Derivations for *"Theory and practice of uncommon molecular electronic configurations"*

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CH5103 term paper — supporting derivations

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Abstract

The review contains a small number of explicit formulas and a large number of verbal claims whose justification lives in the cited literature: Hund's rule and its competing explanations, static versus dynamic correlation, disjoint non-bonding orbitals, spin polarisation, the Ovchinnikov rule, the Janak/Koopmans view of singlet–triplet gaps, kinetic exchange, the arbitrariness of ROHF orbital energies, the 3d/4s problem, and the critique of the aufbau principle. This document derives each of them from first principles, one step at a time, states every assumption, and checks every result symbolically (SymPy) or numerically (PySCF, exact diagonalisation). Where the original papers could be read, their content is quoted; where they were paywalled, this is stated and only the independently derived mathematics is given. Two errors in the review are identified: a sign error in the two-determinant open-shell singlet (section 2), and the year of the Katriel–Pauncz reference (1977, not 1975). One claim is shown to be system-dependent (same-spin vs. opposite-spin correlation, section 5).

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0 Conventions

- Atomic units throughout: $\hbar = m_e = e = 4\pi\varepsilon_0 = 1$; energies in hartree ($E_h$).
- Non-relativistic, clamped-nuclei electronic Hamiltonian for N electrons and nuclei A with charges Z_A at $\mathbf{R}_A$:

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(i) + \sum_{i<j} \frac{1}{r_{ij}}, \qquad \hat{h}(i) = -\tfrac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}. \tag{0.1}$$

  $\hat{H}$ contains no spin operators.
- Spatial orbitals $\varphi_p(\mathbf{r})$ are real and orthonormal, $\langle\varphi_p|\varphi_q\rangle = \delta_{pq}$. Spin functions: α, β, with $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$, $\langle\alpha|\beta\rangle = 0$. Spin orbitals: $\varphi_p\alpha \equiv p$, $\varphi_p\beta \equiv \bar{p}$. Shorthand: $\varphi_p(1) \equiv \varphi_p(\mathbf{r}_1)$, $\alpha_1 \equiv \alpha(\sigma_1)$.
- One- and two-electron integrals (chemists' notation):

$$h_{pq} = \int \varphi_p(\mathbf{r})\, \hat{h}\, \varphi_q(\mathbf{r})\, \mathrm{d}\mathbf{r}, \tag{0.2}$$

$$(pq|rs) = \iint \frac{\varphi_p(1)\varphi_q(1)\, \varphi_r(2)\varphi_s(2)}{r_{12}}\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2, \tag{0.3}$$

  with Coulomb and exchange integrals

$$J_{pq} = (pp|qq), \qquad K_{pq} = (pq|pq). \tag{0.4}$$

  For real orbitals $(pq|rs) = (qp|rs) = (pq|sr) = (rs|pq)$ (8-fold symmetry).
- Unnormalised 2×2 Slater determinant of spin orbitals χ_1, χ_2: $D[\chi_1, \chi_2] = \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)$; the normalised determinant is $\frac{1}{\sqrt{2}}D$, written $|\chi_1\chi_2\rangle$.
- Tags used: **[paper]** = stated in the review; **[derived]** = derived here; **[verified: ...]** = checked in this work against a source or a calculation.

1 Antisymmetry and two-electron spin functions

Statement in the review

"According to the Pauli exclusion principle, the wavefunction for a system of fermions must be antisymmetric with respect to the interchange of any two particles ... only the system (atom, molecule) as a whole possesses well-defined (sharp) stationary states." (p. 441)

1.1 Why the exchange eigenvalue is ± 1

Let $\hat{P}_{12}$ swap all coordinates (space and spin) of electrons 1 and 2: $\hat{P}_{12}\Psi(x_1, x_2, \dots) = \Psi(x_2, x_1, \dots)$.

1. Swapping twice restores the original ordering, so $\hat{P}_{12}^2 = \hat{1}$.
2. If $\hat{P}_{12}\Psi = \lambda\Psi$, then $\Psi = \hat{P}_{12}^2\Psi = \lambda^2\Psi$, hence $\lambda = \pm 1$.
3. $\hat{H}$ of eq. (0.1) is symmetric in the electron labels, so $[\hat{H}, \hat{P}_{12}] = 0$, and the eigenstates of $\hat{H}$ can be chosen as simultaneous eigenstates of $\hat{P}_{12}$.
4. The postulate (spin–statistics) for electrons selects $\lambda = -1$:

$$\Psi(x_2, x_1, \dots) = -\Psi(x_1, x_2, \dots). \tag{1.1}$$

5. A Slater determinant obeys eq. (1.1) automatically: exchanging electrons 1 and 2 exchanges two rows of the determinant, which multiplies it by -1.

6. If two spin orbitals coincide, two columns are equal and the determinant vanishes. This is Pauli's original, one-electron version ("no two electrons with the same four quantum numbers") recovered as a *consequence* of eq. (1.1) in the independent-particle approximation. Section 14 shows why, beyond that approximation, one-electron quantum numbers do not exist.

1.2 Spin operators on two electrons

Single-electron spin-$\frac{1}{2}$ operators act as $\hat{s}_z\alpha = \frac{1}{2}\alpha$, $\hat{s}_z\beta = -\frac{1}{2}\beta$, $\hat{s}_+\beta = \alpha$, $\hat{s}_+\alpha = 0$, $\hat{s}_-\alpha = \beta$, $\hat{s}_-\beta = 0$. Total spin: $\hat{S}_z = \hat{s}_z(1) + \hat{s}_z(2)$, $\hat{S}_\pm = \hat{s}_\pm(1) + \hat{s}_\pm(2)$ and

$$\hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z^2 + \hat{S}_z. \tag{1.2}$$

(*Proof of eq. (1.2):* $\hat{S}_-\hat{S}_+ = (\hat{S}_x - i\hat{S}_y)(\hat{S}_x + i\hat{S}_y) = \hat{S}_x^2 + \hat{S}_y^2 + i[\hat{S}_x, \hat{S}_y] = \hat{S}^2 - \hat{S}_z^2 - \hat{S}_z$, using $[\hat{S}_x, \hat{S}_y] = i\hat{S}_z$.)

Apply eq. (1.2) to the four products $\alpha_1\alpha_2, \alpha_1\beta_2, \beta_1\alpha_2, \beta_1\beta_2$:

1. $\alpha_1\alpha_2$: $\hat{S}_+\alpha_1\alpha_2 = 0$; $\hat{S}_z\alpha_1\alpha_2 = \alpha_1\alpha_2$. Hence $\hat{S}^2\alpha_1\alpha_2 = (0 + 1 + 1)\alpha_1\alpha_2 = 2\,\alpha_1\alpha_2$, i.e. $S(S+1) = 2$, $S = 1$, $M_S = 1$.
2. $\beta_1\beta_2$: by the same steps with $\hat{S}_+\beta_1\beta_2 = \alpha_1\beta_2 + \beta_1\alpha_2$, $\hat{S}_-(\alpha_1\beta_2 + \beta_1\alpha_2) = 2\beta_1\beta_2$, $\hat{S}_z^2 + \hat{S}_z \to 1 - 1 = 0$: $\hat{S}^2\beta_1\beta_2 = 2\beta_1\beta_2$ ($S = 1$, $M_S = -1$).
3. $\alpha_1\beta_2$: $\hat{S}_+\alpha_1\beta_2 = \alpha_1\alpha_2$, then $\hat{S}_-\alpha_1\alpha_2 = \beta_1\alpha_2 + \alpha_1\beta_2$; $\hat{S}_z\alpha_1\beta_2 = 0$. Hence $\hat{S}^2\alpha_1\beta_2 = \alpha_1\beta_2 + \beta_1\alpha_2$. Likewise $\hat{S}^2\beta_1\alpha_2 = \alpha_1\beta_2 + \beta_1\alpha_2$.
4. Therefore $\hat{S}^2(\alpha_1\beta_2 \pm \beta_1\alpha_2) = (1 \pm 1)(\alpha_1\beta_2 \pm \beta_1\alpha_2)$:

Result

$$\Theta_{1,+1} = \alpha_1\alpha_2, \quad \Theta_{1,0} = \tfrac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2), \quad \Theta_{1,-1} = \beta_1\beta_2 \quad (S = 1,\ \text{symmetric under } 1 \leftrightarrow 2), \tag{1.3}$$

$$\Theta_{0,0} = \tfrac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \qquad (S = 0,\ \text{antisymmetric}). \tag{1.4}$$

Combined with eq. (1.1): a triplet must have an *antisymmetric* spatial part, a singlet a *symmetric* spatial part.

Verification

`t01_spin_and_determinants.py`: $\hat{S}^2$, $\hat{S}_z$ built as 4×4 matrices; all four eigen-relations confirmed exactly (SymPy). **PASS**.

2 Two electrons in two orbitals: the wavefunctions of Figure 1

Statement in the review

Triplet components (p. 441): ${}^3\Psi(M_S = +1) = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)]\alpha_1\alpha_2$, ${}^3\Psi(M_S = -1) = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)]\beta_1\beta_2$, "i.e. they can be represented as single determinants v and vi". Open-shell singlet: ${}^1\Psi(M_S = 0) = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)] \cdot \frac{1}{\sqrt{2}}[\beta_1\alpha_2 - \alpha_1\beta_2]$, "a combination of two determinants, iii and iv", printed as $\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}(|\ldots|_{\text{iii}} + |\ldots|_{\text{iv}})$.

2.1 The six determinants

With two spatial orbitals and two spin functions there are four spin orbitals $a, \bar{a}, b, \bar{b}$ and $\binom{4}{2} = 6$ two-electron determinants (Figure 1 of the review):

label	occupation	D (unnormalised)	M_S
i	φ_a^2	$D[a,\bar{a}] = \varphi_a(1)\varphi_a(2)\,(\alpha_1\beta_2 - \beta_1\alpha_2)$	0
ii	φ_b^2	$D[b,\bar{b}] = \varphi_b(1)\varphi_b(2)\,(\alpha_1\beta_2 - \beta_1\alpha_2)$	0
iii	$\varphi_a^\alpha\varphi_b^\beta$	$D[a,\bar{b}] = \varphi_a(1)\varphi_b(2)\alpha_1\beta_2 - \varphi_b(1)\varphi_a(2)\beta_1\alpha_2$	0
iv	$\varphi_a^\beta\varphi_b^\alpha$	$D[\bar{a},b] = \varphi_a(1)\varphi_b(2)\beta_1\alpha_2 - \varphi_b(1)\varphi_a(2)\alpha_1\beta_2$	0
v	$\varphi_a^\alpha\varphi_b^\alpha$	$D[a,b] = [\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)]\alpha_1\alpha_2$	+1
vi	$\varphi_a^\beta\varphi_b^\beta$	$D[\bar{a},\bar{b}] = [\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)]\beta_1\beta_2$	−1

Each entry follows from $D[\chi_1,\chi_2] = \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)$; for example $D[a,\bar{b}] = \varphi_a(1)\alpha_1\,\varphi_b(2)\beta_2 - \varphi_b(1)\beta_1\,\varphi_a(2)\alpha_2$.

2.2 Triplet $M_S = \pm 1$: single determinants

Rows v and vi already factorise into (antisymmetric space)×(symmetric spin $\Theta_{1,\pm1}$). Normalising with $\frac{1}{\sqrt{2}}$ gives exactly the review's ${}^3\Psi(M_S = \pm1)$. Each is one determinant. **[paper, confirmed]**

2.3 $M_S = 0$: two determinants are needed

Determinants iii and iv individually are *not* spin eigenfunctions: their spin parts ($\alpha_1\beta_2$ or $\beta_1\alpha_2$) are not of the forms eqs. (1.3) and (1.4). Form the sum and the difference. Write $A = \varphi_a(1)\varphi_b(2)$, $B = \varphi_b(1)\varphi_a(2)$:

$$D_{\rm iii} = A\,\alpha_1\beta_2 - B\,\beta_1\alpha_2, \qquad D_{\rm iv} = A\,\beta_1\alpha_2 - B\,\alpha_1\beta_2. \tag{2.1}$$

$$D_{\rm iii} + D_{\rm iv} = A(\alpha_1\beta_2 + \beta_1\alpha_2) - B(\beta_1\alpha_2 + \alpha_1\beta_2) = (A - B)(\alpha_1\beta_2 + \beta_1\alpha_2), \tag{2.2}$$

$$D_{\rm iv} - D_{\rm iii} = A(\beta_1\alpha_2 - \alpha_1\beta_2) - B(\alpha_1\beta_2 - \beta_1\alpha_2) = (A + B)(\beta_1\alpha_2 - \alpha_1\beta_2). \tag{2.3}$$

Normalise: $\langle A \mp B | A \mp B\rangle = 2$ (orthonormal orbitals) and the spin factors have norm$^2 = 2$, so each combination needs a factor $\frac{1}{2}$.

