Uncommon Molecular Electronic Configurations

Theory, derivations and verification of Gryn'ova, Coote & Corminboeuf (2015)

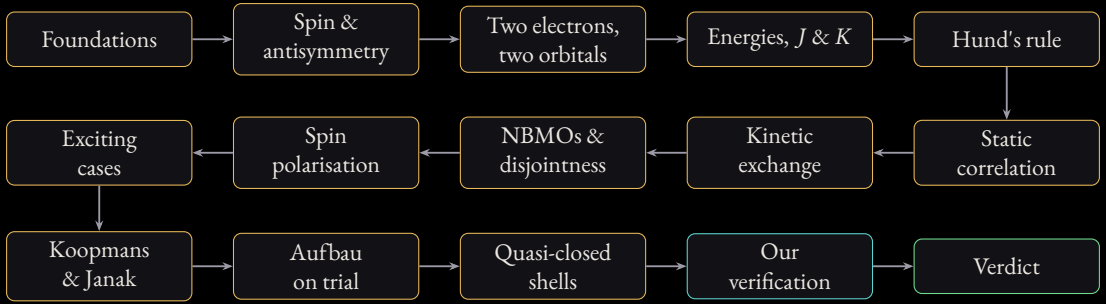
Shuvam Banerji Seal

CH5103 Term Paper

November 9, 2026

The journey

from the Schrödinger equation to a sign error in print



Every equation is derived step by step; every identity used was checked by SymPy, PySCF or Lean.

How to read these slides

The paper says
a statement quoted from the review

Assumptions
what a derivation takes for granted

Result
what the derivation proves

Verified
how we tested it (script / proof)

Erratum
where the paper got it wrong

VERIFIED ERROR OVERSTATED PARTIAL

$E = h + J$ *blue italic: why this step follows*

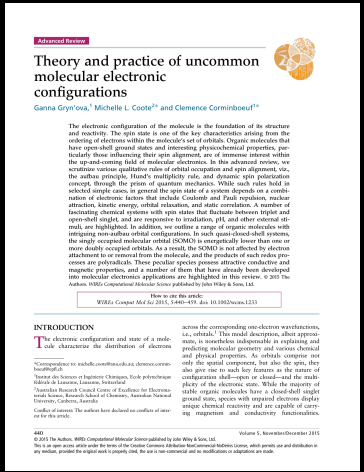
a SYMBOLS strip at the foot of a slide defines its notation

Atomic units throughout: $\hbar = m_e = e = 4\pi\varepsilon_0 = 1$, energies in hartree ($E_\mathrm{h}$).

Part I

The paper

I



Advanced Review

Theory and practice of uncommon molecular electronic configurations

Ganna Gryn'ova,[1] Michelle L. Coote[2]* and Clemence Corminboeuf[1]*

The electronic configuration of the molecule is the foundation of its structure and reactivity. The spin state is one of the key characteristics arising from the ordering of electrons within the molecule's set of orbitals. Organic molecules that have open-shell ground states and interesting physicochemical properties, particularly those influencing their spin alignment, are of immense interest within the up-and-coming field of molecular electronics. In this advanced review, we scrutinize various qualitative rules of orbital occupation and spin alignment, viz., the aufbau principle, Hund's multiplicity rule, and dynamic spin polarization concept, through the prism of quantum mechanics. While such rules hold in selected simple cases, in general the spin state of a system depends on a combination of electronic factors that include Coulomb and Pauli repulsion, nuclear attraction, kinetic energy, orbital relaxation, and static correlation. A number of fascinating chemical systems with spin states that fluctuate between triplet and open-shell singlet, and are responsive to irradiation, pH, and other external stimuli, are highlighted. In addition, we outline a range of organic molecules with intriguing non-aufbau orbital configurations. In such quasi-closed-shell systems, the singly occupied molecular orbital (SOMO) is energetically lower than one or more doubly occupied orbitals. As a result, the SOMO is not affected by electron attachment to or removal from the molecule, and the products of such redox processes are polyradicals. These peculiar species possess attractive conductive and magnetic properties, and a number of them that have already been developed into molecular electronics applications are highlighted in this review. © 2015 The Authors. WIREs Computational Molecular Science published by John Wiley & Sons, Ltd.

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INTRODUCTION

The electronic configuration and state of a molecule characterize the distribution of electrons across the corresponding one-electron wavefunctions, i.e., orbitals.[1] This model description, albeit approximate, is nonetheless indispensable in explaining and predicting molecular geometry and various chemical and physical properties. As orbitals comprise not only the spatial component, but also the spin, they also give rise to such key features as the nature of configuration shell—open or closed—and the multiplicity of the electronic state. While the majority of stable organic molecules have a closed-shell singlet ground state, species with unpaired electrons display unique chemical reactivity and are capable of carrying magnetism and conductivity functionalities.

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Conflict of interests: The authors have declared no conflicts of interest for this article.

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Theory and practice of uncommon molecular electronic configurations

Ganna Gryn′ova, Michelle L. Coote, Clémence Corminboeuf

WIREs Computational Molecular Science **5**, 440–459 (2015)
doi:10.1002/wcms.1233 Advanced Review, open access

- 20 pages, 17 figures, 5 schemes, 118 references
- part theory (what decides a spin state?)
- part catalogue (molecules that break the textbook rules)

Two uncommon configurations

the two halves of the paper

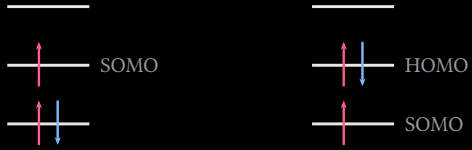
1. Fluctuating multiplicity



two (nearly) degenerate orbitals, two electrons:
parallel or *antiparallel*?

Who wins: Hund's rule, or correlation?

2. Non-Aufbau ordering



the singly occupied orbital lies *below*
a doubly occupied one

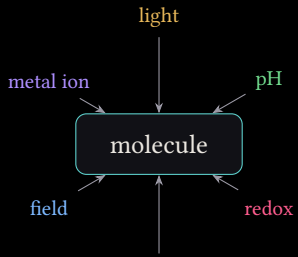
Redox then gives a polyradical
(a diradical in the simplest case).

Why anyone cares

The paper says

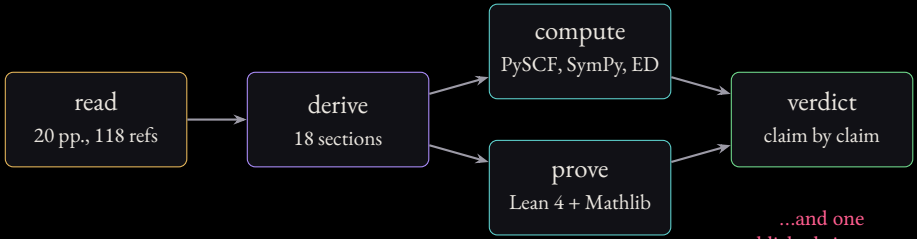
> "species with unpaired electrons display unique chemical reactivity and are capable of carrying magnetism and conductivity functionalities" (p. 440)

- spin valves, switches, field-effect transistors, logic
- wanted: a set spin state that a stimulus can flip
- but few radicals are persistent, crystallisable *and* not Mott insulators



stimuli that switch spin states
(Figures 7–9 of the review)

What we did with it



21 checks (T1–T17, with T1b, T9b, T11a–c)
17 machine-checked theorems

Part II

Foundations

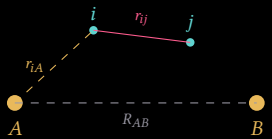
II

Where everything starts

the molecular Schrödinger equation

$$\hat{H}_{\text{mol}}\,\Psi = E\,\Psi$$

$$\hat{H}_{\text{mol}} = \underbrace{-\sum_A \frac{\nabla_A^2}{2M_A}}_{\text{nuclear KE}} \underbrace{-\sum_i \frac{\nabla_i^2}{2}}_{\text{electron KE}} \underbrace{-\sum_{i,A} \frac{Z_A}{r_{iA}}}_{\text{e–n attraction}} \underbrace{+\sum_{i<j} \frac{1}{r_{ij}}}_{\text{e–e repulsion}} \underbrace{+\sum_{A<B} \frac{Z_A Z_B}{R_{AB}}}_{\text{n–n repulsion}}$$



- *kinetic energy is $-\frac{1}{2}\nabla^2$ (second derivatives): curvature of Ψ costs energy*
- *attraction: every electron i to every nucleus A of charge Z_A, falling off as $1/r$*
- *repulsion: every pair of electrons once ($i < j$ avoids double counting)*

SYMBOLS Ψ: total wavefunction of all electrons and nuclei E: total energy A, B: nuclei, i, j: electrons M_A: nuclear mass (units of m_e) Z_A: nuclear charge r_{iA}, r_{ij}, R_{AB}: distances atomic units $\hbar = m_e = e = 1$

Born--Oppenheimer: freeze the nuclei

assume $M_A \gg m_e = 1$: electrons adjust instantly; nuclear positions $\{\mathbf{R}_A\}$ are parameters

1. drop the nuclear kinetic energy — $-\sum_A \nabla_A^2/2M_A \to 0$
2. nuclear repulsion becomes a constant — $V_{nn}(\mathbf{R})$
3. what is left is the electronic Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(i) + \sum_{i<j} \frac{1}{r_{ij}}, \qquad \hat{h}(i) = -\tfrac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

- *a proton is* 1836× *heavier than an electron, so on the electrons' time scale the nuclei stand still*
- $\hat{h}(i)$ = *everything that involves electron i alone;* $1/r_{ij}$ *couples electrons in pairs and is the hard part*

SYMBOLS $\mathbf{R}_A$: position of nucleus A V_{nn}: nuclear repulsion (a number once nuclei are fixed) N: number of electrons $\hat{h}(i)$: one-electron ("core") Hamiltonian $\hat{H}$ has no spin operator: spin enters only via the Pauli principle

The variational principle

assume exact eigenstates $\hat{H}\Psi_n = E_n\Psi_n$: orthonormal, complete, $E_0 \le E_1 \le \cdots$

$$
\begin{aligned}
(1)\quad & \tilde{\Psi} = \textstyle\sum_n c_n \Psi_n, \qquad \sum_n |c_n|^2 = 1 && \text{any function is a mix of eigenstates (completeness)} \\
(2)\quad & \langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle = \textstyle\sum_{m,n} c_m^* c_n E_n \langle\Psi_m|\Psi_n\rangle && \text{insert both sums; } \hat{H}\Psi_n = E_n\Psi_n \\
& = \textstyle\sum_n |c_n|^2 E_n && \text{orthonormality: only } m = n \text{ terms survive} \\
(3)\quad & \ge \textstyle\sum_n |c_n|^2 E_0 = E_0 && \text{each } E_n \ge E_0\text{; then use } \textstyle\sum |c_n|^2 = 1
\end{aligned}
$$

$E[\tilde{\Psi}] \ge E_0$ for every normalised $\tilde{\Psi}$: a lower energy is a better wavefunction

SYMBOLS $\tilde{\Psi}$: any trial wavefunction c_n: (complex) expansion coefficients $\langle f|g\rangle = \int f^* g \, \mathrm{d}\tau$: overlap integral over all coordinates $\langle f|\hat{H}|g\rangle = \int f^* \hat{H} g \, \mathrm{d}\tau$ δ_{mn}: 1 if $m = n$, else 0

Orbitals: the independent-electron picture

Independent-particle model

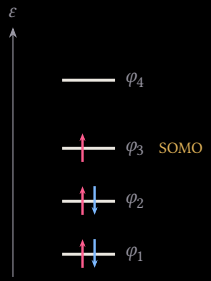
replace $\sum_{i<j} 1/r_{ij}$ by an *average* field felt by each electron

one-electron problem: $\hat{f}\,\varphi_p = \varepsilon_p\,\varphi_p$

LCAO, atom-centred functions:

$\varphi_p(\mathbf{r}) = \sum_\mu c_{\mu p}\,\chi_\mu(\mathbf{r})$

▸ *each electron feels the averaged field of the others; occupations build the configuration*



SYMBOLS $\hat{f}$: Fock (mean-field) operator φ_p: spatial orbital p ε_p: its orbital energy χ_μ: atom-centred basis function (atomic orbital) $c_{\mu p}$: LCAO coefficient ↑↓: spin up (α) / down (β) SOMO: singly occupied MO

Box 1: ``Much ado about orbitals''

The paper says

"The reality is that an orbital is a mathematical construct, an approximate, non-unique solution to the Schrödinger equation." (p. 448)

Non-unique: unitary mixing of occupied orbitals leaves the determinant and every observable unchanged.
Approximate: orbitals are defined within the independent-particle (orbital) model.

A 1999 *Nature* report on "the direct observation of copper's d-orbitals" (p. 448) started a debate: *can an orbital be observed?*

What is observable is the density $\rho(\mathbf{r})$, and orbital *occupations*.

Keep this in mind: it returns when ROHF orbital orderings depend on a convention.

SYMBOLS unitary mixing: replacing the occupied orbitals by orthonormal combinations of themselves $\rho(\mathbf{r})$: electron density, the probability of finding an electron at $\mathbf{r}$ (measurable)

Part III

Spin & antisymmetry

III

Swapping two electrons

why the exchange eigenvalue is ± 1

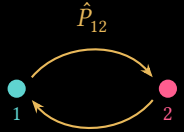
Define $\hat{P}_{12}\Psi(x_1, x_2) = \Psi(x_2, x_1), \quad x = (\mathbf{r}, \sigma).$

(1) $\hat{P}_{12}^2 = \hat{1}$ — *swapping twice restores the order*

(2) $\hat{P}_{12}\Psi = \lambda\Psi \;\Rightarrow\; \Psi = \lambda^2\Psi$ — *apply* $\hat{P}_{12}$ *twice*

(3) $\lambda = \pm 1$ — *since* $\lambda^2 = 1$

(4) $[\hat{H}, \hat{P}_{12}] = 0$ — $\hat{H}$ *treats all electrons alike*



so eigenstates have definite λ; for electrons nature picks -1. The paper: "the wavefunction for a system of fermions must be antisymmetric with respect to the interchange of any two particles" (p. 441)

SYMBOLS $x_i = (\mathbf{r}_i, \sigma_i)$: all coordinates of electron i, position $\mathbf{r}_i$ plus spin coordinate σ_i (↑ or ↓) $\hat{P}_{12}$: operator exchanging electrons 1 and 2 λ: its eigenvalue $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ fermions: half-integer-spin particles (electrons)

Slater determinants

antisymmetry built in

$$D[\chi_1, \chi_2] = \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)$$

▸ *rows label electrons, columns label spin orbitals; the determinant mixes every assignment with a sign*

- swap electrons ⇔ swap two *rows* ⇒ $D \to -D$ — antisymmetric
- two equal spin orbitals ⇔ two equal *columns* ⇒ $D = 0$ — Pauli exclusion
- normalised: $|\chi_1\chi_2\rangle = \frac{1}{\sqrt{2}} D[\chi_1, \chi_2]$

Result

Pauli's 1925 rule (no two electrons with all four quantum numbers equal; p. 448) is a *consequence* of antisymmetry inside the orbital model, not a separate law.

SYMBOLS $\chi(x)$: spin orbital = spatial orbital × spin function, e.g. $\chi = \varphi_a(\mathbf{r})\,\alpha(\sigma)$ $\chi_1(2)$: spin orbital 1 at electron 2's coordinates $\frac{1}{\sqrt{2}}$: D is two orthogonal products of norm 1, so $\langle D|D\rangle = 2$

Spin operators for two electrons

One electron ($s = \frac{1}{2}$):

$$\hat{s}_z\alpha = +\tfrac{1}{2}\alpha, \qquad \hat{s}_z\beta = -\tfrac{1}{2}\beta$$
$$\hat{s}_+\beta = \alpha, \qquad \hat{s}_+\alpha = 0$$
$$\hat{s}_-\alpha = \beta, \qquad \hat{s}_-\beta = 0$$

Two electrons: add each electron's operator

$\hat{S}_z = \hat{s}_z(1) + \hat{s}_z(2),\ \ \hat{S}_\pm = \hat{s}_\pm(1) + \hat{s}_\pm(2)$

A useful identity:

$$\begin{aligned}
\hat{S}_-\hat{S}_+ &= (\hat{S}_x - i\hat{S}_y)(\hat{S}_x + i\hat{S}_y) && \textit{definition of } \hat{S}_\pm \\
&= \hat{S}_x^2 + \hat{S}_y^2 + i[\hat{S}_x, \hat{S}_y] && \textit{multiply out} \\
&= \hat{S}^2 - \hat{S}_z^2 + i(i\hat{S}_z) && [\hat{S}_x, \hat{S}_y] = i\hat{S}_z \\
&= \hat{S}^2 - \hat{S}_z^2 - \hat{S}_z && i \cdot i = -1
\end{aligned}$$

$$\boxed{\hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z^2 + \hat{S}_z}$$

SYMBOLS α, β: spin up / down of one electron $\hat{s}_+$ flips ↓→↑, $\hat{s}_-$ flips ↑→↓ (0 if impossible) $\hat{S}_x, \hat{S}_y, \hat{S}_z, \hat{S}^2$: total spin components and squared magnitude $\hbar = 1$

$\hat{S}^2$ on the four spin products (1/2)

$\alpha_1\alpha_2$ (both up)

$$\hat{S}_+\alpha_1\alpha_2 = 0 \qquad \textit{nothing left to raise}$$

$$\hat{S}_z\alpha_1\alpha_2 = (\tfrac{1}{2}+\tfrac{1}{2})\alpha_1\alpha_2 \qquad \textit{each adds } +\tfrac{1}{2}$$

$$\hat{S}^2\alpha_1\alpha_2 = (0+1+1)\,\alpha_1\alpha_2 \qquad \hat{S}_-\hat{S}_+ + \hat{S}_z^2 + \hat{S}_z$$

$$= 2\,\alpha_1\alpha_2$$

$S(S+1) = 2 \Rightarrow S = 1,\ M_S = +1$

$\beta_1\beta_2$ (both down)

$$\hat{S}_+\beta_1\beta_2 = \alpha_1\beta_2 + \beta_1\alpha_2 \qquad \textit{raise 1 or 2}$$

$$\hat{S}_-(\ldots) = \beta_1\beta_2 + \beta_1\beta_2 \qquad \textit{lower the raised one}$$

$$(\hat{S}_z^2 + \hat{S}_z)\beta_1\beta_2 = (1-1)\beta_1\beta_2 \qquad M_S = -1$$

$$\hat{S}^2\beta_1\beta_2 = 2\,\beta_1\beta_2$$

$S = 1,\ M_S = -1$

SYMBOLS $\alpha_1 \equiv \alpha(\sigma_1)$: electron 1 is spin up $\alpha_1\beta_2$: electron 1 up, electron 2 down eigenvalue of $\hat{S}^2$ is $S(S+1)$ M_S: eigenvalue of $\hat{S}_z$ (sum of the two $\pm\frac{1}{2}$)

$\hat{S}^2$ *on the four spin products (2/2)*

$\alpha_1\beta_2$ and $\beta_1\alpha_2$ ($M_S = 0$; neither is an eigenfunction on its own)

$$\hat{S}_+\alpha_1\beta_2 = \alpha_1\alpha_2$$
$$\hat{S}_z\alpha_1\beta_2 = (\tfrac{1}{2} - \tfrac{1}{2})\,\alpha_1\beta_2 = 0$$

$$\hat{S}_-\alpha_1\alpha_2 = \beta_1\alpha_2 + \alpha_1\beta_2$$
$$\Rightarrow\ \hat{S}^2\alpha_1\beta_2 = \alpha_1\beta_2 + \beta_1\alpha_2$$
$$\hat{S}^2\beta_1\alpha_2 = \alpha_1\beta_2 + \beta_1\alpha_2 \quad \textit{same steps}$$

▸ $\hat{S}^2$ *turns* $\alpha_1\beta_2$ *into a different function: it is not an eigenfunction*

Add and subtract the two results:

$$\hat{S}^2(\alpha_1\beta_2 \pm \beta_1\alpha_2) = (1 \pm 1)\,(\alpha_1\beta_2 \pm \beta_1\alpha_2)$$

+: eigenvalue 2 $\Rightarrow S = 1$ −: eigenvalue 0 $\Rightarrow S = 0$

SYMBOLS $\hat{S}_+$ acts on electron 1 or 2 in turn (it is a sum); only the β of electron 2 can be raised here (1 ± 1): $1 + 1 = 2$ for the sum, $1 - 1 = 0$ for the difference

Triplet and singlet spin functions

The four two-electron spin states

$$\Theta_{1,+1} = \alpha_1\alpha_2$$

$$\Theta_{1,0} = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2)$$

$$\Theta_{1,-1} = \beta_1\beta_2$$

$$\Theta_{0,0} = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$$

- triplet spin functions are symmetric under $1 \leftrightarrow 2$
- the singlet is antisymmetric
- total must be antisymmetric, so

	space	spin
triplet	anti	sym
singlet	sym	anti

▸ $\frac{1}{\sqrt{2}}$: *the two products are orthonormal, so the sum has norm² 2*

✓ T1: $\hat{S}^2, \hat{S}_z$ as 4×4 matrices in SymPy; all eigen-relations exact.

