

Equations – Quantum Chem 1

Early Quantum Mechanics

Basic Equations

$$c = \lambda v \quad ; \quad \lambda = \frac{c}{v} \quad ; \quad v = \frac{c}{\lambda}; \quad \bar{v} = \frac{1}{\lambda}$$

$$\hbar = \frac{h}{2\pi} \quad \text{H bar}$$

$$\lambda = \frac{h}{mv}$$

$$E = hv = \frac{hc}{\lambda} = \hbar\omega \quad \text{Energy quanta}$$

$$p = n \hbar \quad \text{Allowed momentums}$$

Quantum Mechanics

$$\lambda_{\max} T = 2.9 \times 10^{-3} \text{K} \quad \text{Wein's law}$$

$$E(T) = \text{Constant} * T^4 \quad \text{Stephan-Boltzmann (const = } 7.567 \times 10^{-16} \text{ Jm}^{-3}\text{K}^{-4}\text{)}$$

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)} \quad \text{Planck distribution}$$

$$\rho(v, T) = \frac{8\pi hc}{c^3 (e^{hv/kT} - 1)}$$

$$\frac{\hbar}{2} \leq \Delta x \Delta p \quad | \quad \frac{\hbar}{2} \leq \Delta E \Delta t \quad \text{Heisenberg Uncertainty}$$

$$\phi = hv - KE \quad \text{Work function [} \phi \text{ work function, KE electron KE, } hv \text{ emitted photon energy]}$$

$$r = n^2 \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2 Z} \quad \text{Orbital radii (n is the electron orbit)}$$

$$C_{v,m}(T) = 3Rf_E(T) \quad \text{Einstein heat capacity}$$

$$f_E(T) = \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{2T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2}$$

$$\theta_E = \frac{hv}{k} \quad \text{Einstein temp}$$

$$\lambda = \frac{h}{p} = \frac{h}{vm} \quad \text{de Broglie relation}$$

$$E = KE = (\text{particle view}) \frac{p^2}{2m} = (\text{wave view}) = \frac{\hbar^2 k^2}{8m} = \left(v + \frac{1}{2}\right) \hbar\omega = \left(v + \frac{1}{2}\right) \hbar \sqrt{\frac{k_f}{m}}$$

$k_f = \text{force constant, } v = \text{quantum level, } \omega = \text{rotational freq,}$

Table 1: Degeneracy properties of the particle in a 2-D box with $L_x = L$ and $L_y = L$.

$n_x^2 + n_y^2$	Combinations of Degeneracy (n_x, n_y)		Total Energy (E_{n_x, n_y})	Degree of Degeneracy
2	(1, 1)		$\frac{2\hbar^2 \pi^2}{2mL^2}$	1
5	(2, 1)	(1, 2)	$\frac{5\hbar^2 \pi^2}{2mL^2}$	2
8	(2, 2)		$\frac{8\hbar^2 \pi^2}{2mL^2}$	1
10	(3, 1)	(1, 3)	$\frac{10\hbar^2 \pi^2}{2mL^2}$	2
13	(3, 2)	(2, 3)	$\frac{13\hbar^2 \pi^2}{2mL^2}$	2
18	(3, 3)		$\frac{18\hbar^2 \pi^2}{2mL^2}$	1

Probability

Normalization	$\int \psi^* \psi d\tau = 1$		
Probability	$p(x, t) = \int \psi(x) ^2 dx = \int \psi^*(x) \psi(x) dx = \langle \psi \psi \rangle$		
Probability density	$p(x, t) = \int_{x_1}^{x_2} \psi(x) ^2 dx = \int_{x_1}^{x_2} \psi^*(x) \psi(x) dx$		
Probability	$\int \psi^*(x) \hat{\Omega} \psi(x) dx = \langle \psi \hat{\Omega} \psi \rangle$		
Avg value	$\langle x \rangle = \int_{-\infty}^{\infty} x \psi(x) ^2 dx \quad \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 \psi(x) ^2 dx$		
$x_i - \langle x \rangle$	Deviation of the i^{th} from $\langle x \rangle$	$\langle x_i - \langle x \rangle \rangle$	avg deviation from avg $\langle x \rangle$
$(x_i - \langle x \rangle)^2$	square of deviation	$\langle (x_i - \langle x \rangle)^2 \rangle$	variance - σ^2
Std Dev	$= \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$		

Quantum mechanical operators for some physical observables.

Observable	symbol in classical physics	Operator in QM	Operation
Position	\mathbf{r}	$\hat{\mathbf{r}}$	multiply by \mathbf{r}
Momentum	p_x	\hat{p}_x	$-i\hbar \frac{\partial}{\partial x}$
	p_y	\hat{p}_y	$-i\hbar \frac{\partial}{\partial y}$
	p_z	\hat{p}_z	$-i\hbar \frac{\partial}{\partial z}$
Kinetic Energy	T	\hat{T}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential Energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	multiply by $\hat{V}(\mathbf{r})$
Total Energy	E	\hat{H}	$\hat{T} + \hat{V}$
Angular Momentum	l_x	\hat{l}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	l_y	\hat{l}_y	$-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	l_z	\hat{l}_z	$-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

Constants

R = Gas constant = $N_A k$ (8.31446 J/Kmol or Pa \cdot 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) $k_{\text{B}} = 0.694468$

atm = 1.01325 bar = 101325 Pa = 760 torr ; bar = 1.0x10⁵ Pa torr = mmHg = 133.322 Pa

F = Faraday's constant = 96,485 C/mol = $N_A \times e^-$ charge $c = 2.99892458 \times 10^8$ m/s

$h = 6.6261762 \times 10^{-34}$ Js = 4.134733×10^{-15} eVs $\hbar = 1.0545887 \times 10^{-34}$ Js $N_A = 6.022 \times 10^{23}$ molecules/At Wt

eV/J = 6.24x10¹⁸, J/eV = 1.602x10⁻¹⁹ $m_e = 9.11 \times 10^{-31}$ amu = 1.661x10⁻²⁷ kg

\mathcal{R}_H = Rydberg constant = 109677, $\mathcal{R}_\infty = 1096737$ $c =$ speed of light (2.9979z10⁸ m/s)

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 ($\frac{J}{\langle \text{unit} \rangle K}$)

Q = Rxn quotient

R = Gas constant = $N_A k$ (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/s²)

v = electrons/molecule, rxn rate

$C_{V,m} = C_m =$ Molar Heat Capacity, V

R = Thermodynamic Equilibrium Const (= Q_{Equil}) C = Coulomb (6.24x10¹⁸ e⁻)

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 m²/s²)

$C_{V,p} =$ Molar Heat Cap, const p,