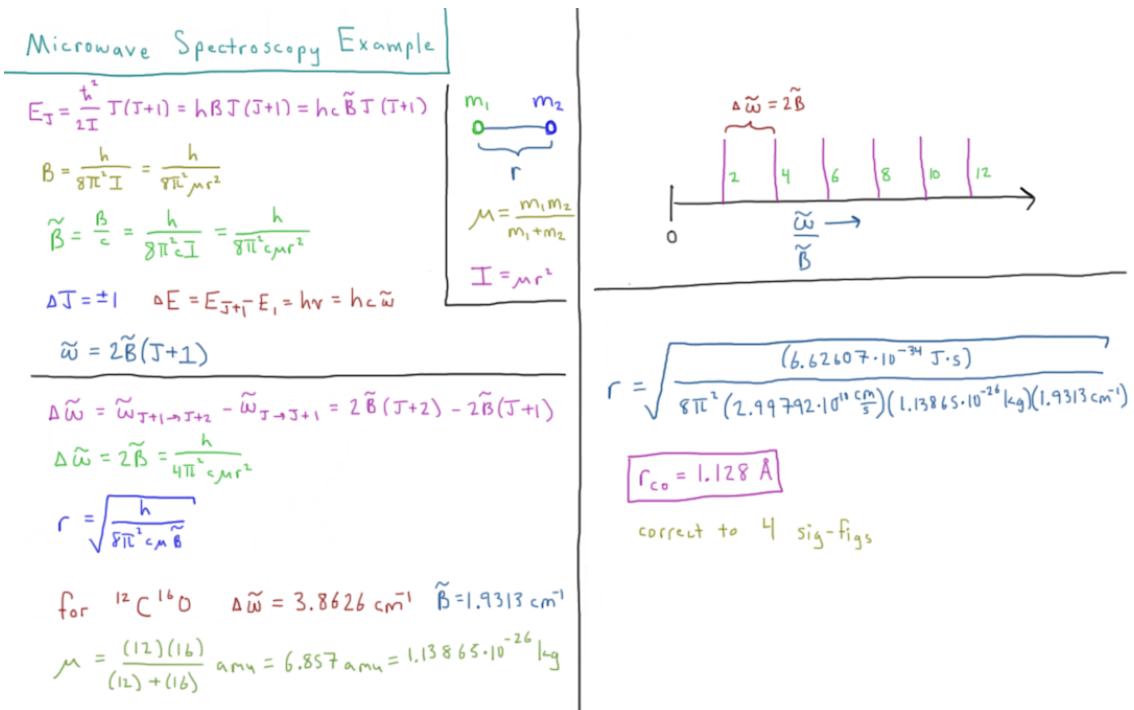
$$\omega = \sqrt{\frac{k}{\mu}} \quad \nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \tilde{\omega}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\tilde{B} = \frac{\hbar}{8\pi^2 I} = \frac{\hbar}{8\pi^2 \mu r^2} \quad \tilde{B} = \frac{\hbar}{8\pi^2 c \mu r^2} = \frac{\hbar}{8\pi^2 c \mu r^2}$$

2.59 Diatomic Rovibrational Spectra



2.60 Microwave Spectroscopy Example



2.61 Rotation-Vibration Interaction

Rotation-Vibration Interaction

$$E_{n,J} = \hbar c [\tilde{\omega}_e(n+\nu_2) + \tilde{B}_n J(J+1)]$$

$$\tilde{\omega}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \tilde{B} = \frac{\hbar}{8\pi c \mu r^2}$$

$$\Delta n = +1 \text{ absorption} \quad \Delta J = \begin{cases} +1 & R \\ -1 & P \end{cases}$$

$$\tilde{\omega}_R = \tilde{\omega}_e + 2\tilde{B}(J+1) \quad \tilde{\omega} = \frac{\Delta E}{\hbar c} \text{ (cm}^{-1}\text{)}$$

$$\tilde{\omega}_P = \tilde{\omega}_e - 2\tilde{B}J$$

$$n \uparrow \rightarrow r \uparrow \rightarrow I \uparrow \rightarrow B \downarrow \quad B \rightarrow B_n$$

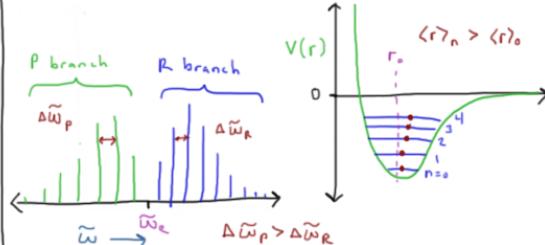
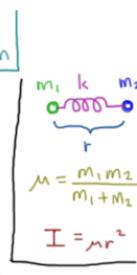
$$E_{n,J} = \hbar c [\tilde{\omega}_e(n+\nu_2) + \tilde{B}_n J(J+1)]$$

$$\tilde{B}_n = \tilde{B}_e - \tilde{\alpha}_e(n+\nu_2)$$

$\tilde{\alpha}_e \rightarrow$ "rotation-vibration interaction" constant

$$\Delta E_R = E_{n+1,J+1} - E_{n,J} = \hbar c [\tilde{\omega}_e(n'+\nu_1 + \nu_2) - (n-\nu_2)] + \tilde{B}_{n+1}(J+1)(J+2) - \tilde{B}_n J(J+1)$$

$$\Delta E_P = E_{n+1,J-1} - E_{n,J} = \hbar c [\tilde{\omega}_e(n+\nu_1 + \nu_2) - (n-\nu_2)] + \tilde{B}_{n+1}(J-1)(J) - \tilde{B}_n J(J+1)$$



$$\tilde{\omega}_R = \tilde{\omega}_e + \tilde{B}_{n+1}(J+1)(J+2) - \tilde{B}_n J(J+1)$$

$$\tilde{\omega}_P = \tilde{\omega}_e + \tilde{B}_{n+1}J(J-1) - \tilde{B}_n J(J+1)$$

$$\Delta \tilde{\omega}_R = (\tilde{\omega}_R)_{J+1} - (\tilde{\omega}_R)_J$$

$$\Delta \tilde{\omega}_P = (\tilde{\omega}_P)_{J+2} - (\tilde{\omega}_P)_{J+1}$$

$$\Delta \tilde{\omega}_P - \Delta \tilde{\omega}_R = -2(\tilde{B}_n - \tilde{B}_{n+1})$$

$$\tilde{B}_n - \tilde{B}_{n+1} = (\tilde{B}_e - \tilde{\alpha}_e(n+\nu_2)) - (\tilde{B}_e - \tilde{\alpha}_e(n+\nu_1))$$

$$\tilde{B}_n - \tilde{B}_{n+1} = \tilde{\alpha}_e \quad \tilde{\alpha}_e > 0$$

$$\Delta \tilde{\omega}_R - \Delta \tilde{\omega}_P = -2\tilde{\alpha}_e < 0$$

$$\boxed{\Delta \tilde{\omega}_R < \Delta \tilde{\omega}_P}$$

2.62 Centrifugal Distortion

Centrifugal Distortion

$$E_J = h_c \tilde{B} J(J+1)$$

$$\tilde{\omega} = \frac{1}{h_c} (E_{J+1} - E_J)$$

$$\tilde{\omega} = 2\tilde{B}(J+1) \quad J=0, 1, 2, \dots$$

$$J \uparrow \rightarrow r \uparrow \rightarrow I \uparrow \rightarrow \tilde{B} \downarrow$$

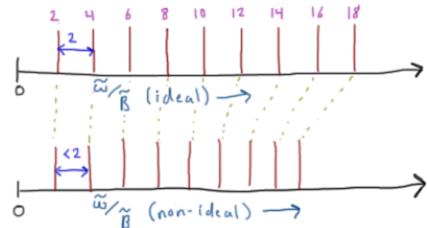
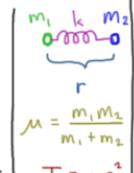
$$\tilde{B}_{J+1} < \tilde{B}_J$$

$$E_J = h_c [\tilde{B} J(J+1) - \tilde{D} J^2(J+1)^3]$$

\tilde{D} → "centrifugal distortion coefficient"

$$\tilde{D} = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3 \quad J=0, 1, 2, \dots$$

$$\tilde{D} \approx 10^{-2} - 10^{-8} \text{ cm}^{-1}$$



2.63 Rigid Rotor Wavefunctions

Rigid Rotor Wavefunctions	
$\hat{H}\Psi_{Jm}(\theta, \phi) = E_J \Psi_{Jm}(\theta, \phi)$ $E_J = \frac{\hbar^2}{2I} J(J+1)$ $\hat{H} = -\frac{\hbar^2}{2I} \hat{L}^2$ $\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$ $\Psi_{Jm}(\theta, \phi) = \Theta_{Jm}(\theta) \Phi_m(\phi)$ $\Theta_{Jm}(\theta) = \frac{1}{\sqrt{2J+1}} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2JE}{\hbar^2} \sin^2 \theta = \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2$ $\Phi_m(\phi + 2\pi) = \Phi_m(\phi)$ $\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$ $m = 0, \pm 1, \pm 2, \dots -J \leq m \leq J$ $\Theta_{Jm}(\theta) = \sqrt{\frac{2J+1}{2}} \frac{(J- m)!}{(J+ m)!} P_J^{ m }(\cos \theta)$ associated Legendre polynomials $P_J^m(x) = \frac{(-1)^m}{2^m m!} (1-x^2)^{m/2} \frac{d^{m/2}}{dx^{m/2}} (x^2-1)^m$	 $J = \frac{m_1 m_2}{m_1 + m_2}$ $I = J r^2$ $\Psi_{Jm}(\theta, \phi) = Y_J^m(\theta, \phi) = \underbrace{\sqrt{\frac{2J+1}{4\pi}} \frac{(J- m)!}{(J+ m)!}}_{\text{normalization}} \underbrace{P_J^{ m }(\cos \theta)}_{\text{polynomial}} \underbrace{e^{im\phi}}_{\text{complex exponential}}$ $Y_0^0 = \frac{1}{\sqrt{4\pi}}$ $Y_1^0 = \sqrt{\frac{3}{8\pi}} \cos \theta$ $Y_1^{\pm 1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$ $Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$ $Y_2^{\pm 1} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$ $Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$ $Y_J^m \rightarrow \text{"Spherical Harmonics"}$

2.64 Orthonormality of Spherical Harmonics

Orthonormality of Spherical Harmonics

$$Y_J^m(\theta, \phi) = \underbrace{\sqrt{\frac{2J+1}{4\pi} \frac{(J-|m|)!}{(J+|m|)!}}}_{\text{normalization constant}} P_J^{|m|}(\cos\theta) e^{im\phi}$$

associated complex Legendre exponential polynomials

$J=0, 1, 2, \dots$ $m=0, \pm 1, \pm 2, \dots, \pm J$

$$\int_{-1}^1 P_J(x) P_{J'}(x) dx = \langle J | J' \rangle = \delta_{JJ'}$$

$$\delta_{ij} = \begin{cases} 1 & \text{if } i=j \\ 0 & \text{if } i \neq j \end{cases}$$

$x \rightarrow \cos\theta \quad -1, 1 \rightarrow \pi, 0 \quad dx \rightarrow \sin\theta d\theta$

$$\int_0^\pi P_J(\cos\theta) P_{J'}(\cos\theta) \sin\theta d\theta = \frac{\delta_{JJ'}}{2J+1}$$

$$\int_0^\pi P_J^{|m|}(\cos\theta) P_{J'}^{|m|}(\cos\theta) \sin\theta d\theta = \frac{2}{2J+1} \frac{(J+|m|)!}{(J-|m|)!} \delta_{JJ'}$$

$$\int_0^{2\pi} \bar{\Phi}_m^*(\phi) \bar{\Phi}_{m'}(\phi) d\phi = \langle m' | m \rangle$$

$$= \int_0^{2\pi} (e^{im'\phi})^* (e^{im\phi}) d\phi$$

$$\langle m' | m \rangle = \int_0^{2\pi} e^{i(m-m')\phi} d\phi = 2\pi \delta_{mm'}$$

$\{\bar{\Phi}_n\} \rightarrow \text{orthonormal}$

$$\langle J'm' | Jm \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta Y_J^{m*}(\theta, \phi) Y_J^m(\theta, \phi) = \delta_{JJ'} \delta_{mm'}$$

$\{Y_J^m(\theta, \phi)\} \rightarrow \text{orthonormal}$

both J and m must be equal

2.65 Angular Momentum Eigenvalues

Angular Momentum Eigenvalues

$$Y_J^m(\theta, \phi) = \sqrt{\frac{2J+1}{4\pi} \frac{(J-|m|)!}{(J+|m|)!}} P_J^{|m|}(\cos \theta) e^{im\phi}$$

$$\hat{H} = \frac{\hat{L}^2}{2I}$$

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

$\hat{L}^2 \rightarrow$ total angular momentum squared

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

✓ X X ✓ Eigenfunctions?

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 Y_J^m(\theta, \phi) = \underbrace{\hbar^2 J(J+1)}_{\text{Eigenvalues}} Y_J^m(\theta, \phi)$$

$$\hat{L}_z Y_J^m(\theta, \phi) = \underbrace{\hbar m}_{\text{Eigenvalues}} Y_J^m(\theta, \phi)$$

Eigenvalues

2.66 Hydrogen Atom Model

Hydrogen Atom Model

Proton fixed at origin
Electron moving in space

$q_p = +e \quad q_e = -e$
 $e = 1.602 \cdot 10^{-19} C$
 $m_p = 1.673 \cdot 10^{-27} kg$
 $m_e = 9.109 \cdot 10^{-31} kg$

$\frac{m_p}{m_e} \approx 1823 \quad \mu = \frac{m_e m_p}{m_e + m_p} = 0.9995 m_e$

$\hat{H} = \hat{T} + \hat{V}$
 $\hat{T} = -\frac{\hbar^2}{2m_e} \nabla^2 \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$

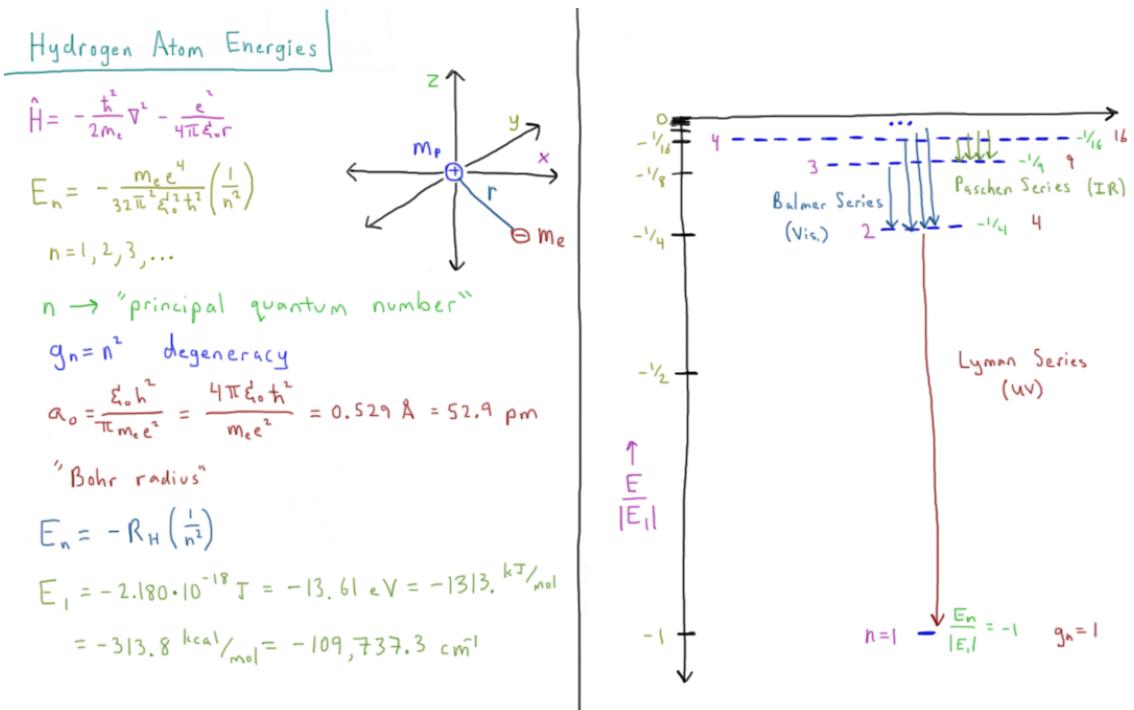
Coulomb potential $V(r) = \frac{q_p q_e}{4\pi \epsilon_0 r} = \frac{-e^2}{4\pi \epsilon_0 r}$
 $E_{10} = 8.854 \cdot 10^{-12} \frac{C^2}{J \cdot m}$

$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi \epsilon_0 r}$

$V = V(r) \rightarrow \Psi = \Psi(r, \theta, \phi)$

$\hat{H} \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$

2.67 Hydrogen Atom Energy Levels



2.68 Hydrogen Atom Radial Wavefunctions

Hydrogen Atom Radial Wavefunctions

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$\hat{H}\Psi_{nlm}(r, \theta, \phi) = E_n \Psi_{nlm}(r, \theta, \phi)$$

$$E_n = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 h^2} \left(\frac{1}{n}\right)^2 \quad n=1, 2, 3, \dots$$

$\Psi_{nlm}(r, \theta, \phi) = \underbrace{R_{nl}(r)}_{\text{Radial Wavefunction}} \underbrace{Y_l^m(\theta, \phi)}_{\text{Spherical Harmonics}}$

$\{n, l, m\} \in \mathbb{Z}$

$n \geq 1 \quad 0 \leq l \leq n \quad -l \leq m \leq l$

$$R_{nl}(r) = \underbrace{\sqrt{\frac{(n-l-1)!}{2^n [(n+1)!]^3}}}_{\text{normalization constant}} \left(\frac{2}{na_0}\right)^{l+1/2} L_{n+l}^{2l+1} \left(\frac{2r}{na_0}\right) r^l e^{-r/na_0}$$

$a_0 = 0.529 \text{ \AA}$
Bohr radius

$\text{associated Laguerre polynomials}$

$$L_a^b(x) = \frac{x^{-b} e^x}{a!} \frac{d^a}{dx^a} \left(x^{a+b} e^{-x} \right) \quad p = \frac{2r}{a_0} \quad z_p = +1$$

$$R_{10}(r) = 2 \left(\frac{z}{a_0}\right)^{1/2} e^{-p} \quad 1s$$

$$R_{20}(r) = \left(\frac{z}{2a_0}\right)^{3/2} (2-p) e^{-p/2} \quad 2s$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{z}{2a_0}\right)^{3/2} p e^{-p/2} \quad 2p$$

$$R_{30}(r) = \frac{1}{27} \left(\frac{z}{3a_0}\right)^{3/2} (27 - 18p + 2p^2) e^{-p/3} \quad 3s$$

$$R_{31}(r) = \frac{1}{27} \left(\frac{2z}{3a_0}\right)^{3/2} p(p-b) e^{-p/3} \quad 3p$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}} \left(\frac{z}{3a_0}\right)^{3/2} p^2 e^{-p/3} \quad 3d$$

2.69 Hydrogen Atom Total Wavefunctions

Hydrogen Atom Total Wavefunctions

$$\hat{H}\Psi_{n\ell m}(r, \theta, \phi) = E_n \Psi_{n\ell m}(r, \theta, \phi)$$

$$\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_\ell^m(\theta, \phi)$$

$$E_n = -\frac{m_e e^4}{32\pi^2 \alpha_0^4 \hbar^3} \left(\frac{1}{n^3}\right) \quad n=1, 2, 3, \dots$$

$$R_{n\ell}(r) = \sqrt{\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} \left(\frac{2}{na_0}\right)^{\ell+3/2} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right) r^\ell e^{-r/na_0}$$

$$Y_\ell^m(\theta, \phi) = \sqrt{\frac{2\ell+1}{4\pi}} \frac{(\ell-|m|)!}{(\ell+|m|)!} P_\ell^{|m|}(\cos\theta) e^{im\phi}$$

$$\{n, \ell, m\} \in \mathbb{Z} \quad n \geq 1 \quad 0 \leq \ell \leq n \quad -\ell \leq m \leq \ell$$

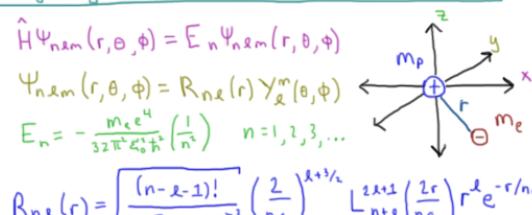
$$\alpha_0 = 0.529 \text{ \AA} \quad Z = \# \text{ of protons}$$

$$\Psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} e^{-r} \quad 1s$$

$$\Psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{2}{a_0}\right)^{3/2} (2-r) e^{-r/2} \quad 2s$$

$$\Psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{2}{a_0}\right)^{3/2} r e^{-r/2} \cos\theta \quad 2p_z$$

$$\Psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} r e^{-r/2} \sin\theta e^{\pm i\phi} \quad 2p_x, 2p_y$$



$$\Psi_{300} = \frac{1}{81\sqrt{5\pi}} \left(\frac{2}{a_0}\right)^{3/2} (27 - 18r + 2r^2) e^{-r/3} \quad 3s$$

$$\Psi_{310} = \frac{\sqrt{5}}{81\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} r(6-r) e^{-r/3} \cos\theta \quad 3p_z$$

$$\Psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} r(6-r) e^{-r/3} \sin\theta e^{\pm i\phi} \quad 3p_x, 3p_y$$

$$\Psi_{320} = \frac{1}{81\sqrt{8\pi}} \left(\frac{2}{a_0}\right)^{3/2} r^2 e^{-r/3} (3\cos^2\theta - 1) \quad 3d_{z^2}$$

$$\Psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} r^2 e^{-r/3} \sin\theta \cos\theta e^{\pm i\phi} \quad 3d_{2xy}$$

$$\Psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} \left(\frac{2}{a_0}\right)^{3/2} r^2 e^{-r/3} \sin^2\theta e^{\pm 2i\phi} \quad 3d_{x^2-y^2}$$

$$e^{\pm im\phi} = \cos(m\phi) \pm i\sin(m\phi)$$

$$\cos(m\phi) = \frac{1}{2} (e^{im\phi} + e^{-im\phi})$$

$$\sin(m\phi) = -\frac{i}{2} (e^{im\phi} - e^{-im\phi})$$

$$\Psi_{2p_x} = \frac{1}{\sqrt{2}} [\Psi_{211} + \Psi_{21-1}]$$

$$\Psi_{2p_y} = \frac{-i}{\sqrt{2}} [\Psi_{211} - \Psi_{21-1}]$$

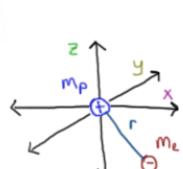
2.70 Hydrogen Atomic Orbital Nodes

Atomic Orbital Nodes

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$\hat{H}\Psi_{n2m}(r, \theta, \phi) = E_n \Psi_{n2m}(r, \theta, \phi)$$

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$



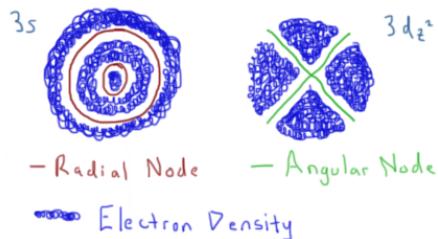
$$\left(\begin{array}{c} \text{Number of} \\ \text{Radial Nodes} \end{array} \right) = n - l - 1$$

$$\left(\begin{array}{c} \text{Number of} \\ \text{Angular Nodes} \end{array} \right) = l$$

$$\left(\begin{array}{c} \text{Number of} \\ \text{Total Nodes} \end{array} \right) = n - 1$$

l	0 1 2 3 4 5 6 7 8 9 10 ...
letter	s p d f g h i k l m n ...

Orbital	N_{ang}	N_{rad}	N_{tot}
1s	0	0	0
2s	0	1	1
2p	1	0	1
3s	0	2	2
3p	1	1	2
3d	2	0	2
4s	0	3	3
4p	1	2	3
4d	2	1	3
4f	3	0	3



2.71 Hydrogen Atom Eigenvalues

Hydrogen Atom Eigenvalues

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

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

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi}$$

$$\hat{H}\Psi_{nem}(r, \theta, \phi) = E_n \Psi_{nem}(r, \theta, \phi)$$

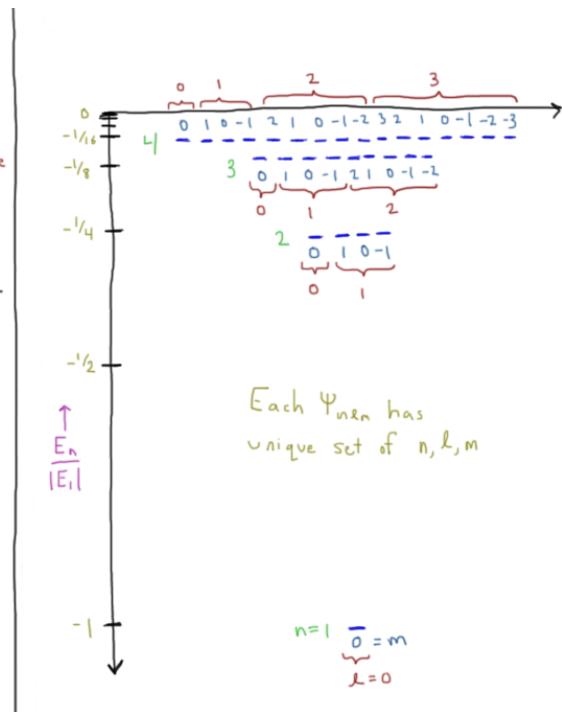
$$\hat{L}^2 \Psi_{nem}(r, \theta, \phi) = \underbrace{\hbar^2 l(l+1)} \Psi_{nlm}(r, \theta, \phi)$$

$$\hat{L}_z \Psi_{nlm}(r, \theta, \phi) = \underbrace{\hbar m} \Psi_{nlm}(r, \theta, \phi)$$

Eigenvalues

$$E_n = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n^2} \right) \quad \{n, l, m\} \in \mathbb{Z}$$

$$n \geq 1, \quad 0 \leq l \leq n, \quad -l \leq m \leq l$$



2.72 Hydrogen Atom Radius

Hydrogen Atom Radius

$$\langle A \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \Psi^*(x, y, z) \hat{A} \Psi(x, y, z)$$

$$\langle A \rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr \Psi^*(r, \theta, \phi) \hat{A} \Psi(r, \theta, \phi)$$

$$\langle r \rangle_{1s} = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \Psi_{100}^* \Psi_{100} r^2 \sin\theta dr d\theta d\phi$$

$$\Psi_{100} = \Psi_{100}^* = \frac{1}{\sqrt{\pi}} \left(\frac{z}{a_0}\right)^{3/2} e^{-2r/a_0} \quad z = +1 \quad (\text{proton})$$

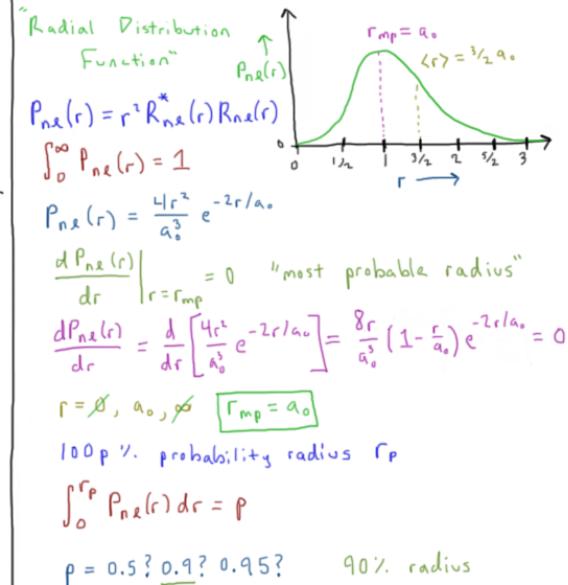
$$\langle r \rangle_{1s} = \left(\int_0^{2\pi} d\phi \right) \left(\int_0^{\pi} \sin\theta d\theta \right) \int_0^{\infty} \left(\frac{1}{\pi}\right) \left(\frac{1}{a_0}\right)^3 r^3 e^{-2r/a_0}$$

$$\langle r \rangle_{1s} = \frac{4\pi}{\pi} \frac{1}{a_0^3} \int_0^{\infty} r^3 e^{-2r/a_0} dr$$

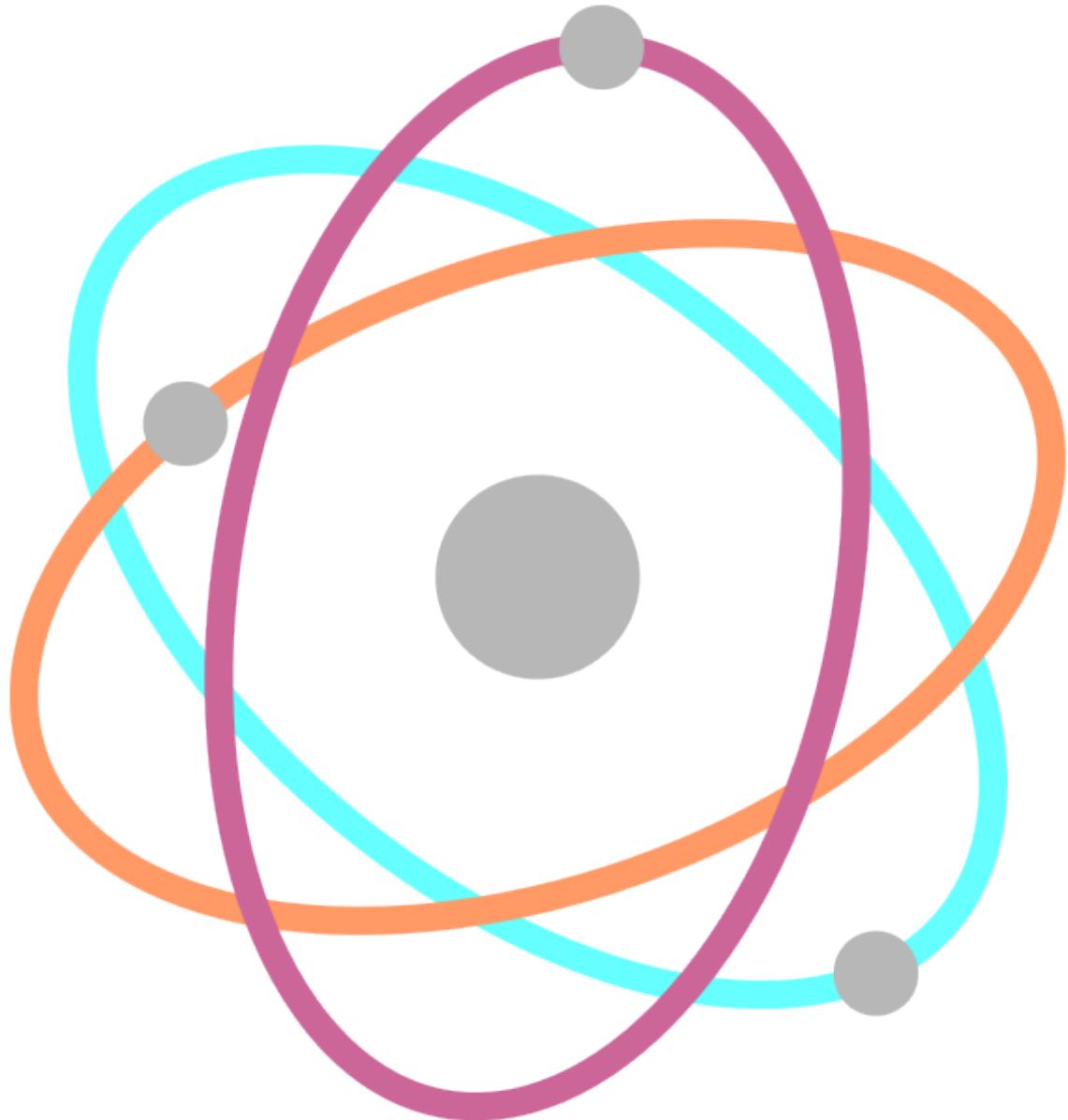
$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad n=3, \quad a=\frac{2}{a_0}$$

$$\langle r \rangle_{1s} = \frac{4}{a_0^3} \cdot 3! \cdot \left(\frac{a_0}{2}\right)^{3+1} = \frac{24a_0^4}{16\pi a_0^6} \quad \boxed{\langle r \rangle_{1s} = \frac{3}{2}a_0}$$

expectation value



2.73 Hydrogen Atom Radial Wavefunction Animation



2.74 Virial Theorem

Virial Theorem

$$E_n = \frac{-m_e e^4}{32\pi^2 \xi_0^2 h^2} \left(\frac{1}{n^2} \right) \quad n=1, 2, 3, \dots$$

$$\hat{H} = \hat{T} + \hat{V} \quad \hat{T} = -\frac{\hbar^2}{2m_e} \nabla^2 \quad \hat{V} = \frac{-e^2}{4\pi \xi_0 r}$$

$$\Psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{a_0} \right)^{3/2} e^{-2r/a_0} \quad z=+1, \quad a_0 = 0.529 \text{ Å}$$

$$\langle A \rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} r^2 dr \Psi_{n,l,m}^* \hat{A} \Psi_{n,l,m}$$

$$\langle V \rangle_{1s} = \int_0^{2\pi} \cancel{d\phi} \int_0^{\pi} \cancel{\sin\theta} d\theta \int_0^{\infty} \left(\frac{1}{4\pi a_0^3} \right) \left(\frac{-e^2}{4\pi \xi_0 r} \right) r^2 e^{-2r/a_0}$$

$$\langle V \rangle_{1s} = \left(\frac{4\pi}{8\pi a_0^3} \right) \left(-\frac{e^2}{8\pi \xi_0} \right) \int_0^{\infty} r^2 e^{-2r/a_0}$$

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad n=1 \quad a = \frac{2}{a_0}$$

$$\langle V \rangle_{1s} = \left(\frac{-e^2}{\pi \xi_0^2 a_0^2} \right) \left(\frac{a_0}{4} \right) = \frac{-e^2}{4\pi \xi_0^2 a_0}$$

$$a_0 = \frac{\xi_0 \hbar^2}{\pi m_e e^2}$$

$$\langle V \rangle_{1s} = \frac{-e^2}{4\pi \xi_0} \left(\frac{4\pi m_e \xi_0^2}{\xi_0 \hbar^2} \right) = \frac{-m_e e^4}{4 \xi_0^2 \hbar^2} = \frac{-m_e e^4}{16 \pi^2 \xi_0^2 \hbar^2}$$

$$\langle v \rangle_{1s} = 2 \langle E \rangle_{1s}$$

$$\langle T \rangle_{1s} + \langle V \rangle_{1s} = \langle E \rangle_{1s}$$

$$\langle T \rangle_{1s} = \langle E \rangle_{1s} - \langle V \rangle_{1s} = \langle E \rangle_{1s} - 2 \langle E \rangle_{1s}$$

$$\langle T \rangle_{1s} = -\langle E \rangle_{2s}$$

$$\langle V \rangle_{1s} = -2 \langle T \rangle_{1s}$$

$$\boxed{\frac{\langle v \rangle}{\langle T \rangle} = -2}$$

True for all atoms and molecules

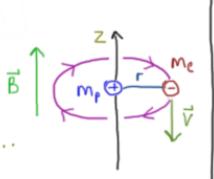
2.75 Zeeman Effect

Zeeman Effect

$$\hat{H} = -\frac{\hbar}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

$$E_n = \frac{-m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n^3} \right) \quad n=1, 2, 3, \dots$$

$$\Psi_{nlm}(r, \theta, \phi) \quad 0 \leq l \leq n \quad -l \leq m \leq l$$



magnetic dipole \vec{m}

$$m = IA = \left(\frac{qV}{2\pi r^2} \right) / (\pi r^2) = \frac{qVr}{2}$$

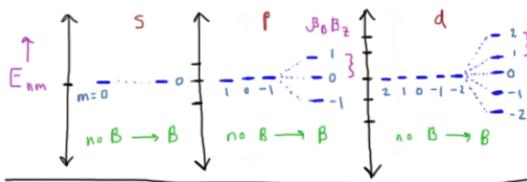
$$I = \frac{qV}{2\pi r} \quad A = \pi r^2$$

$$\vec{L} = \vec{r} \otimes \vec{p} = m(\vec{r} \otimes \vec{v}) \quad p = mv$$

$$\vec{m} = \frac{q(\vec{r} \otimes \vec{v})}{2} = \frac{1}{2m} \vec{L} = \frac{-e}{2m_e} \vec{L} \quad \text{if } |\vec{B}| = B_z$$

$$V_B = -\vec{m} \cdot \vec{B} = -m_z B_z = \frac{e B_z}{2m_e} L_z$$

$$\hat{H} = \hat{H}_0 + \frac{e B_z}{2m_e} \hat{L}_z$$



$$\hat{L}_z \Psi_{nlm} = \hbar m \Psi_{nlm}$$

$$\hat{H} \Psi_{nlm} = E_{nm} \Psi_{nlm} = \left(E_n + \frac{e B_z \hbar}{2m_e} m \right) \Psi_{nlm}$$

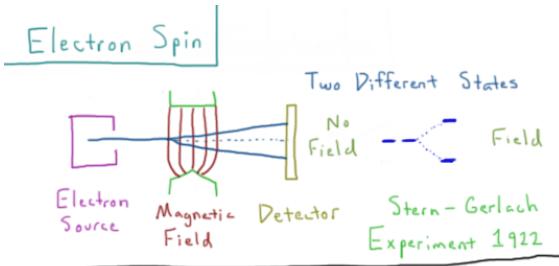
$$\beta_B = \frac{e \hbar}{2m_e} = 9.274 \cdot 10^{-24} \frac{J}{T} \quad \text{"Bohr magneton"}$$

$$E_{nm} = E_n + m \beta_B B_z$$

Lifts degeneracy of m

$$E_n \rightarrow E_{nm}$$

2.76 Electron Spin



"Spin quantum number" $m_s = \pm \frac{1}{2}$ for e^-

Two spin states $|\alpha\rangle$ and $|\beta\rangle$

Spin operators \hat{S}^z and \hat{S}_x

$$\hat{S}^z |\alpha\rangle = \hbar s(s+1) |\alpha\rangle \quad \hat{S}_x |\alpha\rangle = \frac{1}{2}\hbar |\alpha\rangle$$

$$\hat{S}^z |\beta\rangle = \hbar s(s+1) |\beta\rangle \quad \hat{S}_x |\beta\rangle = -\frac{1}{2}\hbar |\beta\rangle$$

$$s = \frac{1}{2}$$

$$m_s = \pm \frac{1}{2}$$

$$\left. \begin{aligned} \langle \alpha | \alpha \rangle &= \langle \beta | \beta \rangle = 1 \\ \langle \alpha | \beta \rangle &= \langle \beta | \alpha \rangle = 0 \end{aligned} \right\} \text{orthonormal}$$

$$|\alpha\rangle = |\frac{1}{2}, \frac{1}{2}\rangle \text{ "spin up"}$$

$$|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle \text{ "spin down"}$$

$$\hat{S}^z |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle$$

$$\hat{S}_x |s, m_s\rangle = \hbar m_s |s, m_s\rangle$$

$$\langle s, m_s | s, m'_s \rangle = \delta_{m_s m'_s}$$

$$\Psi_{n\ell m_\ell m_s}(r, \theta, \phi, \sigma) = \Psi_{n\ell m_\ell}(r, \theta, \phi) \omega(\sigma)$$

$$\omega(\sigma) = (|\alpha\rangle \text{ or } |\beta\rangle)$$

$|n, \ell, m_\ell\rangle \rightarrow \text{"spatial orbital"}$

$|n, \ell, m_\ell, m_s\rangle \rightarrow \text{"spin orbital"}$

$$\langle n, \ell, m_\ell, m_s | n', \ell', m'_\ell, m'_s \rangle = \delta_{nn'} \delta_{\ell\ell'} \delta_{m_\ell m'_\ell} \delta_{m_s m'_s}$$

2.77 Spin-Orbit Coupling

Spin-Orbit Coupling

$$\vec{m}_L = -\frac{e}{2m_e} \vec{L} \quad \text{magnetic moment}$$

$$\hat{L}^2 \Psi_{nlm_l} = \hbar^2 l(l+1) \Psi_{nlm_l} \quad \beta_B = \frac{e\hbar}{2m_e}$$

$$|m_L| = -\frac{e\hbar}{2m_e} \sqrt{l(l+1)} = -\beta_B \sqrt{l(l+1)}$$

$$\vec{m}_s = -\frac{g_e}{2m_e} \vec{s} \quad g=2 \quad \text{"anomalous" spin factor}$$

$$|m_s| = -g\beta_B \sqrt{s(s+1)}$$

$$m_{sz} = -\frac{g_e S_z}{2m_e} = -\frac{g_e \hbar m_s}{2m_e} = -g m_s \beta_B = \pm \beta_B$$

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + \underbrace{f_{so}(r) \hat{L} \cdot \hat{s}}_{\text{spin-orbit interaction term}}$$

$$\hat{T}^2 |j, m_j\rangle = \hbar^2 j(j+1) |j, m_j\rangle$$

$$\hat{T}_z |j, m_j\rangle = \hbar m_j |j, m_j\rangle$$

$l \rightarrow$ orbital angular momentum

$s \rightarrow$ spin angular momentum

$j \rightarrow$ total angular momentum

$m_s = \pm \frac{1}{2} \rightarrow 2$ states

$m_l = 0, \pm 1, \dots, \pm l \rightarrow 2l+1$ states

$m_j \rightarrow 2(2l+1)$ states

$0 \leq l \leq n-1 \quad s = \frac{1}{2}$

$$|l+s| \geq j \geq |l-s|$$

$$-j \leq m_j \leq j$$

$l=0$

$j=\frac{1}{2}$

\downarrow

$m_j = +\frac{1}{2}, -\frac{1}{2}$

$$j=\frac{1}{2}$$

$$-j \leq m_j \leq j$$

$$l=1$$

$$j=\frac{1}{2}$$

$$-\frac{1}{2} \leq m_j \leq \frac{1}{2}$$

$$j=\frac{1}{2}$$

$$-j \leq m_j \leq j$$

$$l=2$$

$$j=\frac{1}{2}$$

$$-\frac{3}{2} \leq m_j \leq \frac{3}{2}$$

$$j=\frac{1}{2}$$

$$-j \leq m_j \leq j$$

2.78 Hydrogen Atom Term Symbols

Hydrogen Atom Term Symbols

Represent electronic states by atomic term symbols

$$2s+1 L_J$$

H atom \rightarrow 1 electron $\rightarrow S = \frac{1}{2}$

$L = 0, 1, 2, 3, 4, 5, 6, \dots$
 S P D F G H I ...

$$|L+S| \geq J \geq |L-S|$$

$$J = |L+\frac{1}{2}|, |L-\frac{1}{2}|$$

$$J \geq m_J \geq -J \quad m_J = J, J-1, \dots$$

$$1s \rightarrow ^2S_{\frac{1}{2}} \quad m_J = \pm \frac{1}{2}$$

$$2p \rightarrow ^2P_{\frac{3}{2}} \quad m_J = \pm \frac{3}{2}, \pm \frac{1}{2}$$

$$2p \rightarrow ^2P_{\frac{1}{2}} \quad m_J = \pm \frac{1}{2}$$

$$3d \rightarrow ^2D_{\frac{5}{2}} \quad m_J = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$$

$$3d \rightarrow ^2D_{\frac{3}{2}} \quad m_J = \pm \frac{3}{2}, \pm \frac{1}{2}$$

$$4f \rightarrow ^2F_{\frac{7}{2}} \quad m_J = \pm \frac{7}{2}, \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$$

$$4f \rightarrow ^2F_{\frac{5}{2}} \quad m_J = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$$

2.79 Hydrogen Atom Spectrum

Hydrogen Atom Spectrum

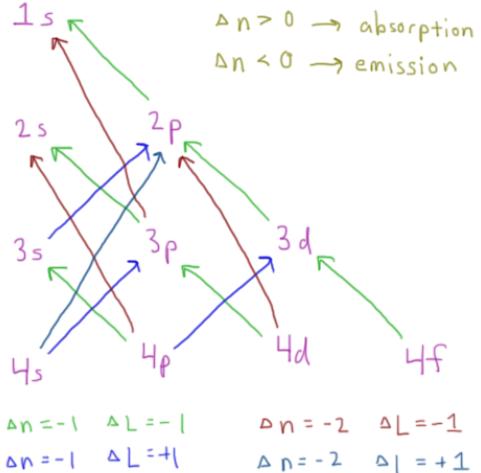
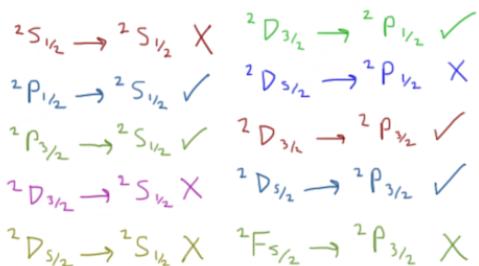
$$E_n = \frac{-m_e e^4}{32\pi^2 \epsilon_0^2 h^3} \left(\frac{1}{n^2} \right) \quad n=1, 2, 3, \dots$$

$$\Delta E = E_{n_2} - E_{n_1} = h\nu = hc\tilde{\nu}$$

$$\tilde{\nu} = R_H \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad R_H = 109,737.3 \text{ cm}^{-1}$$

Selection Rules

$$\Delta S = 0, \Delta L = \pm 1, \Delta J = \pm 1, 0$$



2.80 Helium Atom Hamiltonian

Helium Atom Hamiltonian

$$\begin{aligned} r_1 &= |\vec{r}_1 - \vec{r}_N| \\ r_2 &= |\vec{r}_2 - \vec{r}_N| \\ r_{12} &= |\vec{r}_1 - \vec{r}_2| \\ \nabla_i^2 &= \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \end{aligned}$$

$$\begin{aligned} \hat{H}\Psi(\vec{r}_N, \vec{r}_1, \vec{r}_2) &= E\Psi(\vec{r}_N, \vec{r}_1, \vec{r}_2) \\ \hat{H} &= \hat{T} + \hat{V} \quad \hat{T} = \hat{T}_N + \hat{T}_1 + \hat{T}_2 \\ \hat{T} &= -\frac{\hbar^2}{2M} \nabla_N^2 - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 \end{aligned}$$

B.O. Appx' n → M ≫ m_e → T_N = 0 ↓
 $\Psi = \Psi(\vec{r}_1, \vec{r}_2)$

$$\begin{aligned} \hat{V} &= \hat{V}_{IN} + \hat{V}_{2N} + \hat{V}_{12} \\ \hat{V} &= \underbrace{\frac{-2e^2}{4\pi\epsilon_0 r_1}}_{\text{depends on } r_1} - \underbrace{\frac{2e^2}{4\pi\epsilon_0 r_2}}_{\text{depends on } r_2} + \underbrace{\frac{1e^2}{4\pi\epsilon_0 r_{12}}}_{\text{depends on } r_1 \text{ and } r_2} \end{aligned}$$

"non-separable"
 no exact solution
 need approximate methods

2.81 Variational Principle

Variational Principle

$\Psi_0 \rightarrow$ exact ground state wavefunction

$E_0 \rightarrow$ exact ground state energy

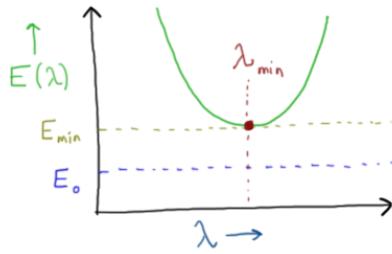
$$\hat{H}\Psi_0 = E_0\Psi_0$$

$\phi \rightarrow$ approximate ground state wavefunction

$$E_\phi = \frac{\int \Psi_0^* \hat{H} \Psi_0 d\tau}{\int \Psi_0^* \Psi_0 d\tau} = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

$$\boxed{E_\phi \geq E_0} \quad \text{for all } \phi$$



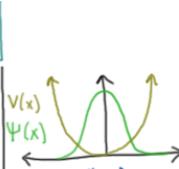
$$E_\phi(\lambda) \geq E_0$$

$\lambda \rightarrow$ parameter

$$\phi = \phi(\lambda)$$

$$\min_{\lambda} E_\phi \quad \text{when} \quad \frac{dE_\phi(\lambda)}{d\lambda} = 0$$

2.82 Variational Principle Example

Variational Principle Example	
$\phi = e^{-\alpha x^2}$ $\hat{V} = \frac{1}{2} k x^2$ $\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ $\hat{H} = \hat{T} + \hat{V}$ $E_\phi = \frac{\langle \phi \hat{H} \phi \rangle}{\langle \phi \phi \rangle}$	
$\langle \phi \phi \rangle = \int_{-\infty}^{\infty} dx (e^{-\alpha x^2})^* (e^{-\alpha x^2})$ $\langle \phi \phi \rangle = \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = \sqrt{\frac{\pi}{2\alpha}}$ $\langle \phi \hat{V} \phi \rangle = \int_{-\infty}^{\infty} dx (e^{-\alpha x^2})^* \left(\frac{1}{2} k x^2 \right) (e^{-\alpha x^2})$ $\langle \phi \hat{V} \phi \rangle = \frac{1}{2} k \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{1}{2} k \left(\frac{1}{4\alpha} \sqrt{\frac{\pi}{2\alpha}} \right)$ $\langle \phi \hat{T} \phi \rangle = \int_{-\infty}^{\infty} dx (e^{-\alpha x^2}) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} (e^{-\alpha x^2}) \right)$ $\frac{d^2}{dx^2} (e^{-\alpha x^2}) = \frac{d}{dx} (-2\alpha x e^{-\alpha x^2}) = -2\alpha c^{-\alpha x^2} (1 - 2\alpha x^2)$ $\langle \phi \hat{T} \phi \rangle = -\frac{\hbar^2}{2m} (-2\alpha) \int_{-\infty}^{\infty} dx (e^{-\alpha x^2} - 2\alpha x^2 e^{-\alpha x^2})$ $\langle \phi \hat{T} \phi \rangle = \frac{\hbar^2 \alpha}{m} \left[\sqrt{\frac{\pi}{2\alpha}} - 2 \times \left(\frac{1}{4\alpha} \sqrt{\frac{\pi}{2\alpha}} \right) \right] = \frac{\hbar^2 \alpha}{2m} \sqrt{\frac{\pi}{2\alpha}}$	$E_\phi = \frac{\langle \phi \hat{T} \phi \rangle + \langle \phi \hat{V} \phi \rangle}{\langle \phi \phi \rangle} = \frac{\frac{\hbar^2 \alpha}{2m} \sqrt{\frac{\pi}{2\alpha}} + \frac{k}{8\alpha} \sqrt{\frac{\pi}{2\alpha}}}{\sqrt{\frac{\pi}{2\alpha}}}$ $E_\phi = \frac{\hbar^2 \alpha}{2m} + \frac{k}{8\alpha}$ $\frac{dE_\phi}{d\alpha} = \frac{\hbar^2}{2m} - \frac{k}{8\alpha^2} = 0$ $\alpha_{\min} = \frac{\sqrt{km}}{2\hbar}$ $E_{\alpha_{\min}} = \frac{\hbar}{2\sqrt{m}} \left(\frac{\sqrt{km}}{2\hbar} \right) + \frac{\sqrt{k}}{4} \left(\frac{2\hbar}{\sqrt{km}} \right)$ $E_{\alpha_{\min}} = \frac{\hbar}{4} \sqrt{\frac{k}{m}} + \frac{\hbar}{4} \sqrt{\frac{k}{m}} = \frac{\hbar}{2} \sqrt{\frac{k}{m}}$ $\omega = \sqrt{\frac{k}{m}}$ $E_{\alpha_{\min}} = \frac{1}{2} \hbar \omega$ $E_{\alpha_{\min}} = E_0 \rightarrow \Psi_{\alpha_{\min}} = \Psi_0$ $\Phi_{\alpha_{\min}}(x) = \left(\frac{2\alpha}{\pi} \right)^{1/4} e^{-\frac{\sqrt{km}}{2\hbar} x^2}$

2.83 Linear Variational Method

<p><u>Linear Variational Method</u></p> <p>$\phi = \sum_{n=1}^k c_n f_n(x)$ $f_n(x) \rightarrow$ "basis functions"</p> <p>$\{f_n(x)\} \rightarrow$ "basis set" $\{c_n\} \rightarrow$ "variational parameters"</p> <p>$\phi = c_1 f_1(x) + c_2 f_2(x) = c_1 1\rangle + c_2 2\rangle = \phi\rangle$</p> <p>Assume $\{c_n\} \in \mathbb{R}$ and $\{f_n(x)\} \in \mathbb{R} \forall x$</p> <p>$\langle E \rangle = \frac{\langle \phi \hat{H} \phi \rangle}{\langle \phi \phi \rangle}$ $H_{ij} = \langle i \hat{H} j \rangle = \int d\tau f_i^* \hat{H} f_j$</p> <p>$S_{ij} = \langle i j \rangle = \int d\tau f_i^* f_j$</p> <p>$\langle \phi \hat{H} \phi \rangle = (c_1 \langle 1 + c_2 \langle 2) \hat{H} (c_1 1\rangle + c_2 2\rangle)$</p> <p>$= c_1^2 \langle 1 \hat{H} 1 \rangle + c_1 c_2 \langle 1 \hat{H} 2 \rangle + c_2 c_1 \langle 2 \hat{H} 1 \rangle + c_2^2 \langle 2 \hat{H} 2 \rangle$</p> <p>$= c_1^2 H_{11} + c_1 c_2 H_{12} + c_2 c_1 H_{21} + c_2^2 H_{22} \quad H_{12} = H_{21}$</p> <p>$= c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$</p> <p>$\langle \phi \phi \rangle = (c_1 \langle 1 + c_2 \langle 2)(c_1 1\rangle + c_2 2\rangle)$</p> <p>$= c_1^2 \langle 1 1 \rangle + c_1 c_2 \langle 1 2 \rangle + c_2 c_1 \langle 2 1 \rangle + c_2^2 \langle 2 2 \rangle$</p> <p>$= c_1^2 S_{11} + c_1 c_2 S_{12} + c_2 c_1 S_{21} + c_2^2 S_{22} \quad S_{12} = S_{21}$</p> <p>$= c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}$</p> <p>$\langle E \rangle = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$</p> <p>$\{S_{ij}\} \rightarrow$ "overlap integrals"</p>	$\frac{\partial}{\partial c_1} \langle \phi \hat{H} \phi \rangle = 2c_1 H_{11} + 2c_2 H_{12} = \frac{\partial}{\partial c_1} [\langle \phi \phi \rangle \langle E \rangle]$ <p>$\frac{\partial}{\partial c_1} \langle \phi \phi \rangle = 2c_1 S_{11} + 2c_2 S_{12}$</p> <p>$\langle \phi \phi \rangle \frac{\partial E}{\partial c_1} + E \frac{\partial \langle \phi \phi \rangle}{\partial c_1} = \frac{\partial \langle \phi \hat{H} \phi \rangle}{\partial c_1}$</p> <p>$\frac{\partial E}{\partial c_1} = 0 = \frac{1}{\langle \phi \phi \rangle} \left[\frac{\partial \langle \phi \hat{H} \phi \rangle}{\partial c_1} - E \frac{\partial \langle \phi \phi \rangle}{\partial c_1} \right]$</p> <p>$2c_1 H_{11} + 2c_2 H_{12} - E (2c_1 S_{11} + 2c_2 S_{12}) = 0$</p> <p>$c_1 (H_{11} - ES_{11}) + c_2 (H_{12} - ES_{12}) = 0$</p> <p>$c_1 (H_{21} - ES_{21}) + c_2 (H_{22} - ES_{22}) = 0$</p> <p>$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$</p> <p>$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$</p> <p>$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad \text{"Secular Determinant"}$</p> <p>$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \quad S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \quad \underline{c} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad H \underline{c} = E S \underline{c}$</p> <p>Matrix Schrödinger Equation $H - ES = 0$</p>
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2.84 Secular Determinant

Secular Determinant

$$\phi = \sum_{n=1}^k c_n \phi_n \quad \text{trial wavefunction}$$

$\phi_n \rightarrow \text{basis function}$ $\{\phi_n\} \rightarrow \text{basis set}$

$\{c_n\} \rightarrow \text{variational parameters}$

$$\langle E \rangle = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \quad |H - E| = 0 \quad H \leq E \leq$$

$$\frac{\partial E}{\partial c_n} = 0 \quad \text{for all } c_n \quad H_{ij} = \langle i | \hat{H} | j \rangle = \int \phi_i^* \hat{H} \phi_j d\tau$$

$$S_{ij} = \langle i | j \rangle = \int \phi_i^* \phi_j d\tau$$

$\phi = c_1 \phi_1 + c_2 \phi_2 \quad S_{ij} = \delta_{ij}$ "orthonormal"

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = \begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0$$

$$(H_{11} - E)(H_{22} - E) - H_{12}^2 = 0$$

$$E^2 + (-H_{11} - H_{22})E + (H_{11}H_{22} - H_{12}^2) = 0$$

$$E = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} + H_{22})^2 - 4(H_{11}H_{22} - H_{12}^2)}}{2(1)}$$

$$RAD = H_{11}^2 + 2H_{11}H_{22} + H_{22}^2 - 4H_{11}H_{22} + 4H_{12}^2$$

$$RAD = (H_{11} - H_{22})^2 + 4H_{12}^2$$

$$E = \left(\frac{H_{11} + H_{22}}{2} \right) \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2} \right)^2 + H_{12}^2}$$

average 1/2 difference coupling

2.85 Linear Variational Example

Linear Variational Example

$$V(x) = \frac{V_0 x}{\lambda} \sin\left(\frac{\pi x}{\lambda}\right)$$

$$\phi_1(x) = \sqrt{\frac{2}{\lambda}} \sin\left(\frac{\pi x}{\lambda}\right)$$

$$\phi_2(x) = \sqrt{\frac{2}{\lambda}} \sin\left(\frac{2\pi x}{\lambda}\right)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{V_0 x}{\lambda}$$

$$E_1 = \frac{\hbar^2}{8m\lambda^2}, \quad E_2 = 4E_1$$

$$S_{ij} = \langle i | j \rangle = \int \psi_i^*(x) \psi_j(x) dx = \delta_{ij}$$

$$H_{ij} = \langle i | \hat{H} | j \rangle = \int \psi_i^*(x) \hat{H} \psi_j(x) dx$$

$$E = \left(\frac{H_{11} + H_{22}}{2} \right) \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2} \right)^2 + H_{11}^2}$$

$$H_{nn} = \underbrace{\langle n | \hat{T} | n \rangle}_{E_n} + \underbrace{\langle n | \hat{V} | n \rangle}_{H_{nn}}$$

$$H_{nn} = E_n + \int_0^\lambda dx \left(\sqrt{\frac{2}{\lambda}} \sin\left(\frac{n\pi x}{\lambda}\right) \right) \left(\frac{V_0 x}{\lambda} \right) \left(\sqrt{\frac{2}{\lambda}} \sin\left(\frac{n\pi x}{\lambda}\right) \right)$$

$$H_{nn} = n^2 E_1 + \cancel{\frac{2}{\lambda}} \left(\frac{V_0}{\lambda} \right) \left(\cancel{\frac{\lambda}{\lambda}} \right) = E_n + \frac{1}{2} V_0$$

$$H_{12} = \langle 1 | \hat{T} | 2 \rangle + \langle 1 | \hat{V} | 2 \rangle$$

$$H_{12} = \int_0^\lambda dx \left(\sqrt{\frac{2}{\lambda}} \sin\left(\frac{\pi x}{\lambda}\right) \right) \left(\frac{V_0 x}{\lambda} \right) \left(\sqrt{\frac{2}{\lambda}} \sin\left(\frac{2\pi x}{\lambda}\right) \right)$$

$$H_{12} = \frac{2}{\lambda} \left(\frac{V_0}{\lambda} \right) \int_0^\lambda x \sin\left(\frac{\pi x}{\lambda}\right) \sin\left(\frac{2\pi x}{\lambda}\right) dx$$

$$H_{12} = \frac{2}{\lambda} \left(\frac{V_0}{\lambda} \right) \left(\cancel{-\frac{8}{9\pi^2}} \right) = \frac{-16}{9\pi^2} V_0$$

$$\frac{H_{11} + H_{22}}{2} = \frac{1}{2} (E_1 + \frac{V_0}{2} + 4E_1 + \frac{V_0}{2}) = \frac{5}{2} E_1 + \frac{V_0}{2}$$

$$\frac{H_{11} - H_{22}}{2} = \frac{1}{2} (E_1 + \cancel{\frac{V_0}{2}} - 4E_1 - \cancel{\frac{V_0}{2}}) = -\frac{3}{2} E_1$$

$$E_{\pm} = \frac{5}{2} E_1 + \frac{V_0}{2} \pm \sqrt{\left(\frac{3}{2} E_1 \right)^2 + \left(\frac{16}{9\pi^2} V_0 \right)^2}$$

$$E_+ = E_1 + \frac{V_0}{2} + \mu \quad E_- = E_1 + \frac{V_0}{2} - \mu$$

2.86 Perturbation Theory

Perturbation Theory

$$\hat{H}\Psi_n = E_n\Psi_n \quad \text{Unknown}$$

$$\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)} \quad \text{Known}$$

$$\hat{H} = \underbrace{\hat{H}^{(0)}}_{\substack{\text{Total} \\ \text{Hamiltonian}}} + \underbrace{\hat{V}}_{\substack{\text{Reference} \\ \text{Hamiltonian}}} \rightarrow \text{Perturbation}$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots \xrightarrow{\text{"Order"}} \text{1st, 2nd, 3rd, ...}$$

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)} + \Psi_n^{(2)} + \dots$$

$$E_n^{(0)} = \langle n | \hat{H}^{(0)} | n \rangle \quad E_n^{(1)} = \langle n | \hat{V} | n \rangle$$

$$\Psi_n^{(1)} = \sum_{m \neq n}^{\infty} \frac{\langle m | \hat{V} | n \rangle}{E_n^{(0)} - E_m^{(0)}} | m \rangle$$

Anharmonic Oscillator

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 + \frac{1}{6} \gamma_3 x^3 + \frac{1}{24} \gamma_4 x^4$$

Particle in a Slanted Box

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{V_0 x}{\lambda}$$

2.87 Perturbation Theory Derivation

Perturbation Theory Derivation

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{V}$$

$$\Psi_n = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$\hat{H}\Psi = E\Psi$$

$$(\hat{H}^{(0)} + \lambda \hat{V})(\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots)$$

$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)(\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \dots)$$

$$\lambda^0 (\hat{H}^{(0)} \Psi_n^{(0)}) = \lambda^0 (E_n^{(0)} \Psi_n^{(0)}) \quad "0^{\text{th}} \text{ order}"$$

$$\lambda^1 (\hat{H}^{(0)} \Psi_n^{(1)} + \hat{V} \Psi_n^{(0)}) = \lambda^1 (E_n^{(0)} \Psi_n^{(1)} + E_n^{(1)} \Psi_n^{(0)}) \quad "1^{\text{st}} \text{ order}"$$

$$\hat{H}^0 |n'\rangle + \hat{V} |n^0\rangle = E_n^0 |n'\rangle + E_n^1 |n^0\rangle$$

$$\langle n^0 | \hat{H}^0 | n' \rangle + \langle n^0 | \hat{V} | n^0 \rangle = \langle n^0 | E_n^0 | n' \rangle + \langle n^0 | E_n^1 | n^0 \rangle$$

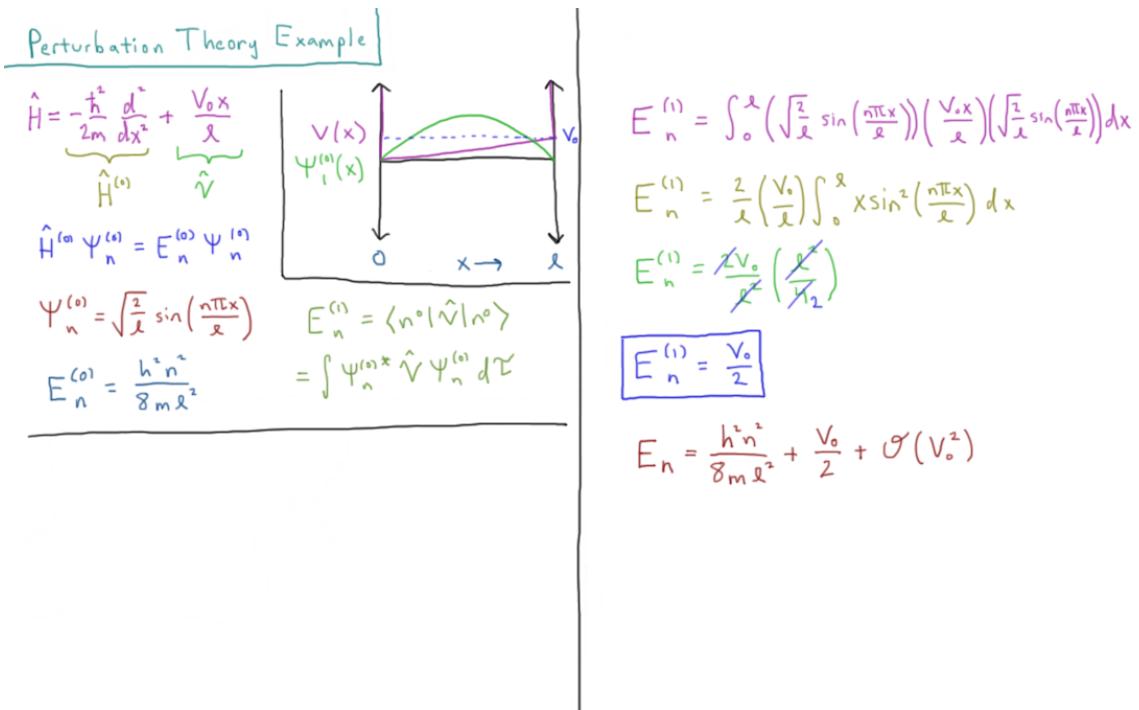
$$\langle n^0 | \hat{H}^0 | n^0 \rangle + \langle n^0 | \hat{V} | n^0 \rangle = E_n^0 \langle n^0 | n' \rangle + E_n^1 \langle n^0 | n^0 \rangle$$

$$E_n^0 \langle n^0 | n' \rangle + \langle n^0 | \hat{V} | n^0 \rangle = \cancel{E_n^0 \langle n^0 | n^0 \rangle} + E_n^1$$

$$E_n^{(1)} = \langle n^0 | \hat{V} | n^0 \rangle$$

$$E_n^{(1)} = \int \Psi_n^{(0)*} \hat{V} \Psi_n^{(0)} d\tau$$

2.88 Perturbation Theory Example

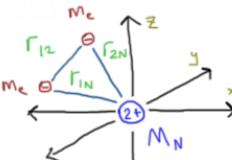


2.89 Atomic Units

Atomic Units

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_{IN}} - \frac{2e^2}{4\pi\epsilon_0 r_{2N}} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$



$$m_e = 1 \quad 9.1094 \cdot 10^{-31} \text{ kg}$$

$$e = 1 \quad 1.6022 \cdot 10^{-19} \text{ C}$$

$$\hbar = 1 \quad 1.0546 \cdot 10^{-34} \text{ J} \cdot \text{s}$$

$$4\pi\epsilon_0 = 1 \quad 1.1127 \cdot 10^{-10} \text{ C}^2 / \text{J} \cdot \text{m}$$

$$a_0 = 1 \quad 5.2918 \cdot 10^{-11} \text{ m}$$

$$E_H = 1 \quad 4.3597 \cdot 10^{-18} \text{ J}$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

$$1 \text{ Bohr} = 0.529 \text{ \AA} = 52.9 \text{ pm}$$

$$E_H = \frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2}$$

$$1 \text{ Hartree} = 4.36 \cdot 10^{-18} \text{ J} = 627.5 \frac{\text{kcal}}{\text{mol}} \\ = 27.2 \text{ eV} = 2625 \frac{\text{kJ}}{\text{mol}}$$

$$\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_{IN}} - \frac{2}{r_{2N}} + \frac{1}{r_{12}}$$

$$E_{100} = -0.5 \text{ H}$$

2.90 Helium Atom Energy Approximations

Helium Atom Energy Approximations	
$\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}}$ $\hat{H}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_{iN}}$ $\Psi_{100} = \sqrt{\frac{Z^3}{4\pi a_0}} e^{-Zr/a_0}$ $\Phi(\vec{r}_1, \vec{r}_2) = \Psi_{100}(1) \Psi_{100}(2)$ $\Phi(1, 2) = \Psi_{100}(1) \Psi_{100}(2)$	
$E = \int_{\mathbb{R}^3} d^3\vec{r}_1 \int_{\mathbb{R}^3} d^3\vec{r}_2 \Phi^*(1, 2) \hat{H} \Phi(1, 2) \quad Z=2$ if $\hat{H} = \hat{H}_1 + \hat{H}_2 \rightarrow E = -2\left(\frac{Z^2}{2}\right) = -4.000 \text{ H}$ Variational $\rightarrow Z$ is a parameter $E_Z = Z^2 - \frac{27}{9}Z \quad \frac{\partial E_Z}{\partial Z} = 0 \quad Z_{\min} = 1.6875$ $E_{Z_{\min}} = -\left(\frac{27}{16}\right)^2 = -2.848 \text{ H}$	perturbative $\rightarrow \hat{H}^{(0)} = \hat{H}_1 + \hat{H}_2 \quad \hat{V} = \frac{1}{r_{12}}$ $\Psi^{(0)} = \Phi(1, 2)$ $E^{(0)} = -2\left(\frac{Z^2}{2}\right) = -Z^2 = -4.000 \text{ H}$ $E^{(1)} = \langle 12 12 \rangle = +1.250 \text{ H}$ $= \int_{\mathbb{R}^3} d\vec{r}_1 \int_{\mathbb{R}^3} d\vec{r}_2 \Psi_{100}^*(1) \Psi_{100}^*(2) \frac{1}{r_{12}} \Psi_{100}(1) \Psi_{100}(2)$ $E_{PT1} = -2.750 \text{ H}$ $E_{PT2} = -2.9077 \text{ H}$ $E_{HF} = -2.8617 \text{ H}$

