Structure of Matter CheatSheet

Mathematical tools

Gamma function $\Gamma(\alpha) = \int_0^\infty x^{\alpha-1} e^{-x} dx$

$\Gamma(n) = (n-1)!$

Laplacian in polar coordinates:

$$\nabla^2 = \left(\frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}\right) - \frac{l^2}{r^2}$$

Angular momentum in polar coordinates

$$l^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

Hermite polynomial $\phi_0(Q) = \left(\frac{b}{\pi}\right)^{\frac{1}{4}} e^{-\frac{b}{2}Q^2}$, $b = \frac{\mu\omega_0}{\hbar}$

Quantum mechanics

Fermi golden rule $W_{12} = \frac{2\pi}{\hbar^2} |\langle 2|H'|1\rangle|^2 \delta(\omega - \omega_{21})$

Density matrix formalism

Density matrix $\rho = \sum_\varphi p_\varphi |\varphi\rangle\langle\varphi|$

Expectation value observable $\langle A\rangle = Tr(\rho A) = \sum_\varphi p_\varphi \langle\varphi|A|\varphi\rangle$

Harmonic oscillator

Ladder Operators: $a_k = \sqrt{\frac{m\omega}{2\hbar}}\left(r_k + \frac{i}{m\omega}p_k\right)$

$$a_k^\dagger |\mathbf{n}\rangle = \sqrt{n_k+1}\,|\mathbf{n}+\mathbf{e}_i\rangle$$

$$a_k |\mathbf{n}\rangle = \sqrt{n_k}\,|\mathbf{n}-\mathbf{e}_i\rangle$$

Second order corrections perturbation theory

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left|\left\langle \psi_m^{(0)}|H'|\psi_n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}$$

Dipole transitions

$$A_{2\to1} = \frac{2\pi}{3\hbar^2}\rho(\nu_{21})\,|R_{12}|^2$$

$$\rho(\nu_{21}) = \frac{8\pi h\nu^3}{c^3}$$

$$|R_{12}|^2 = |\langle 2| - ex|1\rangle|^2 + |\langle 2| - ey|1\rangle|^2 + |\langle 2| - ez|1\rangle|^2$$

Angular momentum operators

$$L_\pm = L_x \pm iL_y$$

$$L_\pm |l, m_z\rangle = \sqrt{(l \mp m_z)(l \pm m_z + 1)}\,|l, m_z \pm 1\rangle$$

Statistical mechanics

Partition function $\mathcal{Z} = \sum_E g(E) e^{-\beta E}$

$g(E) =$ degeneracy of the state

Free energy $A = -NK_B T \ln\mathcal{Z} = U - TS$

$$S = -\frac{\partial A}{\partial T},\ U = -\frac{\partial \ln\mathcal{Z}}{\partial\beta} = K_B T^2 \frac{\partial\ln\mathcal{Z}}{\partial T}$$

Power emitted per unit surface $\varphi(T) = \frac{1}{4}cU$

Velocity distribution

$$\rho(v)dv = \left(\frac{m}{2\pi KT}\right)^{3/2}\exp\left(-\frac{1}{2}m\frac{v^2}{KT}\right)v^2 dv \sin\theta\, d\theta\, d\varphi$$

In one dimension:

$$dn(v_x) = N\rho(v_x)dv_x = N\sqrt{\frac{m}{2\pi kT}}\exp\left(-\frac{mv_x^2}{2KT}\right)dv_x$$

Atom

Bohr radius $a_0 = \frac{\hbar^2}{me^2} = 0.529$(for hydrogen-like a_0/Z)

Rydberg constant $R = -\frac{e^2}{2a_0hc} = 109.678\,\text{cm}^{-1}$

Magnetic moment $\boldsymbol{\mu}_\mathbf{l} = -\frac{e\hbar}{2mc}\mathbf{l}$

Bohr magneton $\frac{e\hbar}{2mc} = 0.927 \times 10^{-20}$ erg/G

Spin orbit $\xi_{nl} = 2Z\mu_B^2 \langle r^{-3}\rangle_{nl}$

Hydrogen-like atom energies

$$E_n = -\frac{m(Ze)^2e^2}{2\hbar}\frac{1}{n^2} = -Z^2R_H hc\frac{1}{n^2} = -Z^2\frac{e^2}{2a_0n^2}$$

Hydrogen-like atom eigenfunctions

n	l	m	eigenfunctions
1	0	0	$\phi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\phi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	±1	$\phi_{21\pm1} = \mp\frac{e^{\pm i\varphi}}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\sin\theta$
2	1	0	$\phi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\theta$

Expectation values

$\langle r\rangle$	$\frac{a_0}{2Z}(3n^2 - l(l+1))$
$\langle r^2\rangle$	$\frac{n^2}{2}\left(\frac{a_0}{Z}\right)^2(5n^2 + 1 - 3l(l+1))$
$\langle r^{-1}\rangle$	$\left(\frac{a_0}{Z}n^2\right)^{-1}$
$\langle r^{-2}\rangle$	$\frac{Z^2}{a_0^2}\left(n^3\left(l + \frac{1}{2}\right)\right)^{-1}$
$\langle r^{-3}\rangle$	$\frac{Z^3}{a_0^3 n^3 (l(l+1)(l+\frac{1}{2}))}$