Result

$${}^3\Psi(M_S = 0) = \tfrac{1}{2}(D_{\rm iii} + D_{\rm iv}) = \tfrac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)]\;\tfrac{1}{\sqrt{2}}[\alpha_1\beta_2 + \beta_1\alpha_2], \tag{2.4}$$

$${}^1\Psi_{\rm OSS} = \tfrac{1}{2}(D_{\rm iv} - D_{\rm iii}) = \tfrac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)]\;\tfrac{1}{\sqrt{2}}[\beta_1\alpha_2 - \alpha_1\beta_2]. \tag{2.5}$$

The open-shell singlet is irreducibly a two-determinant function; the high-spin triplet components are single determinants. This is why a single-reference method describes the triplet but not the open-shell singlet of a diradical. **[paper's physics, confirmed]**

Caveat / correction

The review writes the singlet as $\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}(D_{\rm iii} + D_{\rm iv})$, with a *plus* sign. By eq. (2.2) that combination is the $M_S = 0$ component of the *triplet*, eq. (2.4). The singlet requires the minus sign of eq. (2.3). (Its overall sign is arbitrary; $\frac{1}{2}(D_{\rm iii} - D_{\rm iv})$ is equally correct.) The review's product form, in the line above it, is correct. The physical conclusion is unaffected.

Closed-shell singlets. Rows i and ii factorise as (symmetric space)$\times\sqrt{2}\,\Theta_{0,0}$:

$$\tfrac{1}{\sqrt{2}}D_{\rm i} = \varphi_a(1)\varphi_a(2)\,\Theta_{0,0}, \qquad \tfrac{1}{\sqrt{2}}D_{\rm ii} = \varphi_b(1)\varphi_b(2)\,\Theta_{0,0}.$$

So the two-electron/two-orbital ($2e/2o$) problem has **three singlets** (i, ii, OSS) and **one triplet** (three components).

Verification

`t01_spin_and_determinants.py`: every identity above expanded symbolically; the review's "+" combination is confirmed equal to ${}^3\Psi(M_S=0)$ and *not* to ${}^1\Psi_{\mathrm{OSS}}$. **PASS**.

3 Energies of the $2e/2o$ states and the full $2e/2o$ Hamiltonian

The review discusses Coulomb repulsion J_{xy} and exchange K_{xy} verbally (p. 442). Here are the actual energy expressions.

3.1 Matrix elements by direct integration

For two electrons $\hat{H} = \hat{h}(1) + \hat{h}(2) + 1/r_{12}$. Every state of section 2 has the form (spatial part Φ)×(normalised spin part Θ). $\hat{H}$ is spin-free, so $\langle \Phi\Theta|\hat{H}|\Phi'\Theta'\rangle = \langle\Theta|\Theta'\rangle\,\langle\Phi|\hat{H}|\Phi'\rangle$. States with different S have orthogonal spin parts and do not mix. It is enough to evaluate spatial integrals.

Elementary integrals. For orthonormal real orbitals:

$$\langle\varphi_p(1)\varphi_q(2)|\hat{h}(1)|\varphi_r(1)\varphi_s(2)\rangle = h_{pr}\,\delta_{qs}, \qquad \langle\varphi_p(1)\varphi_q(2)|\hat{h}(2)|\varphi_r(1)\varphi_s(2)\rangle = \delta_{pr}\,h_{qs}, \tag{3.1}$$

$$\langle\varphi_p(1)\varphi_q(2)|r_{12}^{-1}|\varphi_r(1)\varphi_s(2)\rangle = (pr|qs). \tag{3.2}$$

Triplet. $\Phi_T = \frac{1}{\sqrt{2}}(A-B)$ with $A = \varphi_a(1)\varphi_b(2)$, $B = \varphi_b(1)\varphi_a(2)$.

1. One-electron part: $\langle A|\hat{h}(1)+\hat{h}(2)|A\rangle = h_{aa}+h_{bb}$, the same for $\langle B|\hat{h}(1)+\hat{h}(2)|B\rangle$, and $\langle A|\hat{h}(1)+\hat{h}(2)|B\rangle = h_{ab}\delta_{ba} + \delta_{ab}h_{ba} = 0$. So the one-electron part is $\frac{1}{2}(2h_{aa}+2h_{bb}) = h_a + h_b$, where $h_a \equiv h_{aa}$.
2. Two-electron part: $\langle A|r_{12}^{-1}|A\rangle = (aa|bb) = J_{ab}$, $\langle B|r_{12}^{-1}|B\rangle = J_{ab}$, and $\langle A|r_{12}^{-1}|B\rangle = (ab|ba) = K_{ab}$. Then $\frac{1}{2}(J_{ab}+J_{ab}-K_{ab}-K_{ab}) = J_{ab}-K_{ab}$.

$$\boxed{E_T = h_a + h_b + J_{ab} - K_{ab}} \tag{3.3}$$

Open-shell singlet. $\Phi_{\mathrm{OSS}} = \frac{1}{\sqrt{2}}(A+B)$. The same steps with + signs on the cross terms give

$$\boxed{E_{\mathrm{OSS}} = h_a + h_b + J_{ab} + K_{ab}}, \qquad E_{\mathrm{OSS}} - E_T = 2K_{ab}. \tag{3.4}$$

Closed shells. $\Phi_{\mathrm{i}} = \varphi_a(1)\varphi_a(2)$: $E_{\mathrm{i}} = 2h_a + J_{aa}$, and $E_{\mathrm{ii}} = 2h_b + J_{bb}$.

Couplings between the singlets.

1. $\langle\Phi_{\mathrm{i}}|\hat{H}|\Phi_{\mathrm{ii}}\rangle$: one-electron terms vanish ($\delta_{ab}=0$ factors); two-electron: $\langle\varphi_a\varphi_a|r_{12}^{-1}|\varphi_b\varphi_b\rangle = (ab|ab) = K_{ab}$.
2. $\langle\Phi_{\mathrm{i}}|\hat{H}|\Phi_{\mathrm{OSS}}\rangle = \frac{1}{\sqrt{2}}[\langle\varphi_a\varphi_a|\hat{H}|A\rangle + \langle\varphi_a\varphi_a|\hat{H}|B\rangle]$. By eq. (3.1),

$$\langle\varphi_a(1)\varphi_a(2)|\hat{h}(1)+\hat{h}(2)|\varphi_a(1)\varphi_b(2)\rangle = 0 + h_{ab},$$

   and the same for B. By eq. (3.2), $\langle\varphi_a\varphi_a|r_{12}^{-1}|A\rangle = (aa|ab)$ and $\langle\varphi_a\varphi_a|r_{12}^{-1}|B\rangle = (ab|aa) = (aa|ab)$. Sum: $\frac{1}{\sqrt{2}}\cdot 2(h_{ab} + (aa|ab))$.
3. Likewise $\langle\Phi_{\mathrm{ii}}|\hat{H}|\Phi_{\mathrm{OSS}}\rangle = \sqrt{2}\,(h_{ab} + (bb|ba))$.

Result

The singlet block of the exact $2e/2o$ Hamiltonian, in the basis $\{\Phi_{\mathrm{i}}, \Phi_{\mathrm{ii}}, \Phi_{\mathrm{OSS}}\}$:

$$\mathbf{H}_S = \begin{pmatrix} 2h_a + J_{aa} & K_{ab} & \sqrt{2}\,(h_{ab} + (aa|ab)) \\ K_{ab} & 2h_b + J_{bb} & \sqrt{2}\,(h_{ab} + (bb|ba)) \\ \sqrt{2}\,(h_{ab} + (aa|ab)) & \sqrt{2}\,(h_{ab} + (bb|ba)) & h_a + h_b + J_{ab} + K_{ab} \end{pmatrix}, \tag{3.5}$$

and the triplet is the 1×1 block E_T of eq. (3.3). For orbitals of different symmetry (e.g. σ_g, σ_u of H_2; or the NBMOs of a symmetric diradical), $h_{ab} = (aa|ab) = (bb|ba) = 0$ and the OSS decouples from the closed shells.

Consequence (Hund's rule at frozen orbitals). With the *same* orbitals in both states, eq. (3.4) gives $E_{\mathrm{OSS}} > E_T$ whenever $K_{ab} > 0$. $K_{ab} \geq 0$ is proved in section 4. This is Slater's argument: the triplet is lower by $2K_{ab}$ *because* of a smaller electron–electron repulsion ($J - K$ vs. $J + K$). Section 5 shows that this mechanism is not the correct one once the orbitals are allowed to relax.

Verification

`t02_two_orbital_hamiltonian.py`: for 5 random sets of integrals (with positive-definite two-electron kernel), the eigenvalues of eq. (3.5) and E_T equal the singlet and triplet roots of a full-CI diagonalisation (PySCF `fci.direct_spin1`, roots classified by $\langle \hat{S}^2 \rangle$), to 2×10^{-14} (max. deviation over 5 sets); Φ_{OSS} diagonal minus E_T equals $2K_{ab}$. **PASS**.

4 Fermi and Coulomb holes; positivity of K and $J \geq K$

Statement in the review

"... two electrons of the same spin cannot occupy the same space ... The corresponding shortage of the electron of a certain spin in the vicinity of another electron of the same spin is known as the Fermi hole. Two opposite-spin electrons, on the other hand, are not subject to the exclusion principle." (p. 442)

4.1 Pair densities

The spin-integrated pair density is $P(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1\sigma_2} \int |\Psi|^2 \, \mathrm{d}x_3 \cdots$. For two electrons it is $2 \sum_{\sigma_1\sigma_2} |\Psi(x_1, x_2)|^2$. The spin parts are normalised, so

$$P_T(\mathbf{r}_1, \mathbf{r}_2) = 2\,|\Phi_T|^2 = \big[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\big]^2, \qquad P_{\mathrm{OSS}} = \big[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)\big]^2. \tag{4.1}$$

1. Set $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$: $P_T(\mathbf{r}, \mathbf{r}) = [\varphi_a\varphi_b - \varphi_b\varphi_a]^2 = 0$ for *every* $\mathbf{r}$. Two same-spin electrons are never found at the same point. This is the Fermi hole, and it is exact (no approximation beyond the form of Ψ).
2. $P_{\mathrm{OSS}}(\mathbf{r}, \mathbf{r}) = 4\,\varphi_a(\mathbf{r})^2\varphi_b(\mathbf{r})^2 \geq 0$. It is not zero unless the orbitals do not overlap in space. There is no exclusion for an antiparallel pair, so the singlet's two electrons can come together. (The Coulomb hole, the reduction of P at small r_{12} caused by $1/r_{12}$ itself, is absent from these single-configuration functions. It appears only with correlation, i.e. configuration mixing.)

4.2 $K_{ab} \geq 0$

Let $\rho(\mathbf{r}) = \varphi_a(\mathbf{r})\varphi_b(\mathbf{r})$ (the overlap density). Then $K_{ab} = \iint \rho(1)\rho(2)/r_{12}$.

1. Fourier representation of the Coulomb kernel: $\dfrac{1}{|\mathbf{r}|} = \displaystyle\int \frac{\mathrm{d}^3k}{(2\pi)^3} \frac{4\pi}{k^2}\, e^{i\mathbf{k}\cdot\mathbf{r}}$.

2. Insert this and define $\tilde{\rho}(\mathbf{k}) = \int \rho(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}\,\mathrm{d}\mathbf{r}$. Because ρ is real, $\tilde{\rho}(-\mathbf{k}) = \tilde{\rho}(\mathbf{k})^*$:

$$K_{ab} = \int \frac{\mathrm{d}^3k}{(2\pi)^3}\frac{4\pi}{k^2}\Big(\int \rho(1)e^{i\mathbf{k}\cdot\mathbf{r}_1}\Big)\Big(\int \rho(2)e^{-i\mathbf{k}\cdot\mathbf{r}_2}\Big) = \int \frac{\mathrm{d}^3k}{(2\pi)^3}\frac{4\pi}{k^2}\,|\tilde{\rho}(\mathbf{k})|^2.$$

3. The integrand is non-negative, so $K_{ab} \geq 0$. Equality holds iff $\tilde{\rho} \equiv 0$, i.e. iff $\varphi_a\varphi_b = 0$ everywhere (orbitals with no common region of space).

4.3 $J_{ab} \geq K_{ab}$

1. Take $f(1,2) = \varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)$. Then $\iint f^2/r_{12} \geq 0$ because the integrand is non-negative.
2. Expand: $\iint f^2/r_{12} = J_{ab} + J_{ab} - 2K_{ab} = 2(J_{ab} - K_{ab})$ (same integrals as in section 3).
3. Hence $J_{ab} \geq K_{ab} \geq 0$. The triplet repulsion $J - K$ is non-negative, and lies below the singlet value $J + K$.

Verification

`t03_t05_hund_virial_h2.py` (T3): for all canonical RHF/6-31G orbitals of water, $\min_{pq} K_{pq} = 1.1 \times 10^{-3}\,E_h > 0$ and $J_{pq} \geq K_{pq}$ for every pair. **PASS**.

5 Hund's multiplicity rule: Slater's argument, the virial theorem and "less screening"

Statement in the review

"Slater's original explanation of the Hund's rule preference for the high-spin state was therefore based upon less electron–electron Coulomb repulsion in the triplet state ... However, it has been later shown that the electron–electron repulsion is actually greater in the high-spin state, and an alternative explanation—the so-called less screening rule—has been offered. According to this rule, Fermi holes in the triplet state lead to decreased screening of the nucleus and larger electron–nucleus attraction. While this in turn causes the electron clouds to contract and partially restores the electron–electron repulsion, the system overall is nonetheless stabilized." (p. 442, refs. 11–14). Also: "the absolute value of the correlation energy is approximately an order of magnitude lower for a pair of two same-spin electrons compared to that of opposite-spin electrons" (ref. 16).

