Key formulae — Gryn'ova, Coote & Corminboeuf (2015)

1. Pauli antisymmetry [paper, p. 441]

For any two electrons i, j the total wavefunction must satisfy

$$\Psi(\ldots, i, \ldots, j, \ldots) = -\,\Psi(\ldots, j, \ldots, i, \ldots). \tag{1}$$

The paper's argument: only the many-electron system has sharp stationary states; assigning electrons to individual orbitals/quantum numbers is an approximation.

2. Two electrons in two orbitals (Figure 1) [paper, p. 441]

Active space: electrons 1, 2; spatial orbitals φ_a, φ_b; spin functions α, β. Figure 1 determinants: i $= \varphi_a^2$, ii $= \varphi_b^2$, iii $= \varphi_a^\alpha \varphi_b^\beta$, iv $= \varphi_a^\beta \varphi_b^\alpha$, v $= \varphi_a^\alpha \varphi_b^\alpha$ ($M_S = +1$), vi $= \varphi_a^\beta \varphi_b^\beta$ ($M_S = -1$).

Triplet, $M_S = \pm 1$ (single determinants v, vi):

$$^3\Psi(M_S = +1) = \tfrac{1}{\sqrt{2}}\big[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\big]\,\alpha_1\alpha_2, \tag{2}$$

$$^3\Psi(M_S = -1) = \tfrac{1}{\sqrt{2}}\big[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\big]\,\beta_1\beta_2. \tag{3}$$

Open-shell singlet, $M_S = 0$ (two determinants iii, iv):

$$^1\Psi(M_S = 0) = \tfrac{1}{\sqrt{2}}\big[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)\big] \cdot \tfrac{1}{\sqrt{2}}\big[\beta_1\alpha_2 - \alpha_1\beta_2\big]. \tag{4}$$

Written with unnormalised Slater determinants $D_{\mathrm{iii}} = \begin{vmatrix} \varphi_a(1)\alpha_1 & \varphi_b(1)\beta_1 \\ \varphi_a(2)\alpha_2 & \varphi_b(2)\beta_2 \end{vmatrix}$, $D_{\mathrm{iv}} = \begin{vmatrix} \varphi_a(1)\beta_1 & \varphi_b(1)\alpha_1 \\ \varphi_a(2)\beta_2 & \varphi_b(2)\alpha_2 \end{vmatrix}$:

$$^1\Psi(M_S = 0) = \tfrac{1}{2}\big[D_{\mathrm{iv}} - D_{\mathrm{iii}}\big]. \tag{5}$$

Erratum (checked symbolically with SymPy): the paper prints this combination with a "+" sign, $\frac{1}{2}[D_{iii} + D_{iv}]$. Expanding that gives $\frac{1}{2}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)][\alpha_1\beta_2 + \beta_1\alpha_2]$, i.e. the $M_S = 0$ triplet component. The singlet needs the minus sign shown above. The physical point is unaffected: the triplet is single-reference, the open-shell singlet is multireference.

Triplet, $M_S = 0$ [supplementary]:

$$^3\Psi(M_S = 0) = \tfrac{1}{\sqrt{2}}\big[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\big] \cdot \tfrac{1}{\sqrt{2}}\big[\alpha_1\beta_2 + \beta_1\alpha_2\big] = \tfrac{1}{2}\big[D_{\mathrm{iii}} + D_{\mathrm{iv}}\big]. \tag{6}$$

3. Coulomb and exchange [paper, p. 442, qualitative; integrals supplementary]

The paper names the Coulomb repulsion J_{xy} and exchange interaction K_{xy} between electrons x, y. Standard definitions:

$$J_{ab} = \iint \frac{|\varphi_a(1)|^2\,|\varphi_b(2)|^2}{r_{12}}\,d\tau_1 d\tau_2, \qquad K_{ab} = \iint \frac{\varphi_a^*(1)\varphi_b(1)\,\varphi_b^*(2)\varphi_a(2)}{r_{12}}\,d\tau_1 d\tau_2 \;\geq 0. \tag{7}$$