SYMBOLS Θ_{S,M_S}: two-electron spin function with total spin S and projection M_S symmetric: unchanged when $1 \leftrightarrow 2$; antisymmetric: changes sign (anti)×(sym) = anti, as required

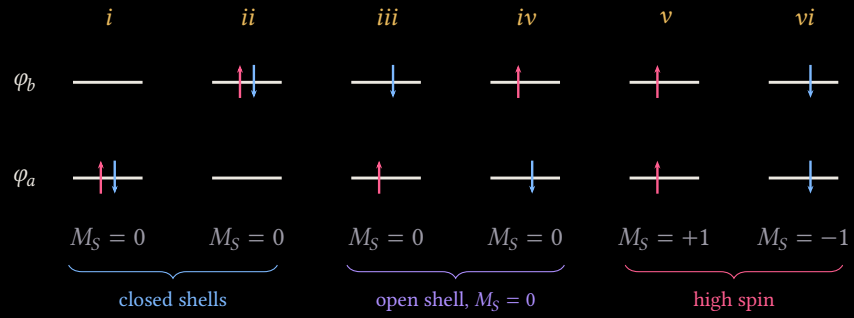
Part IV

Two electrons, two orbitals

IV

Six ways to place two electrons

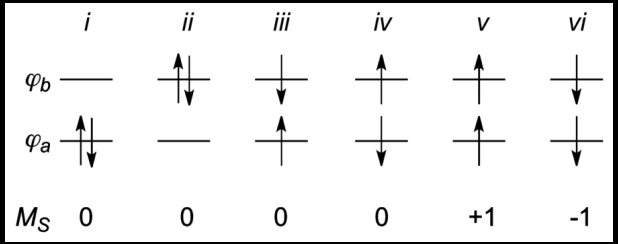
Figure 1 of the review, rebuilt



four spin orbitals $\varphi_a\alpha, \varphi_a\beta, \varphi_b\alpha, \varphi_b\beta$; choose 2 of 4 $\Rightarrow \binom{4}{2} = 6$ determinants

SYMBOLS φ_a, φ_b: the two spatial orbitals (real, orthonormal), e.g. the two frontier orbitals of a diradical $\uparrow/\downarrow$: electron with spin α/β M_S: total S_z = sum of $+\frac{1}{2}$ per $\uparrow$ and $-\frac{1}{2}$ per $\downarrow$

The paper's Figure 1



The paper says

"Various arrangements (determinants) of two electrons in two molecular orbitals and the corresponding values of the secondary spin quantum number." (p. 441)

Matches our reconstruction. Now write each one out.

symbols "secondary spin quantum number" = M_S, the projection of the total spin on the z axis

Writing the determinants out

shorthand: $A \equiv \varphi_a(1)\varphi_b(2)$ (electron 1 in φ_a, 2 in φ_b), $B \equiv \varphi_b(1)\varphi_a(2)$ (swapped)

	spin orbitals χ_1, χ_2	$D = \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2)$
i	$\varphi_a\alpha,\ \varphi_a\beta$	$\varphi_a(1)\varphi_a(2)\,(\alpha_1\beta_2 - \beta_1\alpha_2)$
ii	$\varphi_b\alpha,\ \varphi_b\beta$	$\varphi_b(1)\varphi_b(2)\,(\alpha_1\beta_2 - \beta_1\alpha_2)$
iii	$\varphi_a\alpha,\ \varphi_b\beta$	$A\,\alpha_1\beta_2 - B\,\beta_1\alpha_2$
iv	$\varphi_a\beta,\ \varphi_b\alpha$	$A\,\beta_1\alpha_2 - B\,\alpha_1\beta_2$
v	$\varphi_a\alpha,\ \varphi_b\alpha$	$(A - B)\,\alpha_1\alpha_2$
vi	$\varphi_a\beta,\ \varphi_b\beta$	$(A - B)\,\beta_1\beta_2$

e.g. iii: $\chi_1 = \varphi_a\alpha,\ \chi_2 = \varphi_b\beta$: $\varphi_a(1)\alpha_1\,\varphi_b(2)\beta_2 - \varphi_b(1)\beta_1\,\varphi_a(2)\alpha_2$

▸ *in each product the spatial part and the spin part of the same electron travel together*

SYMBOLS D_X: *unnormalised* determinant of row X (its normalised form is $\frac{1}{\sqrt{2}}D$) $\varphi_a(1)$: orbital φ_a evaluated at electron 1's position $\mathbf{r}_1$ $\alpha_1\beta_2$: electron 1 up, electron 2 down

$M_S = \pm 1$: one determinant each

$$\frac{1}{\sqrt{2}} D_{\mathrm{v}} = \underbrace{\frac{1}{\sqrt{2}}\left[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\right]}_{\text{antisymmetric space}} \underbrace{\alpha_1\alpha_2}_{\Theta_{1,+1}} \qquad \textit{row v: } (A-B)\,\alpha_1\alpha_2$$

$$\frac{1}{\sqrt{2}} D_{\mathrm{vi}} = \frac{1}{\sqrt{2}}\left[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\right] \beta_1\beta_2 \qquad \textit{same space, both spins down}$$

The paper says

"${}^3\Psi(M_s = +1) = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)][\alpha_1\alpha_2]$" … "i.e., they can be represented as single determinants v and vi" (p. 441; $M_s = -1$ analogous with $\beta_1\beta_2$)

VERIFIED exactly right: the high-spin triplet components are single-reference.

SYMBOLS ${}^3\Psi$: triplet ($2S+1 = 3$) one determinant already factorises into (space)×(spin of definite S) $\frac{1}{\sqrt{2}}$ normalises $A - B$, since $\langle A-B|A-B\rangle = 2$

$M_S = 0$: *iii and iv are not spin eigenfunctions*

$$D_{\text{iii}} = A \underbrace{\alpha_1\beta_2}_{\text{not }\Theta} - B \underbrace{\beta_1\alpha_2}_{\text{not }\Theta}$$

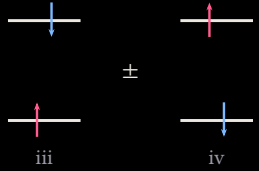
From the spin slides:

$$\hat{S}^2\alpha_1\beta_2 = \alpha_1\beta_2 + \beta_1\alpha_2 \neq \lambda\,\alpha_1\beta_2$$

so D_{iii} is half singlet, half triplet.

Only combinations of iii and iv have definite spin.

- *"half and half":* $\alpha_1\beta_2 = \frac{1}{\sqrt{2}}(\Theta_{1,0} + \Theta_{0,0})$, *so* $\langle \hat{S}^2| = \rangle \frac{1}{2}\cdot 2 + \frac{1}{2}\cdot 0 = 1$ *(T1b measures exactly 1)*



SYMBOLS Θ: a spin eigenfunction (definite S) λ: would-be eigenvalue eigenfunction: $\hat{S}^2 f = \lambda f$ with the *same* f on both sides

The sum $D_{iii} + D_{iv}$, every term tracked

$$
\begin{aligned}
D_{\mathrm{iii}} + D_{\mathrm{iv}} &= A\,\alpha_1\beta_2 - B\,\beta_1\alpha_2 + A\,\beta_1\alpha_2 - B\,\alpha_1\beta_2 && \textit{rows iii, iv}\\
&= A\,(\alpha_1\beta_2 + \beta_1\alpha_2) - B\,(\beta_1\alpha_2 + \alpha_1\beta_2) && \textit{collect A, B}\\
&= (A - B)\,(\alpha_1\beta_2 + \beta_1\alpha_2) && \textit{same bracket}\\
&= \underbrace{\left[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\right]}_{\text{antisymmetric space}}\ \underbrace{(\alpha_1\beta_2 + \beta_1\alpha_2)}_{\sqrt{2}\,\Theta_{1,0}} && \textit{put A, B back}
\end{aligned}
$$

Result

antisymmetric space × symmetric spin: the *sum* is the $M_S = 0$ triplet.

SYMBOLS $A = \varphi_a(1)\varphi_b(2)$, $B = \varphi_b(1)\varphi_a(2)$ $A - B$ changes sign under $1 \leftrightarrow 2$ (antisymmetric) $\Theta_{1,0} = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2)$: triplet, $M_S = 0$

The difference $D_{iv} - D_{iii}$

$$
\begin{aligned}
D_{\mathrm{iv}} - D_{\mathrm{iii}} &= A\,\beta_1\alpha_2 - B\,\alpha_1\beta_2 - A\,\alpha_1\beta_2 + B\,\beta_1\alpha_2 && \textit{iv minus iii}\\
&= A\,(\beta_1\alpha_2 - \alpha_1\beta_2) + B\,(\beta_1\alpha_2 - \alpha_1\beta_2) && \textit{collect A and B}\\
&= (A + B)\,(\beta_1\alpha_2 - \alpha_1\beta_2) && \textit{common bracket}\\
&= \underbrace{\left[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)\right]}_{\text{symmetric space}}\ \underbrace{(\beta_1\alpha_2 - \alpha_1\beta_2)}_{-\sqrt{2}\,\Theta_{0,0}} && \textit{put A, B back}
\end{aligned}
$$

Result

symmetric space × antisymmetric spin: the *difference* is the open-shell singlet.

SYMBOLS $A + B$ is unchanged under $1 \leftrightarrow 2$ (symmetric) $\Theta_{0,0} = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)$: singlet; $\beta_1\alpha_2 - \alpha_1\beta_2 = -\sqrt{2}\,\Theta_{0,0}$ (overall sign of a state is irrelevant)

Normalisation

$$\langle A \pm B | A \pm B \rangle = \langle A|A\rangle + \langle B|B\rangle \pm 2\langle A|B\rangle \qquad \textit{expand}$$

$$\langle A|A\rangle = \langle \varphi_a|\varphi_a\rangle\langle \varphi_b|\varphi_b\rangle = 1 \qquad \textit{split the integrals}$$

$$\langle A|B\rangle = \langle \varphi_a|\varphi_b\rangle\langle \varphi_b|\varphi_a\rangle = \cancel{0 \cdot 0} = 0 \qquad \textit{orthogonal}$$

$$\Rightarrow \langle A \pm B | A \pm B \rangle = 2$$

each combination needs $\dfrac{1}{\sqrt{2}} \cdot \dfrac{1}{\sqrt{2}} = \dfrac{1}{2}$

- *spin part likewise:* $\|\alpha_1\beta_2 \pm \beta_1\alpha_2\|^2 = 2$*; one* $\frac{1}{\sqrt{2}}$ *for space, one for spin*

Result

$$^3\Psi_0 = \frac{1}{2}(D_{\mathrm{iii}} + D_{\mathrm{iv}})$$

$$^1\Psi_{\mathrm{OSS}} = \frac{1}{2}(D_{\mathrm{iv}} - D_{\mathrm{iii}})$$

SYMBOLS $\langle f|g\rangle = \iint f^* g \, \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$ (spin sums for spin functions) $\|f\|^2 = \langle f|f\rangle$ $^3\Psi_0$: triplet, $M_S = 0$ $^1\Psi_{\mathrm{OSS}}$: open-shell singlet

Now read the paper

spot the difference

requires multiple configurations. For example, the open-shell singlet wavefunction

$$^1\Psi_{(M_s=0)} = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)] * \frac{1}{\sqrt{2}}[\beta_1\alpha_2 - \alpha_1\beta_2]$$

is a combination of two determinants, *iii* and *iv*:

$$^1\Psi_{(M_s=0)} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_a(1)\alpha_1 & \varphi_b(1)\beta_1\\ \varphi_a(2)\alpha_2 & \varphi_b(2)\beta_2\end{vmatrix} + \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_a(1)\beta_1 & \varphi_b(1)\alpha_1\\ \varphi_a(2)\beta_2 & \varphi_b(2)\alpha_2\end{vmatrix}\right]$$

Line 1 (product form) … then “is a combination of two determinants, iii and iv:”

SYMBOLS the paper writes each determinant with rows = electrons 1, 2 and columns = spin orbitals, exactly our D_{iii} and D_{iv}; its prefactor $\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} = \frac{1}{2}$ matches ours

Spotted it

requires multiple configurations. For example, the open-shell singlet wavefunction

$$^1\Psi_{(M_s=0)} = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)] * \frac{1}{\sqrt{2}}[\beta_1\alpha_2 - \alpha_1\beta_2]$$

is a combination of two determinants, *iii* and *iv*:

$$^1\Psi_{(M_s=0)} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_a(1)\alpha_1 & \varphi_b(1)\beta_1\\ \varphi_a(2)\alpha_2 & \varphi_b(2)\beta_2\end{vmatrix} + \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_a(1)\beta_1 & \varphi_b(1)\alpha_1\\ \varphi_a(2)\beta_2 & \varphi_b(2)\alpha_2\end{vmatrix}\right]$$

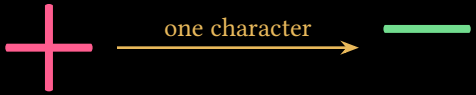
- green: product form, symmetric space × antisymmetric spin VERIFIED
- rose: $\frac{1}{2}(D_{\text{iii}} + D_{\text{iv}})$ is what we just proved to be the triplet ERROR

Erratum

should read $\frac{1}{2}(D_{\text{iv}} - D_{\text{iii}})$

SYMBOLS the two lines contradict each other: line 1 (green) equals $\frac{1}{2}(D_{\text{iv}} - D_{\text{iii}})$; line 2 (rose) does not

Fluctuating multiplicity, live in print



The section is titled *"Fluctuating ground-state multiplicity"*…

…and between two lines the open-shell singlet fluctuates into a triplet.

(It survived peer review and typesetting. Two referees with parallel spins, presumably: the Fermi hole kept them from ever meeting the error.)

Checked three ways: SymPy, $\hat{S}^2$, Lean

SymPy (T1): symbolic expansion

```
3Psi(0)  = (iii+iv)/2          : True
1Psi_OSS = (iv-iii)/2          : True
paper's (iii+iv)/2 == OSS ?    : False
```

$\hat{S}^2$ as an operator (T1b): the paper's matrices on a grid

```
paper:   (1/2)(|iii| + |iv|)  <S^2> = +2.000000  TRIPLET
correct: (1/2)(|iv| - |iii|)  <S^2> = +0.000000  SINGLET
paper's product form (line 1) <S^2> = +0.000000  SINGLET
```

Lean 4 + Mathlib (T17): machine-checked

```
theorem sum_is_triplet (A B ab ba : R) :
    Diii A B ab ba + Div A B ab ba
      = (A - B) * (ab + ba) := by
  unfold Diii Div; ring

theorem erratum_plus_is_not_singlet :
    ¬ (∀ A B ab ba : ℤ,
      Diii A B ab ba + Div A B ab ba
        = (A + B) * (ba - ab)) := by
  intro h
  have := h 1 0 1 0
  simp [Diii, Div] at this
```

SYMBOLS T1b builds the two-electron wavefunctions as numerical tensors from random orthonormal orbitals and applies $\hat{S}^2 = (\hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2)^2$ directly: no algebra is shared with T1 $\langle S^2 \rangle = S(S+1)$: 2 triplet, 0 singlet

What the two-electron problem teaches

- three singlets: i, ii, OSS
- one triplet (three M_S components)
- triplet $M_S = \pm 1$: single determinants (v, vi); $M_S = 0$ needs iii+iv
- open-shell singlet: *irreducibly* two determinants, for every M_S

The paper says

"their triplet state is therefore accurately described by a single reference determinant, however open-shell singlets require multiconfigurational (multireference) treatment." (p. 441)

VERIFIED conclusion right, despite the typo

SYMBOLS single-reference: one determinant is a good starting point (the high-spin component suffices) multireference: several determinants with comparable weights are needed from the start

Part V

Energies: J and K



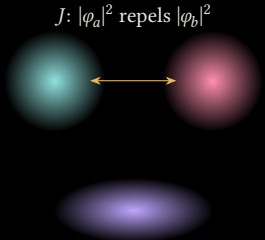
The integrals we need

$$h_{pq} = \int \varphi_p(\mathbf{r})\, \hat{h}\, \varphi_q(\mathbf{r})\, \mathrm{d}\mathbf{r} \qquad \textit{one electron}$$

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

$$J_{pq} = (pp|qq) \qquad \textit{Coulomb}$$

$$K_{pq} = (pq|pq) \qquad \textit{exchange}$$



- $(pq|rs)$: *electron 1 sits in the "charge" $\varphi_p\varphi_q$, electron 2 in $\varphi_r\varphi_s$; they repel as $1/r_{12}$*
- *J: two ordinary charge clouds $|\varphi_a|^2$ and $|\varphi_b|^2$ repelling: classical electrostatics*
- *K: no classical analogue; it comes from antisymmetry (the swapped term B) and is the overlap density $\varphi_a\varphi_b$ repelling itself*

SYMBOLS $\hat{h}$: one-electron Hamiltonian (kinetic + nuclear attraction) h_{pq}: its matrix element; $h_p \equiv h_{pp}$ = energy of one electron in φ_p without the others $\mathrm{d}\mathbf{r}$: volume element $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ chemists' notation $(pq|rs)$: first pair = electron 1

Two elementary integrals

assume real orthonormal orbitals, $\langle\varphi_p|\varphi_q\rangle = \delta_{pq}$; $\hat{h}(1)$ acts only on electron 1

$$\langle\varphi_p(1)\varphi_q(2)|\hat{h}(1)|\varphi_r(1)\varphi_s(2)\rangle = \underbrace{\langle\varphi_p|\hat{h}|\varphi_r\rangle}_{h_{pr}}\ \underbrace{\langle\varphi_q|\varphi_s\rangle}_{\delta_{qs}}$$

the $\mathrm{d}\mathbf{r}_1$ and $\mathrm{d}\mathbf{r}_2$ integrals separate

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

same, roles swapped

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

$1/r_{12}$ ties them: no splitting

- *bookkeeping rule: electron 1 carries the indices p, r (bra, ket), electron 2 carries q, s*

SYMBOLS $\langle f|g\rangle = \int f\, g\, \mathrm{d}\mathbf{r}$ for real orbitals $\langle f|\hat{O}|g\rangle = \int f\, \hat{O}\, g\, \mathrm{d}\mathbf{r}$ $\delta_{qs} = 1$ if $q = s$, else 0 bra $\langle\cdot|$: left function, ket $|\cdot\rangle$: right function

