Equations – Quantum Chem 2

$I = mr^2 = \sum_i m_i r_i^2$ Moment of Intertia

J = Iω Angular momentum

$E_k = \frac{1}{2}I\omega^2 = \frac{J^2}{2I}$ Energy

$J^2 = J_x^2 + J_y^2 + J_z^2;\ J_x^2 = y\rho_z - z\rho_y;\ J_y^2 = z\rho_x - x\rho_z;\ J_z^2 = x\rho_y - y\rho_x$

Cylinder coordinates where -∞ $\le z \le \infty$

x = rcosθ $0 \le r \le \infty$

y = rsinθ $0 \le \theta \le 2\pi$

$\delta\tau = r\delta r\delta\theta$

Volume element $\delta\tau = r\delta r\delta\theta\delta z$

$E_{por} = \frac{n\hbar^2}{2I};\ (sphere)\ E_{l,m_l} = (l(l+1))\frac{\hbar^2}{2I}$ 2,3D

$E_n = -\frac{\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{Z^2}{n^2}; E_e = \frac{J^2}{2I}; E_H = 2hc\tilde{R};\ E_l = l(l+1)\frac{\hbar^2}{2I}$ Energy

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

$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)$

$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$ The Laplacian, cartesian

$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{1}{r^2}\frac{1}{sin^2\theta}\frac{d^2}{d\phi^2} + \frac{1}{r^2}\frac{1}{sin\theta}\frac{d}{d\theta}(sin\theta\frac{d}{d\theta})$ The Laplacian, spherical

$= \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{1}{r^2}\Lambda^2$

$\Lambda^2 = \frac{1}{sin^2\theta}\frac{d^2}{d\phi^2} + \frac{1}{sin\theta}\frac{d}{d\theta}(sin\theta\frac{d}{d\theta})$ The Legendrian

$-\frac{\hbar^2}{2I}\Lambda^2\psi(\theta,\phi) = E\psi(\theta,\phi)$ The Hamiltonian for a particle on a sphere

$\psi(\theta,\phi) = Y_{1,m_l}(\theta,\phi)$ Solution to particle on a sphere

$-\frac{\hbar^2}{2I}\Lambda^2\psi(\theta,\phi) = l(l+1)Y_{l,m_l}(\theta,\phi);\quad E_l = l(l+1)\frac{\hbar^2}{2I}$ All energies at l are equal, not matter m_l

$-\frac{\hbar^2}{2I}\frac{d}{d\phi}Y_{l,m_l}(\theta,\phi) = m_l\hbar Y_{l,m_l}(\theta,\phi);\quad l_z = m_l\hbar$ Angular Momentum along z

$\hat{l_z} = x\hat{p}_y - y\hat{p}_x = -i\,\hbar\left(x\frac{d}{dy} - y\frac{d}{dx}\right) = -i\,\hbar\frac{d}{d\phi}$ if you know l_z then $l_x\ and\ l_y$ are undeterminable

$J = (l(l+1))^{\frac{1}{2}}\hbar;$ Total Angular Momentum

$R_{n,l}(r) = N_{n,l}\rho^l L_{n,l}(\rho)e^{\frac{\rho}{2}}$ Radial wave function

Where $\rho = \frac{2Zr}{na};\ a = \frac{m_e}{\mu}a_o;\ a_o = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2};\ \rho \approx \frac{2Zr}{na_o} = \frac{Zrm_e e^2}{2n\pi\varepsilon_0\hbar^2}$

$a_o = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ Bohr Radius

$1\ electric\ constant = -\frac{1}{4\pi\varepsilon_0} = 8.988x10^9\ \frac{kg\,m}{s^2C^2}$ Coulomb force constant

$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$ Total Wave Function

$nodes_{Radial} = n - l - 1;$ $states_l = 2l+1$

$nodes_{Angular} = l$

orbitals = n^2 = (for a specific n,l) $2l+1$

$\bar{\nu} = Z^2\tilde{R}(n_1^{-2} - n_2^{-2});\ E = hcZ^2\tilde{R}(n_1^{-2} - n_2^{-2})$ Rydberg Equation *Take care, Rydberg is not in SI units*

$hc\tilde{R} = \frac{E_H}{2}$ Hartree/2

$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2m_e r^2}$ Coulomb vs centrifugal potential E