For the wavefunctions above, with frozen orbitals and one-electron energies h_a, h_b [supplementary]:

$$E(^3\Psi) = h_a + h_b + J_{ab} - K_{ab}, \qquad E(^1\Psi_{\mathrm{OSS}}) = h_a + h_b + J_{ab} + K_{ab}, \tag{8}$$

$$\Delta E_{\mathrm{ST}} \equiv E(\mathrm{S}) - E(\mathrm{T}) = 2K_{ab}. \tag{9}$$

This single-configuration estimate is the "Hund's rule" picture the paper criticises. It ignores orbital relaxation, static correlation (mixing with the closed-shell configurations i and ii) and dynamic spin polarisation, which can make the singlet the ground state.

Disjoint NBMOs (Borden–Davidson) [paper, p. 443]: if φ_a and φ_b share no atoms, $\varphi_a(\mathbf{r})\varphi_b(\mathbf{r}) \approx 0$ everywhere, so

$$K_{ab} \approx 0 \;\Rightarrow\; \Delta E_{\mathrm{ST}} \approx 0, \tag{10}$$

and higher-order effects (spin polarisation) decide the ground state; often the singlet (CBD, TME). Non-disjoint NBMOs ($K_{ab} > 0$) give triplet ground states (MX, TriMB).

4. Hund's rule explanations [paper, p. 442]

- **Hund (1925):** among multiplets of one configuration, the highest S is lowest.
- **Slater:** the triplet has less e^-–e^- repulsion because of the Fermi hole (exchange $-K$).
- **Later (less-screening rule):** V_{ee} is actually *larger* in the triplet. The Fermi hole reduces nuclear screening, so $|V_{ne}|$ grows by more:

  $$\Delta V_{ee} > 0, \qquad \Delta V_{ne} < 0, \qquad |\Delta V_{ne}| > \Delta V_{ee} \quad \text{(T relative to S)}. \tag{11}$$

  Virial theorem: $E = -\langle T\rangle = \frac{1}{2}\langle V\rangle$, with $V = V_{ne} + V_{ee} + V_{nn}$ [supplementary].
- **Correlation magnitude:** $|E_{\mathrm{corr}}(\uparrow\uparrow)| \approx \frac{1}{10}\,|E_{\mathrm{corr}}(\uparrow\downarrow)|$ (same-spin vs. opposite-spin pair).

5. Janak / extended Koopmans view [paper, p. 443]

At the Hartree–Fock level, the singlet–triplet gap equals the difference between the HOMO energies of the triplet and the open-shell singlet:

$$\Delta E_{\mathrm{ST}} = \varepsilon^{\mathrm{T}}_{\mathrm{HOMO}} - \varepsilon^{\mathrm{OSS}}_{\mathrm{HOMO}} \tag{12}$$

The paper gives no sign convention; this is a literal transcription of its wording. Janak's theorem in general [supplementary]: $\partial E/\partial n_i = \varepsilon_i$.

6. Topology rules of spin coupling [paper, p. 443; Scheme 1]

Dynamic spin polarisation produces an alternating (damped) spin wave along the chain:

$$\text{sites separated by } \begin{cases} \text{odd number of bonds} & \Rightarrow \text{ferromagnetic (parallel) coupling} \\ \text{even number of bonds} & \Rightarrow \text{antiferromagnetic (antiparallel) coupling} \end{cases} \tag{13}$$

Ovchinnikov's rule (VB): the most spin-alternant determinant has the lowest energy and the largest weight. For alternant hydrocarbons with n^* starred and n° unstarred atoms [supplementary, standard form]:

$$S_{\mathrm{ground}} = \tfrac{1}{2}\,\big|\, n^* - n^\circ \,\big|. \tag{14}$$

7. Aufbau vs. quasi-closed-shell (non-aufbau) occupation [paper, pp. 447–449; Fig. 10]

$$\text{aufbau:} \quad \varepsilon_{\text{doubly occ.}} < \varepsilon_{\mathrm{SOMO}} < \varepsilon_{\mathrm{LUMO}}, \tag{15}$$

$$\text{quasi-closed-shell:} \quad \varepsilon_{\mathrm{SOMO}} < \varepsilon_{\mathrm{HOMO}}\ \text{(doubly occupied)} < \varepsilon_{\mathrm{LUMO}}. \tag{16}$$