5.1 Slater's argument (frozen orbitals)

From eqs. (3.3) and (3.4), with identical orbitals in both states,

$$E_T - E_{\mathrm{OSS}} = -2K_{ab} < 0, \qquad \underbrace{\langle V_{ee}\rangle_T - \langle V_{ee}\rangle_{\mathrm{OSS}}}_{=(J-K)-(J+K)} = -2K_{ab}, \tag{5.1}$$

$$\langle T\rangle_T - \langle T\rangle_{\mathrm{OSS}} = 0, \qquad \langle V_{ne}\rangle_T - \langle V_{ne}\rangle_{\mathrm{OSS}} = 0. \tag{5.2}$$

All of the stabilisation is assigned to V_{ee}.

5.2 The virial theorem (scaling proof)

Proposition 5.1. *For an exact bound eigenstate of an atom (one nucleus at the origin), $2\langle T\rangle + \langle V\rangle = 0$, hence $E = -\langle T\rangle = \frac{1}{2}\langle V\rangle$. The same holds for any approximate wavefunction that is variationally optimal with respect to uniform scaling.*

Proof. 1. For a normalised Ψ define $\Psi_\eta(\mathbf{r}_1,\dots,\mathbf{r}_N) = \eta^{3N/2}\Psi(\eta\mathbf{r}_1,\dots,\eta\mathbf{r}_N)$ with $\eta > 0$. Substituting $\mathbf{s}_i = \eta\mathbf{r}_i$ ($\mathrm{d}^{3N}r = \eta^{-3N}\,\mathrm{d}^{3N}s$) shows that Ψ_η is normalised.

2. Kinetic energy: $\nabla_{\mathbf{r}} = \eta\nabla_{\mathbf{s}}$, so $\langle T\rangle_\eta = \eta^2\langle T\rangle$.

3. Potential energy: every Coulomb term ($-Z/r_i$ and $1/r_{ij}$) is homogeneous of degree -1, $1/r = \eta/s$, so $\langle V\rangle_\eta = \eta\langle V\rangle$.

4. $E(\eta) = \eta^2\langle T\rangle + \eta\langle V\rangle$. The exact eigenstate is a stationary point of the energy functional with respect to *all* variations, in particular this one, so $\mathrm{d}E/\,\mathrm{d}\eta\big|_{\eta=1} = 2\langle T\rangle + \langle V\rangle = 0$.

5. Then $E = \langle T\rangle + \langle V\rangle = \langle T\rangle - 2\langle T\rangle = -\langle T\rangle$, and $E = \frac{1}{2}\langle V\rangle$.

6. (Molecules: the nuclear positions also scale. One finds $2\langle T\rangle + \langle V\rangle = -\sum_A \mathbf{R}_A\cdot\nabla_{\mathbf{R}_A}E$, which vanishes at an equilibrium geometry.) □

5.3 Why the frozen-orbital argument cannot be the true mechanism

1. Apply proposition 5.1 to both exact states and subtract:

$$\Delta E \equiv E_T - E_S = -\Delta\langle T\rangle = \tfrac{1}{2}(\Delta\langle V_{ne}\rangle + \Delta\langle V_{ee}\rangle). \tag{5.3}$$

2. In eq. (5.1) $\Delta\langle T\rangle = 0$. By eq. (5.3) this would force $\Delta E = 0$, contradicting $\Delta E = -2K < 0$. The frozen-orbital pair of states violates the virial theorem, so it cannot describe how the *exact* energy difference is partitioned. (This is precisely the objection of Hongo et al.: "This assumption leaves the kinetic energy T unchanged for different spin states, which cannot be correct as each eigenstate must satisfy the virial theorem.")

3. Since $\Delta E < 0$, eq. (5.3) demands $\Delta\langle T\rangle > 0$ (the triplet electrons are more compressed) and $\Delta\langle V\rangle = 2\Delta E < 0$. If, as the review states, $\Delta\langle V_{ee}\rangle > 0$, then necessarily

$$\Delta\langle V_{ne}\rangle = 2\Delta E - \Delta\langle V_{ee}\rangle < 2\Delta E < 0, \qquad |\Delta\langle V_{ne}\rangle| > \Delta\langle V_{ee}\rangle. \tag{5.4}$$

   The triplet is stabilised by a stronger electron–nucleus attraction that over-compensates the larger electron–electron repulsion: the less-screening mechanism.

4. Physical picture: the Fermi hole (section 4) keeps parallel electrons apart, so each electron screens the nucleus less from the other. The electrons contract towards the nucleus, which lowers V_{ne}, raises T (eq. (5.3)), and also raises V_{ee}, because contracted electrons are on average closer together.

5.4 Numerical test: helium $1s2s$, $2\,^3S$ versus $2\,^1S$

Helium is the simplest case: two electrons, and the same configuration $1s2s$ gives a singlet and a triplet. The two-electron Schrödinger equation was solved exactly within a large even-tempered Gaussian basis ($16s7p4d$). The spatial function $\Psi(1,2) = \sum_{pq} C_{pq}\varphi_p(1)\varphi_q(2)$ is restricted to symmetric C (singlet) or antisymmetric C (triplet), following section 1. The exponents were uniformly scaled by the variationally optimal η^2, which by proposition 5.1 enforces the virial theorem.

state	E	exact E (Drake)	$\langle T\rangle$	$\langle V_{ne}\rangle$	$\langle V_{ee}\rangle$
$2\,^3S$	-2.175212	-2.175229	2.175212	-4.618633	0.268208
$2\,^1S$	-2.145865	-2.145974	2.145865	-4.541465	0.249735
$\Delta(T-S)$	-0.029347	-0.029255	$+0.029347$	-0.077168	$+0.018473$

The virial ratio $-\langle V\rangle/\langle T\rangle = 2.000000$ for both states. Check of eq. (5.3): $\frac{1}{2}(-0.077168+0.018473) = -0.029348 \approx \Delta E$. The triplet has the *larger* electron repulsion ($+0.0185\,E_h$), the opposite of Slater's picture. It is stabilised by a $0.077\,E_h$ gain in nuclear attraction, exactly as in eq. (5.4).

Literature values for carbon (^3P vs. ^1D), Hongo et al. 2004, Table I [verified: arXiv cond-mat/0408147].

method	$\Delta\langle V_{ee}\rangle$	$\Delta\langle V_{en}\rangle$	$\Delta\langle T\rangle$
HF	$+0.032$	-0.145	$+0.057$
DMC (linear estimator)	$+0.074$	-0.169	$+0.048$

(Values in E_h, triplet minus singlet, computed from their Table I.) The pattern is the same as for He.

5.5 Same-spin versus opposite-spin correlation

The review (citing Krylov 2001) states that the correlation energy of a same-spin pair is about an order of magnitude smaller than that of an opposite-spin pair. Krylov's introduction says this [verified: ScienceDirect preview of Chem. Phys. Lett. 338, 375]. The reason is the Fermi hole: the same-spin pair is already kept apart at the mean-field level, so there is less left for correlation to do. Tests:

- He: $E_{\mathrm{corr}}(1\,^1S) = -0.04205$ (one $\uparrow\downarrow$ pair) vs. $E_{\mathrm{corr}}(2\,^3S) = -0.00098\,E_h$ (one $\uparrow\uparrow$ pair; exact minus ROHF in the same basis). Ratio 0.023: the statement holds, and strongly.
- Molecules, MP2/cc-pVTZ, frozen core: same-spin/opposite-spin ratio of the total correlation energy is 0.32 (H_2O), 0.35 (N_2), 0.27 (C_2H_4). *Per pair* it is 0.43, 0.43, 0.32.

Caveat / correction

"An order of magnitude" is right for compact two-electron systems such as He, but overstated for valence electrons in molecules at the MP2 level, where same-spin pairs carry roughly one third of the correlation per pair. This is consistent with the empirical SCS-MP2 scaling ($c_{os} = 6/5$, $c_{ss} = 1/3$; Grimme 2003).

Verification

T4 (`t03_t05_hund_virial_h2.py`): energies within 1.7×10^{-5} and $1.1 \times 10^{-4}\,E_h$ of the exact values; virial satisfied; $\Delta V_{ee} > 0$, $\Delta V_{ne} < 0$, $|\Delta V_{ne}| > \Delta V_{ee}$. **PASS**. T15 (`t09b_t15_correlation.py`): numbers above. **PASS**.

Original sources (status)

Boyd, *Nature* **310**, 480 (1984), doi:10.1038/310480a0. Abstract read: Hund's rule is a consequence of Fermi correlation, which leads to less screening of the nucleus in the high-spin state. Hongo et al., *J. Chem. Phys.* **121**, 7144 (2004): full text read (arXiv). Katriel & Pauncz, *Adv. Quantum Chem.* **10**, 143 (**1977**, not 1975 as cited), doi:10.1016/S0065-3276(08)60580-8: not accessed. Hongo et al., *J. Magn. Magn. Mater.* **310**, e560 (2007): not accessed. Slater (1929): cited by the review only via Kollmar & Staemmler (ref. 9).

6 Static correlation: H_2 dissociation and the weak-interaction limit (Figure 2)

Statement in the review

"...dynamic correlation is weak compared to static correlation effects, i.e. correlation between configurations in the multireference wavefunction ... The weaker the interaction between the two nonbonding molecular orbitals, the stronger the static correlation (Figure 2). This is clearly illustrated by ... the H_2 homolytic dissociation curve or the singlet ground state of square cyclobutadiene ..." (p. 442)

6.1 H_2 in a minimal basis: exact two-configuration treatment

Basis: one $1s$ function on each nucleus, χ_A, χ_B, overlap S. By symmetry the MOs are

$$\sigma_g \equiv \varphi_1 = \frac{\chi_A + \chi_B}{\sqrt{2(1+S)}}, \qquad \sigma_u \equiv \varphi_2 = \frac{\chi_A - \chi_B}{\sqrt{2(1-S)}}. \tag{6.1}$$

φ_1 is even and φ_2 odd under inversion, so $h_{12} = (11|12) = (22|21) = 0$ and eq. (3.5) splits. The OSS ($^1\Sigma_u^+$) is alone, and the two closed shells ($^1\Sigma_g^+$ symmetry) mix:

$$\mathbf{H}(^1\Sigma_g^+) = \begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{12} & 2h_{22} + J_{22} \end{pmatrix}, \qquad E_{\mathrm{CI}} = \tfrac{1}{2}\Big[E_1 + E_2 - \sqrt{(E_2 - E_1)^2 + 4K_{12}^2}\Big], \tag{6.2}$$

with $E_1 = 2h_{11} + J_{11}$ (the RHF energy), $E_2 = 2h_{22} + J_{22}$, and $E(^3\Sigma_u^+) = h_{11} + h_{22} + J_{12} - K_{12}$, $E(^1\Sigma_u^+) = h_{11} + h_{22} + J_{12} + K_{12}$ (nuclear repulsion $1/R$ added to all).

6.2 The dissociation limit, step by step

Let $R \to \infty$, so $S \to 0$ and all two-centre overlap densities $\chi_A\chi_B \to 0$. Define the on-site repulsion $U = (AA|AA)$, the inter-site repulsion $V = (AA|BB) \to 1/R$, and the H-atom energy E_H.

1. Orbital products: $\varphi_1^2 = \frac{1}{2}(\chi_A^2 + \chi_B^2 + 2\chi_A\chi_B) \to \frac{1}{2}(\chi_A^2 + \chi_B^2)$, $\varphi_2^2 \to \frac{1}{2}(\chi_A^2 + \chi_B^2)$, $\varphi_1\varphi_2 \to \frac{1}{2}(\chi_A^2 - \chi_B^2)$.
2. Two-electron integrals (each product contributes $\frac{1}{2}\cdot\frac{1}{2}$):
$$J_{11} = J_{22} = J_{12} \to \tfrac{1}{4}\big[(AA|AA) + (AA|BB) + (BB|AA) + (BB|BB)\big] = \tfrac{1}{2}(U+V),$$
$$K_{12} = (12|12) \to \tfrac{1}{4}\big[(AA|AA) - (AA|BB) - (BB|AA) + (BB|BB)\big] = \tfrac{1}{2}(U-V).$$
3. One-electron integrals: $h_{11} = h_{22} \to h_{AA} = E_H - \frac{1}{R}$ (an electron on A also feels nucleus B as a point charge at distance R).
4. RHF: $E_{\mathrm{RHF}} = 2h_{11} + J_{11} + \frac{1}{R} = 2E_H - \frac{2}{R} + \frac{1}{2}(U+V) + \frac{1}{R} \to 2E_H + \frac{U}{2} - \frac{1}{2R}$. *The RHF error at dissociation is* $U/2$, which does not vanish.
5. Triplet: $E_T = 2h_{11} + J_{12} - K_{12} + \frac{1}{R} = 2E_H - \frac{2}{R} + V + \frac{1}{R} \to 2E_H$. Correct.
6. CI: the diagonal elements are now equal ($E_1 = E_2$), so by eq. (6.2) $E_{\mathrm{CI}} = E_1 - K_{12} = 2E_H + \frac{U}{2} - \frac{1}{2R} - \frac{1}{2}(U-V) \to 2E_H$. Correct. The eigenvector has $c_1 = -c_2 = \frac{1}{\sqrt{2}}$: *two configurations with equal weight*. This is maximal static correlation.
7. What that eigenvector is: $\varphi_1(1)\varphi_1(2) - \varphi_2(1)\varphi_2(2) \to \frac{1}{2}[(\chi_A+\chi_B)(\chi_A+\chi_B) - (\chi_A-\chi_B)(\chi_A-\chi_B)] = \chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2)$, the purely covalent Heitler–London function. By contrast $\varphi_1(1)\varphi_1(2)$ alone is $\frac{1}{2}$[covalent + ionic], which is the origin of the $U/2$ error in step 4.
8. OSS: $E(^1\Sigma_u^+) = E_T + 2K_{12} \to 2E_H + U - V$. It is the antisymmetric *ionic* combination.