Triplet energy, step by step (1/2)

$$\Psi_T = \underbrace{\frac{1}{\sqrt{2}}(A - B)}_{\Phi_T \text{ (space)}} \Theta_{1,M}, \qquad \hat{H} = \hat{h}(1) + \hat{h}(2) + r_{12}^{-1} \text{ (no spin)} \Rightarrow E_T = \langle \Phi_T | \hat{H} | \Phi_T \rangle \langle \Theta | \Theta \rangle, \text{ with}$$

$\langle \Theta | \Theta \rangle = 1$

One-electron part ($\frac{1}{2}$ from $(\frac{1}{\sqrt{2}})^2$; four terms: AA, BB, $-AB$, $-BA$)

$$\langle A | \hat{h}(1) + \hat{h}(2) | A \rangle = h_{aa} \cdot 1 + 1 \cdot h_{bb} = h_a + h_b \qquad p = r = a, q = s = b$$

$$\langle B | \hat{h}(1) + \hat{h}(2) | B \rangle = h_{bb} + h_{aa} \qquad \text{orbitals swapped}$$

$$\langle A | \hat{h}(1) + \hat{h}(2) | B \rangle = h_{ab} \underbrace{\delta_{ba}}_{0} + \underbrace{\delta_{ab}}_{0} h_{ba} = 0 \qquad \text{orthogonality kills it}$$

$$\frac{1}{2}\big[(h_a + h_b) + (h_a + h_b) - 0 - 0\big] = \boxed{h_a + h_b}$$

SYMBOLS Ψ_T: full triplet wavefunction (space × spin) Φ_T: its spatial part $A = \varphi_a(1)\varphi_b(2)$, $B = \varphi_b(1)\varphi_a(2)$ $\Theta_{1,M}$: any triplet spin function; the result is the same for $M = 0, \pm 1$

Triplet energy, step by step (2/2)

Two-electron part (same four terms, now with $1/r_{12}$)

$$\langle A|r_{12}^{-1}|A\rangle = (aa|bb) = J_{ab} \qquad p,r=a;\ q,s=b\text{: two charge clouds}$$

$$\langle B|r_{12}^{-1}|B\rangle = (bb|aa) = J_{ab} \qquad \text{same clouds, labels swapped}$$

$$\langle A|r_{12}^{-1}|B\rangle = (ab|ba) = K_{ab} \qquad p=a,r=b;\ q=b,s=a\text{: overlap densities}$$

$$\tfrac{1}{2}\big[J + J - K - K\big] = J_{ab} - K_{ab} \qquad \text{the minus of } A-B$$

Result

$$E_T = h_a + h_b + J_{ab} - K_{ab}$$ (the cross terms carry the sign of the combination)

SYMBOLS $(ab|ba) = (ab|ab) = K_{ab}$ for real orbitals (8-fold symmetry) $J_{ab} \geq K_{ab} \geq 0$ (proved in Part VI)

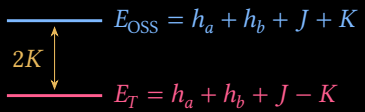
Open-shell singlet and the gap

$\Psi_{\mathrm{OSS}} = \frac{1}{\sqrt{2}}(A + B)\,\Theta_{0,0}$: identical steps, but the cross terms enter with +

$$E_{\mathrm{OSS}} = h_a + h_b + \tfrac{1}{2}\big[J + J + K + K\big] \qquad \textit{the + of } A + B$$

$$= h_a + h_b + J_{ab} + K_{ab}$$

$$E_{\mathrm{OSS}} - E_T = (J_{ab} + K_{ab}) - (J_{ab} - K_{ab}) = \boxed{2K_{ab}} \qquad \textit{h and J cancel}$$



SYMBOLS same orbitals in both states (“frozen orbitals”) the whole singlet–triplet splitting is carried by the exchange integral K_{ab}

The closed shells and their couplings

Diagonal (both electrons in one orbital)

$$E_{\mathrm{i}} = 2h_a + J_{aa}$$
$$E_{\mathrm{ii}} = 2h_b + J_{bb}$$

▸ *two electrons in φ_a: $2h_a$, plus one repulsion J_{aa} of the cloud $|\varphi_a|^2$ with itself*

i – ii: one-electron terms vanish ($\delta_{ab} = 0$)

$$\langle \varphi_a\varphi_a | r_{12}^{-1} | \varphi_b\varphi_b \rangle = (ab|ab) = K_{ab}$$

i – OSS

$$\langle \Phi_{\mathrm{i}} | \hat{H} | \Phi_{\mathrm{OSS}} \rangle = \tfrac{1}{\sqrt{2}} \left[\langle \varphi_a\varphi_a | \hat{H} | A \rangle + \langle \varphi_a\varphi_a | \hat{H} | B \rangle \right]$$
$$\langle \varphi_a\varphi_a | \hat{h}(1) + \hat{h}(2) | A \rangle = 0 + h_{ab}$$
$$\langle \varphi_a\varphi_a | r_{12}^{-1} | A \rangle = (aa|ab) = \langle \varphi_a\varphi_a | r_{12}^{-1} | B \rangle$$
$$\Rightarrow \quad = \sqrt{2}\left(h_{ab} + (aa|ab)\right)$$

▸ *$\hat{h}(1)$ term: $h_{aa}\langle\varphi_a|\varphi_b\rangle = 0$; $\hat{h}(2)$ term: $\langle\varphi_a|\varphi_a\rangle h_{ab} = h_{ab}$*

SYMBOLS $\Phi_{\mathrm{i}} = \varphi_a(1)\varphi_a(2)$: closed shell i (spin part $\Theta_{0,0}$) $\quad \Phi_{\mathrm{OSS}} = \frac{1}{\sqrt{2}}(A + B)$ states of different S never couple (their spin parts are orthogonal)

The full two-electron, two-orbital Hamiltonian

basis $\{\Phi_{\mathrm{i}}, \Phi_{\mathrm{ii}}, \Phi_{\mathrm{OSS}}\}$ (singlets) + the triplet on its own

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

▸ *diagonalising $\mathbf{H}_S$ gives the three exact singlet energies of this model; the matrix is symmetric ($\cdot$ = mirror entries)*

orbitals of different symmetry (e.g. σ_g/σ_u of H_2) $\Rightarrow h_{ab} = (aa|ab) = (bb|ba) = 0$: the OSS decouples

T2: BRUTE FORCE

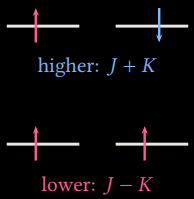
5 random integral sets (positive-definite kernel) → PySCF full CI: singlet and triplet roots reproduce these closed forms to $2 \times 10^{-14}\ E_{\mathrm{h}}$.

SYMBOLS $\mathbf{H}_S$: Hamiltonian matrix in the singlet configurations full CI: exact diagonalisation in all determinants E_{h}: hartree (27.211 eV)

Hund's rule at frozen orbitals

The review states Hund's rule (p. 442)

> "of the different multiplets resulting from different configurations of electrons in degenerate orbitals of an atom those with greatest multiplicity have the lowest energy"



With the *same* orbitals in both states:

$$E_T - E_{\mathrm{OSS}} = -2K_{ab} < 0 \quad \text{if } K_{ab} > 0$$

Two things to prove: $K \geq 0$ (next part), and whether "same orbitals" is legitimate (it is not).

SYMBOLS multiplicity $2S+1$: 3 for the triplet, 1 for the singlet Hund's rule (1925) was found empirically from atomic spectra; the wording quoted is the review's, citing the IUPAC Gold Book

Part VI

Fermi holes

VI

Where can the two electrons be?

the pair density

$P(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1 \sigma_2} \int |\Psi|^2 \, \mathrm{d}x_3 \cdots \mathrm{d}x_N$

▸ *probability density for "one electron at $\mathbf{r}_1$ and another at $\mathbf{r}_2$"*

two electrons, spin summed:

$$P_T = \left[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\right]^2$$

$$P_{\mathrm{OSS}} = \left[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)\right]^2$$

▸ *$N(N-1) = 2$ cancels the $(\frac{1}{\sqrt{2}})^2$; the spin sum gives $\sum |\Theta|^2 = 1$*

set $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$: $\quad P_T(\mathbf{r}, \mathbf{r}) = 0$,

$P_{\mathrm{OSS}}(\mathbf{r}, \mathbf{r}) = 4\varphi_a^2 \varphi_b^2$

Fermi hole

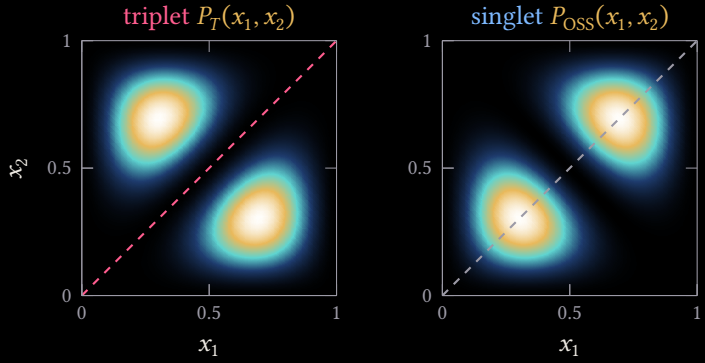
in the triplet the two electrons are *never* at the same point, for every M_S; exact, no approximation beyond the form of Ψ

The *Coulomb* hole (caused by $1/r_{12}$ itself) is absent here: it needs correlation beyond one configuration (dynamic correlation, review p. 442).

SYMBOLS $x_k = (\mathbf{r}_k, \sigma_k)$ $\int \mathrm{d}x$: integrate over position, sum over spin P_T: pair density of the triplet; P_{OSS}: of the open-shell singlet $[A-B]^2$ vanishes when $\mathbf{r}_1 = \mathbf{r}_2$ because then $A = B$

Seeing the Fermi hole

two electrons in a 1-D box, orbitals $\sin \pi x$ *and* $\sin 2\pi x$



dashed line $x_1 = x_2$: dark all along for the triplet, bright for the singlet

SYMBOLS box orbitals $\varphi_a = \sqrt{2} \sin \pi x$, $\varphi_b = \sqrt{2} \sin 2\pi x$ on $0 \le x \le 1$ (normalised; prefactor $(\sqrt{2})^4 = 4$) colour = probability density of finding electron 1 at x_1 and electron 2 at x_2 (black 0, white high)

$K_{ab} \geq 0$: *a three-line proof*

overlap density $\rho(\mathbf{r}) = \varphi_a(\mathbf{r})\varphi_b(\mathbf{r})$ (real) $\quad\Rightarrow\quad K_{ab} = \iint \dfrac{\rho(1)\rho(2)}{r_{12}}$

(1) $$\frac{1}{|\mathbf{r}|} = \int \frac{\mathrm{d}^3k}{(2\pi)^3}\,\frac{4\pi}{k^2}\,e^{i\mathbf{k}\cdot\mathbf{r}}$$ *$1/r$ as a sum of plane waves, all with positive weight $4\pi/k^2$*

(2) $$K_{ab} = \int \frac{\mathrm{d}^3k}{(2\pi)^3}\,\frac{4\pi}{k^2}\,\underbrace{\left(\int \rho\, e^{i\mathbf{k}\cdot\mathbf{r}_1}\right)}_{\tilde\rho(\mathbf{k})^*}\underbrace{\left(\int \rho\, e^{-i\mathbf{k}\cdot\mathbf{r}_2}\right)}_{\tilde\rho(\mathbf{k})}$$ *insert with $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$; integrals separate*

(3) $$= \int \frac{\mathrm{d}^3k}{(2\pi)^3}\,\frac{4\pi}{k^2}\,|\tilde\rho(\mathbf{k})|^2 \geq 0$$ *ρ real $\Rightarrow$ the two factors are complex conjugates*

▸ *a positive weight times a square, integrated: it can never be negative*

equality iff $\varphi_a\varphi_b \equiv 0$ (no common region of space): this returns as *disjointness*

SYMBOLS $\rho = \varphi_a\varphi_b$: overlap density (integrates to 0, but is not zero pointwise) $\mathbf{k}$: wave vector, $k = |\mathbf{k}|$ $\tilde\rho(\mathbf{k}) = \int \rho(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}\mathrm{d}\mathbf{r}$: Fourier transform $|z|^2 = z^*z$

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

(1) $f = \varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2) \qquad = A - B$

(2) $0 \leq \iint \frac{f^2}{r_{12}} \qquad f^2 \geq 0 \text{ and } 1/r_{12} > 0$

$= J_{ab} + J_{ab} - K_{ab} - K_{ab} \qquad f^2 = A^2 + B^2 - 2AB$

$= 2(J_{ab} - K_{ab})$

$$\boxed{J_{ab} \geq K_{ab} \geq 0}$$

▸ *so the triplet's repulsion $J - K$ is never negative, and lies below the singlet's $J + K$*

T3

all canonical RHF/6-31G orbitals of H_2O:
$\min K_{pq} = 1.1 \times 10^{-3}\ E_h > 0$
and $J_{pq} \geq K_{pq}$ for every pair

so $E_T = h_a + h_b + J - K$ really is the lower of the two.

SYMBOLS $\iint A^2/r_{12} = \iint B^2/r_{12} = J_{ab}$ and $\iint AB/r_{12} = K_{ab}$ (the same integrals as in Part V) RHF/6-31G: Hartree–Fock orbitals in a standard Gaussian basis

Part VII

Hund's rule

VII

Two explanations of the same rule

The paper says

Slater's explanation: "less electron–electron Coulomb repulsion in the triplet state" … "However, … the electron–electron repulsion is actually greater in the high-spin state" — hence the "less screening rule" (p. 442)

Slater's argument, read with frozen orbitals

$\Delta V_{ee} = -2K < 0,\ \Delta T = 0,\ \Delta V_{ne} = 0$

triplet wins by lower repulsion

Less screening (relaxed orbitals)

$\Delta V_{ee} > 0,\ \Delta V_{ne} \ll 0,\ \Delta T > 0$

triplet wins by stronger nuclear attraction

Which is right? The virial theorem plus the computed sign of ΔV_{ee} decides.

SYMBOLS $\Delta X \equiv X(\text{triplet}) - X(\text{singlet})$ T: kinetic energy V_{ne}: electron–nucleus attraction (< 0) V_{ee}: electron–electron repulsion (> 0) screening: one electron's charge partly cancelling the nucleus' pull on another

The virial theorem by scaling (1/2)

assume an atom (nucleus at the origin); Ψ exact, or optimised with respect to scaling

---

$$\text{(1)}\quad \Psi_\eta(\mathbf{r}_1, \dots, \mathbf{r}_N) = \eta^{3N/2}\, \Psi(\eta\mathbf{r}_1, \dots, \eta\mathbf{r}_N) \qquad \textit{squeeze } (\eta > 1) \textit{ or stretch } (\eta < 1) \textit{ the whole cloud}$$

$$\text{(2)}\quad \langle \Psi_\eta | \Psi_\eta \rangle = \eta^{3N} \int |\Psi(\eta\mathbf{r})|^2 \mathrm{d}^{3N} r \qquad \textit{the prefactor appears squared}$$

$$= \int |\Psi(\mathbf{s})|^2 \mathrm{d}^{3N} s = 1 \qquad \textit{substitute } \mathbf{s} = \eta\mathbf{r},\ \mathrm{d}^{3N} r = \eta^{-3N} \mathrm{d}^{3N} s$$

- *the scaled function is still normalised, so it is a legal trial function at every η*
- *the factor $\eta^{3N/2}$ exists only to keep the norm 1: 3 coordinates per electron, N electrons*

SYMBOLS η: scaling factor ($\eta = 1$ is the original Ψ) N: number of electrons $\mathrm{d}^{3N} r$: all $3N$ position coordinates $\mathbf{s}$: rescaled coordinates

The virial theorem by scaling (2/2)

$$\langle T\rangle_\eta = \eta^2\langle T\rangle \tag{3}$$ *T has two derivatives; $\nabla_{\mathbf{r}} = \eta\nabla_{\mathbf{s}}$ each*

$$\langle V\rangle_\eta = \eta\langle V\rangle \tag{4}$$ *every Coulomb term is $1/\text{distance}$: $\frac{1}{r} = \eta\frac{1}{s}$*

$$E(\eta) = \eta^2\langle T\rangle + \eta\langle V\rangle \tag{5}$$ *add them*

$$\left.\frac{\mathrm{d}E}{\mathrm{d}\eta}\right|_{\eta=1} = 2\langle T\rangle + \langle V\rangle = 0 \tag{6}$$ *exact state: stationary under any variation*

Result

$$2\langle T\rangle + \langle V\rangle = 0 \quad\Longrightarrow\quad E = \langle T\rangle + \langle V\rangle = -\langle T\rangle = \frac{1}{2}\langle V\rangle$$

SYMBOLS $\langle T\rangle, \langle V\rangle$: expectation values of kinetic and total potential energy $V = V_{ne} + V_{ee}$ for an atom virial ratio $-\langle V\rangle/\langle T\rangle = 2$ Lean: `scaling_derivative` molecules: same at equilibrium geometries

Frozen orbitals cannot be the mechanism

Apply the virial theorem to *both* exact states and subtract:

$$\Delta E \equiv E_T - E_S = -\Delta\langle T\rangle = \frac{1}{2}\big(\Delta\langle V_{ne}\rangle + \Delta\langle V_{ee}\rangle\big)$$

1. frozen-orbital model: same orbitals in both states $\Rightarrow \Delta\langle T\rangle = 0$
2. then the virial theorem forces $\Delta E = 0$, but the same model gives $\Delta E = -2K < 0$ contradiction

Result

frozen orbitals violate the virial theorem: they cannot tell *which* energy component pays

Hongo et al. 2004 (full text): "This assumption leaves the kinetic energy T unchanged … which cannot be correct as each eigenstate must satisfy the virial theorem."

symbols same orbitals $\Rightarrow$ same $\langle T\rangle$, because T is a one-electron operator summed over the same occupied orbitals exact states must obey $E = -\langle T\rangle$, so different E needs different $\langle T\rangle$

Less screening, as inequalities

assume triplet lower ($\Delta E < 0$), both states virial, $\Delta V_{ee} > 0$ (what the calculations show)

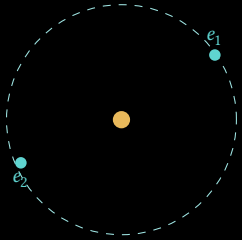
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(1)	$\Delta T = -\Delta E > 0$	*virial: $E = -T$; electrons more compressed*
(2)	$\Delta V = 2\Delta E < 0$	*virial: $E = \frac{1}{2}V$*
(3)	$\Delta V_{ne} = 2\Delta E - \Delta V_{ee} < 2\Delta E < 0$	*$V = V_{ne} + V_{ee}$, and $\Delta V_{ee} > 0$*
(4)	$\lvert\Delta V_{ne}\rvert > \Delta V_{ee}$	*from step 3*

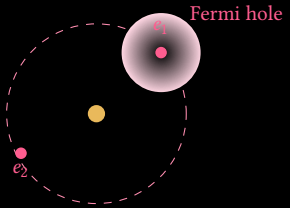
the nucleus wins: stronger attraction over-compensates stronger repulsion (Lean: `less_screening`)

SYMBOLS every inequality follows from the two virial identities and the measured sign of ΔV_{ee}; nothing else is assumed

The physical picture



singlet: electrons may overlap,
each screens the nucleus



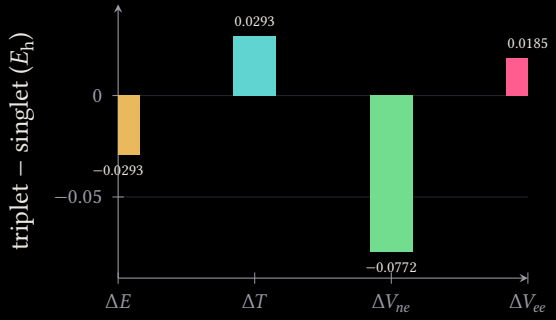
triplet: kept apart, less screening,
both contract towards the nucleus

contraction lowers V_{ne} • raises T • also raises V_{ee} (closer on average)