2.91 Hartree-Fock Helium Atom

Hartree-Fock for Helium

$$\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_{1N}} - \frac{2}{r_{2N}} + \frac{1}{r_{12}}$$

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_1) \Psi(\vec{r}_2)$$

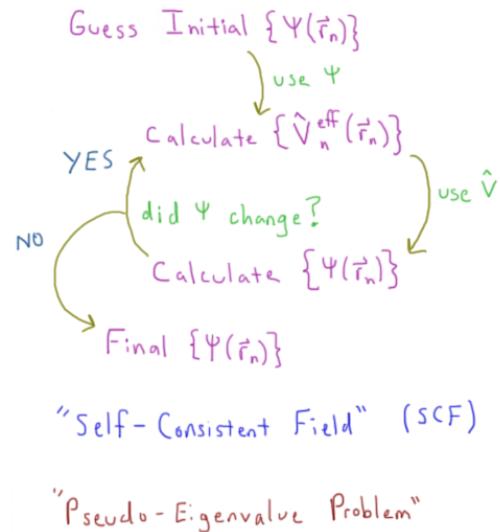
$$E = \int_{\mathbb{R}^3} d^3 \vec{r}_1 \int_{\mathbb{R}^3} d^3 \vec{r}_2 \Psi^*(\vec{r}_1, \vec{r}_2) \hat{H} \Psi(\vec{r}_1, \vec{r}_2)$$

$$\hat{H}_1^{\text{eff}} = -\frac{1}{2} \nabla_1^2 - \frac{2}{r_{1N}} + \underbrace{\hat{V}_1^{\text{eff}}(\vec{r}_1)}_{\text{"mean field"}}$$

$$\hat{V}_1^{\text{eff}}(\vec{r}_1) = \int_{\mathbb{R}^3} d^3 \vec{r}_2 \Psi^*(\vec{r}_1) \Psi(\vec{r}_2) \frac{1}{r_{12}}$$

$$\hat{H}_1^{\text{eff}} \Psi(\vec{r}_1) = \underbrace{\epsilon_1}_{\text{"orbital energy"}} \Psi(\vec{r}_1)$$

$$\hat{H}_2^{\text{eff}} \Psi(\vec{r}_2) = \epsilon_2 \Psi(\vec{r}_2)$$



2.92 Hartree-Fock Helium Energy

Hartree-Fock Helium Energy

$$\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_{1N}} - \frac{2}{r_{2N}} + \frac{1}{r_{12}}$$

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_1) \Psi(\vec{r}_2)$$

$$\hat{H}_1^{\text{eff}} = -\frac{1}{2} \nabla_1^2 - \frac{2}{r_{1N}} + \hat{V}_1^{\text{eff}}(\vec{r}_1)$$

$$\hat{V}_1^{\text{eff}} = \int_{\mathbb{R}^3} d^3 \vec{r}_2 \Psi^*(\vec{r}_2) \Psi(\vec{r}_2) \frac{1}{r_{12}}$$

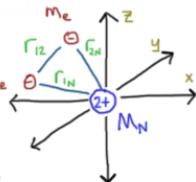
$$\hat{H}_1^{\text{eff}} \Psi(\vec{r}_1) = \xi_1 \Psi(\vec{r}_1)$$

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \frac{2}{r_{iN}}$$

$$h_i = \int_{\mathbb{R}^3} d^3 \vec{r}_i \Psi^*(\vec{r}_i) \hat{h}_i \Psi(\vec{r}_i)$$

$$J_{12} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \Psi^*(\vec{r}_1) \Psi^*(\vec{r}_2) \frac{1}{r_{12}} \Psi(\vec{r}_1) \Psi(\vec{r}_2) d^3 \vec{r}_1 d^3 \vec{r}_2$$

$$\xi_i = \int_{\mathbb{R}^3} \Psi^*(\vec{r}_i) \hat{H}_i^{\text{eff}} \Psi(\vec{r}_i) d^3 \vec{r}_i$$



$$\xi_1 = h_1 + J_{12}$$

$$\xi_2 = h_2 + J_{12}$$

$$E = h_1 + h_2 + J_{12}$$

$$\xi_1 + \xi_2 = h_1 + h_2 + 2J_{12}$$

$$E \neq \sum_{i=1}^n \xi_i$$

I.P. \rightarrow "ionization potential"

$$E - \xi_1 = h_2$$

$$\boxed{\text{I.P.} \approx -\xi_1} \quad \text{"Koopman's Theorem"}$$

2.93 Antisymmetry Principle

Antisymmetry Principle

All electronic wavefunctions must be anti-symmetric under the exchange of any two electrons

$$\Psi(1,2) = -\Psi(2,1)$$

$$\Psi(1,2) = \Psi_1(1)\Psi_2(2) \quad \text{"Hartree Product"}$$

$$\Psi(2,1) = \Psi_1(2)\Psi_2(1)$$

$$\Psi(1,2) \neq -\Psi(2,1) \quad X$$

$$\Psi(1,2) = \Psi_1(1)\Psi_2(2) - \Psi_2(1)\Psi_1(2)$$

$$\Psi(2,1) = \Psi_1(2)\Psi_2(1) - \Psi_2(2)\Psi_1(1)$$

$$\Psi(1,2) = -\Psi(2,1) \quad \checkmark$$

"Slater Determinant"

if $\Psi_1 = \Psi_2$

$$\Psi(1,2) = \Psi_1(1)\Psi_2(2) - \Psi_1(1)\Psi_1(2) = 0$$

if 2 electrons in same orbital

then $\Psi = 0$

"Pauli Exclusion Principle"

2.94 Slater Determinants

Slater Determinants

$$\Psi(1,2) = -\Psi(2,1)$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}} [\Psi_1(1)\Psi_2(2) - \Psi_1(2)\Psi_2(1)]$$

$$\Psi_1(i) = 1s\alpha(\vec{r}_i) \quad \Psi_2(i) = 1s\beta(\vec{r}_i)$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_1(1) & \Psi_2(1) \\ \Psi_1(2) & \Psi_2(2) \end{vmatrix}$$

$$\begin{aligned} \Psi(1,2,3) &= -\Psi(1,3,2) = \Psi(3,1,2) = -\Psi(3,2,1) \\ &= \Psi(2,3,1) = -\Psi(2,1,3) \end{aligned}$$

$$\begin{aligned} \Psi(1,2,3) &= \frac{1}{\sqrt{6}} [\Psi_1(1)\Psi_2(2)\Psi_3(3) - \Psi_1(1)\Psi_2(3)\Psi_1(2) \\ &\quad + \Psi_1(3)\Psi_2(1)\Psi_3(2) - \Psi_1(3)\Psi_2(2)\Psi_3(1) \\ &\quad + \Psi_1(2)\Psi_2(3)\Psi_3(1) - \Psi_1(2)\Psi_2(1)\Psi_3(2)] \end{aligned}$$

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(1) & \Psi_2(1) & \dots & \Psi_N(1) \\ \Psi_1(2) & \Psi_2(2) & \dots & \Psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_1(N) & \Psi_2(N) & \dots & \Psi_N(N) \end{vmatrix}$$

$$\Psi(1,2,\dots,i,j,\dots,N) = -\Psi(1,2,\dots,j,i,\dots,N)$$

2.95 Hartree-Fock Atomic Energy

Hartree-Fock Atomic Energy	
$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(1) & \Psi_2(1) \dots \Psi_N(1) \\ \Psi_1(2) & \Psi_2(2) \dots \Psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_1(N) & \Psi_2(N) \dots \Psi_N(N) \end{vmatrix}$	$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_{iN}}$ $h_i = \int_{\mathbb{R}^3} d^3 \vec{r}_i \Psi_i^*(\vec{r}_i) \hat{h}_i \Psi_i(\vec{r}_i)$ one electron integral
$\Psi(1, 2, \dots, i, j, \dots, N) = -\Psi(1, 2, \dots, j, i, \dots, N)$	$J_{ij} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d^3 \vec{r}_i d^3 \vec{r}_j \Psi_i^*(\vec{r}_i) \Psi_j^*(\vec{r}_j) \frac{1}{r_{ij}} \Psi_i(\vec{r}_i) \Psi_j(\vec{r}_j)$ Coulomb integral
$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_{iN}} \right) + \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{r_{ij}}$	$K_{ij} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d^3 \vec{r}_i d^3 \vec{r}_j \Psi_i^*(\vec{r}_i) \Psi_j^*(\vec{r}_j) \frac{1}{r_{ij}} \Psi_j(\vec{r}_i) \Psi_i(\vec{r}_j)$ Exchange integral
$E = \langle \Psi(1, 2, \dots, N) \hat{H} \Psi(1, 2, \dots, N) \rangle$	$J_{ii} = K_{ii} \rightarrow (J_{ii} - K_{ii}) = 0$ No "self-interaction" in Hartree-Fock
$E = \int_{\mathbb{R}^3} d^3 \vec{r}_1 \int_{\mathbb{R}^3} d^3 \vec{r}_2 \dots \int_{\mathbb{R}^3} d^3 \vec{r}_N \Psi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \hat{H} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$	
$E = \underbrace{\sum_{i=1}^N h_i}_{\text{1 electron energy}} + \underbrace{\sum_{i=1}^N \sum_{j=i+1}^N (J_{ij} - K_{ij})}_{\text{2 electron energy}}$	

2.96 Hartree-Fock Operators

Hartree-Fock Operators

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_{in}} \quad \text{"one electron operator"}$$

$$\hat{T}_i \Psi_i(\vec{r}_i) = \Psi_i(\vec{r}_i) \int_{\mathbb{R}^3} d^3 \vec{r}_2 \Psi_i^*(\vec{r}_2) \Psi_i(\vec{r}_2) \frac{1}{r_{12}}$$

$$\hat{K}_i \Psi_i(\vec{r}_i) = \Psi_i(\vec{r}_i) \int_{\mathbb{R}^3} d^3 \vec{r}_2 \Psi_i^*(\vec{r}_2) \Psi_i(\vec{r}_2) \frac{1}{r_{12}}$$

Coulomb } "two electron operators"
Exchange }

$$h_i = \int_{\mathbb{R}^3} d^3 \vec{r}_i \Psi_i^*(\vec{r}_i) \hat{h}_i \Psi_i(\vec{r}_i) \quad \text{"one electron integral"}$$

$$T_{ij} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d^3 \vec{r}_i d^3 \vec{r}_2 \Psi_i^*(\vec{r}_i) \Psi_j^*(\vec{r}_2) \frac{1}{r_{12}} \Psi_i(\vec{r}_i) \Psi_j(\vec{r}_2)$$

$$K_{ij} = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d^3 \vec{r}_i d^3 \vec{r}_2 \Psi_i^*(\vec{r}_i) \Psi_j^*(\vec{r}_2) \frac{1}{r_{12}} \Psi_i(\vec{r}_i) \Psi_j(\vec{r}_2)$$

coulomb integral } "two electron exchange integral" integrals "

$$\hat{F}(\vec{r}_i) = \hat{h}_i(\vec{r}_i) + \sum_{j=1}^N \underbrace{(\hat{T}_{ij}(\vec{r}_i) - \hat{K}_{ij}(\vec{r}_i))}_{\text{"Fock operator"}}$$

$$\hat{V}_{\text{eff}}(\vec{r}_i)$$

$$\hat{F}(\vec{r}_i) \Psi_i(\vec{r}_i) = \xi_i \Psi_i(\vec{r}_i) \quad i=1, 2, \dots, N$$

$$\xi_i = \int_{\mathbb{R}^3} d^3 \vec{r}_i \Psi_i^*(\vec{r}_i) \hat{F}(\vec{r}_i) \Psi_i(\vec{r}_i)$$

$$\xi_i = h_i + \sum_{j=1}^N (T_{ij} - K_{ij})$$

$$\sum_{i=1}^N \xi_i = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{j=1}^N (T_{ij} - K_{ij})$$

$$E_{HF} = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (T_{ij} - K_{ij})$$

2.97 Hartree-Fock-Roothaan Equations

Hartree-Fock Roothaan Equations

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_{in}} \quad \text{"one electron operator"}$$

$$\hat{T}_i \Psi_i(\vec{r}_i) = \Psi_i(\vec{r}_i) \int_{\mathbb{R}^3} d^3 \vec{r}_2 \Psi_i^*(\vec{r}_2) \Psi_i(\vec{r}_2) \frac{1}{r_{12}}$$

$$\hat{K}_i \Psi_i(\vec{r}_i) = \Psi_i(\vec{r}_i) \int_{\mathbb{R}^3} d^3 \vec{r}_2 \Psi_i^*(\vec{r}_2) \Psi_i(\vec{r}_2) \frac{1}{r_{12}}$$

Coulomb } "two electron operators"
Exchange }

$$\hat{F}(\vec{r}_i) = \hat{h}_i(\vec{r}_i) + \sum_{j=1}^N (\hat{T}_j(\vec{r}_i) - \hat{K}_j(\vec{r}_i))$$

$$\hat{F}(\vec{r}_i) \Psi_i(\vec{r}_i) = \xi'_i \Psi_i(\vec{r}_i)$$

$$\Psi_i(\vec{r}_i) = \sum_{v=1}^k c_{vi} \phi_v(\vec{r}_i) \quad \{\phi_v(\vec{r}_i)\} \text{"basis functions"}$$

$$\phi_v(\vec{r}_i) = N x^a y^b z^c e^{-\beta_v r_{in}} \text{"Slater function"}$$

$$\phi_v(\vec{r}_i) = N x^a y^b z^c e^{-\beta_v r_{in}^2} \text{"Gaussian function"}$$

$$l = a+b+c \quad \text{angular momentum}$$

$$\hat{F}(\vec{r}_i) \left[\sum_{v=1}^k c_{vi} \phi_v(\vec{r}_i) \right] = \xi'_i \left[\sum_{v=1}^k c_{vi} \phi_v(\vec{r}_i) \right]$$

$$F_{mv} = \int_{\mathbb{R}^3} d^3 \vec{r}_1 \phi_m^*(\vec{r}_1) \hat{F}(\vec{r}_1) \phi_v(\vec{r}_1)$$

$$S_{mv} = \int_{\mathbb{R}^3} d^3 \vec{r}_1 \phi_m^*(\vec{r}_1) \phi_v(\vec{r}_1)$$

$$\sum_{v=1}^k F_{mv} c_{vi} = \xi'_i \sum_{v=1}^k S_{mv} c_{vi}$$

$$\boxed{F_c = \xi'_i S_c} \quad F, S \rightarrow K \times K \text{ matrices}$$

N occupied spin orbitals

$K-N$ virtual spin orbitals

2.98 Hartree-Fock Spin

Hartree-Fock Spin

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_{iN}} \quad h_i = \int_{R^3} d^3 r_i \Psi_i^*(\vec{r}_i) \hat{h}_i \Psi_i(\vec{r}_i)$$

$$J_{ij} = \int_{R^3} \int_{R^3} d^3 r_i d^3 r_j \Psi_i^*(\vec{r}_i) \Psi_i(\vec{r}_i) \frac{1}{r_{ij}} \Psi_j^*(\vec{r}_j) \Psi_j(\vec{r}_j)$$

$$K_{ij} = \int_{R^3} \int_{R^3} d^3 r_i d^3 r_j \Psi_i^*(\vec{r}_i) \Psi_j(\vec{r}_i) \frac{1}{r_{ij}} \Psi_j^*(\vec{r}_j) \Psi_i(\vec{r}_j)$$

$$h_i = [i | \hat{h} | i] \quad J_{ij} = [ii | jj] \quad K_{ij} = [ij | ji]$$

$$E_{HF} = \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} (J_{ij} - K_{ij})$$

$$\uparrow = \alpha(\omega_1) = |\alpha\rangle \quad \langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$

$$\downarrow = \beta(\omega_1) = |\beta\rangle \quad \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

$$\langle \omega_1 | \omega_2 \rangle = \int \sigma^*(\omega_1) \sigma(\omega_2) d\omega = \delta_{\omega_1 \omega_2}$$

$$\underbrace{\chi_i(\vec{r})}_{\substack{\text{spin} \\ \text{orbital}}} = \underbrace{\Psi_i(\vec{r})}_{\substack{\text{spatial} \\ \text{orbital}}} \underbrace{\sigma(\omega)}_{\text{spin function}}$$

[] → spin integral

() → spatial integral

$$(i | \hat{h} | i) = [i | \hat{h} | i] \langle \omega_1 | \omega_1 \rangle = [i | \hat{h} | i]$$

$$(ii | jj) = [ii | jj] \langle \omega_1 | \omega_1 \rangle \langle \omega_2 | \omega_2 \rangle = [ii | jj]$$

$$(ij | ij) = [ij | ij] \langle \omega_1 | \omega_2 \rangle^2 = [ij | ij] \delta_{\omega_1 \omega_2}$$

Ψ_3 2p ↑ Boron $E_{HF} = h_i$ for all e⁻
 Ψ_2 2s ↑ atom + J_{ij} for all e⁻ pairs
 Ψ_1 1s ↑ - K_{ij} for all same-spin
e⁻ pairs

$$E_{HF}^B = 2h_1 + 2h_2 + h_3 + J_{11} + 4J_{12} + 2J_{13} + 2J_{23} + J_{22} - 2K_{12} - K_{13} - K_{23}$$

2.99 Post Hartree-Fock Methods

Post Hartree-Fock Methods

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \quad \text{"correlation energy"}$$

- 1). Size of atomic orbital basis set
- 2). Accuracy of electron repulsion method

z-level: # of functions for each ℓ -shell

Polarization: Higher ℓ -value functions

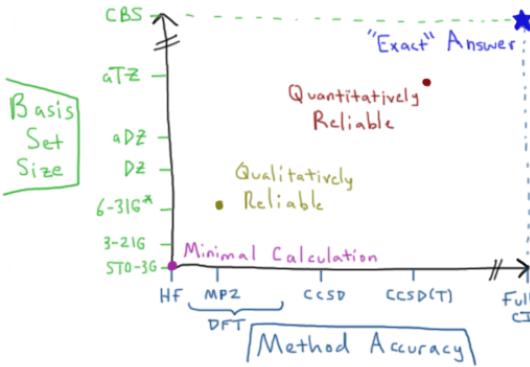
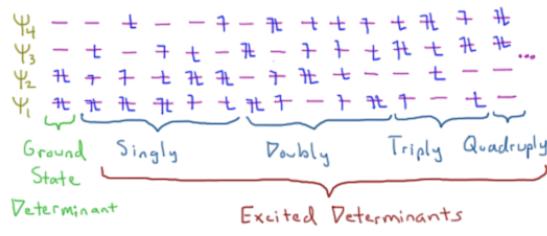
Diffuse: Small α , large, spread out

Type: Pople, Dunning, etc.

Density Functional Theory B3LYP B97
 Moller-Plesset Perturbation Theory PBE MO5-2X
 MP2 MP4

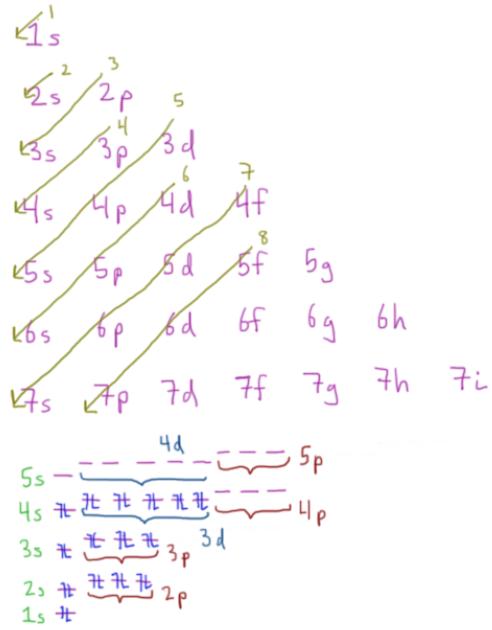
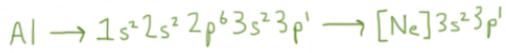
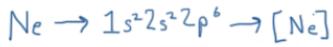
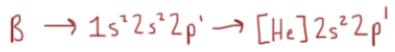
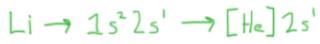
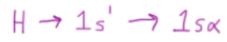
Coupled Cluster Theory CCSD CCSD(T)
 CISD

Configuration Interaction CIS CISD(T)
 Full CI



2.100 Atomic Electron Configurations

Electron Configuration



2.101 Electron Configuration Exceptions

Electron Configuration Exceptions													
4s	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	3d
5s	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	4d
													Exceptions
	K: [Ar] 4s ¹	Z = N = 19						Fe: [Ar] 4s ² 3d ⁶	Z = 26	N = 26			
	Ca: [Ar] 4s ²	20						Fe ²⁺ : [Ar] 3d ⁶	Z = 26	N = 24			
	Sc: [Ar] 4s ² 3d ¹	21							X Cr				
	Cr: [Ar] 4s ¹ 3d ⁵	24								+	+		
	Cu: [Ar] 4s ¹ 3d ¹⁰	29								+	+	+	
	Mo: [Kr] 5s ¹ 4d ⁵	42											
	Ag: [Kr] 5s ¹ 4d ¹⁰	47							X Fe ²⁺				
										+	+	+	
												-	

$\begin{array}{c} \text{Fe: [Ar]} 4s^2 3d^6 \\ \text{Fe}^{2+}: [\text{Ar}] 3d^6 \end{array}$

 Z = 26 N = 26
 Z = 26 N = 24

2.102 Atomic Term Symbols

Atomic Term Symbols

$S \rightarrow$ spin angular momentum

$L \rightarrow$ orbital angular momentum

$J \rightarrow$ total angular momentum

$$\{2S, L, 2J\} \geq 0 \in \mathbb{Z}$$

$$|L+S| \geq J \geq |L-S|$$

$$S \geq m_S \geq -S \quad (S+m_S) \in \mathbb{Z}$$

$$L \geq m_L \geq -L \quad (L+m_L) \in \mathbb{Z}$$

$$J \geq m_J \geq -J \quad (J+m_J) \in \mathbb{Z}$$

Atomic values \rightarrow Capital letters

$$S = 0, 1, 2, \dots \text{ or } \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$$

$$L = 0, 1, 2, \dots \rightarrow S, P, D, \dots$$

$$J = 0, 1, 2, \dots \text{ or } \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$$

$\underbrace{2S+1}_{\text{"Term Symbol"}}$ $\underbrace{L_J}_{\text{Distinct Electronic State}}$

$2S+1 \rightarrow$ "Multiplicity"

1 \rightarrow singlet 3 \rightarrow triplet 5 \rightarrow quintet

2 \rightarrow doublet 4 \rightarrow quartet 6 \rightarrow sextet

$^1S_0, ^1P_1, ^1D_2, ^1F_3, \dots$

$^2S_{1/2}, ^2P_{3/2}, ^2P_{1/2}, ^2D_{5/2}, ^2D_{3/2}, \dots$

$^3P_2, ^3P_1, ^3P_0, ^3D_3, ^3D_2, ^3D_1, \dots$

C $\rightarrow 1s^2 2s^2 \underbrace{2p^2}_{\text{partial subshell}} \rightarrow [^1D_2, ^3P_2, ^3P_1, ^3P_0, ^1S_0]$

2.103 Term Symbols Example 1

Term Symbols Example 1

$m_L + 1$	0	-1	m_L	m_S	Carbon atom
$+ \frac{1}{2} -$	$+1$	$+1$	$+1$	$+1$	$1s^2 2s^2 \underbrace{2p^2}$
$+ - \frac{1}{2}$	0	$+1$	0	$+1$	
$- \frac{1}{2} +$	-1	$+1$			Look at partially filled subshells
$+ \frac{1}{2} -$	$+1$	-1	$+1$	-1	
$+ - \frac{1}{2}$	0	-1	0	-1	
$- \frac{1}{2} +$	-1	-1			$N_{\text{det}} = \binom{k}{n} = \binom{6}{2} = \frac{6!}{2!(4!)} = 15$
$+ \frac{1}{2} -$	$+2$	0	$+1$	0	
$- \frac{1}{2} +$	0	0	-1	0	
$- - \frac{1}{2}$	-2	0			
$+ \frac{1}{2} -$	$+1$	0	$\sum_{i=1}^n m_{L,i}$	0	
$+ - \frac{1}{2}$	0	0	$\sum_{i=1}^n m_{S,i}$	0	
$- \frac{1}{2} +$	-1	0	$2S+1$	L_J	$ L+S \geq J \geq L-S $
$+ \frac{1}{2} -$	$+1$	0			$2p$ subshell
$+ - \frac{1}{2}$	0	0			$l=1, \quad l \geq m_L \geq -l, \quad m_L \in \mathbb{Z}$

$\max(m_L) = 2 \rightarrow \max(L) = 2 \rightarrow L_{\text{poss}} = 0, 1, 2$
 $\max(m_S) = 1 \rightarrow \max(S) = 1 \rightarrow S_{\text{poss}} = 0, 1$
 $(2S+1)_{\text{poss}} = 1, 3$ singlet or triplet

Possible Symbols: ${}^3D, {}^1D, {}^3P, {}^1P, {}^3S, {}^1S$

$$L \geq m_L \geq -L \rightarrow 2L+1 \quad N_{\text{term}} = (2L+1)(2S+1)$$

	MAX m_L	MAX m_S	N_{det}
$X {}^3D$	2	1	15
$X {}^1D$	2	0	5
$X {}^3P$	1	1	9
$X {}^1P$	1	0	3
$X {}^3S$	0	1	3
$X {}^1S$	0	0	1

${}^1D, {}^3P, {}^1S \downarrow$

${}^1D_2, {}^3P_2, {}^3P_1, {}^3P_0, {}^1S_0$

2.104 Term Symbols Example 2

Term Symbols Example 2						
m_L	+2	+1	0	-1	-2	m_S
# # # # #	+2	+1/2				
# # # # #	+2	-1/2				
# # # # #	+1	+1/2				
# # # # #	+1	-1/2				
# # # # #	0	+1/2				
# # - + # #	0	-1/2				
# # # # #	-1	+1/2				
# # # # #	-1	-1/2				
+ # # # #	-2	+1/2				
+ # # # #	-2	-1/2				
nd subshell						
$L \geq m_L \geq -L$	$m_L \in \mathbb{Z}$		$g_L = 2L+1$			
$S \geq m_S \geq -S$	$2m_S \in \mathbb{Z}$		$g_S = 2S+1$			
$N_{\text{det}}^{\text{term}} = (2S+1)(2L+1)$	$ L+S \geq J \geq L-S $					
$N_{\text{det}} = \sum_{i=1}^{N_{\text{terms}}} N_{\text{det}}^i$	$J \geq m_J \geq -J$					

N	+2	+1	0	-1	-2		max m_L	max m_S	N _{det}
+1/2	1	1	1	1	1	X $\sqrt{2}D$	2	1/2	10
-1/2	1	1	1	1	1	X 2P	1	1/2	6
(-2)D						X 2S	0	1/2	2
N	+2	+1	0	-1	-2				
+1/2	0	0	0	0	0	$^2D \rightarrow [^2D_{5/2}, ^2D_{3/2}]$			
-1/2	0	0	0	0	0				

2.105 Term Symbols Example 3

Term Symbols Example 3											
m_L	0	+1	0	-1	m_s	Excited state					
+	+	--	+1	+1	+	Be atom					
+	+	--	+1	0	0	$1s^2 2s^1 3p^1$					
+	-	-	0	+1							
+	-	+	0	0							
+	--	-	-1	+1							
+	--	+	-1	0							
+	-	-	+1	0							
+	-	-	+1	-1							
+	-	-	0	0							
+	-	+	0	-1							
+	--	+	-1	0							
+	-	-	-1	0							
+	-	-	-1	-1							
$\underbrace{2s}_{\text{subshells}}$		$\underbrace{3p}_{\text{subshells}}$		$N_{\text{det}} = \binom{2}{1} \binom{6}{1} = \frac{2!}{1!(2-1)!} \left(\frac{6!}{1!(6-1)!} \right) = \frac{2}{1 \cdot 1} \cdot \frac{720}{1 \cdot 120} = 12$							
$L_{\text{poss}} = 0, 1 \rightarrow S, P$											
$S_{\text{poss}} = 0, 1$											
$(2S+1)_{\text{poss}} = 1, 3$											
$L \geq m_L \geq -L \quad m_L \in \mathbb{Z} \quad g_L = 2L+1$											
$S \geq m_s \geq -S \quad m_s \in \mathbb{Z} \quad g_S = 2S+1 \quad N_{\text{det}} = \sum_{i=1}^{N_{\text{terms}}} N_i$											
$N_{\text{det}}^{+} = (2S+1)(2L+1) \quad L+S \geq J \geq L-S $											

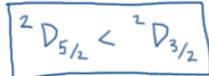
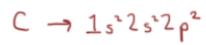
2.106 Hund's Rules

Hund's Rules

To rank energies of term symbols:

- 1) Largest S → most stable
- 2) If same S
 Largest L → most stable
- 3) If same S and L
 If subshell >½ full
 Largest J → most stable
 If subshell <½ full
 Smallest J → most stable

Works best for ground states



2.107 Atomic Spectra

Atomic Spectra

$$\Delta S = S' - S$$

$$\Delta L = L' - L$$

$$\Delta \bar{J} = \bar{J}' - \bar{J}$$

Selection Rules

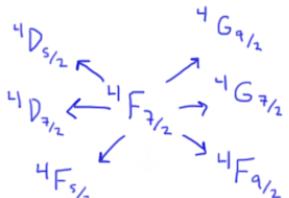
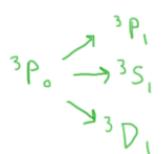
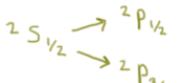
$$\Delta S = 0$$

$$\Delta L = +1, 0, -1 \quad (0 \rightarrow 0)$$

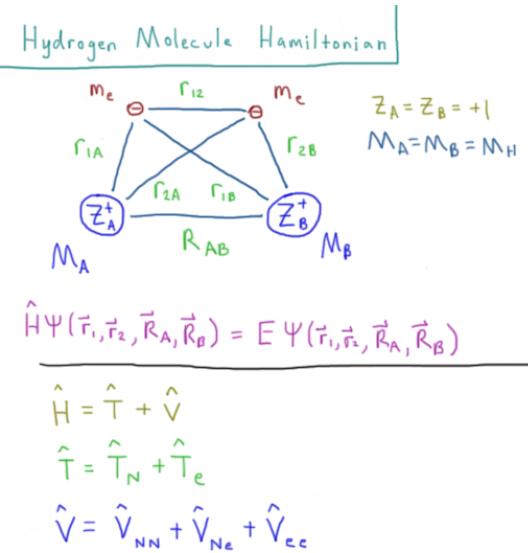
$$\Delta T = +1, 0, -1 \quad (0 \rightarrow 0)$$

$$|L+S| \geq J \geq |L-S|$$

$$S, L, J \geq 0 \quad 2S, L, 2J \in \mathbb{Z}$$



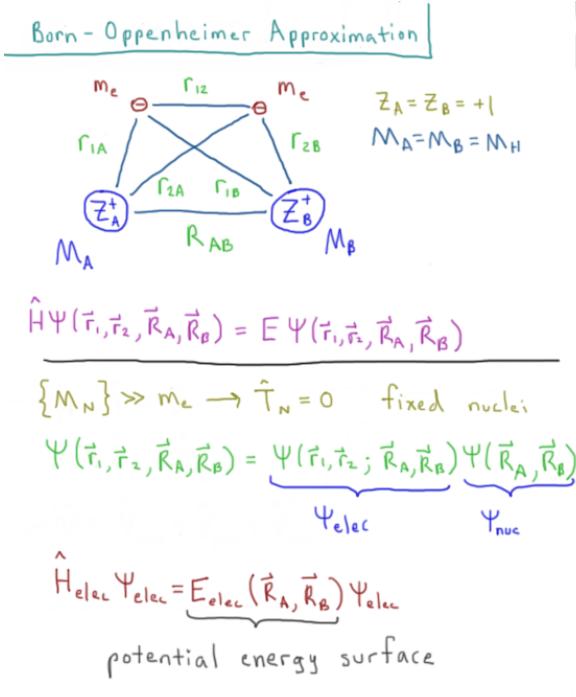
2.108 Hydrogen Molecule Hamiltonian



$$\begin{aligned} \hat{H} &= -\underbrace{\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2}_{\hat{T}_N} - \underbrace{\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2}_{\hat{T}_e} \\ &\quad - \underbrace{\frac{Z_A e^2}{4\pi\epsilon_0 r_{1A}} - \frac{Z_B e^2}{4\pi\epsilon_0 r_{1B}} - \frac{Z_A e^2}{4\pi\epsilon_0 r_{2A}} - \frac{Z_B e^2}{4\pi\epsilon_0 r_{2B}}}_{\hat{V}_{ee}} \\ &\quad + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\hat{V}_{NN}} + \underbrace{\frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}}_{\hat{V}_{Ne}} \end{aligned}$$

$$\begin{aligned} \hat{H} &= -\frac{1}{2M_A} \nabla_A^2 - \frac{1}{2M_B} \nabla_B^2 - \frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 \\ &\quad - \frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{R_{AB}} \end{aligned}$$

2.109 Born-Oppenheimer Approximation



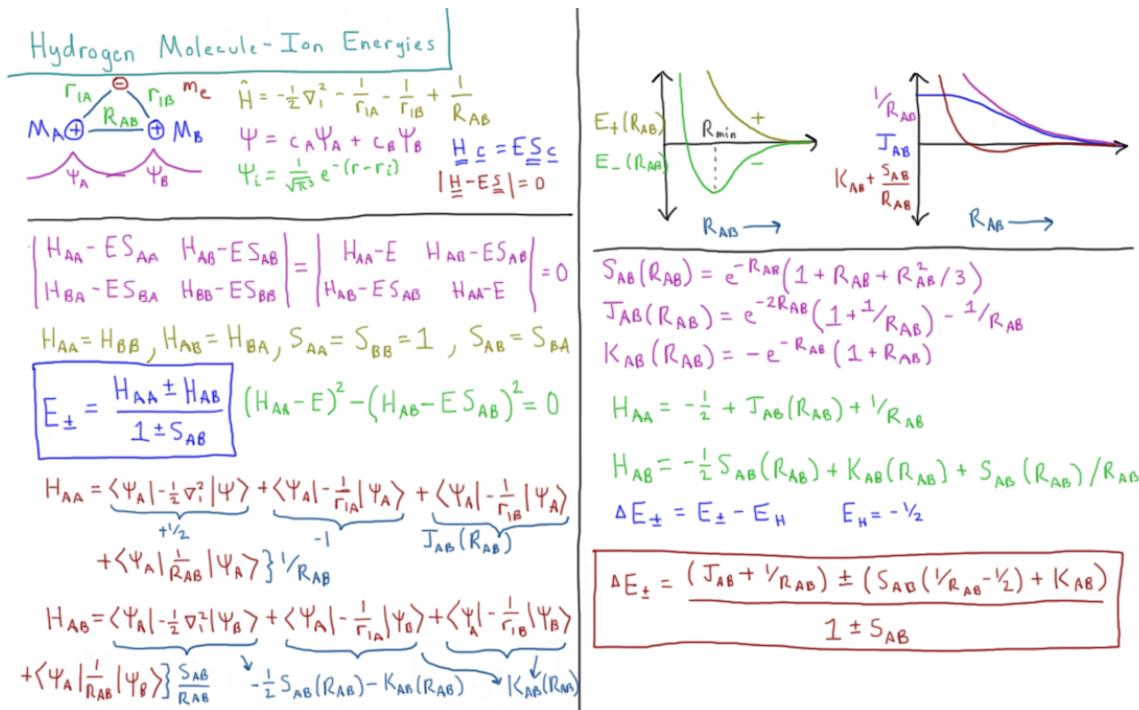
$$\hat{H} = -\frac{1}{2M_A} \nabla_A^2 - \frac{1}{2M_B} \nabla_B^2 - \underbrace{\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2}_{\text{straightforward}} - \underbrace{\frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{R_{AB}}}_{\text{very difficult algebra}}$$

$$\hat{H}_{elec} = -\frac{1}{2} \nabla_1^2 - \frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} - \frac{1}{2} \nabla_2^2 - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{R_{AB}}$$

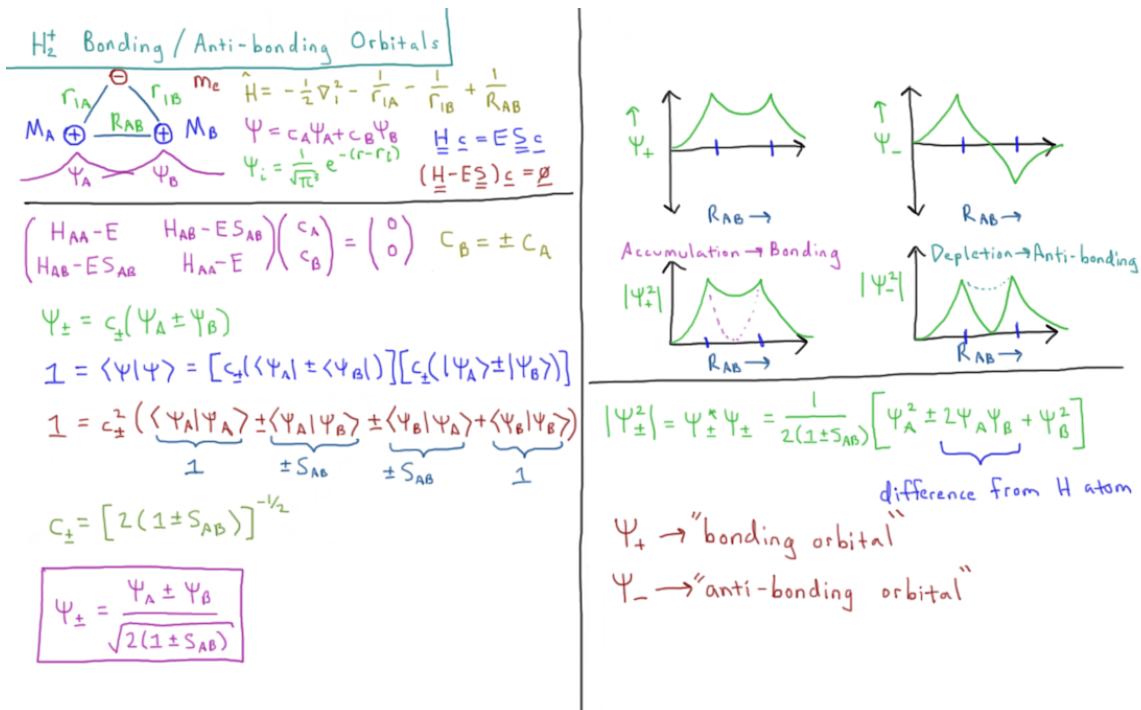
$$\hat{H}_{nuc} = -\frac{1}{2M_A} \nabla_A^2 - \frac{1}{2M_B} \nabla_B^2 + E_{nuc}(\vec{R}_A, \vec{R}_B)$$

$$\hat{H}_{nuc}\Psi_{nuc}(\vec{R}_A, \vec{R}_B) = E_{nuc}\Psi_{nuc}(\vec{R}_A, \vec{R}_B)$$

2.110 Hydrogen Molecule-Ion 1: Energy

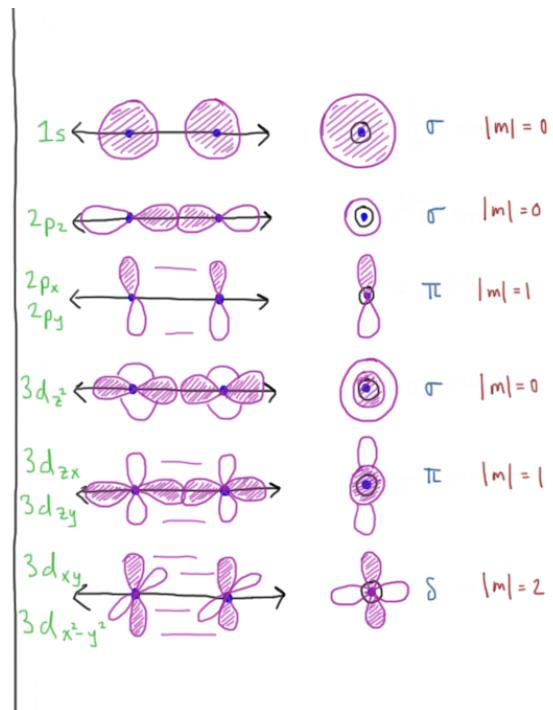


2.111 Hydrogen Molecule-Ion 2: Orbitals

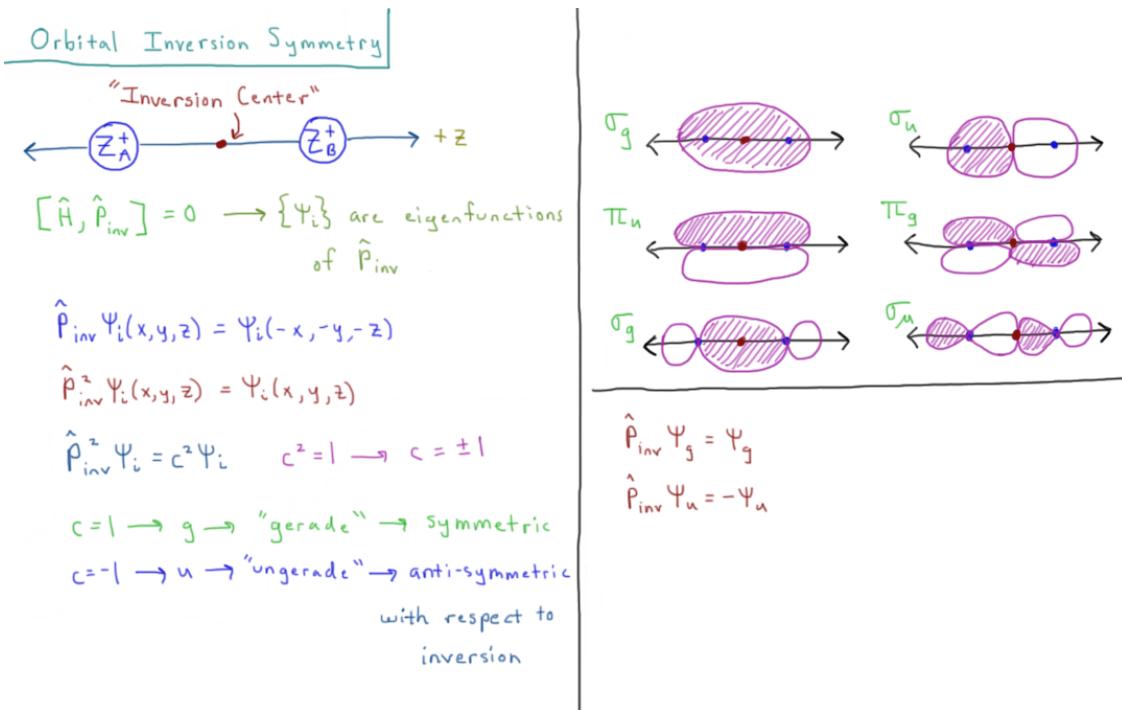


2.112 Molecular Orbital Angular Momentum

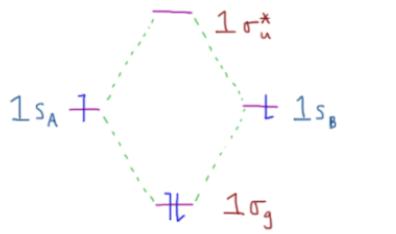
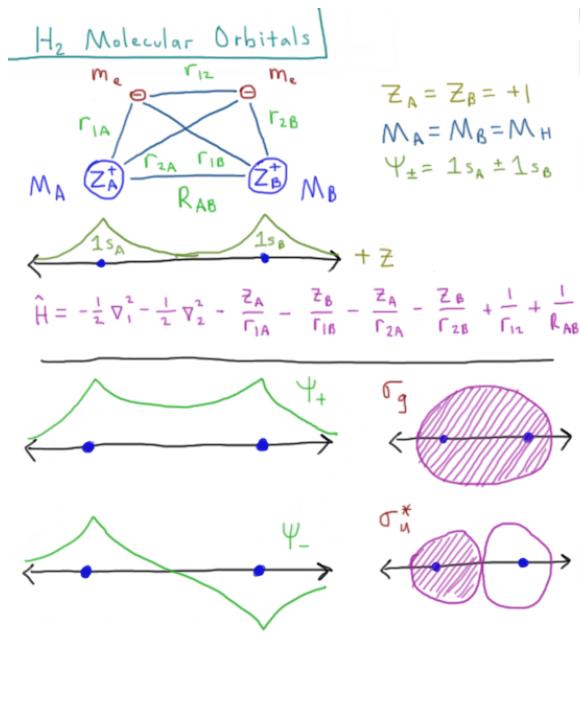
Molecular Orbital Angular Momentum	
Internuclear Axis	\hat{L}_z
$\leftarrow \text{Z}_A^+ \quad \text{Z}_B^+ \rightarrow$	$\curvearrowright +z$
$[\hat{H}, \hat{L}_z] = 0 \rightarrow \{\Psi_i\}$ are eigenfunctions of \hat{L}_z	
$\hat{L}_z \Psi_i = \hbar m_i \Psi_i \quad m_i = 0, \pm 1, \pm 2, \dots$	
$ m $	State Label
0	σ
1	π
2	δ
3	ϕ
:	:



2.113 Molecular Orbital Inversion Symmetry

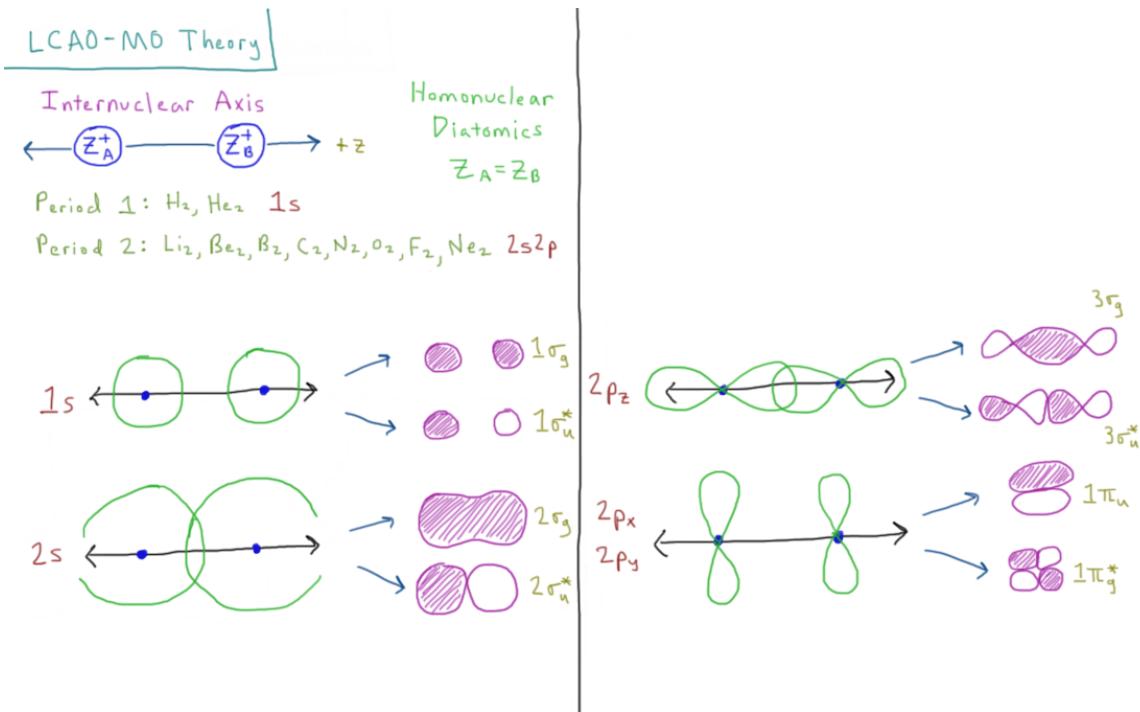


2.114 Hydrogen Molecular Orbital Diagram

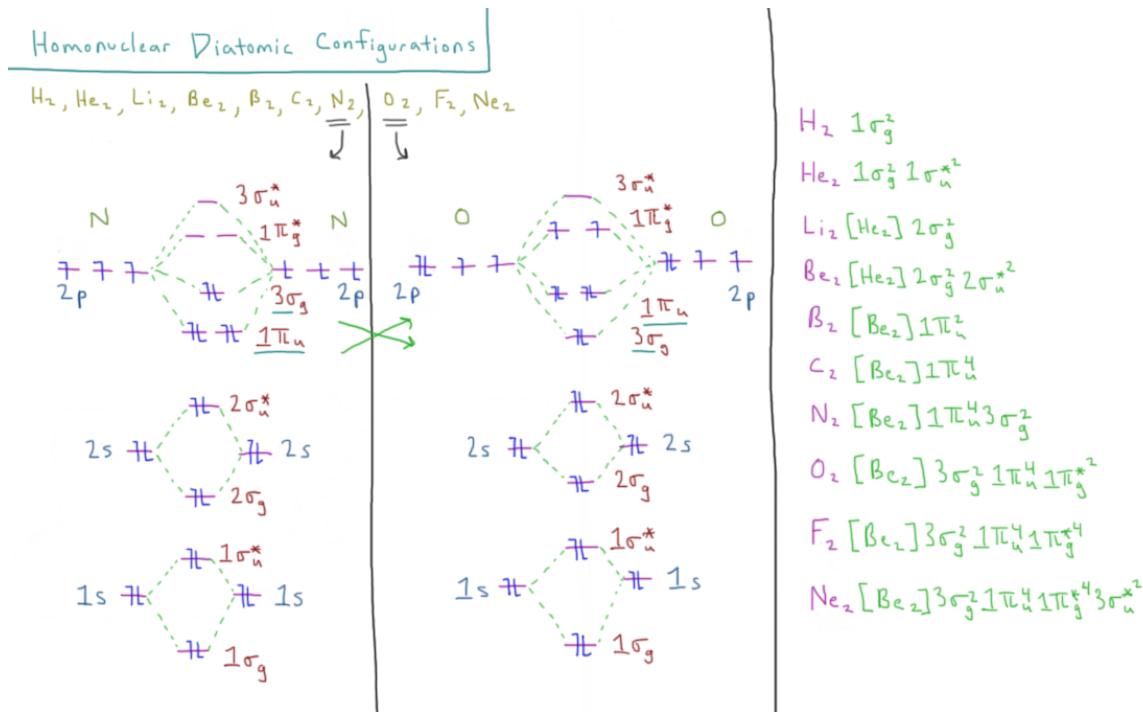


Ground state of $H_2 \rightarrow 1\sigma_g^2$

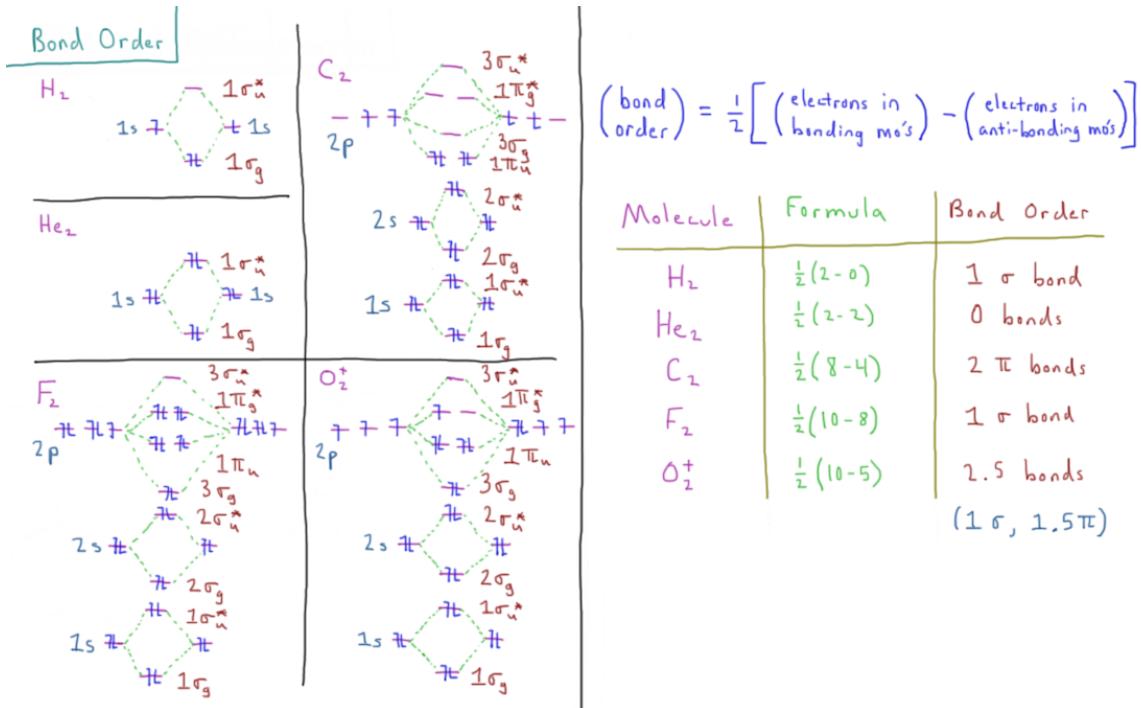
2.115 LCAO-MO Theory



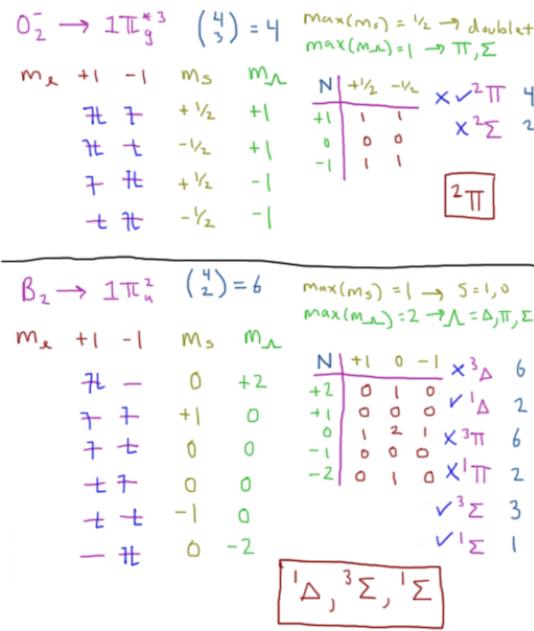
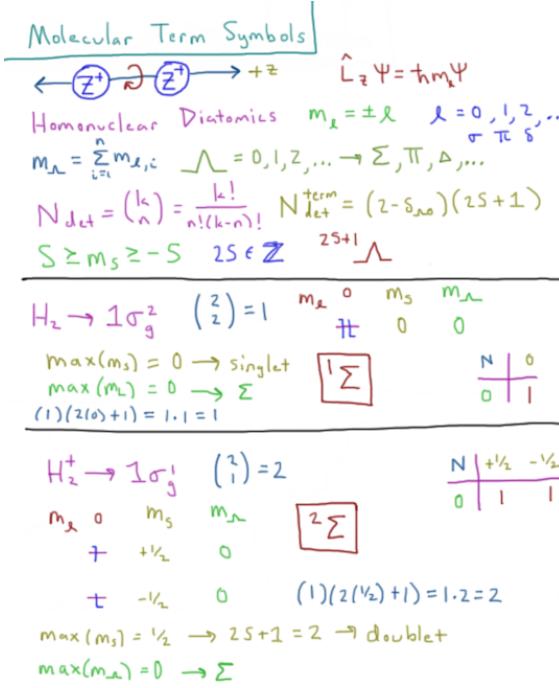
2.116 Diatomic Molecular Orbital Diagrams



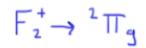
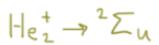
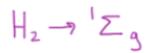
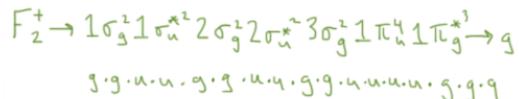
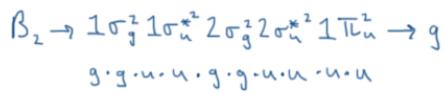
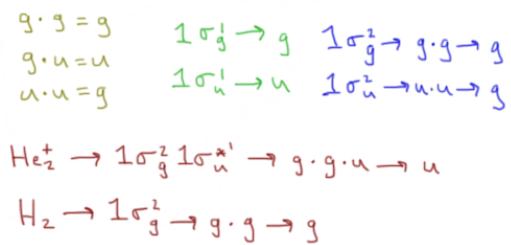
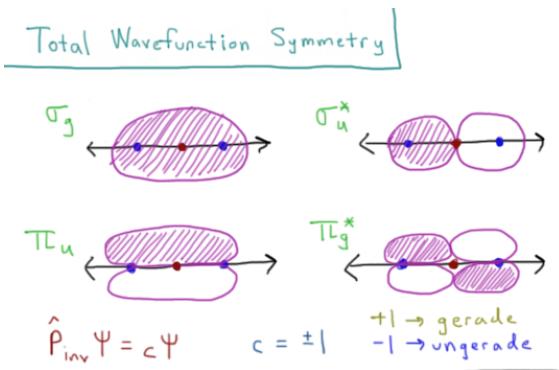
2.117 Bond Order



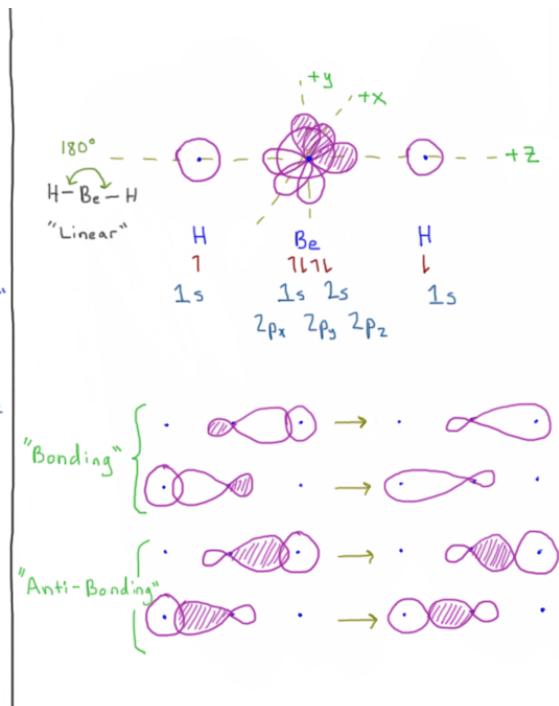
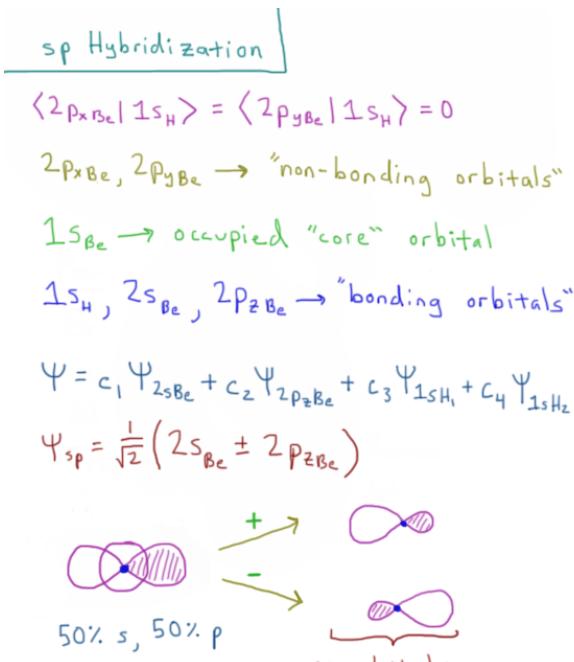
2.118 Diatomic Term Symbols



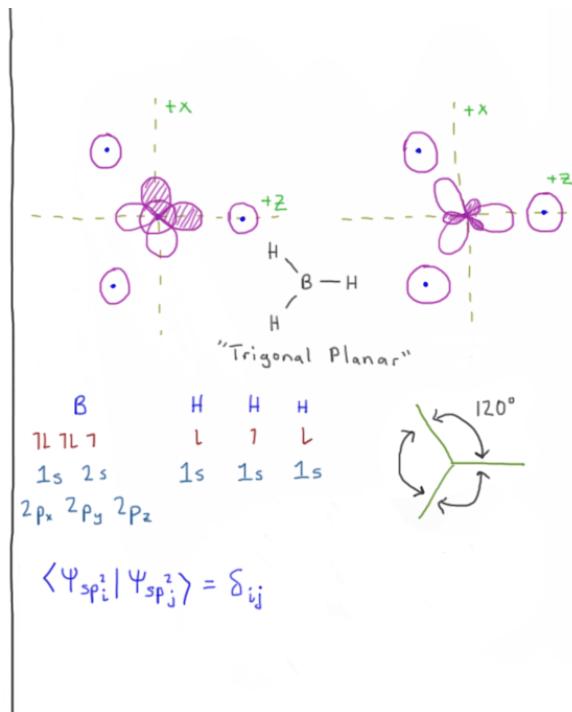
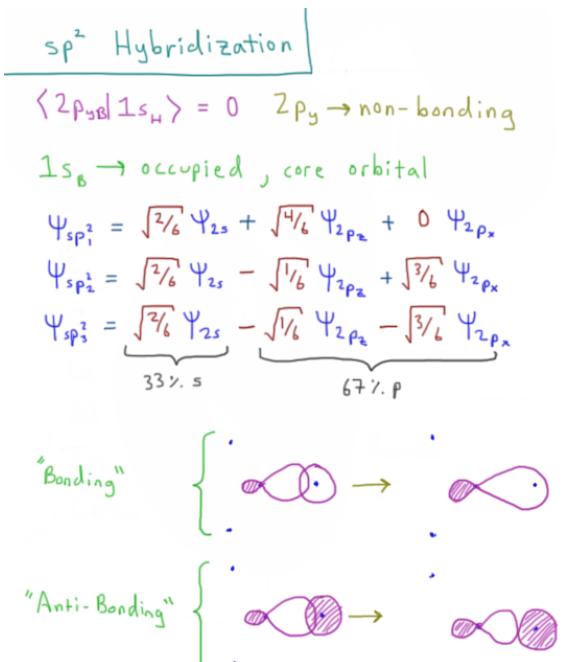
2.119 Total Wavefunction Symmetry



2.120 sp Hybridization



2.121 sp² Hybridization



2.122 sp³ Hybridization

sp³ Hybridization

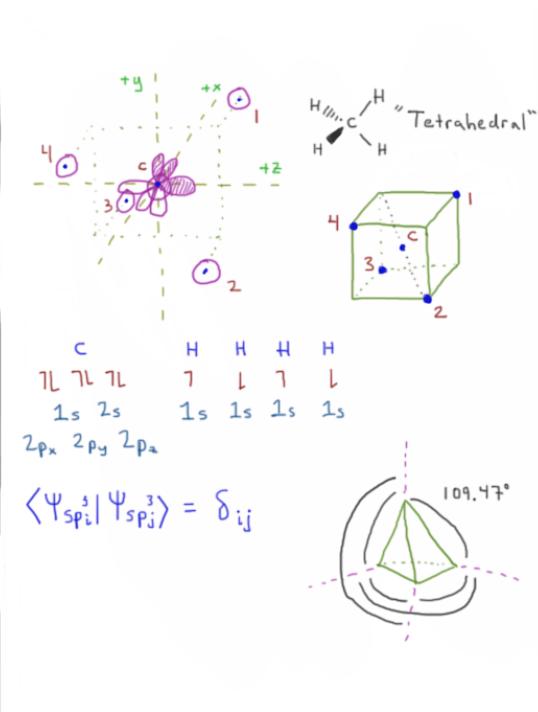
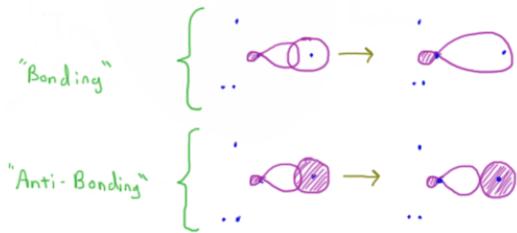
$1s_c \rightarrow$ occupied, core orbital

$$\Psi_{sp_1^3} = \sqrt{\frac{1}{4}} (\Psi_{2s} + \Psi_{2p_x} + \Psi_{2p_y} + \Psi_{2p_z})$$

$$\Psi_{sp_2^3} = \sqrt{\frac{1}{4}} (\Psi_{2s} - \Psi_{2p_x} - \Psi_{2p_y} + \Psi_{2p_z})$$

$$\Psi_{sp_3^3} = \sqrt{\frac{1}{4}} (\Psi_{2s} + \Psi_{2p_x} - \Psi_{2p_y} - \Psi_{2p_z})$$

$$\Psi_{sp_4^3} = \sqrt{\frac{1}{4}} (\underbrace{\Psi_{2s}}_{25\% s} - \underbrace{\Psi_{2p_x} + \Psi_{2p_y} - \Psi_{2p_z}}_{75\% p})$$