Verification

T5 (`t03_t05_hund_virial_h2.py`), STO-3G, PySCF vs. the closed forms at $R = 1.4, 3, 6, 20$ bohr. RHF, 2×2 CI = FCI and ROHF triplet agree with eq. (6.2) to $4\times10^{-16}\,E_h$ (max. deviation, tight SCF). At $R = 20$: $E_{\mathrm{CI}} = E_T = -0.933164 = 2E_H$; $E_{\mathrm{RHF}} - 2E_H = 0.3623 = K_{12}$; $J_{11} - K_{12} = 0.050 = 1/R$ (so $U = J_{11} + K_{12} = 0.7746$); $E(^1\Sigma_u^+) - 2E_H = 0.7246 = U - 1/R$. Every limit in steps 4–8 is reproduced. **PASS**.

6.3 General weak-interaction limit (Figure 2b, twisted ethylene)

Take the $2e/2o$ model with orbitals of different symmetry ($h_{ab} = (aa|ab) = (bb|ba) = 0$), orbital energy gap Δ ($h_a = -\Delta/2$, $h_b = +\Delta/2$), and for simplicity $J_{aa} = J_{bb} \equiv J_d$, $J_{ab} \equiv J_x$. This describes the π/π^* pair of ethylene, where Δ is the π–π^* splitting, which goes to 0 at a 90° twist.

1. Closed-shell block: $\begin{pmatrix} J_d - \Delta & K \\ K & J_d + \Delta \end{pmatrix}$, eigenvalues $J_d \pm \sqrt{\Delta^2 + K^2}$.
2. Ground singlet: $E_S = J_d - \sqrt{\Delta^2 + K^2}$, with coefficient ratio $\dfrac{c_2}{c_1} = \dfrac{E_S - (J_d - \Delta)}{K} = \dfrac{\Delta - \sqrt{\Delta^2 + K^2}}{K}$.
3. Limits: $\Delta \gg K$ gives $c_2/c_1 \to 0$ (one configuration, closed shell, no static correlation); $\Delta \to 0$ gives $c_2/c_1 \to -1$ (two configurations of equal weight, a pure diradical).
4. Gap to the triplet ($E_T = J_x - K$): $E_S - E_T = (J_d - J_x) + K - \sqrt{\Delta^2 + K^2}$.

Result

Static correlation (the weight of the second configuration) is controlled by Δ/K. The smaller the splitting of the two frontier orbitals ("weaker interaction"), the more multiconfigurational the singlet becomes, and the closer it comes to the triplet. This is the content of Figure 2(a,b).

Verification

T6 (`t06_t09_models.py`): eigenvalue, ratio and both limits verified symbolically. **PASS**. Balková & Bartlett, *J. Chem. Phys.* **101**, 8972 (1994), doi:10.1063/1.468057 [abstract]: MR-CC places the square-cyclobutadiene singlet 6.9 kcal/mol below the triplet.

Figure 2(c) (spin crossover in a transition-metal complex) is qualitative in the review and contains no mathematics to derive.

7 Localised orbitals, ionic configurations and kinetic exchange

Statement in the review

"The kinetic exchange picture based on the Hubbard model is a related, yet also simplistic (and not satisfying virial theorem) spin alignment rule. It attributes stability of a singlet state in the case of orthogonal atomic orbitals (AOs) to the fact that perturbation yielding ionic configuration is allowed only from this state, and not from the triplet." (p. 442, ref. 19 Yamanaka et al. 2005). Also: "the importance of resonance between open-shell singlet and closed-shell zwitterionic configurations" (p. 444, Figure 6).

7.1 Two-site model in a localised basis

Two orthonormal localised orbitals l, r (one per radical centre). Parameters:

$$h_{ll} = h_{rr} = 0, \quad h_{lr} = -t, \quad U = (ll|ll) = (rr|rr), \quad V = (ll|rr), \tag{7.1}$$

$$k = (lr|lr)\ (\geq 0), \quad (ll|lr) = (rr|rl) = 0. \tag{7.2}$$

($V = k = 0$ is the Hubbard dimer; $V, k \neq 0$ the "extended" model.)

Configurations. Section 2 with $a \to l$, $b \to r$: covalent singlet $\Phi_{\text{cov}} = \frac{1}{\sqrt{2}}[l(1)r(2) + r(1)l(2)]\Theta_{0,0}$; ionic $l(1)l(2)\Theta_{0,0}$ and $r(1)r(2)\Theta_{0,0}$; triplet $\frac{1}{\sqrt{2}}[l(1)r(2) - r(1)l(2)]\Theta_{1,M}$.

Step 1: the triplet cannot mix with ionic configurations. An ionic configuration has both electrons in the same spatial orbital, so its spatial part $l(1)l(2)$ is symmetric. By section 1 it must carry the singlet spin function. Since $\hat{H}$ is spin-free, $\langle \text{ionic}|\hat{H}|\text{triplet}\rangle = 0$ (orthogonal spin parts). This is the precise meaning of "perturbation yielding ionic configuration is allowed only from" the singlet.

Step 2: matrix elements. Insert the parameters into eqs. (3.3) and (3.5):

$$E_T = V - k, \qquad \mathbf{H}_S = \begin{pmatrix} U & k & -\sqrt{2}t \\ k & U & -\sqrt{2}t \\ -\sqrt{2}t & -\sqrt{2}t & V+k \end{pmatrix} \quad (\text{basis } ll,\ rr,\ \text{cov}). \tag{7.3}$$

Step 3: symmetry-adapt the ionic pair. $\Phi_{\text{ion}\pm} = \frac{1}{\sqrt{2}}(ll \pm rr)$ has energy $U \pm k$. Its coupling to cov is $\frac{1}{\sqrt{2}}(-\sqrt{2}t \mp \sqrt{2}t)$, i.e. $-2t$ for ion+ and 0 for ion−. The ground singlet comes from the 2×2 block $\begin{pmatrix} V+k & -2t \\ -2t & U+k \end{pmatrix}$:

$$E_S = \tfrac{1}{2}\Big[U + V + 2k - \sqrt{(U-V)^2 + 16t^2}\Big]. \tag{7.4}$$

Step 4: singlet–triplet gap and its expansion.

$$E_S - E_T = \tfrac{1}{2}(U-V) + 2k - \tfrac{1}{2}\sqrt{(U-V)^2+16t^2} \;=\; 2k - \frac{4t^2}{U-V} + O\!\left(\frac{t^4}{(U-V)^3}\right), \tag{7.5}$$

using $\sqrt{x^2+16t^2} = x + 8t^2/x + O(t^4/x^3)$ for $x = U - V \gg t$.

Result

Two competing terms:

- $+2k$, *potential (direct) exchange*. It favours the triplet (Hund-like, section 3).
- $-4t^2/(U-V)$, *kinetic exchange*. The covalent singlet lowers its energy by virtual hopping into the ionic configuration (second-order perturbation: $|-2t|^2/[(V+k)-(U+k)]$). The triplet cannot do this (step 1), so it favours the singlet.

Mapped onto $\hat{H}_{\text{spin}} = -2J\,\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ (for which $E_S - E_T = 2J$): $J \simeq k - 2t^2/(U-V)$. For the pure Hubbard dimer ($V = k = 0$), $E_S = \frac{1}{2}(U - \sqrt{U^2+16t^2}) \simeq -4t^2/U$ and $E_T = 0$, i.e. antiferromagnetic coupling $J_{\text{AF}} = 4t^2/U$ in the convention $\hat{H} = J_{\text{AF}}\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$.

Ionic resonance in charged polyradicals (Figure 6). Pyridinium-bridged diradicals (V in Figure 6) are the case where the closed-shell zwitterionic ("ionic") resonance structures are low in energy: effectively $U - V$ is small. By eq. (7.5) the kinetic term $-4t^2/(U-V)$ then grows and can overcome $2k$, reversing the topology-predicted triplet. This is the review's point that this contribution "exceeds the exchange and Coulomb terms". (A qualitative mapping; the review gives no numbers.)

On "not satisfying the virial theorem". The Hubbard model has no separate $\hat{T}$ and $\hat{V}$. Its energy is not a stationary point with respect to coordinate scaling, so proposition 5.1 cannot be imposed. Like the frozen-orbital model of section 5, it cannot say which physical energy component pays for the spin preference.

Relation to delocalised orbitals. With $a, b = (l \pm r)/\sqrt{2}$ one finds $a(1)a(2) - b(1)b(2) = l(1)r(2) + r(1)l(2)$ (as in section 6, step 7). The "two-configuration" singlet of the delocalised picture is the covalent singlet of the localised picture. Static correlation in one basis is the absence of ionic character in the other.

Verification

T7 (`t06_t09_models.py`): eqs. (7.4) and (7.5) verified symbolically, including the series coefficient $-4t^2/U$; and numerically against PySCF full CI with the same integrals ($t = 1$, $U = 6$, $V = 1.5$, $k = 0.2$), and against an independent fermionic exact-diagonalisation code. **PASS**.

Original sources (status)

Yamanaka et al., *Int. J. Quantum Chem.* **105**, 687 (2005): not accessed. The derivation above is the standard Anderson kinetic-exchange argument, reconstructed independently and tested.

8 Non-bonding MOs, disjointness and the sign of K (Borden–Davidson)

Statement in the review

"Borden and Davidson proposed to classify the nonbonding molecular orbitals (NBMOs) φ_a and φ_b as either disjoint or nondisjoint. If the two orbitals do not have common atoms and the probability of two electrons occupying the same space is nil independent of their spins, they are termed disjoint. Under such circumstances, the energy of an open-shell singlet can become comparable to or even lower than that of a triplet." (p. 443) Examples: CBD, TME (disjoint, singlet); MX, TriMB (nondisjoint, high spin) (p. 443–444, Figure 3).

8.1 Hückel NBMOs: the zero-sum rule

Hückel Hamiltonian for a conjugated π system with adjacency matrix $\mathbf{A}$ ($A_{ij} = 1$ if atoms i, j are bonded): $\mathbf{H} = \alpha\mathbf{1} + \beta\mathbf{A}$. Writing $E = \alpha + x\beta$, the secular equation is $\mathbf{Ac} = x\mathbf{c}$.

1. An NBMO has $E = \alpha$, i.e. $x = 0$, so $\mathbf{Ac} = \mathbf{0}$.
2. Row i of this equation reads $\sum_{j\in\mathcal{N}(i)} c_j = 0$. **Zero-sum rule:** for every atom, the NBMO coefficients of its neighbours sum to zero.

8.2 Alternant hydrocarbons: pairing theorem and NBMO count

If the atoms split into "starred" ($\mathcal{A}$, n_A atoms) and "unstarred" ($\mathcal{B}$, n_B atoms) sets with bonds only between the sets (a bipartite graph), then in that ordering $\mathbf{A} = \begin{pmatrix} \mathbf{0} & \mathbf{B} \\ \mathbf{B}^{\mathsf{T}} & \mathbf{0} \end{pmatrix}$, with $\mathbf{B}$ of size $n_A \times n_B$.

1. *Pairing theorem.* If $\mathbf{A}\binom{\mathbf{u}}{\mathbf{v}} = x\binom{\mathbf{u}}{\mathbf{v}}$, i.e. $\mathbf{Bv} = x\mathbf{u}$ and $\mathbf{B}^{\mathsf{T}}\mathbf{u} = x\mathbf{v}$, then $\mathbf{A}\binom{\mathbf{u}}{-\mathbf{v}} = \binom{-\mathbf{Bv}}{\mathbf{B}^{\mathsf{T}}\mathbf{u}} = \binom{-x\mathbf{u}}{x\mathbf{v}} = -x\binom{\mathbf{u}}{-\mathbf{v}}$. Levels come in $\pm x$ pairs, with coefficients equal in magnitude and the sign flipped on one set.
2. *Lower bound from the sublattice imbalance.* $\operatorname{rank}\mathbf{A} = 2\operatorname{rank}\mathbf{B} \le 2\min(n_A, n_B)$. Hence the number of NBMOs (the nullity) is $N - \operatorname{rank}\mathbf{A} \ge N - 2\min(n_A, n_B) = |n_A - n_B|$.
3. *Longuet-Higgins bound.* $\operatorname{rank}\mathbf{B}$ cannot exceed the largest number of non-attacking nonzero entries of $\mathbf{B}$. That is the size T of a maximum matching, which equals the number of double bonds in the best Kekulé structure. So $\#\text{NBMO} \ge N - 2T$ $(\ge |n_A - n_B|)$. **This is a lower bound, not an equality**: square cyclobutadiene has $T = 2$, so $N - 2T = 0$, yet it has two NBMOs (its $\pm x$ pairs include an accidental $x = 0$ pair).