SYMBOLS dashed circle: size of the electron cloud shaded region: Fermi hole, where the other same-spin electron is absent e_1, e_2: the two electrons

Test 1: helium 1s2s, near-exact

T4 --- $2\,^3S$ vs $2\,^1S$, 16s7p4d basis (within 1.7×10^{-5} and 1.1×10^{-4} E_h of exact), scaled to satisfy the virial theorem



	$2\,^3S$	$2\,^1S$
E (ours)	−2.175212	−2.145865
E (exact)	−2.175229	−2.145974
$-\langle V\rangle/\langle T\rangle$	2.000000	2.000000

$\Delta V_{ee} > 0$: Slater's mechanism fails; ΔV_{ne} pays for everything.

check:
$\frac{1}{2}(-0.0772 + 0.0185) = -0.0293 = \Delta E$

SYMBOLS $2\,^3S$, $2\,^1S$: the 1*s*2*s* excited states of He, same configuration, triplet and singlet 16s7p4d: Gaussian basis functions of *s*, *p*, *d* type exact energies: Drake's benchmark values

Test 2: the carbon atom (literature)

Hongo et al., J. Chem. Phys. 121, 7144 (2004), Table I --- read from the arXiv full text

$^3P - {}^1D$ (E_h)	ΔV_{ee}	ΔV_{en}	ΔT
Hartree–Fock	+0.032	−0.145	+0.057
DMC (linear estimator)	+0.074	−0.169	+0.048

same pattern as helium: higher repulsion, much stronger attraction, higher kinetic energy

Result

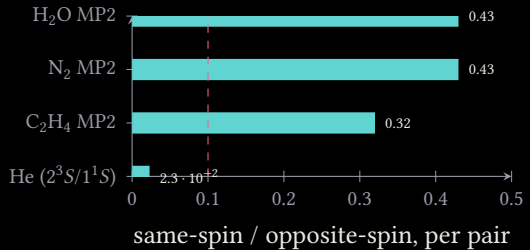
The review's account (less screening, V_{ee} *greater* in the high-spin state) agrees with He (ours) and C (Hongo). VERIFIED

SYMBOLS ^3P, ^1D: lowest triplet and singlet terms of the C atom ($2p^2$) DMC: diffusion quantum Monte Carlo, nearly exact correlation differences computed by us from their Table I

A side claim: same-spin correlation

The paper says

"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" (p. 442, citing Krylov 2001)



dashed: "order of magnitude" (0.1)

He: 0.023, the claim holds

molecular valence shells: ≈ 0.3–0.4 per pair (cf. SCS-MP2 scaling $\frac{1}{3}$ vs $\frac{6}{5}$)

OVERSTATED true for compact two-electron systems, overstated in general (T15)

SYMBOLS correlation energy = $E_{\text{exact}} - E_{\text{Hartree–Fock}}$ He: $2\,^3S$ has one same-spin pair, $1\,^1S$ one opposite-spin pair MP2: second-order perturbation theory, split into same-spin and opposite-spin parts, divided by the number of pairs

Part VIII

Static correlation

VIII

Static versus dynamic correlation

The paper says

> "The weaker the interaction between the two nonbonding molecular orbitals (MOs), the stronger the static correlation (Figure 2)." (p. 442)

dynamic: electrons dodging each other within one configuration

static: several configurations of comparable weight

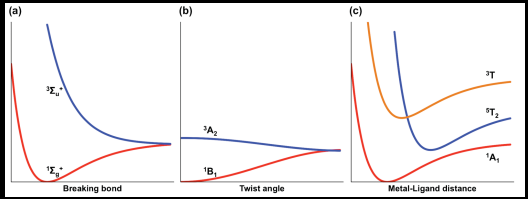


Fig. 2: (a) H_2 bond breaking (b) ethylene twist (c) metal–ligand distance

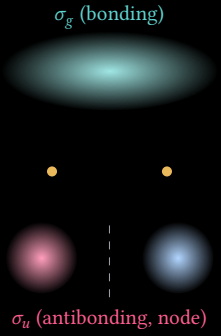
SYMBOLS correlation energy: what a single determinant (Hartree–Fock) misses configuration: one way of filling the orbitals (one determinant or spin-adapted combination) term symbols ($^1\Sigma_g^+$, $^3A_2$, ...): spin multiplicity and spatial symmetry of a state

$\mathcal{H}_2$ in a minimal basis

one 1s function per atom, χ_A, χ_B, overlap S:

$$\sigma_g \equiv \varphi_1 = \frac{\chi_A + \chi_B}{\sqrt{2(1+S)}}$$

$$\sigma_u \equiv \varphi_2 = \frac{\chi_A - \chi_B}{\sqrt{2(1-S)}}$$



- $\sqrt{2(1 \pm S)}$: $\langle \chi_A \pm \chi_B | \chi_A \pm \chi_B \rangle = 1 + 1 \pm 2S$

φ_1 even, φ_2 odd under inversion $\Rightarrow$
$h_{12} = (11|12) = (22|21) = 0$

- *an integral with an odd number of φ_2's has an odd integrand: it integrates to zero*

SYMBOLS χ_A, χ_B: hydrogen 1s atomic orbitals on nuclei A, B $S = \langle \chi_A | \chi_B \rangle$: their overlap g/u: even/odd under inversion through the bond centre indices 1, 2 below mean φ_1, φ_2

The 2 × 2 CI problem

the OSS ($^1\Sigma_u^+$) is alone; the two closed shells σ_g^2, σ_u^2 ($^1\Sigma_g^+$) mix:

$$\mathbf{H} = \begin{pmatrix} E_1 & K_{12} \\ K_{12} & E_2 \end{pmatrix}, \qquad E_1 = 2h_{11} + J_{11}\ \text{(RHF)}, \quad E_2 = 2h_{22} + J_{22}$$

- *the coupling K_{12} is the closed-shell/closed-shell element $\langle\Phi_i|\hat{H}|\Phi_{ii}\rangle$ derived in Part V*

$$\det(\mathbf{H} - E\mathbf{1}) = (E_1 - E)(E_2 - E) - K_{12}^2 = 0 \qquad \textit{eigenvalue condition}$$

$$E^2 - (E_1 + E_2)E + E_1E_2 - K_{12}^2 = 0 \qquad \textit{multiply out}$$

$$E_{\mathrm{CI}} = \frac{1}{2}\Big[E_1 + E_2 - \sqrt{(E_2 - E_1)^2 + 4K_{12}^2}\Big] \qquad \textit{lower root of the quadratic}$$

also: $E(^3\Sigma_u^+) = h_{11} + h_{22} + J_{12} - K_{12}, \quad E(^1\Sigma_u^+) = h_{11} + h_{22} + J_{12} + K_{12}$

SYMBOLS CI: configuration interaction (diagonalise $\hat{H}$ among several configurations) RHF: restricted Hartree–Fock, both electrons in σ_g $^3\Sigma_u^+$, $^1\Sigma_u^+$: the triplet and open-shell singlet of $\sigma_g^1\sigma_u^1$

Pulling the atoms apart (1/2): the integrals

assume $R \to \infty$: $S \to 0$, every overlap density $\chi_A\chi_B \to 0$; $U = (AA|AA)$, $V = (AA|BB) \to 1/R$

$$\varphi_1^2 = \tfrac{1}{2}(\chi_A^2 + \chi_B^2 + \cancel{2\chi_A\chi_B}) \to \tfrac{1}{2}(\chi_A^2 + \chi_B^2) \qquad \textit{the atoms no longer overlap}$$

$$\varphi_2^2 \to \tfrac{1}{2}(\chi_A^2 + \chi_B^2) \qquad \textit{same, minus sign gone}$$

$$\varphi_1\varphi_2 \to \tfrac{1}{2}(\chi_A^2 - \chi_B^2) \qquad \tfrac{1}{2}(\chi_A + \chi_B)(\chi_A - \chi_B)$$

$$J_{11} = J_{22} = J_{12} \to \tfrac{1}{4}\big[U + V + V + U\big] = \tfrac{1}{2}(U + V) \qquad \textit{4 cross terms of two } \tfrac{1}{2}\textit{-clouds}$$

$$K_{12} \to \tfrac{1}{4}\big[U - V - V + U\big] = \tfrac{1}{2}(U - V) \qquad \textit{the } \chi_B^2 \textit{ part enters with } -$$

and $h_{11} = h_{22} \to E_H - \frac{1}{R}$ (an electron on A still feels nucleus B as a point charge)

SYMBOLS R: H–H distance U: repulsion of two electrons on the *same* atom V: repulsion of electrons on *different* atoms ($\to 1/R$, two point charges) E_H: energy of an isolated H atom

Pulling the atoms apart (2/2): the energies

$$E_{\mathrm{RHF}} = 2h_{11} + J_{11} + \frac{1}{R} = 2E_H - \frac{2}{R} + \frac{U}{2} + \frac{V}{2} + \frac{1}{R} \overset{V=1/R}{=} 2E_H + \frac{U}{2} - \frac{1}{2R}$$

$$E_T = 2h_{11} + J_{12} - K_{12} + \frac{1}{R} = 2E_H - \frac{2}{R} + V + \frac{1}{R} \overset{V=1/R}{=} 2E_H$$

$$E_{\mathrm{CI}} = E_1 - K_{12}\ (E_1 = E_2) = 2E_H + \frac{U}{2} - \frac{1}{2R} - \frac{U-V}{2} \to 2E_H$$

$$E(^1\Sigma_u^+) = E_T + 2K_{12} \to 2E_H + U - V$$

- *RHF keeps $U/2$ because half of σ_g^2 is H^+H^-; in CI, $E_1 = E_2$ so the root is $E_1 - K_{12}$, and $K_{12} = \frac{U-V}{2}$ cancels it*

RHF misses the dissociation limit by $U/2$; one extra configuration fixes it exactly.

SYMBOLS $2E_H$: the correct limit, two separate H atoms $E_1 = 2h_{11} + J_{11}$, $E_2 = 2h_{22} + J_{22}$ become equal as $R \to \infty$

What the CI wavefunction is

at $R \to \infty$ the eigenvector is $c_1 = -c_2 = \frac{1}{\sqrt{2}}$ (two configurations, equal weight)

$$\varphi_1(1)\varphi_1(2) = \frac{1}{2}\big[\underbrace{\chi_A\chi_B + \chi_B\chi_A}_{\text{covalent}} + \underbrace{\chi_A\chi_A + \chi_B\chi_B}_{\text{ionic}}\big] \qquad \textit{expand } (\chi_A + \chi_B)^2/2$$

$$\varphi_1\varphi_1 - \varphi_2\varphi_2 = \frac{1}{2}\big[(\chi_A + \chi_B)^2 - (\chi_A - \chi_B)^2\big] \qquad \textit{the CI combination}$$

$$= \chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2) \qquad \textit{ionic terms cancel}$$

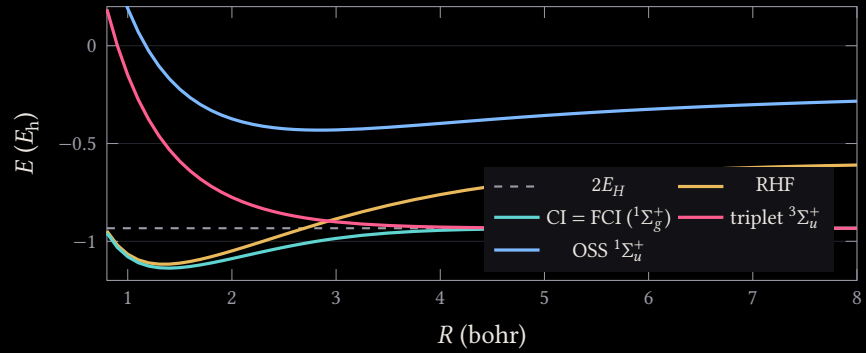
RHF: 50% ionic
H^+H^- at infinity costs $U/2$

CI: purely covalent
Heitler–London H· ·H

SYMBOLS covalent: one electron on each atom ionic: both electrons on one atom (H^- next to H^+) c_1, c_2: CI coefficients of σ_g^2 and σ_u^2 (shorthand $\chi_A\chi_B \equiv \chi_A(1)\chi_B(2)$)

H_2 curves from our calculation

STO-3G, PySCF; closed forms agree to $4 \times 10^{-16}\ E_\mathrm{h}$ *(T5)*



CI and triplet converge on $2E_H$; RHF does not (T5: still $0.362\ E_\mathrm{h} = K_{12}$ too high at $R = 20$ bohr)

SYMBOLS STO-3G: minimal Gaussian basis (one 1*s* function per H) FCI: full CI, exact in this basis bohr = 0.529 Å $2E_H = -0.9332\ E_\mathrm{h}$ in STO-3G

The general rule: orbital gap versus exchange

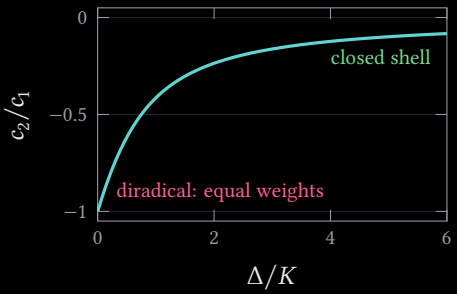
model: $h_a = -\frac{\Delta}{2}$, $h_b = +\frac{\Delta}{2}$, $J_{aa} = J_{bb} = J_d$, $J_{ab} = J_x$

$$\mathbf{H} = \begin{pmatrix} J_d - \Delta & K \\ K & J_d + \Delta \end{pmatrix}$$

$$E_S = J_d - \sqrt{\Delta^2 + K^2}$$

$$\frac{c_2}{c_1} = \frac{\Delta - \sqrt{\Delta^2 + K^2}}{K}$$

$$E_S - E_T = (J_d - J_x) + K - \sqrt{\Delta^2 + K^2}$$



VERIFIED weak interaction ⇒ strong static correlation (T6)

▸ *diagonal $2h + J$; E_S is the lower root; c_2/c_1 from row 1,* $(J_d - \Delta - E_S)c_1 + Kc_2 = 0$; $E_T = J_x - K$

SYMBOLS Fig. 2b: twisting ethylene to 90° closes the π/π^* gap ($\Delta \to 0$; standard result) $\Delta = h_b - h_a$ J_d: same-orbital repulsion, J_x: different-orbital $c_2/c_1 = -1$: two configurations of equal weight (a pure diradical); $\to 0$: one configuration

Part IX

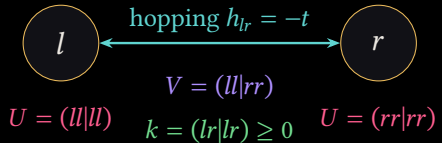
Kinetic exchange

IX

The Hubbard picture

The paper says

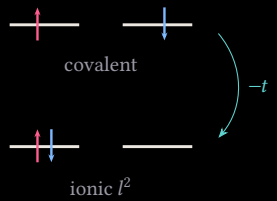
"The kinetic exchange picture based on the Hubbard model … attributes stability of a singlet state in the case of orthogonal atomic orbitals (AOs) to the fact that perturbation yielding ionic configuration is allowed only from this state, and not from the triplet." (p. 442)



SYMBOLS l, r: orthonormal orbitals localised on the left/right radical centre t: hopping (how easily an electron moves between them) U: cost of two electrons on one site V: repulsion between sites k: direct exchange between the sites

Step 1: ionic configurations are pure singlets

1. ionic: both electrons in one orbital, $l(1)l(2)$
2. that spatial part is symmetric: swapping 1 and 2 changes nothing
3. antisymmetry $\Rightarrow$ its spin part must be the antisymmetric singlet $\Theta_{0,0}$
4. $\hat{H}$ is spin-free, so $\langle \text{ionic}|\hat{H}|\text{triplet}\rangle \propto \langle \Theta_{0,0}|\Theta_{1,M}\rangle = 0$



Result

only the singlet can borrow from ionic configurations

symbols covalent: one electron on each site ionic: both on one site $\Theta_{0,0}, \Theta_{1,M}$: singlet / triplet spin functions, orthogonal to each other $\propto$: proportional to

Step 2: the matrix

insert the parameters into the $2e/2o$ Hamiltonian of Part V ($h_{ll} = h_{rr} = 0$, $(ll|lr) = 0$):

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

- *diagonal:* $2h + J$ *becomes* U *for* ll, rr; $h_l + h_r + J + K$ *becomes* $V + k$ *for cov; coupling* $\sqrt{2}(h_{lr} + (ll|lr)) = -\sqrt{2}t$

Step 3: symmetry-adapt the ionic pair, $\Phi_\pm = \frac{1}{\sqrt{2}}(ll \pm rr)$

$$E(\Phi_\pm) = U \pm k \qquad \tfrac{1}{2}(U + U \pm 2k)$$

$$\langle \Phi_\pm | \hat{H} | \mathrm{cov} \rangle = \frac{1}{\sqrt{2}}\left(-\sqrt{2}t \mp \sqrt{2}t\right) = \{-2t,\ 0\} \qquad \textit{the two couplings add or cancel}$$

Φ_- decouples; the ground singlet lives in $\{\mathrm{cov}, \Phi_+\}$

SYMBOLS ll, rr: the two ionic configurations cov: covalent open-shell singlet $\Phi_\pm$: their symmetric and antisymmetric combinations (left–right mirror symmetry)

Step 4: solve and expand

$$\begin{pmatrix} V+k & -2t \\ -2t & U+k \end{pmatrix} \Rightarrow E_S = \frac{1}{2}\Big[U+V+2k-\sqrt{(U-V)^2+16t^2}\Big] \qquad \textit{lower root}$$

$$E_S - E_T = \frac{1}{2}(U-V)+2k-\frac{1}{2}\sqrt{(U-V)^2+16t^2} \qquad \textit{subtract } V-k$$

$$\sqrt{x^2+16t^2} = x+\frac{8t^2}{x}+\cdots \qquad = 2k-\frac{4t^2}{U-V}+O\Big(\frac{t^4}{(U-V)^3}\Big) \qquad \textit{Taylor, } x=U-V\gg t$$

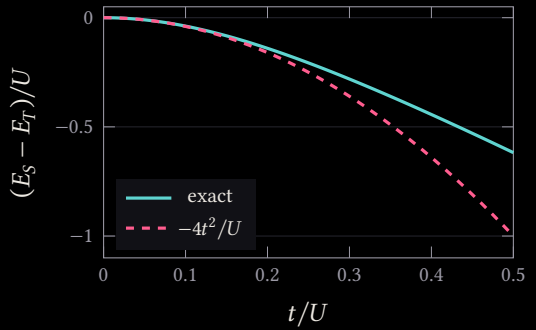
$+2k$: potential exchange, favours the triplet

$-4t^2/(U-V)$: kinetic exchange, favours the singlet

SYMBOLS kinetic exchange: second-order energy gain $|-2t|^2/[(V+k)-(U+k)]$ from virtual hopping into Φ_+; the triplet cannot do this $O(\cdot)$: terms of that order and smaller

Hubbard dimer: exact versus kinetic exchange

$V = k = 0$: $E_S = \frac{1}{2}\left(U - \sqrt{U^2 + 16t^2}\right)$, $E_T = 0$

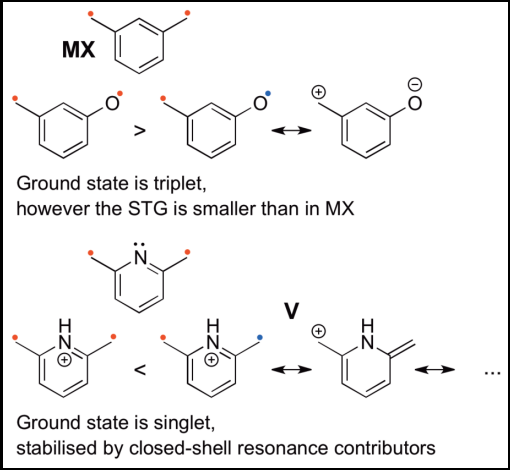


- agree for $t \ll U$ (strong correlation)
- spin Hamiltonian $J_{\mathrm{AF}}\,\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ with $J_{\mathrm{AF}} = 4t^2/U$
- this coupling, bond by bond, will build the *topology rules*