2.123 Lone Pair Hybridization

Lone Pair Hybridization

$$\Psi_1 = 0.45s + 0.71p_x + 0.55p_z$$

$$\Psi_2 = 0.45s - 0.71p_x + 0.55p_z$$

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$$

$0.45^2 = 0.20 \rightarrow 20\% s$ character

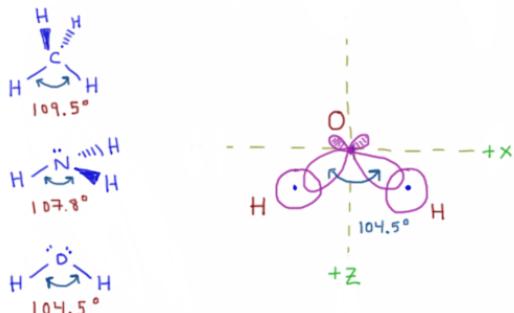
$(\pm 0.71)^2 + 0.55^2 = 0.8 \rightarrow 80\% p$ character

$$sp^n \text{ orbital} \quad n = \frac{\% p}{\% s}$$

$$H_2O \rightarrow n = \frac{0.80}{0.20} = 4.0$$

$sp^{4.0} \rightarrow$ very "p" like

$$n = \frac{1}{\sin(\theta - 90^\circ)}$$

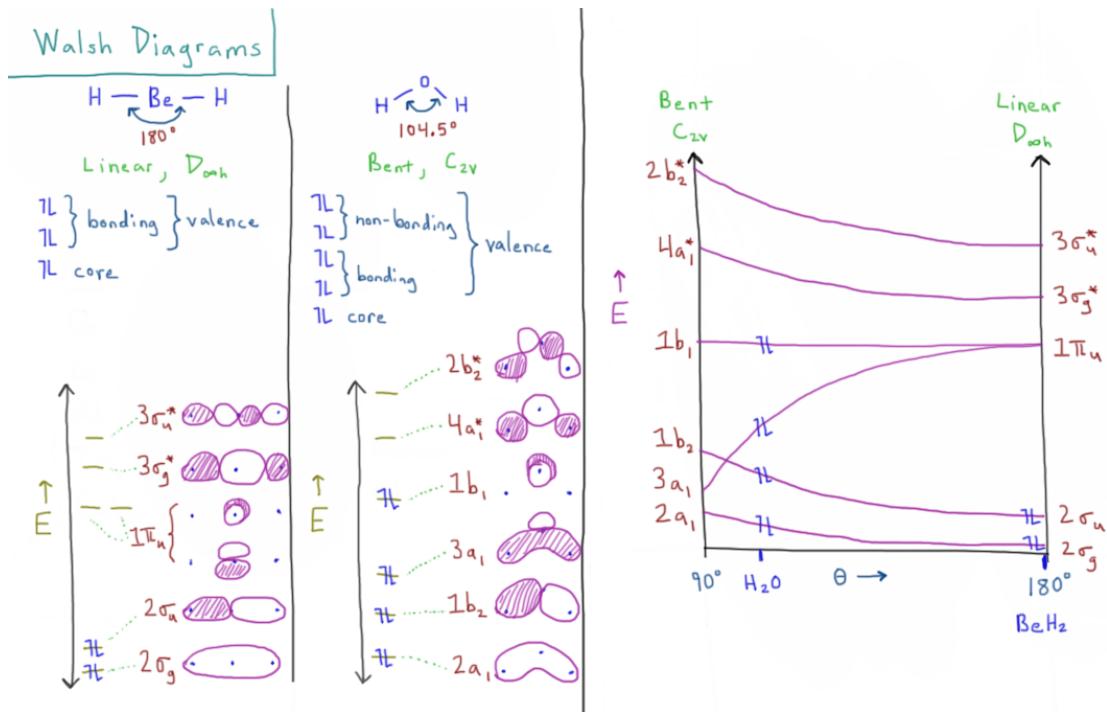


$H_2O \quad 2$ lone pairs $sp^{4.0}$

$NH_3 \quad 1$ lone pair $sp^{3.5}$

$CH_4 \quad 0$ lone pairs $sp^{3.0}$

2.124 Walsh Diagrams



2.125 Huckel Theory

Hückel Theory

π bond \rightarrow weak overlap \rightarrow small energy difference
 $\langle 2p_z | \text{other} \rangle = 0 \rightarrow$ orthogonal to others

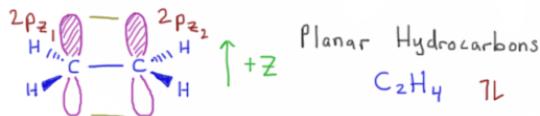
$$\Psi_{\pi}^{(i)} = c_1^{(i)} 2p_{z1} + c_2^{(i)} 2p_{z2}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

assume orthonormal basis $\rightarrow S_{ij} = \delta_{ij}$

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

$$H_{ij} = \begin{cases} \alpha & \text{if } i=j \\ \beta & \text{if adjacent} \\ 0 & \text{otherwise} \end{cases}$$



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

$$(\alpha - E)^2 - \beta^2 = 0$$

$$(1) E^2 + (-2\alpha)E + (\alpha^2 - \beta^2) = 0$$

$E = \alpha \pm \beta$ $\alpha \rightarrow$ defines reference

$\alpha - \beta$ Anti-Bonding $\beta \rightarrow$ scale for energy

$\alpha + \beta$ Bonding $\beta \approx -75 \text{ kJ/mol}$
 empirically

2.126 Pi Resonance

Pi Resonance

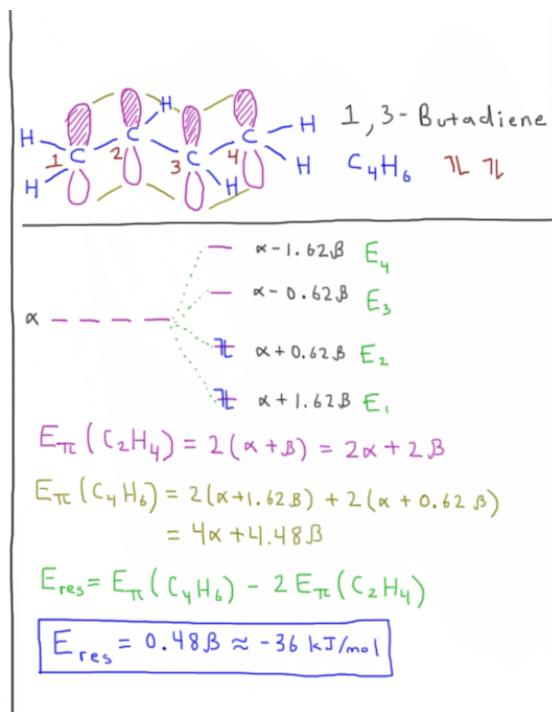
$$\Psi_{\pi_i} = c_1^i 2p_{z_1} + c_2^i 2p_{z_2} + c_3^i 2p_{z_3} + c_4^i 2p_{z_4}$$

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

$$\beta^4 \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \quad \text{define } x = \frac{\alpha - E}{\beta} \quad \text{factor out } \beta$$

$$\beta^4(x^4 - 3x^2 + 1) = 0$$

$$x = \pm \left(\frac{3 \pm \sqrt{5}}{2} \right) = \pm 0.62, \pm 1.62$$



2.127 Aromaticity

Aromaticity

$$\Psi_{\pi_i} = \sum_{j=1}^6 c_{ij} 2p_z j$$

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

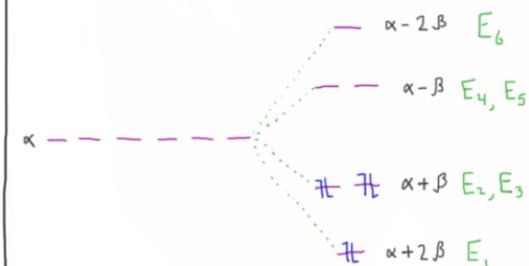
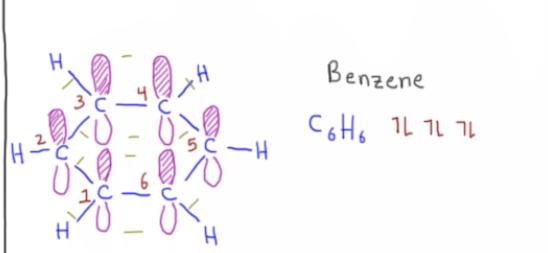
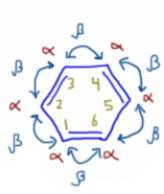
$$x = \frac{\alpha - E}{\beta} = \pm 1, \pm 1, \pm 2$$

$$E_{\pi}(C_2H_4) = 2\alpha + 2\beta$$

$$E_{\pi}(C_6H_6) = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

$$E_{\text{aromaticity}} = E_{\pi}(C_6H_6) - 3E_{\pi}(C_2H_4)$$

$$E_{\text{arom}}(C_6H_6) = 2\beta \approx -150 \text{ kJ/mol}$$



2.128 Symmetry Websites

Molecular Symmetry Websites

symmetry.otterbein.edu

symmetry.jacobs-university.de

Symmetry at Otterbein

- Tutorial
- Gallery
- Challenge

Character tables for
molecular point groups

2.129 Symmetry Operations

Symmetry Operations

geometric operations which leave an object indistinguishable from its original position

Operator	Effect
\hat{E}	identity
\hat{i}	inversion through point
$\hat{\sigma}$	reflection across plane
\hat{C}_n	proper rotation by $360/n^\circ$
\hat{S}_n	improper rotation by $360/n^\circ$

$$\hat{C}_1 = \hat{E} \quad \hat{C}_4^2 = \hat{C}_4 \hat{C}_4 = \hat{C}_2 \quad \hat{C}_n^n = \hat{C}_1 = \hat{E}$$

$$\hat{\sigma}^2 = \hat{E} \quad \hat{S}_n = \hat{\sigma}_h \hat{C}_n \quad \hat{S}_6^2 = \hat{C}_3 \quad \hat{S}_2 = \hat{i}$$

$$\hat{E} \begin{pmatrix} 2 & 0 & 0 & 3 \\ 1 & 0 & 0 & 4 \end{pmatrix} = \begin{pmatrix} 2 & 0 & 0 & 3 \\ 1 & 0 & 0 & 4 \end{pmatrix}$$

$$\hat{i} \quad \hat{C}_4 \begin{pmatrix} 2 & 0 & 0 & 3 \\ 1 & 0 & 0 & 4 \end{pmatrix} = \begin{pmatrix} 3 & 0 & 0 & 4 \\ 2 & 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma} \quad \hat{C}_4^2 \begin{pmatrix} 2 & 0 & 0 & 3 \\ 1 & 0 & 0 & 4 \end{pmatrix} = \begin{pmatrix} 4 & 0 & 0 & 1 \\ 3 & 0 & 0 & 2 \end{pmatrix}$$

$$\hat{\sigma}_v \quad \begin{pmatrix} 2 & 0 & 0 & 3 \\ 1 & 0 & 0 & 4 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 4 \\ 2 & 0 & 0 & 3 \end{pmatrix}$$

$$\square \quad \hat{\sigma}_h \begin{pmatrix} 2 & 0 & 0 & 3 \\ 1 & 0 & 0 & 4 \end{pmatrix} = \begin{pmatrix} 1 & \otimes & \otimes & 3 \\ 1 & \otimes & \otimes & 4 \end{pmatrix}$$

$$\triangle \quad \hat{S}_4 \begin{pmatrix} 2 & 0 & 0 & 3 \\ 1 & 0 & 0 & 4 \end{pmatrix} = \begin{pmatrix} 3 & \otimes & \otimes & 4 \\ 2 & \otimes & \otimes & 1 \end{pmatrix}$$

$$\bullet \quad \hat{i} \begin{pmatrix} 2 & 0 & 0 & 3 \\ 1 & 0 & 0 & 4 \end{pmatrix} = \begin{pmatrix} 4 & \otimes & \otimes & 1 \\ 3 & \otimes & \otimes & 2 \end{pmatrix}$$

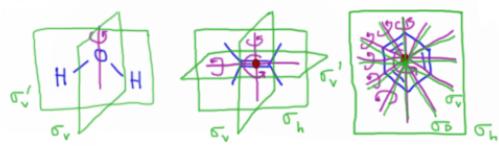
2.130 Symmetry Elements

Symmetry Elements

The set of points, axes, and/or planes through which an object's symmetry operations occur

Element	Description
E	identity
i	inversion center
σ	plane of symmetry
C_n	n-fold proper rotation axis
S_n	n-fold improper rotation axis

all molecules $\rightarrow E$



C_n with max n \rightarrow "principal axis"

σ_h \rightarrow perpendicular to principal axis

σ_v \rightarrow parallel to principal axis

σ_D \rightarrow bisects C_2 which is perpendicular to principal axis

2.131 Groups

Groups

A set of entities that satisfy the following conditions:

- ① There is a rule for combining members, and the result is part of the group
- ② Multiplication is associative
- ③ There is an identity element (\hat{E})
- ④ All members have an inverse (\hat{A}^{-1})

For all $\{\hat{A}, \hat{B}\}$; $\hat{A}\hat{B} = \hat{C}$
and all $\{\hat{C}\} \in$ group

for all $\{\hat{A}, \hat{B}, \hat{C}\}$ $\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$

for all $\{\hat{A}\}$ $\hat{E}\hat{A} = \hat{A}$

for all $\{\hat{A}\}$ $\hat{A}^{-1}\hat{A} = \hat{E}$

2.132 Point Groups

Point Groups

The set of symmetry operations of an object form a "point group"

C: "cyclic groups"

C_1 : only E \rightarrow "no symmetry"

C_i : E, i only inversion

C_s : E, σ only mirror plane

C_n : E, C_n only rotation axis

C_{nv} : E, C_n , $n\sigma_v$

C_{nh} : E, C_n , σ_h , i
if n is even

D: "dihedral groups"

D_n : E, C_n , nC_2

D_{nd} : E, C_n , nC_2 , $n\sigma_d$, S_{2n}

D_{nh} : E, C_n , nC_2 , $n\sigma_v$, σ_h , S_n

"cubic groups"

T_d : "tetrahedral" CH₄

O_h : "octahedral" SF₆

I_h : "icosahedral" C₆₀

"linear groups"

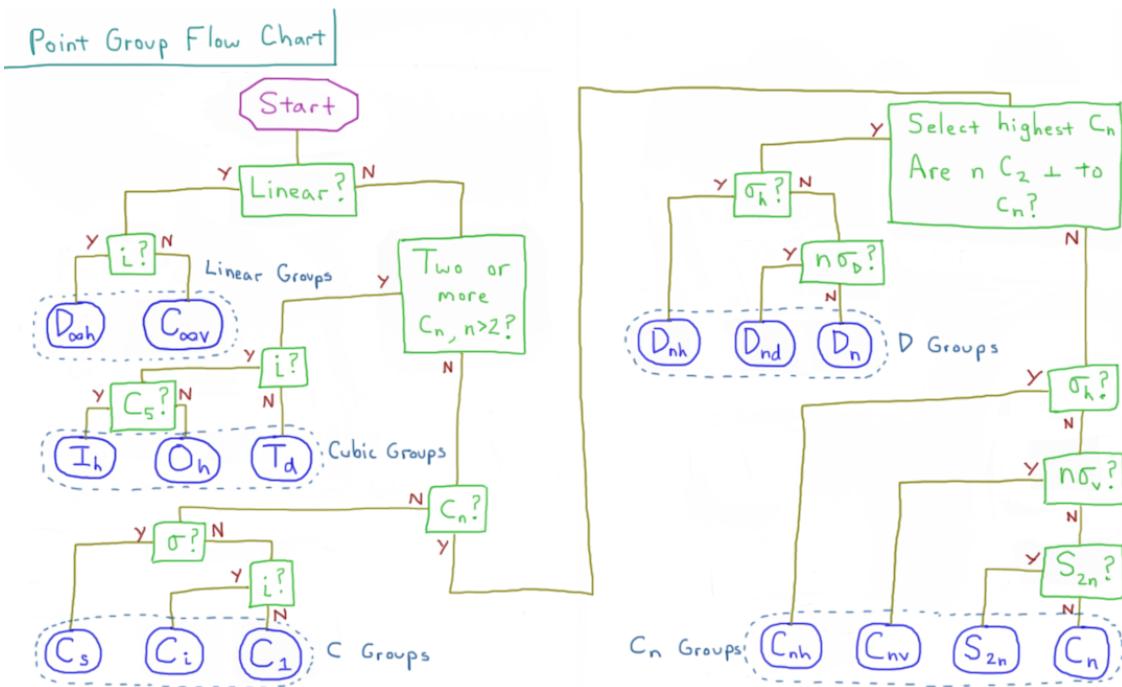
$C_{\infty v}$: E, C_∞ , $\infty\sigma_v$

$D_{\infty h}$: E, C_∞ , $\infty\sigma_h$, ∞C_2 , σ_h , S_∞

2.133 Point Group Examples

Point Group Examples	
Point Group	Molecules
D _∞ h	CO ₂ , C ₂ H ₂ , H ₂ , O ₂
C _∞ v	HCN, CO, HF, OH ⁻
I _h	C ₆₀
O _h	SF ₆ , Mo(CO) ₆ , Fe(CN) ₆ ⁴⁻
T _d	CH ₄ , NH ₄ ⁺ , CF ₄
C ₁	
C _i	
C _s	
D _{2h}	
D _{3h}	
D _{6h}	
D _{2d}	
D _{3d}	
D ₂	
D ₃	
C _{2v}	H ₂ O, F ₂ O, H-C(=O)-H, p-fluorobiphenyl
C _{3v}	NH ₃ , NO ₃ ⁻ ,
C _{3h}	
S ₄	12-crown-4
C ₂	N ₂ H ₄ , H ₂ O ₂ , H-O-H

2.134 Determining Point Groups



2.135 Group Multiplication Tables

Group Multiplication Tables

 staggered $H_2 D_2 \rightarrow C_{2h}$																										
$C_{2h}:$ \hat{E} \hat{C}_2 \hat{i} $\hat{\sigma}_h$ $\hat{\sigma}_d$																										
\hat{O}_1 { <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>C_{2h}</th> <th>\hat{E}</th> <th>\hat{C}_2</th> <th>\hat{i}</th> <th>$\hat{\sigma}_h$</th> </tr> </thead> <tbody> <tr> <td>\hat{E}</td> <td>\hat{E}</td> <td>\hat{C}_2</td> <td>\hat{i}</td> <td>$\hat{\sigma}_h$</td> </tr> <tr> <td>\hat{C}_2</td> <td>\hat{C}_2</td> <td>\hat{E}</td> <td>$\hat{\sigma}_h$</td> <td>\hat{i}</td> </tr> <tr> <td>\hat{i}</td> <td>\hat{i}</td> <td>$\hat{\sigma}_h$</td> <td>\hat{E}</td> <td>\hat{C}_2</td> </tr> <tr> <td>$\hat{\sigma}_h$</td> <td>$\hat{\sigma}_h$</td> <td>\hat{i}</td> <td>\hat{C}_2</td> <td>\hat{E}</td> </tr> </tbody> </table>	C_{2h}	\hat{E}	\hat{C}_2	\hat{i}	$\hat{\sigma}_h$	\hat{E}	\hat{E}	\hat{C}_2	\hat{i}	$\hat{\sigma}_h$	\hat{C}_2	\hat{C}_2	\hat{E}	$\hat{\sigma}_h$	\hat{i}	\hat{i}	\hat{i}	$\hat{\sigma}_h$	\hat{E}	\hat{C}_2	$\hat{\sigma}_h$	$\hat{\sigma}_h$	\hat{i}	\hat{C}_2	\hat{E}	
C_{2h}	\hat{E}	\hat{C}_2	\hat{i}	$\hat{\sigma}_h$																						
\hat{E}	\hat{E}	\hat{C}_2	\hat{i}	$\hat{\sigma}_h$																						
\hat{C}_2	\hat{C}_2	\hat{E}	$\hat{\sigma}_h$	\hat{i}																						
\hat{i}	\hat{i}	$\hat{\sigma}_h$	\hat{E}	\hat{C}_2																						
$\hat{\sigma}_h$	$\hat{\sigma}_h$	\hat{i}	\hat{C}_2	\hat{E}																						

\hat{E}

$=$

\hat{E}

\hat{C}_2

$=$

\hat{C}_2

\hat{i}

$=$

\hat{i}

$\hat{\sigma}_h$

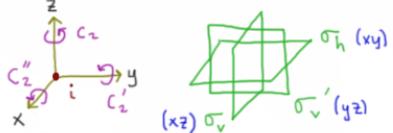
$=$

$\hat{\sigma}_h$

2.136 Symmetry Operator Matrices

Symmetry Operator Matrices

D_{2h} : E, C_2 , C_2' , C_2'' , σ_h , σ_v , σ_v' , i



$$\vec{u} = u_x \hat{x} + u_y \hat{y} + u_z \hat{z}$$

$$\hat{E} \vec{u}_x = \vec{u}_x \quad \hat{E} \vec{u}_y = \vec{u}_y \quad \hat{E} \vec{u}_z = \vec{u}_z$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} = \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} \quad \hat{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ is a 3×3 "representation" of

the \hat{E} operator in the D_{2h} point group

$$\hat{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{i} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\hat{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{C}'_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\hat{C}_2'' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \hat{\sigma}_h = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\hat{\sigma}_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{\sigma}'_v = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

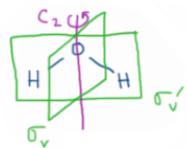
2.137 Irreducible Representations

Irreducible Representations

The minimal set of the simplest possible representations of a group from which all others can be expressed

$$\begin{array}{l} | \cdot 1 = 1 \\ (-1) \cdot (-1) = 1 \end{array} \quad \begin{array}{l} | \cdot (-1) = -1 \\ (-1) \cdot 1 = -1 \end{array}$$

C_{2v}	\hat{E}	\hat{C}_2	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
\hat{E}	\hat{E}	\hat{C}_2	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
\hat{C}_2	\hat{C}_2	\hat{E}	$\hat{\sigma}'_v$	$\hat{\sigma}_v$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	\hat{E}	\hat{C}_2
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	\hat{C}_2	\hat{E}



$$A_1: \hat{E}=1 \quad \hat{C}_2=1 \quad \hat{\sigma}_v=1 \quad \hat{\sigma}'_v=1$$

$$A_2: \hat{E}=1 \quad \hat{C}_2=1 \quad \hat{\sigma}_v=-1 \quad \hat{\sigma}'_v=-1$$

$$B_1: \hat{E}=1 \quad \hat{C}_2=-1 \quad \hat{\sigma}_v=1 \quad \hat{\sigma}'_v=-1$$

$$B_2: \hat{E}=1 \quad \hat{C}_2=-1 \quad \hat{\sigma}_v=-1 \quad \hat{\sigma}'_v=1$$

4 irreducible representations of the C_{2v} point group
"irreps"

2.138 Character Tables 1: Abelian

Abelian Character Tables

$A, B \rightarrow 1\text{-dimensional irreps}$

$A \rightarrow$ symmetric w.r.t. principal C_n

$B \rightarrow$ anti-symmetric w.r.t. principal C_n

Subscript $1, 2, \dots$

$1 \rightarrow$ symmetric w.r.t. $\hat{\sigma}_v$ or \hat{C}_2 (not \hat{C}_n)

$2 \rightarrow$ anti-symmetric w.r.t. $\hat{\sigma}_v$ or \hat{C}_2 (not \hat{C}_n)

Subscript g, u

$g \rightarrow$ "gerade" symmetric w.r.t. inversion

$u \rightarrow$ "ungerade" anti-symmetric w.r.t. inversion

Superscript ', ''

' \rightarrow symmetric w.r.t. σ_h

'' \rightarrow anti-symmetric w.r.t. σ_h

C_{2v}	\hat{E}	\hat{C}_2	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

C_{2h}	\hat{E}	\hat{C}_2	\hat{i}	$\hat{\sigma}_h$
A_g	1	1	1	1
B_g	1	-1	1	-1
A_u	1	1	-1	-1
B_u	1	-1	-1	1

C_s	\hat{E}	$\hat{\sigma}_h$
A'	1	1
A''	1	-1

C_1	\hat{E}
A	1

Every point group has a totally symmetric irrep

A, A', A_1, A_g, A_{1g}

2.139 Character Tables 2: Non-Abelian

Non-Abelian Character Tables

$$\begin{pmatrix} \text{character of} \\ \hat{E} \text{ in irrep.} \end{pmatrix} = \begin{pmatrix} \text{dimensionality} \\ \text{of irrep.} \end{pmatrix}$$

Abelian point group: All irreps are 1-dimensional ($C_n \leq 2$)

$C_1, C_2, C_S, C_i, C_{2v}, C_{2h}, D_2, D_{2h}$

irrep label	dimensions (d)
A, B	1
E	2
T	3
G	4
H	5
...	...

T_d	\hat{E}	$8\hat{C}_3$	$3\hat{C}_2$	$6\hat{S}_4$	$6\hat{\sigma}_b$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

C_{3v}	\hat{E}	$2\hat{C}_3$	$3\hat{\sigma}_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
C_2	\hat{E}	\hat{C}_2	
A	1	1	
B	1	-1	

Order: (h) number of symmetry operations of point group

$$h = \sum_{n=1}^{\text{irreps}} d_n^2$$

$$T_d \rightarrow 1 + 8 + 3 + 6 + 6 = 1^2 + 1^2 + 2^2 + 3^2 + 3^2 = 24$$

$\hat{E} \quad \hat{C}_3 \quad \hat{C}_2 \quad \hat{S}_4 \quad \hat{\sigma}_b \quad A_1 \quad A_2 \quad E \quad T_1 \quad T_2$

2.140 Determining Irreps

Determining Irreps

$\Gamma \rightarrow$ "reducible representation"

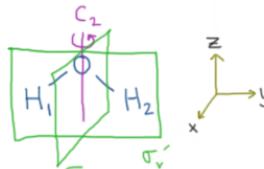
sum of all irreducible representations

- ① apply operation to all objects
- ② compute trace of resulting matrix
- ③ repeat for all operators
- ④ decompose into irreps

$$\hat{E} \begin{pmatrix} 1s_1 \\ 1s_2 \\ 2s \\ 2p_z \\ 2p_y \\ 2p_x \end{pmatrix} = \begin{pmatrix} 1s_1 \\ 1s_2 \\ 2s \\ 2p_z \\ 2p_y \\ 2p_x \end{pmatrix} \quad \hat{E} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\text{tr}(\hat{E}) = \sum_{i=1}^n (\hat{E})_{ii} = \Gamma_{\hat{E}} = 6$$

$$\text{tr}(\hat{C}_2) = 0 + 0 + 1 + 1 - 1 - 1 = 0$$



C_{2v}	\hat{E}	\hat{C}_2	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

$$\text{tr}(\hat{\sigma}_v) = 0 + 0 + 1 + 1 - 1 + 1 = 2$$

$$\text{tr}(\hat{\sigma}'_v) = 1 + 1 + 1 + 1 + 1 - 1 = 4$$

$$\Gamma = (6 \ 0 \ 2 \ 4) = a_1 A_1 + a_2 A_2 + a_3 B_1 + a_4 B_2$$

$$a_1 = \frac{1}{4}(6 \cdot 1 + 0 \cdot 1 + 2 \cdot 1 + 4 \cdot 1) = \frac{12}{4} = 3$$

$$a_2 = \frac{1}{4}(6 \cdot 1 + 0 \cdot 1 - 2 \cdot 1 - 4 \cdot 1) = \frac{0}{4} = 0$$

$$a_3 = \frac{1}{4}(6 \cdot 1 - 0 \cdot 1 + 2 \cdot 1 - 4 \cdot 1) = \frac{4}{4} = 1$$

$$a_4 = \frac{1}{4}(6 \cdot 1 - 0 \cdot 1 - 2 \cdot 1 + 4 \cdot 1) = \frac{8}{4} = 2$$

$$\Gamma = 3A_1 + B_1 + 2B_2 \quad a_i = \frac{1}{h} \sum_R \Gamma_R x_i(\hat{R})$$

2.141 Generating Operators

Generating Operators

$$\Gamma = (6 \ 0 \ 2 \ 4) = 3A_1 + B_1 + 2B_2$$

$$\hat{P}_{A_1}(2s) = \frac{1}{4} (1 \cdot 2s + 1 \cdot 2s + 1 \cdot 2s + 1 \cdot 2s) = 2s$$

$$\hat{P}_{A_2}(2s) = \frac{1}{4} (1 \cdot 2s + 1 \cdot 2s - 1 \cdot 2s - 1 \cdot 2s) = 0$$

		operator			
		\hat{P}_{A_1}	\hat{P}_{A_2}	\hat{P}_{B_1}	\hat{P}_{B_2}
orbital	2s	2s	0	0	0
	2p _z	2p _z	0	0	0
	2p _y	0	0	0	2p _y
	2p _x	0	0	2p _x	0

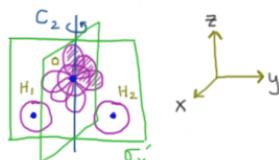
2s → A₁ only

2p_z → A₁ only

2p_y → B₂ only

2p_x → B₁ only

$$\Gamma = 2A_1 - B_2 - B_1 = (2 \ 0 \ 0 \ 2) = \Gamma_H$$



$$O: 2s, 2p_z, 2p_y, 2p_x \quad H: 1s$$

$$irreps: \sum_{i=1}^4 d_i^2 = 1^2 + 1^2 + 1^2 + 1^2 = 4$$

$$h = \sum_{i=1}^4 d_i = 1 + 1 + 1 + 1 = 4$$

$$\hat{P}_i = \frac{d_i}{h} \sum_{\vec{R}} x_i(\vec{R}) \hat{R}$$

$$\Gamma_H = (2 \ 0 \ 0 \ 2) = A_1 + B_2$$

$$\hat{P}_{A_1}(1s_1) = \frac{1}{4} (1 \cdot 1s_1 + 1 \cdot 1s_2 + 1 \cdot 1s_2 + 1 \cdot 1s_1) \\ = \frac{1}{2} (1s_1 + 1s_2) \quad \textcircled{0} \quad \textcircled{0}$$

$$\hat{P}_{B_2}(1s_1) = \frac{1}{4} (1 \cdot 1s_1 - 1 \cdot 1s_1 - 1 \cdot 1s_2 + 1 \cdot 1s_1) \\ = \frac{1}{2} (1s_1 - 1s_2) \quad \textcircled{0} \quad \textcircled{0}$$

2.142 Irrep Direct Products

Irrep Direct Products

$$A_2 \times B_1 = (1 \cdot 1 \quad 1(-1) \quad (-1) \cdot 1 \quad (-1)(-1)) = (1 \quad -1 \quad -1 \quad 1) = B_2$$

$$(x_1 \times x_2)_i = (x_1)_i (x_2)_i$$

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

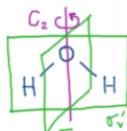
in general:

$$A \times A = A \quad A \times B = B \quad B \times A = B \quad B \times B = A$$

$$g \times g = g \quad g \times u = u \quad u \times g = g \quad u \times u = g$$

$$1 \times 1 = 1 \quad 1 \times 2 = 2 \quad 2 \times 1 = 2 \quad 2 \times 2 = 1$$

$$' \times ' = ' \quad ' \times '' = '' \quad " \times " = "$$



C_{2v}	\hat{E}	\hat{C}_2	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

$$A_1 \times A_2 \times B_1 = A_2 \times B_1 = A_1 \times B_2 = B_2$$

direct product is associative



$$\underbrace{A_1 \times A_1}_{A_1} \times \underbrace{A_1 \times A_1}_{A_1} \times \underbrace{B_2 \times B_2}_{A_1} \times \underbrace{A_1 \times A_1}_{A_1} \times \underbrace{B_1 \times B_1}_{A_1} = A_1$$



2.143 Symmetry IR / Raman Activity

Symmetry IR/Raman Activity

$$\Gamma = (9 - 1 \ 1 \ 3) = 3A_1 + A_2 + 2B_1 + 3B_2$$

$$\alpha_{A_1} = \frac{1}{4}(9 \cdot 1 + (-1) \cdot 1 + 1 \cdot 1 + 3 \cdot 1) = 12/4 = 3$$

$$\alpha_{A_2} = \frac{1}{4}(9 \cdot 1 + (-1) \cdot 1 + 1 \cdot (-1) + 3 \cdot (-1)) = 4/4 = 1$$

$$\alpha_{B_1} = \frac{1}{4}(9 \cdot 1 + (-1) \cdot (-1) + 1 \cdot 1 + 3 \cdot (-1)) = 8/4 = 2$$

$$\alpha_{B_2} = \frac{1}{4}(9 \cdot 1 + (-1) \cdot (-1) + 1 \cdot (-1) + 3 \cdot 1) = 12/4 = 3$$

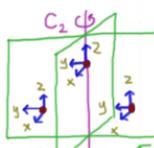
$$\Gamma_{\text{trans}} = A_1 + B_1 + B_2 = (3 - 1 \ 1 \ 1)$$

$$\Gamma_{\text{rot}} = A_2 + B_1 + B_2 = (3 - 1 \ -1 \ -1)$$

$$\Gamma = \Gamma_{\text{trans}} + \Gamma_{\text{rot}} + \Gamma_{\text{vib}}$$

$$\Gamma_{\text{vib}} = \Gamma - \Gamma_{\text{rot}} - \Gamma_{\text{trans}} = (3 \ 1 \ 1 \ 3)$$

$$\boxed{\Gamma_{\text{vib}} = 2A_1 + B_2}$$



C_{2v}	\hat{E}	\hat{C}_2	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz

IR active if same irrep as x, y , or z

Raman active if same irrep as x^2, y^2, z^2, xy, yz , or xz

$$A_1 \rightarrow z, x^2$$

$$B_2 \rightarrow y, yz$$

All 3 modes IR active

All 3 modes Raman active

2.144 Nuclear Spin

Nuclear Spin

$\hat{I}^2 \rightarrow$ total nuclear spin angular momentum squared operator

$\hat{I}_z \rightarrow$ z-component of nuclear spin angular momentum operator

$|\alpha\rangle \rightarrow$ "spin up" $|\beta\rangle \rightarrow$ "spin down"
for protons:

$$\hat{I}^2 |\alpha\rangle = \frac{1}{2} (\frac{1}{2} + 1) \hbar^2 |\alpha\rangle = \frac{3}{4} \hbar^2 |\alpha\rangle$$

$$\hat{I}^2 |\beta\rangle = \frac{1}{2} (\frac{1}{2} + 1) \hbar^2 |\beta\rangle = \frac{3}{4} \hbar^2 |\beta\rangle$$

$$\hat{I}_z |\alpha\rangle = +\frac{1}{2} \hbar |\alpha\rangle$$

$$\hat{I}_z |\beta\rangle = -\frac{1}{2} \hbar |\beta\rangle$$

$$\langle \alpha | \alpha \rangle = \int \alpha^* \alpha d\tau = 1$$

$$\langle \beta | \beta \rangle = 1$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

"orthonormal"

Spin $\frac{1}{2}$ Nuclei:

^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P

2.145 Nuclear Magnetic Dipole

Magnetic Moments

$$\mu = iA$$

$\mu \rightarrow$ magnetic dipole

$i \rightarrow$ electric current

$A \rightarrow$ cross-sectional area of orbit

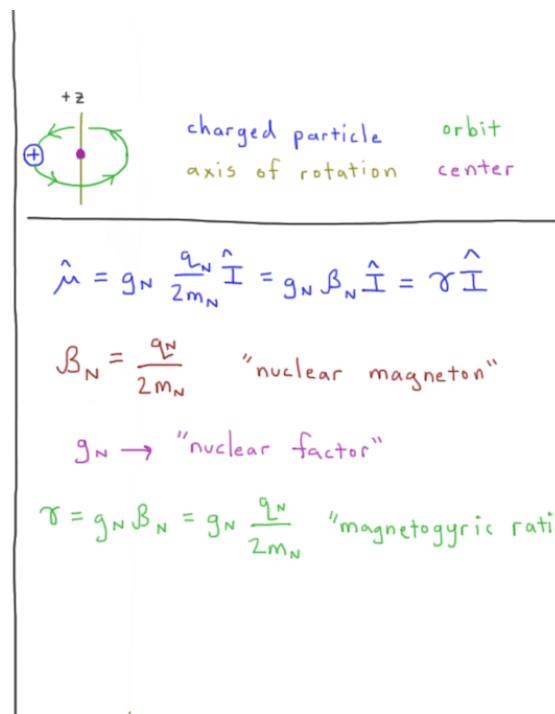
$$i = qv/t = qv/(2\pi r) \quad A = \pi r^2$$

$$\mu = \left(\frac{qv}{2\pi r}\right)(\pi r^2) = \frac{1}{2}qv r \quad (\text{circular})$$

$$\vec{\mu} = \frac{1}{2} q (\vec{r} \otimes \vec{v}) \quad (\text{general})$$

$$\vec{r} \otimes \vec{v} = \frac{1}{m} (\vec{r} \otimes \vec{p}) = \frac{1}{m} \vec{L} \quad \vec{p} = m\vec{v}$$

$$\vec{\mu} = \frac{q}{2m} \vec{L}$$



2.146 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance

$$V = -\vec{\mu} \cdot \vec{B} = -(\mu_x B_x + \mu_y B_y + \mu_z B_z)$$

assume $B_x = B_y = 0$

$$\hat{V} = -\beta_z \hat{\mu}_z = -\gamma B_z \hat{I}_z$$

$$\hat{H} = -\gamma \beta_z \hat{I}_z = -g_N \frac{q_N}{2m_N} B_z \hat{I}_z$$

$$\hat{H} \Psi = E \Psi = -\gamma \beta_z (\hbar m_I \Psi)$$

$$m_I = \pm \frac{1}{2} \quad |\alpha\rangle \rightarrow +\frac{1}{2} \quad |\beta\rangle \rightarrow -\frac{1}{2}$$

$$E_{\pm \frac{1}{2}} = \mp \frac{1}{2} \hbar \gamma \beta_z$$

$$\begin{array}{c} \uparrow \\ \frac{E}{\hbar \gamma \beta_z} \\ \downarrow \\ +\frac{1}{2} \end{array} \quad \begin{array}{c} |\beta\rangle \\ + \\ |\alpha\rangle \\ - \end{array} \quad \begin{array}{l} \hat{\mu} = g_N \frac{q_N}{2m_N} \hat{I} = g_N \beta_N \hat{I} = \gamma \hat{I} \\ \hat{I}_z |\alpha\rangle = +\frac{1}{2} \hbar |\alpha\rangle \\ \hat{I}_z |\beta\rangle = -\frac{1}{2} \hbar |\beta\rangle \end{array}$$

$$\Delta E = h\nu = 2\pi \hbar \nu = E_{+\frac{1}{2}} - E_{-\frac{1}{2}} =$$

$$= \left(\frac{1}{2} - (-\frac{1}{2}) \right) \hbar \gamma \beta_z$$

$$\nu = \frac{1}{2\pi} \gamma \beta_z \quad [\text{Hz}]$$

$$\nu \propto \beta_z$$

2.147 NMR Spectrometer

NMR Spectrometer

$$\nu = \frac{1}{2\pi} \gamma B_z \quad \gamma = g_N \beta_N \quad \beta_N = \frac{e_N}{2m_N}$$

ν → "resonance frequency"

$\nu \propto B_z$ for spectrum, can either

fix ν , vary B or

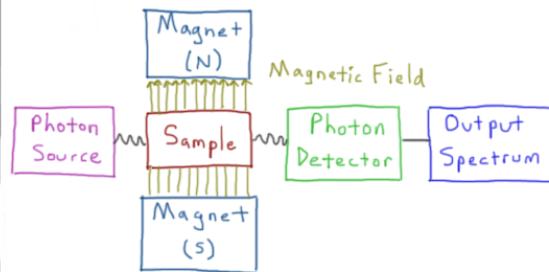
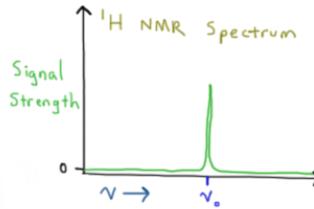
fix B , vary ν

common frequencies [MHz]:

60, 90, 250, 300, 400, 500, 700, 1000

tetramethylsilane (TMS) → $\text{Si}(\text{CH}_3)_4$

- non-reactive
- strong signal
- highly shielded



2.148 Magnetic Shielding

Magnetic Shielding

$$\hat{H} = -\tau B_z \hat{I}_z$$

$$\sigma = g_N \beta_N = g_N \frac{q_N}{2m_N} \quad \Delta E = h\nu = \hbar \tau B_z$$

electrons generate \vec{B}_{elec} which opposes \vec{B}_o

$$\vec{B}_{elec} = -\sigma \vec{B}_o \quad \uparrow \vec{B}_o \quad \downarrow \vec{B}_{elec}$$

σ → "shielding constant"

$$\sigma \approx 10^{-5}$$

$$B_z = B_o(1-\sigma)$$

$$B_o = \frac{2\pi\nu}{\tau(1-\sigma)}$$

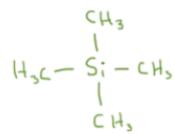
$$E_{\pm\nu} = \mp \frac{1}{2}\hbar\tau B_z$$

$$\sigma \uparrow \rightarrow B_z \downarrow \rightarrow \nu \downarrow$$

σ depends on chemical environment

(more local electron density) → $\sigma \uparrow$

TMS → very high σ



δ → "chemical shift"

$$\delta_H = 10^6 \left(\frac{\nu_H - \nu_{TMS}}{\nu_{spec}} \right) \quad [\text{ppm}] \quad \text{parts per million}$$

ν_{spec} → spectrometer frequencies [Hz]

$\delta_{TMS} = 0.0 \text{ ppm}$ (reference)

2.149 Chemical Shift

Chemical Shift

$$E_{\pm\nu_2} = \mp \frac{1}{2} \hbar \sigma B_z \quad \nu = \frac{\gamma B_z}{2\pi} \quad \delta_H = 10^6 \left(\frac{\nu_H - \nu_{TMS}}{\nu_{spec}} \right)$$

$$\gamma = g_N \beta_N = g_N \frac{q_N}{2m_N} \quad B_z = B_0 (1 - \sigma) \quad \delta_{TMS} = 0.0 \text{ ppm}$$

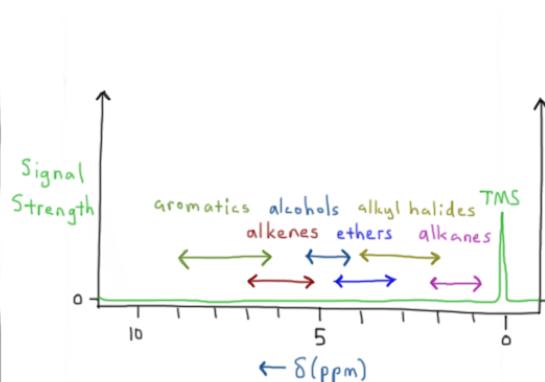
$$\nu_1 = \frac{\gamma B_0}{2\pi} (1 - \sigma_1) \quad \nu_2 = \frac{\gamma B_0}{2\pi} (1 - \sigma_2)$$

$$\delta_2 - \delta_1 = 10^6 \left[\left(\frac{\nu_2 - \nu_{TMS}}{\nu_{spec}} \right) - \left(\frac{\nu_1 - \nu_{TMS}}{\nu_{spec}} \right) \right] =$$

$$= 10^6 \left(\frac{\nu_2 - \nu_1}{\nu_{spec}} \right) = 10^6 \frac{\gamma B_0}{2\pi \nu_{spec}} (\sigma_1 - \sigma_2)$$

$$\beta_0 = \frac{2\pi \nu_{spec}}{\gamma (1 - \sigma)} \quad \sigma \approx 10^{-5} \rightarrow |1 - \sigma| \approx 1$$

$$\delta_2 - \delta_1 = 10^6 \left(\frac{\pi}{2\pi \nu_{spec}} \right) \left(\frac{2\pi \nu_{spec}}{\pi} \right) (\sigma_1 - \sigma_2)$$



$$\boxed{\delta_2 - \delta_1 = -10^6 (\sigma_2 - \sigma_1)}$$

$$\sigma_{TMS} > \sigma_H \rightarrow \delta_H > 0.0 \text{ ppm}$$

almost always

2.150 Spin-Spin Coupling

Spin-Spin Coupling $\sigma_1 > \sigma_2$

$$\hat{H}^{(0)} = -\gamma B_0 (1 - \sigma_1) \hat{I}_{z_1} - \gamma B_0 (1 - \sigma_2) \hat{I}_{z_2}$$

$$\Psi_1 = \alpha(1)\alpha(2)11 \quad \Psi_2 = \alpha(1)\beta(2)1L$$

$$\Psi_3 = \beta(1)\alpha(2)L1 \quad \Psi_4 = \beta(1)\beta(2)LL$$

$$\hat{I}_z |\alpha\rangle = +\frac{1}{2}\hbar |\alpha\rangle \quad \hat{I}_z |\beta\rangle = -\frac{1}{2}\hbar |\beta\rangle$$

$$[E^{(0)} = -\hbar \gamma B_0 [m_1 (1 - \sigma_1) + m_2 (1 - \sigma_2)]]$$

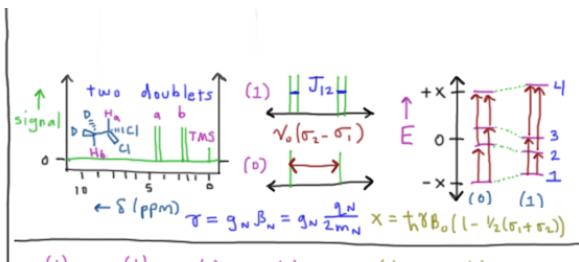
$$m_1 = \pm \frac{1}{2}, \quad m_2 = \pm \frac{1}{2}$$

$$\hat{H}^{(1)} = \frac{\hbar J_{12}}{\hbar} \hat{I}_1 \cdot \hat{I}_2 \quad E(\vec{m}_1, \vec{m}_2) \propto \vec{m}_1 \cdot \vec{m}_2$$

$J_{12} \rightarrow$ "coupling constant" [Hz]

$$\hat{I}_1 \cdot \hat{I}_2 = \hat{I}_{x1} \hat{I}_{x2} + \hat{I}_{y1} \hat{I}_{y2} + \hat{I}_{z1} \hat{I}_{z2}$$

$$\hat{I}_{z1} \hat{I}_{z2} \Psi_i = \hbar^2 m_1 m_2 \Psi_i \quad m_1 m_2 = \pm \frac{1}{4}$$



$$E_1^{(1)} = E_{1x}^{(1)} + E_{1y}^{(1)} + E_{1z}^{(1)} \quad E_{1x}^{(1)} = E_{1y}^{(1)} = 0$$

$$E_{1z}^{(1)} = \left(\frac{\hbar J_{12}}{\hbar} \right) \left(\pm \frac{1}{4} \hbar \right) \quad E_1^{(1)} = \pm \frac{1}{4} \hbar J_{12}$$

$$E_2^{(0)} = -\hbar \gamma B_0 (1 - \frac{1}{2}(\sigma_1 + \sigma_2)) \quad E_2^{(0)} = -\frac{1}{4} \hbar \gamma B_0 (\sigma_2 - \sigma_1)$$

$$E_1 = E_1^{(0)} + \frac{1}{4} \hbar J_{12} \quad E_2 = E_2^{(0)} - \frac{1}{4} \hbar J_{12}$$

$$E_4 = -E_1^{(0)} + \frac{1}{4} \hbar J_{12} \quad E_3 = -E_2^{(0)} - \frac{1}{4} \hbar J_{12}$$

$$\nu_{12} = \nu_0 (1 - \sigma_1) - \frac{1}{2} J_{12} \quad \nu_{13} = \nu_0 (1 - \sigma_2) - \frac{1}{2} J_{12}$$

$$\nu_{34} = \nu_0 (1 - \sigma_1) + \frac{1}{2} J_{12} \quad \nu_{24} = \nu_0 (1 - \sigma_2) + \frac{1}{2} J_{12}$$

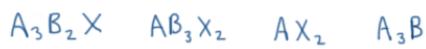
2.151 First Order Spectra

First Order Spectra

if $J_{12} \ll \nu_0 |\sigma_1 - \sigma_2|$, then first-order perturbation theory is valid

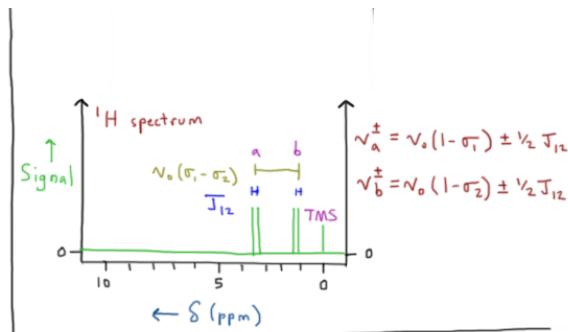
$J_{12} \ll \nu_0 |\sigma_1 - \sigma_2| \rightarrow \text{"AX spectrum"}$

$J_{12} \approx \nu_0 |\sigma_1 - \sigma_2| \rightarrow \text{"AB spectrum"}$



$$\frac{\nu_0 |\sigma_1 - \sigma_2|}{J_{12}} \gg 1 \quad \text{if 1st order}$$

$$\gg \text{ if } \nu_0 |\sigma_1 - \sigma_2| \gtrsim 10 - 20 J_{12}$$



spectrum becomes 1st order at:

- high ν_0
- high $|\sigma_1 - \sigma_2|$
- low J_{12}

2.152 Chemical Equivalence

Chemical Equivalence

$$\hat{H} = -\gamma B_0 (1-\sigma_1) \hat{I}_{z_1} - \gamma B_0 (1-\sigma_2) \hat{I}_{z_2} + \frac{\hbar J_{12}}{h^2} \hat{I}_1 \cdot \hat{I}_2$$

equivalent $\rightarrow \sigma_1 = \sigma_2 = \sigma_A$

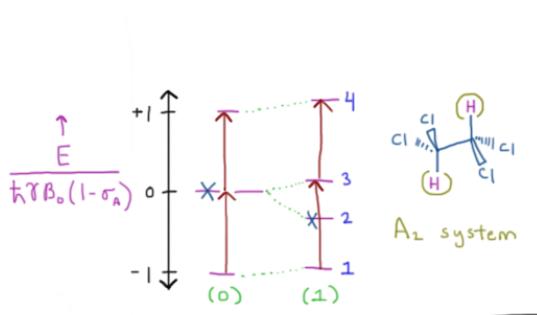
$$\hat{H}^{(0)} = -\gamma B_0 (1-\sigma_A) (\hat{I}_{z_1} + \hat{I}_{z_2})$$

$$\hat{H}^{(1)} = \frac{\hbar J_{AA}}{h^2} \hat{I}_1 \cdot \hat{I}_2$$

$$\Psi_1 = \alpha(1)\alpha(2) \quad \Psi_4 = \beta(1)\beta(2)$$

$$\Psi_2 = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad X$$

$$\Psi_3 = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$



$$E_1 = -\hbar\gamma B_0 (1-\sigma_A) + \frac{1}{4}\hbar J_{AA}$$

$$E_4 = +\frac{1}{4}\hbar J_{AA} (1-\sigma_A) + \frac{1}{4}\hbar J_{AA}$$

$$E_2 = -\frac{3}{4}\hbar J_{AA} \quad E_3 = +\frac{1}{4}\hbar J_{AA}$$

$$\nu_{13} = \frac{E_3 - E_1}{h} = \frac{1}{2\pi} \gamma B_0 (1-\sigma_A) = \nu_0 (1-\sigma_A)$$

$$\nu_{34} = \frac{E_4 - E_3}{h} = \frac{1}{2\pi} \gamma B_0 (1-\sigma_A) = \nu_0 (1-\sigma_A)$$

2.153 N+1 Rule

The N+1 Rule

| singlet

1 L doublet

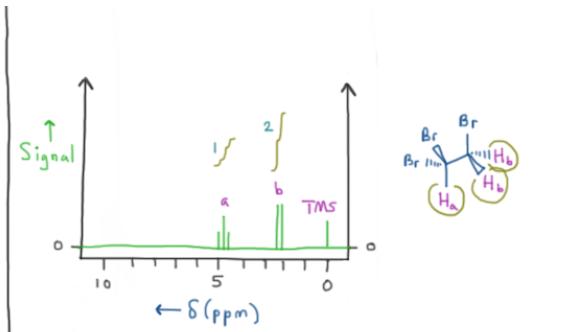
11 1L 1L triplet

111 111 111 quartet

1111 1111 1111 quintet

1 : 3 : 3 : 1

1 : 4 : 6 : 4 : 1



n adjacent protons → n+1 peaks

1	1	"binomial coefficients"				
1	2	1				
1	3	3	1	"Pascal's triangle"		
1	4	6	4	1		
1	5	10	10	5	1	
1	6	15	20	15	6	1
...

2.154 Second Order Spectra

Second Order Spectra

1st order perturbation theory not valid
when $\nu_0 |\sigma_1 - \sigma_2| \approx J_{12}$

use linear variational method instead

$$\hat{H} = -\gamma \beta_0 [(1-\sigma_1) \hat{I}_{z_1} + (1-\sigma_2) \hat{I}_{z_2}] + \frac{\hbar J_{12}}{2} \hat{I}_1 \cdot \hat{I}_2$$

$$\phi_1 = \alpha(1) \alpha(2) \quad \phi_2 = \alpha(1) \beta(2)$$

$$\phi_3 = \beta(1) \alpha(2) \quad \phi_4 = \beta(1) \beta(2)$$

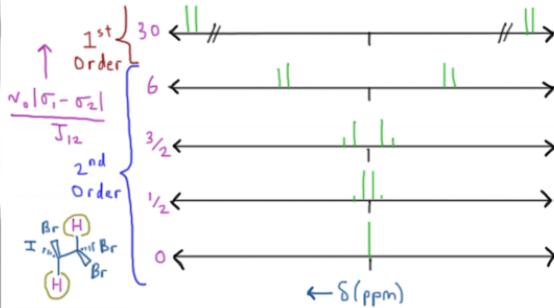
$$\Psi_i = c_{1i} \phi_1 + c_{2i} \phi_2 + c_{3i} \phi_3 + c_{4i} \phi_4$$

$$|\hat{H} - E| = 0 \quad H_{ij} = \int \Psi_i^* \hat{H} \Psi_j d\tau$$

$$d_1 = \frac{1}{2} h \nu_0 (1 - \sigma_1) \quad f = \frac{1}{4} h J_{12}$$

$$H_{11} = -d_1 - d_2 + f \quad H_{22} = -d_1 + d_2 - f$$

$$H_{44} = d_1 + d_2 + f \quad H_{33} = d_1 - d_2 - f$$



$$H_{23} = H_{32} = +f, \text{ all other } H_{i \neq j} = 0$$

$$E_1 = -h\nu_0 (1 - \frac{1}{2}(\sigma_1 + \sigma_2)) + \frac{1}{4}hJ_{12}$$

$$E_2 = -\frac{1}{2}h\sqrt{\nu_0^2(\sigma_1 - \sigma_2)^2 + J_{12}^2} - \frac{1}{4}hJ_{12}$$

$$E_3 = +\frac{1}{2}h\sqrt{\nu_0^2(\sigma_1 - \sigma_2)^2 + J_{12}^2} - \frac{1}{4}hJ_{12}$$

$$E_4 = +h\nu_0 (1 - \frac{1}{2}(\sigma_1 + \sigma_2)) + \frac{1}{4}hJ_{12}$$

2.155 Particle in a Ring Model

Particle in a Ring Model

$$\hat{H}\Psi(r, \theta, \phi) = E\Psi(r, \theta, \phi)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r, \theta, \phi)$$

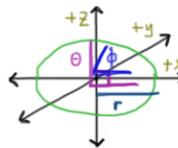
$$V(r, \theta, \phi) = \begin{cases} 0 & \text{if } r=R \text{ and } \theta = \pi/2 \\ \infty & \text{otherwise} \end{cases}$$

$$\Psi(r, \theta, \phi) = 0 \text{ if } r \neq R \text{ or } \theta \neq \pi/2$$

$$\Psi(R, \pi/2, \phi) = \Psi(\phi)$$

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$\nabla^2 = \frac{1}{R^2} \frac{d^2}{d\phi^2} \quad r = R, \sin(\pi/2) = 1$$



$$\hat{H}\Psi(\phi) = E\Psi(\phi)$$

$$\hat{H} = -\frac{\hbar^2}{2mR^2} \frac{d^2}{d\phi^2}$$

2.156 Particle in a Ring Energies

Particle in a Ring Energy

$$-\frac{\hbar^2}{2mR^2} \frac{d^2\Psi(\phi)}{d\phi^2} = E\Psi(\phi)$$

$$\frac{d^2\Psi(\phi)}{d\phi^2} = -\left(\frac{2mR^2E}{\hbar^2}\right)\Psi(\phi) = -k^2\Psi(\phi)$$

$$\Psi(\phi) = e^{\pm ik\phi} \quad k = \frac{R}{\hbar} \sqrt{2mE}$$

$$\Psi(\phi + 2\pi) = \Psi(\phi)$$



$$e^{ik\phi} = e^{ik(\phi+2\pi)} = e^{ik\phi} e^{i2\pi k}$$

$$| = e^{i2\pi k} = \underbrace{\cos(2\pi k)}_1 + i\underbrace{\sin(2\pi k)}_0$$

$$\hat{H}\Psi(\phi) = E\Psi(\phi) \quad r=R$$

$$\hat{H} = -\frac{\hbar^2}{2mR^2} \frac{d^2}{d\phi^2} \quad \theta = \pi/2$$

$$0 \leq \phi < 2\pi$$

$$\sin(2\pi k) = 0 \rightarrow \sin^{-1}(0) = n\pi = 2k\pi \quad n \in \mathbb{Z}$$

$$\cos(2\pi k) = 1 \rightarrow \cos^{-1}(1) = 2n\pi = 2k\pi \quad n \in \mathbb{Z}$$

$$\sin \rightarrow k = n/2 \quad \cos \rightarrow k = n \quad \therefore k = n$$

$$n = \frac{R}{\hbar} \sqrt{2mE} \quad \frac{\hbar^2 n^2}{R^2} = 2mE$$

$$E_n = \frac{\hbar^2 n^2}{2mR^2} = \frac{\hbar^2 n^2}{8\pi^2 m R^2} \quad n = 0, \pm 1, \pm 2, \dots$$

2.157 Particle in a Ring Wavefunctions

Particle in a Ring Wavefunctions

$$\Psi_n(\phi) = N e^{in\phi} \quad n = 0, \pm 1, \pm 2, \dots$$

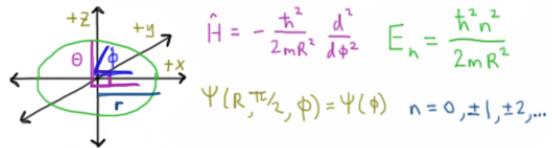
$$I = \int_0^{2\pi} \Psi^*(\phi) \Psi(\phi) d\phi$$

$$I = \int_0^{2\pi} (N e^{in\phi})^* (N e^{in\phi}) d\phi$$

$$(e^{in\phi})^* = e^{-in\phi} \quad e^{-in\phi} \cdot e^{in\phi} = 1$$

$$I = N^2 \int_0^{2\pi} d\phi = 2\pi N^2 \quad N = \frac{1}{\sqrt{2\pi}}$$

$$\boxed{\Psi_n(\phi) = \frac{1}{\sqrt{2\pi}} e^{in\phi}}$$



$$\hat{H} = -\frac{\hbar^2}{2mR^2} \frac{d^2}{d\phi^2} \quad E_n = \frac{\hbar^2 n^2}{2mR^2}$$

$$\Psi(R, \theta, z, \phi) = \Psi(\phi) \quad n = 0, \pm 1, \pm 2, \dots$$

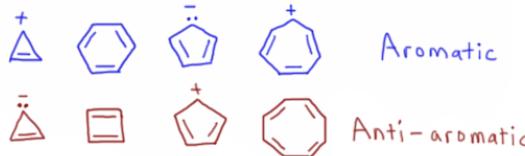
$$\Psi_0(\phi) = \frac{1}{\sqrt{2\pi}} \quad E_0 = 0$$

$$\Psi_{\pm 1}(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i\phi} \quad E_{\pm 1} = \frac{\hbar^2}{2mR^2}$$

$$\Psi_{\pm 2}(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi} \quad E_{\pm 2} = \frac{4\hbar^2}{2mR^2}$$

2.158 Huckel's Rule

Huckel's Rule



$4n \rightarrow \frac{1}{2}$ shell $4n+2 \rightarrow$ full shell

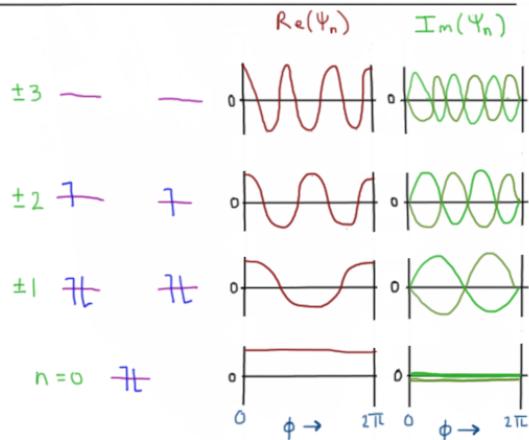
$4n+2 \rightarrow$ aromatic

$4n \rightarrow$ anti-aromatic

$\max(n)$	orbitals	electrons
0	1	2
1	3	6
2	5	10
n	$2n+1$	$4n+2$

$$\hat{H} = -\frac{\hbar^2}{2mR^2} \frac{d^2}{d\phi^2} \quad E_n = \frac{\hbar^2 n^2}{2mR^2}$$

$$\Psi_n(\phi) = \frac{1}{\sqrt{2\pi}} e^{in\phi} \quad n = 0, \pm 1, \pm 2, \dots$$



2.159 Aromatic UV-Vis Spectra

UV-Vis Spectra of Aromatics

calculate wavelength of $\pi \rightarrow \pi^*$ transition in benzene



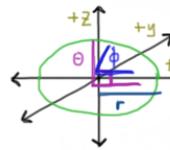
$$\begin{array}{c} \pm 2 \\ \pm 1 \\ n=0 \end{array} \xrightarrow{\text{hv}} \begin{array}{c} + \\ - \\ \mp \end{array} \xrightarrow{\text{hv}} \begin{array}{c} + \\ - \\ \mp \end{array}$$

$$\Delta E = E_f - E_i = (2E_0 + 3E_1 + E_2) - (2E_0 + 4E_1)$$

$$\Delta E = E_2 - E_1 = \frac{\hbar^2}{2mR^2} (2^2 - 1^2) = \frac{3\hbar^2}{8\pi^2 m R^2}$$

$$\Delta E = h\nu = hc/\lambda \quad \lambda = hc/\Delta E$$

$$\lambda = Kc \left(\frac{8\pi^2 m R^2}{3\hbar^2} \right)$$



$$\hat{H} = -\frac{\hbar^2}{2mR^2} \frac{d^2}{dr^2} \quad E_n = \frac{\hbar^2 n^2}{2mR^2}$$

$$\Psi_n(\theta, \phi) = \frac{1}{\sqrt{2\pi}} e^{in\theta} \quad n=0, \pm 1, \pm 2, \dots$$

$$\boxed{\lambda = \frac{8\pi^2 m c R^2}{3h}}$$



$$R_{c-c} = R = 1.38 \cdot 10^{-10} \text{ m}$$

$$\lambda = \frac{8\pi^2 (9.109 \cdot 10^{-31} \text{ kg})(2.998 \cdot 10^8 \text{ m/s}) (1.38 \cdot 10^{-10} \text{ m})^2}{3(6.626 \cdot 10^{-34} \text{ J}\cdot\text{s})}$$

$$\boxed{\lambda_{\text{theory}} = 207 \text{ nm}}$$

$$\lambda_{\text{expt}} = 255 \text{ nm} \quad \sim 20\% \text{ error}$$

2.160 Particle in a Ring Eigenvalues

Particle in a Ring Eigenvalues

$$\hat{H} = \frac{-\hbar^2}{2mR^2} \frac{d^2}{d\phi^2} \quad \hat{L}_z = -i\hbar \frac{d}{d\phi}$$

$$\hat{H} \Psi_n(\phi) = E_n \Psi_n(\phi) \quad \hat{L}_z \Psi_n(\phi) = \hbar n \Psi_n(\phi)$$

$E_{+k} = E_{-k}$ need to distinguish $\pm k$

$$\hat{L}_z \Psi_k(\phi) = -\hat{L}_z \Psi_{-k}(\phi)$$

$$\hat{L}_z \Psi_0(\phi) = 0 \rightarrow \text{no angular momentum}$$

$\Psi_{+k}, \Psi_{-k} \rightarrow \text{equal magnitude, opposite direction}$

$$\hat{H} = \frac{-\hbar^2}{2mR^2} \frac{d^2}{d\phi^2} \quad E_n = \frac{\hbar^2 n^2}{2mR^2}$$

$$\Psi_n(\phi) = \frac{1}{\sqrt{2\pi}} e^{in\phi} \quad n=0, \pm 1, \pm 2, \dots$$

$$e^{+2i\phi} \quad +2 \circlearrowleft +2\hbar \quad -2 \circlearrowright -2\hbar \quad e^{-2i\phi}$$

$$e^{+i\phi} \quad +1 \circlearrowleft +\hbar \quad -1 \circlearrowright -\hbar \quad e^{-i\phi}$$

$$n=0 \quad \circlearrowleft \quad \langle L_z \rangle = 0$$

$$\Psi_0(\phi) \propto 1$$

3 Chemical Thermodynamics

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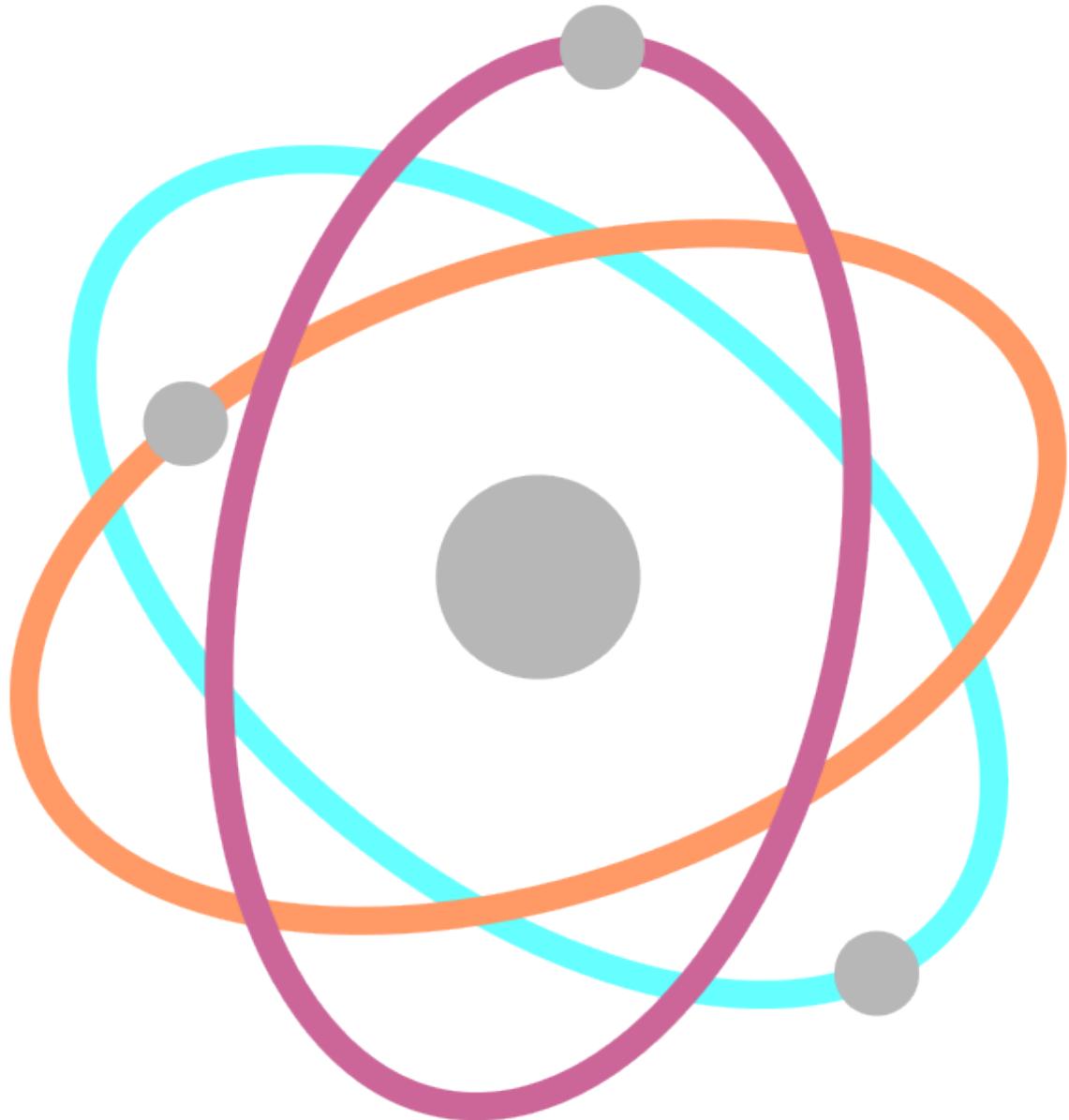
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3.1 Introduction



3.2 Ideal Gas Equation

Ideal Gas Equation

$$PV = nRT \quad P\bar{V} = RT \quad \bar{V} = V/n$$

if true, gas behaves "ideally"

as $P \rightarrow 0$, all gases become ideal

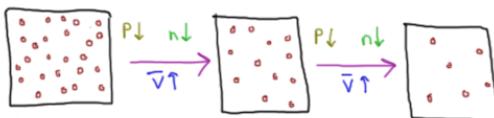
\bar{V} → "molar volume"

$\bar{V} \rightarrow \infty$ as $P \rightarrow 0$

$$\bar{T} = \lim_{P \rightarrow 0} \left(\frac{P\bar{V}}{R} \right)$$

always in Kelvin, "absolute" T

273.15 K = 0°C = 32°F



$$1 \text{ atm} = 101,325 \quad P_A = 1.013 \text{ bar} = 760 \text{ mmHg}$$

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} = 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = k_b N_A$$

$$1 \text{ m}^3/\text{mol} = 10^3 \text{ L/mol} = 10^6 \text{ cm}^3/\text{mol}$$

$$L = \text{dm}^3 \quad mL = \text{cm}^3 \quad kL = \text{m}^3$$

$V \propto n$ → "extensive" n, m, E, ...