8.3 Which NBMO pairs are disjoint? Explicit constructions

TME (atoms 1,2 central; 3,4 on C1; 5,6 on C2). Zero-sum at atoms 3 and 4 (single neighbour 1) gives $c_1 = 0$. At atoms 5 and 6 it gives $c_2 = 0$. At atom 1: $c_2 + c_3 + c_4 = 0$, so $c_4 = -c_3$. At atom 2: $c_5 = -c_6$. The NBMO space is spanned by

$$\varphi_a = \tfrac{1}{\sqrt{2}}(\chi_3 - \chi_4), \qquad \varphi_b = \tfrac{1}{\sqrt{2}}(\chi_5 - \chi_6), \tag{8.1}$$

which share no atom: **disjoint** (two allyl-type NBMOs on separate halves).

Square CBD (ring 1-2-3-4). Zero-sum at atom 1: $c_2 + c_4 = 0$; at atom 2: $c_1 + c_3 = 0$. So $\varphi_a = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3)$ and $\varphi_b = \frac{1}{\sqrt{2}}(\chi_2 - \chi_4)$: **disjoint**.

TMM (centre 0, terminals 1,2,3). $c_0 = 0$ (zero-sum at a terminal), and $c_1 + c_2 + c_3 = 0$ (zero-sum at the centre). Every nonzero vector in this plane has at least two nonzero entries (one nonzero entry cannot sum to zero). Two such vectors with disjoint supports would need at least $2 + 2 = 4$ terminal atoms, but there are only 3. So no basis of the NBMO space is disjoint: **nondisjoint**.

8.4 Why disjointness kills K_{ab}: zero differential overlap

Expand $\varphi_a = \sum_\mu a_\mu \chi_\mu$, $\varphi_b = \sum_\nu b_\nu \chi_\nu$ in atomic p_π orbitals:

1. $K_{ab} = (ab|ab) = \sum_{\mu\nu\lambda\sigma} a_\mu b_\nu a_\lambda b_\sigma (\mu\nu|\lambda\sigma)$.
2. ZDO approximation: $(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}\gamma_{\mu\lambda}$, with $\gamma_{\mu\lambda}$ the Coulomb repulsion between charges on atoms μ and λ.
3. Then $K_{ab} = \sum_{\mu\lambda}(a_\mu b_\mu)(a_\lambda b_\lambda)\gamma_{\mu\lambda}$.
4. *Disjoint* $\Rightarrow a_\mu b_\mu = 0$ for every atom $\Rightarrow K_{ab} = 0$ exactly (within ZDO). By eq. (3.4), $E_{\mathrm{OSS}} - E_T = 2K_{ab} = 0$: the first-order Hund preference vanishes, and higher-order effects (spin polarisation, section 9) decide the ground state.
5. *Nondisjoint* $\Rightarrow$ some $a_\mu b_\mu \neq 0$. Since γ is a positive-definite Coulomb matrix (section 4), $K_{ab} > 0$ and the triplet is favoured at first order.
6. In the Hubbard limit ($\gamma_{\mu\lambda} = U\delta_{\mu\lambda}$): $K_{ab} = U\sum_\mu a_\mu^2 b_\mu^2$.

Verification

T8 (`t06_t09_models.py`): Hückel spectra of CBD, TMM, TME, MX, TriMB, 1,2,4,5-TetraMB and *p*-xylylene. Pairing theorem, zero-sum rule and #NBMO $\geq N - 2T \geq |n_A - n_B|$ hold in every case; CBD shows the strict inequality. Minimising $\sum_\mu a_\mu^2 b_\mu^2$ over all rotations of the degenerate NBMO pair gives ≈ 0 for CBD, TME and TetraMB (disjoint), and 1/6 (TMM) and 1/16 (MX) (nondisjoint). T9b (`t09b_t15_correlation.py`): in the Hubbard model at small U the triplet–singlet gap of TMM and MX is linear in U (fitted exponent 0.97, 0.96). For TMM -0.01643 at $U = 0.05t$ matches $-2U \cdot \frac{1}{6} = -0.0167$, and MX matches $-2U \cdot \frac{1}{16}$. For disjoint CBD and TME the gap is $\propto U^{1.97}, U^{1.95}$, i.e. zero at first order, as derived. **PASS**.

Original sources (status)

Borden & Davidson, *J. Am. Chem. Soc.* **99**, 4587 (1977), doi:10.1021/ja00456a010: not accessed; definition as quoted in the review. Longuet-Higgins, *J. Chem. Phys.* **18**, 265 (1950): the matching bound as cited in arXiv:1906.08544. The proofs above are self-contained.

9 Dynamic spin polarisation, topology rules, Ovchinnikov and Lieb

Statement in the review

"...instantaneous correlation effects, in particular the dynamic spin polarization (Scheme 1). A damped spin wave so formed generates ferromagnetic coupling between the spins separated by an odd number of sites, and antiferromagnetic between those separated by an even number of sites, thus yielding the topology rules of spin coupling. Within the spin-Hamiltonian VB theory, Ovchinnikov's qualitative rule dictates that the most spin-alternant determinant is expected to have the lowest energy and the highest contribution." (p. 443)

9.1 Spin polarisation is a correlation effect

1. In Hückel (independent-electron) theory the unpaired electron of an odd alternant radical sits in the NBMO. By section 8 the NBMO vanishes on the smaller (unstarred) set. The spin density on unstarred atoms is therefore *exactly zero*.
2. Add on-site repulsion $U\sum_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$ (Hubbard model). An $\uparrow$ electron in the NBMO repels $\downarrow$ density on the starred atoms more than $\uparrow$ density. Paired electrons therefore rearrange so that $\downarrow$ density accumulates on the neighbouring (unstarred) atoms: a negative spin density appears between positive ones. This is Scheme 1 of the review.

Verification

T9: pentadienyl radical (5-site chain, 5 electrons, $S_z = \frac{1}{2}$), exact diagonalisation. $U = 0$: $\rho_s = (0.333, 0, 0.333, 0, 0.333)$. $U = 3t$: $\rho_s = (0.451, -0.182, 0.462, -0.182, 0.451)$, sum $= 1$. The alternation appears only with $U \neq 0$. **PASS**.

9.2 Odd/even rule from the bipartite structure

1. From section 7, for $U \gg t$ each bond carries an antiferromagnetic coupling $J_{\mathrm{AF}} = 4t^2/U$. At half filling the low-energy physics is the Heisenberg model $\hat{H} = J_{\mathrm{AF}}\sum_{\langle ij\rangle}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$.
2. On a bipartite graph every bond joins $\mathcal{A}$ to $\mathcal{B}$. The energy is lowest when neighbours are antiparallel: spins on $\mathcal{A}$ point one way and spins on $\mathcal{B}$ the other (the Néel pattern).
3. Two sites are in the same set iff the path between them has an even number of bonds, i.e. an *odd* number of intervening atoms. Hence: same set $\Rightarrow$ parallel (ferromagnetic); different sets $\Rightarrow$ antiparallel.
4. Example: in *m*-xylylene the radical CH_2 carbons are joined via 3 intervening ring atoms (odd), so they couple ferromagnetically (triplet). In *p*-xylylene there are 4 (even), so the coupling is antiferromagnetic: a singlet (actually Kekulé, closed shell). This is the review's rule.

9.3 Ovchinnikov's rule and Lieb's theorem

1. Counting the Néel configuration: n_A spins up and n_B spins down gives $S = \frac{1}{2}|n_A - n_B|$. This is **Ovchinnikov's rule** for the ground-state spin of an alternant hydrocarbon, $S = \frac{1}{2}|n^* - n^\circ|$.
2. The rule was conjectured from VB/Heisenberg arguments. Lieb (1989) proved it rigorously for the repulsive Hubbard model at half filling on any bipartite graph: *the ground state is unique and has* $S = \frac{1}{2}||\mathcal{B}| - |\mathcal{A}||$, for every $U > 0$ [verified: *Phys. Rev. Lett.* **62**, 1201 (1989)].
3. Consequences: CBD and TME ($n_A = n_B$) have singlet ground states; TMM (1/3) and MX (3/5) are triplets; TriMB (3/6) is a quartet; 1,2,4,5-tetramethylenebenzene (5/5) is a singlet. These are the review's Figure 3 assignments.

Verification

T9: Hubbard model ($t = 1$, $U = 3$), exact diagonalisation in every S_z sector. The ground-state S equals $\frac{1}{2}|n_A - n_B|$ for all 7 graphs: CBD 0, TMM 1, TME 0, MX 1, TriMB $\frac{3}{2}$, TetraMB 0, *p*-xylylene 0. **PASS**.

9.4 Disjoint diradicals: the singlet is selected by spin polarisation (Kollmar–Staemmler)

For disjoint NBMOs (CBD, TME) the first-order gap $2K_{ab}$ vanishes (section 8). The degeneracy is lifted only at second order, through the spin-polarised configurations above. In D_{4h} CBD, "the bonding π-electrons can partially localize on the same pair of atoms as the same-spin unpaired

electrons; however, in the triplet state such advantageous spin polarization is not possible" (review, p. 443). The numerical signature is a gap $\propto U^2$, with the singlet lower.

Verification

T9b: gap $E_T - E_S > 0$ (singlet lower), scaling as $U^{1.97}$ (CBD) and $U^{1.95}$ (TME) for $U \to 0$; cf. linear scaling with the triplet lower for the nondisjoint TMM and MX. **PASS**.

Original sources (status)

Kollmar & Staemmler, *Theor. Chim. Acta* **48**, 223 (1978), doi:10.1007/BF00549021 (not accessed). Ovchinnikov, *Theor. Chim. Acta* **47**, 297 (1978), doi:10.1007/BF00549259: $S = (N_A - N_B)/2$ as quoted in arXiv:1906.08544. Lieb 1989: statement verified.

Caveat / correction

Ovchinnikov's rule and Lieb's theorem apply to *alternant* (bipartite) π systems described by Hubbard/Heisenberg-type models. The review's own counterexamples (pyridinium analogue V, Figure 6; σ–π diradicals such as the didehydrotoluenes) lie outside these assumptions. This is consistent with its warning that such rules "inevitably" have "limited scope".

10 Orbital energies: Koopmans, Janak, and the singlet–triplet gap as a HOMO difference

Statement in the review

"An alternative theoretical interpretation of the Hund's multiplicity rule has been proposed on the basis of Janak theorem (or extended Koopmans' theorem) in excited state density functional theory (DFT) for multiplets: at the Hartree–Fock level, the singlet–triplet gap (STG) is equal to the difference between the energies of the triplet's and open-shell singlet's HOMOs. This explanation echoes Pearson's maximum hardness principle, but lacks dynamic electron correlation." (p. 442–443, ref. 20 Liu & Langenaeker 2003)

10.1 Koopmans' theorem

For a single determinant of spin orbitals $\{\chi_i\}$ write $[ij|kl]$ for spin-orbital integrals. Then

$$E_N = \sum_i \langle i|\hat{h}|i\rangle + \tfrac{1}{2}\sum_{i,j}\big([ii|jj] - [ij|ji]\big). \tag{10.1}$$

1. Remove spin orbital k *without changing the others* (frozen orbitals). Every term containing k disappears: $E_N - E^{(k)}_{N-1} = \langle k|\hat{h}|k\rangle + \frac{1}{2}\sum_j([kk|jj] - [kj|jk]) + \frac{1}{2}\sum_i([ii|kk] - [ik|ki])$. The $i = j = k$ term, counted in both sums, is $[kk|kk] - [kk|kk] = 0$.
2. The two sums are equal by the symmetry of the integrals, so $E_N - E^{(k)}_{N-1} = \langle k|\hat{h}|k\rangle + \sum_j([kk|jj] - [kj|jk])$.
3. The right-hand side is the diagonal Fock element, i.e. the canonical orbital energy ε_k. Hence

$$\mathrm{IP}_k \equiv E^{(k)}_{N-1} - E_N = -\varepsilon_k \qquad \text{(frozen orbitals)}. \tag{10.2}$$

Relaxation of the remaining orbitals lowers E_{N-1}. Correlation acts in the other direction, so eq. (10.2) is an approximation with partially cancelling errors.

10.2 Janak's theorem

In Kohn–Sham DFT with fractional occupations n_i: $E = \sum_i n_i \langle\psi_i| -\frac{1}{2}\nabla^2|\psi_i\rangle + \int v\rho + E_H[\rho] + E_{xc}[\rho]$, with $\rho = \sum_i n_i |\psi_i|^2$.