✓ T7: symbolic + PySCF FCI (t=1, U=6, V=1.5, k=0.2)

SYMBOLS Hubbard dimer: two sites, hopping t, on-site repulsion U only $J_{\mathrm{AF}} > 0$: antiferromagnetic coupling (antiparallel favoured) $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = -\frac{3}{4}$ (singlet), $+\frac{1}{4}$ (triplet)

Ionic resonance reverses a spin state (Figure 6)



The paper says

> "In the pyridinium analog of MX (V in Figure 6) this contribution exceeds the exchange and Coulomb terms, which formally favor the triplet state of this system with nondisjoint NBMOs." (p. 444–445)

low-lying zwitterionic structures = small effective $U - V$

$\Rightarrow 4t^2/(U - V)$ grows past $2k$ $\Rightarrow$ singlet (our qualitative mapping: the review gives no numbers)

SYMBOLS "this contribution": resonance with closed-shell zwitterionic (ionic) configurations MX: *m*-xylylene NBMO: non-bonding MO (Part X)

Delocalised and localised: two views of one state

$$a, b = \frac{1}{\sqrt{2}}(l \pm r) \quad \Rightarrow \quad a(1)a(2) - b(1)b(2) = l(1)r(2) + r(1)l(2)$$

▸ *expand:* $\frac{1}{2}[(l+r)(l+r) - (l-r)(l-r)]$*; the ll and rr (ionic) terms cancel, the cross terms add*

delocalised orbitals a, b

two closed-shell configurations of equal weight: static correlation

localised orbitals l, r

one covalent configuration with no ionic part

same state, different bookkeeping: the static-correlation and kinetic-exchange descriptions agree

SYMBOLS a, b: delocalised (bonding/antibonding-like) orbitals l, r: localised site orbitals the unitary rotation between them leaves the two-electron state unchanged

Part X

NBMOs & disjointness

X

Borden & Davidson's classification

The paper says

"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)

three things to derive: (1) how to find NBMOs, (2) when they can be disjoint, (3) why disjoint means $K \approx 0$

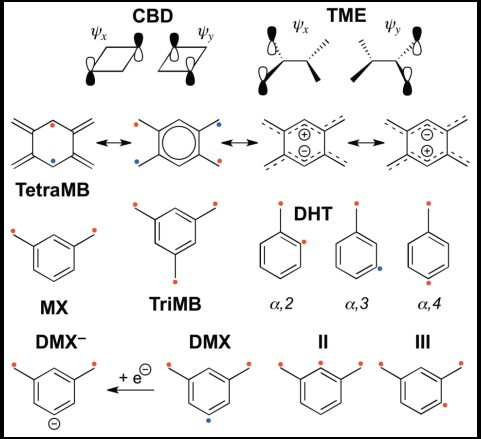


Fig. 3: high- and low-spin polyradicals

SYMBOLS NBMO: non-bonding MO, orbital energy equal to that of an isolated *p* orbital disjoint: the two NBMOs share no atom CBD cyclobutadiene, TME tetramethyleneethane, TMM trimethylenemethane, MX *m*-xylylene, TriMB 1,3,5-trimethylenebenzene

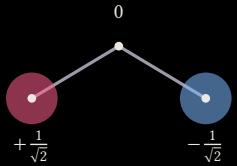
Hückel theory and the zero-sum rule

assume (Hückel) one p_π per carbon; $H_{ii} = \alpha$, $H_{ij} = \beta$ if bonded, else 0; zero overlap

$$\mathbf{H} = \alpha\mathbf{1} + \beta\mathbf{A}, \quad E = \alpha + x\beta \;\Rightarrow\; \mathbf{Ac} = x\,\mathbf{c}$$

$$\text{NBMO: } E = \alpha \;\Leftrightarrow\; \mathbf{Ac} = \mathbf{0}$$

$$\text{row } i: \quad \sum_{j \in \mathcal{N}(i)} c_j = 0$$



allyl NBMO: centre sees $c_1 + c_3 = 0$

▸ *subtract α, divide by β; NBMO means $x = 0$; row i of* **Ac** *adds the coefficients of i's neighbours*

for every atom, the NBMO coefficients of its neighbours sum to zero

SYMBOLS **here α, β are Hückel energies, not spin**: α = energy of a p_π electron on one carbon, $\beta < 0$ = coupling of bonded neighbours **A**: adjacency matrix ($A_{ij} = 1$ if i, j bonded) **c**: MO coefficients $\mathcal{N}(i)$: neighbours of atom i

Alternant hydrocarbons: the pairing theorem

star every other atom; bonds only join starred ($\mathscr{A}$) to unstarred ($\mathscr{B}$):

$$\mathbf{A} = \begin{pmatrix} \mathbf{0} & \mathbf{B} \\ \mathbf{B}^{\mathsf{T}} & \mathbf{0} \end{pmatrix}$$

- *zero diagonal blocks: no bond joins two starred atoms or two unstarred atoms*

$$\mathbf{A}\begin{pmatrix} \mathbf{u} \\ \mathbf{v} \end{pmatrix} = x\begin{pmatrix} \mathbf{u} \\ \mathbf{v} \end{pmatrix} \;\Leftrightarrow\; \mathbf{B}\mathbf{v} = x\mathbf{u}, \quad \mathbf{B}^{\mathsf{T}}\mathbf{u} = x\mathbf{v}$$

multiply the blocks

$$\mathbf{A}\begin{pmatrix} \mathbf{u} \\ -\mathbf{v} \end{pmatrix} = \begin{pmatrix} -\mathbf{B}\mathbf{v} \\ \mathbf{B}^{\mathsf{T}}\mathbf{u} \end{pmatrix} = \begin{pmatrix} -x\mathbf{u} \\ x\mathbf{v} \end{pmatrix} = -x\begin{pmatrix} \mathbf{u} \\ -\mathbf{v} \end{pmatrix}$$

flip the sign on one set

levels come in $\pm x$ pairs, mirrored about α (Lean: `pairing`)

SYMBOLS alternant: atoms can be split into two sets with bonds only between the sets (no odd rings) $\mathbf{u}, \mathbf{v}$: coefficients on the starred and unstarred atoms $\mathbf{B}$: bonds from starred to unstarred T: transpose

How many NBMOs?

$$\begin{aligned} \operatorname{rank} \mathbf{A} &= 2 \operatorname{rank} \mathbf{B} \\ &\leq 2 \min(n_A, n_B) \\ \#\text{NBMO} = N - \operatorname{rank} \mathbf{A} &\geq |n_A - n_B| \end{aligned}$$

▸ *each nonzero level of* $\mathbf{B}$ *gives a* $\pm x$ *pair; a rank can never exceed the smaller side;* $N = n_A + n_B$

sharper (Longuet-Higgins): $\operatorname{rank} \mathbf{B} \leq T$, the size of a maximum matching (largest set of bonds sharing no atom) $\Rightarrow$ $\#\text{NBMO} \geq N - 2T$

Careful: only a bound

square cyclobutadiene: $N = 4$, $T = 2$, so $N - 2T = 0$, yet it has *two* NBMOs

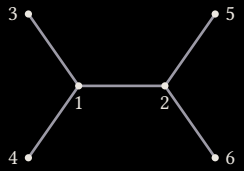


perfect matching

T8 caught our own wrong assumption here.

SYMBOLS rank: number of nonzero eigenvalues #NBMO: number of zero eigenvalues ($x = 0$) n_A, n_B: sizes of the starred and unstarred sets N: number of π atoms

Tetramethyleneethane: solving the zero-sum equations



atom 3: $c_1 = 0$ atom 5: $c_2 = 0$

atom 1: $c_2 + c_3 + c_4 = 0 \Rightarrow c_4 = -c_3$

atom 2: $c_1 + c_5 + c_6 = 0 \Rightarrow c_6 = -c_5$

▸ *atom 3 has one neighbour (atom 1), so the rule forces* $c_1 = 0$*; likewise atom 5 forces* $c_2 = 0$

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

no common atom: disjoint

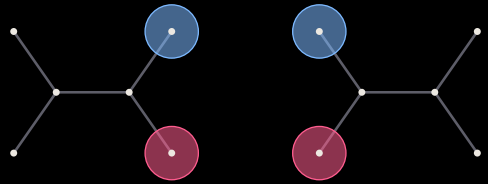
SYMBOLS c_i: NBMO coefficient on atom i χ_i: the p_π atomic orbital on carbon i two free parameters $(c_3, c_5) \Rightarrow$ two NBMOs $\frac{1}{\sqrt{2}}$: normalisation

Disjoint pairs, drawn by our JavaScript

lobe area $\propto |c_i|^2$; *rose* $+$, *blue* $-$

tetramethyleneethane

φ_a φ_b



disjoint: $\Sigma\, a_i^2\, b_i^2 = 0 \Rightarrow K_{ab} = 0$

cyclobutadiene (D_4h)

φ_a φ_b



disjoint: $\Sigma\, a_i^2\, b_i^2 = 0 \Rightarrow K_{ab} = 0$

JS code: Hückel matrix → Jacobi diagonalisation → rotate the degenerate pair to minimise $\sum_i a_i^2 b_i^2$ → SVG → PDF

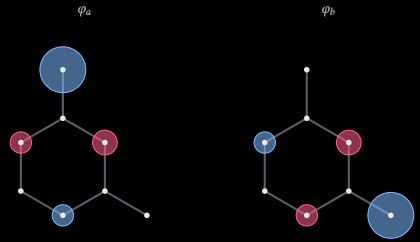
SYMBOLS a_i, b_i: coefficients of φ_a, φ_b on atom i degenerate NBMOs can be mixed freely; we pick the mixture that overlaps least $\sum_i a_i^2 b_i^2 = 0$: no atom carries both orbitals

Trimethylenemethane cannot be made disjoint

1. zero-sum at a terminal $\Rightarrow c_0 = 0$
2. zero-sum at the centre $\Rightarrow c_1 + c_2 + c_3 = 0$
3. a vector in this plane with one nonzero entry cannot sum to zero: at least 2 nonzero
4. two such vectors with disjoint supports need ≥ 4 terminal atoms; there are 3

nondisjoint, for every choice of basis

m-xylylene



nondisjoint: min $\Sigma\, a_i^2\, b_i^2 = 0.0625 \Rightarrow K_{ab} > 0$

m-xylylene: also nondisjoint

SYMBOLS atoms: centre 0, terminals 1–3 support of a vector: the atoms where it is nonzero "for every basis": no rotation of the two NBMOs can separate them

Why disjoint means $K_{ab} = 0$

assume zero differential overlap (ZDO): $(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}\,\gamma_{\mu\lambda}$

$$K_{ab} = (ab|ab) = \sum_{\mu\nu\lambda\sigma} a_\mu b_\nu a_\lambda b_\sigma\,(\mu\nu|\lambda\sigma) \qquad \textit{insert } \varphi_a = \sum a_\mu \chi_\mu,\ \varphi_b = \sum b_\nu \chi_\nu$$

$$= \sum_{\mu\lambda} (a_\mu b_\mu)(a_\lambda b_\lambda)\,\gamma_{\mu\lambda} \qquad \textit{ZDO keeps only } \nu = \mu,\ \sigma = \lambda$$

disjoint $(a_\mu b_\mu = 0\ \forall \mu)$: $K_{ab} = 0$ — *every product vanishes*

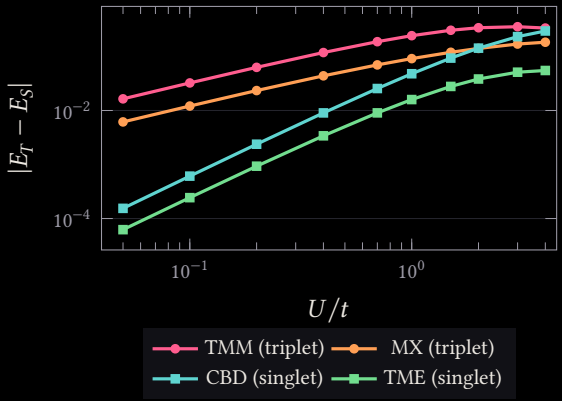
Hubbard $(\gamma_{\mu\lambda} = U\delta_{\mu\lambda})$: $K_{ab} = U \sum_\mu a_\mu^2 b_\mu^2$ — *on-site repulsion only*

TMM: $\min \sum a^2 b^2 = \frac{1}{6}$ MX: $\frac{1}{16}$ (Python *and* JavaScript agree)

SYMBOLS ZDO: products of two different atomic orbitals are treated as zero $\gamma_{\mu\lambda}$: repulsion between an electron on atom μ and one on atom λ γ is positive definite, so nondisjoint $\Rightarrow K_{ab} > 0$

The test: how the gap grows with U

T9b: exact Hubbard diagonalisation, $t = 1$



- nondisjoint: slope ≈ 1; at $U = 0.05$: TMM 0.0164 vs $2U \cdot \frac{1}{6} = 0.0167$
- disjoint: slope ≈ 2 (fit 1.97, 1.95), singlet below triplet
- first-order K vanishes; something second-order picks the singlet…

SYMBOLS log–log axes: slope 1 means gap $\propto U$ (first order, $2K$), slope 2 means gap $\propto U^2$ (second order) exact diagonalisation: all determinants of the Hubbard model, no approximation

Part XI

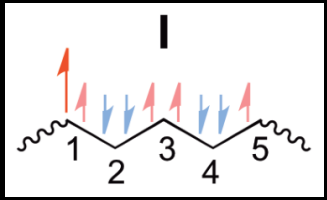
Spin polarisation

XI

Dynamic spin polarisation

The paper says

"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." (p. 443)



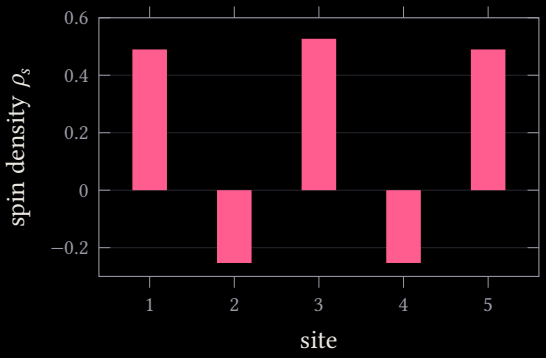
Scheme 1

1. Hückel: the unpaired electron sits in the NBMO, which is zero on unstarred atoms
2. add on-site repulsion U: an ↑ electron pushes ↓ density onto its neighbours
3. negative spin density appears between positive ones: a correlation effect

SYMBOLS spin density $\rho_s = \rho_\uparrow - \rho_\downarrow$ on each atom ferromagnetic: parallel spins; antiferromagnetic: antiparallel "sites" = atoms; "separated by an odd number of sites" = odd number of atoms in between

Measured on the pentadienyl radical

T9: exact Hubbard diagonalisation, 5 sites, 5 electrons, $S_z = \frac{1}{2}$



$U = 6t$: -0.25; the "damped spin wave"

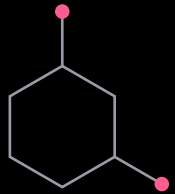
total is always 1; positive on starred, negative on unstarred atoms

SYMBOLS pentadienyl: chain of 5 carbons, one unpaired electron U/t: strength of on-site repulsion relative to hopping $S_z = \frac{1}{2}$: three ↑, two ↓ electrons starred sites 1, 3, 5

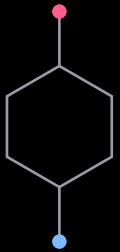
From bonds to topology

1. strong U: each bond carries $J_{\mathrm{AF}} = 4t^2/U$ (kinetic exchange, Part IX)
2. bipartite graph: every bond joins $\mathscr{A}$ to $\mathscr{B}$
3. lowest energy: $\mathscr{A}$ spins one way, $\mathscr{B}$ spins the other (Néel)
4. same set ⇔ even number of bonds ⇔ odd number of atoms in between

same set: parallel; different sets: antiparallel



meta: 3 atoms between
parallel, triplet



para: 4 atoms between
antiparallel, singlet

SYMBOLS Néel state: neighbours antiparallel everywhere meta / para: *m*- / *p*-xylylene, CH_2 groups at ring positions 1,3 / 1,4 a path of an even number of bonds returns to the same set

Ovchinnikov's rule, and Lieb's theorem behind it

count the Néel arrangement: n_A up, n_B down

$$S = \frac{1}{2}\,|n_A - n_B|$$

Ovchinnikov's rule, as the review states it (p. 443): the most spin-alternant determinant "is expected to have the lowest energy and the highest contribution"

Lieb, Phys. Rev. Lett. 62, 1201 (1989)

repulsive Hubbard model, bipartite graph, half filling, any $U > 0$: unique ground state with $S = \frac{1}{2}\big||\mathscr{B}| - |\mathscr{A}|\big|$

T9 ($U = 3t$)	n_A/n_B	rule	exact
CBD	2/2	0	0
TMM	1/3	1	1
TME	3/3	0	0
MX	3/5	1	1
TriMB	3/6	$\frac{3}{2}$	$\frac{3}{2}$
TetraMB	5/5	0	0
p-xylylene	4/4	0	0

TriMB: the review (p. 444) groups it with MX as having "triplet ground states"; three unpaired electrons give a *quartet* ($S = \frac{3}{2}$).

SYMBOLS n_A, n_B: starred / unstarred atom counts half filling: one π electron per carbon $S = 0$ singlet, 1 triplet, $\frac{3}{2}$ quartet rule = Ovchinnikov count; exact = our diagonalisation

Disjoint diradicals: who picks the singlet?

The paper says

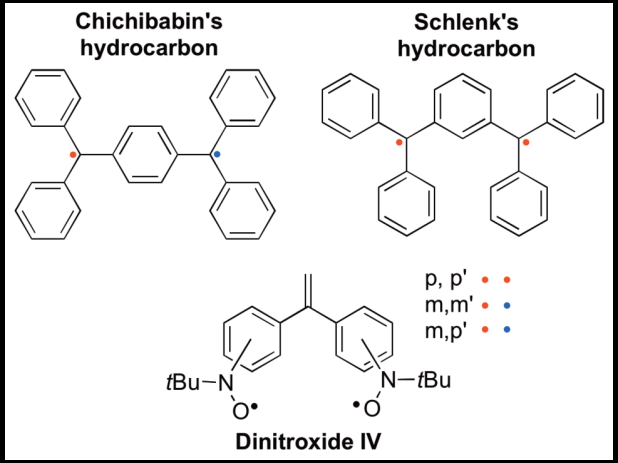
"In the singlet state of D_{4h} CBD, the bonding π-electrons can partially localize on the same pair of atoms as the same-spin unpaired electrons; however, in the triplet state such advantageous spin polarization is not possible." (p. 443)

- first order: $2K_{ab} = 0$ (disjoint)
- second order: spin polarisation of the paired electrons, $\propto U^2$
- our scaling test: gap $\propto U^{1.97}$ (CBD), $U^{1.95}$ (TME), singlet lower

VERIFIED consistent with the spin-polarisation mechanism of the review's ref. 9 (Kollmar & Staemmler, "Violation of Hund's rule by spin polarization"; not accessed)

SYMBOLS D_{4h}: square geometry first order: energy from the exchange integral alone second order: energy from mixing in excited (spin-polarised) configurations, scaling as U^2

Topology in the paper: Figure 4



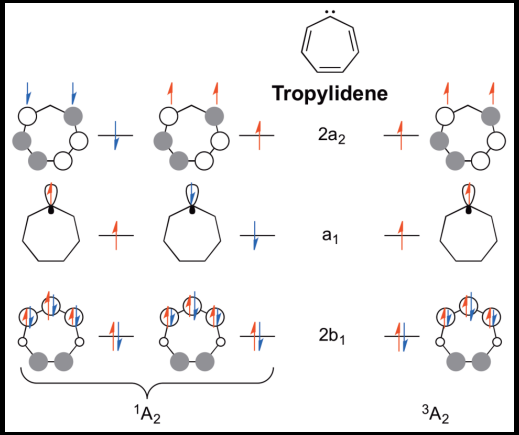
The paper says

simple polyradicals "can also be thought of as coupling units that sustain certain spin alignment depending on topology, as seen in Schlenk's and Chichibabin's hydrocarbons, or in isomers of dinitroxide IV" (p. 444)

in Fig. 4, IV with p, p' links: parallel spins; m, m' and m, p': antiparallel. Same atoms, different topology.