Selection rules

Electric dipole neglecting spin $\Delta l = \pm1$ and $\Delta m = 0, \pm1$

Electric dipole with spin-orbit $\Delta j = 0, \pm1$ but $j = 0 \leftrightarrow j = 0$ not allowed, $\Delta m = 0, \pm1$ but $m = 0 \leftrightarrow m = 0$ not allowed if $\Delta j = 0$

Magnetic dipole $\Delta l = 0$ e $\Delta m = 0, \pm1$

Electric quadrupole $\Delta l = 0, \pm2$ e $\Delta m = 0, \pm1, \pm2$ but $l = 0 \leftrightarrow l = 0$ not allowed

Magnetic field

Landé factor $g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$

Magnetization $M = \frac{Ng^2\mu_B^2 J(J+1)}{3KT}H$

Magnetic susceptivities

Curie $\chi_C = \frac{Ng^2\mu_B^2 j(j+1)}{3KT} = C/T$

Diamagnetic $\chi_{dia} = -\frac{e^2}{4mc^2}\sum_i \langle\varphi|r_i^2\sin^2\theta_i|\varphi\rangle$

Magnetic nuclear moment $\mu_{\mathbf{I}} = \gamma\hbar\mathbf{I}$

Quadrupole Hamiltonian

$$\mathcal{H} = \frac{eQV_{zz}}{4I(2I-1)}(3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2))$$

$$\eta = \frac{V_{xx} - Vyy}{V_{zz}}$$

Hamiltonian in e.m. field $\mathcal{H} = \frac{1}{2m}(\mathbf{p} + \frac{e}{c}\mathbf{A})^2$

$$\mathbf{A} = \frac{1}{2}\mathbf{H}\times\mathbf{r}$$

Molecule

Ground state energy biatomic molecule

$$E(R) = \frac{\mathcal{H}_{11} + \mathcal{H}_{12}}{1 + S_{12}}$$

for H_2^+ molecule, with $x = R/a_0$

$$S_{12}(x) = \mathrm{e}^{-x}\left(1 + x + \frac{x^2}{3}\right)$$

$$\mathcal{H}_{11} = \frac{e^2}{a_0}\mathrm{e}^{-2x}\left(1 + \frac{1}{x}\right) - \frac{\mathrm{e}^2}{2a_0}$$

$$\mathcal{H}_{12}(x) = \frac{e^2}{a_0}\mathrm{e}^{-x}\left(\frac{1}{x} - \frac{1}{2} - \frac{7x}{6} - \frac{x^2}{6}\right)$$

Zero point energy frequency $\nu = \frac{1}{2\pi}\sqrt{\frac{k_{\text{el}}}{\mu}}$

$k_{el} = \frac{\partial^2 E}{\partial R^2}\Big|_{R_{\text{eq}}}$

$E^{\text{atoms}}_{\text{dissociation}} = |V(R_{\text{eq}})| - E_{\text{ionization}} + E_{\text{aff}}$

Born-Meyer potential $V(R) = -\frac{e^2}{R} + B\mathrm{e}^{-\frac{R}{\rho}}$

Wave functions $\sigma_{g,u1s} = \frac{1}{\sqrt{2(1\pm S_{AB})}}(\phi_{1s}^A(\mathbf{r}_A) \pm \phi_{1s}^B(\mathbf{r}_B))$

$S_{AB} \simeq 0.58$

Rotational states

Fundamental rotational constant $B = \frac{\hbar}{4\pi\mu R_{\text{eq}}^2 c} = \frac{\hbar}{4\pi Ic}$

Rotational state energies $E_k = Bhck(k+1)$

$\theta_{\text{rot}} = \frac{\hbar^2}{2IK_{\text{B}}}$

$\omega_{\text{rot}} = \frac{\hbar\sqrt{k(k+1)}}{\mu R_{\text{eq}}^2}$

$\mathcal{Z}_{\text{rot}} = \sum_{k=0}^{\infty}(2k+1)\exp\left(-\frac{\theta_{\text{rot}}}{T}k(k+1)\right)$, for $T \gg \theta_{\text{rot}}$,

$\mathcal{Z}_{\text{rot}} = \frac{T}{\theta_{\text{rot}}}$, for $T \to 0$ count only first two levels

$\mathcal{Z}_{\text{vib}} = \sum_{v=0}^{\infty}\exp\left(-\frac{\theta_{\text{vib}}}{T}\left(v + \frac{1}{2}\right)\right)$

$\theta_{\text{vib}} = \frac{h\nu_0}{K_{\text{B}}}$

Statistical population

$N_k(T) = N_{k=0}(T)(2k+1)\exp\left(-\frac{\theta_{rot}}{T}k(k+1)\right)$

$\Delta E(0,0) = -\frac{\mu_e^2\mathcal{E}^2 I}{3\hbar^2}$; for $k \neq 0$,

$\Delta E(k, M_k) = \frac{\mu_e^2\mathcal{E}^2 I}{\hbar^2}\left(\frac{k(k+1) - 3M_k^2}{k(k+1)(2k-1)(2k+3)}\right)$

Rotazional polarizability $\alpha = -\frac{\partial^2\Delta E}{\partial\mathcal{E}^2} = \frac{2\mu_e^2 I}{3\hbar^2}$,

$\langle\alpha(T)\rangle = \frac{N}{\mathcal{Z}_{\text{rot}}}\alpha$

Vibrazional polarizability $\alpha_{\text{vib}} = \frac{e^2}{k_{\text{el}}}$, electric pol.