1. Differentiate with respect to n_i. The explicit dependence (through the prefactor n_i and through ρ) gives $\langle\psi_i| - \frac{1}{2}\nabla^2|\psi_i\rangle + \int (v + v_H + v_{xc})|\psi_i|^2 = \langle\psi_i|\hat{h}_{KS}|\psi_i\rangle = \varepsilon_i$.
2. The implicit dependence through $\partial\psi_j/\partial n_i$ gives

$$\sum_j n_j \left[\langle \partial_{n_i}\psi_j|\hat{h}_{KS}|\psi_j\rangle + \text{c.c.}\right] = \sum_j n_j \varepsilon_j \, \partial_{n_i}\langle\psi_j|\psi_j\rangle = 0,$$

   because each ψ_j is an eigenfunction of $\hat{h}_{KS}$ and stays normalised.
3. Hence $\partial E/\partial n_i = \varepsilon_i$, for any E_{xc} [verified: Janak, *Phys. Rev. B* **18**, 7165 (1978), abstract]. Integrating, $E(n_i = 1) - E(n_i = 0) = \int_0^1 \varepsilon_i(n)\,\mathrm{d}n \approx \varepsilon_i(\frac{1}{2})$ (Slater's transition state).

10.3 The singlet–triplet gap as a HOMO-energy difference (frozen-orbital derivation)

Use the $2e/2o$ states of section 3 and define, for each state $X \in \{T, \text{OSS}\}$, the "HOMO energy" as minus the energy needed to remove the electron from φ_b, leaving φ_a frozen (the Koopmans/ΔSCF definition, eq. (10.2)). The ion has energy $E_{\text{ion}} = h_a$ in both cases.

1. $\varepsilon_b^T = E_T - E_{\text{ion}} = h_b + J_{ab} - K_{ab}$.
2. $\varepsilon_b^{\text{OSS}} = E_{\text{OSS}} - E_{\text{ion}} = h_b + J_{ab} + K_{ab}$.
3. Subtract:

$$\boxed{E_{\text{OSS}} - E_T = \varepsilon^{\text{OSS}}_{\text{HOMO}} - \varepsilon^{T}_{\text{HOMO}} = 2K_{ab}.} \tag{10.3}$$

Result

Within frozen orbitals the singlet–triplet gap *is* the difference of the HOMO energies. The triplet's HOMO lies lower by $2K_{ab}$: it is more strongly bound, i.e. "harder". That is the sense in which the argument "echoes" the maximum-hardness principle. The sign convention is now fixed: STG $\equiv E_S - E_T = \varepsilon^S_{\text{HOMO}} - \varepsilon^T_{\text{HOMO}}$. Like Slater's argument, eq. (10.3) has no dynamic correlation and no orbital relaxation, so it inherits the limitations discussed in section 5.

Verification

T10 (`t10_t12_t13_symbolic.py`): eq. (10.3) symbolically. T2: the Koopmans identity $\varepsilon_k = E_N - E^{(k)}_{N-1}$ checked numerically for random integrals in a 3-electron case. **PASS**.

Original sources (status)

Liu & Langenaeker, *Theor. Chem. Acc.* **110**, 338 (2003), doi:10.1007/s00214-003-0487-6: not accessed (search summaries only state $\Delta E_{ST} = \Delta\varepsilon_{\text{HOMO}}$). The maximum-hardness connection is the review's wording and was not verified against the original.

11 Quasi-closed-shell (non-aufbau) radicals

Statement in the review

"In molecular systems with unpaired electrons, the violation of the aufbau principle in electron configuration is reflected in the conversion of the SOMO and HOMO orbital energies, yielding a so-called quasi-closed-shell state (Figure 10). Its main fingerprint is the electron attachment or removal pattern: upon ionization an electron is removed from the higher energy doubly occupied MO, leaving another unpaired electron behind, while upon addition new electron enters the former LUMO; essentially, SOMO does not participate in these processes." (p. 448–449) "... a rigorous support for the non-aufbau occupation can be obtained a posteriori from the ionization potentials and electron affinities ... as well as from the determination of the spin state ... of the corresponding open-shell oxidation/reduction products." (p. 449)

11.1 Frozen-orbital model of the redox fingerprint

Three relevant orbitals: SOMO s, the highest doubly occupied orbital h, and the LUMO l. Ground configuration (core) s^1h^2 (a doublet).

1. UHF orbital energies, from eq. (10.2) applied to each spin orbital (Slater–Condon, section 10):

$$\varepsilon_h^\alpha = h_h + J_{hh} + J_{hs} - K_{hs}, \qquad \varepsilon_h^\beta = h_h + J_{hh} + J_{hs}, \tag{11.1}$$

$$\varepsilon_s^\alpha = h_s + 2J_{hs} - K_{hs}, \qquad \varepsilon_s^\beta(\text{virtual}) = h_s + J_{ss} + 2J_{hs} - K_{hs}. \tag{11.2}$$

   (Interactions with the core are absorbed into h_h, h_s.)

2. **Spin polarisation of the donor HOMO (Scheme 3).** From eq. (11.1), $\varepsilon_h^\beta - \varepsilon_h^\alpha = K_{hs} \geq 0$: the α electron of h (parallel to the unpaired spin) is stabilised by exchange with the SOMO electron, while the β electron is not. The donor's α and β HOMOs split. That is the content of Scheme 3.

3. **Condition for SOMO–HOMO conversion** (within the α manifold): $\varepsilon_s^\alpha < \varepsilon_h^\alpha \iff h_s + 2J_{hs} - K_{hs} < h_h + J_{hh} + J_{hs} - K_{hs} \iff h_s + J_{hs} < h_h + J_{hh}$. In words: the SOMO's one-electron energy plus its repulsion with *one* h electron lies below h's one-electron energy plus its *self*-repulsion. A stable, low-lying radical orbital and a separate, electron-rich (high h_h, e.g. anionic) fragment favour this.

4. **Oxidation.** Koopmans: $\mathrm{IP}(h) = -\varepsilon_h < \mathrm{IP}(s) = -\varepsilon_s$, so the electron leaves h. The product (core) s^1h^1 is a diradical cation (or diradical, if the parent was an anion). Its triplet and open-shell singlet are split by $E_{\mathrm{OSS}} - E_T = 2K_{sh}$ (eq. (3.4) with $a, b \to s, h$). With $K_{sh} > 0$ the triplet is lower: the observed "triplet cation diradicals with nondegenerate SOMOs".

5. **Reduction.** The added electron can enter the β SOMO, at cost ε_s^β of eq. (11.2), giving a closed-shell anion; or the LUMO, at ε_l, giving the diradical $s^1h^2l^1$. Koopmans picks the lower: the diradical forms iff $\varepsilon_l < \varepsilon_s^\beta = h_s + J_{ss} + 2J_{hs} - K_{hs}$. The large on-site repulsion J_{ss} makes this possible. Note that this is a *separate* condition, not implied by step 3; the review's Figure 10 depicts the case where it holds, and Figure 17 gives examples.

6. **Protonation switch.** Protonating the anionic fragment strongly lowers h_h (Coulomb attraction of H^+). Once $h_h + J_{hh} < h_s + J_{hs}$ the aufbau order is restored, and oxidation removes the SOMO electron, giving a closed-shell cation. This is the pH-switchable conversion of Figure 16.

Caveat / correction

Steps 1–5 use frozen orbitals and canonical orbital energies. By section 12 orbital energies are convention-dependent, and by section 10 relaxation shifts them. As the review says, the *observable* criterion is energetic: compare the two possible oxidised states directly, $E(\text{diradical}, T)$ vs. $E(\text{closed shell})$ (ΔSCF).

11.2 Numerical test: a distonic radical anion and its conjugate acid

Model: the aminoxyl radical $^{\bullet}ON(Me)CH_2CH_2COO^-$, with a carboxylate that is not conjugated to the radical, and its protonated form $^{\bullet}ON(Me)CH_2CH_2COOH$. UB3LYP/6-31+G*; radical geometries optimised (geomeTRIC). Vertical oxidation at the radical geometry to (i) the triplet (one electron removed from below the SOMO, the diradical) and (ii) the closed-shell singlet (SOMO electron removed).

radical	α-SOMO position	IE→triplet	IE→closed shell	Δ(T−CS)
acid (COOH)	is the α-HOMO	9.489 eV	8.179 eV	+1.31 eV
anion (COO^-)	3 levels below the α-HOMO	4.008 eV	3.946 eV	+0.06 eV

1. *Orbital level: confirmed.* In the anion the α-SOMO (−2.40 eV) lies below three doubly occupied levels (character not analysed) (α-HOMO −1.62 eV). In the acid the SOMO is the HOMO. This is the pH-switchable SOMO–HOMO conversion of step 6.

2. *Energetic level: shifted, but no crossover.* Deprotonation moves the triplet–closed-shell preference by 1.25 eV towards the diradical, but at this level the closed-shell product of the anion remains lower, by 0.06 eV. For this short-linker model, the orbital inversion alone does not guarantee that oxidation yields the diradical. This is exactly why the review insists on the energetic, observable criterion (caveat above). T11c below shows that this verdict depends on the functional.

Functional and separation dependence (T11c). The same vertical test was repeated on UB3LYP/6-31G* geometries with B3LYP and with the range-separated CAM-B3LYP, which has less delocalisation error. The larger TEMPO-4-carboxylate was added to vary the radical–anion separation.

radical	functional	IE→T (eV)	IE→CS (eV)	Δ(T−CS) (eV)
short anion	B3LYP	4.012	3.939	+0.072
short anion	CAM-B3LYP	4.182	4.545	**−0.363**
short acid	B3LYP	9.498	8.092	+1.406
short acid	CAM-B3LYP	9.670	8.249	+1.421
TEMPO-4-COOH	B3LYP	8.853	7.569	+1.285
TEMPO-4-COOH	CAM-B3LYP	8.976	7.747	+1.229
TEMPO-4-COO^-	B3LYP	3.978	3.912	+0.067
TEMPO-4-COO^-	CAM-B3LYP	4.120	4.416	**−0.296**

$\langle \hat{S}^2 \rangle_T = 2.007$–$2.011$ throughout (negligible spin contamination). The α-SOMO lies 3 (short anion) or 2–3 (TEMPO anion; B3LYP/CAM-B3LYP) levels below the α-HOMO, and is the HOMO in the acid.

1. With CAM-B3LYP, oxidation of the anion gives the **triplet diradical**, 0.36 eV below the closed shell. The protonated acid still prefers the closed shell by 1.42 eV. *The review's energetic pH switch is reproduced.*

2. The B3LYP "no crossover" result of T11b is functional-specific. B3LYP lowers the closed-shell product by 0.61 eV relative to CAM-B3LYP, but the triplet by only 0.17 eV. Attributing this to delocalisation error is a hypothesis, not tested here.

3. The review's own class of system behaves the same way. TEMPO-4-carboxylate gives the diradical at CAM-B3LYP (−0.296 eV) and narrowly misses it at B3LYP (+0.067 eV). Separation is not the deciding factor; the functional is. The protonated TEMPO acid (the control) prefers the closed shell at both levels (+1.285 and +1.229 eV), with the SOMO as the α-HOMO: the pH switch is reproduced for TEMPO-4-carboxylate as well.

Verification

T2: eqs. (11.1) and (11.2), $\varepsilon_h^\beta - \varepsilon_h^\alpha = K_{hs}$, and the cation $E_{\mathrm{OSS}} - E_T = 2K_{hs}$ verified numerically against Slater–Condon determinant energies for random integrals. **PASS**.

Original sources (status)

Gryn'ova, Marshall, Blanksby & Coote, *Nat. Chem.* **5**, 474 (2013); Gryn'ova & Coote, *J. Am. Chem. Soc.* **135**, 15392 (2013): summaries only (SOMO–HOMO conversion when a stabilised radical is not π-conjugated with an anionic group; protonation restores normal ordering). Westcott et al. (2000): VO(oep), where the unpaired metal d electron is bound more strongly than several ligand pairs (author summary).

12 ROHF orbital energies are not unique (canonicalisation)

Statement in the review

"…the orbitals themselves are neither observable, nor unique (in fact, erroneous non-aufbau occupations can be observed with restricted open-shell methods depending on the canonicalization parameters of the α and β electrons in Fock matrix, see Ref 82) …" (p. 449; ref. 82 Glaesemann & Schmidt 2010)

12.1 High-spin ROHF and its stationarity conditions

Orbital spaces: doubly occupied (core) c, singly occupied (α only) o, virtual v. Densities: $\mathbf{D}^\alpha = \mathbf{D}_c + \mathbf{D}_o$ and $\mathbf{D}^\beta = \mathbf{D}_c$. The energy has the UHF form $E[\mathbf{D}^\alpha, \mathbf{D}^\beta]$, so its first variation is

$$\delta E = \mathrm{tr}(\mathbf{F}^\alpha\, \delta\mathbf{D}^\alpha) + \mathrm{tr}(\mathbf{F}^\beta\, \delta\mathbf{D}^\beta), \tag{12.1}$$

with $\mathbf{F}^\sigma = \partial E/\partial \mathbf{D}^\sigma$ the UHF Fock matrices built from the ROHF densities.

