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

Density matrix formalism

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

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

Harmonic oscillator

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

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

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

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

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

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

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

Angular momentum operators

$L_\pm = L_x \pm iL_y$

$L_\pm\left|l, m_z\right\rangle = \sqrt{(l\mp m_z)(l\pm m_z+1)}\left|l, m_z\pm1\right\rangle$

Statistical mechanics

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

$g(E) =$ degeneracy of the state

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

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

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

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

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

Bohr magneton $\frac{e\hbar}{2mc} = 0.927\times10^{-20}\,\mathrm{erg/G}$

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

Hydrogen-like atom energies

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

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

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

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

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

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

Magnetic susceptivities

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

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

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

Quadrupole Hamiltonian

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

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

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

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

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 $\nu = \frac{1}{2\pi}\sqrt{\frac{k_{\mathrm{el}}}{\mu}}$

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

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

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 $B = \frac{\hbar}{4\pi\mu R_{\mathrm{eq}}^2 c} = \frac{\hbar}{4\pi Ic}$

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

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

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

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

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

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

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

Statistical population

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

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

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

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

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

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

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

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

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

Secular equation for ciclobutadiene with LCAO method

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