Redox fingerprint (core = lower doubly occupied MOs):

$$\text{aufbau:}\quad (\text{core})^2\,(\text{SOMO})^1 \xrightarrow{-e^-} (\text{core})^2(\text{SOMO})^0 \quad \text{(closed shell)} \tag{17}$$

$$\text{non-aufbau:}\quad (\text{core})^2(\text{SOMO})^1(\text{HOMO})^2 \xrightarrow{-e^-} (\text{core})^2(\text{SOMO})^1(\text{HOMO})^1 \quad \text{(T or OSS diradical)} \tag{18}$$

$$(\text{core})^2(\text{SOMO})^1(\text{HOMO})^2 \xrightarrow{+e^-} (\ldots)(\text{SOMO})^1(\text{HOMO})^2(\text{LUMO})^1 \quad \text{(diradical)} \tag{19}$$

The SOMO is not touched by electron removal or addition. Evidence must come from observables (IP/EA, CV redox potentials, ESR/magnetic data of the products), not from orbital energies alone: ROHF orbital ordering depends on canonicalisation [paper, p. 449].

Spin-polarised donor (Scheme 3) [paper, p. 449]: in an unrestricted picture the unpaired α spin splits the donor HOMO into $\varepsilon^{\alpha}_{\text{HOMO}} \neq \varepsilon^{\beta}_{\text{HOMO}}$; the α-HOMO can lie above the α-SOMO.

Distonic radical anions (Fig. 16) [paper, p. 452]:

$$^{\bullet}\text{R}\sim\text{A}^- \text{ (non-aufbau)} \underset{-\text{H}^+}{\overset{+\text{H}^+}{\rightleftharpoons}} {}^{\bullet}\text{R}\sim\text{AH} \text{ (aufbau)}, \qquad {}^{\bullet}\text{R}\sim\text{A}^- \xrightarrow{-e^-} {}^{\bullet}\text{R}\sim\text{A}^{\bullet} \text{ (diradical, not } \text{R}^+\sim\text{A}^-\text{)}. \tag{20}$$

Radical stabilisation is measured by methyl-transfer equilibria $\text{Me}-\text{R}\sim\text{A} \rightleftharpoons {}^{\bullet}\text{R}\sim\text{A} + {}^{\bullet}\text{Me}$ (radical stabilisation energy), as drawn in Fig. 16.

8. Historical statements quoted in the paper [paper, p. 448]

- **Ehrenfest adiabatic principle (1917):** "if a system be affected in a reversible adiabatic way, the allowed motions are transformed into allowed motions."
- **Pauli (1925), original form:** "it should be forbidden for more than one electron with the same value of the main quantum number n to have the same value for the other three quantum numbers k, j and m."
- **Modern form:** antisymmetry, Eq. (1). Individual-electron quantum numbers do not commute with $\hat{H}$; only total quantities (e.g. $\hat{J}^2$, $\hat{S}^2$) do: $[\hat{H}, \hat{\mathbf{l}}_i^2] \neq 0$ in general, while $[\hat{H}, \hat{\mathbf{J}}^2] = 0$.
- **3d/4s:** in neutral transition-metal atoms $\varepsilon_{4s} > \varepsilon_{3d}$ when both are populated (4s ionised first), yet 4s fills first because the 4s–3d repulsion is smaller than the 3d–3d repulsion.

9. State labels appearing in the figures

Fig. 2a	H_2 dissociation	ground $^1\Sigma_g^+$, excited $^3\Sigma_u^+$; degenerate at $r \to \infty$
Fig. 2b	ethylene C=C twist	$^1B_1$ and $^3A_2$; degenerate at 90°
Fig. 2c	TM complex, M–L distance	$^1A_1$, $^5T_2$, ^3T (spin crossover)
Fig. 5	tropylidene	$^1A_2$ (two determinants) vs. $^3A_2$; orbitals $2b_1$, a_1, $2a_2$