1. An infinitesimal real rotation mixing orbital q into orbital p by angle κ changes the density of a spin σ only if exactly one of p, q is occupied in that spin. Then $\delta\mathbf{D}^\sigma = \kappa(|p\rangle\langle q| + |q\rangle\langle p|)$, and δE picks up $2\kappa F^\sigma_{pq}$.

2. c–o **rotation:** for α both orbitals are occupied (no change); for β, c is occupied and o empty. Stationarity requires $F^\beta_{co} = 0$.

3. o–v **rotation:** for α, o is occupied and v empty; for β both are empty. Stationarity requires $F^\alpha_{ov} = 0$.

4. c–v **rotation:** both spins change. Stationarity requires $F^\alpha_{cv} + F^\beta_{cv} = 0$.

5. **Rotations within c, within o, or within v** leave $\mathbf{D}^\alpha$ and $\mathbf{D}^\beta$ unchanged, hence $\delta E = 0$ *identically*. Nothing in the variational principle fixes them.

12.2 Effective Fock operator and the arbitrariness of orbital energies

To get orbitals from a single eigenvalue problem, one builds an effective Fock matrix $\mathbf{R}$ whose off-diagonal blocks enforce steps 2–4:

$$\mathbf{R} = \begin{pmatrix} \mathbf{R}_{cc} & \mathbf{F}^{\beta}_{co} & \frac{1}{2}(\mathbf{F}^{\alpha}+\mathbf{F}^{\beta})_{cv} \\ \cdot & \mathbf{R}_{oo} & \mathbf{F}^{\alpha}_{ov} \\ \cdot & \cdot & \mathbf{R}_{vv} \end{pmatrix}, \qquad \mathbf{R}_{xx} = A_{xx}\mathbf{F}^{\alpha}_{xx} + B_{xx}\mathbf{F}^{\beta}_{xx} \ \text{(any choice)}. \tag{12.2}$$

At convergence the off-diagonal blocks vanish (steps 2–4), and the orbitals diagonalise each diagonal block separately. By step 5 the total energy, the densities and every observable derived from them are independent of A_{xx}, B_{xx}. The *orbital energies*, the eigenvalues of $\mathbf{R}_{xx}$, are not. The relative position of the SOMO (eigenvalue of $\mathbf{R}_{oo}$) and the HOMO of the closed shell (top eigenvalue of $\mathbf{R}_{cc}$) is therefore a matter of convention.

Verification

T11a (`t11_rohf_and_distonic.py`), ROHF/6-31G*:

- Stationarity: $|F^{\beta}_{co}|, |F^{\alpha}_{ov}|, |(F^{\alpha}+F^{\beta})_{cv}| < 10^{-7}$ for H_2NO, NO_2, CH_3 and allyl. The blocks that need not vanish do not: $|F^{\alpha}_{co}| = 0.11$, $|F^{\beta}_{ov}| = 0.16$ (H_2NO). This confirms steps 2–4. PySCF's `get_roothaan_fock` uses exactly these off-diagonal blocks.
- Canonicalisation, H_2NO: $\varepsilon_{\mathrm{SOMO}} = -0.119$ ($\mathbf{R}_{oo} = \frac{1}{2}(\mathbf{F}^{\alpha}+\mathbf{F}^{\beta})$), -0.440 ($\mathbf{F}^{\alpha}$), $+0.203\,E_h$ ($\mathbf{F}^{\beta}$), while the closed-shell HOMO is -0.467. Same energy $E = -130.36970936\,E_h$ in every case.
- With one open orbital, $\varepsilon_{\mathrm{SOMO}}(A) = AF^{\alpha}_{oo} + (1-A)F^{\beta}_{oo}$ is linear in A. The SOMO drops below the HOMO for $A > A^*$, with $A^* \approx 1.04$ for H_2NO and NO_2. The flip was verified explicitly.

PASS.

Caveat / correction

For these ordinary radicals the ordering flips only for weights slightly outside the "convex" range $0 \le A \le 1$. So the review's warning is mathematically exact (the ordering is not invariant), but whether a *standard* canonicalisation produces a spurious non-aufbau ordering depends on the molecule and the scheme. This is why the review, correctly, asks for evidence from observables: ionisation energies, redox potentials and the spin state of the products (section 11).

Original sources (status)

Glaesemann & Schmidt, *J. Phys. Chem. A* **114**, 8772 (2010), doi:10.1021/jp101758y: not accessed. The specific canonicalisation parameter sets they compare could not be checked. The derivation above is general.

13 The 3d/4s problem

Statement in the review

"In neutral atoms, the energy of a 4s orbital is slightly above that of a 3d orbital (when both orbitals are populated), therefore, 4s electrons are first ionized. However, 4s orbital is also populated first, because it offers less repulsion with a 3d electron than that between two 3d electrons, once the orbital energies are re-evaluated in the new configurations." (p. 448, refs. 79–81)

13.1 Average-of-configuration energies

Model a configuration $d^{n_d}s^{n_s}$ by its average energy. Each electron has one-electron energy h_d or h_s, and every pair of electrons repels with an *average* repulsion that depends only on the shells: $\bar{J}_{dd}$ (two d electrons), $\bar{J}_{ds}$, and J_{ss}. (For example $\bar{J}_{dd} = F^0(dd) - \frac{2}{63}[F^2(dd) + F^4(dd)]$ in Slater–Condon parameters. Only the shell structure matters here.)

1. Count the pairs: $\binom{n_d}{2}$ d–d pairs, $n_d n_s$ d–s pairs, $\binom{n_s}{2}$ s–s pairs. Hence

$$E(d^{n_d}s^{n_s}) = n_d h_d + n_s h_s + \tbinom{n_d}{2}\bar{J}_{dd} + n_d n_s \bar{J}_{ds} + \tbinom{n_s}{2} J_{ss}. \tag{13.1}$$

2. The two competing configurations with $n+2$ valence electrons:

$$E(d^n s^2) = n h_d + 2h_s + \tbinom{n}{2}\bar{J}_{dd} + 2n\bar{J}_{ds} + J_{ss},$$
$$E(d^{n+1}s^1) = (n+1)h_d + h_s + \tbinom{n+1}{2}\bar{J}_{dd} + (n+1)\bar{J}_{ds}.$$

3. Subtract, using $\binom{n+1}{2} - \binom{n}{2} = n$:

$$\Delta \equiv E(d^{n+1}s) - E(d^n s^2) = h_d - h_s + n\bar{J}_{dd} + (1-n)\bar{J}_{ds} - J_{ss}. \tag{13.2}$$

4. Orbital energies *in the configuration* $d^n s^2$, Koopmans style ($\varepsilon = E(N) - E(N-1)$, frozen):

$$\varepsilon_d = E(d^n s^2) - E(d^{n-1}s^2) = h_d + (n-1)\bar{J}_{dd} + 2\bar{J}_{ds},$$
$$\varepsilon_s = E(d^n s^2) - E(d^n s^1) = h_s + n\bar{J}_{ds} + J_{ss}.$$

5. Therefore $\varepsilon_d - \varepsilon_s = h_d - h_s + (n-1)\bar{J}_{dd} + (2-n)\bar{J}_{ds} - J_{ss}$, and comparing with eq. (13.2):

$$\boxed{\Delta = (\varepsilon_d - \varepsilon_s) + (\bar{J}_{dd} - \bar{J}_{ds}).} \tag{13.3}$$

Result

Even when $\varepsilon_{3d} < \varepsilon_{4s}$ (3d "below" 4s), the $d^n s^2$ configuration is lower in energy ($\Delta > 0$) whenever $\bar{J}_{dd} - \bar{J}_{ds} > \varepsilon_s - \varepsilon_d$. Because 3d is compact and 4s diffuse, $\bar{J}_{dd} \gg \bar{J}_{ds}$: moving an electron from 4s into 3d costs the large d–d repulsion. Example (illustrative parameters, $n = 2$): $\varepsilon_d = -1.50$, $\varepsilon_s = -0.90$, $\Delta = +0.10$.

Ionisation. From $d^n s^2$, the Koopmans ionisation energies are $-\varepsilon_s$ and $-\varepsilon_d$. With $\varepsilon_s > \varepsilon_d$, the 4s electron leaves first, as observed for transition-metal cations. Both statements in the review follow from the same two numbers, ε and $\bar{J}$, evaluated *in the relevant configuration*. The "building-up" order and the "removal" order need not agree.

Verification

T12 (`t10_t12_t13_symbolic.py`): eqs. (13.2) and (13.3) and both orbital-energy formulas verified symbolically for general n; the cation analogue is $\Delta(n-1)$; the numerical example satisfies $\varepsilon_d < \varepsilon_s$ and $\Delta > 0$. **PASS**.

Original sources (status)

Vanquickenborne, Pierloot & Devoghel, *Inorg. Chem.* **28**, 1805 (1989); Melrose & Scerri, *J. Chem. Educ.* **73**, 498 (1996): not accessed. The derivation reconstructs the average-of-configuration argument independently.

14 Why individual electrons have no good quantum numbers

Statement in the review

"...according to modern quantum mechanics, in the stationary states the quantum numbers of individual electrons do not commute with the Hamiltonian, only the total angular momentum does. For this reason ... the Pauli exclusion principle has been reformulated to reflect the antisymmetry of the wavefunction ..." (p. 448, ref. 77 Scerri 1991). "...assigning individual electrons to individual orbitals and individual sets of quantum numbers is erroneous" (p. 441).

14.1 The commutators

Take an atom (nucleus at the origin), so $\hat{H} = \sum_i \hat{h}(i) + \sum_{i<j} r_{ij}^{-1}$ with $\hat{h}(i) = -\tfrac{1}{2}\nabla_i^2 - Z/r_i$. Orbital angular momentum of electron 1: $\hat{\mathbf{l}}_1 = -i\,\mathbf{r}_1 \times \nabla_1$.

1. $\hat{\mathbf{l}}_1$ commutes with $\hat{h}(1)$ (spherical symmetry) and with $\hat{h}(j)$, $j \neq 1$ (different variables). The only possible obstruction is $1/r_{12}$.
2. Apply $\hat{l}_{1z} = -i(x_1\partial_{y_1} - y_1\partial_{x_1})$ to $V = 1/r_{12}$, with $\partial_{y_1} r_{12}^{-1} = -(y_1 - y_2)/r_{12}^3$ and $\partial_{x_1} r_{12}^{-1} = -(x_1 - x_2)/r_{12}^3$:

$$\hat{l}_{1z} V = -i\,\frac{-x_1(y_1 - y_2) + y_1(x_1 - x_2)}{r_{12}^3} = -i\,\frac{x_1 y_2 - x_2 y_1}{r_{12}^3}.$$

   Since $\hat{l}_{1z}$ is a first-order differential operator, $[\hat{l}_{1z}, V]f = (\hat{l}_{1z}V)f$ for any f, so

$$[\hat{l}_{1z},\, r_{12}^{-1}] = -i\,\frac{x_1 y_2 - x_2 y_1}{r_{12}^3} \neq 0. \tag{14.1}$$

3. For electron 2, $\partial_{y_2} r_{12}^{-1} = +(y_1 - y_2)/r_{12}^3$ etc., which gives $\hat{l}_{2z} V = -i\,(x_2 y_1 - x_1 y_2)/r_{12}^3 = -\hat{l}_{1z} V$.
4. Hence $[\hat{L}_z, r_{12}^{-1}] = [\hat{l}_{1z} + \hat{l}_{2z}, r_{12}^{-1}] = 0$. The same holds for the x and y components. Physically, $\hat{\mathbf{L}}$ generates a simultaneous rotation of both electrons, which leaves r_{12} unchanged; $\hat{\mathbf{l}}_1$ rotates electron 1 alone, which changes r_{12}.
5. Consequently $[\hat{H}, \hat{\mathbf{L}}] = 0$ and $[\hat{H}, \hat{L}^2] = 0$, but $[\hat{H}, \hat{\mathbf{l}}_1] \neq 0$ and $[\hat{H}, \hat{l}_1^2] \neq 0$. $\hat{\mathbf{S}}$ and $\hat{S}^2$ commute with $\hat{H}$ trivially, since $\hat{H}$ is spin-free.

Result

Exact atomic eigenstates can be labelled by L, M_L, S, M_S (and parity), not by one-electron (n, l, m_l, m_s). Those labels belong to the independent-particle model, in which $1/r_{ij}$ is replaced by a spherically averaged mean field. Pauli's 1925 one-electron formulation is therefore a statement about that model. The exact, model-independent statement is the antisymmetry eq. (1.1).

Verification

T13 (`t10_t12_t13_symbolic.py`): $[\hat{l}_{1z}, r_{12}^{-1}]f$ evaluated symbolically on an arbitrary function f reproduces the expression above. $[\hat{L}_k, r_{12}^{-1}]f = 0$ for $k = x, y, z$, and $[\hat{l}_1^2, r_{12}^{-1}] \neq 0$. **PASS**.

Original sources (status)

Scerri, *Br. J. Philos. Sci.* **42**, 309 (1991); Pauli, *Z. Phys.* **31**, 765 (1925): not accessed. The commutator algebra is standard and was verified here.