$V(r_i) = -\frac{Ze^2}{4\pi\varepsilon_0 r_i}$ Electrostatic potential E

The total wave function

Recall that the total electronic wave function for hydrogen-like atoms is:

$$\Psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$$

Radial wave functions

n	l	$R_{n,l}(r)$
1	0	$2\left(\frac{Z}{a}\right)^{3/2} e^{-\rho/2}$
2	0	$\frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2}(2-\rho)e^{-\rho/2}$
2	1	$\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2}$
3	0	$\frac{1}{243^{1/2}}\left(\frac{Z}{a}\right)^{3/2}(6-6\rho+\rho^2)e^{-\rho/2}$
3	1	$\frac{1}{486^{1/2}}\left(\frac{Z}{a}\right)^{3/2}(4-\rho)\rho e^{-\rho/2}$
3	2	$\frac{1}{2430^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho^2 e^{-\rho/2}$

Spherical Harmonics

l	m_l	$Y_{l,m_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta e^{\pm 3i\phi}$

$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla_N^2 - \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i\neq j} V(r_{i,j})$ Generic Atomic Hamiltonian

Hamilton Generalized to any system $N\ nuclei, M\ e^-$

$$\widehat{H} = -\sum_A^N \frac{\hbar^2}{2m_A}\nabla_A^2 - \sum_i^M \frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_A^N \sum_{B>A}^N \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r_{AB}} + \sum_i^M \sum_{j>i}^M \frac{e^2}{4\pi\varepsilon_0 r_{ij}} - \sum_A^N \sum_i^M \frac{Z_A e^2}{4\pi\varepsilon_0 r_{Ai}}$$

<r> = $\frac{3}{2}\frac{a_0}{Z}$ s orbital;

$P(r) = |R_{1,0}^2| r^2 = 4\left(\frac{Z^3}{a_0^3}\right) r^2 e^{\frac{-2Zr}{a_0}}$; $\frac{dP}{dr} = 4\left(\frac{Z^3}{a_0^3}\right)\left(1-\frac{Z_r}{a_0}\right)2re^{\frac{-2Zr}{a_0}}$ derivative 0 at 2 pts, r=0, and $\frac{a_0}{Z}$

Constants

R = Gas constant = N_Ak *(8.31446 J/Kmol or Pa m³ /K mol)* = 0.0831445 *(dm³ bar /K mol)*
= *(0.0820574 dm³ atm /K mol)* = *(62.364 dm³ Torr/K mol)* = *(1.98721 cal/K mol)*
k = Boltzmann's constant *(1.38065x10^{-23} J/K)* c = speed of light (2.9979z10^8 m/s)
atm = 1.01325 bar = 101325 Pa = 760 torr; bar = 1.0x10^5 Pa torr = mmHg = 133.322 Pa
F= Faraday's constant = 96,485 C/mol = N_A x e^- charge c = 2.99892458x10^8 m/s
h = 6.6261762x10^{-34} Js=4.134733x10^{-15}eVs ħ = 1.0545887 x10^{-34} Js N_A = 6.022x10^{23} molecules/At Wt
eV/J= 6.24x10^1, J/eV=1.602x10^{-19} m_e=9.11x10^-31 amu = 1.661x10^{-27}kg
$\mathcal{R}_H$ = Rydberg constant = 109677, $\mathcal{R}_\infty$ = 1096737

Legend

d = distance, Collision diam
V = volume
U = Internal energy
M = molar mass (Kg/mol)
$\mathcal{N}$ = number density (N/V)
$C_{V,s}$ = C_s = Specific Heat Capacity ($\frac{J}{\text{<unit> } K}$)
Q = Rxn quotient
R = Gas constant = N_Ak *(8.31446* J/Kmol)
E = Energy

A = area, Helmholtz free energy
V_m = molar volume (V/n)
w = work (J)
F = force (N; Kg m/s^2)
v = electrons/molecule, rxn rate
$C_{V,m}$ = C_m = Molar Heat Capacity, V
R = Thermodynamic Equilibrium Const (= Q_{Equil})
k = Boltzmann's constant *(1.38065x10^{-23} J/K)*

Z = atomic number
V_m^0 = molar vol of ideal gas
q = heat energy (J)
n = moles (mol) or orbit level
J = Joules (Nm or kg m^2/s^2)
$C_{V,p}$ = Molar Heat Cap, const p,
C = Coulomb (6.24x10^{18} e^-)