SYMBOLS dots: rose spin up, blue spin down p, m: para / meta attachment on each ring Schlenk, Chichibabin: classic hydrocarbon diradicals

Tropylidene: a singlet from spin polarisation (Figure 5)



1. unpaired electron in the $2a_2$ π orbital
2. polarises the bonding π electrons in $2b_1$
3. opposite spin accumulates on the carbenic carbon
4. it couples *ferromagnetically* with the electron in the orthogonal a_1 orbital on the same atom
5. net result: the $^1A_2$ singlet is lower

our summary: Hund's rule obeyed locally, violated globally.

SYMBOLS tropylidene: cycloheptatrienylidene, a carbene in a 7-ring $2a_2$, $2b_1$, a_1: orbital symmetry labels (a_1 in-plane, the others π) $^1A_2$ / $^3A_2$: singlet / triplet states

Where the rules stop

- Ovchinnikov / Lieb: *alternant* π systems, Hubbard/Heisenberg-type physics
- pyridinium V (Fig. 6): ionic resonance overturns the topology prediction
- σ–π diradicals (didehydrotoluenes): ortho, para triplet; *meta* open-shell singlet

The paper says

"Crucially, all of these rules are not the direct consequences of quantum mechanics and only mimic the dynamic and static correlation effects with the help of simplifying assumptions, thus inevitably having limited scope." (p. 443)

VERIFIED fair: the topology rule is a theorem only of the Hubbard model (Lieb); the others are model heuristics

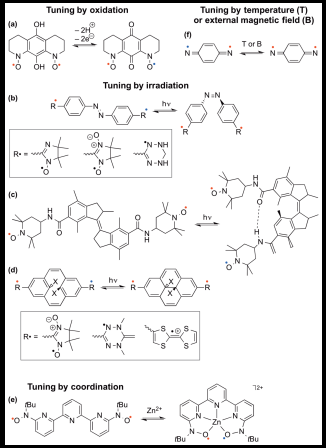
SYMBOLS alternant: no odd-membered rings, so atoms split into two sets σ–π diradical: one unpaired electron in an in-plane σ orbital, one in a π orbital didehydrotoluene: toluene with two H removed

Part XII

Switching spin states

XII

Spin-state crossover by external stimuli (Figure 7)



- (a) oxidation: quinone coupler switches two nitroxides between ferro- and antiferromagnetic coupling
- (b) light: *trans*-azobenzene (antiparallel, singlet) → *cis*, which loses planarity: triplet (predicted computationally)
- (c) light: *trans*→*cis* alkene brings two TEMPO units close, H-bonded, antiferromagnetic
- (d) light: photo-induced bond formation changes the orbital topology
- (e) Zn^{2+}: O–Zn–O superexchange and O···O through-space exchange favour antiferromagnetic coupling
- (f) *T* or *B*: 1,4-phenylenedinitrene, open-shell singlet → triplet

SYMBOLS dots in the figure: rose ↑, blue ↓ *hν*: light TEMPO: a stable nitroxide radical superexchange: coupling of two spins through an intervening atom *T*: temperature, *B*: magnetic field

A wording slip in (e)?

The paper says

"Coordination to Zn^{2+} brings about O–Zn–O superexchange and O···O through-space exchange, which favor antiferromagnetic coupling and override the preference for the triplet ground state, predicted on the basis of *disjoint* NBMOs in parent dinitroxide ligand" (p. 445)

review, p. 443: disjoint NBMOs make the singlet *competitive*; its triplet examples (MX, TriMB) are nondisjoint

so "disjoint" here probably means "nondisjoint", or the triplet preference has another origin

INCONSISTENT wording vs p. 443; original (ref. 52) not checked

SYMBOLS disjoint / nondisjoint NBMOs: Part X (no shared atoms ⇒ $K \approx 0$; shared atoms ⇒ $K > 0$, triplet favoured)

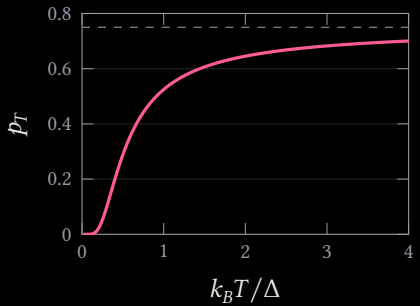
Panel (f), quantitatively: temperature

assume a singlet ground state, triplet Δ above; Boltzmann statistics; degeneracies 1 and 3

$$Z = 1 + 3e^{-\Delta/k_BT}$$ *Boltzmann weights*

$$p_T = \frac{3e^{-\Delta/k_BT}}{1 + 3e^{-\Delta/k_BT}}$$ *triplet weight /Z*

$$p_T(T \to \infty) \to \frac{3}{4}$$ $e^0 = 1$: $3/(1+3)$



"increased temperature … promotes electrons to populate the triplet state" (p. 445) VERIFIED

SYMBOLS Z: partition function k_B: Boltzmann constant $\Delta = E_T - E_S > 0$ degeneracy 3: the triplet's $M_S = -1, 0, +1$ p_T: fraction of molecules in the triplet

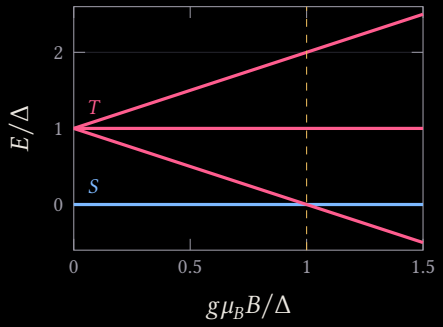
Panel (f), quantitatively: magnetic field

assume a Zeeman term $g\mu_B B M_S$; the singlet is unaffected; $g \approx 2$

$$E_T(M_S) = \Delta + g\mu_B B\, M_S \qquad M_S = 0, \pm 1 \text{ split apart}$$

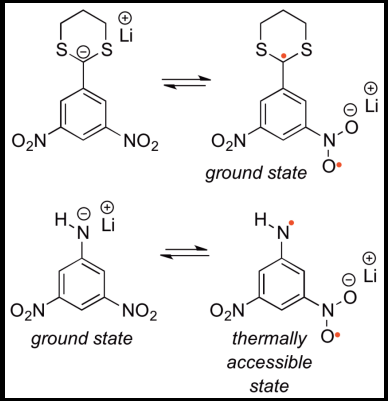
$$E_T(-1) = E_S \;\Leftrightarrow\; B^* = \frac{\Delta}{g\mu_B} \qquad \Delta - g\mu_B B = 0$$

"external magnetic field that splits the triplet into microstates, one of which approaches the energy of the ground-state singlet" (p. 445) VERIFIED



SYMBOLS g: electron g-factor (≈ 2) μ_B: Bohr magneton B: magnetic field M_S: spin projection along B the singlet has $M_S = 0$ only, so it does not shift

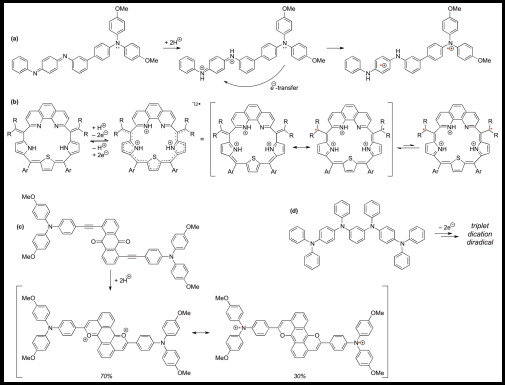
Closed shell or diradical? (Figures 8 and 9)



- Fig. 8: 1,3-dinitrophenyls with anionic substituents transfer an electron intramolecularly to give anionic diradicals; triplet is the ground state or only negligibly above the closed shell; cation binding to the nitro group stabilises the diradical
- Fig. 9: protonation (and oxidation) creates diradicals: donor–acceptor electron transfer after double protonation, a sapphyrin-derived singlet biradicaloid, a dipyrylium diradical salt, high-spin building blocks for polaronic ferromagnets
- singlet fission: one excited singlet shares its excitation with a neighbour; both end in a low triplet

SYMBOLS closed shell: all electrons paired diradical: two unpaired electrons biradicaloid: partial diradical character polaron: a charge carrier with its own spin in a polymer

Protonation-induced magnetisation (Figure 9)



descriptive part of the review: no mathematics to derive, only claims about specific molecules (not re-checked)

SYMBOLS arrows: reactions (H^+ added / removed, electrons transferred) dots: unpaired electrons, coloured by spin

Part XIII

Koopmans & Janak

XIII

The claim

The paper says

"An alternative theoretical interpretation of the Hund's multiplicity rule has been proposed on the basis of Janak theorem (or extended Koopmans' theorem) …: 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." (p. 442–443)

three steps: Koopmans' theorem → Janak's theorem → the gap

(which difference, which sign? the review does not say; the derivation will)

SYMBOLS STG: $E_S - E_T$ HOMO: highest occupied molecular orbital Koopmans: orbital energy ≈ minus the ionisation energy (Hartree–Fock) Janak: orbital energy = slope of E with occupation (DFT) "…" omits "in excited state DFT for multiplets"

Assumptions

single determinant of spin orbitals χ_i; remove χ_k *without* relaxing the others

$$
\begin{aligned}
E_N &= \sum_i \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{i,j}\big([ii|jj] - [ij|ji]\big) && \text{Slater--Condon rules}\\
E_N - E_{N-1}^{(k)} &= \langle k|\hat{h}|k\rangle + \frac{1}{2}\sum_j (\dots)_{kj} + \frac{1}{2}\sum_i (\dots)_{ik} && \text{keep only terms containing } k\\
&= \langle k|\hat{h}|k\rangle + \sum_j \big([kk|jj] - [kj|jk]\big) && \text{halves equal, } [ab|cd] = [cd|ab];\ j{=}k \text{ cancels}\\
&= \varepsilon_k && \text{definition of the Fock eigenvalue}
\end{aligned}
$$

$$
\mathrm{IP}_k = E_{N-1}^{(k)} - E_N = -\varepsilon_k \qquad \text{(frozen orbitals)}
$$

SYMBOLS χ_i: spin orbital (space × spin) $\hat{h}$: kinetic + nuclear attraction $[ij|kl] = \iint \chi_i^*(1)\chi_j(1) r_{12}^{-1} \chi_k^*(2)\chi_l(2)$ $[ii|jj]$: Coulomb, $[ij|ji]$: exchange (zero unless same spin) ε_k: orbital energy IP: ionisation potential

Janak's theorem

Kohn–Sham with fractional occupations n_i

$$E = \sum_i n_i \langle \psi_i | -\tfrac{1}{2}\nabla^2 | \psi_i \rangle + \int v\rho + E_H[\rho] + E_{xc}[\rho], \qquad \rho = \sum_i n_i |\psi_i|^2$$

$$\left.\frac{\partial E}{\partial n_i}\right|_{\text{explicit}} = \langle \psi_i | -\tfrac{1}{2}\nabla^2 + v + v_H + v_{xc} | \psi_i \rangle = \varepsilon_i$$

n_i enters ρ linearly; chain rule

$$\left.\frac{\partial E}{\partial n_i}\right|_{\text{via } \psi_j} = \sum_j n_j \varepsilon_j \, \partial_{n_i} \langle \psi_j | \psi_j \rangle = 0$$

$\delta E/\delta \psi_j^* = n_j \varepsilon_j \psi_j$; norms stay 1

$$\boxed{\partial E/\partial n_i = \varepsilon_i} \quad \text{for any } E_{xc} \qquad \text{(Janak, Phys. Rev. B 18, 7165, 1978)}$$

- *integer occupations and frozen orbitals turn this slope into a finite difference: Koopmans' theorem again*

SYMBOLS $n_i \in [0,1]$: occupation ψ_i: Kohn–Sham orbital v: nuclear potential E_H, $v_H = \delta E_H/\delta\rho$: Hartree (classical) repulsion E_{xc}, v_{xc}: exchange–correlation ρ: electron density

The gap as a HOMO difference

HOMO energy of a state := minus the cost of removing its φ_b electron, φ_a frozen; ion: $E_{ion} = h_a$

$$\varepsilon_b^T = E_T - E_{\text{ion}} = h_b + J_{ab} - K_{ab} \qquad E_T = h_a + h_b + J - K \text{ (Part V)}$$

$$\varepsilon_b^{\text{OSS}} = E_{\text{OSS}} - E_{\text{ion}} = h_b + J_{ab} + K_{ab} \qquad E_{\text{OSS}} = h_a + h_b + J + K$$

$$E_{\text{OSS}} - E_T = \varepsilon_{\text{HOMO}}^{\text{OSS}} - \varepsilon_{\text{HOMO}}^{T} = 2K_{ab} \qquad E_{ion} \text{ cancels}$$

Result

frozen orbitals: the triplet's HOMO is lower ("harder") by $2K$, cf. Pearson. Review's caveat (ref. 20): "lacks dynamic electron correlation"; relaxation is missing too. VERIFIED

SYMBOLS h_a, h_b: one-electron energies J_{ab}: Coulomb, $K_{ab} \geq 0$: exchange integral ion: one electron left, in φ_a hardness: resistance to losing an electron

Part XIV

Aufbau on trial

XIV

The prosecution

The paper says

"the aufbau principle, by assuming the existence of unchanging stationary individual electronic states, violates the Pauli exclusion principle. Only the many-electron system as a whole possesses stationary states." (p. 448)

Exhibit A
one-electron quantum numbers are not conserved

Exhibit B
the adiabatic argument behind "building up"

Exhibit C
the 3d/4s paradox

SYMBOLS aufbau (German "building up"): fill orbitals in order of energy, two electrons each stationary state: eigenstate of $\hat{H}$, unchanged in time apart from a phase conserved: its quantum number commutes with $\hat{H}$

Exhibit A: $[\hat{l}_{1z}, 1/r_{12}] \neq 0$

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

▸ *chain rule on* $r_{12}^{-1} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{-1/2}$

$$\begin{aligned}
\hat{l}_{1z}\, r_{12}^{-1} &= -i\,\frac{-x_1(y_1 - y_2) + y_1(x_1 - x_2)}{r_{12}^3} && \textit{insert both derivatives} \\
&= -i\,\frac{\cancel{-x_1 y_1} + x_1 y_2 + \cancel{y_1 x_1} - y_1 x_2}{r_{12}^3} && \textit{multiply out} \\
&= -i\,\frac{x_1 y_2 - x_2 y_1}{r_{12}^3} \neq 0 && \textit{only the cross terms survive}
\end{aligned}$$

first-order operator: $[\hat{l}_{1z}, V]f = (\hat{l}_{1z}V)f \quad \Rightarrow \quad l_{1z}$ is not a constant of motion

SYMBOLS $\hat{l}_{1z}$: z-angular momentum of electron 1 alone ($\hbar = 1$) $\quad r_{12}$: distance between electrons 1 and 2 $\quad [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ $\quad f$: any test function $\quad$ first-order: $\hat{l}_{1z}(Vf) = (\hat{l}_{1z}V)f + V\hat{l}_{1z}f$

…but the total is conserved

$$\hat{l}_{2z}\, r_{12}^{-1} = -i\,\frac{x_2 y_1 - x_1 y_2}{r_{12}^3}$$

same steps; $\partial_{y_2} r_{12}^{-1} = +\frac{y_1 - y_2}{r_{12}^3}$ flips the sign

$$(\hat{l}_{1z} + \hat{l}_{2z})\, r_{12}^{-1} = -i\,\frac{(x_1 y_2 - x_2 y_1) + (x_2 y_1 - x_1 y_2)}{r_{12}^3} = 0$$

equal and opposite

Result

atom (central field, spin-free $\hat{H}$):
$[\hat{H}, \hat{\mathbf{L}}] = 0,\ [\hat{H}, \hat{S}^2] = 0$, but $[\hat{H}, \hat{\mathbf{l}}_i] \neq 0$

$\hat{\mathbf{L}}$ rotates both electrons together (keeps r_{12}); $\hat{\mathbf{l}}_1$ rotates one (changes r_{12}). In a molecule even $\hat{\mathbf{L}}$ is lost; $\hat{S}^2$ survives.

✓ T13, SymPy on an arbitrary f

SYMBOLS $\hat{\mathbf{L}} = \sum_i \hat{\mathbf{l}}_i$: total orbital angular momentum $\hat{S}^2$: total spin squared central field: the nuclear attraction depends only on $|\mathbf{r}_i|$

The paper says

Bohr assumed stationary states survive "addition of an electron and a proton"; this rests on Ehrenfest's adiabatic principle, which "does not apply to aperiodic systems" (p. 448)

$$\Psi(t) = \sum_n c_n(t)\, e^{i\theta_n(t)} \psi_n(t), \qquad \theta_n = -\int_0^t E_n \, \mathrm{d}t' \qquad \textit{expand in snapshot eigenstates}$$

$$\dot{c}_m = -\sum_n c_n \langle \psi_m | \dot{\psi}_n \rangle e^{i(\theta_n - \theta_m)}, \quad \langle \psi_m | \dot{\psi}_n \rangle = \frac{\langle \psi_m | \dot{\hat{H}} | \psi_n \rangle}{E_n - E_m} \qquad \textit{insert in } i\dot{\Psi} = \hat{H}\Psi\textit{, project on } \psi_m$$

slow $\dot{\hat{H}}$, finite gaps ⇒ the system stays in the *continuously connected* eigenstate. But: adding a particle changes the Hilbert space (no continuous path), and the conserved labels are L, S of the *whole* system, never one-electron labels.

