# A&M Cheatsheet

**Energy levels:**

$$E_n = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{Z_{core}^2}{n^2}$$

**Emission & Absorption**

$$\frac{\Delta E}{hc} = \tilde{\nu} = R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$R = \frac{m_e}{4\pi\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

**Reduced mass**

$$\mu_m = \frac{m_e m_p}{m_e + m_p}$$

**Rydberg constants**

$$R_m = \frac{R_\infty Z_{core}^2 \mu_m}{m_e}$$

$$R_\infty = 109737.31\,\mathrm{cm}^{-1}$$

**Parity**

$$\hat{P} f(r) = f(-r) \begin{cases} f(r) \text{ (even)} \\ -f(r) \text{ (odd)} \end{cases}$$

**Degeneracy:**

$$\sum_{j=0}^{n-1}(2\ell+1) = n^2$$

**Quantum Defects:**

$$\frac{E_{n,l}}{hc} = -\frac{R_m}{(n-\Delta_{n,l})^2}$$

**Orbital Angular momentum**

$$\hat{L}^2 Y = \hbar^2(\ell(\ell+1))Y$$

$$\hat{L}_z Y = m\hbar Y$$

**Spin**

$$\hat{S}^2\chi = \hbar^2 s(s+1)\chi$$

$$\hat{S}_z\chi = m_s\hbar\chi$$

**General wavefunctions**

$$\psi = \phi_T \chi_S$$

$$\psi = \phi_S \chi_T$$

**Triplet:**

$$\alpha(1)\alpha(2) = \uparrow\uparrow = \chi^T_{m=1}$$

$$\beta(1)\beta(2) = \downarrow\downarrow = \chi^T_{m=-1}$$

$$\left(\alpha(1)\beta(2) + \alpha(2)\beta(1)\right)/\sqrt{2} = (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2} = \chi^T_{m=0}$$

**Singlet**

$$\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)/\sqrt{2} = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2} = \chi^S$$

**Exchange splitting**

$$E = J \pm K \begin{cases} (+)\ \chi^S \\ (-)\ \chi^T \end{cases}$$

**Term Symbols**

$${}^{2S+1}L_J \quad \text{(SO coupling)}$$

**Magnetic moment due to spin**

$$\mu_s^{classical} = -\frac{e}{2m_e}\underline{S}$$

$$\mu_s^{Dirac} = -2\frac{e}{2m_e}\underline{S}$$

$$V_{mag} = H_{SO} = -\frac{e}{2m_e^2c^2r}\frac{d\phi}{dr}\underline{\ell}\cdot\underline{s}$$

$$\phi = \frac{e}{4\pi\varepsilon_0 r} \quad / \quad c = \frac{1}{\sqrt{\mu_0\varepsilon_0}}$$

**Spin orbit operator**

$$\hat{H}_{SO} = \frac{-e}{2m_e^2c^2r}\frac{d\phi}{dr}\hat{\underline{L}}\cdot\hat{\underline{S}}$$

$$\hat{\underline{L}} = \sum_i \hat{\underline{\ell}}_i$$

$$\hat{\underline{S}} = \sum_i \hat{\underline{s}}_i$$

$$H_{SO} \propto \frac{Z^4}{n^3}$$

**Shift in energy levels**

$$\Delta E_{SO} = \langle \hat{H}_{SO}\rangle$$

$$= \frac{hcA}{2}\left[\langle \hat{\underline{J}}^2 - \hat{\underline{L}}^2 - \hat{\underline{S}}^2\rangle\right]$$

$$= \frac{hcA}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

**Landé's Interval Rule:**

$$\Delta E_{SO}(J) - \Delta E_{SO}(J-1) = hcA(L,S)J$$

**Parity of terms:** spatial inversion

$$(-)^{\sum_i \ell_i}$$

$$I = \frac{1}{A}$$

**Nuclear magnetic moment**

$$\mu_I = g_N \mu_N \frac{I}{\hbar}$$

$$\mu_N = \frac{m_e}{m_N}\mu_B$$

**Fermi's Golden Rule:**

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}|\langle f|\hat{H}_{int}|i\rangle|^2\delta(E_i - E_f - \hbar\omega)$$

**Selection Rules:**

| | |
|---|---|
| $\Delta\ell = \pm 1$ | $\Delta J = 0, \pm 1$ |
| $\Delta m_\ell = 0, \pm 1$ | $\Delta M_J = 0, \pm 1$ |
| $\Delta s = 0$ | $J=0 \nrightarrow J'=0$ |
| [strong SO] | [strong transit] |
| $\hookrightarrow \Delta j = 0, \pm 1$ | $\hookrightarrow \Delta S = 0$ |
| $j=0 \nrightarrow j'=0$ | $\Delta L = \pm 1$ |
| | $L=0 \nrightarrow L'=0$ |