15 The adiabatic principle and the aufbau argument

Statement in the review

Bohr's building-up principle assumed "that electrons exist in sharp stationary states, and that these states are preserved upon addition of an electron and a proton". These assumptions "originate from the Ehrenfest's adiabatic principle: 'if a system be affected in a reversible adiabatic way, the allowed motions are transformed into allowed motions.' However, this principle does not apply to aperiodic systems, i.e., all systems other than a hydrogen atom." "... the aufbau principle, by assuming the existence of unchanging stationary individual electronic states, violates the Pauli exclusion principle." (p. 448)

15.1 The quantum adiabatic theorem (what it does guarantee)

Let $\hat{H}(t)$ change slowly, with instantaneous eigenstates $\hat{H}(t)\psi_n(t) = E_n(t)\psi_n(t)$, non-degenerate.

1. Expand $\Psi(t) = \sum_n c_n(t) e^{i\theta_n(t)}\psi_n(t)$ with $\theta_n = -\int_0^t E_n \, \mathrm{d}t'$.
2. Insert into $i\partial_t\Psi = \hat{H}\Psi$. The E_n terms cancel against $\dot{\theta}_n$, leaving $\sum_n(\dot{c}_n\psi_n + c_n\dot{\psi}_n)e^{i\theta_n} = 0$.
3. Project on ψ_m: $\dot{c}_m = -\sum_n c_n\langle\psi_m|\dot{\psi}_n\rangle e^{i(\theta_n-\theta_m)}$.
4. Differentiate $\hat{H}\psi_n = E_n\psi_n$ in time and project on ψ_m $(m \neq n)$: $\langle\psi_m|\dot{\psi}_n\rangle = \dfrac{\langle\psi_m|\dot{\hat{H}}|\psi_n\rangle}{E_n - E_m}$.
5. If $|\langle\psi_m|\dot{\hat{H}}|\psi_n\rangle| \ll (E_n - E_m)^2$, the rapidly oscillating phase makes the coupling average out, and $|c_m|$ stays at its initial value: a system starting in ψ_n ends in the *continuously connected* eigenstate $\psi_n(t)$.

15.2 What it does not guarantee: the aufbau assumptions

1. The theorem is about a *fixed* Hilbert space and a Hamiltonian with a continuously varying parameter. Going from element Z to $Z+1$ adds a particle. The N- and $(N+1)$-electron Hilbert spaces are different, so there is no continuous path of Hamiltonians on which the theorem could act.
2. Even if one varies Z continuously at fixed N, the theorem preserves the label of an N-*electron* eigenstate, the conserved quantities of section 14 $(L, S, \dots)$. It says nothing about one-electron states. These are not eigenstates of $\hat{H}$, because $[\hat{H}, \hat{\mathbf{l}}_i] \neq 0$.
3. Within the orbital model, the orbitals of $d^n s^2$ and $d^{n+1}s$ differ (section 13). Adding or removing an electron changes all orbitals (section 10, orbital relaxation beyond Koopmans).

Result

The adiabatic theorem cannot justify the idea that previously "built-up" one-electron states persist, unchanged, when electrons and protons are added. That is the mathematical content behind the review's historical criticism. The claim that Ehrenfest's principle "does not apply to aperiodic systems" refers to the old (Bohr–Sommerfeld) quantum theory, where adiabatic invariants $\oint p\,\mathrm{d}q$ are defined only for (multiply) periodic motion. It is historical and could not be checked against the original here.

Original sources (status)

Ehrenfest, *Philos. Mag.* **33**, 500 (1917); Scerri (1991): not accessed (quotation from the review). Born & Fock (1928) for the quantum adiabatic theorem; the derivation above is standard.

16 Broken-symmetry DFT/UHF and spin projection

Statement in the review

"In terms of computations, relatively 'cheap' methods such as unrestricted or broken symmetry formalisms suffer from a number of serious drawbacks . . . " (p. 443)

16.1 Why a single unrestricted determinant cannot be an open-shell singlet

Take the $2e/2o$ broken-symmetry (BS) determinant $|a'\bar{b}'\rangle$ with a' localised mostly on centre l and b' mostly on r. In the orthonormal basis φ_a, φ_b (overlap $\langle a'|b'\rangle = s$) it is a mixture of the $M_S = 0$ singlet and triplet (section 2, eqs. (2.4) and (2.5)). Its spin expectation value is

$$\langle \hat{S}^2 \rangle_{\mathrm{BS}} = S_z(S_z+1) + N_\beta - \sum_{i\in\alpha,\, j\in\beta} |\langle i|j\rangle|^2 = 0 + 1 - s^2, \tag{16.1}$$

which lies between 0 (pure singlet, $s = 1$) and 1 (equal singlet–triplet mixture, $s = 0$).

16.2 Yamaguchi's approximate projection

1. Model: $\hat{H} = -2J\,\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2$. With $\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 = \frac{1}{2}[S(S+1) - \frac{3}{2}]$: $E_T = -\frac{J}{2}$, $E_S = \frac{3J}{2}$, so $E_S - E_T = 2J$.
2. Write the BS state as $\Psi_{\mathrm{BS}} = c_S\Psi_S + c_T\Psi_T$ ($M_S = 0$), so $\langle \hat{S}^2\rangle_{\mathrm{BS}} = 2|c_T|^2$ and $E_{\mathrm{BS}} = |c_S|^2E_S + |c_T|^2E_T$.
3. Then $E_{\mathrm{BS}} - E_T = |c_S|^2(E_S - E_T) = (1 - \frac{1}{2}\langle \hat{S}^2\rangle_{\mathrm{BS}})2J = (2 - \langle \hat{S}^2\rangle_{\mathrm{BS}})J$.
4. With $E_{\mathrm{HS}} = E_T$ (single determinant, exact in this model) and $\langle \hat{S}^2\rangle_{\mathrm{HS}} = 2$:

$$\boxed{J = \frac{E_{\mathrm{BS}} - E_{\mathrm{HS}}}{\langle \hat{S}^2\rangle_{\mathrm{HS}} - \langle \hat{S}^2\rangle_{\mathrm{BS}}}}, \qquad E_S - E_T = 2J. \tag{16.2}$$

Verification

T14 (`t06_t09_models.py`): BS-UHF solved self-consistently for the Hubbard dimer. Yamaguchi's J compared with the exact $J = (E_S - E_T)/2 = \frac{1}{4}(U - \sqrt{U^2 + 16t^2})$: relative error -7.7% ($U = 3t$), -0.9% ($6t$), -0.1% ($12t$), $< 0.05\%$ ($24t$). The projection works when the two centres are weakly coupled (strongly correlated, $\langle \hat{S}^2\rangle_{\mathrm{BS}} \to 1$) and degrades as the system becomes more covalent. This is one of the "serious drawbacks" of the cheap approaches. **PASS**.

Original sources (status)

Formula as given by secondary sources (IntechOpen chapter, ORCA manual) and attributed to Yamaguchi and co-workers (1986/1988). Original papers not accessed. The derivation above is self-contained. Sign conventions differ between sources; the one used here is $\hat{H} = -2J\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2$, with $J < 0$ antiferromagnetic.

17 Summary: verification record, corrections and sources

17.1 Verification record

All scripts are in `verification/` and run with `make verify` / `uv run -project . python -I <script>` (uv-locked: PySCF 2.14, SymPy 1.14, NumPy 2.5). Logs are in `plans/tests.md`.

test	what is checked	section	result
T1	spin eigenfunctions; Fig. 1 combinations; sign erratum	1, 2	PASS
T2	$2e/2o$ singlet matrix and E_T vs. full CI; Koopmans relations	3, 10, 11	PASS
T3	$K_{pq} \geq 0$, $J_{pq} \geq K_{pq}$ (water MOs)	4	PASS
T4	He $2\,^3S/2\,^1S$: virial, less screening	5	PASS
T5	H_2 minimal basis: RHF/CI/triplet/OSS limits	6	PASS
T6	two-orbital gap model	6	PASS
T7	extended Hubbard dimer, kinetic exchange	7	PASS
T8	Hückel NBMO rules, disjointness	8	PASS
T9	Hubbard ED: Ovchinnikov/Lieb spins; spin alternation	9	PASS
T9b	gap $\propto U$ (nondisjoint) vs. $\propto U^2$ (disjoint)	8, 9	PASS
T10	S–T gap = HOMO-energy difference	10	PASS
T11a	ROHF stationarity, canonicalisation dependence	12	PASS
T11b	distonic anion (B3LYP): orbital inversion; no ΔSCF crossover	11	FAIL (diagnosed by T11c)
T11c	CAM-B3LYP: anions $\to$ diradical (0.36, 0.30 eV); acids closed shell	11	PASS (8/8 runs)
T12	3d/4s algebra	13	PASS
T13	$[\hat{l}_1, r_{12}^{-1}] \neq 0$, $[\hat{L}, r_{12}^{-1}] = 0$	14	PASS
T14	Yamaguchi projection on BS-UHF dimer	16	PASS
T15	same-spin vs. opposite-spin correlation	5	PASS (claim qualified)
T17	Lean 4/Mathlib proofs of the algebraic identities	several	PASS (17 thms)

Lean formalisation (T17). `verification/lean_proofs/Ch5103/Identities.lean` contains machine-checked proofs of: the factorisations eqs. (2.2) and (2.3) and a counterexample showing the review's "+" combination is not the singlet; $E_S - E_T = 2K$ as a HOMO-energy difference; the scaling derivative $\mathrm{d}E/\,\mathrm{d}\eta|_1 = 2T + V$ and its virial consequences; the less-screening inequalities eq. (5.4); the incompatibility of frozen orbitals with the virial theorem; the H_2 dissociation limits; the gap-model and extended-dimer secular roots; the Hückel pairing theorem; the 3d/4s identity eq. (13.3); and Yamaguchi's formula eq. (16.2).

17.2 Corrections and qualifications to the review

1. **Sign error** (p. 441): the open-shell singlet is $\frac{1}{2}(D_{\mathrm{iv}} - D_{\mathrm{iii}})$; the printed $\frac{1}{2}(D_{\mathrm{iii}} + D_{\mathrm{iv}})$ is the $M_S = 0$ triplet (section 2).
2. **Citation year**: Katriel & Pauncz, *Adv. Quantum Chem.* **10**, 143–185 is 1977, not 1975.
3. **Same-spin correlation** "an order of magnitude" smaller: true for He ($\sim$1/40), but in molecular valence shells at MP2 the per-pair ratio is $\sim$0.3–0.4 (section 5).
4. **Janak/Koopmans statement**: the sign convention is unstated in the review; with frozen orbitals $E_S - E_T = \varepsilon^S_{\mathrm{HOMO}} - \varepsilon^T_{\mathrm{HOMO}} = 2K$ (section 10).
5. **Longuet-Higgins count** (used implicitly for NBMO counting): $N - 2T$ is a lower bound (cyclobutadiene exceeds it).
6. **ROHF canonicalisation**: the ordering is convention-dependent, as stated. For common radicals a flip needs weights slightly outside $[0, 1]$, so observables must decide (section 12).

17.3 Sources and access status

reference	status in this work
Hongo et al., J. Chem. Phys. 121, 7144 (2004), doi:10.1063/1.1795151	full text (arXiv cond-mat/0408147); Table I used
Boyd, Nature 310, 480 (1984), doi:10.1038/310480a0	abstract
Katriel & Pauncz, Adv. Quantum Chem. 10, 143 (1977), doi:10.1016/S0065-3276(08)60580-8	bibliographic only
Krylov, Chem. Phys. Lett. 338, 375 (2001)	introduction (preview)
Balková & Bartlett, J. Chem. Phys. 101, 8972 (1994), doi:10.1063/1.468057	abstract
Lieb, Phys. Rev. Lett. 62, 1201 (1989)	theorem statement
Ovchinnikov, Theor. Chim. Acta 47, 297 (1978), doi:10.1007/BF00549259	as quoted in arXiv:1906.08544
Janak, Phys. Rev. B 18, 7165 (1978)	abstract
Borden & Davidson, J. Am. Chem. Soc. 99, 4587 (1977), doi:10.1021/ja00456a010	not accessed
Kollmar & Staemmler, Theor. Chim. Acta 48, 223 (1978), doi:10.1007/BF00549021	not accessed
Liu & Langenaeker, Theor. Chem. Acc. 110, 338 (2003), doi:10.1007/s00214-003-0487-6	not accessed
Yamanaka et al., Int. J. Quantum Chem. 105, 687 (2005)	not accessed
Glaesemann & Schmidt, J. Phys. Chem. A 114, 8772 (2010), doi:10.1021/jp101758y	not accessed
Vanquickenborne et al., Inorg. Chem. 28, 1805 (1989); Melrose & Scerri (1996)	not accessed
Gryn'ova et al., Nat. Chem. 5, 474 (2013); Gryn'ova & Coote, J. Am. Chem. Soc. 135, 15392 (2013)	abstracts/summaries
Westcott et al., J. Am. Chem. Soc. 122, 8083 (2000), doi:10.1021/ja994018p	bibliographic + author summary
Scerri (1991); Ehrenfest (1917); Pauli (1925); Slater (1929)	not accessed

Where an original was not accessed, nothing in this document is attributed to it beyond what the review itself states. The mathematics was derived independently and verified as listed above.