\bar{V} independent of n → "intensive"

P, T, \bar{V}

3.3 van der Waals Gas Equation

van der Waal's Equation of State

$$P\bar{V} = RT \quad \bar{V} = V/n$$

true for all gases as $P \rightarrow 0$

$$Z = \frac{P\bar{V}}{RT}$$

"compressibility factor"

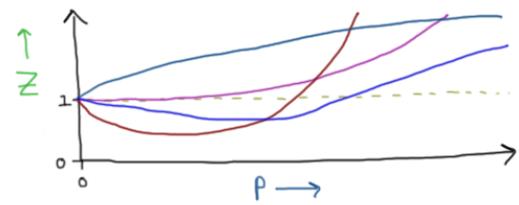
$$Z_{\text{ideal}} = 1 \quad 0 < Z_{\text{real}} < \infty$$

$\circ \rightarrow \leftarrow \circ$ real gases attract one another

$\leftarrow \circ \circ \rightarrow$ real gases take up space

$V_{\text{real}} < V_{\text{ideal}}$ $V_{\text{real}} > V_{\text{ideal}}$

competing effects



$$\left(P + \frac{a}{V^2} \right) \left(\bar{V} - b \right) = RT$$

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

$a \rightarrow$ attraction strength
 $b \rightarrow$ molecular size } empirical

3.4 Virial Equation of State

Virial Equation of State

$$Z = \frac{PV}{RT} = 1 + \frac{B_{2V}(T)}{V} + \frac{B_{3V}(T)}{V^2} + \dots$$

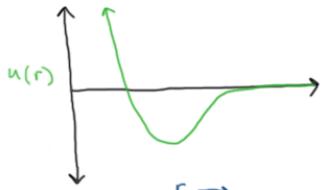
Taylor series for Z in $(\frac{1}{V})$

$$Z = \frac{PV}{RT} = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + \dots$$

$B_{2V}(T), B_{2P}(T) \rightarrow$ "second virial coefficient"

$\{B_{nV}(T)\}$ depend on $u(r)$

$u(r) \rightarrow$ inter-particle interactions



$$B_{2V}(T) = -2\pi N_A \int_0^\infty (e^{-u(r)/kT} - 1) r^2 dr$$

If $B_{2V}(T) = 0$, gas is ideal at low T

$B_{2V}(T_{Boyle}) = 0$ "Boyle temperature"

3.5 Gas Equation Example

Gas Equation Example

0.2540m 1.471 mol Ar gas
0.3250m 300.0 K
0.2200m P = ?

Ideal $P\bar{V} = RT$ $P = \frac{RT}{\bar{V}}$

$$\bar{V} = (0.2200\text{m})(0.3250\text{m})(0.2540\text{m}) = 1.816 \cdot 10^{-2} \text{ m}^3$$

$$\bar{V} = \frac{V}{n} = \frac{1.816 \cdot 10^{-2} \text{ m}^3}{1.471 \text{ mol}} = 1.2346 \cdot 10^{-2} \text{ m}^3/\text{mol}$$

$$P_{\text{ideal}} = \frac{(8.31446 \text{ J/mol}\cdot\text{K})(300.0 \text{ K})}{(1.2346 \cdot 10^{-2} \text{ m}^3/\text{mol})} = 202,036 \text{ Pa}$$

$$vdW \quad (P + \frac{a}{\bar{V}^2})(\bar{V} - b) = RT \quad P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

$$P_{\text{vdw}} = P_{\text{ideal}} \left(\frac{1}{1 - b/\bar{V}} - \frac{a}{RT\bar{V}} \right)$$

$$a_{\text{Ar}} = 1.3483 \frac{\text{L}^2 \cdot \text{bar}}{\text{mol}^2} \quad b_{\text{Ar}} = 0.031830 \text{ L/mol}$$

$$\frac{b}{\bar{V}} = \frac{3.1830 \cdot 10^{-5} \text{ m}^3/\text{mol}}{1.2346 \cdot 10^{-2} \text{ m}^3/\text{mol}} = 2.5782 \cdot 10^{-3}$$

$$\frac{a}{RT\bar{V}} = \frac{0.13483 \text{ m}^6 \cdot \text{Pa}/\text{mol}^3}{(8.31446 \text{ J/mol}\cdot\text{K})(300.0 \text{ K})(1.2346 \cdot 10^{-2} \text{ m}^3/\text{mol})} = 4.361 \cdot 10^{-3}$$

$$P_{\text{vdw}} = P_{\text{ideal}} (1.00258 - 0.004361) = 0.99822 P_{\text{ideal}}$$

Virial $\frac{P\bar{V}}{RT} = 1 + \frac{B_{2v}(T)}{\bar{V}} + \dots \quad P = \frac{RT}{\bar{V}} \left(1 + \frac{B_{2v}(T)}{\bar{V}} + \dots \right)$

$$B_{2v}(300.0 \text{ K})_{\text{Ar}} = -15.7 \text{ cm}^3/\text{mol}$$

$$\frac{B_{2v}(T)}{\bar{V}} = \frac{-1.57 \cdot 10^{-5} \text{ m}^3/\text{mol}}{1.2346 \cdot 10^{-2} \text{ m}^3/\text{mol}} = -1.27167 \cdot 10^{-3}$$

$$P_{\text{vir}} = P_{\text{ideal}} (1 - 1.27 \cdot 10^{-3}) = 0.99873 P_{\text{ideal}}$$

$$P_{\text{ideal}} = 1.9939 \text{ atm}$$

$$P_{\text{vdw}} = 1.9904 \text{ atm}$$

$$P_{\text{vir}} = 1.9914 \text{ atm}$$

1 atm = 101,325 Pa

3.6 Gas Interaction Functions

Interaction Functional Forms

$$B_{2V}(T) = -2\pi N_A \int_0^\infty (e^{-u(r)/k_b T} - 1) r^2 dr$$

$$\bar{Z} = \frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + \dots$$

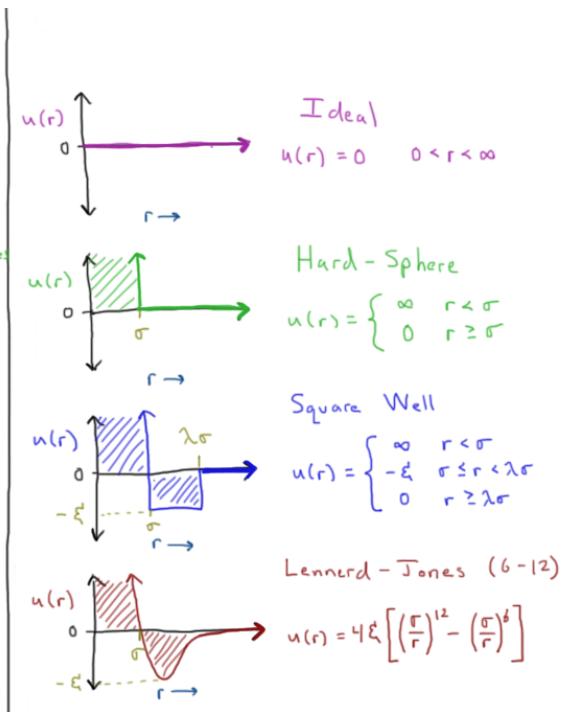
$u(r) \rightarrow$ potential energy between particles
 $r \rightarrow$ distance between particles

$$(P + \frac{n}{V^2})(\bar{V} - b) = RT$$

$$B_{2V}(T) = b - \frac{a}{RT}$$

$$a = \frac{8\pi N_A^3 \xi^4 \sigma^3}{3}$$

$$b = \frac{2\pi N_A \sigma^3}{3}$$



3.7 Critical Point

Critical Point

$$\text{Ideal gas} \rightarrow P = \frac{RT}{V}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} \neq 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{V^3} \neq 0$$

no interactions \rightarrow no liquid

$$vdW \text{ gas} \rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2}$$

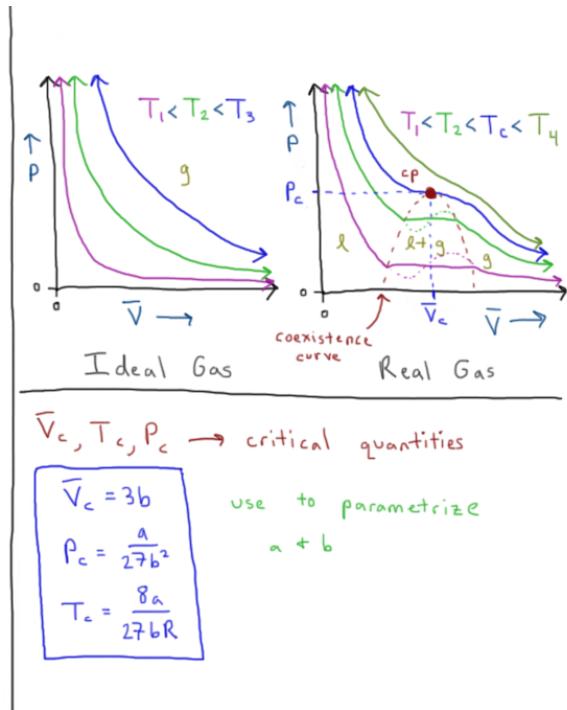
$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3}$$

interactions result

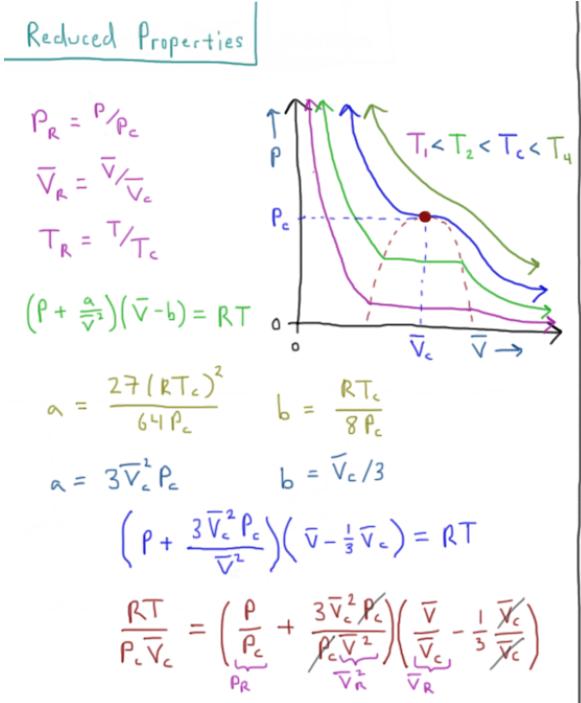
$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

in liquid during compression

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad \text{at the critical point}$$



3.8 Reduced Properties



$$\left(P_r + \frac{3}{\bar{V}_r^2} \right) \left(\bar{V}_r - \frac{1}{3} \right) = \frac{RT}{P_c \bar{V}_c}$$

$$P_c = \frac{a}{27b^2} \quad \bar{V}_c = 3b$$

$$P_c \bar{V}_c = \frac{3ab}{27b^2} = \frac{a}{9b} = \frac{1}{R} \left(\frac{27(RT_c)}{64P_c} \right) \left(\frac{8P_c}{P_c T_c} \right) = \frac{3}{8} RT_c$$

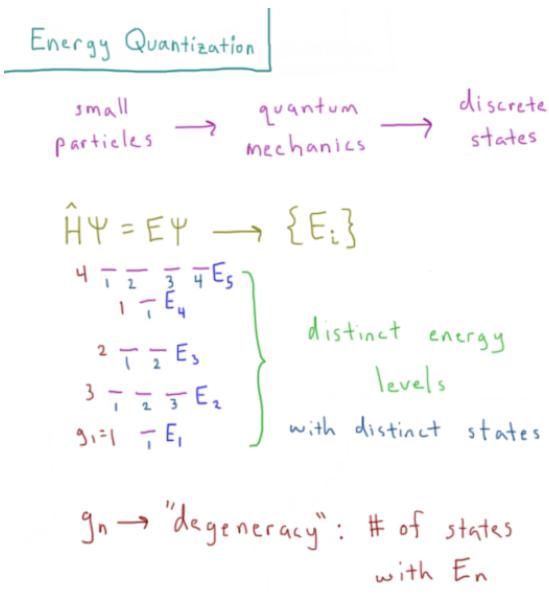
$$\frac{RT}{P_c \bar{V}_c} = \frac{RT}{\frac{3}{8} RT_c} = \frac{8}{3} T_r$$

$$\boxed{(P_r + \frac{3}{\bar{V}_r^2})(\bar{V}_r - \frac{1}{3}) = \frac{8}{3} T_r}$$

"Law of Corresponding States"

All gases at same (P_r, T_r, \bar{V}_r)
have the same properties

3.9 Energy Quantization



$p_i \rightarrow$ probability particle is in state i

Ergodic Hypothesis - all states

with same E have same p

$$p_{21} = p_{22} = p_{23} \quad p_{31} = p_{32}$$

$$p_{51} = p_{52} = p_{53} = p_{54}$$

$$p_{ij} = p_{ik}$$

3.10 Boltzmann Factor

Boltzmann Factor		
$p_{ij} = p_{ik}$	$E_3 - \frac{1}{2} - \frac{3}{4} - \frac{4}{5} g_3 = 4$	
$p_i = \sum_{j=1}^{g_i} p_{ij} = g_i p_{i1}$	$E_2 - \frac{1}{2} - \frac{3}{4} - \frac{4}{5} g_2 = 5$	
$p_i \propto g_i$	$E_1 - \frac{1}{2} - \frac{3}{4} g_1 = 3$	
$f(E_i) = \underbrace{e^{-E_i/k_b T}}_{\text{"Boltzmann factor"}} = e^{-\beta E_i}$	$\beta = \frac{1}{k_b T}$	
$E_j > E_i$	$\frac{p_j}{p_i} = \frac{\cancel{g_j} e^{-E_j/k_b T}}{\cancel{g_i} e^{-E_i/k_b T}} = \frac{g_j}{g_i} e^{-\Delta E_{ji}/k_b T}$	
$\Delta E_{ji} = E_j - E_i > 0$		

ΔE_{ji}	$e^{-\Delta E_{ji}/k_b T}$	p_i/p_j
0	1	g_j/g_i
$k_b T$	0.368	$0.37 g_i/g_j$
$3k_b T$	0.0498	$0.05 g_j/g_i$
$10k_b T$	$4.5 \cdot 10^{-4}$	$0.0004 g_j/g_i$
∞	0	0

$0 < T < \infty \rightarrow$ always Kelvin

$$0 < p_i/p_j < g_j/g_i$$

$$T = 0 \quad p_i = 1 \quad p_{\neq i} = 0$$

$$T = \infty \quad p_i = C g_i$$

3.11 Partition Function

Partition Function

$$p_i \propto g_i e^{-E_i/k_B T}$$

$$p_i = C g_i e^{-E_i/k_B T}$$

$$\sum_{i=1}^n p_i = 1 \quad \text{"normalization"}$$

$$Q = \sum_{i=1}^{\text{states}} e^{-E_i/k_B T} = \sum_{i=1}^{\text{levels}} g_i e^{-E_i/k_B T}$$

"partition function"

contains all information
about the system

$$E_3 - 1 - 2 - 3 \quad g_3=3$$

$$E_2 - 1 \quad g_2=1$$

$$E_1 - 1 - 2 \quad g_1=2$$

$$p_i = \frac{g_i e^{-\beta E_i}}{\sum_{j=1}^n g_j e^{-\beta E_j}}$$

$$\beta = \frac{1}{k_B T}$$

$$p_i = \frac{1}{Q} g_i e^{-\beta E_i}$$

3.12 Ensemble Energy

Ensemble Energy

Ensemble → (probability distribution for the states of a system)

$\langle A \rangle$ → "expectation value": average value of A

$$\langle A \rangle = \sum_{i=1}^n p_i A_i \quad \text{weighted average}$$

$$p_i = \frac{1}{Q} g_i e^{-\beta E_i} \quad \beta = \frac{1}{k_b T}$$

$$Q = \sum_{j=1}^n g_j e^{-\beta E_j}$$

$$\boxed{\langle E \rangle = \frac{\sum_{i=1}^n E_i g_i e^{-\beta E_i}}{\sum_{j=1}^n g_j e^{-\beta E_j}}}$$

$$\frac{\partial \ln Q}{\partial \beta} = \frac{\partial \ln Q}{\partial Q} \left(\frac{\partial Q}{\partial \beta} \right) = \frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right) =$$

$$= \frac{1}{Q} \frac{\partial}{\partial \beta} \left(\sum_{i=1}^n g_i e^{-\beta E_i} \right) =$$

$$= \frac{1}{Q} \sum_{i=1}^n g_i \frac{\partial}{\partial \beta} (e^{-\beta E_i}) =$$

$$= \sum_{i=1}^n -E_i \left(\frac{1}{Q} g_i e^{-\beta E_i} \right) =$$

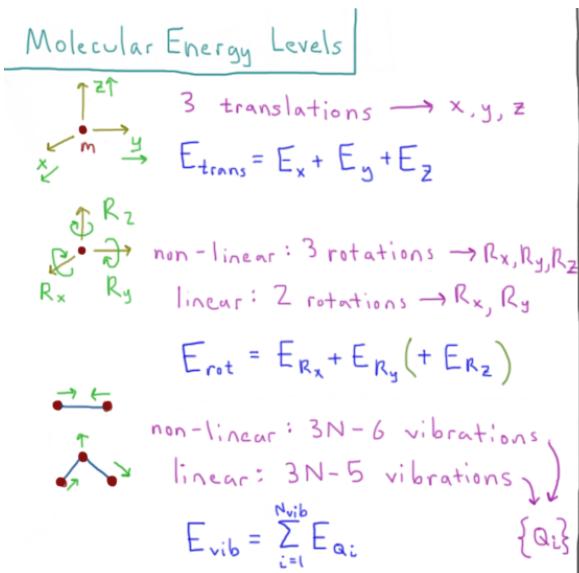
$$= - \sum_{i=1}^n E_i p_i = -\langle E \rangle$$

$$\boxed{\langle E \rangle = - \frac{\partial \ln Q}{\partial \beta}}$$

3.13 Ensemble Energy Example

Average Energy Example		$E_3 = 100 \text{ cm}^{-1}$ -- $g_3=3$	$E_2 = 50 \text{ cm}^{-1}$ -- $g_2=2$	$E_1 = 0 \text{ cm}^{-1}$ -- $g_1=1$	T (K)	Q	p_1	p_2	p_3	$E (\text{cm}^{-1})$
$\langle E \rangle = \sum_{i=1}^3 p_i E_i$					0	1	1	0	0	0
$p_i = \frac{1}{Q} g_i e^{-E_i/k_b T}$					25	1.12	0.89	0.10	0.0085	5.86
$Q = \sum_{i=1}^3 g_i e^{-E_i/k_b T}$					50	1.64	0.61	0.29	0.10	24.71
$\frac{k_b}{hc} = \frac{(1.3806 \cdot 10^{-23} \text{ J/K})}{(6.6261 \cdot 10^{-34} \text{ J} \cdot \text{s})(2.9979 \cdot 10^{10} \frac{\text{cm}}{\text{s}})} = 0.69503 \text{ cm}^{-1}\text{K}$					100	2.69	0.37	0.36	0.27	44.63
$Q = 1 \exp\left(\frac{-0}{0.69503}\right) + 2 \exp\left(\frac{-50}{0.69503}\right) + 3 \exp\left(\frac{-100}{0.69503}\right)$					300	4.43	0.23	0.35	0.42	59.67
$Q = 1 + 2e^{-71.94/T} + 3e^{-143.9/T}$					1000	5.46	0.18	0.34	0.48	64.64
$p_1 = 1/Q$	$p_2 = 2/Q e^{-71.94/T}$	$p_3 = 3/Q e^{-143.9/T}$			∞	6	1/6	1/3	1/2	66.67
$E = 1/Q (E_1 + 2E_2 e^{-71.94/T} + 3E_3 e^{-143.9/T})$										

3.14 Molecular Energy Levels



$\hat{H}\Psi = E_{\text{elec}}\Psi \rightarrow$ electronic states

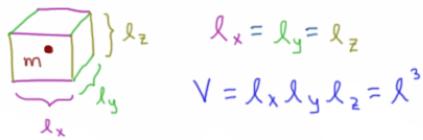
$E_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$

$$q_{\text{mol}} = \sum_{i=1}^{\text{states}} e^{-E_{\text{tot}}^{(i)} / k_b T}$$

need to find $\{E_{\text{tot}}^{(i)}\}$

3.15 Translational Partition Function

Translational Partition Function



$$E_{n_x n_y n_z} = \frac{h^2}{8m\lambda^2} (n_x^2 + n_y^2 + n_z^2)$$

$$g_{n_x n_y n_z} = 1 \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

$$q_{\text{trans}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left(-\frac{\beta h^2}{8m\lambda^2} (n_x^2 + n_y^2 + n_z^2) \right)$$

$$q_{\text{trans}} = q_x q_y q_z \quad \beta = \frac{1}{k_B T}$$

$$q_x = \sum_{n_x=1}^{\infty} \exp \left(-\frac{\beta h^2}{8m\lambda^2} n_x^2 \right) \approx \int_0^{\infty} dn_x \exp \left(-\frac{\beta h^2}{8m\lambda^2} n_x^2 \right)$$

$$\int_0^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{4\alpha}} \quad \alpha = \frac{\beta h^2}{8m\lambda^2}$$

$$q_x = q_y = q_z = \sqrt{\frac{2\pi m}{\beta h^2}} \lambda$$

$$q_{\text{trans}} = \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \lambda^3$$

$$q_{\text{trans}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \lambda^3$$

All Atoms and Molecules

3.16 Rotational Partition Function

Rotational Partition Function

$$q_r = \sum_{i=1}^n g_i e^{-\beta E_i} \quad \beta = \frac{1}{k_b T}$$

$$E_J = \frac{\hbar^2}{2I} J(J+1) = \hbar B J(J+1) = \hbar c \tilde{B} J(J+1)$$

$$M = \frac{m_1 m_2}{m_1 + m_2} \quad I = Mr^2 \quad B = \frac{\hbar}{8\pi^2 I} \quad \tilde{B} = \frac{\hbar}{8\pi^2 c I}$$

$$(kg) \quad (kg \cdot m^2) \quad (Hz) \quad (cm^{-1})$$

$$g_J = 2J+1 \quad J = 0, 1, 2, \dots \quad \tilde{B} \approx 1 - 10 \text{ cm}^{-1}$$

$$\theta_{\text{rot}} = \frac{\hbar B}{k_b} = \frac{\hbar c \tilde{B}}{k_b} = \frac{\tilde{B}}{0.695 \text{ cm}^{-1} / \text{K}} \quad (\text{K})$$

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{\theta_{\text{rot}}}{T} J(J+1)}$$

$$q_{\text{rot}} \approx \int_0^{\infty} dJ (2J+1) e^{-\frac{\theta_{\text{rot}}}{T} T(J+1)}$$

if $T \gg \theta_{\text{rot}}$

$$x = J(J+1) \quad dx = \frac{dJ}{2J+1}$$

$$dx = (2J+1)dJ$$

$$q_{\text{rot}} \approx \int_0^{\infty} e^{-\theta_{\text{rot}} x / T} dx = \frac{T}{\theta_{\text{rot}}}$$

$$q_{\text{rot}} = \frac{T}{\sigma \theta_{\text{rot}}} = \frac{k_b T}{\sigma \hbar c \tilde{B}} = \frac{8\pi^2 \mu r^2 k_b T}{\sigma \hbar^2}$$

Diatomlic / Linear

$$\sigma_{A_2} = 2$$

$$\sigma \rightarrow \text{"symmetry number"} \quad \sigma_{AB} = 1$$

Polyatomic: $I \rightarrow I_A, I_B, I_C$

$$\theta_R \rightarrow \theta_A, \theta_B, \theta_C$$

$$q_{\text{rot}} = \frac{1}{\sigma} \sqrt{\frac{\pi T^3}{\theta_A \theta_B \theta_C}} \quad \{\theta_A, \theta_B, \theta_C\} \rightarrow \text{tables}$$

Non-linear Polyatomic

3.17 Vibrational Partition Function

Vibrational Partition Function

$$q_v = \sum_{i=1}^n g_i e^{-\beta E_i} \quad \beta = \frac{1}{k_b T}$$

$$E_n = h\nu (n + \frac{1}{2}) \quad g_n = 1$$

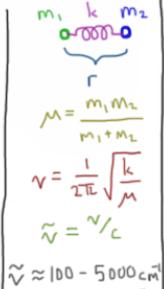
$$q_{vib} = \sum_{n=0}^{\infty} e^{-\frac{h\nu}{k_b T} (n + \frac{1}{2})}$$

$$\theta_{vib} = \frac{h\nu}{k_b} = \frac{h c \tilde{\nu}}{k_b} = \frac{\tilde{\nu}}{0.695 \text{ cm}^3 / \text{K}} \quad (\text{K})$$

$$q_{vib} = \sum_{n=0}^{\infty} e^{-\frac{\theta_{vib}}{T} (n + \frac{1}{2})} = e^{-\theta_{vib}/2T} \sum_{n=0}^{\infty} (e^{-\theta_{vib}/T})^n$$

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \quad \text{if } x < 1 \quad e^{-\theta_{vib}/T} < 1$$

$$\sum_{n=0}^{\infty} (e^{-\theta_{vib}/T})^n = \frac{1}{1 - e^{-\theta_{vib}/T}}$$



$$q_{vib} = \frac{e^{-\theta_{vib}/2T}}{1 - e^{-\theta_{vib}/T}}$$

(exact)

Diatom

Non-Linear Polyatomic $N_{vib} = 3N - 6$

Linear Polyatomic $N_{vib} = 3N - 5 \quad \{N_i\}$

$$q_{vib} = q_{vib}^{(1)} q_{vib}^{(2)} \cdots q_{vib}^{(N_{vib})} = \prod_{i=1}^{N_{vib}} q_{vib}^{(i)}$$

$$q_{vib} = \prod_{i=1}^{N_{vib}} \frac{e^{-\theta_{vib}^{(i)}/2T}}{1 - e^{-\theta_{vib}^{(i)}/T}}$$

Polyat

3.18 Electronic Partition Function

Electronic Partition Function

$$\hat{H}_{\text{elec}} \Psi_{\text{elec}} = E_{\text{elec}} \Psi_{\text{elec}}$$

$$\text{H-atom} \rightarrow E_n = -\frac{\hbar c R_H}{n^2} \quad n=1, 2, 3, \dots$$

$$g_n = n^2 \quad R_H = 109,737 \text{ cm}^{-1}$$

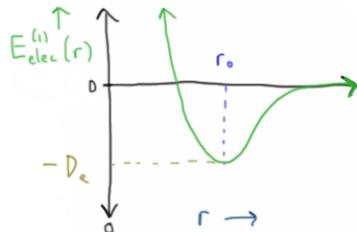
$$q_{\text{elec}}^H = \sum_{n=1}^{\infty} n^2 \exp\left(\frac{+\hbar c R_H}{k_B T n^2}\right)$$

$$\frac{P_2}{P_1} = \frac{2 \exp(h c R_H / 4 k_B T)}{1 \exp(h c R_H / k_B T)} = 4 \exp\left(-\frac{3 h c R_H}{4 k_B T}\right)$$

$$P_2/P_1 (300 \text{ K}) \approx 10^{-134}$$

$$\therefore q_{\text{elec}}^H = g_1 e^{-E_1/k_B T} = e^{h c R_H / k_B T}$$

for most atoms/molecules, $E_n - E_1 \gg k_B T$



$$E_1 = -D_e$$

$$q_{\text{elec}} = g_1 e^{-D_e/k_B T}$$

most molecules $g_1 = 1$

$$\hbar c D_e \approx 10,000 - 100,000 \text{ cm}^{-1}$$

$$\text{O}_2 \rightarrow g_1 = 3$$

g_1	name
1	singlet
2	doublet
3	triplet
4	quartet
...	...

3.19 Molecular Partition Function

Molecular Partition Function

$$E_{\text{mol}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

$$q_{\text{mol}} = \sum_{i=1}^{\text{states}} e^{-E_i / k_b T} = \sum_{i=1}^{\text{states}} e^{-(E_t^i + E_r^i + E_v^i + E_e^i) / k_b T}$$

$$q_{\text{mol}} = \sum_{i=1}^{\text{states}} (e^{-E_t^i / k_b T})(e^{-E_r^i / k_b T})(e^{-E_v^i / k_b T})(e^{-E_e^i / k_b T})$$

$$q_{\text{mol}} = \left(\sum_{i=1}^{\text{states}} e^{-E_t^i / k_b T} \right) \left(\sum_{j=1}^{\text{states}} e^{-E_r^j / k_b T} \right) \left(\sum_{k=1}^{\text{states}} e^{-E_v^k / k_b T} \right) \cdot \left(\sum_{l=1}^{\text{states}} e^{-E_e^l / k_b T} \right)$$

$$q_{\text{mol}} = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

$$q = \left(\frac{2\pi m k_b T}{h^2} \right)^{3/2} \cdot V \cdot g_i e^{\frac{D_e}{k_b T}}$$

Atomic

$$q = \left(\frac{2\pi m k_b T}{h^2} \right)^{3/2} \cdot V \cdot \frac{T}{\sigma \theta_{\text{rot}}} \left(\prod_{i=1}^{3N-5} \frac{e^{-\theta_{\text{vib}}^{(i)} / 2T}}{1 - e^{-\theta_{\text{vib}}^{(i)} / T}} \right) \cdot g_i e^{\frac{D_e}{k_b T}}$$

Diatomic / Linear

$$q = \left(\frac{2\pi m k_b T}{h^2} \right)^{3/2} \cdot V \cdot \frac{1}{\sigma \sqrt{\theta_A \theta_B \theta_C}} \prod_{i=1}^{3N-b} \frac{e^{-\theta_i^{(i)} / 2T}}{1 - e^{-\theta_i^{(i)} / T}} \cdot g_i e^{\frac{D_e}{k_b T}}$$

Non-Linear Polyatomic

3.20 System Partition Function

System Partition Function

$$q = \sum_{i=1}^n g_i e^{-\beta E_i} \quad \beta = \frac{1}{k_b T}$$

$$q_{\text{mol}} = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

$$Q_{\text{sys}} = q_{\text{mol}}^{(1)} q_{\text{mol}}^{(2)} \dots q_{\text{mol}}^{(N)} = \prod_{i=1}^N q_{\text{mol}}^{(i)} = (q_{\text{mol}})^N$$

N - distinguishable particles $Q = q^N$

N -indistinguishable particles $Q = \frac{1}{N!} q^N$

$N!$ permutations

$$\begin{array}{ll} 12 & 123 \\ 21 & 132 \\ \underbrace{\hspace{1cm}} & 213 \\ 2! \text{ ways} & 231 \\ & 312 \\ & 321 \\ \underbrace{\hspace{1cm}} & 3! \text{ ways} \end{array}$$

$$Q_{\text{trans}} = \frac{V^N}{N!} \left(\frac{2\pi m k_b T}{h^2} \right)^{3N/2}$$

$$Q_{\text{rot}} = \left(\frac{T}{\sigma \theta_{\text{rot}}} \right)^N \quad Q_{\text{rot}} = \frac{1}{\sigma^N} \left(\frac{\pi T^3}{\theta_A \theta_B \theta_c} \right)^{N/2}$$

$$Q_{\text{vib}} = \left(\prod_{i=1}^{n_{\text{vib}}} \frac{e^{-\theta_v^{(i)}/2T}}{1 - e^{-\theta_v^{(i)}/T}} \right)^N$$

$$Q_{\text{elec}} = g_i^N e^{ND_e/k_b T}$$

3.21 Statistical Molecular Energy

Molecular Energy

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} \quad \beta = \frac{1}{k_b T}$$

$$Q_{trans} = \frac{V^N}{N!} \left(\frac{2\pi m k_b T}{h^2} \right)^{3N/2}$$

$$\ln Q_{trans} = \frac{3N}{2} \left[\ln(T) + \ln \left(\frac{2\pi m k_b}{h^2} \right) \right] + N \ln V - \ln N!$$

$$\ln Q_{trans} = +\frac{3N}{2} \ln(k_b T) + \dots = -\frac{3N}{2} \ln(\beta) + \dots$$

$$-\frac{\partial \ln Q_{trans}}{\partial \beta} = -\left(-\frac{3N}{2}\right)\left(\frac{1}{\beta}\right)$$

$$\langle E_{trans} \rangle = \frac{3}{2} N k_b T = \frac{3}{2} n R T$$

$$Q_{rot} = \left(\frac{\pi T^3}{\theta_A \theta_B \theta_C} \right)^{N/2} \quad \ln Q_{rot} = \frac{3N}{2} \ln(T) + \dots$$

$$\langle E_{rot} \rangle = \frac{3}{2} N k_b T \quad (\text{Nk}_b T \text{ if linear})$$

$$Q_{elec} = g_i^N e^{ND_e/k_b T} \quad \ln Q_{elec} = \frac{ND_e}{k_b T} + N \ln g_i$$

$$\langle E_{elec} \rangle = -ND_e$$

$$Q_{vib} = \left(\prod_{i=1}^{3n-6} \frac{e^{-\theta_{vib}^{(i)} / 2T}}{1 - e^{-\theta_{vib}^{(i)} / T}} \right)^N$$

$$\ln Q_{vib} = N \sum_{i=1}^{3n-6} \left(-\frac{\theta_{vib}^{(i)}}{2T} + \ln(1 - e^{-\theta_{vib}^{(i)} / T}) \right)$$

$$\langle E_{vib} \rangle = N k_b \sum_{i=1}^{3n-6} \theta_{vib}^{(i)} \left(\frac{1}{2} + \frac{1}{\exp(\theta_{vib}^{(i)} / T) - 1} \right)$$

(3n-5 if linear)

$$\langle E \rangle = -ND_e + 3Nk_b T + Nk_b \sum_{i=1}^{3n-6} \theta_{vib}^{(i)} \left[\frac{1}{2} + \left(e^{\theta_{vib}^{(i)} / T} - 1 \right)^{-1} \right]$$

Non-Linear Polyatomic

3.22 Molecular Energy Example

Molecular Energy Example

$$^{12}\text{C}^{16}\text{O}: \quad \tilde{B} = 1.9225 \text{ cm}^{-1} \quad \tilde{\nu} = 2169.8 \text{ cm}^{-1}$$

$$D_e = 1084.92 \text{ kJ/mol} \quad 1.0000 \text{ mol}$$

$$\langle E_{\text{trans}} \rangle = \frac{3}{2} N k_b T = \frac{3}{2} n R T \quad R = N_A k_b = 8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$@ 20^\circ\text{C} \rightarrow \langle E_{\text{trans}} \rangle = \frac{3}{2} (1.0000 \text{ mol}) (8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}}) (293.15)$$

$$\boxed{\langle E_{\text{trans}} \rangle = 3.6561 \text{ kJ}} \quad E_{\text{trans}} \propto T$$

$$\Theta_{\text{rot}} = \frac{\hbar c \tilde{B}}{k_b} = \frac{\tilde{B}}{0.69503 \text{ cm}^2/\text{K}} = \frac{1.9225 \text{ cm}^2}{0.69503 \text{ cm}^2/\text{K}} = 2.7661 \text{ K}$$

$$\text{if } T \gg \Theta_{\text{rot}}, \quad \langle E_{\text{rot}} \rangle = N k_b T = n R T$$

$$293 \text{ K} \gg 2.8 \text{ K} \quad \checkmark \quad \boxed{\langle E_{\text{rot}} \rangle = 2.4374 \text{ kJ}}$$

$$\Theta_{\text{vib}} = \frac{\hbar c \tilde{\nu}}{k_b} = \frac{2169.8 \text{ cm}^{-1}}{0.69503 \text{ cm}^2/\text{K}} = 3122.0 \text{ K}$$

$$\langle E_{\text{vib}} \rangle = N k_b \Theta_{\text{vib}} \left(\frac{1}{2} + \frac{1}{e^{\Theta_{\text{vib}}/T} - 1} \right)$$

T / Θ _{vib}	$\langle E_{\text{vib}} \rangle / N k_b \Theta_{\text{vib}}$	$(\partial \langle E_{\text{vib}} \rangle / \partial T) / N k_b \Theta_{\text{vib}}$
0	1/2	0
0.1	0.50004	0.0045
0.2	0.5068	0.1707
0.5	0.6565	0.7241
1.0	1.0820	0.9207
2.0	2.0415	0.9794
5.0	5.0167	0.9967
T > Θ _{vib}	T	1

$$[\exp(3122.0 \text{ K} / 293.15 \text{ K}) - 1]^{-1} = 2.371 \cdot 10^{-5}$$

$$\boxed{\langle E_{\text{vib}} \rangle = 12.979 \text{ kJ}}$$

$$\langle E_{\text{elec}} \rangle = -N D_e \quad \boxed{\langle E_{\text{elec}} \rangle = -1084.92 \text{ kJ}}$$

$$\langle E \rangle = \langle E_{\text{trans}} \rangle + \langle E_{\text{rot}} \rangle + \langle E_{\text{vib}} \rangle + \langle E_{\text{elec}} \rangle$$

$$\boxed{\langle E \rangle = -1065.85 \text{ kJ/mol} \quad @ 293.15 \text{ K}}$$

3.23 First Law

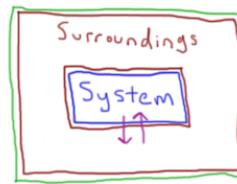
1st Law of Thermodynamics

The energy of an isolated system is constant

Conservation of Energy

$$\Delta E_{\text{universe}} = \Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0$$

System Type	Exchanges Energy	Exchanges Matter
Isolated	No	No
Closed	Yes	No
Open	Yes	Yes



Universe

Exchange matter and/or energy

Work: energy input from the surroundings to the system from imbalanced forces

Heat: energy input from the surroundings to the system from imbalanced temperature

ΔE_{sys}	work	heat
>0	done on system	input into system
<0	done on surroundings	released from system

3.24 Pressure-Volume Work

Pressure-Volume Work

Closed System \rightarrow Gas Cylinder

Surroundings \rightarrow External Environment

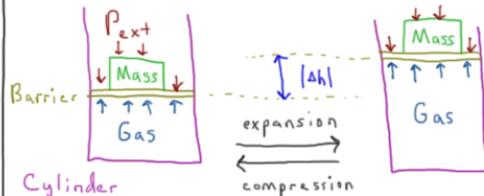
$$w = F \cdot d = (-mg)(h_f - h_i) = \left(-\frac{mg}{A}\right)(A \Delta h) = -P_{ext} \Delta V$$

if P_{ext} is constant,

$$\text{then } w = -P_{ext} \Delta V$$

if P_{ext} varies,

$$\text{then } w = - \int_{V_i}^{V_f} P_{ext}(V) dV$$



A = cross-sectional area of barrier

$\Delta V > 0 \rightarrow$ expansion: $w \leq 0$

$\Delta V < 0 \rightarrow$ compression: $w \geq 0$

3.25 State and Path Functions

State and Path Functions

State: The set of all variables needed to completely specify the conditions of a system

Path: The set of states connecting an initial state and a final state

State Function: A variable whose value depends only on the state

Path Function: A variable whose value depends on a path

ideal gas: $P\bar{V} = RT \rightarrow$ "equation of state"

state: P, \bar{V}, T

$U \rightarrow$ internal energy \rightarrow state function

$w, q \rightarrow$ work, heat \rightarrow path functions

$dx \rightarrow$ exact differential (state)

$\delta x \rightarrow$ inexact differential (path)

$$\int_i^f dU = U_f - U_i = \Delta U$$

$$\int_i^f \delta w = w \quad \int_i^f \delta q = q$$

$$dU = \delta w + \delta q \quad \text{differential form}$$

$$\Delta U = w + q \quad \text{integrated form}$$

3.26 Reversible Processes

Reversible Expansion / Compression

$$w = - \int_{V_i}^{V_f} P_{\text{ext}}(V) dV$$

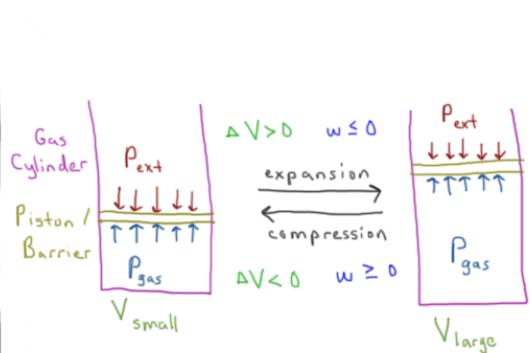
to expand: $P_{\text{ext}} \leq P_{\text{gas}}$

to compress: $P_{\text{ext}} \geq P_{\text{gas}}$

$$\underbrace{|w(V_i \rightarrow V_s)|}_{\text{compression work}} \geq \underbrace{\left| \int_{V_s}^{V_e} P_{\text{gas}}(V) dV \right|}_{\text{reversible work}} \geq \underbrace{|w(V_s \rightarrow V_e)|}_{\text{expansion work}}$$

when $P_{\text{ext}} = P_{\text{gas}}$ $\begin{cases} \text{minimum compression work} \\ \text{maximum expansion work} \end{cases}$ for all V

"reversible" if $|w_{\text{exp}}| = |w_{\text{comp}}|$



Reversible Process: a process whose direction can be reversed via infinitesimal changes

$$P_{\text{ext}} = P_{\text{gas}} = \frac{nRT}{V} \quad \text{if ideal}$$

$$w_{\text{rev}} = - \int_{V_i}^{V_f} \frac{nRT}{V} dV \quad \boxed{w_{\text{rev}} = -nRT \ln(V_f/V_i)}$$

3.27 Isothermal Processes

Isothermal Processes

for a monatomic ideal gas:

$$U = \frac{3}{2} nRT = \frac{3}{2} Nk_b T$$

$$U \propto T \rightarrow \Delta U \propto \Delta T$$

if $\Delta T = 0$, then $\Delta U = 0$

$\Delta T = 0 \rightarrow$ isothermal process

$$\Delta U = q + w = 0$$

$$q = -w$$

reversible, isothermal expansion / compression

$$w_{rev} = -nRT \ln(V_f/V_i)$$

$$q_{rev} = +nRT \ln(V_f/V_i)$$

3.28 Adiabatic Processes

Adiabatic Processes

adiabatic \rightarrow no heat $\rightarrow q = 0$

$$dU = \cancel{\delta q} + \delta w = \delta w$$

monatomic ideal gas $\rightarrow U = \frac{3}{2} nRT$

$$C_v(T) = \left(\frac{\partial U}{\partial T} \right)_V = \frac{d}{dT} \left(\frac{3}{2} nRT \right) = \frac{3}{2} nR$$

$$dU = C_v(T) dT = \delta w$$

$$w_{rev} = -nRT \ln(V_f/V_i)$$

$$\delta w_{rev} = -\frac{nRT}{V} dV$$

$$C_v(T) dT = -\frac{nRT}{V} dV$$

$$\int_{T_i}^{T_f} \frac{C_v(T)}{T} dT = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

Assume $C_v(T) = C_v$, constant

$$C_v \ln(T_f/V_i) = -nR \ln(V_f/V_i)$$

$\bar{C}_v = C_v/n$ \rightarrow molar heat capacity

$$-\frac{\bar{C}_v}{R} \ln(T_f/T_i) = \ln(V_f/V_i)$$

$$\boxed{\left(\frac{T_f}{T_i} \right)^{-\frac{\bar{C}_v}{R}} = \frac{V_f}{V_i}} \text{ Reversible, Adiabatic Expansion/Compression of an Ideal Gas}$$

$$\frac{\bar{C}_v}{R} = \begin{cases} 3/2 & \text{monatomic} \\ 5/2 & \text{diatomic/linear} \\ 6/2 & \text{non-linear polyatomic} \end{cases}$$

3.29 Adiabatic / Isothermal Comparison

Adiabatic vs. Isothermal Processes

$$PV = nRT \quad T = \frac{PV}{nR} \quad n, R \rightarrow \text{constant}$$

$$\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i}$$

$$\text{isothermal} \rightarrow \frac{T_f}{T_i} = 1 = \frac{P_f V_f}{P_i V_i}$$

$P_i V_i = P_f V_f$ Reversible, Isothermal Expansion/Compression of an Ideal Gas

$$\text{adiabatic} \rightarrow \left(\frac{T_f}{T_i}\right)^{\frac{R}{C_v}} = \frac{V_f}{V_i}$$

$$\left(\frac{V_f}{V_i}\right)^{\frac{R}{C_v}} = \frac{P_f V_f}{P_i V_i}$$

$P_i V_i^{1+\frac{R}{C_v}} = P_f V_f^{1+\frac{R}{C_v}}$ Reversible, Adiabatic Expansion/Compression of an Ideal Gas

quantity	isothermal	adiabatic
ΔU	0	$C_v(T_f - T_i)$
w	$-nRT \ln(V_f/V_i)$	$C_v(T_f - T_i)$
q	$+nRT \ln(V_f/V_i)$	0
T_f	T_i	$T_i(V_f/V_i)^{-\frac{R}{C_v}}$

$$\frac{C_v}{R} = \begin{cases} 3/2 & \text{monatomic} \\ 5/2 & \text{diatomic/ linear} \\ 6/2 & \text{non-linear polyatomic} \end{cases}$$

3.30 Statistical Heat and Work

Microscopic Heat and Work

$$U = \langle E \rangle = \sum_i^{\text{states}} p_i E_i$$

$$p_i = \frac{1}{Q} e^{-E_i/k_b T} = \frac{1}{Q} e^{-\beta E_i} \quad \beta = \frac{1}{k_b T}$$

$$Q = \sum_i^{\text{states}} e^{-E_i/k_b T} = \sum_i^{\text{states}} e^{-\beta E_i}$$

$$E_i = E_i(N, V) \quad p_i = p_i(N, V, T)$$

$$dE_i = \left(\frac{\partial E_i}{\partial V}\right)_N dV + \left(\frac{\partial E_i}{\partial N}\right)_V dN$$

$$\text{if } dN=0, \quad dE_i = \left(\frac{\partial E_i}{\partial V}\right) dV$$

(closed system)

$$dU = \sum_i^{\text{states}} [p_i dE_i + E_i dp_i]$$

$$dU = \sum_i^{\text{states}} p_i \left(\frac{\partial E_i}{\partial V}\right)_N dV + \sum_i^{\text{states}} E_i dp_i$$

$$dU = \delta w_{\text{rev}} + \delta q_{\text{rev}}$$

$$dU = -P dV + \delta q_{\text{rev}}$$

$$P = - \sum_i^{\text{states}} p_i \left(\frac{\partial E_i}{\partial V}\right)_N = - \left\langle \left(\frac{\partial E}{\partial V}\right)_N \right\rangle$$

$$\delta w_{\text{rev}} = \sum_i^{\text{states}} p_i \left(\frac{\partial E_i}{\partial V}\right)_N dV$$

$$\delta q_{\text{rev}} = \sum_i^{\text{states}} E_i dp_i$$

$$\delta q_{\text{rev}} = dU - \delta w_{\text{rev}}$$

3.31 Statistical Pressure

Statistical Pressure

$$P = -\left\langle \left(\frac{\partial E}{\partial V} \right)_N \right\rangle = - \sum_{i=1}^N P_i \left(\frac{\partial E_i}{\partial V} \right)_N$$

$$P = \frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} \quad \beta = \frac{1}{k_b T}$$

$$Q_{trans} = \frac{V^N}{N!} \left(\frac{2\pi m k_b T}{h^2} \right)^{N/2}$$

$$\ln Q_{trans} = N \ln V - N \ln N + N + \frac{N}{2} \ln \left(\frac{2\pi m k_b T}{h^2} \right)$$

$$\frac{\partial \ln Q_{trans}}{\partial V} = \frac{N}{V}$$

$$\frac{1}{\beta} \frac{\partial \ln Q_{trans}}{\partial V} = \frac{1}{\beta} \left(\frac{N}{V} \right) = \left(k_b T \right) \frac{N}{V}$$

$$P = \frac{N k_b T}{V} = \frac{n R T}{V} \quad N k_b = n R$$

$$P = \frac{n R T}{V}$$

Ideal Gas Law

3.32 Enthalpy

Enthalpy

consider a reversible process with only PV work

$$\Delta U = q_{rev} + w_{rev} = q_{rev} - \int_{V_i}^{V_f} P(V) dV$$

$$\text{if } \Delta V = 0 \rightarrow V_f = V_i \rightarrow w_{rev} = 0$$

$$\text{then } \Delta U = q_{rev} = q_v$$

$$\Delta U = q_v \text{ at constant volume}$$

$$? = q_p \text{ at constant pressure}$$

most chemical processes occur at constant pressure

$$q_p = \Delta U - w_p = \Delta U + P \int_{V_i}^{V_f} dV =$$

$$= \Delta U + P(V_f - V_i) = \Delta U + P\Delta V$$

$$H = U + PV \quad \text{"enthalpy"}$$

$$dH = dU + PdV + VdP \quad \text{at constant } P$$

$$\Delta H = \int (dU + PdV) = \Delta U + P\Delta V = q_p$$

✓ $\Delta H = q_p$ for reversible processes at constant pressure

3.33 Enthalpy Example

Enthalpy Example

at 1 atm, $(T_{\text{vap}})_{\text{N}_2(\text{L})} = -195.8^\circ\text{C}$,
 $\rho_{\text{N}_2(\text{L})} = 0.808 \text{ g/mL}$, $q_{\text{vap}} = +5.56 \text{ kJ/mol}$
 $\Delta_{\text{vap}} \bar{U} = ?$

$$\bar{H} = \bar{U} + P\bar{V} \quad \bar{H} = H/n \quad \bar{U} = U/n \quad \bar{V} = V/n$$

$$\Delta_{\text{vap}} \bar{H} = \underbrace{\Delta_{\text{vap}} \bar{U} + P \Delta_{\text{vap}} \bar{V}}_{{\text{at constant pressure}}} = q_p = 5.56 \text{ kJ/mol}$$

at constant pressure

$$\Delta_{\text{vap}} \bar{V} = \bar{V}_g - \bar{V}_l$$

$$\bar{V}_l = \frac{1}{P} = \left| \begin{array}{c|c|c|c} 1 \text{ mL} & 14.02 \text{ g N}_2 & 1 \text{ cm}^3 & (1 \text{ m})^3 \\ \hline 0.808 \text{ g N}_2 & 1 \text{ mol N}_2 & 1 \text{ mL} & (100 \text{ cm})^3 \end{array} \right| = 1.24 \cdot 10^{-6} \text{ m}^3/\text{mol}$$

$$\bar{V}_g = \frac{RT}{P} = \frac{(8.314 \text{ J/mol} \cdot \text{K})(-195.8 + 273.15 \text{ K})}{(1 \text{ atm})(101,325 \text{ Pa/atm})} = 6.35 \cdot 10^{-3} \text{ m}^3/\text{mol}$$

$$\Delta_{\text{vap}} \bar{V} = (6.35 \cdot 10^{-3} - 1.24 \cdot 10^{-6}) \frac{\text{m}^3}{\text{mol}} = 6.35 \cdot 10^{-3} \frac{\text{m}^3}{\text{mol}}$$

$$P \Delta_{\text{vap}} \bar{V} = (101,325 \text{ Pa})(6.35 \cdot 10^{-3} \frac{\text{m}^3}{\text{mol}}) \frac{1 \text{ kT}}{1000 \text{ K}} = 0.643 \text{ kJ/mol}$$

$$\Delta_{\text{vap}} \bar{U} = \Delta_{\text{vap}} \bar{H} - P \Delta_{\text{vap}} \bar{V} = (5.56 \text{ kJ/mol}) - (0.643 \text{ kJ/mol}) = 4.92 \text{ kJ/mol}$$

$$\boxed{\Delta_{\text{vap}} \bar{U} = +4.92 \text{ kJ/mol}}$$

$$q_{\text{vap}} = +5.56 \text{ kJ/mol}$$

$$w_{\text{vap}} = -0.643 \text{ kJ/mol}$$

3.34 Heat Capacity

Heat Capacity

Energy required to raise temperature of a substance by 1 K

C_v → extensive path function

$\bar{C}_v = \frac{C_v}{n}$ → intensive path function

$$\text{if } \Delta V = (V_f - V_i) = 0 \rightarrow w_v = - \int_{V_i}^{V_f} P_{\text{ext}} dV = 0$$

$$\text{then } \Delta U = \cancel{w_v} + q_v = q_v$$

$$C_v(T) = \left(\frac{\partial U}{\partial T} \right)_V \approx \frac{\Delta U}{\Delta T} = \frac{q_v}{\Delta T}$$

$$\text{if } \Delta P = (P_f - P_i) = 0 \rightarrow w_p = - \int_{V_i}^{V_f} P_{\text{ext}} dV = - P \Delta V$$

$$\text{then } \Delta U = w_p + q_p \rightarrow q_p = \Delta U + P \Delta V = \Delta H$$

$$C_p(T) = \left(\frac{\partial H}{\partial T} \right)_p \approx \frac{\Delta H}{\Delta T} = \frac{q_p}{\Delta T}$$

for an ideal gas $H = U + PV = U + nRT$

$$U = U(T, N) \propto T$$

$$\text{if } dN=0, \quad dU = \left(\frac{\partial U}{\partial T} \right)_N dT = C_v(T) dT$$

$$C_p(T) = \frac{\partial H}{\partial T} = \frac{\partial}{\partial T}(U + nRT) = \frac{\partial U}{\partial T} + nR$$

$$C_p(T) = C_v(T) + nR \quad \bar{C}_p = \frac{C_p}{n} \quad \bar{C}_v = \frac{C_v}{n}$$

$$\bar{C}_p(T) = \bar{C}_v(T) + R$$

$$\boxed{\bar{C}_p - \bar{C}_v = R} \quad \text{for ideal gas} \quad \bar{C}_v(T) = \bar{C}_v \quad \bar{C}_p(T) = \bar{C}_p$$

$$\frac{\bar{C}_v}{R} = \begin{cases} 3/2 & \text{monatomic} \\ 5/2 & \text{diatomic / linear} \\ 6/2 & \text{non-linear polyatomic} \end{cases}$$

3.35 Transition Enthalpy

Enthalpy of Transition

$$\bar{H}(T_2) - \bar{H}(T_1) = \int_{T_1}^{T_2} \left(\frac{\partial \bar{H}}{\partial T} \right)_P dT = \int_{T_1}^{T_2} \bar{C}_P(T) dT$$

if no phase change between T_1 and T_2

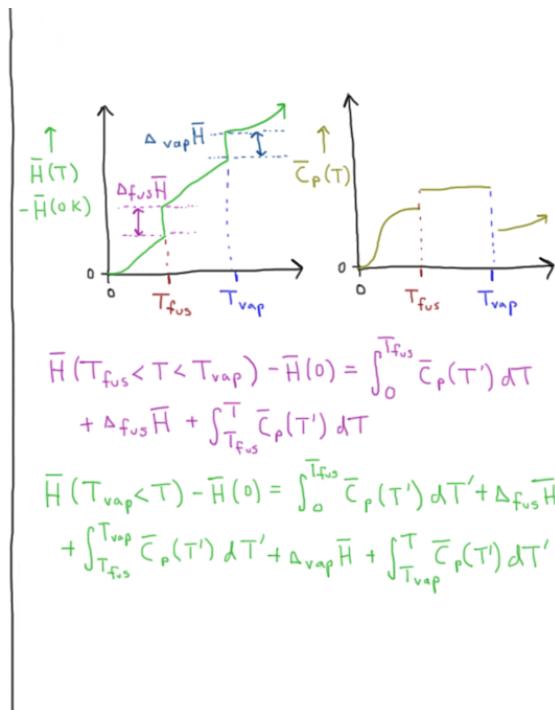
$$\Delta_{\text{trs}} \bar{H} = \begin{pmatrix} \text{heat input during constant} \\ \text{pressure phase transitions} \end{pmatrix}$$

$\Delta_{\text{fus}} \bar{H}$ = heat of fusion (melting)

$\Delta_{\text{vap}} \bar{H}$ = heat of vaporization (boiling)

$\Delta_{\text{fus}} \bar{H} > 0$, $\Delta_{\text{vap}} \bar{H} > 0 \rightarrow$ endothermic

$$\bar{H}(T < T_{\text{fus}}) - \bar{H}(0) = \int_0^T \bar{C}_P(T') dT'$$



$$\bar{H}(T_{\text{fus}} < T < T_{\text{vap}}) - \bar{H}(0) = \int_0^{T_{\text{fus}}} \bar{C}_P(T') dT' + \Delta_{\text{fus}} \bar{H} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \bar{C}_P(T') dT'$$

$$\bar{H}(T_{\text{vap}} < T) - \bar{H}(0) = \int_0^{T_{\text{vap}}} \bar{C}_P(T') dT' + \Delta_{\text{fus}} \bar{H} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \bar{C}_P(T') dT' + \Delta_{\text{vap}} \bar{H}$$

3.36 Reaction Enthalpy

Enthalpy of Reaction

for most chemical reactions, $\Delta F = P_f - P_i = 0$

$H \rightarrow$ extensive state function

$\Delta_r H \rightarrow$ "enthalpy of reaction"

$$\Delta_r H = H_{\text{products}} - H_{\text{reactants}}$$

if $H_{\text{prod}} > H_{\text{react}}$ then $\Delta_r H > 0$

if $H_{\text{prod}} < H_{\text{react}}$ then $\Delta_r H < 0$

$\Delta_r H > 0 \rightarrow$ heat absorbed \rightarrow endothermic

$\Delta_r H < 0 \rightarrow$ heat released \rightarrow exothermic

$$\Delta_r H = q_r \text{ at constant pressure}$$

$\Delta_r H^\circ \rightarrow$ "standard (molar) enthalpy of reaction"

$\Delta_r H^\circ \rightarrow$ intensive state function

$$\Delta_r H^\circ = (\Delta_r H \text{ per mole of reagent at standard conditions})$$

Standard State	Pressure	Temperature
STP	1 bar	273.15 K
SATP	1 bar	298.15 K
NTP	1 atm	293.15 K

3.37 Hess's Law

Hess's Law

$H \rightarrow$ state function

$$\Delta H(1 \rightarrow 2) = H(2) - H(1)$$

$$\Delta H(2 \rightarrow 3) = H(3) - H(2)$$

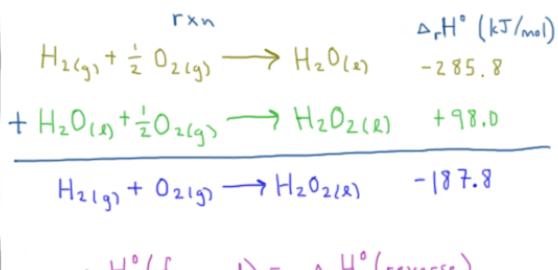
$$\Delta H(1 \rightarrow 3) = H(3) - H(1)$$

$$\Delta H(1 \rightarrow 2) + \Delta H(2 \rightarrow 3) = H(2) - H(1) + H(3) - H(1)$$

$$\Delta H(1 \rightarrow 3) = \Delta H(1 \rightarrow 2) + \Delta H(2 \rightarrow 3)$$

$$\Delta H(1 \rightarrow n) = \sum_{i=1}^{n-1} \Delta H(i \rightarrow i+1)$$

$$\Delta_{rxn}H(\text{total rxn}) = \sum_i^{\text{rxns}} \Delta_{rxn}H(\text{rxn } i)$$



$$\Delta_r H^\circ (\text{forward}) = -\Delta_r H^\circ (\text{reverse})$$

3.38 Formation Enthalpy

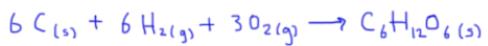
Enthalpy of Formation

$\Delta_f H^\circ = \Delta_{rxn} \bar{H}(1\text{ bar}, 273.15\text{ K})$ for
forming species from elements in
standard states

Standard states:

$H_{(g)}$ $He_{(g)}$ $Li_{(s)}$ $Be_{(s)}$ $B_{(s)}$
 $C_{(s)}$ $N_{2(g)}$ $O_{2(g)}$ $F_{2(g)}$ $Ne_{(g)}$
 $Cl_{2(g)}$ $Br_{2(g)}$ $I_{2(g)}$ $Ar_{(g)}$ $Hg_{(l)}$

$\Delta_f H^\circ = 0$ for elements



$$\Delta_f H^\circ(C_6H_{12}O_6(s)) = -1271 \text{ kJ/mol}$$

3.39 Standard Reaction Enthalpy

Reaction Enthalpy from Formation Enthalpy

elements \longrightarrow A	$\Delta_f H^\circ(A)$
elements \longrightarrow aA	$a \Delta_f H^\circ(A)$
elements \longrightarrow aA + bB	$a \Delta_f H^\circ(A) + b \Delta_f H^\circ(B)$
aA + bB \longrightarrow elements	$-a \Delta_f H^\circ(A) - b \Delta_f H^\circ(B)$
elements \longrightarrow cC + dD	$c \Delta_f H^\circ(C) + d \Delta_f H^\circ(D)$
aA + bB \longrightarrow cC + dD	$[c \Delta_f H^\circ(C) + d \Delta_f H^\circ(D)]$ $- [a \Delta_f H^\circ(A) + b \Delta_f H^\circ(B)]$

$$\Delta_r H^\circ = \sum_j^{products} n_j \Delta_f H^\circ(J) - \sum_i^{reactants} n_i \Delta_f H^\circ(I)$$



compound	$\Delta_f H^\circ (kJ/mol)$
C ₆ H ₁₂ O ₆ (s)	-1271
O ₂ (g)	0
H ₂ O(l)	-285.8
CO ₂ (g)	-393.5

$$\Delta_r H^\circ = 6(-285.8 \text{ kJ/mol}) + 6(-393.5 \text{ kJ/mol}) \\ - 1(-1271 \text{ kJ/mol}) - 6(0 \text{ kJ/mol})$$

$$\Delta_r H^\circ = -2805 \text{ kJ/mol}$$

3.40 Enthalpy Temperature Dependence

Reaction Enthalpy Temperature Dependence

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p(T) dT$$

$$\Delta_r H(T_2) - \Delta_r H(T_1) = \int_{T_1}^{T_2} \Delta_r C_p(T) dT$$

$$C_p(T) = \left(\frac{\partial H}{\partial T} \right)_P \quad \Delta_r C_p(T) = \left(\frac{\partial \Delta_r H}{\partial T} \right)_P$$



$$\Delta_r H = a \Delta_f H(A) + c \Delta_r H(C) - b \Delta_r H(B) - a \Delta_r H(A)$$

$$\Delta_r C_p(T) = a C_{p,A}(T) + c C_{p,C}(T) - b C_{p,B}(T) - a C_{p,A}(T)$$

$$\boxed{\Delta_r C_p(T) = \sum_j^{products} n_j C_{p,j}(T) - \sum_i^{reactants} n_i C_{p,i}(T)}$$

3.41 Spontaneous Processes

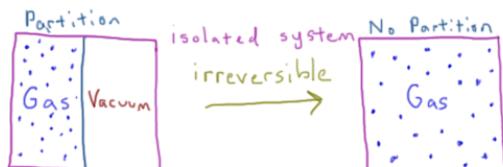
Spontaneous Processes

An irreversible process which occurs without energy input to the system

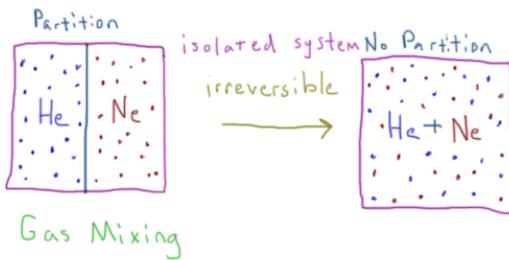
isolated system $\rightarrow \Delta U = q + w = 0 + 0 = 0$

if $\Delta U = 0$, why irreversible?

increasing disorder



Expansion into Vacuum



Gas Mixing

3.42 Entropy

Entropy

want:

- quantitative measure of disorder
- extensive state function

reversible processes:

$$dU = \delta q_{rev} + \delta w_{rev}$$

$$\delta q_{rev} = dU - \delta w_{rev}$$

$$\underbrace{\delta q_{rev}}_{\text{path function}} = \underbrace{C_v(T) dT}_{\substack{\text{exact} \\ \text{differential}}} + \underbrace{\frac{nRT}{V} dV}_{\substack{\text{inexact} \\ \text{differential}}}$$

$$\underbrace{\frac{\delta q_{rev}}{T}}_{\text{state function}} = \underbrace{\frac{C_v(T)}{T} dT}_{\substack{\text{exact} \\ \text{differential}}} + \underbrace{\frac{nR}{V} dV}_{\substack{\text{exact} \\ \text{differential}}}$$

$$dS = \frac{\delta q_{rev}}{T}$$

$\frac{1}{T}$ → "integrating factor" of δq_{rev}

$$\oint dS = \int_i^f dS = S_f - S_i = 0$$

3.43 Expansion Entropy

Expansion Entropy

for reversible processes:

$$dS = \frac{\delta q_{rev}}{T}$$

$$\Delta S = S_f - S_i = \int_i^f dS = \int_i^f \frac{\delta q_{rev}}{T}$$

for reversible isothermal processes:

$$dU = 0 = \delta q_{rev} + \delta w_{rev}$$

$$\delta q_{rev} = -\delta w_{rev} = \frac{nRT}{V} dV$$

$$\Delta S = \int_i^f dS = \int_i^f \frac{\delta q_{rev}}{T} = \int_i^f \frac{nR}{V} dV$$

$$\boxed{\Delta S = nR \ln(V_f/V_i)}$$

$V \uparrow \rightarrow S \uparrow$

for reversible adiabatic processes

$$\delta q_{rev} = 0$$

$$dS = \frac{\delta q_{rev}}{T} = 0$$

$$\Delta S = \int_i^f dS = \int_i^f 0 = 0$$

$$\boxed{\Delta S = 0}$$

$$\left. \begin{array}{l} V \uparrow \rightarrow S \uparrow \\ T \downarrow \rightarrow S \downarrow \end{array} \right\} \text{effects cancel}$$

3.44 Second Law

2nd Law of Thermodynamics

The entropy of an isolated system cannot decrease

$S \rightarrow$ "entropy" \rightarrow extensive state function

Clausius Inequality

$$dS \geq \frac{\delta Q}{T}$$

= when reversible

> when irreversible

$dS_{universe} \geq 0$ for any process

$S_{universe}$ can only increase over time

first two laws:

$$\textcircled{1} \quad dU_{universe} = 0$$

$$\textcircled{2} \quad dS_{universe} \geq 0$$

3.45 Heat Flow Direction

Heat Flow Direction

$$dV_L = dV_R = 0$$

$$\delta w_L = \delta w_R = 0$$

$$dU_L = \delta q_L = \delta q$$

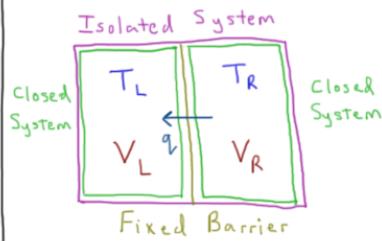
$$dU_R = \delta q_R = -\delta q$$

$$dS_L = \frac{\delta q_L}{T_L} = \frac{\delta q}{T_L}$$

$$dS_R = \frac{\delta q_R}{T_R} = -\frac{\delta q}{T_R}$$

$$dS = dS_L + dS_R = \frac{\delta q}{T_L} - \frac{\delta q}{T_R}$$

$$dS = \delta q \left(\frac{1}{T_L} - \frac{1}{T_R} \right) \geq 0$$



if $T_L > T_R$ then $\delta q < 0$, $T_L \downarrow, T_R \uparrow$

if $T_L < T_R$ then $\delta q > 0$, $T_L \uparrow, T_R \downarrow$

the 2nd law requires that heat flows from hot to cold in an **isolated** system

3.46 Degenerate Entropy

Degenerate Entropy

"Ergodic Hypothesis": all states with equal energy are equally likely

$W \rightarrow$ "degeneracy" of system

$S \rightarrow$ extensive state function

$$S = k_b \ln W$$

1 particle in g_1 degenerate states

$$W = g_1 \quad S = k_b \ln g_1$$

2 particles in g_1 degenerate states

$$W = g_1^2 \quad S = k_b \ln g_1^2 = 2k_b \ln g_1$$

$$\ln(a^n) = n \ln(a) \quad \text{extensive } \checkmark$$

$$\left(\begin{array}{cc} \bullet & - \\ - & \bullet \\ \bullet & - \\ - & \bullet \\ \end{array} \right) = \underbrace{\left(\begin{array}{cc} \bullet & - \\ - & \bullet \\ \end{array} \right)}_{\substack{1 \text{ particle} \\ \text{in 2 states}}} \cdot \underbrace{\left(\begin{array}{cc} \bullet & - \\ - & \bullet \\ \end{array} \right)}_{\substack{1 \text{ particle} \\ \text{in 2 states}}}$$

$$W_{12} = \frac{W_1}{2} \cdot \frac{W_2}{2}$$

N particles \rightarrow particle i in g_i states

$$W = \prod_{i=1}^N g_i$$

$$\begin{aligned} S &= k_b \ln W = k_b \ln \left(\prod_{i=1}^N g_i \right) = k_b \sum_{i=1}^N \ln(g_i) = \\ &= \sum_{i=1}^N k_b \ln W_i = \sum_{i=1}^N S_i \quad \checkmark \end{aligned}$$