$\alpha_{\text{el}} \propto R_{\text{eq}}^3$

$k_{\text{el}}\langle Q^2(T)\rangle = \langle E(T)\rangle$

Radial equation $-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 u}{\mathrm{d}R^2} + \left(E(R) + \frac{k(k+1)\hbar^2}{2\mu R_{eq}^2}\right)u = Eu$

Franck-Condon factor $S_{\text{FC}}(\nu_1,\nu_2) = \int \phi_{\text{vib}}^{\nu_2 *}\phi_{\text{vib}}^{\nu_1}\mathrm{d}\tau$

Secular equation for ciclobutadiene with LCAO method

$$\det\begin{bmatrix} E_0 - E & \beta & 0 & \beta \\ \beta & E_0 - E & \beta & 0 \\ 0 & \beta & E_0 - E & \beta \\ \beta & 0 & \beta & E_0 - E \end{bmatrix} = 0$$

Solids

Effective mass $m^*(k) = \hbar^2\left(\frac{\partial^2 E}{\partial k^2}\right)^{-1}$

Energy weakly bound electron

$$E(k) = \frac{\hbar^2 k^2}{2m} + \bar{V} + \sum_{\vec{g}}\frac{|V_{\vec{g}}|^2}{E^0_{\vec{k}} - E^0_{\vec{k}-\vec{g}}}$$

State density $D(\vec{k}) = \frac{L^n}{(2\pi)^n}$

Energy density in n dimensions

$$D(E) = \alpha_n\left(\frac{2m}{\hbar}\right)^{n/2}\left(\frac{L}{2\pi}\right)^n E^{(n-2)/2}\ ,\ \alpha_n = 2, 2\pi, 4\pi$$

Delta change of variable

$$\int \mathrm{d}k\, D(\vec{k})\delta(E(\vec{k} - E)) = \int_{E(k)=E} D(\vec{k})\frac{\mathrm{d}S_{n-1}}{|\boldsymbol{\nabla}E(\vec{k})|}$$

Fermi Pressure $P = -\frac{\partial U}{\partial V} = \frac{2}{3}\frac{U}{V} = \frac{2}{5}nE_{\text{F}}$

Thermal wavelength $\lambda = \frac{h}{\sqrt{3mK_BT}}$

Magnetization $M = N\langle m_H\rangle_T = -N\frac{\partial}{\partial H}\ln Z$

Compression module $B = -V\frac{\partial P}{\partial V} = \frac{2}{3}nE_F = \frac{5}{3}P$

Energy in conduction band $E_c(k) = E_{c,0} + \frac{\hbar^2 k^2}{2m_c}$

Electron contribution to C_V (low T)

$$C_V = \frac{\pi^2}{3} D(E_F) k_B^2 T \overset{3D}{=} \frac{\pi^2}{2} N K_B \frac{T}{T_F}$$

Two level C_V $C_V = K_B N_A \left(\frac{\Delta E}{K_B T}\right) \frac{\mathrm{e}^{-\Delta E/K_B T}}{(\mathrm{e}^{-\Delta E/K_B T} + 1)^2}$

Energy to take a Fermi gas at temperature T

$$U(T) = \int_{E_F}^{\infty} (E - E_F) f(E,T) D(E)\, \mathrm{d}E - \int_0^{E_F} (E - E_F)(1 - f(E,T)) D(E)\, \mathrm{d}E\,,$$

$f(E,T) =$statistic population function

Pauli magnetic susceptibility

$$\chi_P = -\mu_B \int_0^{\infty} \left.\frac{\delta f}{\delta E}\right|_{E'} D(E')\, \mathrm{d}E$$

if $E - E_F \gg K_B T \implies f \sim \mathrm{e}^{-(E-E_F)/K_B T}$

Strongly bound electron $E(k) = E_a + V_0 + \sum_{h \neq 0} \mathrm{e}^{\mathrm{i}kh} t_h$

Born-Mayer potential $E(R) = -\frac{Ne^2\alpha}{R} + NzB\mathrm{e}^{-R/\rho}$

Resistivity $\rho = \frac{m}{ne^2\tau}$

Debye density states $D(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{v^3}$

Debye $C_V^D = \frac{12\pi^4}{5} N K_B \left(\frac{T}{\theta_D}\right)$, $\theta_D = \frac{\hbar\omega_D}{K_B}$, $\omega_D^3 = v^3 \frac{6\pi^2}{v_c}$

Einstein $C_V^E = \frac{3NK_B}{V} (\theta_E/T)^2 \mathrm{e}^{-\theta_E/T}$