**Decay and Excited state lifetimes**

$$\Gamma_{spon} = A = \frac{8\pi^2\nu_{12}^3}{3\varepsilon_0 hc^3}|\langle\psi_f|e\underline{r}|\psi_i\rangle|^2$$

$$\tau_{spon} = \frac{1}{A} \qquad \tau_i = \frac{1}{\Gamma_i} = \left(\sum_f A_{if}\right)^{-1}$$

$$\Gamma_i = \sum_f A_{if}$$

## Zeeman effect

Normal ($S=0$)

$$\Delta E = \mu_B B_z m_e = -\mu_z B_z$$

Anomalous ($S \neq 0$)

$$\Delta E = -\mu_z B_z$$

$$= g_j \mu_B m_j B_z$$

Paschen-Back (s to strong B-field)

$$\Delta E = \mu_B B_z (m_L + 2m_s)$$

## Stark Effect

Quadratic (non-degen lvls)

$$\Delta E_F = -\frac{1}{2}\alpha F_z^2$$

Linear (degen lvls)

$$\Delta E_F^{\pm} = \mp 3 e a_H F_z$$

$$M_{elec}^{\pm} = \pm 3 e a_H$$

Ionisation (strong E-field)

$$V(z) = V_c(z) + V_F$$

$$= -\frac{e^2}{4\pi\varepsilon |z|} + e F_z z$$

$$V_{saddle} = -2\sqrt{\frac{e^3 F_z}{4\pi\varepsilon}}$$

$$\simeq -\frac{hcR_H}{n^2}$$

$$F_{ion} = \frac{\pi\varepsilon(hcR_H)^2}{e^3 n^4} \propto \frac{1}{n^4}$$

## Variational Method

$$E_{var} = \frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle}$$

$$E_{var} \geq E_{exact}$$

Secular determinant

$$\begin{vmatrix} H_{AA} - S_{AA}E & H_{AA} - S_{AA}E & \cdots & H_{NA} - S_{NA}E \\ \vdots & \ddots & & \vdots \\ H_{AN} - S_{AN}E & & & H_{NN} - S_{NN}E \end{vmatrix} = 0$$

Linear Combination of Atomic Orbitals

LCAO

$$\Psi = \sum_{i=1}^{N} c_i \phi_i^{AO}$$

Dipole moment

$$\mu = Q \times d$$

## Molecular spectroscopy

$$E_{int} = E_{elec} + E_{vib} + E_{rot}$$

Vibrational (HO)

$$\omega_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\bar{\omega}_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$E_{vib} = (v + \tfrac{1}{2})\hbar\omega_0$$

$$\bar{E}_{vib} = (v + \tfrac{1}{2})\bar{\omega}_0$$

$$\underline{D_0 = D_e - \tfrac{1}{2}\hbar\omega_0}$$

Anharmonic

$$E_{vib} = \hbar\omega_0(v + \tfrac{1}{2}) - \hbar\omega_0 x_e (v + \tfrac{1}{2})^2$$

$$\bar{\omega}_{osc} = \bar{\omega}_0 (1 - \omega_0 x_e (v + \tfrac{1}{2}))$$

Populations

$$\frac{N_{v=1}}{N_{v=0}} = \exp\left(-\frac{\Delta E}{kT}\right)$$

## Rotational

$$E_{rot, J_m} = B_e J(J+1)$$

$$B_e = \frac{\hbar}{4\pi I_c} = \frac{\hbar}{4\pi \mu R_e^2 c}$$

$$\bar{\nu}_{rot}(J) = 2B_e(J+1)$$

$$\Delta J = \pm 1$$

$$N_J \sim (2J+1)\exp\left[-\frac{BJ(J+1)}{kT}\right]$$

$$J_{max} = \sqrt{\frac{kT_r}{2hcB}} - \frac{1}{2}$$

Vib-Rot

$$\Delta v = \pm 1 \quad \Delta v = 0$$

$$\Delta J = \pm 1 \quad \Delta J = 0$$

$$E_{rot} = \frac{J(J+1)\hbar^2}{2\mu R^2} + \frac{1}{2}k(R - R_e)^2$$

$$D_c = \frac{\hbar^3}{4\pi c k \mu^2 R_e^6}$$

$$D = \frac{4B^3}{v^2}$$

$$\frac{E_{n,J_m}}{hc} = D_e + (n + \tfrac{1}{2})\omega_e - (n + \tfrac{1}{2})^2 x_e \omega_e$$

$$+ B_n J(J+1) - D_c J^2 (J+1)^2$$

$$B_n = B_e - \alpha_e (n + \tfrac{1}{2})$$

$$\frac{I_J}{I_0} = \frac{N_J}{N_0} = \frac{g_J}{g_0} e^{-\frac{\Delta E}{kT_r}}$$

$$= (2J+1)\exp\left[-\frac{B_n hc J(J+1)}{kT_r}\right]$$

## Franck Condon factor

$$f_{v'v''} = |\langle v' | v'' \rangle|^2$$

$$= \left| \int F_f(R) F_i(R)\, dR \right|^2$$