3.47 Gibbs Entropy

Gibbs Entropy

if $E_1 = E_2$, then $p_1 = p_2$

if $E_1 \neq E_2$, then $p_i \propto e^{-E_i/k_b T}$

$$p_i = \frac{1}{Q} e^{-\beta E_i} \quad Q = \sum_{i=1}^{\text{states}} e^{-\beta E_i} = \sum_{i=1}^{\text{levels}} g_i e^{-\beta E_i}$$

$$S = -k_b \sum_{i=1}^{\text{states}} p_i \ln p_i$$

$$\beta = \frac{1}{k_b T}$$

if $T=0$, $p_i = 1$ $p_{\neq i} = 0 \rightarrow S = k_b \ln g_i$

if $T=\infty$ $p_i = p_j \rightarrow S = k_b \ln(n_{\text{states}})$

N degenerate states $\rightarrow p_i = p_j = \frac{1}{N}$

$$S = -k_b \sum_{i=1}^N \left(\frac{1}{N}\right) \ln \left(\frac{1}{N}\right) = -k_b \ln \left(\frac{1}{N}\right) = k_b \ln N$$

1 state $\rightarrow S = k_b \ln 1 = 0$

$\{p_i\}$	S/k_b
1.0	0.0
0.5 0.5	0.693
0.33 0.33 0.33	1.099
0.25 0.25 0.25 0.25	1.386
0.99 0.01	0.056
0.9 0.1	0.325
0.75 0.25	0.562
0.5 0.25 0.13 0.06 0.03 0.02 0.01	1.357
0.75 0.19 0.04 0.01 0.01	0.752
0.4 0.3 0.2 0.1	1.280

$$S(0 K) \leq S(T) \leq S(\infty)$$

$$k_b \ln g_i$$

$$k_b \ln(n_{\text{states}})$$

3.48 Statistical Entropy

Statistical Entropy		
$P_i = \frac{1}{Q} g_i e^{-\beta E_i}$	$Q = \sum_{i=1}^{\text{levels}} g_i e^{-\beta E_i}$	$\beta = \frac{1}{k_b T}$
$S = -k_b \sum_{i=1}^{\text{states}} p_i \ln p_i$	$S = k_b T \frac{\partial \ln Q}{\partial T} + k_b \ln Q$	
$Q_{\text{trans}} = \frac{V^N}{N!} \left(\frac{2\pi m k_b T}{h^2} \right)^{3N/2}$	$\ln(N!) \approx N \ln N - N$	
$\ln Q_{\text{trans}} = \frac{3N}{2} \ln \left(\frac{2\pi m k_b T}{h^2} \right) + N \ln V - N \ln N + N$		
$\frac{\partial \ln Q_{\text{trans}}}{\partial T} = \frac{3N}{2T}$		
$k_b T \frac{\partial \ln Q_{\text{trans}}}{\partial T} + k_b \ln Q = k_b T \left(\frac{3N}{2T} \right) + \frac{3Nk_b}{2} \ln \left(\frac{2\pi m k_b T}{h^2} \right)$		
$S_{\text{trans}} = Nk_b \left[\frac{5}{2} + \ln \left(\left(\frac{2\pi m k_b T}{h^2} \right)^{3/2} \frac{V}{N} \right) \right] + Nk_b \ln \left(\frac{V}{N} \right) + Nk_b$		
All Atoms and Molecules ($T > 15 \text{ K}$)		
		$Q_{\text{rot}} = \left(\frac{T}{\sigma \theta_{\text{rot}}} \right)^N \quad Q_{\text{rot}} = \left(\frac{\pi T^3}{\theta_A \theta_B \theta_C} \right)^{N/2} \cdot \frac{1}{\sigma^N}$
		$S_{\text{rot}} = Nk_b \left[1 + \ln \left(\frac{T}{\sigma \theta_{\text{rot}}} \right) \right]$ Diatomic / Linear ($T \gg \theta_{\text{rot}}$)
		$S_{\text{rot}} = Nk_b \left[\frac{3}{2} + \frac{1}{2} \ln \left(\frac{\pi T^3}{\theta_A \theta_B \theta_C} \right) \right]$ Non-Linear Polyatomic
		$Q_{\text{vib}} = \left(\frac{e^{-\theta_{\text{vib}}/2T}}{1 - e^{-\theta_{\text{vib}}/T}} \right)^N \quad (T \gg \{\theta_A, \theta_B, \theta_C\})$
		$S_{\text{vib}} = Nk_b \left[\left(\frac{\theta_{\text{vib}}}{T} \right) \frac{1}{e^{\theta_{\text{vib}}/T} - 1} - \ln \left(1 - e^{-\theta_{\text{vib}}/T} \right) \right]$
		Diatomic (exact) $S_{\text{vib}} = \sum_{i=1}^{N_{\text{vib}}} S_{\text{vib}}^{(i)}$
		$Q_{\text{elec}} = (g_i e^{\nu_i / k_b T})^N$ Polyatomic $\{\theta_{\text{vib}}\}$
		$S_{\text{elec}} = Nk_b \ln(g_i)$ $N_{\text{vib}} = \begin{cases} 3n-5 & \text{linear} \\ 3n-b & \text{non-linear} \end{cases}$
		Most Atoms and Molecules

3.49 Reversible Entropy

Reversible Entropy

$$dS \geq \frac{\delta q}{T} \quad dS_{rev} = \frac{\delta q_{rev}}{T}$$

$dS > 0$ for irreversible processes

$dS = 0$ for reversible processes

Reversible Isothermal Processes

$$dS = dS_{sys} + dS_{surr}$$

$$dS = \frac{\delta q_{sys}}{T} + \frac{\delta q_{surr}}{T}$$

$$dU = 0 = \delta q + \delta w$$

$$\delta q = -\delta w = -\left(-\frac{nRT}{V} dV\right) = \frac{nRT}{V} dV$$

$$\delta q_{surr} = -\delta q_{sys} = -\frac{nRT}{V} dV$$

$$dS = \frac{nR}{V} dV - \frac{nR}{V} dV = 0 \quad \checkmark$$

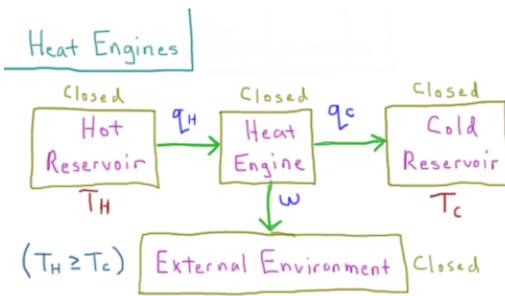
Reversible Adiabatic Processes

$$\delta q_{sys} = -\delta q_{surr} = 0$$

$$dS = dS_{sys} + dS_{surr}$$

$$dS = \frac{\delta q_{sys}}{T} + \frac{\delta q_{surr}}{T} = \frac{0}{T} + \frac{0}{T} = 0 \quad \checkmark$$

3.50 Heat Engines



$$\Delta U_{\text{engine}} = q_H + q_C + w = 0$$

$$\Delta S_{\text{engine}} = \frac{\delta q_{\text{rev},H}}{T_H} + \frac{\delta q_{\text{rev},C}}{T_C} = 0$$

$$-w = q_H + q_C$$

if $|w| = |q_H| \rightarrow 100\% \text{ efficiency}$

if $|w| = 0 \rightarrow 0\% \text{ efficiency}$

$$\left(\begin{array}{l} \text{maximum} \\ \text{efficiency} \end{array} \right) = \frac{-w}{q_H} = \frac{q_H + q_C}{q_H} = 1 + \frac{q_C}{q_H}$$

$$\frac{q_H}{T_H} = -\frac{q_C}{T_C} \quad \frac{q_C}{q_H} = -\frac{T_C}{T_H}$$

$$\left(\begin{array}{l} \text{maximum} \\ \text{efficiency} \end{array} \right) = 1 - \frac{T_C}{T_H}$$

100% efficiency when $T_C = 0 \text{ K}$
0% efficiency when $T_C = T_H$

3.51 Entropy Temp Dependence 1

Temperature Dependence of Entropy 1

$$dU = \delta q_{rev} + \delta w_{rev}$$

$$\delta q_{rev} = T dS \quad \delta w_{rev} = -P dV$$

$$dU = T dS - P dV \rightarrow U = U(S, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \rightarrow U = U(T, V)$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \rightarrow S(U, V)$$

$$dS = \frac{1}{T} \left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \right] + \frac{P}{T} dV$$

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] dV \rightarrow S(T, V)$$

$$dS = \underbrace{\frac{C_V(T)}{T}}_{\text{constant}} dT + \underbrace{\frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right]}_{\text{constant}} dV$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V(T)}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} dS = \\ = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_V dT = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT$$

3.52 Entropy Temp Dependence 2

Temperature Dependence of Entropy 2

$$dU = \underbrace{T dS}_{\delta q_{rev}} + \underbrace{P dV}_{\delta w_{rev}} \quad \left(\frac{\partial S}{\partial T} \right)_V = \frac{C_v(T)}{T}$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_v(T)}{T} dT \quad \text{when } dV=0$$

$$dH = \delta q_{p,rev} \quad \text{when } dP=0$$

$$H = U + PV$$

$$dH = d(U + PV) = dU + PdV + VdP$$

$$dH = TdS - \cancel{PdV} + \cancel{PdV} + VdP$$

$$dH = TdS + VdP$$

$$dS = \underbrace{\frac{C_p(T)}{T} dT}_{dS = \left(\frac{\partial S}{\partial T} \right)_P dT} + \underbrace{\frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right] dP}_{\left(\frac{\partial S}{\partial P} \right)_T dP}$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p(T)}{T}$$

$$\left(\frac{\partial S}{\partial P} \right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right]$$

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T} \right)_P dT$$

$$= \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT \quad \text{when } dP=0$$

$$S(T) = S(0) + \Delta S(0 \rightarrow T)$$

$$S(T) = S(0) + \underbrace{\int_0^T \frac{C_p(T')}{T'} dT'}$$

how to find? \rightarrow 3rd Law

3.53 Third Law

3rd Law of Thermodynamics

The entropy of a perfect crystal at 0 K is zero

$$S = -k_b \sum_i^{\text{states}} p_i \ln p_i \quad p_i \propto e^{-E_i/k_b T}$$

$$\text{as } T \rightarrow 0, \quad p_{E>E_{\min}} = 0 \quad \text{and} \quad p_{E=E_{\min}} = \frac{1}{g_i}$$

for most systems, $g_i = 1$

if $g_i = 1$ then $S(0 \text{ K}) = 0 \text{ J/K}$

$$S(T) = \underbrace{S(0)}_{k_b \ln g_i} + \int_0^T \frac{C_p(T')}{T'} dT' \quad \text{if } df = 0$$

usually zero

$$S(T) = \int_0^T \frac{C_p(T')}{T'} dT'$$

three laws:

$$\textcircled{1} \quad dU_{\text{universe}} = 0$$

$$\textcircled{2} \quad dS_{\text{universe}} \geq 0$$

$$\textcircled{3} \quad S_{\text{universe}} \geq 0$$

3.54 Transition Entropy

Entropy of Transition

$$dS = \frac{S_{\text{rev}}}{T} \quad S_{\text{rev}} = dH \quad \text{if } dP=0$$

$$dS = \frac{dH}{T} \quad \text{at phase transitions, } dT=0$$

$$\Delta_{\text{trs}} S = S_f - S_i = \int_i^f dS = \int_i^f \frac{dH}{T} = \frac{1}{T} \int_i^f dH \\ = \frac{1}{T} (H_f - H_i) = \frac{\Delta_{\text{trs}} H}{T}$$

$$\boxed{\Delta_{\text{trs}} S = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}}}$$

$$T < T_{\text{fus}} \quad S(T) = \int_0^T \frac{C_p^s(T')}{T'} dT'$$

$$T_{\text{fus}} < T < T_{\text{vap}}$$

$$S(T) = \int_0^{T_{\text{fus}}} \frac{C_p^s(T')}{T'} dT' + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} + \int_{T_{\text{fus}}}^T \frac{C_p^l(T')}{T'} dT'$$

$$T > T_{\text{vap}}$$

$$S(T) = \int_0^{T_{\text{fus}}} \frac{C_p^s(T')}{T'} dT' + \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \frac{C_p^l(T')}{T'} dT' \\ + \frac{\Delta_{\text{vap}} H}{T_{\text{vap}}} + \int_{T_{\text{vap}}}^T \frac{C_p^g(T')}{T'} dT'$$

$C_p^s \rightarrow \text{solid}$

$C_p^l \rightarrow \text{liquid}$

$C_p^g \rightarrow \text{gas}$

3.55 Debye T³ Law

Debye T³ Law

$$C_p^s(T) \propto T^3 \text{ as } T \rightarrow 0 \quad T < \sim 15 \text{ K}$$

$$\lim_{T \rightarrow 0} [C_p^s(T)] = 0$$

$$\text{metallic solids } C_p^s(T) = aT + bT^3$$

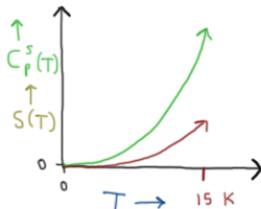
$$\text{non-metallic solids } C_p^s(T) = cT^3$$

$a, b, c \rightarrow \text{constants}$

$$S(T) = \int_0^T \frac{C_p^s(T')}{T'} dT'$$

$$S(T < 15 \text{ K}) \approx \int_0^T \frac{c(T')^3}{T'} dT' = \int_0^T c(T')^2 dT'$$

$$S(T < 15 \text{ K}) \approx \frac{1}{3} c T^3$$



3.56 Calorimetric Entropy

Absolute Calorimetric Entropy

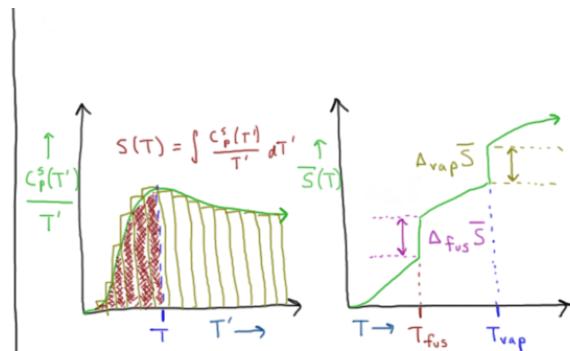
"Calorimetry": measurement of heat transfer during a process

$$C_p(T) = \left(\frac{\partial H}{\partial T}\right)_p \quad dH = \delta q_{rev} \text{ when } dP=0$$

can measure $C_p(T)$ for all T and $\Delta_{trs}H$ for all trs

$$\Delta S = \int_{T_i}^{T_2} \frac{C_p(T')}{T'} dT' \text{ between trs}$$

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}} \quad S(0) = 0 \quad \text{for most systems}$$



$$\bar{S}(T) = S(T)/n$$

$\bar{S}(T) \rightarrow \text{"molar entropy"}$

$S^\circ(T) \rightarrow \text{"standard molar entropy"}$

standard state $\rightarrow 1 \text{ bar} = 10^5 \text{ Pa}$

3.57 Statistical Entropy Example

Absolute Statistical Entropy

Calculate \bar{S} for O_2 at 298 K, 1 bar

$$S = k_b \left[T \frac{\partial \ln Q}{\partial T} + \ln Q \right] \quad Q = \sum_{\text{states}}^{\text{states}} e^{-E_i/k_b T}$$

$$E_i = E_{\text{trans}}^{(i)} + E_{\text{rot}}^{(i)} + E_{\text{vib}}^{(i)} + E_{\text{elec}}^{(i)}$$

$$\bar{S} = \bar{S}_{\text{trans}} + \bar{S}_{\text{rot}} + \bar{S}_{\text{vib}} + \bar{S}_{\text{elec}}$$

$$S \propto Nk_b = nR \quad \bar{S} = S/n \propto R$$

$$\bar{S}_{\text{trans}}/R = \frac{5}{2} + \frac{3}{2} \ln \left(\frac{2\pi m k_b T}{h^2} \right) + \ln \left(\frac{V}{N} \right)$$

$$PV = nRT = Nk_b T \quad \text{if ideal} \quad \frac{V}{N} = \frac{k_b T}{P}$$

$$\bar{S}_{\text{rot}}/R = 1 + \ln \left(\frac{T}{\sigma \theta_{\text{rot}}} \right)$$

$$\bar{S}_{\text{vib}}/R = \frac{\theta_{\text{vib}}}{T} \left(e^{\theta_{\text{vib}}/T} - 1 \right)^{-1} + \ln \left(1 - e^{-\theta_{\text{vib}}/T} \right)$$

$$\bar{S}_{\text{elec}}/R = \ln g_i$$

for O_2 : $m = 32.00 \text{ g/mol}$, $\theta_{\text{rot}} = 2.07 \text{ K}$, $\theta_{\text{vib}} = 2256 \text{ K}$
 $\sigma = 2$, $g_i = 3$

$$\bar{S}_{\text{elec}} = (8.3145 \text{ J/mol·K}) \ln(3) = 9.134 \text{ J/mol·K}$$

$$\frac{\theta_{\text{vib}}}{T} = \frac{2256 \text{ K}}{298.15 \text{ K}} = 7.5667$$

$$\bar{S}_{\text{vib}} = (8.3145 \text{ J/mol·K}) \left[7.5667 \left(\exp(7.5667) - 1 \right)^{-1} \right]$$

$$\bar{S}_{\text{vib}} = 0.0369 \text{ J/mol·K} + \ln(1 - \exp(-7.5667))$$

$$\bar{S}_{\text{rot}} = (8.3145 \text{ J/mol·K}) \left[1 + \ln \left(\frac{298.15 \text{ K}}{2 \cdot 2.07 \text{ K}} \right) \right] = 43.875 \text{ J/mol·K}$$

$$\bar{S}_{\text{trans}} = (8.3145 \text{ J/mol·K}) \left[\frac{5}{2} + \frac{3}{2} \ln \left(\frac{2 \cdot \pi \cdot (32.00 \text{ g/mol})}{(6.6261 \cdot 10^{-34})^2} \right) \right. \\ \left. + \frac{(10^{-3} \text{ kg/m}) (1.3806 \cdot 10^{-23} \text{ J/K}) (298.15 \text{ K})}{(6.022 \cdot 10^{23} \text{ mol}^{-1})} \right) + \ln \left(\frac{k_b \cdot T}{100,000 \text{ Pa}} \right)$$

$$\boxed{\bar{S} = 205.13 \text{ J/mol·K}}$$

$$\bar{S}_{\text{trans}} = 152.08 \text{ J/mol·K}$$

$$\bar{S}_{\text{expt}} = 205.2 \text{ J/mol·K} \longrightarrow \text{very accurate}$$

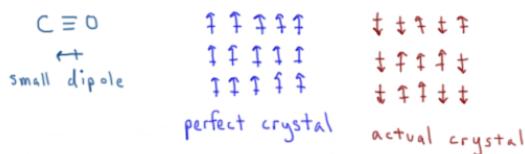
3.58 Residual Entropy

Residual Entropy

Sometimes $\bar{S}_{\text{calc}} > \bar{S}_{\text{expt}}$

$$\bar{S}_{\text{res}} = \bar{S}_{\text{calc}} - \bar{S}_{\text{expt}}$$

"residual entropy"



$$\bar{S}_{\text{res}}(CO) = 4.7 \text{ J/mol·K}$$

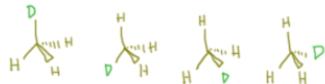
$$W_{\text{rand}} = 2^n \quad 2 \text{ configurations each}$$

$$S_{\text{rand}} = k_b \ln W = k_b \ln(2^n) = N k_b \ln 2 = n R \ln 2$$

$$\bar{S}_{\text{rand}} = R \ln 2 = (8.314 \text{ J/mol·K})(0.693) = 5.8 \text{ J/mol·K}$$

$\bar{S}_{\text{rand}} \approx 1.2 \bar{S}_{\text{res}} \rightarrow \text{organization is } \sim 85\% \text{ random}$

$$\bar{S}_{\text{res}}(CH_3D) = 11.7 \text{ J/mol·K}$$



4 configurations each

$$\bar{S}_{\text{rand}} = \frac{k_b}{n} \ln(4^n) = \frac{N k_b}{n} \ln 4 = \frac{R}{N} \ln 4$$

$$\bar{S}_{\text{rand}} = (8.314 \text{ J/mol·K})(1.386) = 11.5 \text{ J/mol·K}$$

$\bar{S}_{\text{rand}} = 0.98 \bar{S}_{\text{res}} \rightarrow \text{accounts for } \sim 98\% \text{ of residual entropy}$

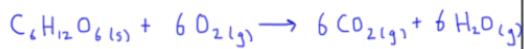
3.59 Reaction Entropy

Reaction Entropy



$$\Delta_r S^\circ = dS^\circ(D) + cS^\circ(C) - aS^\circ(A) - bS^\circ(B)$$

$$\Delta_r S^\circ = \sum_j n_j S^\circ(\text{products}) - \sum_i n_i S^\circ(\text{reactants})$$



$$\begin{aligned}\Delta_r S^\circ &= 6(213.8 \text{ J/mol·K}) + 6(188.7 \text{ J/mol·K}) \\ &\quad - 1(209.2 \text{ J/mol·K}) - 6(205.2 \text{ J/mol·K})\end{aligned}$$

$$\boxed{\Delta_r S^\circ = +974.6 \text{ J/mol·K}}$$

Compound	$S^\circ \text{ (J/mol·K)}$
$C_6H_{12}O_6(s)$	209.2
$O_2(g)$	205.2
$CO_2(g)$	213.8
$H_2O(g)$	188.7

3.60 Helmholtz Energy

Helmholtz Energy

$$1^{\text{st}} \text{ Law: } dU = \delta q + \delta w$$

$$2^{\text{nd}} \text{ Law: } dS \geq \frac{\delta q}{T}$$

$$\delta q \leq TdS \quad \delta w = -PdV$$

$$dU \leq TdS - PdV \xrightarrow[constant volume]{} 0$$

$$dU - TdS \leq 0$$

$$dU - (TdS + SdT) \xrightarrow[constant temperature]{} 0$$

$$d(U - TS) \leq 0$$

$dA \leq 0$ for spontaneous processes at

$$A = U - TS$$

$$dV = dT = 0$$

$A \rightarrow$ "Helmholtz free energy"

extensive state function

must stay the same (reversible)
or decrease (irreversible) for closed
systems at constant volume and
temperature

$$\Delta A = \Delta U - T\Delta S \leq 0$$

$$\Delta U = q_{\text{rev}} + w_{\text{rev}}$$

$$T\Delta S = T(q_{\text{rev}}/\Delta T) = q_{\text{rev}}$$

$$\Delta A = (q_{\text{rev}} + w_{\text{rev}}) - (q_{\text{rev}})$$

$\boxed{\Delta A = w_{\text{rev}}}$ maximum reversible work
at $\Delta V = \Delta T = 0$

3.61 Gibbs Energy

Gibbs Energy

$$dU = \delta_q + \delta_w \quad dS \geq \delta_q/T$$

$$\delta_q \leq T dS \quad \delta_w = - P dV$$

$$dU \leq TdS - PdV$$

$$dU - TdS + PdV \leq 0$$

$$dU - (TdS + SdT) + (pdV + VdP) \leq 0$$

$$d(u - TS + PV) \leq 0$$

$dG \leq 0$ for spontaneous processes at $dT = dP = 0$

$$G = A + \rho V$$

$$G = H - TS$$

$$A = U - TS$$

$$H = U + PV$$

$G \rightarrow$ "Gibbs free energy"

extensive state function

must stay the same (reversible) or decrease (irreversible) for closed systems at constant temperature and pressure

$$\Delta G = \Delta H - T\Delta S \leq 0$$

$$dG = dU + d(-TS + PV)$$

$$dG = \cancel{TdS} - \cancel{PdV} + \delta w_{\text{non-PV}} - \cancel{TdS} - \cancel{SdT} + \cancel{PdV} + VdP$$

at $dT = dP = 0$

$$dG = -SdT + VdP + S_{\text{non-PV}}$$

$$\Delta G = \omega_{\text{non-PV}} \quad \text{maximum reversible non-PV}$$

work at $\Delta T = \Delta P = 0$

3.62 Natural Variables

<u>Natural Variables</u>	
$U, H, A, G, S \rightarrow$ extensive state functions	
$dU = TdS - PdV$	$U = U(S, V)$
$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$	$S, V \rightarrow$ "natural variables" for U
$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$	
$dS = \frac{1}{T} dU + \frac{P}{T} dV$	$S = S(U, V)$
$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$	
$H = U + PV$	$dH = d(U + PV)$
$dH = dU + PdV + VdP$	
$dH = TdS - PdV + PdV + VdP$	
	$dH = TdS + VdP$
	$H = H(S, P)$
	$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V$
	$A = U - TS$
	$dA = -SdT - PdV$
	$A = A(T, V)$
	$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$
	$G = U - TS + PV = A + PV = H - TS$
	$dG = -SdT + VdP$
	$G = G(T, P)$
	$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V$

3.63 Maxwell Relations 1: Concept

Maxwell Relations - Concept

$$f = f(x, y)$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \quad \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y$$

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y} \rightarrow \text{equality of mixed partial derivatives}$$

$$dU = T dS - P dV \quad U = U(S, V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V = \frac{\partial}{\partial V} (T) = \left(\frac{\partial T}{\partial V} \right)_S$$

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S = \frac{\partial}{\partial S} (-P) = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$\boxed{\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V}$$

"Maxwell Relation"

3.64 Maxwell Relations 2: Summary

Maxwell Relations - Summary	
Functions	Natural Variables
U internal energy	$U = U(s, v)$
$H = U + PV$ enthalpy	$H = H(s, P)$
$A = U - TS$ Helmholtz free energy	$A = A(T, v)$
$G = U - TS + PV$ Gibbs free energy = $A + PV$ = $H - TS$	$G = G(T, P)$
Differentials	Maxwell Relations
$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V$
$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$dA = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$

3.65 Maxwell Relations 3: Example

Maxwell Relations - Example

find the entropy change of a reversible, isothermal expansion of an ideal gas

$$\Delta S = S_f - S_i = \int_i^f dS = \int_i^f \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$PV = nRT \rightarrow P = \frac{nRT}{V}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{nRT}{V} \right) = \frac{nR}{V}$$

$$\Delta S = \int_{V_i}^{V_f} \left(\frac{nR}{V} \right) dV = nR \left[\ln(V_f) - \ln(V_i) \right]$$

$$\boxed{\Delta S = nR \ln(V_f/V_i)}$$

3.66 Standard Entropy Correction

Standard Entropy Correction

\bar{S} → molar entropy → intensive state function
 S° → standard state molar entropy
 (ideal gas at 1 bar)

$S^\circ - \bar{S}(1 \text{ bar})$ = correction for non-ideal gas

$$\Delta \bar{S}_1 = \bar{S}(\sim 0 \text{ bar}) - \bar{S}(1 \text{ bar}) = \int_1^{\sim 0} \left(\frac{\partial \bar{S}}{\partial P} \right)_T dP = - \int_{\sim 0}^1 \left(\frac{\partial \bar{S}}{\partial P} \right)_T dP$$

$$\Delta \bar{S}_2 = S^\circ - \bar{S}(\sim 0 \text{ bar}) = \int_{\sim 0}^1 \left(\frac{\partial \bar{S}}{\partial P} \right)_T dP = - \int_{\sim 0}^1 \left(\frac{\partial \bar{V}}{\partial T} \right) dP$$

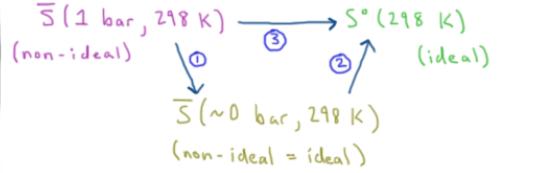
$$\left(\frac{\partial \bar{S}}{\partial P} \right)_T = - \left(\frac{\partial \bar{V}}{\partial T} \right)_P \quad P \bar{V}_{id} = RT \quad \bar{V}_{id} = \frac{RT}{P} \quad \left(\frac{\partial \bar{V}_{id}}{\partial T} \right)_P = \frac{R}{P}$$

$$\Delta \bar{S}_3 = \Delta \bar{S}_1 + \Delta \bar{S}_2 = \int_{\sim 0}^1 \left[\left(\frac{\partial \bar{V}}{\partial T} \right)_P - \left(\frac{\partial \bar{V}_{id}}{\partial T} \right)_P \right] dP$$

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{B_{2v}(T)}{RT} P + \dots$$

$$\bar{V} = \frac{RT}{P} + B_{2v}(T) + \dots$$

$$\left(\frac{\partial \bar{V}}{\partial T} \right)_P = \frac{R}{P} + \frac{d B_{2v}(T)}{dT} + \dots$$



$$S^\circ - \bar{S}(1 \text{ bar}) = \Delta \bar{S}_3 = \int_{\sim 0}^1 \left[\left(\frac{\partial \bar{V}}{\partial P} \right)_T + \frac{d B_{2v}(T)}{dT} + \dots \right] - \frac{P}{P} dP$$

$$\Delta \bar{S}_3 = \left(\frac{d B_{2v}(T)}{dT} \right) \int_{\sim 0}^1 dP$$

$$\boxed{S^\circ(T) - \bar{S}(T, 1 \text{ bar}) = \frac{d B_{2v}(T)}{dT} (1 \text{ bar})}$$

$$vdW_{gas} \rightarrow B_{2v}(T) = b - \frac{a}{RT}$$

$$\frac{d B_{2v}(T)}{dT} = \frac{a}{RT^2} \quad a_{O_2} = 1.382 \frac{L^2 \cdot \text{bar}}{\text{mol}^2}$$

$$S^\circ(298) - \bar{S}(298, 1 \text{ bar}) = 0.0187 \text{ J/mol}\cdot\text{K} \text{ for } O_2$$

~0.01% of S°

3.67 Gibbs-Helmholtz Equation

Gibbs - Helmholtz Equation

$$G = G(T, P)$$

$$dG = -SdT + VdP$$

$$\Delta G = G_f - G_i = \int_i^f dG = \int_i^f (-SdT + VdP)$$

$$\text{if } dT=0, \Delta G = \int_{P_i}^{P_f} VdP$$

$$PV = nRT \quad V = \frac{nRT}{P} \quad \bar{G} = \frac{G}{n} \quad \bar{V} = \frac{V}{n}$$

$$\Delta \bar{G} = \int_{P_i}^{P_f} \bar{V}dP = \int_{P_i}^{P_f} \frac{RT}{P} dP = RT(\ln P_2 - \ln P_1)$$

$$\boxed{\Delta \bar{G} = RT \ln(P_f/P_i)}$$

$\Delta \bar{H} \rightarrow$ independent of P for ideal gases

$$\Delta \bar{G} = -T \Delta \bar{S}$$

$$\boxed{\Delta \bar{S} = -R \ln(P_f/P_i)}$$

$$\left(\frac{\partial \bar{G}}{\partial T} \right)_P = -\bar{S}$$

$$G(T) = H(T) - TS(T)$$

$$\frac{G(T)}{T} = \frac{H(T)}{T} - S(T)$$

$$\left(\frac{\partial G(T)/T}{\partial T} \right)_P = -\frac{H(T)}{T^2} + \frac{1}{T} \left(\frac{\partial H(T)}{\partial T} \right)_P - \left(\frac{\partial S(T)}{\partial T} \right)_P$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_P(T)}{T} = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P$$

$$C_P(T) = \left(\frac{\partial H}{\partial T} \right)_P$$

$$\boxed{\left(\frac{\partial (G/T)}{\partial T} \right)_P = -\frac{H}{T^2}}$$

$$\left(\frac{\partial (\Delta G/T)}{\partial T} \right)_P = -\frac{\Delta H}{T^2}$$

3.68 Fugacity

Fugacity

$$G^\circ(T) = \bar{G}(T, P^\circ) = G(T, P^\circ) / n \quad P^\circ = 1 \text{ bar} \quad (\text{ideal})$$

$$dG = -S dT + V dP \quad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S} \quad \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$$

$$\chi = \frac{P\bar{V}}{RT} = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + \dots$$

$$\bar{V} = \frac{RT}{P} + RT B_{2P}(T) + RT B_{3P}(T)P + \dots$$

$$\bar{G}(T, P) = \bar{G}(T, \infty) + \int_{\infty}^P d\bar{G}$$

$$\begin{aligned} \int_{\infty}^P d\bar{G} &= \int_{\infty}^P (-\bar{S} dT + \bar{V} dP) = \int_{\infty}^P \bar{V} dP = \\ &= \int_{\infty}^P \left(\frac{RT}{P} + RT B_{2P}(T) + RT B_{3P}(P)P + \dots \right) dP = \\ &= RT \ln(P/P_\infty) + RT B_{2P}(T)P + \frac{1}{2} RT B_{3P}(T)P^2 + \dots \end{aligned}$$

$$\bar{G}(T, P) = \bar{G}(T, \infty) + RT \ln(P/P_\infty) + \dots$$

$$\bar{G}(T, \infty) = G^\circ(T, P) + RT \ln(P_\infty/P^\circ)$$

$$RT \ln(P/P_\infty) + RT \ln(P_\infty/P^\circ) = RT \ln\left(\frac{P}{P_\infty} \cdot \frac{P_\infty}{P^\circ}\right)$$

$$\bar{G}(T, P) = \underbrace{G^\circ(T, P^\circ)}_{\text{ideal behavior}} + \underbrace{RT \ln\left(\frac{P}{P^\circ}\right)}_{\text{non-ideal behavior}} + RT \left[B_{2P}(T)P + \frac{1}{2} B_{3P}(T)P^2 + \dots \right]$$

$f(P, T) \rightarrow \text{"fugacity"}$

$$\lim_{P \rightarrow 0} [f(P, T)] = P \quad f^\circ = P^\circ = 1 \text{ bar}$$

$$f(T, P) = P e^{B_{2P}(T)P + \frac{1}{2} B_{3P}(T)P^2 + \dots}$$

$$\bar{G}(T, P) = G^\circ(T) + RT \ln\left(\frac{f(T, P)}{f^\circ}\right)$$

3.69 Fugacity Coefficient

Fugacity Coefficient

$$\bar{G}(T, P) = G^\circ(T) + RT \ln\left(\frac{P}{P^\circ}\right) \quad \text{ideal}$$

$$\bar{G}(T, P) = G^\circ(T) + RT \ln\left(\frac{f}{f^\circ}\right) \quad \text{non-ideal}$$

$$f(T, P) = P e^{B_{2P}(T)P + \frac{1}{2}B_{3P}(T)P^2 + \dots} \quad f^\circ = P^\circ = 1 \text{ bar}$$

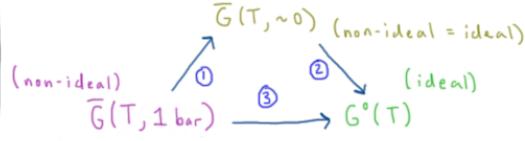
$$\Delta \bar{G}_1 = \int_{P^\circ}^P d\bar{G} = - \int_{P^\circ}^P \left(\frac{\partial \bar{G}}{\partial P'} \right)_T dP' = - \int_{P^\circ}^P \bar{V} dP'$$

$$\Delta \bar{G}_2 = \int_{P^\circ}^P d\bar{G}_{\text{id}} = \int_{P^\circ}^P \left(\frac{\partial \bar{G}_{\text{id}}}{\partial P'} \right) dP' = \int_{P^\circ}^P \bar{V}_{\text{id}} dP'$$

$$\Delta \bar{G}_3 = \Delta \bar{G}_1 + \Delta \bar{G}_2 = \int_{P^\circ}^P (\bar{V}_{\text{id}} - \bar{V}) dP'$$

$$P \bar{V}_{\text{id}} = RT \quad \bar{V}_{\text{id}} = \frac{RT}{P} \quad Z = \frac{P \bar{V}}{RT}$$

$$\begin{aligned} \Delta \bar{G}_3 &= \int_{P^\circ}^P \left(\frac{RT}{P} - \bar{V} \right) dP' = RT \int_{P^\circ}^P \left(\frac{1}{P'} - \frac{\bar{V}}{RT} \right) dP' = \\ &= RT \int_{P^\circ}^P \frac{dP'}{P'} \left(1 - \frac{P' \bar{V}}{RT} \right) = RT \int_{P^\circ}^P \frac{dP'}{P'} \left(1 - Z \right) = \\ &= - RT \int_{P^\circ}^P \left(\frac{Z-1}{P'} \right) dP' \end{aligned}$$



$$\begin{aligned} \Delta \bar{G}_3 &= G^\circ(T) - \bar{G}(T, 1 \text{ bar}) = \\ &= G^\circ(T) + RT \ln\left(\frac{P}{P^\circ}\right) - G^\circ(T) - RT \ln\left(\frac{f}{f^\circ}\right) = \\ &= RT \ln\left(\frac{P}{P^\circ} \cdot \frac{f^\circ}{f}\right) = RT \ln(P/f) \\ &= -RT \ln\left(\frac{f}{P}\right) = -RT \ln\gamma \end{aligned}$$

$\gamma = \frac{f}{P}$ "fugacity coefficient"

ideal gas $\rightarrow f = P \rightarrow \gamma = 1 \rightarrow \ln\gamma = 0$

$$\ln\gamma = \int_{P^\circ}^P \left(\frac{Z-1}{P'} \right) dP'$$

$$G^\circ(T) - \bar{G}(T, 1 \text{ bar}) = -RT \ln\gamma$$

3.70 Phase Diagrams

Phase Diagrams

graph of the equilibrium phase as a function of P and T

$$G = G(T, P) \quad \text{equilibrium} \rightarrow \text{lowest } G$$

$(s) \rightarrow \text{solid}$	$G_s < (G_l, G_g)$
$(l) \rightarrow \text{liquid}$	$G_l < (G_s, G_g)$
$(g) \rightarrow \text{gas}$	$G_g < (G_s, G_l)$

solid-gas coexistence curve $G_s = G_g < G_l$

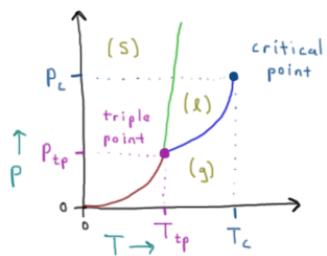
liquid-gas coexistence curve $G_l = G_g < G_s$

solid-liquid coexistence curve $G_s = G_l < G_g$

triple point $G_s = G_l = G_g$

$s, l \rightarrow$ condensed phases

$l, g \rightarrow$ fluid phases



$f \rightarrow$ "degrees of freedom"

$p \rightarrow$ number of phases in equilibrium

$$f = 3 - p$$

general $T, P \rightarrow 2$

coexistence curve $\rightarrow 1$

triple point $\rightarrow 0$

3.71 Gibbs Energy of Phases

Gibbs Energy of Phases

$$dG = -SdT + VdP \quad G = G(T, P)$$

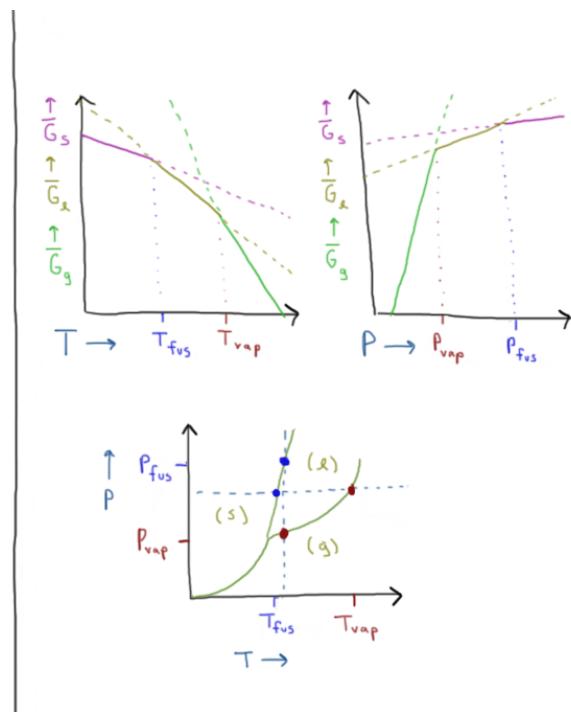
$$d\bar{G}_\alpha = -\bar{S}_\alpha dT + \bar{V}_\alpha dP \quad \alpha = s, l, g$$

$$\left(\frac{\partial \bar{G}_\alpha}{\partial T}\right)_P = -\bar{S}_\alpha \quad \left(\frac{\partial \bar{G}_\alpha}{\partial P}\right)_T = \bar{V}_\alpha$$

$$\bar{S}_g > \bar{S}_l > \bar{S}_s$$

$$\bar{V}_g \gg \bar{V}_l > \bar{V}_s$$

usually



3.72 Chemical Potential

Chemical Potential

$dG = 0$ in equilibrium

solid-liquid coexistence

$$G = G_s + G_x$$

$$dG = \left(\frac{\partial G_s}{\partial n_s}\right)_{P,T} dn_s + \left(\frac{\partial G_x}{\partial n_x}\right)_{P,T} dn_x$$

$$n = n_s + n_x$$

$$dn = dn_s + dn_x = 0$$

$$dn_x = -dn_s$$

$$dG = \left[\left(\frac{\partial G_s}{\partial n_s}\right)_{P,T} - \left(\frac{\partial G_x}{\partial n_x}\right)_{P,T}\right] dn_s$$

$$\mu_\alpha = \left(\frac{\partial G_x}{\partial n_\alpha}\right)_{P,T} \quad \mu_\alpha = \mu_\alpha(P, T)$$

μ_α → "chemical potential"

$$dG = (\mu_s - \mu_x) dn_s \leq 0 \text{ when } dT = dP = 0$$

$$\text{if } \mu_s > \mu_x \rightarrow dn_s \leq 0$$

$$\text{if } \mu_s < \mu_x \rightarrow dn_s \geq 0$$

$$\text{if } \mu_s = \mu_x \rightarrow dG = 0 \rightarrow \text{equilibrium}$$

for single phase:

$$\mu = \frac{\partial G}{\partial n} = \frac{\partial(n\bar{G})}{\partial n} = \bar{G}$$

3.73 Clapeyron Equation

Clapeyron Equation

if phases α and β are in equilibrium

$$\mu_\alpha(T, P) = \mu_\beta(T, P)$$

$$\left(\frac{\partial \mu_\alpha}{\partial T}\right)_P dT + \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T dP = \left(\frac{\partial \mu_\beta}{\partial T}\right)_P dT + \left(\frac{\partial \mu_\beta}{\partial P}\right)_T dP$$

$$\mu_\alpha = \bar{G}_\alpha \quad \left(\frac{\partial \bar{G}_\alpha}{\partial T}\right)_P = -\bar{S}_\alpha \quad \left(\frac{\partial \bar{G}_\alpha}{\partial P}\right)_T = \bar{V}_\alpha$$

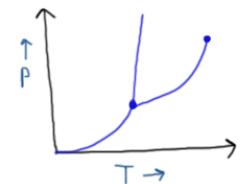
$$-\bar{S}_\alpha dT + \bar{V}_\alpha dP = -\bar{S}_\beta dT + \bar{V}_\beta dP$$

$$\frac{dP}{dT} = \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} = \frac{\Delta_{trs} \bar{S}}{\Delta_{trs} \bar{V}}$$

$$\Delta_{trs} \bar{G} = \Delta_{trs} \bar{H} - T \Delta_{trs} \bar{S} = 0 \quad \text{at equilibrium}$$

$$\Delta_{trs} \bar{S} = \frac{\Delta_{trs} \bar{H}}{T}$$

$$\frac{dP}{dT} = \frac{\Delta_{trs} \bar{H}}{T \Delta_{trs} \bar{V}}$$



$$\left. \begin{array}{l} \Delta_{fus} \bar{H} > 0 \\ \Delta_{vap} \bar{H} > 0 \\ \Delta_{sub} \bar{H} > 0 \end{array} \right\} \text{always}$$

$$\left. \begin{array}{l} \Delta_{fus} \bar{V} > 0 \\ \Delta_{vap} \bar{V} > 0 \\ \Delta_{sub} \bar{V} > 0 \end{array} \right\} \text{usually}$$

$$\Delta_{sub} \bar{V} > 0 \quad \left. \begin{array}{l} \text{always} \\ T_{trs} > 0 \end{array} \right\} \text{always}$$

$$\frac{dP}{dT} > 0 \quad \left. \begin{array}{l} \text{almost} \\ \text{always} \end{array} \right.$$

3.74 Clausius-Clapeyron Equation

Clausius-Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta_{trs}\bar{H}}{T\Delta_{trs}\bar{V}}$$

assumes $\Delta_{trs}\bar{V} \approx \text{constant}$

vaporization \rightarrow liquid-gas coexistence

$$\frac{dP}{dT} = \frac{\Delta_{vap}\bar{H}}{T\Delta_{vap}\bar{V}}$$

$$\Delta_{vap}\bar{V} = \bar{V}_g - \bar{V}_l \approx \bar{V}_g \quad \bar{V}_g \gg \bar{V}_l$$

$$\text{ideal gas } P\bar{V}_g = RT \rightarrow \bar{V}_g = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta_{vap}\bar{H}}{T} \left(\frac{P}{RT} \right) \quad \int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta_{vap}\bar{H}}{RT^2} dT$$

$$[\ln P]_{P_1}^{P_2} = \left[-\frac{\Delta_{vap}\bar{H}}{RT} \right]_{T_1}^{T_2}$$

$$\ln \left(\frac{P_2}{P_1} \right) = - \frac{\Delta_{vap}\bar{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Given $\Delta_{vap}\bar{H}$, T_{vap_1} , and P_{vap_1} , can calculate T_{vap_2} and P_{vap_2}

"standard" T_{vap} at 1 bar

"normal" T_{vap} at 1 atm

Given two sets of T_{vap} , P_{vap}

Plot $\ln P$ vs. $1/T$

Slope is $-\frac{\Delta_{vap}\bar{H}}{R}$

3.75 Statistical Chemical Potential

Statistical Chemical Potential

$$E_{\text{mol}}^{(i)} = E_{\text{trans}}^{(i)} + E_{\text{rot}}^{(i)} + E_{\text{vib}}^{(i)} + E_{\text{elec}}^{(i)}$$

$$Q_{\text{mol}} = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}} Q_{\text{elec}}$$

$$Q = \sum_{i=1}^n e^{-\beta E_i} \quad \beta = \frac{1}{k_B T}$$

$$U = \langle E \rangle = \left(\frac{\partial \ln Q}{\partial \beta} \right)_{P,V} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{P,T} = -k_B T \left(\frac{\partial \ln Q}{\partial n} \right)_{P,T}$$

$$Q_{\text{trans}} = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}$$

$$Q_{\text{rot}} = \left(\frac{T}{\sigma \theta_{\text{rot}}} \right)^N \quad Q_{\text{rot}} = \frac{1}{\sigma^N} \left(\frac{\pi T^3}{\theta_A \theta_B \theta_C} \right)^{N/2}$$

$$Q_{\text{vib}} = \left(\prod_{i=1}^{n_{\text{vib}}} \frac{e^{-\theta_v(i)/2T}}{1 - e^{-\theta_v(i)\omega_i/T}} \right)^N \quad n_{\text{vib}} = 3n - 6 \quad (\text{or } 5)$$

$$Q_{\text{elec}} = \left(g_e e^{D_e / k_B T} \right)^N$$

$$\mu = \mu_{\text{trans}} + \mu_{\text{rot}} + \mu_{\text{vib}} + \mu_{\text{elec}}$$

$$n = N/N_A \quad \frac{\partial}{\partial n} = \frac{\partial N}{\partial n} \left(\frac{1}{N} \right) = \frac{\partial (N_A n)}{\partial n} \left(\frac{1}{N_A n} \right) = N_A \frac{\partial}{\partial N}$$

$$N_A k_B = n R = \frac{N R}{N_A} \quad N_A k_B = R$$

$$\mu_{\text{trans}} = -RT \left[1 + \ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

$$\mu_{\text{rot}} = -RT \ln \left(\frac{T}{\sigma \theta_{\text{rot}}} \right)$$

$$\mu_{\text{vib}} = \sum_{i=1}^{n_{\text{vib}}} \left[\frac{1}{2} R \theta_{\text{vib}}^{(i)} - RT \ln \left(1 - e^{-\theta_{\text{vib}}^{(i)}/T} \right) \right]$$

$$\mu_{\text{elec}} = -D_e - RT \ln g_1$$

3.76 Partial Molar Quantities

Partial Molar Quantities

$G = G(T, P, n_1, n_2)$ for 2 component system

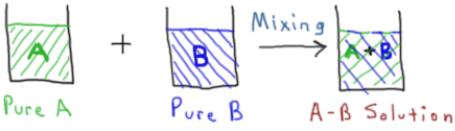
$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1} dn_2$$

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_1, n_2} = -S(T, P, n_1, n_2)$$

$$\left(\frac{\partial G}{\partial P}\right)_{T, n_1, n_2} = V(T, P, n_1, n_2)$$

$$\left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_2} = \mu_1(T, P, n_1, n_2) = \mu_1 = \bar{G}_1$$

$$\left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_1} = \mu_2(T, P, n_1, n_2) = \mu_2 = \bar{G}_2$$



$\Delta_{\text{mix}} H, \Delta_{\text{mix}} S, \Delta_{\text{mix}} G$

$\bar{X}_i \rightarrow \text{"partial molar quantity"}$

$$\bar{X}_i = \bar{X}_i(T, P, \{n_j\}) = \left(\frac{\partial X}{\partial n_i}\right)_{T, P, n_j \neq i}$$

$$\mu_i, \bar{V}_i, \bar{S}_i, \bar{H}_i$$

3.77 Gibbs-Duhem Equation

Gibbs-Duhem Equation

$$G = H - TS \quad G = G(T, P, \{n_j\})$$

$$\underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i}}_{\mu_i} = \underbrace{\left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_j \neq i}}_{\bar{H}_i} - T \underbrace{\left(\frac{\partial S}{\partial n_i}\right)_{T, P, n_j \neq i}}_{\bar{S}_i}$$

$$\boxed{\mu_i = \bar{G}_i = \bar{H}_i - T \bar{S}_i}$$

$$\bar{S}_i = \frac{\partial S}{\partial n_i} = \frac{\partial}{\partial n_i} \left(- \frac{\partial G}{\partial T} \right) = - \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial n_i} \right) = - \frac{\partial \mu_i}{\partial T}$$

$$\bar{V}_i = \frac{\partial V}{\partial n_i} = \frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P} \right) = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i} \right) = \frac{\partial \mu_i}{\partial P}$$

$$\mu_i = \mu_i(T, P) \quad d\mu_i = \left(\frac{\partial \mu_i}{\partial T} \right)_P dT + \left(\frac{\partial \mu_i}{\partial P} \right)_T dP$$

$$\boxed{d\mu_i = -\bar{S}_i dT + \bar{V}_i dP}$$

$$G = G(T, P, n_1, n_2)$$

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \quad \text{at} \quad dT = dP = 0$$

$$G(T, P, \lambda n_1, \lambda n_2) = \lambda G(T, P, n_1, n_2)$$

(extensive state function when $\lambda n_2 = \text{constant}$)

$$G(T, P, n_1, n_2) = \mu_1(T, P)n_1 + \mu_2(T, P)n_2$$

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2$$

$$\cancel{\mu_1 dn_1} + \cancel{\mu_2 dn_2} = \cancel{\mu_1 dn_1} + n_1 d\mu_1 + \cancel{\mu_2 dn_2}$$

$$\boxed{n_1 d\mu_1 + n_2 d\mu_2 = 0} \quad + n_2 d\mu_2$$

"Gibbs-Duhem equation"

3.78 Solution Chemical Potential

Solution Chemical Potential

$$n_A = n_{A,vap} + n_{A,sol} \quad n_B = n_{B,vap} + n_{B,sol}$$

$$dn_A = dn_{A,vap} + dn_{A,sol} \quad dn_B = dn_{B,vap} + dn_{B,sol}$$

$$dn_A = 0, \quad dn_B = 0$$

assume $dn_{B,vap} = dn_{B,sol} = 0$

$$dn_{A,sol} = -dn_{A,vap}$$

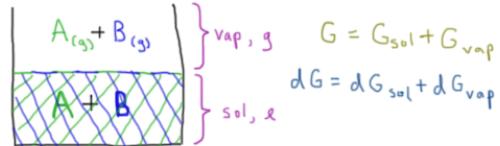
$$dG = \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} dn_{A,sol} + \left(\frac{\partial G}{\partial n_A}\right)_{vap} dn_{A,vap} + \left(\frac{\partial G}{\partial n_B}\right)_{sol} dn_{B,sol} + \left(\frac{\partial G}{\partial n_B}\right)_{vap} dn_{B,vap}$$

$$dG = \mu_{A,sol} dn_{A,sol} + \mu_{A,vap} dn_{A,vap}$$

$$dG = (\mu_{A,sol} - \mu_{A,vap}) dn_{A,sol}$$

$dG = 0$ at equilibrium

$$\boxed{\mu_{A,sol} = \mu_{A,vap}}$$



if vapor is ideal $P^{\circ} = 1 \text{ bar}$

$$\mu_{A,sol} = \mu_{A,vap} = \mu_A^{\circ}(T) + RT \ln\left(\frac{P_A}{P^{\circ}}\right)$$

$\mu_A^{\circ} \rightarrow$ chemical potential of pure A

$$\boxed{\mu_A^{\circ}(x) = \mu_A^{\circ}(g) = \mu_A^{\circ}(T) + RT \ln\left(\frac{P_A^{\circ}}{P_0}\right)}$$

$$\boxed{\mu_{A,sol} = \mu_A^{\circ}(x) + RT \ln\left(\frac{P_A}{P_A^{\circ}}\right)}$$

$$\mu_{A,sol} \rightarrow \mu_A^{\circ}(x) \quad \text{as } P_A \rightarrow P_A^{\circ}$$

3.79 Raoult's Law

Raoult's Law

$P_i \rightarrow$ "partial vapor pressure" of i

$P_i^* \rightarrow$ "pure vapor pressure" of i

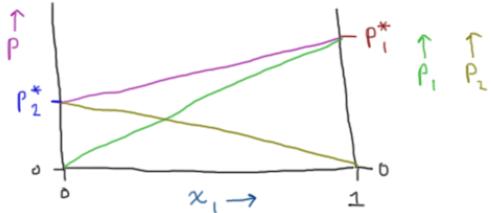
$x_i \rightarrow$ "mole fraction" of i $x_i = \frac{n_i}{n} = \frac{n_i}{\sum_j n_j}$

$$P_i = x_i P_i^* \quad \text{"Raoult's Law"} \quad 0 \leq \{x_{ij}\} \leq 1$$

Ideal Solutions: solutions which obey Raoult's law for all components and mole fractions

True if:

- 1) all components have similar size / shape
- 2) interactions among and between all components are the same



$$\mu_{i,sol} = \mu_i^*(x) + RT \ln \left(\frac{P_i}{P_i^*} \right)$$

$$\text{if ideal } \frac{P_i}{P_i^*} = \frac{x_i P_i^*}{P_i^*} = x_i$$

$$\mu_{i,sol} = \mu_i^*(x) + RT \ln x_i \quad \text{if ideal}$$

if one component behaves ideally, the other will as well $x_2 = 1 - x_1$

$$P = P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = P_2^* + x_1 (P_2^* - P_1^*)$$

3.80 Pressure-Composition Diagrams

Pressure - Composition Diagram

$x_i^g \rightarrow$ vapor phase mole fraction of *i*
 $x_i^s \rightarrow$ solution phase mole fraction of *i*
 $x_i^{tot} \rightarrow$ total mole fraction of *i*

$$n_{tot}^g = \sum_i n_i^g \quad n_{tot}^s = \sum_i n_i^s \quad n_{tot} = n_{tot}^g + n_{tot}^s$$

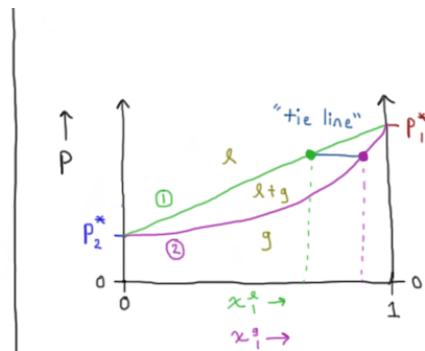
$$x_i^g = \frac{n_i^g}{n_{tot}^g} \quad x_i^s = \frac{n_i^s}{n_{tot}^s} \quad x_i^{tot} = \frac{n_i^g + n_i^s}{n_{tot}}$$

$$x_i^{tot} = \frac{x_i^g n_g + x_i^s n_g}{n_g + n_g}$$

$$\frac{n_g}{n_g} = \frac{x_i^g - x_i^{tot}}{x_i^{tot} - x_i^g}$$

"Lever Rule"

$x_i^s \rightarrow x_i^{tot}$ as $n_g \rightarrow 0$
 $x_i^g \rightarrow x_i^{tot}$ as $n_g \rightarrow 0$



$$P = P_1 + P_2 = P_1^* x_i^g + P_2^* x_i^s \quad (\text{Raoult's Law})$$

$$P = P_2^* - x_i^g (P_2^* - P_1^*) \quad ①$$

$$P_1 = P x_i^g \rightarrow P = \frac{P_1^* x_i^g}{x_i^g} = \frac{P_1^* x_i^g}{x_i^s} \quad (\text{Dalton's Law})$$

$$P = P_2^* \left(1 + \frac{x_i^g}{P_1^*} (P_2^* - P_1^*) \right)^{-1} \quad ②$$

if $P_1^* > P_2^*$ then $x_i^g \geq x_i^s$

vapor "enriched" with more volatile component

3.81 Temperature-Composition Diagrams

Temperature-Composition Diagram

$$P = P_2^* - x_1^g (P_2^* - P_1^*)$$

$$P = P_2^* \left(1 + \frac{x_1^g}{P_1^*} (P_2^* - P_1^*) \right)^{-1}$$

$$P_1^* = P_1^*(T) \quad P_2^* = P_2^*(T)$$

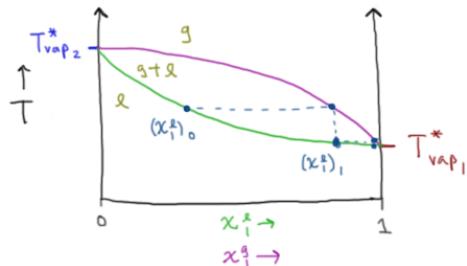
$$P_i^*(T_{\text{vap}_i}) = P$$

$T < \min(T_{\text{vap}_1}, T_{\text{vap}_2}) \rightarrow$ only l

$T > \max(T_{\text{vap}_1}, T_{\text{vap}_2}) \rightarrow$ only g

in between \rightarrow mixture of g+l

if $T_{\text{vap}_1}^* < T_{\text{vap}_2}^*$ then $x_1^g > x_1^l$



① start with mixture $0 < (x_i^g)_0 < 1$

② heat to vaporization $T > T_{\text{vap}_1}^*$

③ collect vapor $(x_i^g)_1 > (x_i^g)_0$

④ condense vapor $(x_i^g)_0 = (x_i^g)_1$

⑤ repeat n times until $(x_i^g)_n \rightarrow 1$

Basis of distillation

3.82 Mixing Energy

Energy of Mixing

$$\Delta_{\text{mix}} G = G_{\text{sol}}(T, P, \{n_i\}) - \sum_i G_i^*(T, P, n_i)$$

$$\Delta_{\text{mix}} G = \sum_i (M_i^{\text{sol}} - M_i^*) n_i$$

$$M_i^{\text{sol}} = M_i^* + RT \ln x_i \quad \text{if ideal}$$

$$\Delta_{\text{mix}} G_{\text{id}} = RT \sum_i n_i \ln x_i \quad n_i = n x_i$$

$$\boxed{\Delta_{\text{mix}} \bar{G}_{\text{id}} = RT \sum_i x_i \ln x_i}$$

$$\Delta_{\text{mix}} \bar{S}_{\text{id}} = - \left(\frac{\partial \Delta_{\text{mix}} \bar{G}_{\text{id}}}{\partial T} \right)_{P, \{n_i\}}$$

$$\boxed{\Delta_{\text{mix}} \bar{S}_{\text{id}} = - R \sum_i x_i \ln x_i}$$

$$\Delta_{\text{mix}} \bar{V}_{\text{id}} = \left(\frac{\partial \Delta_{\text{mix}} \bar{G}_{\text{id}}}{\partial P} \right)_{T, \{n_i\}}$$

$$\boxed{\Delta_{\text{mix}} \bar{V}_{\text{id}} = 0}$$

$$\Delta_{\text{mix}} \bar{G}_{\text{id}} = \Delta_{\text{mix}} \bar{H}_{\text{id}} - T \Delta_{\text{mix}} \bar{S}_{\text{id}}$$

$$\boxed{\Delta_{\text{mix}} \bar{H}_{\text{id}} = 0}$$

$\Delta_{\text{mix}} \bar{V}_{\text{id}} = 0$ because molecules have similar size and shape

$\Delta_{\text{mix}} \bar{H}_{\text{id}} = 0$ because molecules have similar interactions

3.83 Henry's Law

Henry's Law

most solutions are non-ideal



$$r_A \neq r_B$$

and / or

$$2(A \cdots B) \neq (A \cdots A) + (B \cdots B)$$

$P_i \rightarrow x_i P_i^*$ as $x_i \rightarrow 1$ Raoult's Law

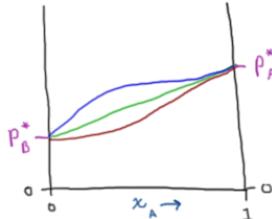
$P_i \rightarrow x_i k_{H,i}$ as $x_i \rightarrow 0$ Henry's Law

$k_{H,i} \rightarrow$ "Henry's Law Constant"

Reflects interactions between A and B

$k_{H,i} = P_i^*$ for ideal solutions

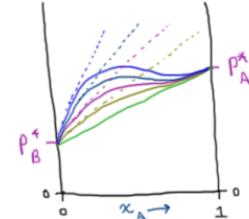
$$k_{H,i} = \left. \frac{\partial P}{\partial x_i} \right|_{x_i=0}$$



Raoult's Law

(+) Deviation

(-) Deviation



$A \cdots B = A \cdots A$
 $A \cdots B < A \cdots A$
 $A \cdots B > A \cdots A$



$$R_5 > R_4 > R_3 > R_2 > R_1$$



3.84 Activity

Activity

$$M_i^{\text{sol}} = M_i^*(x) + RT \ln(p_i / p_i^*)$$

if ideal $\rightarrow p_i = x_i p_i^*$

$$M_i^{\text{sol}} = M_i^* + RT \ln(x_i)$$

want replacement for x_i for non-ideal solutions

$$M_i^{\text{sol}} = M_i^*(x) + RT \left[\ln x_i + \alpha x_i^2 + \beta x_i^3 + \dots \right]$$

$$P_i = x_i p_i^* \exp(\alpha x_i^2 + \beta x_i^3 + \dots) = a_i p_i^*$$

$$a_i = x_i \exp(\alpha x_i^2 + \beta x_i^3 + \dots)$$

$a_i \rightarrow$ "activity"

$$a_i = p_i / p_i^* \quad \text{if ideal}$$

$a_i \rightarrow x_i \quad \text{as } x_i \rightarrow 1$

$$a_i \rightarrow \frac{x_i k_{H,i}}{p_i^*} \quad \text{as } x_i \rightarrow 0$$

$$M_i^{\text{sol}} = M_i^*(x) + RT \ln(a_i)$$

$$\gamma_i = a_i / x_i$$

$\gamma_i \rightarrow$ "activity coefficient"

ideal if $\{\gamma_i\} = 1$ for all $\{x_i\}$

3.85 Standard Activity

Standard Activity

$$\alpha_i = \frac{P_i}{P_i^*} \text{ "Raoult's law standard state"}$$

$\alpha_i \rightarrow x_i$ as $x_i \rightarrow 1$

$$\gamma_i = \frac{P_i}{P_i^* x_i} \quad \gamma_i = 1 \text{ when } P_i = P_i^* x_i$$

- solvent reference

- good for miscible solutions

$$\alpha_i = \frac{P_i}{k_{H,i}} \text{ "Henry's law standard state"}$$

$\alpha_i \rightarrow x_i$ as $x_i \rightarrow 0$

$$\gamma_i = \frac{P_i}{k_{H,i} x_i} \quad \gamma_i = 1 \text{ when } P_i = k_{H,i} x_i$$

- solute reference

- good at low concentrations

$$\mu_i^{\text{sol}(R)} = \mu_i^* + RT \ln(\alpha_{i,R})$$

$$\mu_i^{\text{sol}(H)} = \mu_i^* + RT \ln(\alpha_{i,H})$$

$$\mu_i^{\text{sol}(H)} = \mu_i^{\text{sol}(R)} + RT \ln\left(\frac{k_{H,i}}{P_i}\right)$$

3.86 Molarity and Molality

Molality and Molarity

$x_1 \approx 1 \rightarrow$ solvent (Raoult's Law)

$x_2 \approx 0 \rightarrow$ solute (Henry's Law)

$$\alpha_1 = \frac{P_1}{P_1^*} \quad \gamma_1 = \frac{\alpha_1}{x_1} = \frac{P_1}{x_1 P_1^*}$$

$$x_2 = \frac{n_2}{n_1 + n_2} \quad \text{"mole fraction"}$$

$$m_2 = \frac{n_2}{\text{kg's solvent}} \quad \text{"molality"}$$

$$c_2 = \frac{n_2}{\text{L's solution}} \quad \text{"molarity"}$$

$\alpha_{2x} \rightarrow x_2$ as $x_2 \rightarrow 0$

$\alpha_{2m} \rightarrow m_2$ as $m_2 \rightarrow 0$

$\alpha_{2c} \rightarrow c_2$ as $c_2 \rightarrow 0$

$$\gamma_{2x} = \frac{\alpha_{2x}}{x_2} \quad \alpha_{2x} = \frac{P_2}{k_{H,2x}}$$

$$\gamma_{2m} = \frac{\alpha_{2m}}{m_2} \quad \alpha_{2m} = \frac{P_2}{k_{H,2m}}$$

$$\gamma_{2c} = \frac{\alpha_{2c}}{c_2} \quad \alpha_{2c} = \frac{P_2}{k_{H,2c}}$$