SYMBOLS $\psi_n(t)$, $E_n(t)$: eigenstates/energies of $\hat{H}$ at time t c_n: amplitudes θ_n: dynamic phase dot: time derivative off-diagonal coupling: differentiate $\hat{H}\psi_n = E_n\psi_n$ and project ($m \neq n$)

Exhibit C: the 3d/4s paradox

The paper says

in neutral atoms 4s lies slightly above 3d when both are populated, so 4s is ionised first; "however, 4s orbital is also populated first, because it offers less repulsion with a 3d electron than that between two 3d electrons" … "re-evaluated in the new configurations" (p. 448)

Average of configuration

one-electron energies h_d, h_s; one average repulsion per pair type: $\bar{J}_{dd}$, $\bar{J}_{ds}$, J_{ss}; each electron pays h once, each of the $\binom{n}{2} = n(n-1)/2$ pairs pays its J once

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

symbols $d^{n_d}s^{n_s}$: n_d electrons in 3d, n_s in 4s h: kinetic + nuclear + core terms J: repulsion averaged over spin/orbital arrangements (exchange folded in)

3d/4s: the algebra

$$E(d^n s^2) = n h_d + 2h_s + \binom{n}{2}\bar{J}_{dd} + 2n\bar{J}_{ds} + J_{ss} \qquad n_d = n,\ n_s = 2$$

$$E(d^{n+1} s) = (n+1)h_d + h_s + \binom{n+1}{2}\bar{J}_{dd} + (n+1)\bar{J}_{ds} \qquad \text{move one 4s electron to 3d}$$

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

$$\varepsilon_d = E(d^n s^2) - E(d^{n-1} s^2) = h_d + (n-1)\bar{J}_{dd} + 2\bar{J}_{ds} \qquad \text{remove a 3d electron}$$

$$\varepsilon_s = E(d^n s^2) - E(d^n s^1) = h_s + n\bar{J}_{ds} + J_{ss} \qquad \text{remove a 4s electron}$$

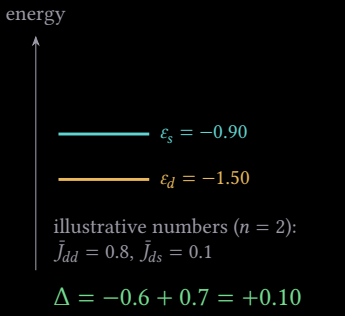
Result

$$\Delta = (\varepsilon_d - \varepsilon_s) + \left(\bar{J}_{dd} - \bar{J}_{ds}\right) \qquad \text{(T12; Lean } \texttt{three_d_four_s}\text{)}$$

SYMBOLS $\Delta > 0$: $d^n s^2$ is lower $\varepsilon_d, \varepsilon_s$: orbital energies *in* $d^n s^2$, as frozen-orbital removal energies (Koopmans)

3d/4s: reading the identity

- compact 3d, diffuse 4s suggests $\bar{J}_{dd} > \bar{J}_{ds}$ (a heuristic, not derived)
- even with $\varepsilon_d < \varepsilon_s$: $\Delta > 0$ if $\bar{J}_{dd} - \bar{J}_{ds} > \varepsilon_s - \varepsilon_d$
  $d^n s^2$ wins: 4s "fills first"
- from $d^n s^2$: Koopmans IPs $-\varepsilon_s < -\varepsilon_d$
  4s leaves first



orbital energies belong to a *configuration*: the building-up and removal orders need not agree

SYMBOLS compact: small mean radius, so two 3d electrons sit close together diffuse: spread out IP: ionisation potential numbers in E_h, chosen only to show the mechanism

Verdict on the aufbau critique

right

- one-electron quantum numbers are model labels (Exhibit A)
- orbital energies depend on the configuration (Exhibit C)
- non-aufbau occupations are observed via measurable properties (VO(oep), quantum dots, LiF dissociation, the radicals ahead)

overstated

- an aufbau-filled *determinant* is fully antisymmetric: within the orbital model it does not "violate" Pauli
- "obsolescence" of aufbau and Hund's rule: both remain useful rules of thumb for atomic ground states, with known exceptions (e.g. Cr, Cu)

OVERSTATED

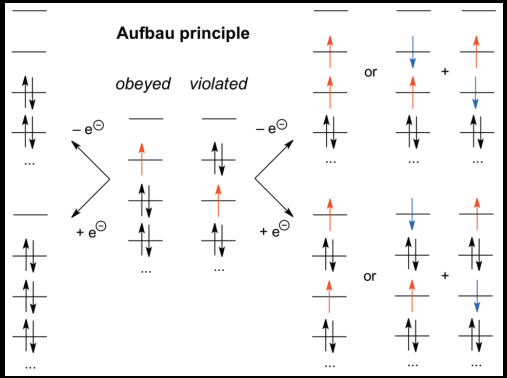
SYMBOLS VO(oep): a vanadyl porphyrin whose unpaired electron is not in the highest occupied orbital model label: a quantum number that is exact only for one electron in a central field

Part XV

Quasi-closed shells

XV

SOMO below HOMO (Figure 10)



The paper says

"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. 449)

the fingerprint is redox: products are polyradicals (diradicals in the simplest case), not closed shells

symbols SOMO: singly occupied MO HOMO: here the highest *doubly* occupied MO LUMO: lowest unoccupied MO quasi-closed shell: SOMO below one or more doubly occupied MOs redox: electron removal (oxidation) or addition (reduction)

UHF orbital energies of s^1h^2 (1/2)

Assumptions

frozen orbitals; SOMO s (α only), doubly occupied h; core absorbed into h_s, h_h; $\varepsilon_k = E_N - E^{(k)}_{N-1}$ (Koopmans)

configuration: $s\alpha,\ h\alpha,\ h\beta$ pairs: $(s\alpha, h\alpha)$ same spin, $(s\alpha, h\beta)$, $(h\alpha, h\beta)$

$$E_N = h_s + 2h_h + \underbrace{(J_{hs} - K_{hs})}_{s\alpha,h\alpha} + \underbrace{J_{hs}}_{s\alpha,h\beta} + \underbrace{J_{hh}}_{h\alpha,h\beta}$$

each pair: J; same-spin pair: also $-K$

$$\varepsilon_h^\alpha = E_N - E(s\alpha, h\beta) = h_h + J_{hh} + J_{hs} - K_{hs}$$

$h\alpha$ leaves with its two pairs

$$\varepsilon_h^\beta = E_N - E(s\alpha, h\alpha) = h_h + J_{hh} + J_{hs}$$

$h\beta$ has no same-spin partner: no K

SYMBOLS s: SOMO, h: HOMO h_s, h_h: one-electron energies $J_{hs} = (hh|ss)$: Coulomb $K_{hs} = (hs|sh) \geq 0$: exchange UHF: unrestricted HF (α and β orbitals may differ; frozen and equal here) $E(\cdot)$: energy of the $N-1$ electron ion

UHF orbital energies of s^1h^2 (2/2)

$$\varepsilon_s^{\alpha} = E_N - E(h\alpha, h\beta) = h_s + 2J_{hs} - K_{hs}$$

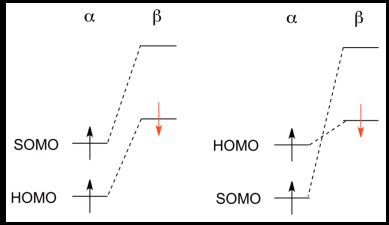
$s\alpha$ leaves: pairs with $h\alpha$ ($J - K$), $h\beta$ (J)

$$\varepsilon_s^{\beta}\ (\text{empty; add } s\beta) = h_s + J_{ss} + 2J_{hs} - K_{hs}$$

$E_{N+1} - E_N$: new pairs with $s\alpha$, $h\alpha$, $h\beta$ (same spin)

Scheme 3, derived

$\varepsilon_h^{\beta} - \varepsilon_h^{\alpha} = K_{hs} \geq 0$: the donor's α HOMO is pulled down by exchange with the unpaired electron; its β HOMO is not



✓ T2: all four checked against determinant energies

SYMBOLS ε_k^{σ}: Koopmans energy of orbital k with spin σ occupied: $E_N - E_{N-1}$; empty: $E_{N+1} - E_N$ J_{ss}: repulsion of two electrons in s (large, on-site) Scheme 3: donor HOMO split by the radical's spin

When does the SOMO drop below the HOMO?

compare within the α manifold:

$$\varepsilon_s^\alpha < \varepsilon_h^\alpha \iff h_s + 2J_{hs} - K_{hs} - K_{hs} \qquad \textit{insert the two } \alpha \textit{ energies}$$
$$\iff h_s + J_{hs} < h_h + J_{hh} \qquad \textit{cancel } -K_{hs} \textit{ and one } J_{hs}$$

radical orbital: its energy plus repulsion with *one* h electron, vs. h's energy plus its *self*-repulsion

favours conversion: a stable radical (low h_s) beside an electron-rich, e.g. anionic, fragment (high h_h)

The paper says

"spatially separated stable radical center and molecular fragment serving as a source of high-energy doubly occupied orbitals" (p. 454)

SYMBOLS conversion: SOMO–HOMO conversion, i.e. $\varepsilon_s^\alpha < \varepsilon_h^\alpha$ J_{hh}: self-repulsion of the HOMO pair stable radical: low-lying, well-protected SOMO (e.g. a nitroxide)

The redox fingerprint, derived

oxidation

- Koopmans: $\mathrm{IP}(h) = -\varepsilon_h < \mathrm{IP}(s)$
- product s^1h^1: a diradical
- its states: $E_{\mathrm{OSS}} - E_T = 2K_{sh} > 0$
- triplet cation diradicals with nondegenerate SOMOs, as observed

reduction

- into $s\beta$ at ε_s^β, or into l at ε_l
- at frozen orbitals: diradical $s^1h^2l^1$ iff $\varepsilon_l < h_s + J_{ss} + 2J_{hs} - K_{hs}$
- a separate condition: SOMO–HOMO conversion alone does not imply it

the large on-site J_{ss} is what pushes ε_s^β up

SYMBOLS Koopmans: the electron leaves from (or enters) the orbital with the cheapest $\pm\varepsilon$ l: former LUMO $2K_{sh}$: the singlet–triplet gap of Part V nondegenerate SOMOs: the two singly occupied orbitals differ in energy

ROHF: are these orbital energies even real?

The paper says

> "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" (p. 449)

spaces: core c (doubly), open o (α), virtual v; $\quad \mathbf{D}^\alpha = \mathbf{D}_c + \mathbf{D}_o,\ \mathbf{D}^\beta = \mathbf{D}_c$

$$\delta E = \mathrm{tr}(\mathbf{F}^\alpha \delta\mathbf{D}^\alpha) + \mathrm{tr}(\mathbf{F}^\beta \delta\mathbf{D}^\beta), \qquad \text{rotation } p \leftrightarrow q: \ \delta\mathbf{D}^\sigma = \kappa(|p\rangle\langle q| + |q\rangle\langle p|)$$

a rotation changes $\mathbf{D}^\sigma$ only if exactly one of p, q is occupied in spin σ

SYMBOLS ROHF: restricted open-shell HF (one set of spatial orbitals) $\mathbf{D}^\sigma$: spin-σ density matrix $\mathbf{F}^\sigma = \partial E/\partial \mathbf{D}^\sigma$: Fock matrix κ: small rotation angle canonicalisation: the choice of matrix whose eigenvectors define the orbitals

ROHF stationarity, rotation by rotation

rotation	changes $\mathbf{D}^\alpha$?	changes $\mathbf{D}^\beta$?	condition
$c \leftrightarrow o$	no (both α-occ.)	yes	$F^\beta_{co} = 0$
$o \leftrightarrow v$	yes	no (both β-empty)	$F^\alpha_{ov} = 0$
$c \leftrightarrow v$	yes	yes	$F^\alpha_{cv} + F^\beta_{cv} = 0$
within c, o or v	no	no	none: $\delta E \equiv 0$

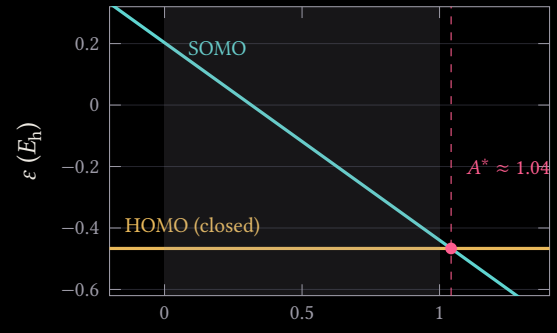
Result

diagonal blocks are *arbitrary*: any $A\mathbf{F}^\alpha + (1-A)\mathbf{F}^\beta$ gives the same energy and density, but different orbital energies

✓ T11a: required blocks $< 10^{-7}$, others ~ 0.1 (H_2NO, NO_2, CH_3, allyl); PySCF's Roothaan Fock uses exactly these off-diagonal blocks

SYMBOLS F^σ_{pq}: Fock element between spaces p, q $\delta E \equiv 0$: the energy is blind to that rotation A: any real weight

How arbitrary? H_2NO, ROHF/6-31G*



- energy identical for every A: $-130.369709\ E_h$
- SOMO crosses the HOMO at $A^* \approx 1.04$
- shaded: the "natural" range $0 \le A \le 1$, no crossing here

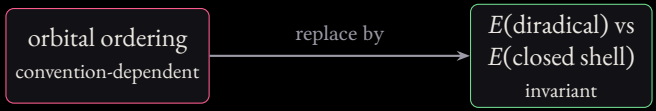
OVERSTATED the review is right in principle; for ordinary radicals the standard choices do not flip

SYMBOLS H_2NO: aminoxyl, the smallest nitroxide $\mathbf{R}_{oo}$: open–open block of the ROHF effective Fock matrix A^*: weight where SOMO and HOMO cross E_h: hartree

Hence: trust observables

The paper says

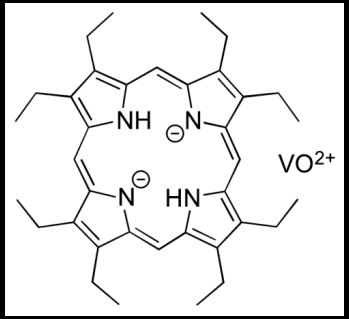
"a rigorous support for the non-aufbau occupation can be obtained a posteriori from the ionization potentials and electron affinities (or redox potentials in solution) … as well as from the determination of the spin state and magnetic properties of the corresponding open-shell oxidation/reduction products." (p. 449)



this is exactly the test we ran on a distonic radical anion (a few slides ahead)

SYMBOLS a posteriori: after the fact, from measured or computed total energies invariant: the same for every canonicalisation electron affinity: energy released on adding an electron

Inorganic precedents (Scheme 2)



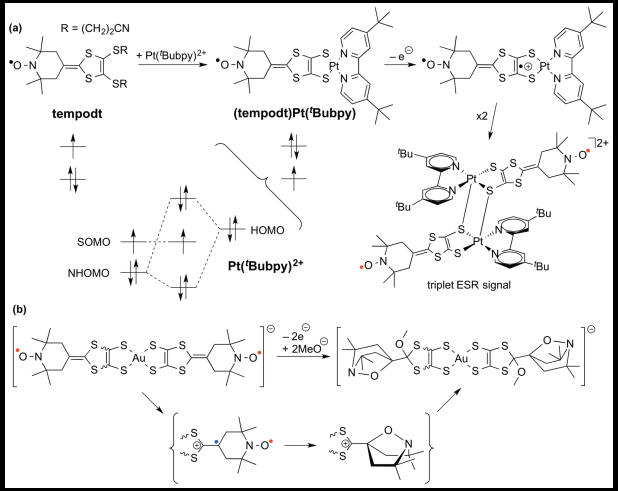
VO(oep)

- unpaired electron localised on vanadium
- one-electron *oxidation* uses an occupied porphyrin orbital
- one-electron *reduction* uses an unoccupied porphyrin orbital

also reported: quantum dots, the LiF dissociation curve

SYMBOLS VO(oep): vanadyl octaethylporphyrin the unpaired electron sits in a vanadium d orbital, below the porphyrin's highest filled π orbital oep: octaethylporphyrin

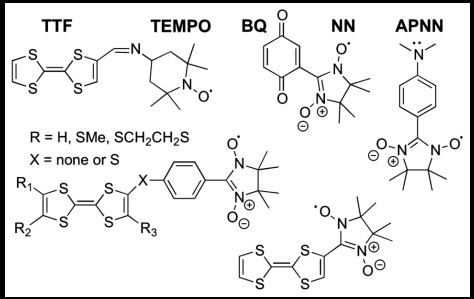
A TEMPO-dithiolate on platinum (Figure 11)



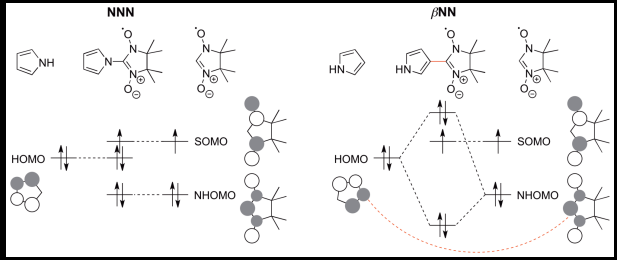
- oxidation of (tempodt)Pt(tBubpy) removes an electron from the dithiolate HOMO
- evidence: UV–Vis, ESR, CV, DFT and the dimerisation product
- free tempodt is a normal radical; the conversion comes from an antibonding interaction of its NHOMO with the HOMO of $Pt(tBubpy)^{2+}$
- (b) a ditempo metalladithiolene: oxidation-generated biradicals couple to a bicyclic product

SYMBOLS tempodt: TEMPO-substituted dithiolate ligand tBubpy: di-*tert*-butyl-bipyridine NHOMO: next-highest occupied MO CV: cyclic voltammetry ESR: electron spin resonance

Spin-polarised donors (Figures 12, 13)



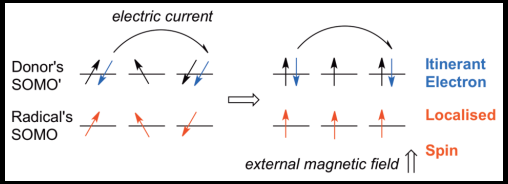
nitronyl nitroxide (NN) radicals on TTF, BQ, amine donors: one-electron oxidation gives triplet cation diradicals

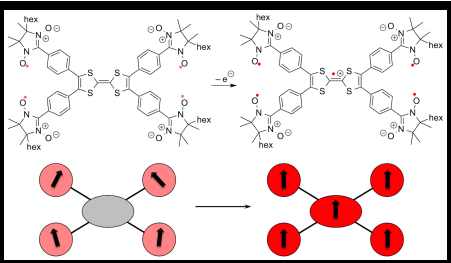


NNN (1-pyrrolyl): donor HOMO disjoint from SOMO/NHOMO. *β*NN (3-pyrrolyl): donor HOMO and NHOMO nondisjoint; their combination rises above the SOMO.