3.87 Non-Volatile Activity

Non-volatile Activity

$$a_{2m} = \frac{P_2}{k_{H,m}} \quad P_2 \ll 1 \text{ bar}$$

$$a_{2m} \rightarrow m_2 \quad \text{as } M_2 \rightarrow 0 \quad a_1 = \frac{P_1}{P_1^*}$$

$$a_1 \rightarrow x_1 \quad \text{as } x_1 \rightarrow 1$$

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \quad \text{if } n_1 \gg n_2$$

$$m_2 = \frac{n_2}{n_1 M_1} \quad M_1 \rightarrow \begin{array}{l} \text{molar mass of solvent} \\ \text{in (kg/mol)} \end{array}$$

$$x_2 \approx m_2 M_1 \quad \text{for } m_2 \approx 0$$

$$\ln(a_1) \approx \ln(x_1) = \ln(1-x_2) \approx -x_2 \approx -m_2 M_1$$

$$\ln(a_1) \approx -m_2 M_1 \quad \text{for dilute solutions}$$

$$\phi = \frac{-\ln(a_1)}{m_2 M_1} \quad \phi \rightarrow \text{"osmotic coefficient"}$$

$$\boxed{\ln(a_1) = -m_2 \phi M_1}$$

$\phi = 1$ for ideal solutions

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 = n_1 d(\ln a_1) + n_2 d(\ln a_2)$$

$$n_2 = m_2 M_1 n_1$$

$$n_1 d(-m_2 \phi M_1) + m_2 M_1 n_1 d(\ln a_2) = 0$$

$$\cancel{M_1 n_1 d(m_2 \phi)} = \cancel{M_1 n_1 m_2 d(\ln(x_{2m} m_2))}$$

$$m_2 d\phi + \phi dm_2 = m_2 (d \ln x_{2m} + dm_2)$$

$$\int d \ln x_{2m} = \int d\phi + \int \frac{\phi-1}{m_2} dm_2$$

when $m_2 = 0$, $x_{2m} = 1$ and $\phi = 1$

$$\int_0^1 d \ln x_{2m} = \int_1^\phi d\phi + \int_0^{m_2} \frac{\phi-1}{m_2} dm_2'$$

$$\boxed{\ln x_{2m} = \phi - 1 + \int_0^{m_2} \left(\frac{\phi-1}{m_2} \right) dm_2'}$$

3.88 Colligative Properties

Colligative Properties

properties that depend only on the concentration of solute particles in dilute solution, and not on their identity

- freezing point depression
- boiling point elevation
- osmotic pressure

$$\Delta T_{\text{fus}} = -K_f m_2$$

$$\Delta T_{\text{vap}} = +K_b m_2$$

$$\Pi = c_2 RT$$

3.89 Freezing Point Depression

Freezing Point Depression +
 Boiling Point Elevation

$$M_i^s(T_{fus}) = M_i^*(T_{fus})$$

$$M_{i,1}^{s+1} = M_i^*(x_1) + RT \ln(a_1)$$

$$M_i^s(T_{fus}) = M_i^*(T_{fus}) + RT \ln(a_1)$$

$$\ln a_1 = \frac{M_i^s - M_i^*}{RT}$$

$$\left(\frac{\partial (\bar{G}/T)}{\partial T} \right)_{P, x_1} = \left(\frac{\partial (M_i/T)}{\partial T} \right)_{P, x_1} = -\frac{\bar{H}_i}{T^2}$$

$$\left(\frac{\partial \ln a_1}{\partial T} \right)_{P, x_1} = \frac{\bar{H}_i^2 - \bar{H}_i^s}{RT^2} = \frac{\Delta_{fus}\bar{H}_i}{RT^2}$$

$$\int d\ln a_1 = \int_{T_{fus}^*}^{T_{fus}} \frac{\Delta_{fus}\bar{H}_i}{RT^2} dT$$

$$\ln a_1 \approx \ln x_1 = \ln(1-x_2) \approx -x_2$$

$$x_1 \approx 1 \rightarrow a_1 \approx x_1 \quad \ln(1-x) \approx -x$$

$$-x_2 = \frac{\Delta_{fus}\bar{H}_i}{R} \int_{T_{fus}^*}^{T_{fus}} \frac{dT}{T^2} \quad x_2 \approx M_1 m_2 \quad \text{if dilute}$$

$$-M_1 m_2 = -\frac{\Delta_{fus}\bar{H}_i}{R} \left(\frac{1}{T_{fus}} - \frac{1}{T_{fus}^*} \right) \quad T_{fus} \approx T_{fus}^* \quad \Delta T_{fus} = T_{fus}^* - T_{fus}$$

$$M_1 m_2 = \frac{\Delta_{fus}\bar{H}_i}{R} \left(\frac{T_{fus}^* - T_{fus}}{T_{fus}^* T_{fus}} \right) = -\frac{\Delta_{fus}\bar{H}_i}{R} \left(\frac{\Delta T_{fus}}{(T_{fus}^*)^2} \right)$$

$$\Delta T_{fus} = -\frac{M_1 R (T_{fus}^*)^2}{\Delta_{fus}\bar{H}_i} \cdot m_2$$

$K_f = \frac{M_1 R (T_{fus}^*)^2}{\Delta_{fus}\bar{H}_i}$

$K_b = \frac{M_1 R (T_{vap}^*)^2}{\Delta_{vap}\bar{H}_i}$

$\Delta T_{fus} = -K_f m_2$

$\Delta T_{vap} = +K_b m_2$

usually $\frac{(T_{fus}^*)^2}{\Delta_{fus}\bar{H}_i} > \frac{(T_{vap}^*)^2}{\Delta_{vap}\bar{H}_i} \rightarrow K_f > K_b$

3.90 Osmotic Pressure

Osmotic Pressure

$$\mu_i^*(T, P) = \mu_i^{sol}(T, P + \Pi, a_i)$$

$$\mu_i^*(T, P) = \mu_i^*(T, P + \Pi) + RT \ln(a_i)$$

$$\underbrace{\mu_i^*(T, P + \Pi) - \mu_i^*(T, P)}_{\int_P^{P+\Pi} \left(\frac{\partial \mu_i^*}{\partial P'} \right) dP'} = -RT \ln(a_i)$$

$$\int_P^{P+\Pi} \left(\frac{\partial \mu_i^*}{\partial P'} \right) dP' = \int_P^{P+\Pi} \bar{V}_i^* dP' = \bar{V}_i^* \Pi$$

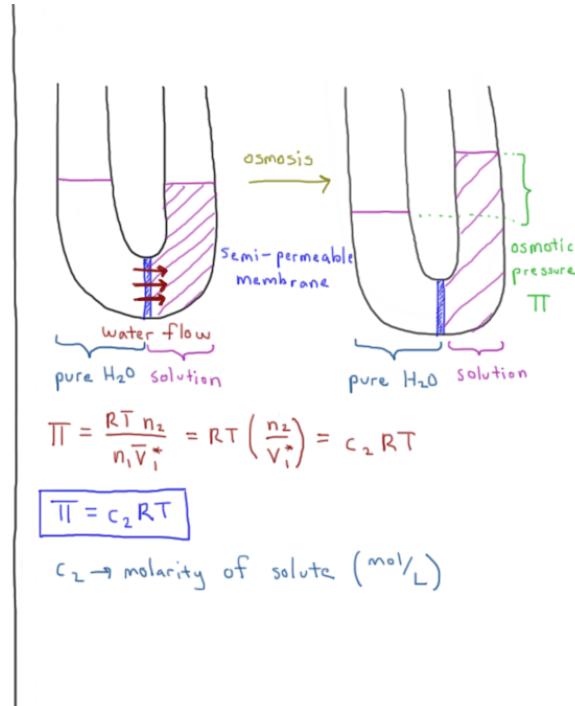
$$\left(\frac{\partial \mu_i^*}{\partial P} \right)_T = \bar{V}_i^* \rightarrow \bar{V}_i^* \approx \text{constant versus } P$$

$$\Pi \bar{V}_i^* = -RT \ln(a_i) \quad (x_1 \approx 1)$$

$$\ln a_i \approx \ln x_1 = \ln(1-x_2) \approx -x_2 \text{ if dilute}$$

$$x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} \quad \text{if } n_1 \gg n_2$$

$$\Pi \bar{V}_i^* = -RT(-x_2) = RT \frac{n_2}{n_1}$$



3.91 Electrolyte Activity

Electrolyte Activity

"Electrolyte": substance that ionizes when dissolved in solution

Coulomb's Law \rightarrow Strong Interactions \rightarrow Non-Ideal at Low χ_2



$$M_2 = M_2^0 + RT \ln(a_2) = v_+ M_+ + v_- M_-$$

$$M_+ = M_+^0 + RT \ln a_+ \quad M_- = M_-^0 + RT \ln a_-$$

$$\ln a_2 = v_+ \ln a_+ + v_- \ln a_-$$

$$a_2 = a_+^v a_-^v = a_\pm^v \quad v = v_+ + v_-$$

a_\pm → "mean ionic activity"

$$a_+ = m_+ \gamma_+ \quad a_- = m_- \gamma_-$$

m_i → molarity γ_i → activity coefficient

$$a_2 = a_\pm^v = (m_+^v m_-^v)(\gamma_+^v \gamma_-^v)$$

$$m_\pm^v = m_+^v m_-^v$$

m_\pm → "mean ionic molality"

$$\gamma_\pm^v = \gamma_+^v \gamma_-^v$$

γ_\pm → "mean ionic activity coefficient"

$$\phi = \frac{-\ln(a_1)}{v m_2 M_1}$$

$$\ln \gamma_\pm = \phi - 1 + \int_0^{m_2} \left(\frac{\phi-1}{m'} \right) dm'$$

$$\Delta T_{fus} = -v K_f m_2$$

$$\Delta T_{vap} = +v K_b m_2$$

$$\Pi = v c_2 RT$$

3.92 Debye-Hückel Law

Debye-Hückel Limiting Law

$\{i\}$ → ions

$$\ln \tau_i = \frac{-K z_i}{8\pi \epsilon_0 \epsilon_r k_b T}$$

$$\ln \tau_{\pm} = \frac{-|q_+ q_-| K}{8\pi \epsilon_0 \epsilon_r k_b T}$$

$\frac{1}{K}$ → "Debye screening length" (m)

ϵ_r → "dielectric constant" (unitless)

$\epsilon_r \approx 1-100$ (80.1 for H₂O at 20°C)

$$K = \left(\frac{2e^2 N_A (1000 I_c)}{\epsilon_0 \epsilon_r k_b T} \right)^{1/2}$$

I_c → "ionic strength" (mol/L)

$$I_c = \frac{1}{2} \sum_i z_i^2 c_i$$

z_i → integer ionic charge (unitless)

c_i → molarity of ions (mol/L)

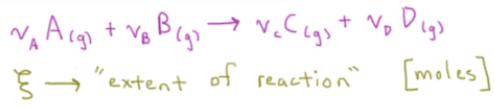
$$K \propto \sqrt{I_c} \propto \sqrt{\{c_i\}}$$

ϕ → expanded as series in $C^{1/2}$

exact at very low concentrations
for all ions

3.93 Extent of Reaction

Extent of Reaction



$$\{i\} \rightarrow \text{reactants} \quad \{j\} \rightarrow \text{products}$$

$$n_i = n_{i,0} - v_i \xi \quad n_j = n_{j,0} + v_j \xi$$

$$dn_i = -v_i d\xi \quad dn_j = +v_j d\xi$$

$$G = G(T, P, n_A, n_B, n_C, n_D)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, \{n_i\}} dT + \left(\frac{\partial G}{\partial P}\right)_{T, \{n_i\}} dP + \sum_{i=1}^{ABCD} \left(\frac{\partial G}{\partial n_i}\right)_{T, P, \{n_j \neq i\}} dn_i$$

$$\frac{\partial G}{\partial T} = -S \quad \frac{\partial G}{\partial P} = V \quad \frac{\partial G}{\partial n_i} = \mu_i$$

$$dG = \sum_i^{\text{ABCD}} \mu_i dn_i \quad \text{if } dT = dP = 0$$

$$dG = (v_C \mu_C + v_D \mu_D - v_A \mu_A - v_B \mu_B) d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T, P} = v_C \mu_C + v_D \mu_D - v_A \mu_A - v_B \mu_B$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{T, P}$$

$\Delta_r G \rightarrow$ "Gibbs energy change of reaction"

change in G per mole of reaction extent (ξ)

3.94 Equilibrium Constant

Equilibrium Constant

$$\Delta_r G = \left(\frac{\partial G}{\partial \bar{S}} \right)_{T, P} = \sum_j^{\text{products}} \nu_j M_j - \sum_i^{\text{reactants}} \nu_i M_i$$

$$M_i(T, P) = M_i^\circ(T) + RT \ln \left(\frac{P_i}{P^\circ} \right)$$



$$\Delta_r G = \sum_j^{\text{products}} \nu_j (M_j^\circ(T) + RT \ln(P_j/P^\circ)) - \sum_i^{\text{reactants}} \nu_i (M_i^\circ(T) + RT \ln(P_i/P^\circ))$$

$$\Delta_r G = \nu_C M_C^\circ(T) + \nu_D M_D^\circ(T) - \nu_A M_A^\circ(T) - \nu_B M_B^\circ(T) + RT [\nu_C \ln \left(\frac{P_C}{P^\circ} \right) + \nu_D \ln \left(\frac{P_D}{P^\circ} \right) - \nu_A \ln \left(\frac{P_A}{P^\circ} \right) - \nu_B \ln \left(\frac{P_B}{P^\circ} \right)]$$

$$\boxed{\Delta_r G = \Delta_r G^\circ + RT \ln Q}$$

$\Delta_r G^\circ \rightarrow$ "standard reaction Gibbs energy"

$$\Delta_r G^\circ = \sum_j^{\text{products}} \nu_j M_j^\circ(T) - \sum_i^{\text{reactants}} \nu_i M_i^\circ(T)$$

$\Delta_r G^\circ = \Delta_r G$ when $P_i = P^\circ$ for all $\{i\}$

$$Q = \frac{(P_C/P^\circ)^{\nu_C} (P_D/P^\circ)^{\nu_D}}{(P_A/P^\circ)^{\nu_A} (P_B/P^\circ)^{\nu_B}}$$

$Q =$ "reaction quotient"

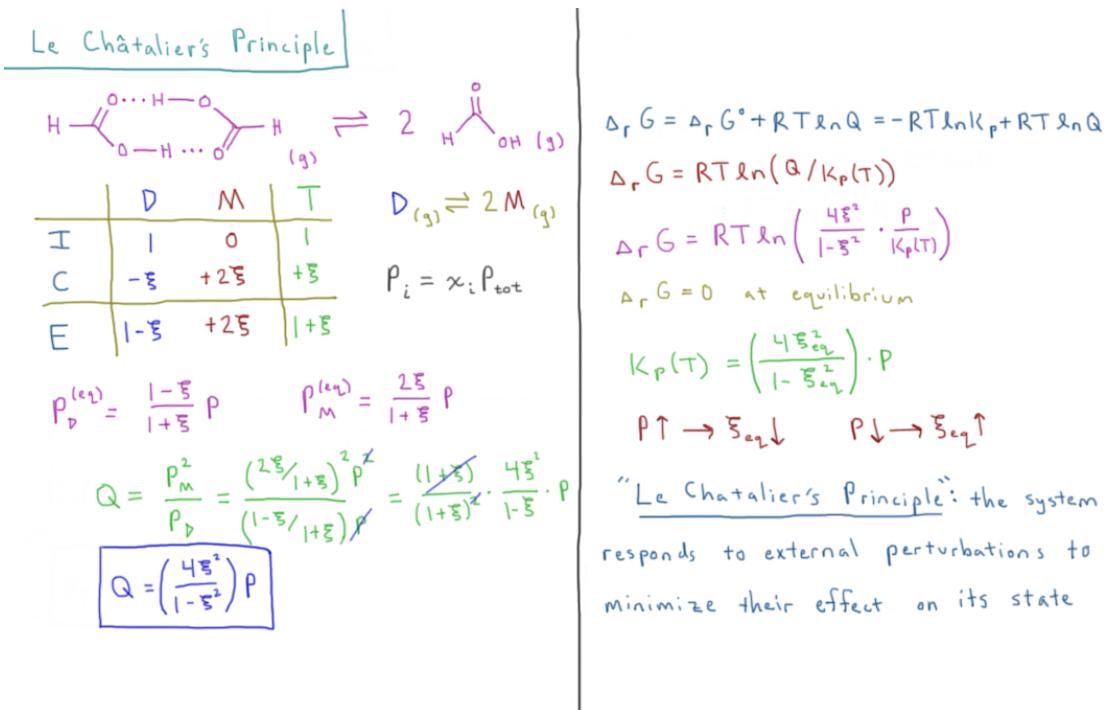
$$\left(\frac{\partial G}{\partial \bar{S}} \right)_{T, P} = \Delta_r G = 0 \text{ at equilibrium}$$

$$\Delta_r G^\circ = -RT \ln \left(\frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq} \quad \{P_i\} \text{ [bar]} \quad P^\circ = 1 \text{ bar}$$

$Q_{eq} \rightarrow K_p \rightarrow$ "equilibrium constant"

$$\boxed{\Delta_r G^\circ = -RT \ln K_p(T)}$$

3.95 Le Chatelier's Principle



3.96 Concentration Equilibrium Constant

Concentration Equilibrium Constant

$$PV = nRT \quad c = \frac{n}{V} = \frac{P}{RT}$$



$$P_i^{v_i} = c_i^{v_i} (RT)^{v_i}$$

$$K_p = \frac{\left(\frac{P_c}{P^\circ}\right)^{v_c} \left(\frac{P_D}{P^\circ}\right)^{v_D}}{\left(\frac{P_A}{P^\circ}\right)^{v_A} \left(\frac{P_B}{P^\circ}\right)^{v_B}} = \frac{\left(\frac{c_c}{c^\circ}\right)^{v_c} \left(\frac{c_D}{c^\circ}\right)^{v_D}}{\left(\frac{c_A}{c^\circ}\right)^{v_A} \left(\frac{c_B}{c^\circ}\right)^{v_B}} \left(\frac{RT}{P^\circ}\right)^{v_c + v_D - v_A - v_B}$$

$$K_c = \frac{c_c^{v_c} c_D^{v_D}}{c_A^{v_A} c_B^{v_B}}$$

$$P^\circ = 1 \text{ bar}$$

$$c^\circ = 1 \text{ mol/L} = 1 \text{ M}$$

$$V = V_c + V_D - V_A - V_B$$

$$K_p = K_c \left(\frac{c^\circ RT}{P^\circ} \right)^V$$

choose correct units of c , P , and R
based on P° and c°

3.97 Gibbs Energy of Reaction

Standard Reaction Gibbs Energy



$$\Delta_r G^\circ = -RT \ln K_p(T) \quad G = H - TS$$

$$\Delta_f G^\circ = \Delta_f H^\circ - T \Delta_f S^\circ$$

$$\Delta_f G^\circ = \Delta_f H^\circ - T \Delta_f S^\circ$$

$\Delta_f G^\circ \rightarrow$ "standard Gibbs energy of formation"

$\{\Delta_f G^\circ\} \rightarrow$ compiled in tables

$$\begin{aligned} \Delta_r G^\circ &= v_C \Delta_f G^\circ [C] + v_D \Delta_f G^\circ [D] \\ &\quad - v_A \Delta_f G^\circ [A] - v_B \Delta_f G^\circ [B] \end{aligned}$$

$$\boxed{\Delta_r G^\circ = \sum_j^{products} v_j \Delta_f G^\circ [J] - \sum_i^{reactants} v_i \Delta_f G^\circ [I]}$$

compound	$\Delta_f G^\circ (\text{kJ/mol})$
$C_6H_{12}O_6(s)$	-910.52
$O_2(g)$	0.0
$CO_2(g)$	-394.39
$H_2O(g)$	-228.58



$$\begin{aligned} \Delta_r G^\circ &= 6(-228.58) + 6(-394.39) \\ &\quad - 1(-910.52) - 6(0.0) = -2827.30 \end{aligned}$$

$$\boxed{\Delta_r G^\circ = -2827.30 \text{ kJ/mol}}$$

3.98 Equilibrium Example

Extent of Reaction Example



	Z	E	T
I	1	0	1
C	$-\xi$	$+\xi$	0
E	$1-\xi$	$+\xi$	1

$$P_z = \left(\frac{1-\xi}{1}\right) P = 1-\xi \quad P_E = \left(\frac{\xi}{1}\right) P = \xi$$

$$K_p = \frac{P_E}{P_z} = \frac{\xi}{1-\xi}$$

$$\Delta_f G^\circ = -RT \ln K_p(T) = \Delta_f G^\circ [E] - \Delta_f G^\circ [Z]$$

$$\Delta_f G^\circ [Z] = 65.9 \text{ kJ/mol}$$

$$\Delta_f G^\circ [E] = 63.0 \text{ kJ/mol}$$

$$\Delta_f G^\circ = (63.0 \text{ kJ/mol}) - (65.9 \text{ kJ/mol}) = -2.9 \text{ kJ/mol}$$

$$K_p(T) = \exp(-\Delta_f G^\circ / RT) = \exp\left(-(-2.9 \text{ kJ/mol}) / ((0.008314 \frac{\text{kJ}}{\text{mol K}})(298 \text{ K}))\right)$$

$$K_p(298 \text{ K}) = 3.222 = \frac{\xi}{1-\xi}$$

$$(1-\xi)(3.222) = \xi \quad \xi = \frac{3.222}{4.222}$$

$$\boxed{\xi = 0.76}$$

$$(P_z)_{eq} = P(1-\xi) = (1 \text{ bar})(1-0.76) = 0.24 \text{ bar}$$

$$(P_E)_{eq} = P(\xi) = (1 \text{ bar})(0.76) = 0.76 \text{ bar}$$

$$\boxed{(P_z)_{eq} = 0.24 \text{ bar}}$$

$$\boxed{(P_E)_{eq} = 0.76 \text{ bar}}$$

3.99 Reaction Direction

Reaction Quotient

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G = -RT \ln K + RT \ln Q$$

$$\Delta_r G = RT \ln(Q/K)$$

Q	$\Delta_r G$	reaction status
$>K$	>0	reverse spontaneous
$<K$	<0	forward spontaneous
$=K$	$=0$	equilibrium

3.100 Reaction Spontaneity

Reaction Spontaneity

$\Delta_r G > 0 \rightarrow$ endergonic \rightarrow not spontaneous

$\Delta_r G < 0 \rightarrow$ exergonic \rightarrow spontaneous

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

$\Delta_r H > 0 \rightarrow$ endothermic

$\Delta_r H < 0 \rightarrow$ exothermic

$\Delta_r S > 0 \rightarrow$ entropically favored

$\Delta_r S < 0 \rightarrow$ entropically disfavored

sign of			
$\Delta_r H$ (all T)	$\Delta_r S$ (all T)	$\Delta_r G$ ($T < \frac{\Delta_r H}{\Delta_r S}$)	$\Delta_r G$ ($T > \frac{\Delta_r H}{\Delta_r S}$)
(-)	(+)	(-)	(-)
(+)	(+)	(+)	(-)
(-)	(-)	(-)	(+)
(+)	(-)	(+)	(+)

$T < \frac{\Delta_r H}{\Delta_r S}$ enthalpically controlled

$T > \frac{\Delta_r H}{\Delta_r S}$ entropically controlled

3.101 Van't Hoff Equation

Van't Hoff Equation

$$\left(\frac{\partial \Delta_r G^\circ / T}{\partial T} \right)_p = - \frac{\Delta_r H^\circ}{T^2} \quad \text{Gibbs-Helmholtz equation}$$

$$\Delta_r G^\circ(T) = -RT \ln K_p(T)$$

$$\ln K_p(T) = -\frac{1}{R} \left(\frac{\Delta_r G^\circ(T)}{T} \right)$$

$$\frac{d \ln K_p(T)}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

sign of $\Delta_r H^\circ$	effect on reaction when $T \uparrow$
(+)	$\ln K \uparrow \rightarrow \Delta_r G^\circ \downarrow \rightarrow \ddot{S} \uparrow$
(-)	$\ln K \downarrow \rightarrow \Delta_r G^\circ \uparrow \rightarrow \ddot{S} \downarrow$
0	$\ln K \rightarrow \Delta_r G^\circ \rightarrow \ddot{S} \rightarrow$

$$\int_{\ln K_p(T_1)}^{\ln K_p(T_2)} d \ln K_p(T) = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ}{RT^2} dT$$

$$\ln \left(\frac{K_p(T_2)}{K_p(T_1)} \right) = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Assumes $\Delta_r H^\circ \approx \text{constant}$ from $T_1 \rightarrow T_2$

$$\ln K_p(T) \propto \frac{1}{T} \rightarrow \text{slope is } -\frac{\Delta_r H^\circ}{T}$$

$$\ln K_p(T_2) = \ln K_p(T_1) + \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{T^2} dT$$

valid over large range of T

3.102 Fugacity Equilibrium Constant

Fugacity Equilibrium Constant

$$\mu_i(T, P) = \mu_i^\circ(T) + RT \ln \left(\frac{f_i}{f_i^\circ} \right) \quad \text{real gases}$$

$f^\circ = P^\circ = 1 \text{ bar}$



$$\Delta_f G = N_C \mu_C + N_D \mu_D - N_A \mu_A - N_B \mu_B$$

$$\Delta_f G^\circ = N_C \mu_C^\circ + N_D \mu_D^\circ - N_A \mu_A^\circ - N_B \mu_B^\circ$$

$$\Delta_f G = \Delta_f G^\circ + RT \ln \left(\frac{(f_C/f^\circ)^{N_C} (f_D/f^\circ)^{N_D}}{(f_A/f^\circ)^{N_A} (f_B/f^\circ)^{N_B}} \right)$$

$$\Delta_f G = 0 \text{ at equilibrium} \rightarrow \Delta_f G^\circ = -RT \ln K_f$$

$$K_f(T) = \left(\frac{(f_C/f^\circ)^{N_C} (f_D/f^\circ)^{N_D}}{(f_A/f^\circ)^{N_A} (f_B/f^\circ)^{N_B}} \right)_{\text{eq}}$$

"Thermodynamic equilibrium constant"

exact for all gases at all conditions

3.103 Activity Equilibrium Constant

Activity Equilibrium Constant

$$\mu_i(T) = \mu_i^\circ(T) + RT \ln(a_i)$$

general system

a_i → activity of species i

$$a_i = \frac{P_i}{P^\circ} \text{ for gases } (P^\circ = 1 \text{ bar})$$

$$a_i \rightarrow x_i \text{ as } x_i \rightarrow 1 \quad \mu_i^\circ = \mu_i^* \text{ for solvents}$$

$$a_i \rightarrow m_i \text{ as } m_i \rightarrow 0 \quad \mu_i^\circ = \mu_i(1 \text{ M})$$

$$\rightarrow c_i \text{ as } c_i \rightarrow 0 \quad \mu_i^\circ = \mu_i(1 \text{ M})$$

for solutes

all phases on same footing



$$\Delta_r G = \Delta_r G^\circ + RT \ln \left(\frac{a_c^{v_c} a_d^{v_d}}{a_a^{v_a} a_b^{v_b}} \right)$$

"Lewis Equation"

$$a^\circ = 1, 1 \text{ bar}, 1 \text{ mol/L}, 1 \text{ mol/kg}, \dots$$

$$Q_A = \frac{a_c^{v_c} a_d^{v_d}}{a_a^{v_a} a_b^{v_b}} \quad \text{activity quotient}$$

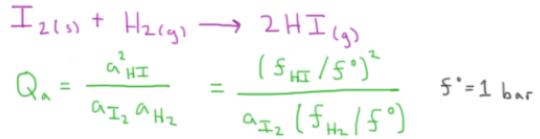
$$\Delta_r G = \Delta_r G^\circ + RT \ln Q_A$$

$$\Delta_r G^\circ = -RT \ln K_a(T)$$

$$K_a(T) = (Q_a)_{eq}$$

3.104 Condensed Phase Activity

Condensed Phase Activity



need to define α_i for (s) and (l)

$$\mu_i(T, P) = \mu_i^\circ(T) + RT \ln(\alpha_i)$$

$$d\mu_i(T, P) = \left(\frac{\partial \mu_i}{\partial P}\right)_T dP + \left(\frac{\partial \mu_i}{\partial T}\right)_P dT$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i \quad \left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}_i$$

$$\text{if } dT=0 \rightarrow d\mu_i = \bar{V}_i dP = RT d\ln \alpha_i$$

$$\bar{V}_i dP = RT d\ln \alpha_i$$

$$\int_0^{\ln \alpha_i} d\ln \alpha_i = \int_1^P \frac{\bar{V}}{RT} dP'$$

for solids and liquids, $\bar{V} \approx \text{constant}$

$$\ln(\alpha_i) = \frac{\bar{V}(P-1)}{RT}$$

$$\text{at } P = 1 \text{ bar } \ln(\alpha_i) = 0 \rightarrow \alpha_i = 1$$

$$\alpha_{(s)} = 1 \text{ and } \alpha_{(l)} = 1 \text{ at } P^\circ$$

generally not included in Q_a

$$Q_a = \frac{(f_{HI}/f^\circ)^2}{(f_{H_2}/f^\circ)}$$

3.105 Electrochemical Cells

Electrochemical Cells



Sn → oxidized

Ni → reduced

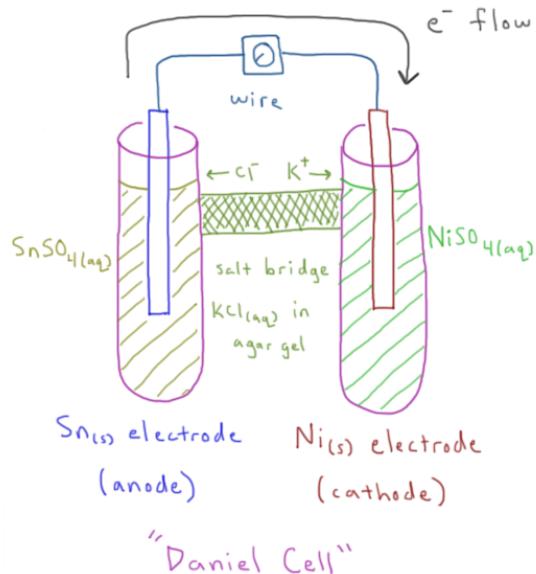
want to separate reactions
to create current and do work

reduction
at cathode

oxidation
at anode

reduction
is
gain

oxidation
is
loss

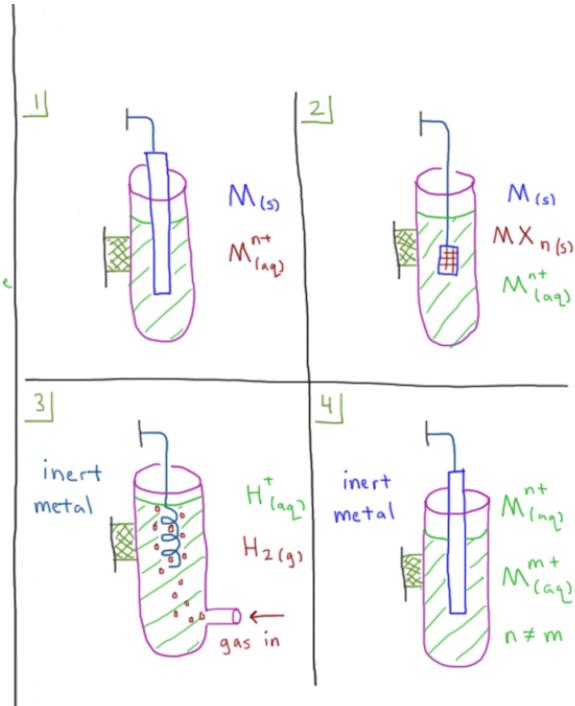
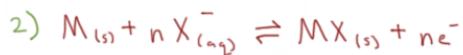
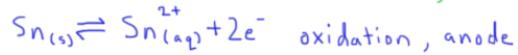


3.106 Half Cell Reactions

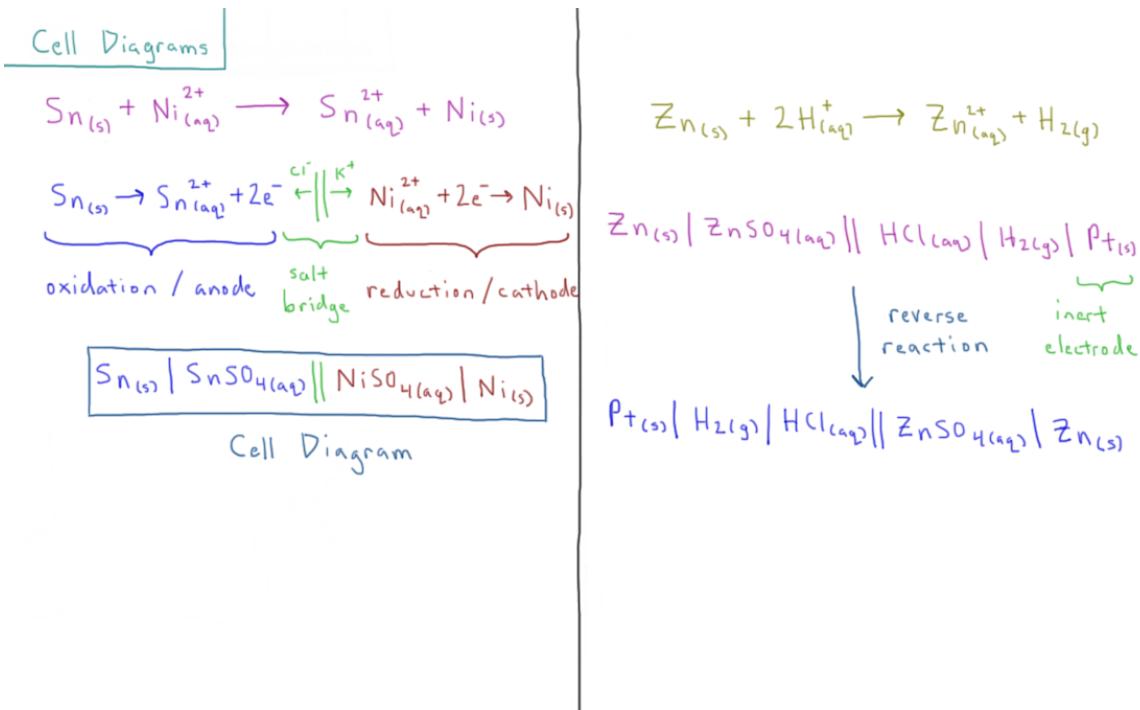
Half Cell Reactions



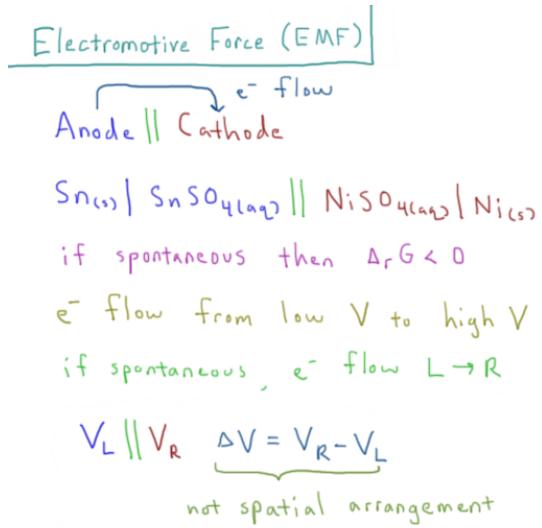
can separate reaction into
2 half cell reactions



3.107 Cell Diagrams



3.108 Electromotive Force (EMF)



E → "electromotive force"

$$E = \Delta V|_{I=0}$$

$$\lim_{I \rightarrow 0} (\Delta V(I)) = E \quad \text{if cell is reversible}$$

sign of E	reaction status
(+)	spontaneous
(-)	not spontaneous
0	at equilibrium

3.109 Nernst Equation

Nernst Equation

$$\text{Anode} \parallel \text{Cathode}$$

$n \text{ moles } e^-$

$$\Delta V = V_R - V_L \quad E = \Delta V|_{I=0}$$

$E > 0 \rightarrow \Delta_r G < 0 \rightarrow \text{spontaneous reaction}$

total charge $q = n \cdot N_A \cdot q_e = n F$

$F \rightarrow \text{"Faraday's constant"}$
total charge of one mole of electrons

$$F = N_A q_e = (6.022 \cdot 10^{23} \text{ mol}^{-1})(1.602 \cdot 10^{-19} \text{ C})$$

$$F = 96,485 \text{ C/mol}$$

$$w_{elec} = q \Delta V = n F E$$

$$\Delta G = -w_{non-pv} = -w_{elec}$$

$$\boxed{\Delta_r G = -n F E_{cell}} \text{ Nernst equation}$$

$$\Delta_r G^\circ = -n F E_{cell}^\circ = -RT \ln K$$

$$\boxed{E_{cell}^\circ = \frac{RT}{n F} \ln K}$$

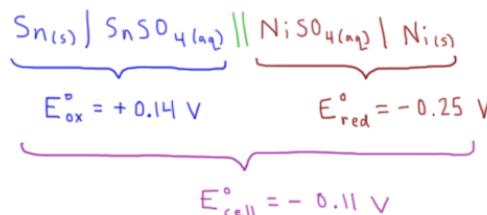
$$E_{cell} = E_{cell}^\circ \text{ when } \{a_i\} = 1$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q = -n F E_{cell} = -n F E_{cell}^\circ + RT \ln Q$$

$$\boxed{E_{cell} = E_{cell}^\circ - \frac{RT}{n F} \ln Q}$$

3.110 Standard Reduction Potential

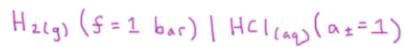
Standard Reduction Potential



$$\Delta_r G^{\circ} = \Delta_{ox} G^{\circ} + \Delta_{red} G^{\circ}$$

$$E_{cell}^{\circ} = E_{ox}^{\circ} + E_{red}^{\circ}$$

$$E_{red}^{\circ} = E_{cell}^{\circ} - E_{ox}^{\circ}$$



"standard hydrogen electrode" (SHE)

$$E_{ox}^{\circ}[\text{SHE}] = -E_{red}^{\circ}[\text{SHE}] = 0 \text{ V}$$

$$E_{red}^{\circ}[\text{1/2 cell}] = E_{cell}^{\circ}[\text{SHE} | \text{1/2 cell}]$$

$$E_{ox}^{\circ} = -E_{red}^{\circ}$$

$$E_{cell}^{\circ} = E_{red}^{\circ}[R] - E_{red}^{\circ}[L]$$

$\{E_{red}^{\circ}\} \rightarrow \text{tables}$

3.111 Electrochemistry Example

Electrochemistry Example

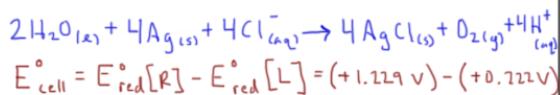
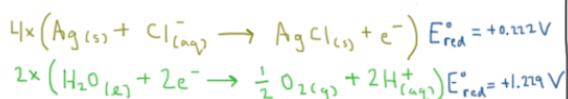
Calculate E_{cell}° , E_{cell} , $\Delta_f G^{\circ}$, and $\Delta_f G$ for

$$\text{Ag}_{(s)} \mid \text{AgCl}_{(s)} \mid \text{HCl}_{(\text{aq})} \parallel \text{HCl}_{(\text{aq})} \mid \text{O}_2_{(\text{g})} \mid \text{H}_2\text{O}_{(\text{l})}$$

0.1 M 0.2 M 0.8 bar

anode

cathode



$$E_{\text{cell}}^{\circ} = +1.007 \text{ V}$$

$$\Delta_f G^{\circ} = -nF E_{\text{cell}}^{\circ} = -(4)(96,485 \text{ C/mol})(+1.007 \text{ V})$$

$$\Delta_f G^{\circ} = -388.6 \text{ kJ/mol}$$

$$\Delta_f G = \Delta_f G^{\circ} + RT \ln Q$$

$$Q = \frac{\alpha_{\text{AgCl}}^4 \alpha_{\text{O}_2} \alpha_{\text{H}^+}^4}{\alpha_{\text{H}_2\text{O}}^2 \alpha_{\text{Ag}}^4 \alpha_{\text{Cl}^-}^4} \quad \alpha_{\text{AgCl}} = \alpha_{\text{Ag}} = \alpha_{\text{H}_2\text{O}} = 1$$

$$Q = \frac{(0.8)(0.2)^4}{(0.1)^4} = 12.8$$

$$\Delta_f G = (-388.6 \text{ kJ/mol}) + (0.008314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}})(298 \text{ K}) \cdot \ln(12.8)$$

$$\Delta_f G = -382.3 \text{ kJ/mol}$$

$$\Delta_f G = -nF E_{\text{cell}}$$

$$E_{\text{cell}} = \frac{-\Delta_f G}{nF} = \frac{-(-382.3 \text{ kJ/mol})}{(4)(96,485 \text{ C/mol})} = 9.906 \cdot 10^{-4} \text{ kJ/C}$$

$$E_{\text{cell}} = +0.991 \text{ V} \quad 1 \text{ V} = 1 \text{ J/C}$$

3.112 Electrochemical Enthalpy and Entropy

Electrochemical Enthalpy and Entropy

$$\Delta_r G = -nF E_{\text{cell}}$$

$$\Delta_r S = - \left(\frac{\partial \Delta_r G}{\partial T} \right)_P = - \frac{\partial}{\partial T} (-nF E_{\text{cell}}) = nF \frac{\partial E_{\text{cell}}}{\partial T}$$

$$\boxed{\Delta_r S = +nF \left(\frac{\partial E_{\text{cell}}}{\partial T} \right)_P}$$

$$\Delta_r G = \Delta_r H - T \Delta_r S$$

$$\Delta_r H = \Delta_r G + T \Delta_r S$$

$$\boxed{\Delta_r H = nF \left[T \left(\frac{\partial E_{\text{cell}}}{\partial T} \right)_P - E_{\text{cell}} \right]}$$

measure E_{cell} over range of T
interpolate $E_{\text{cell}}(T)$ as polynomial

$$\text{compute } \frac{\partial E_{\text{cell}}(T)}{\partial T}$$

compute $\Delta_r H, \Delta_r S, \Delta_r G$ versus T

3.113 Ionic Gibbs Energy

Ionic Gibbs Energy



$$\Delta_f G^\circ = -n F E^\circ_{cell}$$

$$E^\circ_{cell} = E^\circ_{red, R} - E^\circ_{red, L} = (0.0 V) - (-0.136 V)$$

$$\Delta_f G^\circ = -(2)(96,485 \text{ C/mol})(+0.136 \text{ V})$$

$$\Delta_f G^\circ = -26.2 \frac{\text{kJ}}{\text{mol}} \quad 1 \text{ V} = 1 \text{ J/C}$$

$$\Delta_r G^\circ = \Delta_f G^\circ[H_2(g)] + \Delta_f G^\circ[Sn^{2+}]$$

$$- \Delta_f G^\circ[Sn_{(s)}] - 2 \Delta_f G^\circ[H^+]$$

$$\Delta_f G^\circ[Sn^{2+}] - 2 \Delta_f G^\circ[H^+] = -26.2 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G^\circ[H^+] = 0 \quad \text{by definition}$$

$$\boxed{\Delta_f G^\circ[Sn^{2+}] = -26.2 \frac{\text{kJ}}{\text{mol}}}$$

3.114 Solubility Product

Solubility Product



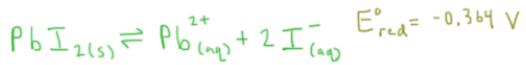
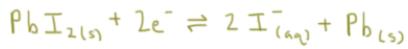
$$K_s = \left(\frac{\alpha_M^x \alpha_A^y}{\alpha_{MxHy}} \right)_{eq}$$

$$K_{sp} = \alpha_M^x \alpha_A^y \quad \text{"solubility product"}$$

$$\Delta_f G^\circ = -nF E_{cell}^\circ = -RT \ln K_{sp}$$

$$\ln K_{sp} = \frac{nF}{RT} E_{cell}^\circ$$

$$K_{sp} = \exp(nF E_{cell}^\circ / RT)$$



$$E_{cell}^\circ = (-0.364 \text{ V}) - (-0.126 \text{ V}) = -0.238 \text{ V}$$

$$K_{sp} = \exp \left(\frac{(2)(96,485 \text{ C/mol})(-0.238 \text{ V})}{(8.314 \text{ J/mol}\cdot\text{K})(298.15 \text{ K})} \right)$$

$$K_{sp} = 8.98 \cdot 10^{-9}$$

3.115 Batteries

Batteries

Electrochemical cells which convert chemical energy into electrical energy

Primary: one use, not rechargeable, irreversible, ex: Hg, Li

Secondary: multi use, rechargeable, reversible, ex: Pb acid, Li ion, NiCd

Hg battery:

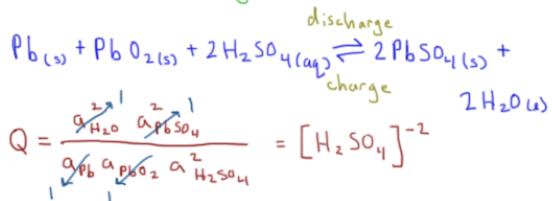


$$\Delta_r G = \Delta_r G^\circ + RT \ln Q = -n F E_{\text{cell}}$$

$$Q = \frac{\alpha_{\text{ZnO}} \alpha_{\text{Hg}}}{\alpha_{\text{Zn}} \alpha_{\text{HgO}}} = \frac{(1)(1)}{(1)(1)} = 1 \quad \text{always}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ = +1.35 \text{ V} \quad \text{always}$$

Pb acid battery:

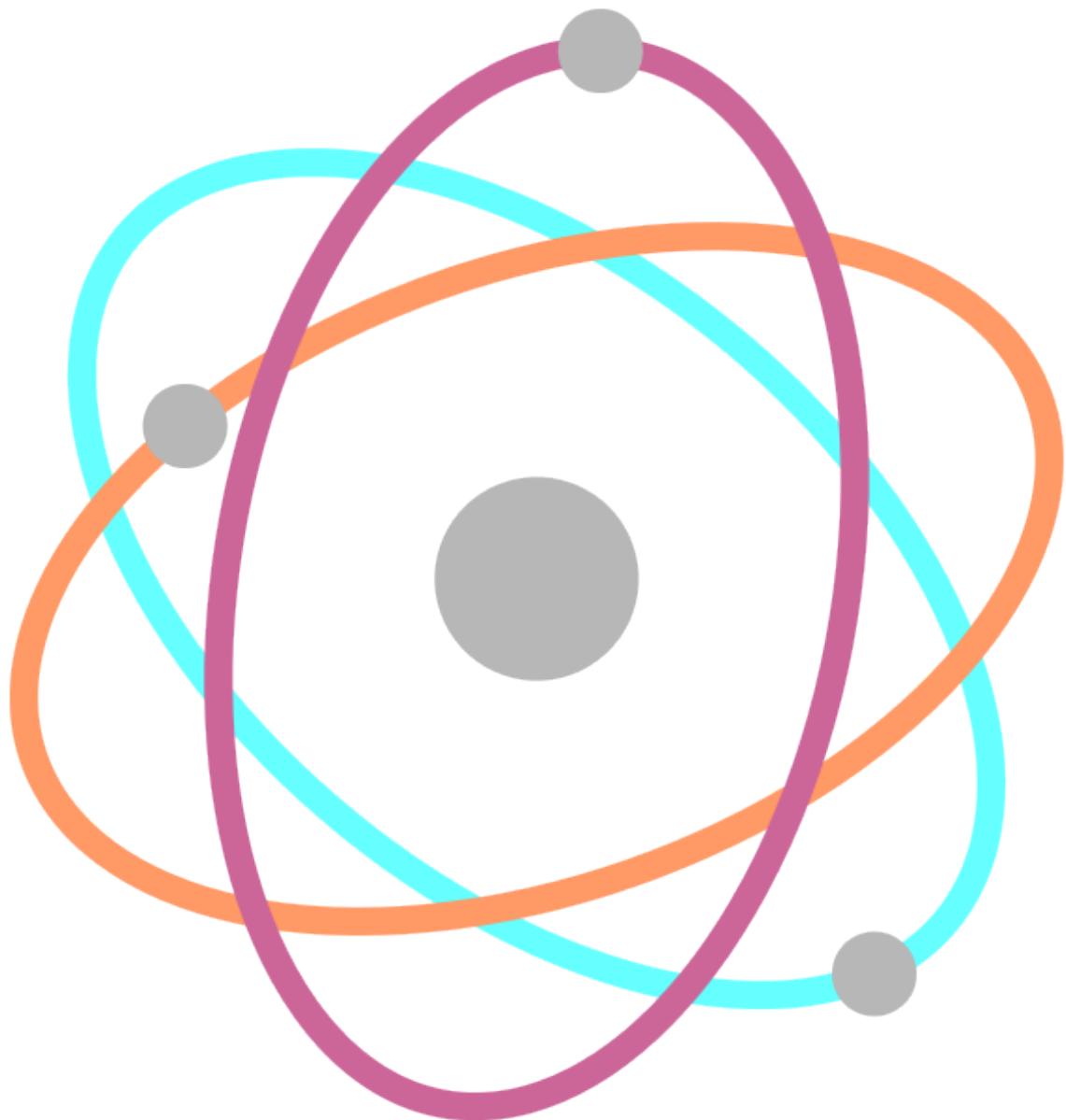


4 Chemical Kinetics

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4.1 Introduction

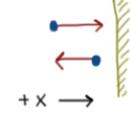


4.2 Average Kinetic Energy

Average Kinetic Energy

$$\text{before collision} \quad p_{1x} = +mu_{1x}$$

$$\text{after collision} \quad p_{1x} = -mu_{1x}$$



$$|\Delta p| = |p_f - p_i| = |(mu_{1x}) - (-mu_{1x})| = 2mu_{1x}$$

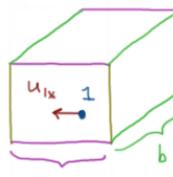
$$u_{1x} = \frac{\Delta d_{1x}}{\Delta t} \quad \Delta t = \frac{\Delta d_{1x}}{u_{1x}} = \frac{2a}{u_{1x}}$$

$$|F_{1x}| = \frac{|\Delta p|}{\Delta t} = \frac{2mu_{1x}}{(2a/u_{1x})} = \frac{mu_{1x}^2}{a}$$

$$P_i = \frac{|F_i|}{A} = \left(\frac{mu_{1x}^2}{a}\right)\left(\frac{1}{bc}\right) = \frac{mu_{1x}^2}{V} \quad V=abc$$

$$P = \sum_{i=1}^N P_i = \frac{m}{V} \sum_{i=1}^N u_{ix}^2 = \frac{Nm \langle u_x^2 \rangle}{V}$$

$$\langle u_x^2 \rangle = \frac{1}{N} \sum_{i=1}^N u_{xi}^2$$



c box with gas particles
particles are non-interacting
elastic collisions with walls

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$$

$$\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle = 3\langle u_x^2 \rangle$$

$$P = \frac{Nm \langle u^2 \rangle}{3V} = \frac{2N}{3V} \left(\frac{1}{2}m\langle u^2 \rangle\right) = \frac{2N}{3V} \langle E \rangle$$

$$\langle E \rangle = \frac{1}{N} \sum_{i=1}^N \frac{1}{2} mu_i^2 = \frac{m}{2N} \sum_{i=1}^N u_i^2 = \frac{m}{2N} (N\langle u^2 \rangle) = \frac{1}{2} m \langle u^2 \rangle$$

$$\langle E \rangle = \frac{3}{2N} (PV) = \frac{3}{2N} (Nk_b T)$$

$$\boxed{\langle E \rangle = \frac{3}{2} k_b T} \quad \text{ideal gas } PV = nRT = Nk_b T$$

4.3 Average Velocity

Average Velocity

$$\langle E \rangle = \frac{3}{2} k_b T$$

$$\langle E \rangle = \langle \frac{1}{2} m u^2 \rangle = \frac{1}{2} m \langle u^2 \rangle$$

$$\langle u^2 \rangle = \frac{2\langle E \rangle}{m} = \frac{\pi}{m} \left(\frac{3}{2} k_b T \right) = \frac{3k_b T}{m} = \frac{3RT}{M}$$

$$PV = nRT = Nk_b T \quad R = N_A k_b \quad M = N_A m$$

$$\frac{k_A}{m} = \frac{(N_A R)}{(N_A M)} = \frac{R}{M}$$

$u_{rms} = \sqrt{\langle u^2 \rangle}$ "root mean squared velocity"

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$R \left[\text{J/mol} \cdot \text{K} \right] \quad T \left[\text{K} \right] \quad M \left[\text{kg/mol} \right]$$

$$u_{rms} \left[\text{m/s} \right]$$

$u_{rms} (\text{m/s})$ for various $T (\text{K})$ and $M (\text{kg/mol})$

$T (\text{K})$	He	N_2	O_2
0	0	0	0
100	789	298	279
298.15	1363	515	482
500	1765	667	624
1000	2496	944	883

$$M_{\text{He}} = 0.004002$$

$$M_{\text{N}_2} = 0.02802 \quad [\text{kg/mol}]$$

$$M_{\text{O}_2} = 0.03200$$

4.4 Maxwell-Boltzmann Distribution

Maxwell - Boltzmann Distribution

$$f(u_x) = \left(\frac{m}{2\pi k_b T} \right)^{1/2} e^{-mu_x^2/2k_b T}$$

$$F(u) = \left(\frac{m}{2\pi k_b T} \right)^{1/2} u^2 e^{-mu^2/2k_b T}$$

$$\langle u_x \rangle = \int_{-\infty}^{\infty} u_x f(u_x) du_x = 0$$

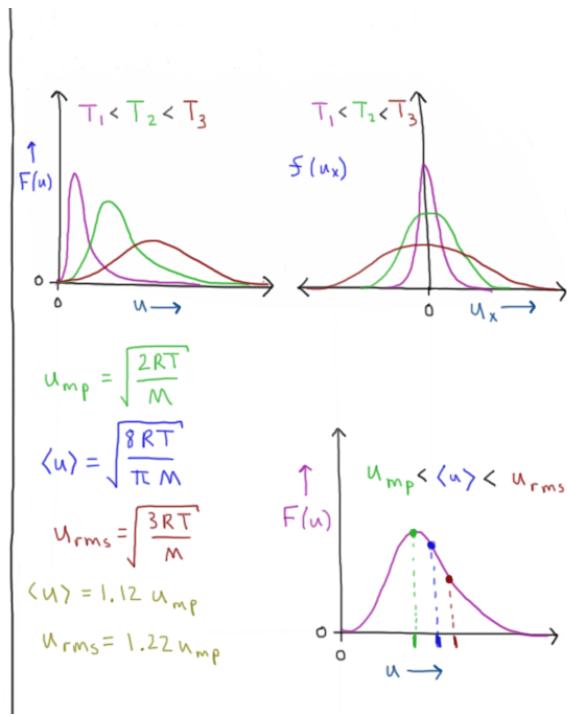
$$\langle u_x^2 \rangle = \int_{-\infty}^{\infty} u_x^2 f(u_x) du_x = \frac{k_b T}{m} = \frac{RT}{M}$$

$$\langle u \rangle = \int_{-\infty}^{\infty} u F(u) du = \sqrt{\frac{8k_b T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

$$\langle u^2 \rangle = \int_{-\infty}^{\infty} u^2 F(u) du = \frac{3k_b T}{m} = \frac{3RT}{M}$$

$$\frac{dF(u)}{du} = 0 \quad \text{and} \quad \frac{d^2 F(u)}{du^2} < 0 \quad \text{only at } u_{mp}$$

$$u_{mp} = \sqrt{\frac{2k_b T}{m}} = \sqrt{\frac{2RT}{M}} \quad u_{rms} = \sqrt{\langle u^2 \rangle}$$



4.5 Mean Free Path

Mean Free Path

if $r_{ij} < d \rightarrow i$ and j collide

$$dN_{\text{coll}} = V_p = (\sigma \langle u \rangle dt) (p)$$

dN_{coll} → number of collisions from $t \rightarrow t+dt$

$$V = A \cdot h = (\sigma) (\langle u \rangle dt)$$

σ → cross-sectional area of particle

$$Z_A = \frac{dN_{\text{coll}}}{dt} = \sigma p \sqrt{\frac{8RT}{\pi M}} = \sigma p \sqrt{\frac{8k_b T}{\pi m}}$$

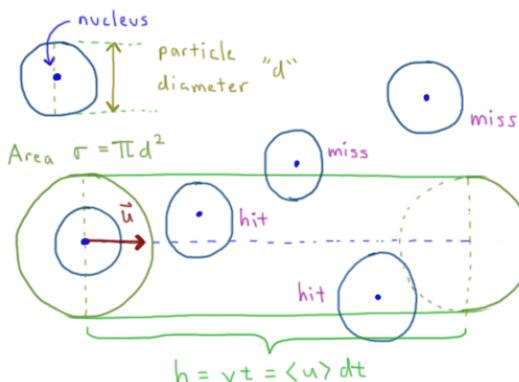
Z_A → "collision frequency"

$$m \rightarrow M \quad M = \frac{m_1 m_2}{m_1 + m_2}$$

when $m_1 = m_2 \quad M = m/2$

$$\langle u_r \rangle = \sqrt{2} \langle u \rangle$$

$$Z_A = \sqrt{2} p \sigma \langle u \rangle \quad J^0 = \frac{N}{V} = \frac{N_A P}{R T} \quad \text{ideal}$$



$h = vt = \langle u \rangle dt$

$l \rightarrow$ "mean free path"

$$l = \frac{\langle u \rangle}{Z_A} = \frac{\langle u \rangle}{\sqrt{2} p \sigma \langle u \rangle} = \frac{1}{\sqrt{2} p \sigma} = \frac{V}{\sqrt{2} \sigma N}$$

$$l = \frac{RT}{\sqrt{2} N_A \sigma p}$$

4.6 Total Collision Rate

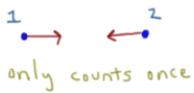
Total Collision Rate

$Z_{AA} \rightarrow$ collision frequency between all A particles per unit volume and time

$$Z_{AA} = \frac{1}{2} \rho Z_A$$

$$Z_{AA} = \frac{1}{2} \rho (\sqrt{2} \rho \sigma \langle u \rangle)$$

$$Z_{AA} = \frac{1}{\sqrt{2}} \sigma \rho^2 \langle u_A \rangle$$



$Z_{AB} \rightarrow$ collision frequency between all A and B particles per unit volume and time

$$Z_{AB} = \sigma_{AB} \rho_A \rho_B \langle u_r \rangle$$

$$\sigma_{AB} = \left(\frac{d_A + d_B}{2} \right)^2$$

$$\langle u_r \rangle = \sqrt{\frac{8k_B T}{\pi M}}$$

$$M = \frac{m_A m_B}{m_A + m_B}$$

$$\rho_i = \frac{N_i}{V} = \frac{RT}{N_A P_i} \quad \text{if ideal}$$

for $N_2(g)$ at 1 bar and 298.15 K

$$Z_{AA} = 8.9 \cdot 10^{28} \text{ mL}^{-1} \text{ s}^{-1}$$

4.7 Reaction Rates

Reaction Rates



$$n_A(t) = n_{A,0} - v_A \xi(t) \quad \xi(t)$$

$$n_B(t) = n_{B,0} - v_B \xi(t) \quad \text{"extent of reaction"}$$

$$n_C(t) = n_{C,0} + v_C \xi(t) \quad [mol]$$

$$n_D(t) = n_{D,0} + v_D \xi(t)$$

$$\frac{dn_A(t)}{dt} = -v_A \frac{d\xi(t)}{dt}$$

$$\frac{dn_B(t)}{dt} = -v_B \frac{d\xi(t)}{dt}$$

$$\frac{dn_C(t)}{dt} = +v_C \frac{d\xi(t)}{dt}$$

$$\frac{dn_D(t)}{dt} = +v_D \frac{d\xi(t)}{dt}$$

$$\frac{d[A]_t}{dt} = -\frac{v_A}{V} \frac{d\xi(t)}{dt} \quad c = \frac{n}{V}$$

$$\frac{d[B]_t}{dt} = -\frac{v_B}{V} \frac{d\xi(t)}{dt} \quad [A]_t = \frac{n_A(t)}{V}$$

$$\frac{d[C]_t}{dt} = +\frac{v_C}{V} \frac{d\xi(t)}{dt}$$

$$\frac{d[D]_t}{dt} = +\frac{v_D}{V} \frac{d\xi(t)}{dt}$$

$$v(t) = \frac{1}{V} \frac{d\xi(t)}{dt} \quad \text{"rate of reaction"} \quad \left[\frac{mol}{L \cdot s} \right]$$

$$v(t) = -\frac{1}{v_A} \frac{d[A]_t}{dt} = -\frac{1}{v_B} \frac{d[B]_t}{dt} = +\frac{1}{v_C} \frac{d[C]_t}{dt} = +\frac{1}{v_D} \frac{d[D]_t}{dt}$$

4.8 Rate Laws

Rate Laws



$$v(t) = \frac{1}{V} \frac{d[\mathbb{E}(t)]}{dt} = -\frac{1}{v_A} \frac{d[A]_t}{dt} = +\frac{1}{v_C} \frac{d[C]_t}{dt} = \dots$$

$$v(t) = \underbrace{k}_{\substack{\text{reaction} \\ \text{rate} \\ \text{constant}}} \underbrace{[A]_t^{m_A} [B]_t^{m_B}}_{\substack{\text{molarity of} \\ \text{A and B}}} \text{ rate law}$$

m_A and m_B do not necessarily equal
 v_A and v_B

must be determined experimentally

often $\{m_A, m_B\} = 0, 1, \text{ or } 2$

reaction is m_A^{th} order in A

reaction is m_B^{th} order in B

reaction is $(m_A + m_B)^{\text{th}}$ order overall

$$v(t) \rightarrow \frac{\text{mol}}{\text{L} \cdot \text{s}} = \frac{M}{s}$$

$$[I] \rightarrow \frac{\text{mol}}{\text{L}} = M$$

$k \rightarrow$ depends on $(m_A + m_B) = m$

[k]	total order
$\text{M} \cdot \text{s}^{-1}$	0
s^{-1}	1
$\text{M}^{-1} \text{s}^{-1}$	2

4.9 First Order Reactions

First Order Reactions



$$v(t) = -\frac{1}{[A]} \frac{d[A]_t}{dt} = k[A]_t \quad \text{assume } v_A = 1 \text{ for simplicity}$$

$$-d[A]_t = k[A]_t dt$$

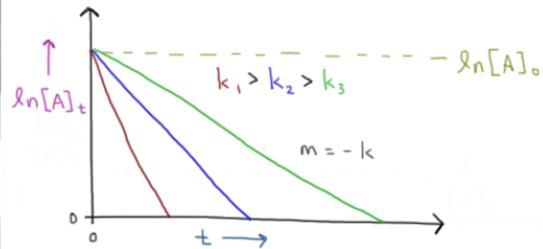
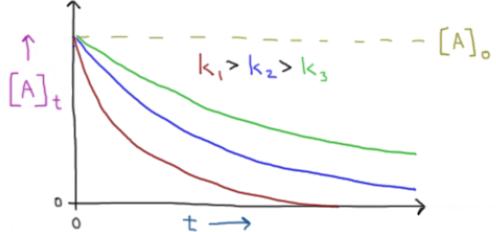
$$\int_{[A]_0}^{[A]_t} \frac{d[A]_t'}{[A]_t'} = \int_0^t -k dt'$$

$$\ln[A]_t - \ln[A]_0 = \ln([A]_t/[A]_0) = -kt$$

$$[A]_t / [A]_0 = e^{-kt}$$

$$[A]_t = [A]_0 e^{-kt} \quad \text{"integrated rate law"}$$

$$\ln[A]_t = -kt + \ln[A]_0$$



4.10 Second Order Reactions

Second Order Reactions



$$v(t) = k[A]_t^2 = -\frac{1}{[A]} \frac{d[A]_t}{dt} \quad \text{assume } v_A=1 \text{ for simplicity}$$

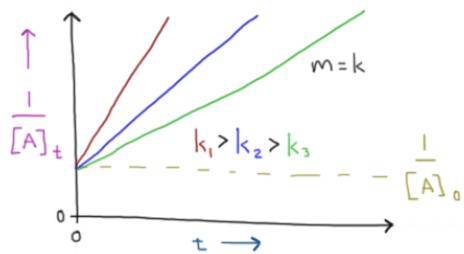
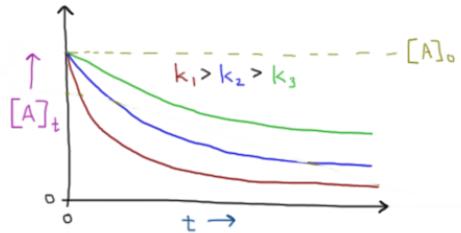
$$-\frac{d[A]}{dt} = k[A]^2 dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]_t'}{[A]_t^2} = \int_0^t -k dt'$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$[A]_t = \left(\frac{1}{[A]_0} + kt \right)^{-1} \quad \text{"integrated rate law"}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$



4.11 Half Life

Half Life

Time required to go from $[A]_t$ to $\frac{1}{2}[A]_t$

$$1^{\text{st}} \text{ order} \quad [A]_t = \frac{1}{2}[A]_0 = [A]_0 e^{-kt}$$

$$\frac{1}{2} = e^{-kt} \quad \ln\left(\frac{1}{2}\right) = -\ln 2 = -kt$$

$$t_{1/2} = \frac{\ln 2}{k} \quad 1^{\text{st}} \text{ order half life}$$

$$\ln 2 \approx 0.693$$

$$2^{\text{nd}} \text{ order} \quad \frac{1}{[A]_t} = \frac{1}{\frac{1}{2}[A]_0} = \frac{1}{[A]_0} + kt$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0} = kt \quad t_{1/2} = \frac{1}{k[A]_0}$$

$t_{1/2}$ order half life

$t_{1/2}$ increases with time

0th order

$$v(t) = k[A]_t^0 = k = -\frac{d[A]_t}{dt}$$

$$\int_0^t k dt' = \int_{[A]_0}^{[A]_t} d[A]_t'$$

$$-kt = [A_t] - [A]_0$$

$$[A]_t = \frac{1}{2}[A]_0 = [A]_0 - kt$$

$$\frac{1}{2}[A]_0 = kt$$

0th order half life

$$t_{1/2} = \frac{[A]_0}{2k} \quad t^{1/2} \text{ decreases with time}$$

order	$t_{1/2}$	$t_{1/4}$	$t_{1/8}$
0	0.50	0.75	0.88
1	0.69	1.38	2.08
2	1.00	3.00	7.00

$$k = 1$$

$$[A]_0 = 1 \text{ M}$$

4.12 Finding Rate Laws

Finding Rate Laws



$$v(t) = k [A]^{m_A} [B]^{m_B}$$

how to find $\{m_i\}$?