SYMBOLS NN: nitronyl nitroxide radical TTF: tetrathiafulvalene BQ: benzoquinone donor: electron-rich group that is oxidised first disjoint: no shared atoms (Part X)

Conducting magnets (Scheme 4, Figure 14, Scheme 5)

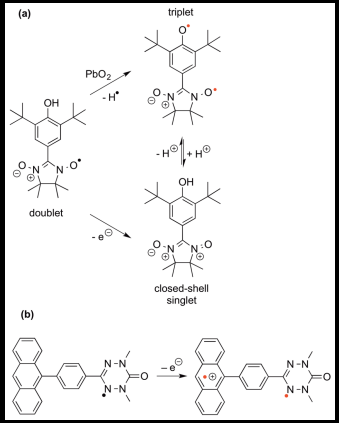




- two nondegenerate SOMOs: the donor's (higher) carries an itinerant electron, the radical's (lower) a localised spin
- ETBN, ESBN perchlorate salts: "first genuine paramagnetic conductors"
- neutral crystals: negative magnetoresistance; field-effect transistors
- Fig. 14: several radicals on one donor; oxidation gives a strongly ferromagnetic high-spin system

SYMBOLS itinerant: free to move through the crystal (carries current) localised spin: stays on the radical (carries magnetism) magnetoresistance: resistance that changes with magnetic field ETBN, ESBN: radical-substituted TTF-type donors

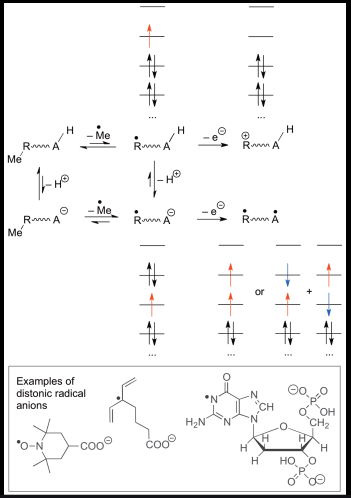
Other radicals, and a pH sensor (Figure 15)



- (a) NN with a phenol-based donor: (de)protonation switches between *triplet* and *closed-shell singlet*: a pH sensor
- (b) anthracene–*p*-phenylene–oxoverdazyl (AnOV): high-spin oxidation products

SYMBOLS phenol: Ar–OH; deprotonated, the phenolate is a strong donor oxoverdazyl: a stable nitrogen-rich radical high spin: parallel unpaired electrons

Distonic radical anions (Figure 16)



The paper says

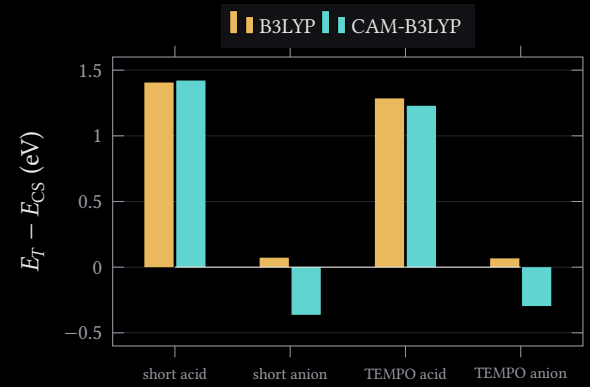
a stabilised radical plus an anionic group not π-conjugated to it: the anion's HOMO lies above the SOMO; "if the anion is protonated, the aufbau orbital occupation is restored", switchable "via changing pH"; on oxidation it "has been shown computationally to yield diradical species preferentially over the closed-shell zwitterion" (p. 452–453)

testable (and so far computational): compute both oxidised states, with and without the proton

symbols distonic: charge and radical on different atoms not π-conjugated: no shared π system between them zwitterion: closed shell carrying + and − charges

Our test: two radicals, two protonation states, two functionals

T11/T11c: UB3LYP/6-31G geometries, vertical oxidation at 6-31+G**



< 0: oxidation gives the diradical
> 0: the closed shell

- acids: closed shell by 1.2–1.4 eV, SOMO = HOMO
- anions, CAM-B3LYP: diradical by 0.36 and 0.30 eV
- anions, B3LYP: misses by 0.06–0.07 eV

SYMBOLS E_T: oxidised diradical (triplet) E_{CS}: oxidised closed shell vertical: same geometry as the radical + in 6-31+G*: diffuse functions for anions
CAM-B3LYP: range-separated (more HF exchange at long range)

What the test says

reproduced

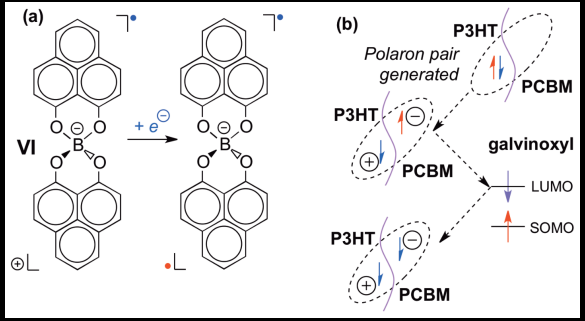
- SOMO 2–3 levels below the HOMO in the anions; equal to the HOMO in the acids
- protonation moves $E_T - E_{CS}$ by $\sim$ 1.2–1.8 eV
- with CAM-B3LYP, the anions oxidise to diradicals: VERIFIED

caveat

- B3LYP lowers the closed shell by 0.61 eV vs. CAM-B3LYP, the triplet by only 0.17
- verdict flips at $\sim$ 0.07 eV: a functional-sensitive claim
- delocalisation error is a plausible cause (not tested)

SYMBOLS delocalisation error: approximate functionals over-stabilise charge spread over many atoms; range separation reduces it functional-sensitive: the sign depends on the method

Non-aufbau by electron addition (Figure 17)



- (a) spirobiphenalenyl VI is reduced to an open-shell singlet; it crystallises without dimerising: an intrinsic molecular metal
- (b) galvinoxyl in P3HT/PCBM: its LUMO mediates singlet→triplet crossing of polaron pairs via exchange, preventing recombination and raising photovoltaic efficiency
- self-doping: in $TTFCOO^{-}NH_4^{+}$ the SOMO of the $TTF^{+\bullet}$ unit is not the highest occupied orbital, according to calculations on a model tetramer

SYMBOLS P3HT/PCBM: polymer/fullerene solar-cell blend polaron pair: an electron and a hole on neighbouring chains self-doping: radicals formed inside the crystal without an external dopant

Part XVI

Broken symmetry

XVI

Cheap methods for diradicals

The paper says

"relatively 'cheap' methods such as unrestricted or broken symmetry formalisms suffer from a number of serious drawbacks" (p. 443); rigorous methods are too costly for large systems

BS determinant $|a'\bar{b}'\rangle$: a' on l, b' on r, $s = \langle a'|b'\rangle$

$$\langle \hat{S}^2 \rangle_{\text{UHF}} = S_z(S_z+1) + N_\beta - \sum_{i\alpha,j\beta} |\langle i|j\rangle|^2$$

$$\langle \hat{S}^2 \rangle_{\text{BS}} = 0 + 1 - s^2$$

$s = 1$: closed shell, $\langle \hat{S}^2 \rangle = 0$
$s = 0$: half singlet, half triplet, $\langle \hat{S}^2 \rangle = 1$
a single determinant cannot be the open-shell singlet (Part IV)

▸ *exact for a determinant; BS: $S_z = 0$, $N_\beta = 1$, one overlap s*

SYMBOLS BS: broken symmetry, α and β electrons in different spatial orbitals $\bar{b}'$: b' with β spin S_z: total M_S N_β: number of β electrons

Yamaguchi's projection, derived

Assumptions

two-centre Heisenberg model $\hat{H} = -2J\,\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2$; BS state $= c_S\Psi_S + c_T\Psi_T$ ($M_S = 0$)

(1) $\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 = \frac{1}{2}\left[S(S+1) - \frac{3}{2}\right] \Rightarrow E_T = -\frac{J}{2},\ E_S = \frac{3J}{2}$ — $\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{\mathbf{s}}_1\cdot\hat{\mathbf{s}}_2$, $\hat{s}_i^2 = \frac{3}{4}$

(2) $\langle\hat{S}^2\rangle_{\mathrm{BS}} = 2|c_T|^2, \qquad E_{\mathrm{BS}} = |c_S|^2E_S + |c_T|^2E_T$ — *S^2: 0 and 2; no cross terms*

(3) $E_{\mathrm{BS}} - E_T = |c_S|^2(E_S - E_T) = \left(1 - \frac{1}{2}\langle\hat{S}^2\rangle_{\mathrm{BS}}\right)2J$ — $|c_T|^2 = 1 - |c_S|^2$; $E_S - E_T = 2J$

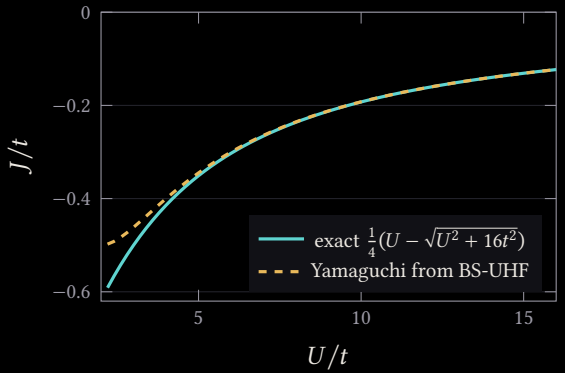
(4) $J = \dfrac{E_{\mathrm{BS}} - E_{\mathrm{HS}}}{\langle\hat{S}^2\rangle_{\mathrm{HS}} - \langle\hat{S}^2\rangle_{\mathrm{BS}}}$ — *solve for J; HS = triplet, $\langle\hat{S}^2\rangle_{HS} = 2$*

Lean: `yamaguchi`; sign conventions differ between sources, here $J < 0$ is antiferromagnetic

SYMBOLS Heisenberg model: spins only, coupling J $\hat{\mathbf{S}}_1, \hat{\mathbf{S}}_2$: spin-$\frac{1}{2}$ operators of the two centres c_S, c_T: amplitudes, $|c_S|^2 + |c_T|^2 = 1$ HS: high-spin determinant (an exact triplet)

How good is it? The Hubbard dimer

T14: self-consistent BS-UHF vs the exact singlet–triplet gap



- $U = 3t$: error -7.7%
- $U = 12t$: -0.1%
- good when the centres are weakly coupled ($\langle \hat{S}^2 \rangle_{\mathrm{BS}} \to 1$), poor when covalent

VERIFIED "serious drawbacks" is fair

SYMBOLS U: on-site repulsion t: hopping exact $J = \frac{1}{2}(E_S - E_T)$ from the Hubbard dimer (Part VI) weakly coupled: large U/t, electrons localised on their centres covalent: small U/t, a real bond

Part XVII

Our verification

XVII

The repository

`CH5103_Term_Paper/`	
`paper/`	the review (PDF)
`derivations/`	18 LaTeX sections
`verification/`	T1–T15 scripts, logs, results/
`lean_proofs/`	Lean 4 + Mathlib (T17)
`assets/`	figures, captions (JSONL)
`presentation/`	this deck
`docs/`	findings, test matrix
`plans/`	working log, audit
`site/`	web page (GitHub Pages)
`pyproject.toml, uv.lock`	pinned environment
`Makefile`	one command per artefact

```
make sync        # uv, locked env
make verify      # T1--T15 > results/
make verify-dft # T11, T11c
make lean        # T17
make derivations
make figures     # byte-identical
```

Python 3.12 pinned by `uv.lock`
PySCF 2.14, SymPy 1.14
Lean 4.29.1, Mathlib 4.29.1

The test matrix (1/2)

test	what	method	result
T1	spin functions, Fig. 1 combinations, sign erratum	SymPy	VERIFIED
T1b	sign erratum again: $\hat{S}^2$ on numerical tensors	NumPy	VERIFIED
T2	$2e/2o$ Hamiltonian vs full CI (5 random sets)	PySCF FCI	VERIFIED
T3	$K_{pq} \geq 0$, $J_{pq} \geq K_{pq}$	RHF/6-31G H_2O	VERIFIED
T4	He $2\,^3S/2\,^1S$: virial, less screening	exact 2-electron	VERIFIED
T5	H_2 dissociation limits	STO-3G closed forms	VERIFIED
T6	two-orbital gap model	SymPy	VERIFIED
T7	kinetic exchange, extended dimer	SymPy + FCI	VERIFIED
T8	Hückel NBMO rules, disjointness	NumPy	VERIFIED
T9	Ovchinnikov/Lieb spins; spin alternation	exact diagonalisation	VERIFIED

SYMBOLS SymPy: exact symbolic algebra PySCF: quantum-chemistry package FCI: full configuration interaction (exact in the basis) RHF: restricted HF 6-31G, STO-3G: basis sets exact diagonalisation: all eigenstates of a model Hamiltonian

The test matrix (2/2)

test	what	method	result
T9b	gap $\propto U$ vs $\propto U^2$	exact diagonalisation	VERIFIED
T10	S–T gap = HOMO difference	SymPy	VERIFIED
T11a	ROHF stationarity, canonicalisation	ROHF/6-31G*	VERIFIED
T11b	distonic anion, B3LYP	UB3LYP ΔSCF	FAIL
T11c	distonic anions/acids, two functionals	UKS ΔSCF; `t11c_check.py`	VERIFIED
T12	3d/4s identity	SymPy	VERIFIED
T13	$[\hat{l}_1, r_{12}^{-1}] \neq 0$, $[\hat{L}, r_{12}^{-1}] = 0$	SymPy	VERIFIED
T14	Yamaguchi projection	BS-UHF dimer	VERIFIED
T15	same- vs opposite-spin correlation	MP2, He	VERIFIED
T17	17 algebraic theorems	Lean 4 + Mathlib	VERIFIED

T11b fails as recorded: B3LYP misses the crossover by 0.06–0.07 eV; T11c shows the outcome depends on the functional. T16 (citations checked by hand against publisher records) has no script.

SYMBOLS ΔSCF: energy difference of two separate SCF calculations UKS: unrestricted Kohn–Sham DFT MP2: second-order perturbation theory BS-UHF: broken-symmetry unrestricted HF

Inside T4: helium, exact in a 16s7p4d basis

verification/t03_t05_hund_virial_h2.py (excerpt, unedited)

```python
# Exact two-electron problem in the spatial pair space Psi(1,2) = sum_pq C_pq phi_p(1) phi_q(2):
#   H[(p,q),(r,s)] = h_pr d_qs + d_pr h_qs + (pr|qs)
# singlet <-> C symmetric, triplet <-> C antisymmetric (spin factor carries the other symmetry).
I = np.eye(n)
H = (np.einsum("pr,qs->pqrs", h, I) + np.einsum("pr,qs->pqrs", I, h)
     + eri.transpose(0, 2, 1, 3)).reshape(n * n, n * n)
sign = +1 if which == "1S" else -1
cols = []
for p in range(n):
    for q in range(p if sign > 0 else p + 1, n):
        v = np.zeros((n, n)); v[p, q] += 1; v[q, p] += sign
        cols.append(v.ravel() / np.linalg.norm(v))
B = np.array(cols).T
w, Y = np.linalg.eigh(B.T @ H @ B)
pick = 1 if which == "1S" else 0          # 1S: root 0 is 1^1S, root 1 is 2^1S ; 3S: root 0 is 2^3S
e = w[pick]; C = (B @ Y[:, pick]).reshape(n, n)
Tex = 2 * np.einsum("pq,pr,rq", C, T, C)
Vne = 2 * np.einsum("pq,pr,rq", C, V, C)
Vee = np.einsum("pq,prqs,rs", C, eri, C)
assert np.isclose(Tex + Vne + Vee, e, atol=1e-8)
return e, Tex, Vne, Vee
```

SYMBOLS symmetric C ↔ singlet, antisymmetric C ↔ triplet (Part III) `C[p,q]`: coefficient of $\phi_p(1)\phi_q(2)$ `h`, `T`, `V`: one-electron, kinetic, nuclear matrices `eri`: $(pq|rs)$ `B`: basis of (anti)symmetric pairs `Tex`, `Vne`, `Vee`: virial components

Inside T11a: ROHF Fock blocks

verification/t11_rohf_and_distonic.py (excerpt)

```python
def rohf_blocks(atom, spin, charge=0, basis="6-31g*"):
    mol = gto.M(atom=atom, spin=spin, charge=charge, basis=basis, verbose=0)
    mf = scf.ROHF(mol).run(conv_tol=1e-11)
    dm = mf.make_rdm1()
    vhf = mf.get_veff(mol, dm)
    h1 = mf.get_hcore()
    C = mf.mo_coeff
    Fa = C.T @ (h1 + vhf[0]) @ C; Fb = C.T @ (h1 + vhf[1]) @ C
    occ = mf.mo_occ
    c, o, v = np.where(occ == 2)[0], np.where(occ == 1)[0], np.where(occ == 0)[0]
    return mol, mf, Fa, Fb, c, o, v
    g_co = np.abs(Fb[np.ix_(c, o)]).max(); g_ov = np.abs(Fa[np.ix_(o, v)]).max()
    g_cv = np.abs((Fa + Fb)[np.ix_(c, v)]).max()
    n_co = np.abs(Fa[np.ix_(c, o)]).max(); n_ov = np.abs(Fb[np.ix_(o, v)]).max()
    stat = max(g_co, g_ov, g_cv) < 1e-5 and max(n_co, n_ov) > 1e-3
```

UHF Fock matrices from the ROHF densities, then the blocks the stationarity table says must vanish

SYMBOLS Fa, Fb: $\mathbf{F}^{\alpha}, \mathbf{F}^{\beta}$ in the MO basis c, o, v: core, open, virtual indices g_*: blocks that must vanish n_*: blocks free to be non-zero

Inside T17: Lean proves the less-screening logic

verification/lean_proofs/Ch5103/Identities.lean (excerpt)

```
/-- Less screening: if the triplet is lower (ΔE < 0), both states obey the virial theorem and the
triplet has the larger e-e repulsion (ΔVee > 0), then ΔT > 0 and ΔVne < 2ΔE < 0 with |ΔVne| > ΔVee. -/
theorem less_screening (dT dVne dVee dE : ℝ)
    (hvir : 2 * dT + (dVne + dVee) = 0) (hE : dE = dT + dVne + dVee)
    (hlow : dE < 0) (hee : 0 < dVee) :
    0 < dT ∧ dVne < 2 * dE ∧ dVne < 0 ∧ dVee < -dVne := by

/-- Frozen orbitals (ΔT = 0) are incompatible with the virial theorem unless ΔE = 0. -/
theorem frozen_orbitals_violate_virial (dT dV dE : ℝ)
    (hvir : 2 * dT + dV = 0) (hE : dE = dT + dV) (hfrozen : dT = 0) : dE = 0 := by
  subst hfrozen; linarith
```

Axiom audit

`#print axioms`, all 17 theorems: only `propext`, `Classical.choice`, `Quot.sound`

SYMBOLS `dT`, `dVne`, `dVee`, `dE`: triplet minus singlet `hvir`: virial theorem for both states `linarith`: proves linear inequalities automatically axioms: the standard three of Lean's logic

What the tests caught in our own work

- T8: we assumed #NBMO $= N - 2T$; cyclobutadiene says $\geq$
- T9b: lowest $S_z = 0$ level was the triplet's $M_S = 0$ component, not a singlet
- T11a: we expected a SOMO/HOMO flip in standard schemes; it needs $A > 1$
- T5: a symmetry tolerance of 10^{-10} failed on round-off at $S \sim 10^{-16}$
- T12: our illustrative numbers had the wrong sign of Δ

Result

every failure was diagnosed before the test changed, and each is logged in `plans/tests.md`

a check that is able to fail is what turns "I believe" into "checked"

Part XVIII

Verdict

XVIII

Scorecard (1/2): confirmed

claim	verdict
triplet single-, open-shell singlet multi-reference	VERIFIED
less screening, not lower V_{ee}, explains Hund's rule	VERIFIED
static correlation grows as orbital interaction weakens	VERIFIED
kinetic exchange; disjoint NBMOs; topology / Ovchinnikov rules	VERIFIED
3d/4s; one-electron quantum numbers not conserved	VERIFIED
ROHF orbital energies are convention-dependent	VERIFIED OVERSTATED

Scorecard (2/2): qualified or wrong

claim	verdict
distonic anions oxidise to diradicals, switchable by pH	PARTIAL
same-spin correlation “an order of magnitude” smaller	OVERSTATED
aufbau “violates” Pauli; “the obsolescence of” aufbau and Hund’s rule	OVERSTATED
$^{1}\Psi_{\mathrm{OSS}} = \frac{1}{2}(D_{\mathrm{iii}} + D_{\mathrm{iv}})$ (p. 441)	ERROR
Katriel & Pauncz cited as 1975 (it is 1977)	ERROR
TriMB called a “triplet” ground state (three unpaired electrons: a quartet)	IMPRECISE

The errors, once more

Sign error, p. 441

$\frac{1}{2}(D_{\mathrm{iii}} + D_{\mathrm{iv}})$ is the $M_S = 0$ triplet; the open-shell singlet is $\frac{1}{2}(D_{\mathrm{iv}} - D_{\mathrm{iii}})$

Citation, ref. ii

Katriel & Pauncz, *Adv. Quantum Chem.* 10, 143 is from 1977

Possible slip, p. 445

"triplet ground state, predicted on the basis of disjoint NBMOs" contradicts the review's own disjoint/nondisjoint rule

these errata do not change the review's chemistry; but its distonic pH switch we reproduce only with CAM-B3LYP

Take-home

1. a spin state is decided by correlation, not by a single term: Hund's rule, aufbau and topology rules are derived within *models* (orbital, Hückel, Hubbard)
2. the virial theorem plus the computed $\Delta V_{ee} > 0$ explain Hund's rule in He: the high-spin state wins on nuclear attraction
3. disjointness removes first-order exchange; second-order spin polarisation then picks the singlet
4. orbital energies are not observables: judge non-aufbau claims by redox energetics
5. distonic radical anions do oxidise to diradicals at CAM-B3LYP, *but* B3LYP misses by 0.06–0.07 eV: a functional-sensitive claim

Even the open-shell singlet in print can fluctuate.

Key references

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full access status of every source: derivations, §17

Thank you

derivations • code • proofs • slides

`github.com/Shuvam-Banerji-Seal/CH5103_Term_Paper`