"method of initial rates" $\{v(0)\}$

"method of isolation" $[A] \gg [B]$

$$v_1(0) = k [A]_0^{m_A} [B]_1^{m_B}$$

$$v_2(0) = k [A]_0^{m_A} [B]_2^{m_B}$$

$$v_1(t) = k [A]^{m_A} [B]_t^{m_B}$$

$$v_2(t) = \underbrace{k [A]^{m_A} [B]_t^{m_B}}_{k' \rightarrow \text{constant}} \quad [A] \gg [B]$$

$$\frac{v_1}{[B]_1^{m_B}} = \frac{v_2}{[B]_2^{m_B}}$$

$$\frac{v_1}{v_2} = \left(\frac{[B]_1}{[B]_2} \right)^{m_B}$$

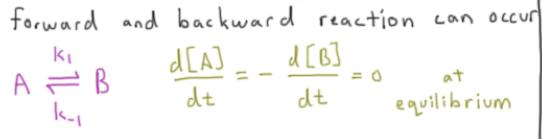
$$\ln \left(\frac{v_1}{v_2} \right) = m_B \ln \left(\frac{[B]_1}{[B]_2} \right)$$

$$m_B = \frac{\ln(v_1/v_2)}{\ln([B]_1/[B]_2)}$$

assumes reactants mix instantly
 $(t_{\text{mix}} \approx 10^{-3} \text{ s})$

4.13 Reversible Reactions

Reversible Reactions



$$K_c = \frac{[B]_{eq}}{[A]_{eq}} \quad \text{"dynamic equilibrium"}$$

$$-\frac{d[A]}{dt} = \underbrace{k_1[A]}_{\text{forward}} - \underbrace{k_{-1}[B]}_{\text{reverse}}$$

$$\text{at } t=0 \quad [A]=[A]_0, \quad [B]=0$$

$$[B]_t = [A]_0 - [A]_t$$

$$\begin{aligned} -\frac{d[A]}{dt} &= k_1[A] - k_{-1}([A]_0 - [A]) \\ &= (k_1 + k_{-1})[A] - k_{-1}[A]_0 \end{aligned}$$

$$[A]_t = [A]_{eq} + ([A]_0 - [A]_{eq}) e^{-(k_1 + k_{-1})t}$$

$$\text{at equilibrium} \quad k_1[A]_{eq} = k_{-1}[B]_{eq}$$

$$\frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_{-1}} = K_c$$

$K_c = \frac{k_1}{k_{-1}}$ gives ratio of k_1 and k_{-1}

4.14 Activation Energy

Activation Energy

$v(t) \rightarrow$ very T dependent

$$\text{empirically: } \frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

assume $E_a \approx \text{constant}$ versus T

$$\int d \ln k = \int \frac{E_a}{RT^2} dT$$

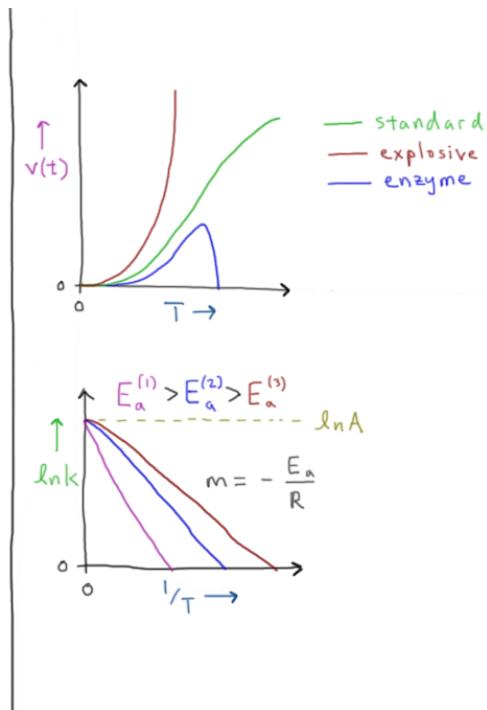
$$\ln k + C = -\frac{E_a}{RT}$$

$$k = e^{-C} e^{-E_a/RT}$$

$A = e^C$
"Arrhenius
equation"

$$k = A \exp(-E_a/RT)$$

rate constant pre-exponential factor activation energy



4.15 Reaction Coordinates

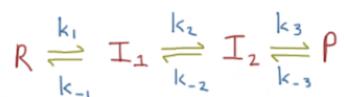
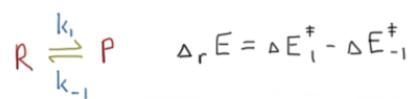
Reaction Coordinate

$q \rightarrow$ reaction coordinate

$\Delta_r E \rightarrow$ energy of reaction

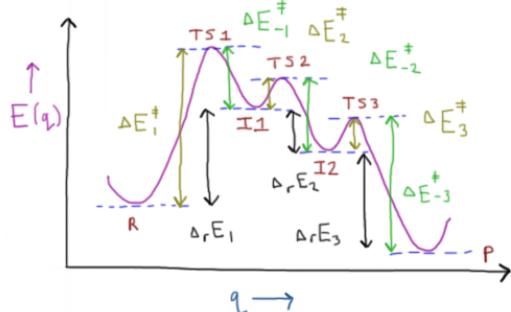
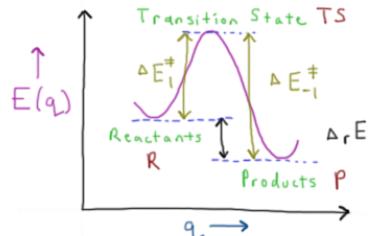
$\Delta E^\ddagger \rightarrow$ energy of activation (E_a)

$\ddagger \rightarrow$ activation



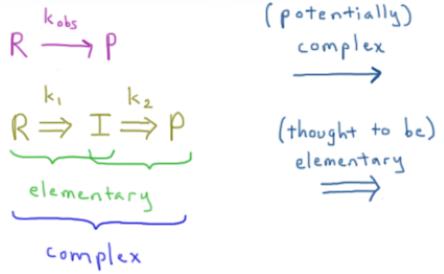
$$\Delta_r E = \Delta_r E_1 + \Delta_r E_2 + \Delta_r E_3$$

$$\Delta_r E_i = \Delta E_i^\ddagger - \Delta E_{-i}^\ddagger$$



4.16 Reaction Mechanisms

Reaction Mechanisms



Mechanism: the sequence of elementary reactions which compose a complex reaction

Molecularity: number of species involved in an elementary reaction

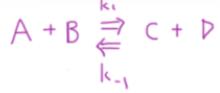


$$v(t) = k_1[A][B] \qquad v(t) = k_2[D]$$

reaction stoichiometry implies rate law for elementary reactions

4.17 Detailed Balance

Detailed Balance



$$v_1 = k_1 [A][B]$$

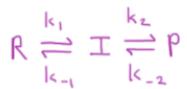
$$v_{-1} = k_{-1} [C][D]$$

at equilibrium $v_1 = v_{-1}$

$$k_1 [A]_{eq} [B]_{eq} = k_{-1} [C]_{eq} [D]_{eq}$$

$$\frac{k_1}{k_{-1}} = \frac{[C]_{eq} [D]_{eq}}{[A]_{eq} [B]_{eq}} = K_c$$

$$K_c = \frac{k_1}{k_{-1}} \quad \text{"principle of detailed balance"}$$



$$K_c^1 = \frac{[I]_{eq}}{[R]_{eq}} = \frac{k_1}{k_{-1}}$$

$$K_c^2 = \frac{[P]_{eq}}{[I]_{eq}} = \frac{k_2}{k_{-2}}$$

$$K_c = K_c^1 K_c^2 = \frac{[P]_{eq}}{[R]_{eq}} = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

$$K_c = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

4.18 Rate-Determining Step



$$[R]_t = [R]_0 e^{-k_{obs} t}$$

$$[P]_t = [R]_0 (1 - e^{-k_{obs} t})$$

$$\frac{d[R]}{dt} = -k_1 [R]$$

$$\frac{d[I]}{dt} = +k_1 [R] - k_2 [I]$$

$$\frac{d[P]}{dt} = +k_2 [I]$$

$$[R]_t = [R]_0 e^{-k_1 t}$$

$$[I]_t = \frac{k_1 [R]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$[P]_t = [R]_0 \left(1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} + k_1 e^{-k_2 t}) \right)$$

if $k_2 \gg k_1$

k_1 is the "rate-determining step"

$$[P]_t = [R]_0 \left(1 - \frac{\cancel{k_2}}{\cancel{k_2} - k_1} e^{-k_1 t} - \frac{k_1}{\cancel{k_2} - k_1} e^{-k_1 t} \right)$$

$$[P]_t = [R]_0 (1 - e^{-k_1 t})$$

4.19 Steady-State Approximation

Steady-State Approximation



assume at $t=0$ $[R]=[R]_0$ and $[I]=[P]=0$

if $k_1 \gg k_2$, $[I]$ builds up, then $[P]$

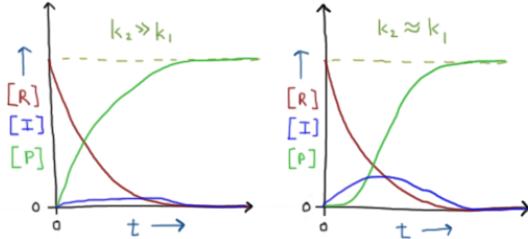
if $k_1 \ll k_2$, $[I]$ consumed immediately to $[P]$

$$\frac{d[I]}{dt} = 0 \text{ "steady-state approximation"}$$

$$\frac{d[I]}{dt} = +k_1[R] - k_2[I] = 0$$

$$[I] = \frac{k_1[R]}{k_2}$$

$$\frac{d[R]}{dt} = -k_1[R] \quad [R] = [R]_0 e^{-k_1 t}$$



$$[I] = \frac{k_1[R]_0}{k_2} e^{-k_1 t}$$

$$\frac{d[I]}{dt} = -\frac{k_1^2 [R]_0}{k_2} e^{-k_1 t} = 0$$

s.s. appx'n valid if $k_2 \gg k_1^2 [R]_0$

4.20 Unimolecular Reactions

Unimolecular Reactions

Most reactions occur through bimolecular collisions. How do unimolecular reactions occur?

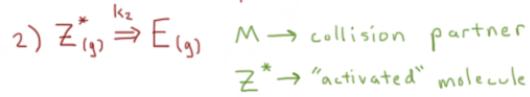
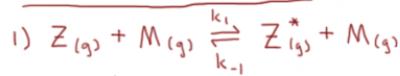


$$\text{high } [Z]: v = k_{obs}[Z] \text{ (1st order)}$$

$$\text{low } [Z]: v = k_{obs}[Z]^2 \text{ (2nd order)}$$

$E_a \gg k_b T$, where does E come from?

Lindemann Mechanism



$$\frac{d[E]}{dt} = +k_2[Z^*] = k_{obs}[Z]$$

$$\frac{d[Z^*]}{dt} = +k_1[Z][M] - k_{-1}[Z^*][M] - k_2[Z^*] = 0$$

$$[Z^*] = \frac{k_1[Z][M]}{k_2 + k_{-1}[M]}$$

$$\frac{d[E]}{dt} = k_{obs}[Z] = k_2[Z^*] = \frac{k_2 k_1 [Z][M]}{k_2 + k_{-1}[M]}$$

$$k_{obs} = \frac{k_2 k_1 [M]}{k_2 + k_{-1}[M]}$$

$$\text{at high } [M], k_{-1}[M] \gg k_2, k_{obs} = \frac{k_1 k_2}{k_{-1}}$$

$$\text{at low } [M], k_{-1}[M] \ll k_2, k_{obs} = k_1[M]$$

$$v_{\text{high}} = \frac{k_1 k_2}{k_{-1}} [Z] \quad (\text{1st order})$$

$$v_{\text{low}} = k_1 [Z]^2 \quad (\text{2nd order})$$

4.21 Catalysis

Catalysis

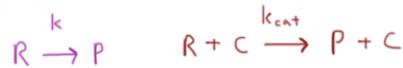
usually $T \uparrow \rightarrow k \uparrow \rightarrow v \uparrow$

can't always raise T. need alternative

Catalyst: species that participates in a reaction without being consumed
doesn't change $\Delta_r E$, does change $\Delta E^\ddagger \downarrow$

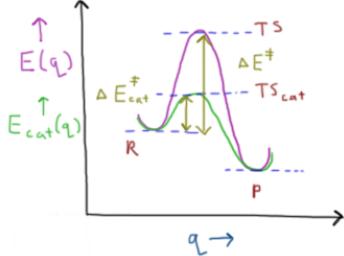
Homogeneous Catalysis: same phase

Heterogeneous Catalysis: different phase



$$-\frac{d[R]}{dt} = +k[R] + k_{cat}[R][C]$$

$$\frac{d[R]}{dt} = -[R](k + k_{cat}[C])$$



often $k_{cat} \gg k$

still 1st order in [R]

1st order in [C]

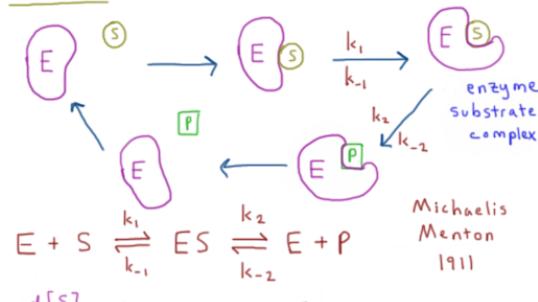
even at low [C], $k_{cat}[C]$ is still large

small $\Delta\Delta E^\ddagger \rightarrow$ big Δk_{obs}

4.22 Michaelis-Menton Mechanism

Michaelis -Menton Mechanism

Enzyme: protein catalyst for specific biological rxn
Substrate: enzyme target reactant



Michaelis
Menton
1911

$$-\frac{d[S]}{dt} = k_1[E][S] - k_{-1}[ES]$$

$$-\frac{d[ES]}{dt} = (k_2 + k_{-1})[ES] - k_1[E][S] - k_{-2}[E][P] = 0$$

$$+\frac{d[P]}{dt} = k_2[ES] - k_{-2}[E][P]$$

$$[E] = [E]_0 - [ES]$$

$$0 = [ES](k_1[S] + k_{-1} + k_2 + k_{-2}[P]) - [E]_0(k_1[S] + k_{-2}[P])$$

$$[ES] = \frac{k_1[S] + k_2[P]}{k_1[S] + k_{-2}[P] + k_{-1} + k_2} [E]_0$$

$$v(t) = -\frac{d[S]}{dt} = \frac{k_1 k_2 [S] - k_{-1} k_{-2} [P]}{k_1[S] + k_{-2}[P] + k_{-1} + k_2} [E]_0$$

at $t=0$, $[S]=[S]_0$ and $[P]=0$

$$v_0 = \frac{k_1 k_2 [S]_0 [E]_0}{k_1[S]_0 + k_{-1} + k_2} \quad V_{max} = k_2 [E]_0 \quad \begin{matrix} \text{rate when} \\ \text{enzyme} \\ \text{is} \\ \text{saturated} \end{matrix}$$

$$V_0 = \frac{V_{max}[S]_0}{K_m + [S]_0} \quad K_m = \frac{k_2 + k_{-1}}{k_1} \quad \text{"Michaelis constant"}$$

$k_2 \rightarrow$ "turnover number" $[1/s] 1-10^7$

$[S]_0 \gg K_m \rightarrow v_0 = V_{max}$ (0th order)

$[S]_0 \ll K_m \rightarrow v_0 = \frac{V_{max}}{K_m} [S]_0$ (1st order)

5 Computational Chemistry

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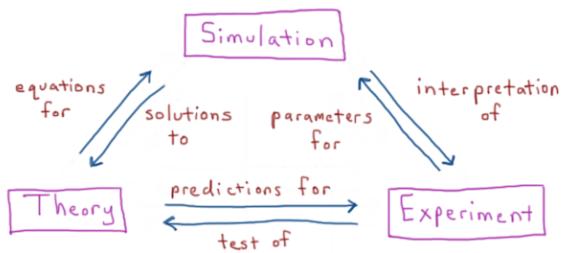
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5.1 Introduction

Introduction to Computational Chemistry

The use of computers to solve the equations of a theory or model for the properties of chemical systems



Model: simplified representation of a physical system

Computing much faster now

- Moore's Law
- parallel computing
- cheaper hardware
- better software

Properties include:

- energies
- structures
- spectra

5.2 XYZ File Format

XYZ File Format

filename.xyz

no spaces, slashes, special characters

1^{st} { 3 2^{nd} { comment line 3^{rd} { 0 0.53890 0.65566 0.00000 $-$ { H 1.50890 0.65566 0.00000 $(N+2)^{\text{th}}$ { H 0.21557 1.56969 -0.03013
1^{st} 2^{nd} 3^{rd} 4^{th}

1^{st} line - number of atoms

2^{nd} line - comment (anything)

3^{rd} to $(N+2)^{\text{th}}$ lines - atoms

1^{st} column - atomic symbol [or Bohr]

$2^{\text{nd}}\text{-}4^{\text{th}}$ column - atomic coordinates (angstrom)

"Cartesian (XYZ) coordinates"

N atoms

$3N$ coordinates

$3N-6^*$ unique coordinates

"internal degrees of freedom"

3 translations

3^* rotations

* $3N-5$ if linear

* 2 if linear

5.3 PDB File Format

PDB File Format

Standard file format for biological macromolecules and many molecular modeling packages

"Protein Data Bank" filename.pdb
column specific - exact location on line

Many types of "records"

ATOM
HETATM
HEADER
SOURCE
HELIX
SHEET

record	atom	residue	(angstrom)			beta
			type	number	XYZ coordinates	
ATOM	6	CG	PRO	A 1	29.296 37.591 7.162	1.0 38.40 C
ATOM	7	CD	PRO	A 1	28.778 39.015 7.019	1.0 38.74 C
ATOM	8	N	GLN	A 2	30.607 37.334 3.305	1.0 41.76 N

atom residue chain occupancy element
number

"occupancy" → fraction of atoms that appear at that location

"β factor" → average displacement of atom

$$\beta_i = 8\pi^2 u_i^2$$

$$u_i = \frac{1}{\pi} \sqrt{\frac{\beta_i}{8}} \quad u_i \rightarrow \text{displacement}$$

5.4 Avogadro and VMD

Avogadro ; VMD

Avogadro: molecule editor for constructing
and manipulating atoms

VMD: (Visual Molecular Dynamics)
molecular modeling and visualization program

Download from:

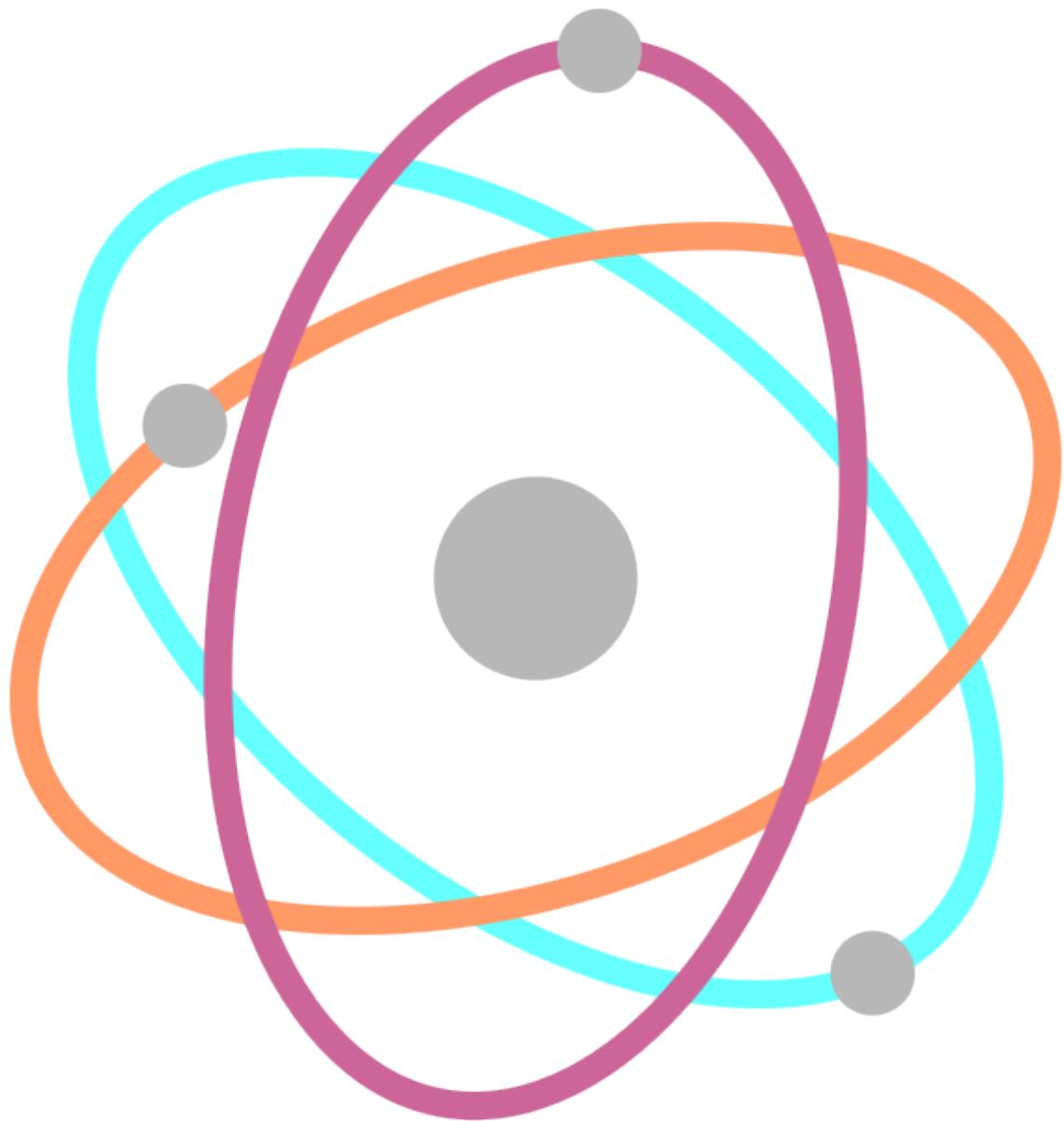
avogadro.cc

www.ks.uiuc.edu/research/vmd

Use for:

- drawing / cleaning up structures
- manipulating atoms
- generating XYZ coordinates
- viewing trajectories
- structure preparation
- high quality images

5.5 Drawing Molecules



5.6 Python and Jupyter

Python & Jupyter

Python: general purpose, high-level programming language

Anaconda: Python distribution with many libraries for scientific computing

Numpy: Python library for large arrays and matrices

Jupyter: (IPython notebook) browser-based interactive computing environment for Python

Matplotlib: Python library for plotting graphs and functions

Pandas: Python library for data analysis

Download from:

continuum.io

jupyter.org

5.7 Bond Lengths

Bond Lengths

F	-0.29502	0.75280	0.00000
H	0.64417	0.75280	0.00000

distance between two points: Pythagorean theorem



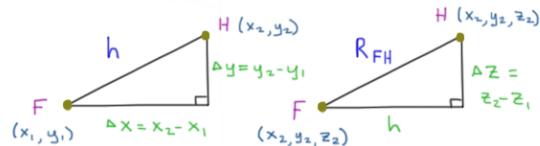
$$\overbrace{\quad\quad}^{R_{FH}}$$

$$h = \sqrt{(\Delta x)^2 + (\Delta y)^2}$$

$$R_{FH} = \sqrt{h^2 + (\Delta z)^2}$$

$$R_{ij} = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2}$$

$$0 \leq R_{ij} < \infty$$



$$R_{FH} = \left\{ [(-0.29502) - (0.64417)]^2 + [(0.75280) - (0.75280)]^2 + [(0.00000) - (0.00000)]^2 \right\}^{1/2}$$

$$R_{FH} = \sqrt{0.93919^2 + 0.00000^2 + 0.00000^2}$$

$$R_{FH} = 0.939 \text{ \AA}$$

5.8 Covalent Radius

Covalent Radius

atomic "radius" for covalent bonding

if $R_{ij} \leq k(r_i + r_j)$, then $i:j$ are bonded

$k \rightarrow$ threshold factor ≈ 1.20

H 0.37 Å

C 0.77 Å

N 0.75 Å

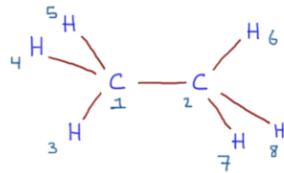
O 0.73 Å

N atoms $\rightarrow \frac{N(N-1)}{2}$ pairs $\rightarrow \mathcal{O}(N^2)$ pairs

$\mathcal{O}(N)$ bonds C ≤ 4 O ≤ 2

$\mathcal{O}(N^2)$ pairs N ≤ 3 H, F, Cl, ... ≤ 1

build "bond graph"



1	C	2	3	4	5
2	C	1	6	7	8
3	H	1			
4	H	1			
5	H	1			
6	H	2			
7	H	2			
8	H	2			

5.9 Bond Angles

Bond Angles

Angle between 3 points or 2 vectors

$$\vec{r}_{ab} = (x_b - x_a)\hat{x} + (y_b - y_a)\hat{y} + (z_b - z_a)\hat{z}$$

$$\|\vec{r}_{ab}\| = \sqrt{(x_b - x_a)^2 + (y_b - y_a)^2 + (z_b - z_a)^2}$$

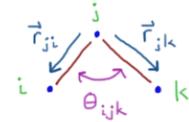
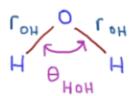
"Magnitude of \vec{r}_{ab} " (length)

$$\vec{a} \cdot \vec{b} = a_x b_x + a_y b_y + a_z b_z \quad \text{"dot product"}$$

$$\hat{r}_{ab} = \frac{\vec{r}_{ab}}{\|\vec{r}_{ab}\|} \quad \text{"unit vector"} \quad \|\hat{r}_{ab}\| = 1$$

$$\hat{r}_{ji} \cdot \hat{r}_{jk} = (\|\hat{r}_{ji}\|)(\|\hat{r}_{jk}\|) \cos(\theta_{ijk})$$

$$\hat{r}_{ji} \cdot \hat{r}_{ik} = \cos(\theta_{jik})$$



$$\theta_{ijk} = \cos^{-1}(\hat{r}_{ji} \cdot \hat{r}_{ik})$$

$$0^\circ \leq \theta_{ijk} \leq 180^\circ \quad \theta_{ijk} = \theta_{kji}$$

$$\theta_{ijk} + \theta_{jki} + \theta_{kij} = 180^\circ$$

only count if $R_{ij} \cap R_{jk}$ are bonds

$$\frac{N(N-1)(N-2)}{2} \quad \text{unique atomic trios}$$

$\Theta(N)$ angles

$\Theta(N^3)$ atom trios

5.10 Torsion Angles

Torsion Angles

Angle between 2 normal vectors between 2 planes from 4 points

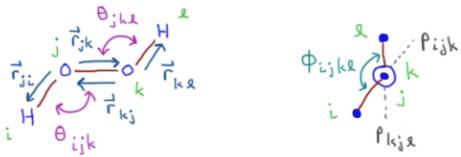
need R_{ij} , R_{jk} , and R_{kl} to be bonds

$\phi_{ijkl} \rightarrow$ angle between planes ijk and jkl

$$\vec{a} \otimes \vec{b} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ a_x & a_y & a_z \\ b_x & b_y & b_z \end{vmatrix} \quad \text{"cross product"}$$

$$\vec{a} \otimes \vec{b} = (a_y b_z - a_z b_y) \hat{x} + (a_z b_x - a_x b_z) \hat{y} + (a_x b_y - a_y b_x) \hat{z}$$

$$\left(\begin{array}{l} \text{normal vector} \\ \text{to plane } abc \end{array} \right) = \frac{\hat{r}_{ba} \cdot \hat{r}_{bc}}{\sin \theta_{abc}} = \hat{n}_{abc}$$



$$\hat{n}_{ijk} \cdot \hat{n}_{jkl} = \cos(\phi_{ijkl})$$

$$\phi_{ijkl} = \cos^{-1} \left(\frac{(\hat{r}_{ji} \otimes \hat{r}_{jk}) \cdot (\hat{r}_{kj} \otimes \hat{r}_{kl})}{\sin \theta_{ijk} \sin \theta_{jkl}} \right)$$

$$-180^\circ < \phi_{ijkl} \leq 180^\circ \quad \phi_{ijkl} = \phi_{klij}$$

$$\text{sign of } \phi_{ijkl} = \text{sign of } \hat{n}_{jkl} \cdot \hat{r}_{ji}$$

$\mathcal{O}(N)$ torsions

$$\cos^2 \theta + \sin^2 \theta = 1$$

$\mathcal{O}(N^4)$ atom quartets

$$\sin \theta = \pm \sqrt{1 - \cos^2 \theta}$$

5.11 Z-Matrix Format

Z-Matrix Format

N_{atoms}

$3N$ xyz coordinates

$3N - 6$ unique coordinates

6 redundant \rightarrow 3 translations
 \rightarrow 3 rotations

3N - 6 z-matrix coordinates

$n-1$ bond lengths

N - 2 bond angles

N - 3 torsion angles

1	C						
2	C	1	1.51				
3	H	1	1.09	2	110.6		
4	H	1	1.09	2	110.6	3	-120.0
5	H	1	1.09	2	110.6	3	120.0
6	H	2	1.09	1	110.6	5	180.0
7	H	2	1.09	1	110.6	5	60.0
8	H	2	1.09	1	110.6	5	-60.0

elements	bond lengths (Å)	bond angles (°)	torsion angles (°)
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5.12 Out-of-Plane Angles

Out of Plane Angles

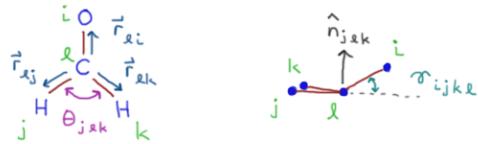
Angle by which a vector lies out of a plane
need R_{il} , R_{jx} , and R_{ke} to be bonds

$$\hat{n}_{jlk} = \frac{\hat{r}_{jl} \otimes \hat{r}_{lk}}{\sin \theta_{jlk}} = \begin{pmatrix} \text{normal vector} \\ \text{to plane } jlk \end{pmatrix}$$

$$\hat{n}_{jlk} \cdot \hat{r}_{li} = \cos(90^\circ - \tau_{ijkl}) = \sin(\tau_{ijkl})$$

$$\boxed{\tau_{ijkl} = \sin^{-1} \left(\frac{(\hat{r}_{lj} \otimes \hat{r}_{lk}) \cdot \hat{r}_{li}}{\sin \theta_{jlk}} \right)}$$

$$-90^\circ \leq \tau_{ijkl} \leq 90^\circ \quad \tau_{ijkl} = -\tau_{ikjl}$$



$$\frac{N(N-1)(N-2)(N-3)}{2} = \Theta(N^4) \text{ atomic quartets}$$

$\Theta(N)$ out of plane angles

$\Theta(N^4)$ atom quartets

5.13 Center of Mass

Center of Mass

0^{th} moment of mass \rightarrow total mass (scalar)

1^{st} moment of mass \rightarrow center of mass (vector)

$$m = \sum_{i=1}^N m_i \quad (\text{sum over all atoms})$$

$$\left. \begin{array}{l} H \rightarrow 1.01 \text{ amu} \\ C \rightarrow 12.01 \text{ amu} \\ N \rightarrow 14.01 \text{ amu} \\ O \rightarrow 16.00 \text{ amu} \end{array} \right\} \{m_i\}$$

$$1 \text{ amu} = 1.66054 \cdot 10^{-27} \text{ kg}$$

$$\vec{c} = \begin{pmatrix} x_{cm} \\ y_{cm} \\ z_{cm} \end{pmatrix} = \begin{pmatrix} \frac{1}{n} \sum_{i=1}^n m_i x_i \\ \frac{1}{n} \sum_{i=1}^n m_i y_i \\ \frac{1}{n} \sum_{i=1}^n m_i z_i \end{pmatrix}$$

translating coordinates such that $\vec{c} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$
removes 3 redundant coordinates

$$\begin{pmatrix} x_{i,cm} \\ y_{i,cm} \\ z_{i,cm} \end{pmatrix} = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} - \begin{pmatrix} x_{cm} \\ y_{cm} \\ z_{cm} \end{pmatrix} = \begin{pmatrix} x_i - x_{cm} \\ y_i - y_{cm} \\ z_i - z_{cm} \end{pmatrix}$$

5.14 Moment of Inertia

Moment of Inertia

0th moment of mass → total mass (scalar)

1st moment of mass → center of mass (vector)

2nd moment of mass → moment of inertia
(matrix)

resistance to torque / angular acceleration

$$I = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}$$

S.I. units → [kg · m²]

$$I_{xx} = \sum_{i=1}^N m_i (y_i^2 + z_i^2)$$

$$I_{yy} = \sum_{i=1}^N m_i (z_i^2 + x_i^2) \quad [\text{amu} \cdot \text{\AA}^2]$$

$$I_{zz} = \sum_{i=1}^N m_i (x_i^2 + y_i^2)$$

$$I_{xy} = I_{yx} = - \sum_{i=1}^N m_i x_i y_i$$

$$I_{xz} = I_{zx} = - \sum_{i=1}^N m_i x_i z_i \quad [\text{amu} \cdot \text{\AA}^2]$$

$$I_{yz} = I_{zy} = - \sum_{i=1}^N m_i y_i z_i$$

symmetric, real 3×3 matrix

5.15 Rotational Constants

Principal Moments of Inertia

$$\underline{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \quad \begin{array}{l} \text{moment of inertia tensor} \\ \text{symmetric, real } 3 \times 3 \text{ matrix} \end{array}$$

3 eigenvalues \rightarrow rotational constants [amu·Å²]

3 eigenvectors \rightarrow principal axes of rotation

convert constants (I_a, I_b, I_c) to MHz or cm⁻¹

$$I_a \leq I_b \leq I_c \rightarrow A \geq B \geq C$$

$$A = 10^{-6} \frac{\hbar}{8\pi^2 c I_a} \quad \tilde{A} = \frac{\hbar}{8\pi^2 c I_a} \quad c = 3.0 \cdot 10^{10} \text{ cm/s}$$

$$B = 10^{-6} \frac{\hbar}{8\pi^2 c I_b} \quad \tilde{B} = \frac{\hbar}{8\pi^2 c I_b} \quad A, B, C \rightarrow [\text{MHz}]$$

$$C = 10^{-6} \frac{\hbar}{8\pi^2 c I_c} \quad \tilde{C} = \frac{\hbar}{8\pi^2 c I_c} \quad \tilde{A}, \tilde{B}, \tilde{C} \rightarrow [\text{cm}^{-1}]$$

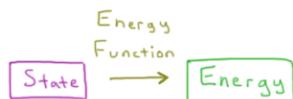
case	molecule type	symmetry
$A > B > C > 0$	asymmetric top	Abelian
$A = B = C = 0$	monatomic	K_h
$A = B > C = 0$	linear	D_{nh} or $C_{\infty v}$
$A = B > C > 0$	oblate symmetric top	non-Abelian
$A > B = C > 0$	prolate symmetric top	non-Abelian
$A = B = C > 0$	spherical top	cubic

translate to
center of mass \rightarrow rotate to
principal axes \rightarrow unique
coordinates

5.16 Energy Functions

Energy Functions

A mathematical algorithm that inputs the state of a system and outputs the energy



System state may include:

- coordinates
- bonded structure
- external elements
- empirical parameters
- charge, spin

Energy function may include:

- logic
- arithmetic
- algebra
- calculus
- numerical procedures

Simple or Complex

Analytic or Numerical

QM or MM or other

Ab initio or Empirical

Atomistic or Coarse-grained

5.17 Molecular Mechanics

Molecular Mechanics

A set of models which use an empirical, algebraic, atomistic energy function for chemical systems

$$E_{\text{total}} = E_{\text{bonded}} + E_{\text{non-bonded}}$$

$$E_{\text{bonded}} = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{torsions}}$$

$$E_{\text{non-bonded}} = E_{\text{elst}} + E_{\text{vdw}}$$

Force Field Models

- atoms: 3-d point particles
- structure: bonds, angles, torsions

Examples

- AMBER
- CHARMM
- OPLS
- GROMOS
- MMFF

Force fields vary in:
• energy functional form
• empirical parameters
• simulation target

Limitations:

- Up to 1,000,000s of atoms
- Up to 10^{15} configurations
- Accuracy of energy
- Scope of parameters

5.18 Force Field Parameters

Force Field Parameters

An arbitrary constant whose value characterizes an element of a system

$$E_{\text{total}} = \sum_{\text{bonds}} K_b (r - r_{\text{eq}})^2 + \dots$$

$$E \rightarrow [\text{kcal/mol}] \quad r \rightarrow [\text{\AA}]$$

$$r_{\text{eq}} \rightarrow [\text{\AA}] \quad K_b \rightarrow \left[\frac{\text{kcal}}{\text{mol} \cdot \text{\AA}^2} \right]$$

Ex: O-H in H₂O in AMBER95

$$r_{\text{eq}} = 0.960 \text{\AA}, \quad K_b = 553.0 \frac{\text{kcal}}{\text{mol} \cdot \text{\AA}^2}$$

Sources: structures, spectra, simulation

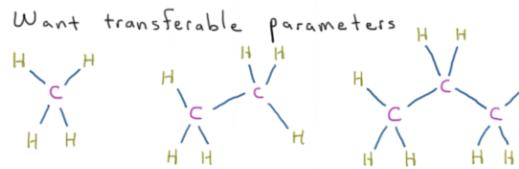
↓ ↓ ↓ ↓ ↓
crystal density IR NMR P.E.S.

Desired properties

- General
- Transferable
- Accurate

5.19 Atom Types

Atom Types



Use same parameters for similar atoms

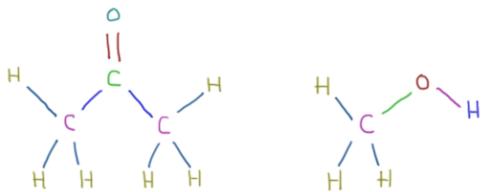
$$\epsilon_{\text{Me}} \approx \epsilon_{\text{Et}} \approx \epsilon_{\text{Pr}}$$

$$(r_{\text{eq}})_{\text{C}-\text{C}_{\text{Et}}} \approx (r_{\text{eq}})_{\text{C}-\text{C}_{\text{Pr}}}$$

aliphatic sp^3 C atom \rightarrow CT "atom type"

oxygen types in AMBER

- OW: water
- OH: alcohols
- OS: ethers
- O: amides (carbonyl)
- O2: carboxylates



5.20 MM Bond Stretch Terms

Bond Stretch Terms

$$E_{\text{bonds}} = \sum_{\text{bonds}} K_b (r - r_{\text{eq}})^2$$

parameters $\begin{cases} r_{\text{eq}} \rightarrow \text{equilibrium bond length } [\text{\AA}] \\ K_b \rightarrow \text{bond spring constant } [\frac{\text{kcal}}{\text{mol} \cdot \text{\AA}^2}] \end{cases}$

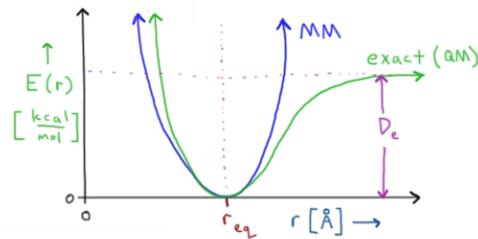
variable $\begin{cases} r \rightarrow \text{bond length } [\text{\AA}], 0 \leq r < \infty \end{cases}$

$$E_{\text{MM}}(0) = K_b r_{\text{eq}}^2 \quad E_{\text{QM}}(0) = \infty$$

$$E_{\text{MM}}(\infty) = +\infty \quad E_{\text{QM}}(\infty) = +D_e$$

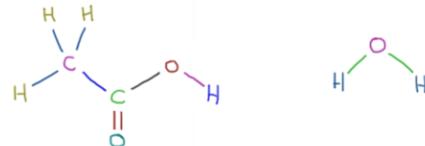
$$E_{\text{MM}}(r_{\text{eq}}) = 0 \quad E_{\text{QM}}(r_{\text{eq}}) = 0$$

$$E(r) \approx E(r_{\text{eq}}) + \frac{1}{1!} \frac{dE(r_{\text{eq}})}{dr} (r - r_{\text{eq}}) + \frac{1}{2!} \frac{d^2E(r_{\text{eq}})}{dr^2} (r - r_{\text{eq}})^2 + \dots$$



$$K_b = \frac{1}{2} \frac{d^2 E(r_{\text{eq}})}{dr^2}$$

typical $K_b \approx 300 - 600 \frac{\text{kcal}}{\text{mol} \cdot \text{\AA}^2}$



5.21 MM Angle Bend Terms

Angle Bend Terms

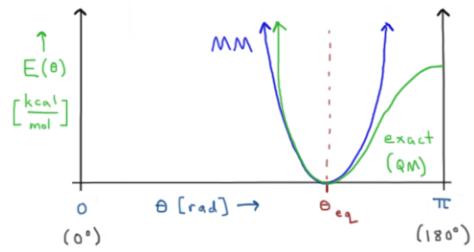
$$E_{\text{angles}} = \sum_{\text{angles}} K_a (\theta - \theta_{\text{eq}})^2$$

parameters $\begin{cases} \theta_{\text{eq}} \rightarrow \text{equilibrium bond angle [rad]} \\ K_a \rightarrow \text{angle spring constant} \left[\frac{\text{kcal}}{\text{mol} \cdot \text{rad}^2} \right] \end{cases}$

variable $\begin{cases} \theta \rightarrow \text{bond angle [rad]}, 0 \leq \theta \leq \pi \end{cases}$

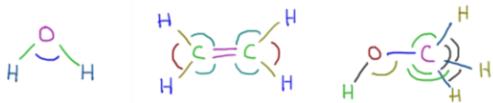
$$E_{\text{MM}}(\theta_{\text{eq}}) = 0$$

$$\frac{dE_{\text{MM}}(\theta_{\text{eq}})}{d\theta} = 0$$



$$K_a = \frac{1}{2} \frac{d^2 E(\theta_{\text{eq}})}{d\theta^2}$$

typical $K_a \approx 100-150 \frac{\text{kcal}}{\text{mol} \cdot \text{rad}^2}$



5.22 MM Torsion Strain Terms

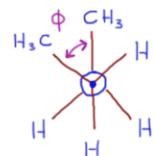
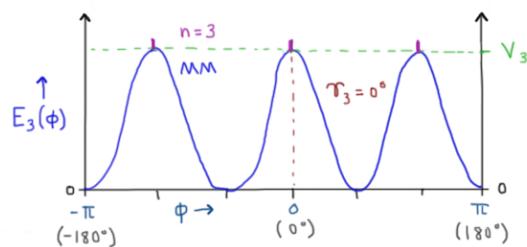
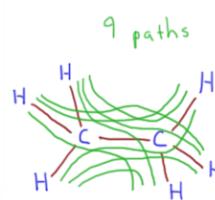
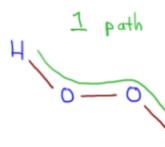
Torsion Strain Terms

$$E_{tors} = \sum_{tors} \sum_{n=1}^{\infty} V_n [1 + \cos(n\phi - \tau_n)]$$

parameters $\begin{cases} V_n \rightarrow n\text{-fold rotation barrier [kcal/mol]} \\ \tau_n \rightarrow \text{phase offset [rad]} \end{cases}$

variable $\begin{cases} \phi \rightarrow \text{dihedral (torsion) angle [rad]} \\ 0 \leq E_n \leq V_n \quad -180^\circ < \phi \leq 180^\circ \end{cases}$

$$V_{3_{HCCH}} = 1.40 \text{ kcal/mol}$$



5.23 MM Out-of-Plane Terms

Out of Plane Terms

$$E_{oop} = \sum_{oop} \frac{1}{2} V [1 + \cos(2\phi - 180^\circ)]$$

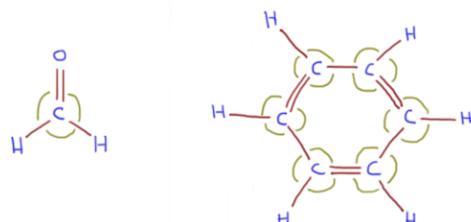
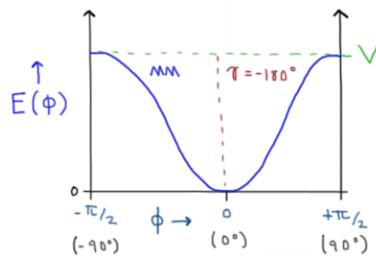
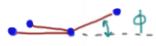
out-of-plane angle / improper torsion

parameter $\{ V \rightarrow \text{rotation barrier} [\frac{\text{kcal}}{\text{mol}}] \}$

variable $\{ \phi \rightarrow \text{out of plane angle [rad]} \}$

$$0 \leq E_{oop} \leq V \quad -90^\circ \leq \phi \leq 90^\circ$$

$$V_{xxch} = 1.1 \text{ kcal/mol}$$



5.24 MM van der Waals Terms

van der Waals Terms

$$E_{vdw} = \sum_{i=1}^N \sum_{j=i+1}^N \xi_{ij} \left[\left(\frac{r_0}{r_{ij}} \right)^2 - 2 \left(\frac{r_0}{r_{ij}} \right)^6 \right]$$

parameters $\begin{cases} \xi_{ij} \rightarrow \text{interaction strength} [\text{kcal/mol}] \\ r_0 \rightarrow \text{van der waals radius (\AA)} \end{cases}$

variable $\{ r_{ij} \rightarrow \text{interatomic distance (\AA)}$

$$E_{vdw}(0) = \infty \quad 0 \leq r_{ij} < \infty$$

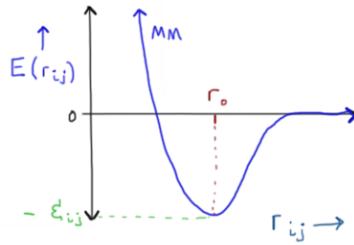
$$E_{vdw}(r_0) = -\xi_{ij} \quad -\xi_{ij} \leq E_{vdw} < \infty$$

$$E_{vdw}(\infty) = 0 \quad \cancel{\text{He} \text{He}} \rightarrow \quad \text{He} \rightarrow \leftarrow \text{He}$$

short range \rightarrow exchange / sterics repulsion

long range \rightarrow London dispersion attraction

$$\mathcal{O}(N) \rightarrow \text{bonded terms} \quad \mathcal{O}(N^2) \rightarrow \text{non-bonded pairs}$$



"Combining rules"

$$\xi_{ij} = \sqrt{\xi_i \xi_j} \quad \text{"geometric mean"}$$

$$r_0 = \frac{1}{2} (r_i + r_j) \quad \text{"arithmetic mean"}$$

$\xi_i, r_i \rightarrow$ atomic parameters

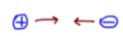
5.25 MM Electrostatics Terms

Electrostatics Terms

$$E_{\text{elst}} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}}$$

parameters $\{q_i, q_j \rightarrow \text{atomic partial charges (e)}\}$

variable $\{r_{ij} \rightarrow \text{interatomic distance (\AA)}\}$



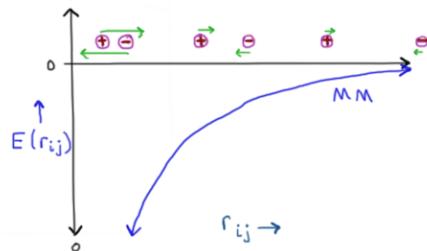
repulsion

attraction

$$q_{\text{tot}} = \sum_{i=1}^N q_i = 0 \quad \text{usually}$$

$\mathcal{O}(N)$ bonded terms

$\mathcal{O}(N^2)$ non-bonded terms



vdw $\propto \left(\frac{1}{r}\right)^6 \rightarrow$ quick decay

elst $\propto \left(\frac{1}{r}\right)^1 \rightarrow$ slow decay

elst is rate limiting step of MM

5.26 MM Cross Terms

Cross Terms

Does changing r change θ_{eq} ?



2nd order Taylor series

$$E(r, \theta) \approx E(r_{eq}, \theta_{eq}) + \frac{\partial E(r_{eq}, \theta_{eq})}{\partial r} (r - r_{eq}) + \frac{\partial E(r_{eq}, \theta_{eq})}{\partial \theta} (\theta - \theta_{eq}) + \frac{1}{2} \underbrace{\frac{\partial^2 E(r_{eq}, \theta_{eq})}{\partial r^2} (r - r_{eq})^2}_{E_{bond}} + \underbrace{\frac{1}{2} \frac{\partial^2 E(r_{eq}, \theta_{eq})}{\partial \theta^2} (\theta - \theta_{eq})^2}_{E_{angle}} + \underbrace{\frac{\partial^2 E(r_{eq}, \theta_{eq})}{\partial r \partial \theta} (r - r_{eq})(\theta - \theta_{eq})}_{\text{Cross Term}}$$

$$K_{a,r} = \frac{\partial^2 E(r_{eq}, \theta_{eq})}{\partial r \partial \theta}$$

$K_{a,r} \rightarrow$ bond-angle cross-term force constant
(kcal/mole·Å·rad)

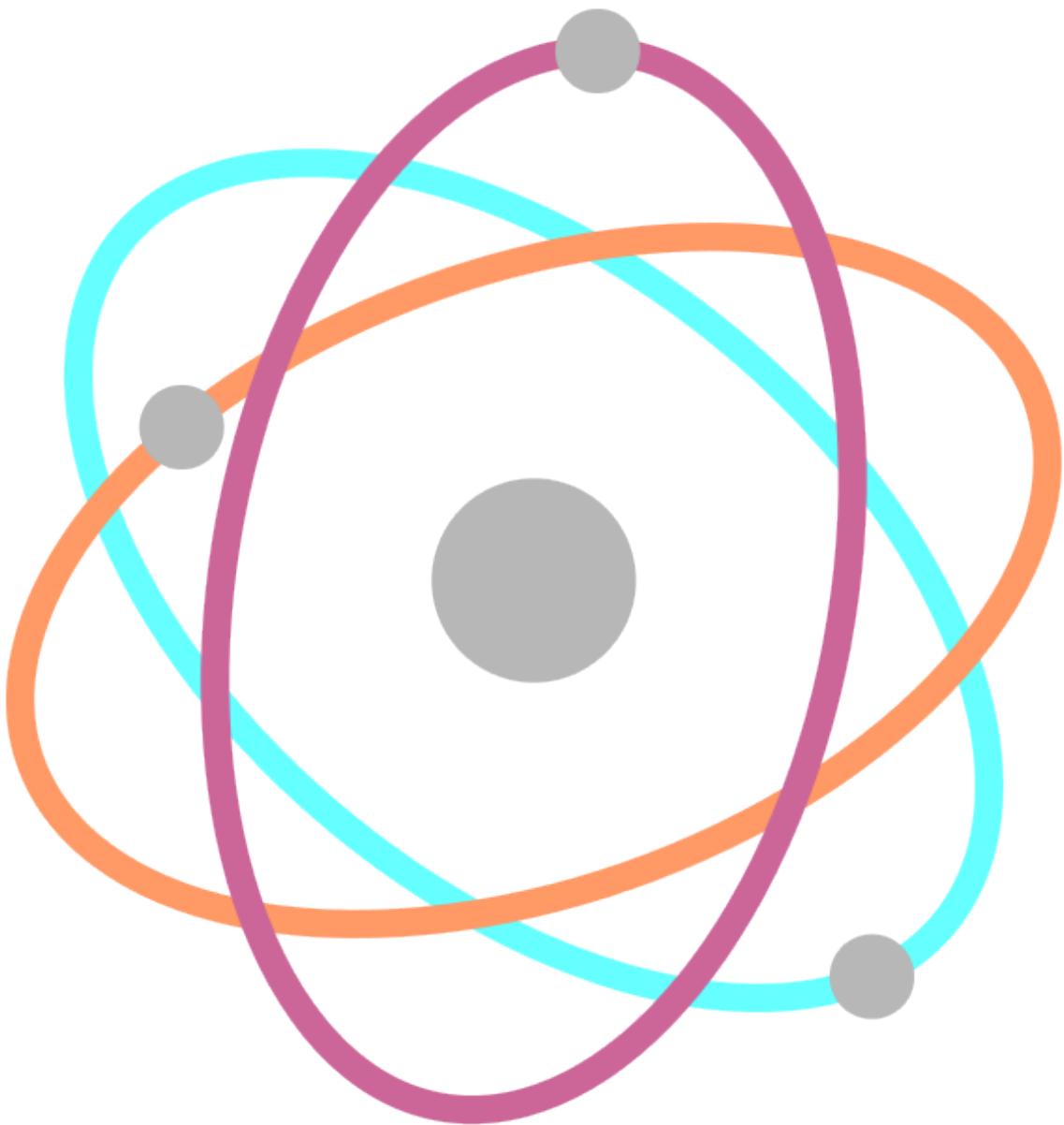
hope $\{K_{a,i}\} \approx 0 \rightarrow$ set to zero

$$E_{\text{bond-angle}} = K_{a,r} (r - r_{eq})(\theta - \theta_{eq})$$

can have

- bond-bond
- bond-angle
- angle-angle
- ...
- etc.

5.27 MM Program



5.28 Energy Gradient

Energy Gradient

$$V(x) \rightarrow \text{potential energy} \quad \frac{1}{2} kx^2$$

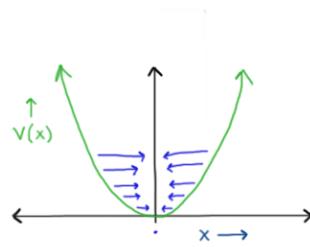
$$F(x) = -\frac{dV(x)}{dx} \rightarrow \text{force} \quad -kx$$

$$\text{in 3-D} \quad V(x) \rightarrow V(x, y, z)$$

$$-\frac{dV(x)}{dx} \rightarrow -\left(\underbrace{\frac{\partial V}{\partial x} \hat{x} + \frac{\partial V}{\partial y} \hat{y} + \frac{\partial V}{\partial z} \hat{z}}_{-\nabla V(x, y, z)} \right)$$

$$\text{"gradient"} \quad -\nabla V(x, y, z)$$

$$N \text{ atoms} \rightarrow 3N \text{ coordinates}$$



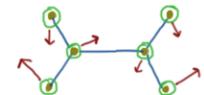
$$V = V(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N)$$

$$= V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

$$= V(\vec{r}^{3N})$$

$$V(\vec{r}^{3N}) \rightarrow \text{energy}$$

$$-\nabla V(\vec{r}^{3N}) \rightarrow \text{force}$$



5.29 Energy Minimization

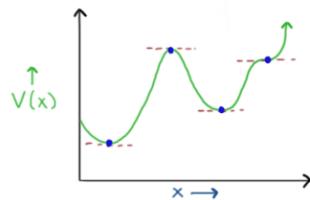
Energy Minimization

$\frac{dV(x)}{dx} = 0 \rightarrow \text{"stationary point"}$

$$\frac{d^2V(x)}{dx^2} \begin{cases} > 0 & \text{local minimum} \\ < 0 & \text{local maximum} \\ = 0 & \text{unknown} \end{cases}$$

1D	3D
$\frac{dV(x)}{dx} = 0$	$ \nabla V(\vec{r}^{3N}) = 0$
$\frac{d^2V(x)}{dx^2} > 0$	$\{\lambda_H\} \geq 0, H_{ij} = \frac{\partial^2 V(\vec{r}^{3N})}{\partial q_i \partial q_j}$

$\underline{H} \rightarrow 3N \times 3N$ real, symmetric "Hessian matrix"



$\left(\begin{array}{l} \text{lowest } V(\vec{r}^{3N}) \text{ among} \\ \text{local minima} \end{array} \right) \rightarrow \text{global minimum}$

"Geometry Optimization" \rightarrow algorithm to find $\{\vec{r}^{3N}\}$ with minimum P.E.

5.30 Steepest Descent

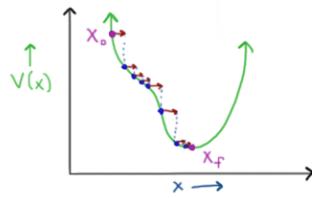
Steepest Descent

Method for obtaining local stationary points of a multi-dimensional function

Simple method for geometry optimization

- 1) Guess \underline{x}_0 "initial geometry"
- 2) Compute $V(\underline{x}_i)$ and $\nabla V(\underline{x}_i)$ energy and gradient
- 3) Update $\underline{x}_{i+1} = \underline{x}_i - \gamma_i \nabla V(\underline{x}_i)$ displacement
- 4) Check for convergence
if yes: done $\underline{x}_f = \underline{x}_i$
if no: return to step 2

various methods for choosing γ_i



Convergence checks

- $\|\nabla V(\underline{x}_i)\| \approx 0$ gradient
- $|V(\underline{x}_i) - V(\underline{x}_{i-1})| \approx 0$ energy
- $\|\underline{x}_i - \underline{x}_{i-1}\| \approx 0$ displacement

5.31 Conjugate Gradient

Conjugate Gradient

More advanced energy minimization algorithm than steepest descent

Use step history to accelerate convergence

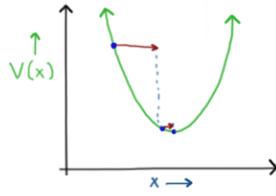
Same algorithm as S.D. except update

$$S.D. \rightarrow \underline{x}_{i+1} = \underline{x}_i - \gamma_i \nabla V(\underline{x}_i)$$

$$C.G. \rightarrow \underline{x}_{i+1} = \underline{x}_i - \gamma_i (\nabla V(\underline{x}_i) + \beta \underline{h}_{i-1})$$

$$\underline{h}_i = \nabla V(\underline{x}_i) + \beta \underline{h}_{i-1}$$

various methods for γ , β , \underline{h}_0



more advanced options

- Newton-Raphson

- R.F.O.

- ...

- etc.

5.32 Ensemble Properties

Ensemble Properties

energy minimization → lowest energy structure
need to average over contributions of
all structures

$A \rightarrow$ any physical property

$$\langle A \rangle = \bar{A} = \sum_{i=1}^{\text{states}} p_i A_i \quad \text{"discrete"}$$

probability of state i value of A in i

$$p_i \propto e^{-E_i/k_b T} \quad \text{"Boltzmann factor"}$$

$$q = \sum_{i=1}^{\text{states}} e^{-E_i/k_b T} = \int_{\mathbb{R}^N} d\vec{r}^N e^{-E(\vec{r}^N)/k_b T}$$

$$p_i = \frac{1}{q} e^{-E_i/k_b T} \quad \text{"partition function"}$$

$$\bar{A} = \int_{\mathbb{R}^N} d\vec{r}^N \left(\frac{1}{q} e^{-E(\vec{r}^N)/k_b T} \right) A(\vec{r}^N)$$

$$\bar{A} = \frac{\int_{\mathbb{R}^N} d\vec{r}^N A(\vec{r}^N) e^{-E(\vec{r}^N)/k_b T}}{\int_{\mathbb{R}^N} d\vec{r}^N e^{-E(\vec{r}^N)/k_b T}}$$

"Boltzmann-weighted average"

Analytic (exact) integration → very difficult

Numerical (approximate) integration

- grid → time consuming (naive)
- time average → molecular dynamics
- random average → Monte Carlo

5.33 Thermal Energy

Thermal Energy

$3N$ coordinates $\rightarrow x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N$

$3N$ velocities $\rightarrow v_{x1}, v_{y1}, v_{z1}, v_{x2}, v_{y2}, v_{z2}, \dots, v_{xN}, v_{yN}, v_{zN}$

coordinates $\rightarrow PE$

velocities $\rightarrow KE$

$$PE = V(\{x_i, y_i, z_i\})$$

$$KE = \sum_{i=1}^N \frac{1}{2} m_i (v_{xi}^2 + v_{yi}^2 + v_{zi}^2)$$

$$T \propto KE \rightarrow v_{rms} \propto \sqrt{T}$$

$$v_i = \sqrt{v_{xi}^2 + v_{yi}^2 + v_{zi}^2} \quad v_{rms} = \sqrt{\langle v_i^2 \rangle}$$

$$PV = nRT = Nk_b T = \sum_{i=1}^N \frac{1}{2} m_i v_i^2$$

$$\langle mv^2 \rangle = \frac{1}{N} \sum_{i=1}^N m_i v_i^2$$

$$Nk_b T = \frac{N}{2} \left(\frac{1}{N} \sum_{i=1}^N m_i v_i^2 \right) = \frac{N}{2} \langle mv^2 \rangle$$

$$2k_b T = \langle mv^2 \rangle = \langle mv_x^2 \rangle + \langle mv_y^2 \rangle + \langle mv_z^2 \rangle$$

$$\langle mv_x^2 \rangle = \langle mv_y^2 \rangle = \langle mv_z^2 \rangle$$

$$2k_b T = 3 \langle mv_x^2 \rangle$$

$$|\bar{v}_{xi}| \approx \sqrt{\frac{2k_b T}{3m_i}}$$

5.34 Boundary Conditions

Boundary Conditions

Represent infinite system with finite repeating sample

$$\left. \begin{array}{l} 0 \leq x < D_x \\ 0 \leq y < D_y \\ 0 \leq z < D_z \end{array} \right\} \text{repeating unit cell}$$

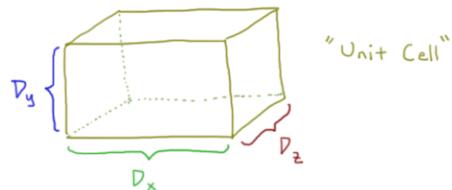
original particle at (x, y, z)

image particles at

$$(x + n_x D_x, y + n_y D_y, z + n_z D_z)$$

$$\{n_x, n_y, n_z\} \in \mathbb{Z}$$

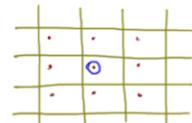
$$-\infty < (n_x, n_y, n_z) < \infty$$



$v_{dw} \rightarrow$ converges quickly ($\propto \frac{1}{r^6}$)

$E_{elst} \rightarrow$ converges slowly ($\frac{1}{r}$)

must have neutral unit cell for finite E_{elst}



5.35 Molecular Dynamics

Molecular Dynamics

calculate system properties by propagating through time and averaging

Classical Mechanics \rightarrow Newton's Laws

MM \rightarrow conservative, time-independent PE

$$F = ma = m \frac{d^2(x)}{dt^2} = \frac{d}{dt} \left(m \frac{dx(t)}{dt} \right) = \frac{d}{dt} (mv) = \frac{dp}{dt}$$

$$F = - \frac{dV(x)}{dx} \quad p = mv = m \frac{dx(t)}{dt}$$

$$\frac{\partial p_{xi}}{\partial t} = - \frac{\partial V}{\partial x_i}$$

solve for all $3N$ coordinates

can't solve exactly \rightarrow approximate numerically

- 1) Assign initial $x_0, p_0, t=0$
 - 2) Compute $V(x_i), \nabla V(x_i)$
 - 3) Update $x_{i+1} = x_i + \frac{1}{m} p_i \Delta t$
 - 4) Update $p_{i+1} = p_i - \nabla V(x_i) \Delta t$
- $t = t + \Delta t$
- 5) Repeat until $t \geq t_f$
 - 6) Compute desired properties

$\Delta t \rightarrow$ timestep ($1 \text{ fs} = 10^{-15} \text{ s}$)

$t \rightarrow$ depends on goal

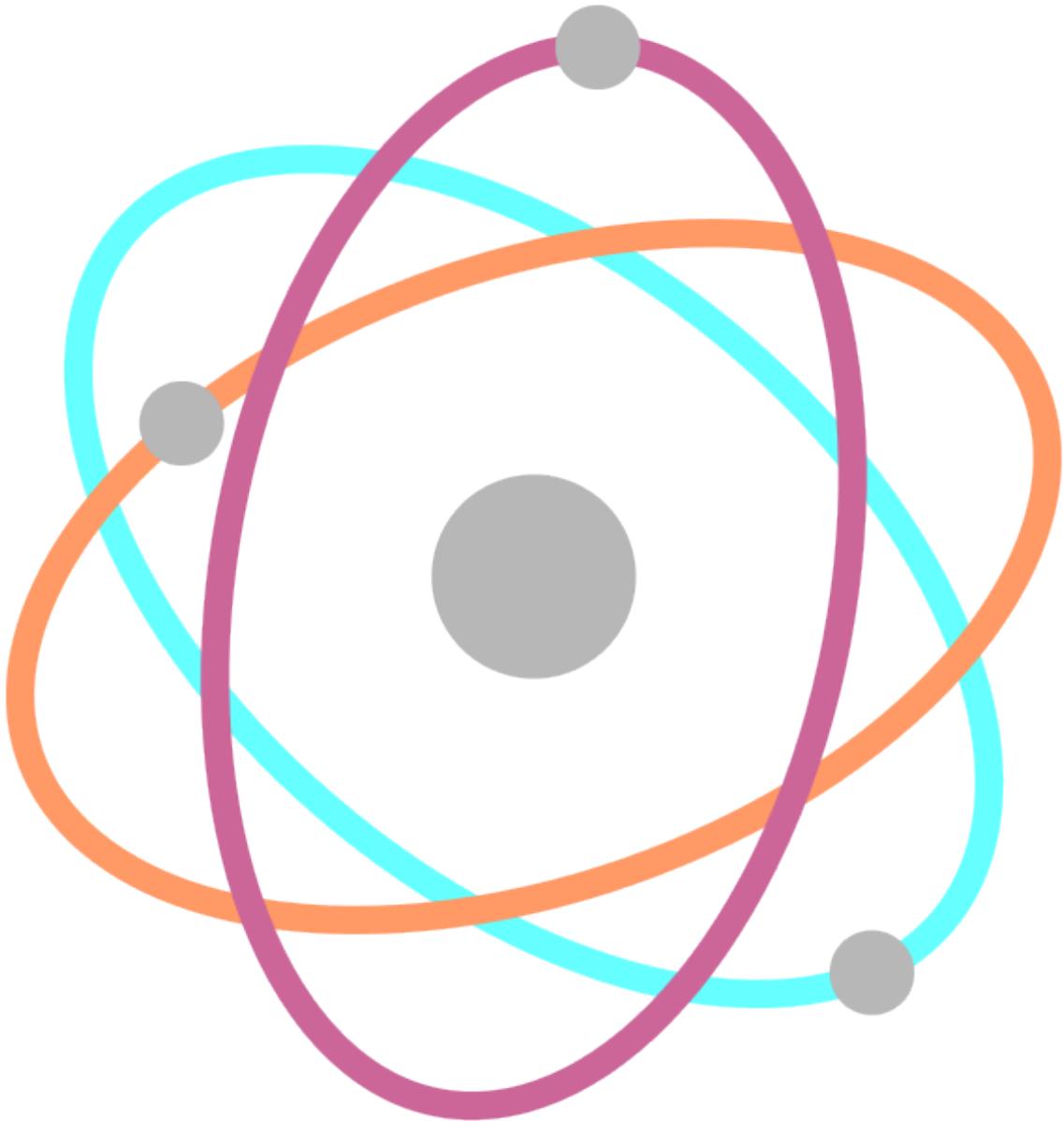
vibrations $\rightarrow 10-1,000 \text{ fs}$

conformation changes $\rightarrow \text{ps}-\text{ns}$

diffusion / interaction $\rightarrow \text{ns}-\mu\text{s}$

protein folding $\rightarrow \mu\text{s}-\text{s}$

5.36 MD Program



5.37 Monte Carlo

Monte Carlo

N atoms $\rightarrow 3N$ coordinates

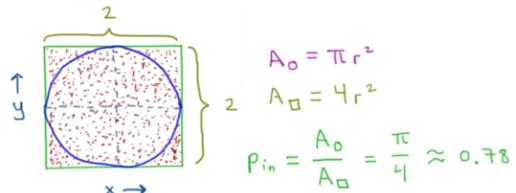
$$E = E(\vec{r}^{3N})$$

$$\bar{E} = \frac{\int_{\mathbb{R}^{3N}} d\vec{r}^{3N} E(\vec{r}^{3N}) e^{-E(\vec{r}^{3N})/k_b T}}{\int_{\mathbb{R}^{3N}} d\vec{r}^{3N} e^{-E(\vec{r}^{3N})/k_b T}}$$

$$\bar{E} \approx -\frac{\sum_{i=1}^M E_i e^{-E_i/k_b T}}{\sum_{i=1}^M e^{-E_i/k_b T}}$$

choose M random points for sum

choose random values for each coordinate



$$\pi \approx 4(\rho_{in}) \quad \lim_{m \rightarrow \infty} (4\rho_{in}) = \pi$$

very inefficient

need large number of points

most structures don't contribute

$$E_i \gg k_b T \rightarrow \rho_i \approx 0$$

need better algorithm

5.38 Metropolis Monte Carlo

Metropolis Monte Carlo

MC method biased towards low E

Most structures don't contribute to properties
if $E_i \gg k_b T$, then $p_i \approx 0$

- 1) Assign initial \underline{x} .
- 2) Randomly perturb $\underline{x}_{i+1} = \underline{x}_i + \Delta \underline{x}_{\text{rand}}$
- 3) Compute E_{i+1}
- 4) If $E_{i+1} \leq E_i$, accept \underline{x}_{i+1}
Else choose random a , $0 \leq a \leq 1$
If $\exp(-(E_{i+1} - E_i)/k_b T) > a$, accept
Else reject \underline{x}_{i+1} , keep \underline{x}_i \underline{x}_{i+1}
- 5) Repeat until N_{trials} reached

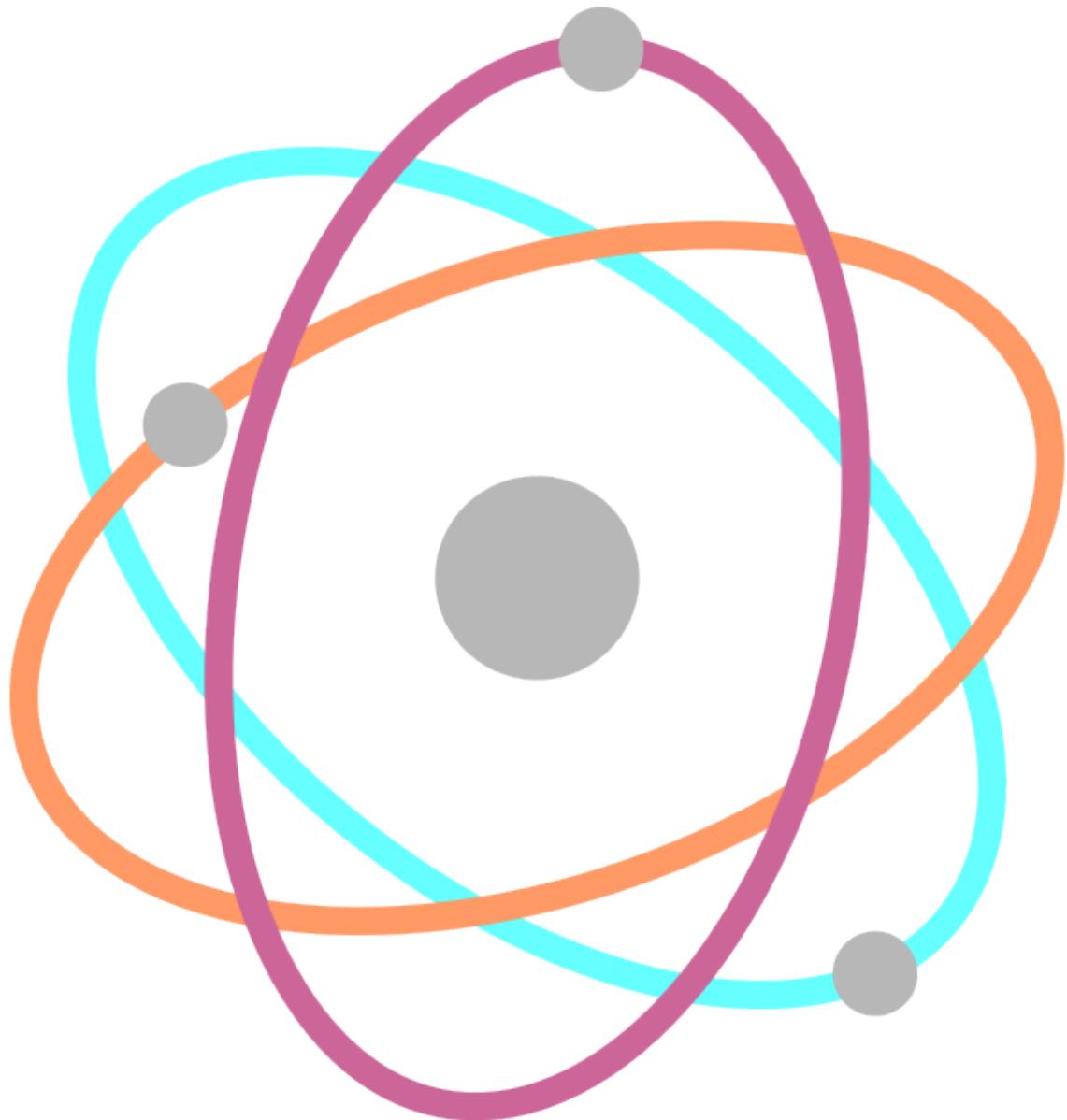
Adjust $\langle \|\Delta \underline{x}_{\text{rand}}\| \rangle$ such that
 $\sim 50\%$ of $\{\underline{x}_{i+1}\}$ are accepted

"Multiple minima problem"

not trajectory \rightarrow jagged path

no time \rightarrow just trials

5.39 MC Program



5.40 Simulated Annealing

Simulated Annealing

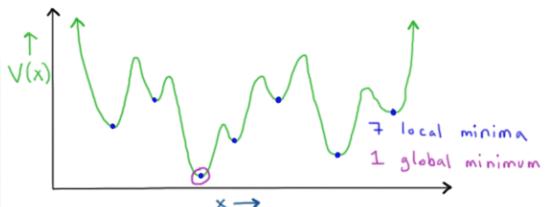
Method for generating multiple minimum energy structures

- SD, CG, NR, RFO
- local minimum only
- deterministic
- downhill only

SA

- multiple minima
- stochastic
- uphill and downhill

Better results as $T_0 \rightarrow \infty$ and/or $\alpha \rightarrow 0$



- 1) Assign initial x_0 .
- 2) Propagate $x_i \rightarrow x_{i+1}$ MM, MC, etc.
- 3) Decrease T $T_{i+1} = T_0(1-\alpha)$
- 4) Repeat until $T_i = 0$

$$\alpha = i / N_{\text{trials}}$$

$$\rho_{\min} \approx q_{\min} / q_{\max}$$

5.41 Molecular Hamiltonian

Molecular Hamiltonian

time-independent, non-relativistic Schrödinger equation

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

\hat{H} → Hamiltonian operator

E → molecular total energy

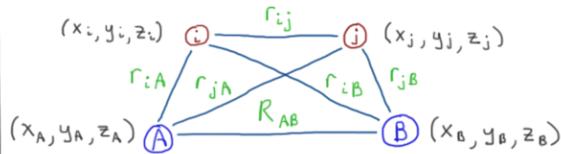
$|\psi\rangle$ → molecular wavefunction

N electrons i, j, k, \dots $\vec{r}_i = (x_i, y_i, z_i)$

M nuclei A, B, C, \dots $\vec{r}_A = (x_A, y_A, z_A)$

$$\vec{r}_{12} = (x_2 - x_1, y_2 - y_1, z_2 - z_1)$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \quad \text{"Laplacian"}$$



$$\hat{H} = \underbrace{\hat{T}}_{\text{kinetic energy}} + \underbrace{\hat{V}}_{\text{potential energy}} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{Ne} + \hat{V}_{ee}$$

kinetic energy potential energy
of particles of particle pairs

$$\begin{aligned} \hat{H} = & - \sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{A=1}^M \sum_{B=A+1}^M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} \\ & - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i=1}^N \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} \end{aligned}$$

$$V_{12} = \frac{q_1 q_2}{4\pi\epsilon_0 r_{12}} \quad \text{"Coulomb's Law"}$$

5.42 Atomic Units

Atomic Units

$m, kg, C, J, \dots \rightarrow$	inconvenient at molecular scale
mass $\rightarrow m_e = 1$	$9.109 \cdot 10^{-31} \text{ kg}$
charge $\rightarrow e = 1$	$1.602 \cdot 10^{-19} \text{ C}$
angular momentum $\rightarrow \hbar = 1$	$1.055 \cdot 10^{-34} \text{ J}\cdot\text{s}$
permittivity $\rightarrow 4\pi\epsilon_0 = 1$	$1.113 \cdot 10^{-10} \frac{\text{C}^2}{\text{J}\cdot\text{m}}$
length $\rightarrow a_0 = 1$	$5.292 \cdot 10^{-11} \text{ m}$
$\hat{T}_e = -\sum_{i=1}^N \frac{k^2}{2m_e} \nabla_i^2 = -\sum_i \frac{1}{2} \nabla_i^2$	
$\hat{T}_N = -\sum_{A=1}^M \frac{k^2}{2M_A} \nabla_A^2 = -\sum_A \frac{1}{2M_A} \nabla_A^2$	
$M_A \rightarrow [m_e]$	$M_H \approx 1,836$

$$\hat{V}_{NN} = \sum_{A=1}^M \sum_{B=A+1}^M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} = \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$$

$$\hat{V}_{Ne} = -\sum_{A=1}^M \sum_{i=1}^N \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} = -\sum_{iA} \frac{Z_A}{r_{iA}}$$

$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} = \sum_{i < j} \frac{1}{r_{ij}}$$

$$Z_A \rightarrow [e] \quad Z_H = 1$$

$$\hat{H} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{i < j} \frac{1}{r_{ij}} \\ + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$$

5.43 Born-Oppenheimer Approximation

Born - Oppenheimer Approximation

$\hat{H}|\psi\rangle = E|\psi\rangle \rightarrow$ can't solve exactly

N charged particles $\rightarrow \frac{N(N-1)}{2!}$ interacting pairs

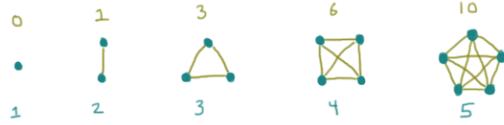
"many-body problem" \rightarrow unsolvable for $N > 2$

"NP-complete" $\rightarrow \mathcal{O}(e^N)$ difficulty

$\{M_A\} \gg m_e \rightarrow \{A\}$ move very slow relative to $\{i\}$

Approximate $\{\vec{R}_A\}$ fixed $\rightarrow \hat{T}_N = 0$

nuclei \rightarrow classical point particles



$$\hat{H}_{\text{mol}} = \underbrace{\sum_A -\frac{i}{2M_A} \nabla_A^2}_{0} + \underbrace{\sum_{A < B} \frac{Z_A Z_B}{R_{AB}}}_{\text{constant}} + \underbrace{\sum_i -\frac{1}{2} \nabla_i^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{ij} \frac{1}{r_{ij}}}_{\text{still difficult}}$$

$$\hat{H}_{\text{elec}} |\Psi_{\text{elec}}\rangle = E_{\text{elec}} |\Psi_{\text{elec}}\rangle$$

$$\hat{H}_{\text{elec}} = - \sum_i \frac{1}{2} \nabla_i^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{ij} \frac{1}{r_{ij}}$$

$V_{NN} = \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$ \rightarrow constant, can be added or not
only affects E , not $|\psi\rangle$

5.44 Spin Orbitals

Spin Orbitals

"orbital" → 1-electron wavefunction
 occupied → electron exists in orbital
 virtual → unoccupied, no electron
 spatial → specifies x, y, z coords (no spin)
 spin → specifies x, y, z coords and spin
 $\vec{r} = (x, y, z)$ $\omega \rightarrow \text{spin}$ $\omega = |\alpha\rangle \text{ or } |\beta\rangle$
 $\vec{x} = (\vec{r}, \omega) = (x, y, z, \omega)$ spin up spin down
 $\int d\omega \alpha^*(\omega) \alpha(\omega) = \int d\omega \beta^*(\omega) \beta(\omega) = 1$
 $\int d\omega \alpha^*(\omega) \beta(\omega) = \int d\omega \beta^*(\omega) \alpha(\omega) = 0$
 $\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$ $\{|\alpha\rangle, |\beta\rangle\} \rightarrow \text{orthonormal}$
 $\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$

$$\underbrace{\chi(\vec{x}_i)}_{\substack{\text{spin} \\ \text{orbital}}} = \underbrace{\phi(\vec{r}_i)}_{\substack{\text{spatial} \\ \text{orbital}}} \underbrace{\sigma(\omega_i)}_{\substack{\text{spin} \\ \text{function}}}$$

$$\chi(\vec{x}_i) = \begin{cases} \phi(\vec{r}_i) |\alpha\rangle \\ \text{or} \\ \phi(\vec{r}_i) |\beta\rangle \end{cases}$$

$$\phi^*(\vec{r}_i) \phi(\vec{r}_i) d^3 r_i = \begin{pmatrix} \text{probability of finding} \\ \text{electron 1 near point } r_i \end{pmatrix}$$

$$\int d^3 r_i \phi^*(\vec{r}_i) \phi(\vec{r}_i) = \langle \phi | \phi \rangle = 1 \rightarrow \text{normalized}$$

if $\{\phi_i\}$ are "complete" then

$$f(\vec{r}) = \sum_i a_i \phi_i(\vec{r}) \quad \text{for any } f(\vec{r})$$

just need $\{a_i\}$ from $a_i = \langle \phi_i | f \rangle$

5.45 Hartree Product

Hartree Products

imagine $\hat{V}_{ee} = 0$ (not correct)

$$\text{then } \hat{H}_{\text{elec}} = \sum_{i=1}^N \hat{h}(i)$$

$$\text{where } \hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}}$$

and $\chi(\vec{x}_i)$ becomes an eigenfunction of $\hat{h}(i)$

$$\hat{h}(i) \chi(\vec{x}_i) = \epsilon_i \chi(\vec{x}_i)$$

$\epsilon_i \rightarrow \text{orbital energy}$

then

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \chi_1(\vec{x}_1) \chi_2(\vec{x}_2) \dots \chi_N(\vec{x}_N)$$

$$\Psi(\{\vec{x}_i\}) = \prod_{i=1}^N \chi_i(\vec{x}_i)$$

independent, "uncorrelated" electrons

$$|\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_N = \\ |\chi_1(\vec{x}_1)|^2 d\vec{x}_1 |\chi_2(\vec{x}_2)|^2 d\vec{x}_2 \dots |\chi_N(\vec{x}_N)|^2 d\vec{x}_N$$

problem: we know which electron is in which orbital (distinguishable)

5.46 Anti-Symmetry Principle

Antisymmetry Principle

no spin in \hat{H} , fix problems with:

$$\Psi(\vec{x}_1, \dots, \vec{x}_i, \vec{x}_{\underline{i}}, \dots, \vec{x}_N) = -\Psi(\vec{x}_1, \dots, \vec{x}_j, \vec{x}_{\underline{j}}, \dots, \vec{x}_N)$$

must be true for all $1 \leq \{i, j\} \leq N$

not true for Hartree products

$$\Psi(1, 2) = \Psi_1(1) \Psi_2(2)$$

$$\Psi(2, 1) = \Psi_1(2) \Psi_2(1) = \Psi_1(1) \Psi_2(2) = +\Psi(1, 2) \quad \times \\ \neq -\Psi(1, 2)$$

instead, use linear combination

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} [\Psi_1(1) \Psi_2(2) - \Psi_2(1) \Psi_1(2)]$$

$$\Psi(2, 1) = \frac{1}{\sqrt{2}} [\Psi_1(2) \Psi_2(1) - \Psi_2(2) \Psi_1(1)] \\ = -\Psi(1, 2) \quad \checkmark$$

$$\Psi(1, 2, 3) = \frac{1}{\sqrt{6}} [\Psi_1(1) \Psi_2(2) \Psi_3(3) \\ - \Psi_1(1) \Psi_2(3) \Psi_3(2) \\ + \Psi_1(2) \Psi_2(1) \Psi_3(3) \\ - \Psi_1(2) \Psi_2(3) \Psi_3(1) \\ + \Psi_1(3) \Psi_2(1) \Psi_3(2) \\ - \Psi_1(3) \Psi_2(2) \Psi_3(1)]$$

switch sign on all exchanges

N electrons \rightarrow $N!$ terms \rightarrow $\frac{1}{\sqrt{N!}}$ normalization constant

5.47 Slater Determinants

Slater Determinants

formalize anti-symmetric wavefunctions

$$\Psi(1, \dots, \underline{i}, \underline{j}, \dots, N) = -\Psi(1, \dots, \underline{j}, \underline{i}, \dots, N)$$

for all $1 \leq \{i, j\} \leq N$

$$\Psi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) \end{vmatrix}$$

rows \rightarrow electrons

columns \rightarrow spin orbitals

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \dots & \chi_N(N) \end{vmatrix}$$

if 2 electrons in same orbital
or 2 orbitals are the same $\rightarrow \Psi = 0$

$$\langle \Psi_A | \Psi_B \rangle = \begin{cases} 1 & \text{if all } \{x_i\} \text{ are same} \\ 0 & \text{otherwise} \end{cases}$$

5.48 Excited Determinants

Excited Determinants

N electrons

K basis functions
 $2K$ spin orbitals

$$\binom{2K}{N} = \frac{(2K)!}{(2K-N)!N!} = \mathcal{O}(K!) \text{ excited determinants}$$

$|\Psi_0\rangle = |x_1 x_2 \dots x_a x_b \dots x_N\rangle \rightarrow \text{ground state}$

$|\Psi_{ab}^r\rangle = |x_1 x_2 \dots x_r x_b \dots x_N\rangle \rightarrow \text{singly excited}$

$|\Psi_{ab}^{rs}\rangle = |x_1 x_2 \dots x_r x_s \dots x_N\rangle \rightarrow \text{doubly excited}$

$|\Psi_{ab\dots gm}^{rs\dots em}\rangle \rightarrow M\text{-fold excited}, 0 \leq M \leq N$

N occupied orbitals
 $2K-N$ virtual orbitals

$1 \rightarrow \mathcal{O}(1)$ ground state x_K

$(2K-N)N \rightarrow \mathcal{O}(N^2)$

singly excited

$(2K-N)(2K-N-1)N(N-1)/4 x_{N+2}$

$\hookrightarrow \mathcal{O}(N^4)$ doubly excited

M -fold excited

$\hookrightarrow \mathcal{O}(N^{2M})$

x_K

x_{N+1}

x_N

x_{N-1}

x_b

x_a

x_z

x_1

$|\Psi_0\rangle$

$|\Psi_{ab}^r\rangle$

5.49 N-Electron Wavefunctions

N-Electron Wavefunctions

can represent any N-electron wavefunction as a linear combination of all determinants of a complete set of spin orbitals

$$|\Psi\rangle = c_0 |\Psi_0\rangle + \underbrace{\sum_{\alpha r} c_{\alpha r} |\Psi_{\alpha r}\rangle}_{\text{ground state}} + \underbrace{\sum_{\alpha < b} \sum_{r s} c_{\alpha b}^{rs} |\Psi_{\alpha b}^{rs}\rangle}_{\text{singles}} + \underbrace{\sum_{\alpha < b} \sum_{r s t} c_{\alpha b c}^{rst} |\Psi_{\alpha b c}^{rst}\rangle}_{\text{doubles}} + \dots$$

$$\sum_{\alpha r} \rightarrow \sum_{\alpha=1}^N \sum_{r=N+1}^{2K} \rightarrow \mathcal{O}(N) \cdot \mathcal{O}(K) \approx \mathcal{O}(N^2)$$

$$\sum_{\alpha < b} \sum_{r s} \rightarrow \sum_{\alpha=1}^N \sum_{b=\alpha+1}^N \sum_{r=N+1}^{2K} \sum_{s=r+1}^{2K} \rightarrow \mathcal{O}(N^4)$$

$$\sum_{\alpha < b < c} \rightarrow \sum_{\alpha=1}^N \sum_{b=\alpha+1}^N \sum_{c=b+1}^N \sum_{r=N+1}^{2K} \sum_{s=r+1}^{2K} \sum_{t=s+1}^{2K} \rightarrow \mathcal{O}(N^6)$$

$|\Psi_0\rangle \rightarrow \text{HF}$

$|\Psi_0\rangle, \{|\Psi_{ab}^{rs}\rangle\} \rightarrow \text{CID}$

$|\Psi_0\rangle, \{|\Psi_{\alpha r}\rangle\}, \{|\Psi_{ab}^{rs}\rangle\} \rightarrow \text{CISD}$

"", "", $\{|\Psi_{abc}^{rst}\rangle\} \rightarrow \text{CISDT}$

CISDTQ5

CISDTQ56

:

Full CI

5.50 Restricted Determinants

Restricted Determinants

"restricted" $\rightarrow \alpha, \beta$ pairs must have same spatial orbital

- closed shell $\frac{+}{+}$
- most common $\frac{-}{-}$
- simple $\frac{-}{-}$

"unrestricted" $\rightarrow \alpha, \beta$ pairs can have different spatial orbitals

- open shell $\frac{+}{-}$
- less common $\frac{-}{+}$
- more complex $\frac{-}{+}$



$$\Psi_1 = \Psi_1 |\alpha\rangle \quad \bar{\Psi}_1 = \bar{\Psi}_1 |\beta\rangle$$

$$|\Psi_0\rangle = |x_1 x_2 \dots x_N\rangle = |\Psi_1 \bar{\Psi}_1 \Psi_2 \bar{\Psi}_2 \dots \Psi_{N/2} \bar{\Psi}_{N/2}\rangle \\ = |1\ 1\ 2\ 2\ \dots\ N/2\ N/2\rangle$$

RHF

UHF

ROHF

5.51 One-Electron Integrals

One-Electron Integrals

$$|\Psi_0\rangle = |\underline{x}_1 \underline{x}_2 \dots \underline{x}_N\rangle \quad E = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

two types of operators in \hat{H} :

$$\cdot \hat{O}_1 \rightarrow 1\text{-electron: } \hat{T}_e, \hat{V}_{Ne}$$

$$\cdot \hat{O}_2 \rightarrow 2\text{-electron: } \hat{V}_{ee}$$

$$\hat{H} = \sum_i \hat{O}_1^{(i)} + \sum_{i,j} \hat{O}_2^{(ij)}$$

$$E = \sum_i \langle \Psi_0 | \hat{O}_1^{(i)} | \Psi_0 \rangle + \sum_{i,j} \langle \Psi_0 | \hat{O}_2^{(ij)} | \Psi_0 \rangle$$

$$\hat{O}_1 = \sum_{i=1}^N \hat{h}_i \quad \hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \xrightarrow{\text{"core"}} \text{Hamiltonian}$$

for 2-electron system:

$$|\Psi_0\rangle = |\underline{x}_1 \underline{x}_2\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} x_1(1) & x_2(1) \\ x_1(2) & x_2(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} x_1(1)x_2(2) \\ -x_1(2)x_2(1) \end{bmatrix}$$

$$\langle \Psi_0 | \hat{O}_1^{(i)} | \Psi_0 \rangle = \int d\underline{x}_1 d\underline{x}_2 \left[\frac{1}{\sqrt{2}} (x_1(\underline{x}_1) x_2(\underline{x}_2) - x_1(\underline{x}_2) x_2(\underline{x}_1)) \right] \hat{O}_1^{(i)} \left[\frac{1}{\sqrt{2}} (x_1(\underline{x}_1) x_2(\underline{x}_2) - x_1(\underline{x}_2) x_2(\underline{x}_1)) \right]$$

$$\begin{aligned} &= \frac{1}{2} \left[\int d\underline{x}_1 d\underline{x}_2 x_1^*(\underline{x}_1) x_2^*(\underline{x}_2) \hat{O}_1^{(i)} x_1(\underline{x}_1) x_2(\underline{x}_2) \right. \\ &\quad - \int d\underline{x}_1 d\underline{x}_2 x_1^*(\underline{x}_1) x_2^*(\underline{x}_2) \hat{O}_1^{(i)} x_2(\underline{x}_1) x_1(\underline{x}_2) \\ &\quad - \int d\underline{x}_1 d\underline{x}_2 x_2^*(\underline{x}_1) x_1^*(\underline{x}_2) \hat{O}_1^{(i)} x_1(\underline{x}_1) x_2(\underline{x}_2) \\ &\quad \left. + \int d\underline{x}_1 d\underline{x}_2 x_2^*(\underline{x}_1) x_1^*(\underline{x}_2) \hat{O}_1^{(i)} x_2(\underline{x}_1) x_1(\underline{x}_2) \right] \\ &\quad \text{factor out all } f(\underline{x}_2), \hat{O}_1^{(i)} = f(\underline{x}_1) \\ &= \frac{1}{2} \int d\underline{x}_1 x_1^*(\underline{x}_2) x_2^*(\underline{x}_2) \int d\underline{x}_1 x_1^*(\underline{x}_1) \hat{O}_1^{(i)} x_1(\underline{x}_1) \\ &\quad - \frac{1}{2} \int d\underline{x}_2 x_1^*(\underline{x}_2) x_2^*(\underline{x}_2) \int d\underline{x}_1 x_2^*(\underline{x}_1) \hat{O}_1^{(i)} x_2(\underline{x}_1) \\ &\quad - \frac{1}{2} \int d\underline{x}_2 x_1^*(\underline{x}_2) x_2^*(\underline{x}_2) \int d\underline{x}_1 x_1^*(\underline{x}_1) \hat{O}_1^{(i)} x_1(\underline{x}_1) \\ &\quad + \frac{1}{2} \int d\underline{x}_2 x_1^*(\underline{x}_2) x_2^*(\underline{x}_2) \int d\underline{x}_1 x_2^*(\underline{x}_1) \hat{O}_1^{(i)} x_2(\underline{x}_1) \\ &= \frac{1}{2} (\langle 1 | \hat{O}_1^{(i)} | 1 \rangle + \langle 2 | \hat{O}_1^{(i)} | 2 \rangle) \xrightarrow{\text{X2 for 2 electrons}}$$

$$E_i = \sum_{i=1}^N \langle i | \hat{h}_i | i \rangle \quad h_i = \langle i | \hat{h}_i | i \rangle = \int d\underline{x}_1 x_i^*(\underline{x}_1) \hat{h}_i x_i(\underline{x}_1)$$

5.52 Two-Electron Integrals

Two-Electron Integrals

$$\hat{O}_2 = \hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{r_{ij}} = \sum_{i < j} \frac{1}{r_{ij}}$$

$$\langle \Psi_0 | \frac{1}{r_{12}} | \Psi_0 \rangle =$$

$$\begin{aligned} & \frac{1}{2} \int dx_1 dx_2 \underline{\chi}_1^*(1) \underline{\chi}_2^*(2) \frac{1}{r_{12}} \underline{\chi}_1(1) \underline{\chi}_2(2) \\ & - \frac{1}{2} \int dx_1 dx_2 \underline{\chi}_2^*(1) \underline{\chi}_1^*(2) \frac{1}{r_{12}} \underline{\chi}_1(1) \underline{\chi}_2(2) \\ & - \frac{1}{2} \int dx_1 dx_2 \underline{\chi}_1^*(1) \underline{\chi}_2^*(2) \frac{1}{r_{12}} \underline{\chi}_2(1) \underline{\chi}_1(2) \\ & + \frac{1}{2} \int dx_1 dx_2 \underline{\chi}_2^*(1) \underline{\chi}_1^*(2) \frac{1}{r_{12}} \underline{\chi}_2(1) \underline{\chi}_1(2) \end{aligned}$$

exchange dummy indices $1 \leftrightarrow 2$ in lines 3+4

$$\begin{aligned} & = \int dx_1 dx_2 \underline{\chi}_1^*(x_1) \underline{\chi}_2^*(x_2) \frac{1}{r_{12}} \underline{\chi}_1(x_1) \underline{\chi}_2(x_2) \\ & - \int dx_1 dx_2 \underline{\chi}_1^*(x_1) \underline{\chi}_2^*(x_2) \frac{1}{r_{12}} \underline{\chi}_2(x_1) \underline{\chi}_1(x_2) \end{aligned}$$

$$= \langle 12 | 12 \rangle - \langle 12 | 21 \rangle = \langle 12 | 21 \rangle$$

$$\begin{aligned} E_2 &= \sum_{i=1}^N \sum_{j=i+1}^N (\langle ij | ij \rangle - \langle ij | ji \rangle) \\ &= \sum_{i < j} \langle ij | ij \rangle = \sum_{i < j} v(i, j) \end{aligned}$$

$$\langle ij | kl \rangle \equiv \int dx_1 dx_2 \underline{\chi}_i^*(1) \underline{\chi}_j^*(2) \frac{1}{r_{12}} \underline{\chi}_k(1) \underline{\chi}_l(2)$$

physicist's notation

$$[ik | jl] \equiv \int dx_1 dx_2 \underline{\chi}_i^*(1) \underline{\chi}_k(1) \frac{1}{r_{12}} \underline{\chi}_j^*(2) \underline{\chi}_l(2)$$

chemist's notation

5.53 Spin Integration

Spin Integration

$$E_0 = \sum_{i=1}^N h(i) + \sum_{i=1}^N \sum_{j=i+1}^N v(i, j)$$

$$h(i) = \langle i | \hat{h}_i | i \rangle = \int dx_i x_i^*(x_i) \hat{h}_i x_i(x_i)$$

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad dx_i = dr_i d\omega_i$$

$$x_i = \begin{cases} \Psi_{i/2}|\alpha\rangle & i = 1, 3, \dots, N-1 \\ \Psi_{i/2}|\beta\rangle & i = 2, 4, \dots, N \end{cases}$$

$$\begin{aligned} \langle i | \hat{h}_i | i \rangle &= \int dr_i d\omega_i \Psi_{i/2}^*(r_i) \sigma_i^*(\omega_i) \hat{h}_i \Psi_{i/2}(r_i) \sigma_i(\omega_i) \\ &= \int d\omega_i \sigma_i^*(\omega_i) \sigma_j(\omega_i) \int dr_i \Psi_{i/2}^*(r_i) \hat{h}_i \Psi_{i/2}(r_i) \\ &= \delta_{\sigma_i \sigma_j} \langle i | h_i | i \rangle \end{aligned}$$

$$h_i = \delta_{\sigma_i \sigma_i}^{-1} \langle i | h_i | i \rangle$$

$$h_i = \langle i | h_i | i \rangle \quad \langle i | h_i | j \rangle = \int dr_i \Psi_{i/2}^*(r_i) \hat{h}_i \Psi_{j/2}(r_i)$$

$$[ij|kl] = \int d\omega_i \sigma_i^*(\omega_i) \sigma_j(\omega_i) \int d\omega_k \sigma_k^*(\omega_k) \sigma_l(\omega_k)$$

$$= \delta_{\sigma_i \sigma_j} \delta_{\sigma_k \sigma_l} \langle ij | kl \rangle$$

$$[ii|jj] = \delta_{\sigma_i \sigma_i}^{-1} \delta_{\sigma_j \sigma_j}^{-1} \langle ii | jj \rangle = \langle ii | jj \rangle$$

$$[ij|ji] = \delta_{\sigma_i \sigma_j} \delta_{\sigma_j \sigma_i} \langle ij | ji \rangle = \delta_{\sigma_i \sigma_j} \langle ij | ij \rangle$$

$$E_0 = \sum_{i=1}^N \underbrace{\langle i | h_i | i \rangle}_{\text{core}} + \sum_{i=1}^N \sum_{j=i+1}^N \underbrace{\langle ii | jj \rangle}_{\text{coulomb}} - \underbrace{\delta_{\sigma_i \sigma_j} \langle ij | ji \rangle}_{\text{exchange}}$$

5.54 Hartree-Fock Approximation

Hartree - Fock Approximation

$$\hat{H}_{\text{elec}} = \sum_{i=1}^N -\frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{r_{ij}}$$

$\hat{O}_1 \rightarrow \text{separable}$ $\hat{O}_2 \rightarrow \text{non-separable}$
 $\sum_{i=1}^N \hat{h}_i(i)$ \downarrow
 approximate!

average over "mean field" of other electrons

$$\hat{f}(i) = \hat{h}(i) + \hat{v}^{\text{HF}}(i)$$

Fock operator core Hamiltonian mean field operator

$$f(i) \chi_i(x_i) = \xi_i \chi_i(x_i)$$

$\chi_i \rightarrow \text{spin orbital}$

$\xi_i \rightarrow \text{orbital energy}$

pseudo - eigenvalue problem

$v_i^{\text{HF}} \rightarrow i \text{ feels effect of } \{1, 2, \dots, i-1, i+1, \dots, N\}$
averaged over all \vec{r}_i

electron i interacts with $N-1$ electrons
 (not itself)

5.55 Hartree-Fock Energy

Hartree-Fock Energy

$$E_0 = \underbrace{\sum_{i=1}^N \langle i | h_i | i \rangle}_{\text{each } e^- \text{ has K.E.}} + \underbrace{\sum_{i=1}^N \sum_{j=i+1}^N \langle ii | jj \rangle - \delta_{\sigma_i \sigma_j} \langle ij | ji \rangle}_{\text{each pair of } e^- \text{ has nuc. attraction coulomb + exchange interaction}}$$

$$h_i = \langle i | h_i | i \rangle = [i | h_i | i] = (\langle i | h_i | i \rangle)$$

$$J_{ij} = \langle ij | ij \rangle = [ii | jj] = (\langle ii | jj \rangle)$$

$$K_{ij} = \langle ij | ji \rangle = [ij | ji] = \delta_{\sigma_i \sigma_j} (\langle ij | ji \rangle)$$

$$E_0 = \sum_i h_i + \sum_{i < j} J_{ij} - K_{ij}$$

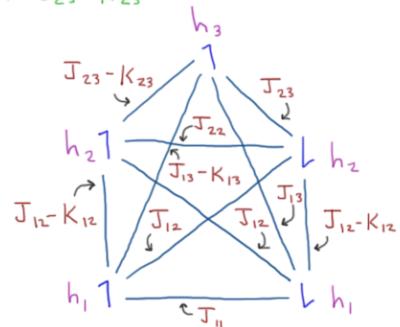
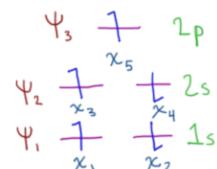
$J_{ij} \rightarrow$ elst interaction between all pairs

$K_{ij} \rightarrow$ exch interaction between all

same-spin pairs

ex: Boron atom

$$\begin{aligned} E_{RHF} = & 2h_1 + 2h_2 + h_3 \\ & + J_{11} + 4J_{12} - 2K_{12} \\ & + 2J_{13} - K_{13} + J_{22} \\ & + 2J_{23} - K_{23} \end{aligned}$$



5.56 Coulomb and Exchange Operators

Coulomb / Exchange Operators

$$\hat{f}(x_i) \chi_\alpha(x_i) = \epsilon_\alpha \chi_\alpha(x_i)$$

$$\hat{f}(x_i) = \hat{h}_i(x_i) + \hat{v}_\alpha^{\text{HF}}(x_i)$$

$$\hat{v}_\alpha^{\text{HF}}(x_i) = \hat{v}_\alpha^{\text{coul}}(x_i) + \hat{v}_\alpha^{\text{exch}}(x_i)$$

$$\hat{v}_\alpha^{\text{coul}}(x_i) = \sum_{b \neq \alpha} \hat{J}_b(x_i)$$

$$\hat{v}_\alpha^{\text{exch}}(x_i) = \sum_{b \neq \alpha} \hat{K}_b(x_i)$$

$$\hat{J}_b(x_i) \equiv \int dx_2 \chi_b^*(x_2) \chi_b(x_2) \frac{1}{r_{12}}$$

$$\hat{K}_b(x_i) \chi_\alpha(x_i) \equiv \left[\int dx_2 \chi_b^*(x_2) \chi_\alpha(x_2) \frac{1}{r_{12}} \right] \chi_b(x_i)$$

$$[\hat{h}_i(x_i) + \sum_{b \neq \alpha} \hat{J}_b(x_i) - K_b(x_i)] \chi_\alpha(x_i) = \epsilon_\alpha \chi_\alpha(x_i)$$

$$\sum_{\alpha \neq b} \rightarrow \sum_{\alpha=1}^{b-1} + \sum_{\alpha=b+1}^N$$

5.57 Fock Operator

Fock Operator

$$\left[\hat{h}_1(x_1) + \sum_{b \neq a} \hat{T}_b(x_1) - \hat{K}_b(x_1) \right] \chi_a(x_1) = \xi_a \chi_a(x_1)$$

pseudo-eigenvalue problem because

$\hat{V}_{\alpha}^{\text{HF}}$ depends on $\{x_1, x_2, \dots, x_{a-1}, x_{a+1}, \dots, x_N\}$

$\hat{\theta}_{12}$ → permutation operator, exchanges 1+2

$$\hat{\theta}_{12} \chi_1(x_1) \chi_2(x_2) = \chi_2(x_1) \chi_1(x_2)$$

$$\hat{K}_b(x_1) \chi_a(x_1) = \left[\int dx_2 \chi_b^*(x_2) \frac{1}{r_{12}} \hat{\theta}_{ab} \chi_b(x_2) \right] \chi_a(x_1)$$

$$\hat{f}(x_1) = \hat{h}_1(x_1) + \sum_{b=1}^N \int dx_2 \chi_b^*(x_2) \frac{1}{r_{12}} (1 - \hat{\theta}_{ab}) \chi_b(x_2)$$

$$\hat{K}_a(x_1) \chi_a(x_1) = \hat{T}_a(x_1) \chi_a(x_1)$$

$$(\hat{K}_a - \hat{T}_a) \chi_a = 0$$

$\therefore \Sigma$ can include a

$$\langle nallaa \rangle = \langle nala \rangle - \langle naa \rangle = 0$$

5.58 Functional Variation

Functional Variation

$\tilde{\Psi} \rightarrow$ trial wavefunction

$$E[\tilde{\Psi}] = \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle$$

$E \rightarrow$ functional of $\tilde{\Psi}$

$\tilde{\Psi} \rightarrow \tilde{\Psi} + \delta \tilde{\Psi}$ first variation

$$\begin{aligned} E[\tilde{\Psi} + \delta \tilde{\Psi}] &= \langle (\tilde{\Psi} + \delta \tilde{\Psi}) | \hat{H} | (\tilde{\Psi} + \delta \tilde{\Psi}) \rangle \\ &= E[\tilde{\Psi}] + \langle \delta \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle + \langle \tilde{\Psi} | \hat{H} | \delta \tilde{\Psi} \rangle \\ &= E[\tilde{\Psi}] + \delta E + \dots \end{aligned}$$

find min(E) when $\delta E = 0$

$$|\tilde{\Psi}\rangle = \sum_{i=1}^k c_i |\psi_i\rangle$$

$$E = \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \sum_{i=1}^k \sum_{j=1}^k c_i^* c_j \langle \psi_i | \hat{H} | \psi_j \rangle$$

minimize E subject to $\langle \tilde{\Psi} | \tilde{\Psi} \rangle = 1$

$$\mathcal{L} = \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle - E(\langle \tilde{\Psi} | \tilde{\Psi} \rangle - 1)$$

$$= \sum_{ij} c_i^* c_j \langle \psi_i | \hat{H} | \psi_j \rangle - E \left(\sum_{ij} c_i^* c_j \langle \psi_i | \psi_j \rangle - 1 \right)$$

$$\begin{aligned} \delta \mathcal{L} &= \sum_{ij} \left(\delta c_i^* c_j \langle \psi_i | \hat{H} | \psi_j \rangle - E \delta c_i^* c_j \langle \psi_i | \psi_j \rangle \right. \\ &\quad \left. + c_i^* \delta c_j \langle \psi_i | \hat{H} | \psi_j \rangle - E c_i^* \delta c_j \langle \psi_i | \psi_j \rangle \right) = 0 \end{aligned}$$

$$H_{ij} \equiv \langle \psi_i | \hat{H} | \psi_j \rangle \quad S_{ij} = \langle \psi_i | \psi_j \rangle$$

$$\sum_i \delta c_i^* \left(\sum_j H_{ij} c_j - E S_{ij} c_j \right)$$

$$+ \sum_j \delta c_j \left(\sum_i H_{ij} c_i^* - E S_{ij} c_i^* \right) = 0$$

$$\sum_j H_{ij} c_j = E \sum_j S_{ij} c_j \quad \text{true for all } j \in \{1, 2, \dots, k\}$$

$$\boxed{H \leq E \leq E}$$

5.59 Minimum Determinant Energy

$ \Psi_0\rangle = x_1 x_2 \dots x_a x_b \dots x_N\rangle = 12\dots ab\dots N\rangle$ $E_0(\{x_i\}) = \langle \Psi_0 \hat{H} \Psi_0 \rangle$ minimize E w.r.t. $\{x_i\}$ enforce constraint $\int dx_i x_a^*(i) x_b(i) = [a b] = \delta_{ab}$ $\mathcal{L}[\{x_i\}] = E_0[\{x_i\}] - \sum_{a=1}^N \sum_{b=1}^N \xi_{ab} ([a b] - \delta_{ab})$ $E_0[\{x_i\}] = \sum_{a=1}^N [a h_i a] + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N ([aa bb] - [ab ba])$ $\mathcal{L} \in \mathbb{R} \rightarrow \underline{\xi} = \underline{\xi}^+ \rightarrow \xi_{ab} = \xi_{ba}^*$ $x_a \rightarrow x_a + \delta x_a \quad \delta \mathcal{L} = \delta E_0 - \sum_{a=1}^N \sum_{b=1}^N \xi_{ab} \delta [a b] = 0$ $\delta E_0 = \sum_{a=1}^N ([\delta a h_i a] + [a h_i \delta a])$ $+ \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N ([\delta aa bb] + [a\delta a bb] + [aa \delta bb] + [aa b\delta b])$ $- [\delta ab ba] + [a\delta b ba] + [ab \delta ba] + [ab b\delta a])$ $[\delta aa bb] = [bb \delta aa] = [a\delta a bb]^* = [bb a\delta a]^*$	$\sum_{ab} \xi'_{ab} ([\delta a b] + [a \delta b]) = \sum_{ab} \xi'_{ab} [\delta a b] + \sum_{ab} \xi'_{ba} [b \delta a]$ $= \sum_{ab} \xi'_{ab} [\delta a b] + \sum_{ab} \xi'^*_{ab} [\delta a b]^*$ $= \sum_{ab} \xi'_{ab} [\delta a b] + (\sum_{ab} \xi'_{ab} [\delta a b])^*$ $\delta \mathcal{L} = 0 = \sum_{a=1}^N ([\delta a h_i a] + [\delta a h_i a]^*)$ $+ \sum_{a=1}^N \sum_{b=1}^N ([\delta aa bb] - [\delta ab ba] + [\delta aa bb]^* - [\delta ab ba]^*)$ $- \sum_{a=1}^N \sum_{b=1}^N (\xi'_{ab} [\delta a b] + \xi'^*_{ab} [\delta a b]^*)$ $\delta \mathcal{L} = \sum_{a=1}^N \int dx_i \delta x_a^*(i) \left[\left(\hat{h}_i(i) + \sum_{b=1}^N (\hat{J}_b(i) - \hat{K}_b(i)) \right) \chi_a(i)$ $- \sum_{b=1}^N \xi'_{ab} \chi_b(i) \right] = 0$ $\left[h_i(i) + \sum_{b=1}^N (J_b(i) - K_b(i)) \right] \chi_a(i) = \sum_{b=1}^N \xi'_{ab} \chi_b(i)$ $\boxed{\hat{f}[\chi_a] = \sum_{b=1}^N \xi'_{ab} \chi_b\rangle}$ non-canonical form
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5.60 Canonical Hartree-Fock Equations

Canonical HF Equations

$\{x'_\alpha\} \rightarrow$ "transformed" orbitals

$$x'_\alpha = \sum_b U_{ab} x_b \quad \{x'_\alpha\} \rightarrow [a' | b'] = \delta_{ab}$$

$$\underline{U}^\dagger = \underline{U}^{-1} \rightarrow \underline{U}^\dagger \underline{U} = \underline{\mathbb{I}}$$

$$\underline{A} = \begin{pmatrix} x_1(1) & x_2(1) & \cdots & x_N(1) \\ x_1(2) & x_2(2) & \cdots & x_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ x_1(N) & x_2(N) & \cdots & x_N(N) \end{pmatrix}$$

$$|\Psi_0\rangle = \frac{1}{\sqrt{N!}} |\underline{A}| = N!^{-1/2} \det(\underline{A})$$

$$\det(\underline{A}') = \det(\underline{U}) \det(\underline{A})$$

$$1 = \det(\underline{\mathbb{I}}) = \det(\underline{U}^\dagger \underline{U}) = \det(\underline{U}^\dagger) \det(\underline{U}) \\ = \det(\underline{U})^* \det(\underline{U}) = |\det(\underline{U})|^2$$

$$\det(\underline{U}) = e^{i\phi} \rightarrow \langle E \rangle \text{ invariant to } \{x'_\alpha\}$$

$$\sum_\alpha J'_\alpha(i) = \sum_\alpha \int dx_2 x'^*_\alpha(2) \frac{1}{r_{12}} x'_\alpha(2) \\ = \sum_\alpha \int dx_2 \left(\sum_b U_{ab}^* x_b^*(2) \right) \frac{1}{r_{12}} \left(\sum_c U_{ac} x_c(2) \right) \\ = \sum_{bc} \left(\sum_a U_{ba}^\dagger U_{ac} \right) \int dx_2 x_b^*(2) \frac{1}{r_{12}} x_c(2) \\ = \sum_b \int dx_2 x_b^*(2) \frac{1}{r_{12}} x_b(2) = \sum_b J_b(i)$$

$\{\hat{T}_\alpha, \hat{K}_\alpha\} \rightarrow$ invariant to orbitals

$$\hat{f}'(i) = \hat{f}(i)$$

$$\langle x_c | f | x_\alpha \rangle = \sum_b \xi'_{ba} \langle x_c | x_b \rangle = \xi'_{ca}$$

$$\xi'_{ab} = \int dx_1 x'^*_a(i) \hat{f}(i) x'_b(i) \\ = \left(\sum_{cd} U_{ca}^* \left(\int dx_1 x_c^*(i) \hat{f}(i) x_d(i) \right) U_{db} \right)$$

$$\boxed{\underline{\xi}' = \underline{U}^\dagger \underline{\xi} \underline{U}}$$

$$\hat{f} | x'_\alpha \rangle = \xi'_{\alpha i} | x'_\alpha \rangle$$

when $\xi'_{ab} = \xi'_{ia} \delta_{ab}$ can always diagonalize $\underline{\xi}'$

5.61 Koopman's Theorem

Koopman's Theorem

$$\hat{f}|x_j\rangle = \xi_j |x_j\rangle \quad j=1, 2, \dots$$

$$\langle x_i | f | x_j \rangle = \xi_j \langle x_i | x_j \rangle = \xi_j \delta_{ij}$$

$$\begin{aligned} \xi_i &= \langle x_i | f | x_i \rangle = \langle x_i | h_i + \sum_b (J_b - K_b) | x_i \rangle \\ &= \langle x_i | h_i | x_i \rangle + \sum_b (\langle x_i | J_b | x_i \rangle - \langle x_i | K_b | x_i \rangle) \\ &= \langle i | h_i | i \rangle + \sum_b (\langle i b | i b \rangle - \langle i b | b i \rangle) \\ &= \langle i | h_i | i \rangle + \sum_b \langle i b | i b \rangle \end{aligned}$$

$$\langle x_i | J_b | x_j \rangle = \langle i b | j b \rangle = [ij]_{bb} \quad \langle aa | aa \rangle = 0$$

$$\langle x_i | K_b | x_j \rangle = \langle i b | b j \rangle = [ib]_{bj}$$

$$\xi_a = \langle a | h_i | a \rangle + \sum_{b \neq a} (\langle ab | ab \rangle - \langle ab | ba \rangle)$$

$$\xi_r = \langle r | h_i | r \rangle + \sum_b (\langle rb | rb \rangle - \langle rb | br \rangle)$$

$$\sum_{a=1}^N \xi_a = \sum_{a=1}^N \langle a | h_i | a \rangle + \sum_{a=1}^N \sum_{b=1}^N \langle ab | ab \rangle$$

$$E_o = \sum_{a=1}^N \langle a | h_i | a \rangle + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N \langle ab | ab \rangle$$

$E_o \neq \sum_{a=1}^N \xi_a$ double counts e⁻ repulsion

$${}^N E_o = \langle {}^N \Psi_o | \# | {}^N \Psi_o \rangle \quad {}^{N-1} E_c = \langle {}^{N-1} \Psi_c | \# | {}^{N-1} \Psi_c \rangle$$

$$E = \sum_i^{\text{occ}} \langle i | h_i | i \rangle + \frac{1}{2} \sum_i^{\text{occ}} \sum_j^{\text{occ}} \langle ij | ij \rangle$$

$${}^{N-1} E_c = \sum_{a \neq c} \langle a | h_i | a \rangle + \frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \langle ab | ab \rangle$$

$${}^{N+1} E_r = \sum_{\{a,r\}} \langle a | h_i | a \rangle + \frac{1}{2} \sum_{\{a,r\}} \sum_{\{b,r\}} \langle ab | ab \rangle$$

$$IP_c \equiv {}^{N-1} E_c - E_o = - \langle c | h_i | c \rangle - \sum_a \langle ca | ca \rangle$$

$$EA_r \equiv E_o - {}^{N+1} E_r = - \langle r | h_i | r \rangle - \sum_a \langle ral | ral \rangle$$

$$IP_c = - \xi_c$$

$$EA_r = - \xi_r$$

5.62 Restricted Hartree-Fock

Restricted Hartree-Fock

$$\begin{aligned} \alpha_i(x_i) &= \begin{cases} \Psi_{iL}(r_i) \alpha(\omega_i) & \text{for odd } i \\ \Psi_{iL}(r_i) \beta(\omega_i) & \text{for even } i \end{cases} \\ |\Psi_0\rangle &= |\chi_1 \chi_2 \dots \chi_{N-1} \chi_N\rangle = |\psi_1 \bar{\psi}_1 \dots \psi_{N_L} \bar{\psi}_{N_L}\rangle \\ \hat{f}(x_i) \chi_i(x_i) &= \xi'_i \chi_i(x_i) \\ \hat{f}(x_i) \Psi_j(r_i) \sigma(\omega_i) &= \xi'_j \Psi_j(r_i) \sigma(\omega_i) \\ \left[\int d\omega_1 \sigma^*(\omega_1) \hat{f}(x_1) \sigma(\omega_1) \right] \Psi_j(r_i) &= \xi'_j \Psi_j(r_i) \\ \hat{f}(x_i) &= \hat{h}_i(r_i) + \sum_{c=1}^N \int dx_2 x_c^*(x_2) \frac{1}{r_{12}} (1 - \hat{\theta}_{12}) \chi_c(x_2) \\ \hat{f}(r_i) \Psi_j(r_i) &= \left[\int d\omega_1 \sigma_j^*(\omega_1) \hat{f}(x_1) \sigma_j(\omega_1) \right] \Psi_j(r_i) \\ &= \left[\int d\omega_1 \sigma_j^*(\omega_1) \hat{h}_i(r_i) \sigma_j(\omega_1) \right] \Psi_j(r_i) \\ &+ \left[\sum_{c=1}^N \int d\omega_1 dx_2 \sigma_j^*(\omega_1) x_c^*(x_2) \frac{1}{r_{12}} (1 - \hat{\theta}_{12}) \chi_c(x_2) \alpha(\omega_1) \right] \Psi_j(r_i) \\ \hat{f}(r_i) \Psi_j(r_i) &= \hat{h}_i(r_i) \Psi_j(r_i) + \sum_{c=1}^N \int dx_2 d\omega_1 \sigma_j^*(\omega_1) x_c^*(x_2) \frac{1}{r_{12}} (1 - \hat{\theta}_{12}) \chi_c(x_2) \alpha(\omega_1) \Psi_j(r_i) \\ &+ \chi_c(x_2) \sigma_j^*(\omega_1) \Psi_j(r_i) + \chi_c(x_2) \sigma_j^*(\omega_2) \Psi_j(r_2) \end{aligned}$$

$$\begin{aligned} \hat{f}(r_i) \Psi_j(r_i) \sigma_j(\omega_i) &= \hat{h}_i(r_i) \Psi_j(r_i) \\ + \sum_{c=1}^{N/2} \int d\omega_1 d\omega_2 dr_2 &\left[\alpha^*(\underline{\omega}_1) \Psi_c^*(r_2) \alpha^*(\underline{\omega}_2) \frac{1}{r_{12}} \Psi_c(r_2) \alpha(\underline{\omega}_2) \Psi_j(r_1) \alpha(\underline{\omega}_1) \right. \\ &+ \alpha^*(\underline{\omega}_1) \Psi_c^*(r_2) \beta^*(\underline{\omega}_2) \frac{1}{r_{12}} \Psi_c(r_2) \beta(\underline{\omega}_2) \Psi_j(r_1) \alpha(\underline{\omega}_1) \\ &- \alpha^*(\underline{\omega}_1) \Psi_c^*(r_2) \alpha^*(\underline{\omega}_2) \frac{1}{r_{12}} \Psi_c(r_1) \alpha(\underline{\omega}_1) \Psi_j(r_2) \alpha(\underline{\omega}_2) \\ &\left. - \alpha^*(\underline{\omega}_1) \Psi_c^*(r_2) \beta^*(\underline{\omega}_2) \frac{1}{r_{12}} \Psi_c(r_1) \beta(\underline{\omega}_1) \Psi_j(r_2) \alpha(\underline{\omega}_2) \right] \\ \hat{f}(1) &= \hat{h}_i(1) + \sum_{a=1}^{N/2} (2 \hat{T}_a(1) - \hat{K}_a(1)) \\ \hat{f}(r_i) &= \hat{h}(r_i) + \sum_{a=1}^{N/2} \int dr_2 \Psi_a^*(r_2) (2 - \hat{\theta}_{12}) \frac{1}{r_{12}} \Psi_a(r_2) \\ E_0 &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = 2 \sum_{a=1}^{N/2} (a | h_i | a) + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} 2 J_{ab} - K_{ab} \\ &= 2 \sum_{a=1}^{N/2} h_a + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} 2 J_{ab} - K_{ab} \\ \xi_a &= (\Psi_i | \hat{f} | \Psi_i) = (\psi_i | h_i | \psi_i) + \sum_{b=1}^{N/2} 2 (a a | b b) - (a b | b a) \\ &= h_a + \sum_{b=1}^{N/2} 2 J_{ab} - K_{ab} \end{aligned}$$

5.63 Hartree-Fock-Roothaan Equations

Hartree-Fock-Roothaan Equations

$$\hat{f}(r_i) \Psi_i(r_i) = \epsilon'_i \Psi_i(r_i)$$

can't solve exactly → introduce basis set

$$\Psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_\mu \quad i=1, 2, \dots, K$$

$\{\phi_\mu\}$ → basis set, basis functions

$$f(1) \sum_n C_{ni} \phi_n(1) = \epsilon'_i \sum_n C_{ni} \phi_n(1)$$

$$\sum_n C_{ni} \int dr_i \phi_\mu^*(r_i) f(1) \phi_n(r_i) = \epsilon'_i \sum_n C_{ni} \int dr_i \phi_\mu^*(r_i) \phi_n(r_i)$$

$$F_{\mu\nu} \equiv \int dr_i \phi_\mu^*(r_i) f(1) \phi_\nu(r_i)$$

$$S_{\mu\nu} \equiv \int dr_i \phi_\mu^*(r_i) \phi_\nu(r_i)$$

$$\sum_n F_{\mu\nu} C_{ni} = \epsilon'_i \sum_n S_{\mu\nu} C_{ni} \quad n=1, 2, \dots, K$$

$$\underline{F} \underline{C} = \underline{S} \underline{C}$$

$$\underline{\epsilon}' \rightarrow \epsilon'_{ij} = \epsilon'_i \delta_{ij}$$

$$\underline{\epsilon}' = \begin{pmatrix} \epsilon'_1 & & & \\ & \ddots & & \\ & & \epsilon'_K & \end{pmatrix}$$

$$\underline{C} = \begin{pmatrix} C_{11} & C_{12} & \dots & C_{1K} \\ C_{21} & C_{22} & \dots & C_{2K} \\ \vdots & \vdots & \ddots & \vdots \\ C_{K1} & C_{K2} & \dots & C_{KK} \end{pmatrix} \begin{matrix} \phi_1 \\ \phi_2 \\ \vdots \\ \phi_K \end{matrix}$$

problem:

$$\underline{F} = \underline{F}(\underline{C})$$

non-linear!

$$\Psi_1 \quad \Psi_2 \dots \Psi_K$$

5.64 Density Matrix

Density Matrix

$$\rho(r) = 2 \sum_{\alpha=1}^{N/2} \Psi_{\alpha}^*(r) \Psi_{\alpha}(r) = 2 \sum_{\alpha=1}^{N/2} |\Psi_{\alpha}(r)|^2$$

$$\int dr \rho(r) = 2 \sum_{\alpha=1}^{N/2} \int dr \Psi_{\alpha}^*(r) \Psi_{\alpha}(r) = 2 \sum_{\alpha=1}^{N/2} 1 = N$$

$\rightarrow N$ electrons in system

$$\rho(r) = 2 \sum_{\alpha=1}^{N/2} \Psi_{\alpha}^*(r) \Psi_{\alpha}(r)$$

$$= 2 \sum_{\alpha=1}^{N/2} \left(\sum_{m=1}^K C_{ma}^* \phi_m^*(r) \right) \left(\sum_{n=1}^K C_{na} \phi_n(r) \right)$$

$$= \sum_{mn} \left(2 \sum_{\alpha=1}^{N/2} C_{ma}^* C_{na} \right) \phi_m^*(r) \phi_n(r)$$

$$= \sum_{mn} P_{mn} \phi_m^*(r) \phi_n(r)$$

$$P_{mn} \equiv \sum_{\alpha=1}^{N/2} C_{ma}^* C_{na}$$

P \equiv density matrix

- completely specifies charge density
- invariant to orbitals given $\{\phi_m\}$

can factor:

$$f(r_1) = h_1(r_1) + v^{HF}(r_1)$$

$$= h_1(r_1) + \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} \int dr_2 \phi_{\lambda}^*(r_2) \frac{1}{r_{12}} (2 - \rho_{12}) \phi_{\sigma}(r_2)$$

5.65 Fock Matrix

Fock Matrix

$$\hat{f}(r_i) = \hat{h}_i(r_i) + \sum_{\alpha=1}^{N/2} (2\hat{T}_{\alpha}(r_i) - \hat{K}_{\alpha}(r_i))$$

$$\begin{aligned} F_{\mu\nu} &\equiv \int dr_i \phi_{\mu}^*(r_i) \hat{f}(r_i) \phi_{\nu}(r_i) \\ &= \int dr_i \phi_{\mu}^*(r_i) \hat{h}_i(r_i) \phi_{\nu}(r_i) \\ &\quad + \sum_{\alpha=1}^{N/2} \int dr_i \phi_{\mu}^*(r_i) [2\hat{T}_{\alpha}(r_i) - \hat{K}_{\alpha}(r_i)] \phi_{\nu}(r_i) \\ &= H_{\mu\nu}^{\text{core}} + \sum_{\alpha=1}^{N/2} (2(\mu\nu|\alpha\alpha) - (\mu\alpha|\alpha\nu)) \end{aligned}$$

$$H_{\mu\nu}^{\text{core}} \equiv \int dr_i \phi_{\mu}^*(r_i) \hat{h}_i(r_i) \phi_{\nu}(r_i)$$

$$\hat{h}_i(r_i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}}$$

$$T_{\mu\nu} \equiv \int dr_i \phi_{\mu}^*(r_i) \left(-\frac{1}{2} \nabla_i^2\right) \phi_{\nu}(r_i)$$

$$V_{\mu\nu}^{\text{nuc}} \equiv \int dr_i \phi_{\mu}^*(r_i) \left(-\sum_A \frac{Z_A}{r_{iA}}\right) \phi_{\nu}(r_i)$$

$$H_{\mu\nu}^{\text{core}} = T_{\mu\nu} + V_{\mu\nu}^{\text{nuc}}$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\alpha=1}^{N/2} \sum_{\lambda\sigma} C_{\lambda\alpha}^* C_{\sigma\alpha} (2(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu))$$

$$= H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu)]$$

$$= H_{\mu\nu}^{\text{core}} + G_{\mu\nu}$$

$$G_{\mu\nu} \equiv \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu)]$$

$$(\mu\nu|\lambda\sigma) = \int dr_1 dr_2 \phi_{\mu}^*(r_1) \phi_{\nu}(r_1) \frac{1}{r_{12}} \phi_{\lambda}^*(r_2) \phi_{\sigma}(r_2)$$

$$\underline{E} = \underline{E}(\underline{\underline{C}}) = \underline{E}(\underline{\underline{C}}) \quad \underline{E}(\underline{\underline{C}}) \underline{\underline{C}} = \underline{\underline{C}} \underline{\underline{C}}^t$$

$$\text{if } S_{\mu\nu} = \delta_{\mu\nu} \text{ then } \underline{E}(\underline{\underline{C}}) \underline{\underline{C}} = \underline{\underline{C}} \underline{\underline{C}}^t$$

if orthonormal basis, find $\underline{\underline{C}}$ by

diagonalizing \underline{E}

5.66 Orthogonalization

Orthogonalization

$$S_{\mu\nu} \equiv \int dr \phi_\mu^*(r) \phi_\nu(r) \quad \phi'_\mu = \sum_{\nu=1}^K X_{\mu\nu} \phi_\nu \quad \mu = 1, 2, \dots, K$$

$$\int dr \phi_\mu'^*(r) \phi_\nu(r) = \int dr \left(\sum_{\lambda=1}^K X_{\mu\lambda}^* \phi_\lambda^*(r) \right) \left(\sum_{\sigma=1}^K X_{\nu\sigma} \phi_\sigma(r) \right)$$

$$= \sum_{\lambda=1}^K \sum_{\sigma=1}^K X_{\mu\lambda}^* X_{\nu\sigma} \int dr \phi_\lambda^*(r) \phi_\sigma(r) = \sum_{\lambda\sigma} X_{\mu\lambda}^* S_{\lambda\sigma} X_{\nu\sigma}$$

$$= \delta_{\mu\nu} \quad X^\dagger \underline{S} \underline{X} = \underline{D} \quad \underline{\underline{S}} \rightarrow \text{Hermitian}$$

1) symmetric orthogonalization

$$\underline{X} = \underline{\underline{S}}^{-1/2} = \underline{\underline{U}}^{-1/2} \underline{U}^\dagger \quad \underline{\underline{S}}^{-1/2} \underline{\underline{S}}^{-1/2} = \underline{\underline{S}}^0 = \underline{\underline{1}} \quad \checkmark$$

2) canonical orthogonalization

$$\underline{X} = \underline{\underline{U}} \underline{\underline{S}}^{-1/2} \quad X_{ij} = U_{ij} / \sqrt{s_{jj}}$$

$$\underline{\underline{X}}^\dagger \underline{\underline{S}} \underline{\underline{X}} = (\underline{\underline{U}} \underline{\underline{S}}^{-1/2})^\dagger \underline{\underline{S}} (\underline{\underline{U}} \underline{\underline{S}}^{-1/2})$$

$$= \underline{\underline{S}}^{-1/2} (\underline{\underline{U}}^\dagger \underline{\underline{S}} \underline{\underline{U}}) \underline{\underline{S}}^{-1/2}$$

$$= \underline{\underline{S}}^{-1/2} \underline{\underline{S}}^{-1/2} = \underline{\underline{S}}^0 = \underline{\underline{1}} \quad \checkmark$$

$\rightarrow \text{sort } \{s_{ii}\} \rightarrow \text{discard smallest } m \text{ values}$

$$\tilde{\underline{X}} = \begin{pmatrix} U_{1,1}/s_{11}^{1/2} & U_{1,2}/s_{21}^{1/2} & \cdots & U_{1,K-m}/s_{K-m,1}^{1/2} \\ U_{2,1}/s_{11}^{1/2} & U_{2,2}/s_{22}^{1/2} & \cdots & U_{2,K-m}/s_{K-m,2}^{1/2} \\ \vdots & \vdots & \ddots & \vdots \\ U_{K,1}/s_{11}^{1/2} & U_{K,2}/s_{22}^{1/2} & \cdots & U_{K,K-m}/s_{K-m,K-m}^{1/2} \end{pmatrix}$$

$$\tilde{\underline{X}} \rightarrow K \text{ rows} \times (K-m) \text{ columns}$$

$$\phi'_\mu(r) = \sum_{\nu=1}^K \tilde{X}_{\nu\mu} \phi_\nu(r) \quad \mu = 1, 2, \dots, K-m$$

$$\underline{\underline{C}}' = \underline{\underline{X}}^{-1} \underline{\underline{C}} \quad \underline{\underline{C}} = \underline{\underline{X}} \underline{\underline{C}}'$$

$$\underline{\underline{F}} \underline{\underline{X}} \underline{\underline{C}}' = \underline{\underline{S}} \underline{\underline{X}} \underline{\underline{C}}' \quad \underbrace{(\underline{\underline{X}}^\dagger \underline{\underline{F}} \underline{\underline{X}})}_{\underline{\underline{F}}'} \underline{\underline{C}}' = \underbrace{(\underline{\underline{X}}^\dagger \underline{\underline{S}} \underline{\underline{X}})}_{\underline{\underline{1}}} \underline{\underline{C}}' \underline{\underline{S}} \underline{\underline{X}}$$

$$\underline{\underline{F}}' \underline{\underline{C}}' = \underline{\underline{C}}' \underline{\underline{S}}$$

$$F'_{\mu\nu} = \int dr \phi_\mu'^*(r) \hat{f}(r) \phi_\nu(r) \quad \underline{\underline{F}}' = \underline{\underline{X}}^\dagger \underline{\underline{F}} \underline{\underline{X}}$$

$$\Psi_i = \sum_m C'_{mi} \phi'_m$$

5.67 Self-Consistent Field

Self-Consistent Field

procedure to solve for optimal orbitals

- 1) Specify molecule: $\{\vec{R}_A\}, \{Z_A\}, \{\phi_M\}, N$
- 2) Calculate integrals $S_{\mu\nu}, T_{\mu\nu}, V_{\mu\nu}, (\mu\nu|\lambda\sigma)$
- 3) Diagonalize $\underline{\underline{S}}$, obtain $\underline{\underline{X}}$
- 4) Obtain guess $\underline{\underline{P}}^{(0)}$
- 5) Calculate $\underline{\underline{G}}^{(0)}$
- 6) Calculate $\underline{\underline{E}}^{(0)} = \underline{\underline{H}}^{\text{core}} + \underline{\underline{G}}^{(0)}$
- 7) Calculate $\underline{\underline{F}}^{(0)} = \underline{\underline{X}}^T \underline{\underline{E}}^{(0)} \underline{\underline{X}}$
- 8) Diagonalize $\underline{\underline{F}}^{(0)}$ to get $\underline{\underline{C}}^{(0)}$ and $\underline{\underline{\xi}}^{(0)}$
- 9) Calculate $\underline{\underline{C}}^{(0)} = \underline{\underline{X}} \underline{\underline{C}}^{(0)}$
- 10) Form $\underline{\underline{P}}^{(i+1)}$ from $\underline{\underline{C}}^{(0)}$

- 11) Determine if $\underline{\underline{P}}^{(i+1)} \approx \underline{\underline{P}}^{(i)}$

· yes \rightarrow go to 12

· no $\rightarrow i += 1$, go to 5

- 12) Use final $\underline{\underline{C}}$ to calculate $\{\langle A \rangle\}$

5.68 Population Analysis

Population Analysis

$$E_0 = 2 \sum_{a=1}^{N/2} h_a + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} (2J_{ab} - K_{ab}) = \sum_{a=1}^{N/2} (h_a + \xi_a)$$

$$= \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu})$$

$$\xi_a = h_a + \sum_{b=1}^{N/2} (2J_{ab} - K_{ab})$$

$$E_{\text{tot}} = E_0 + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$$

most operators look like $\hat{O}_i = \sum_{i=1}^N \hat{o}(i)$

$$\langle \hat{O}_i \rangle = \langle \Psi_0 | \hat{O}_i | \Psi_0 \rangle = 2 \sum_{a=1}^{N/2} (\Psi_a | \hat{o} | \Psi_a) = \sum_{\mu\nu} P_{\mu\nu} (M | \hat{o} | N)$$

for $\{q_i\}$, $\vec{m} = \sum_i q_i \vec{r}_i$

$$\text{for } |\Psi_0\rangle, \vec{m} = \langle \Psi_0 | -\sum_{i=1}^N \vec{r}_i | \Psi_0 \rangle + \sum_{A=1}^M Z_A \vec{R}_A$$

$$\vec{m} = -\sum_{\mu\nu} P_{\mu\nu} (M | \vec{r} | N) + \sum_A Z_A \vec{R}_A$$

$$(M | r | N) = \int dr \phi_M^*(r) \hat{r} \phi_N(r) \quad \hat{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$N = 2 \sum_{a=1}^{N/2} \int dr |\Psi_a(r)|^2 = 2 \sum_{a=1}^{N/2} \int dr \left(\sum_{\mu=1}^K C_{\mu a}^* \phi_\mu^*(r) \right) \left(\sum_{\nu=1}^K C_{\nu a} \phi_\nu(r) \right)$$

$$= \sum_{\mu\nu} \left(2 \sum_{a=1}^{N/2} C_{\mu a}^* C_{\nu a} \right) \int dr \phi_\mu^*(r) \phi_\nu(r)$$

$$= \sum_{\mu\nu} P_{\mu\nu} S_{\mu\nu} = \sum_{\mu} \left(\frac{P}{S} \right)_{\mu\mu} = \text{tr} \left(\frac{P}{S} \right)$$

$$q_A = Z_A - \sum_{\mu \in A} \left(\frac{P}{S} \right)_{\mu\mu} \quad \text{Mulliken charges}$$

$$N = \sum_{\mu} \left(\frac{S^\alpha P}{S} \right)_{\mu\mu}^{1-\alpha} \quad \text{for any } \alpha, \text{ choose } \frac{1}{2}$$

$$N = \sum_{\mu} \left(\frac{S^{1/2} P}{S} \right)_{\mu\mu}^{1/2} = \sum_{\mu} P'_{\mu\mu} = \text{tr}(P')$$

symmetrically orthogonalized

$$\rho(r) = \sum_{\mu\nu} P'_{\mu\nu} \phi_\mu'^*(r) \phi_\nu(r)$$

$$\phi'_\mu(r) = \sum_{\nu} \left(\frac{S^{-1/2}}{S} \right)_{\mu\nu} \phi_\nu(r)$$

$$q'_A = Z_A - \sum_{\mu \in A} \left(\frac{S^{1/2} P}{S} \right)_{\mu\mu}^{1/2} \quad \text{Löwdin charges}$$