Uncommon Molecular Electronic Configurations

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

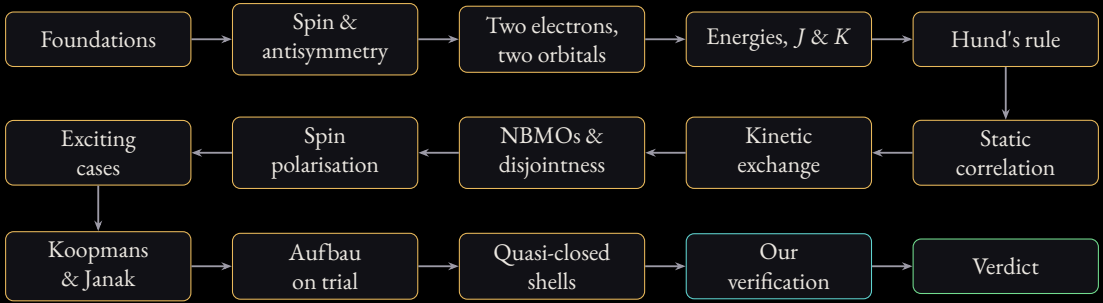
Shuvam Banerji Seal

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*

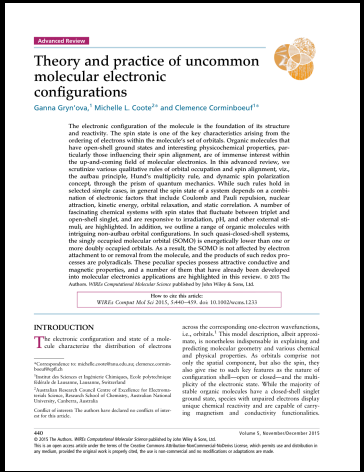
a SYMBOLS strip at the foot of a slide defines its notation

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]*

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How to cite this article:
WIREs Comput Mol Sci 2015, 5:440–459. doi: 10.1002/wcms.1233

INTRODUCTION

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[2]Australian Research Council Centre of Excellence for Electromaterials Science, Research School of Chemistry, Australian National University, Canberra, Australia

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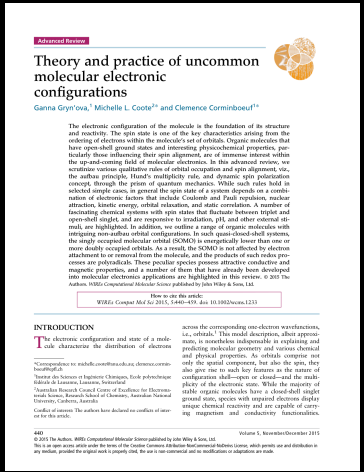

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[3]Laboratory for Computational Molecular Design, Institut des Sciences et Ingénierie Chimiques, Ecole polytechnique fédérale de Lausanne, Lausanne, Switzerland
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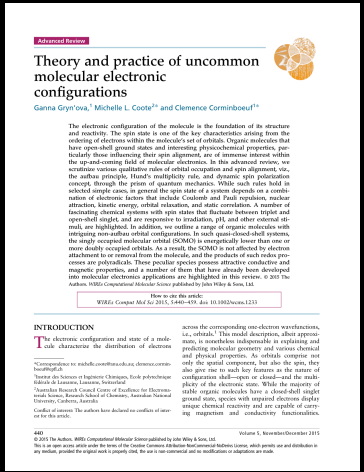

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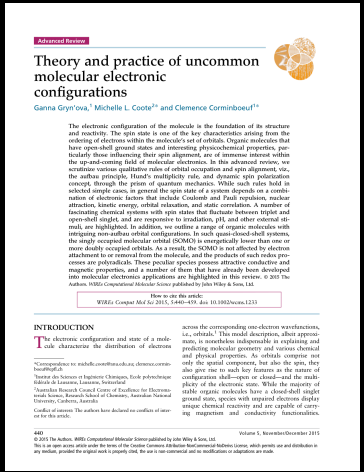
- 20 pages, 17 figures, 5 schemes, 118 references
- part theory (what decides a spin state?)



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- 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

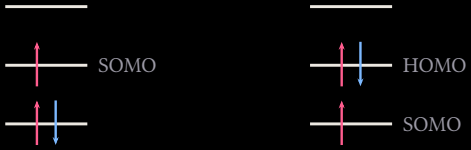
1. FLUCTUATING MULTIPLICITY



triplet — open-shell singlet

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

2. NON-AUFBAU ORDERING



aufbau — quasi-closed shell

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

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Who wins: Hund's rule, or correlation?

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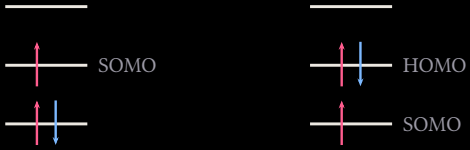


aufbau — quasi-closed shell

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

Two uncommon configurations

the two halves of the paper

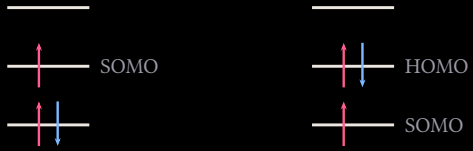
1. Fluctuating multiplicity



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

Who wins: Hund's rule, or correlation?

2. Non-aufbau ordering



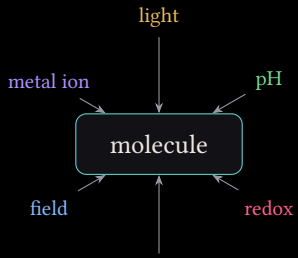
the singly occupied orbital lies *below*
a doubly occupied one

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)



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

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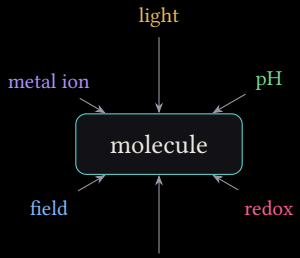

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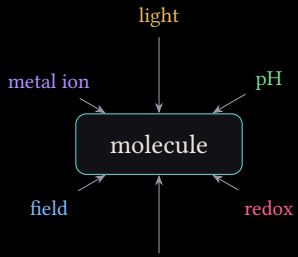

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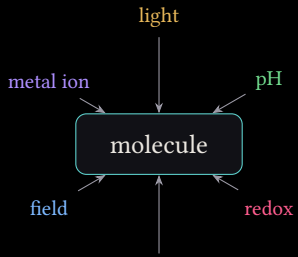
> "species with unpaired electrons display unique chemical reactivity and are capable of carrying magnetism and conductivity functionalities" (p. 440)

- 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
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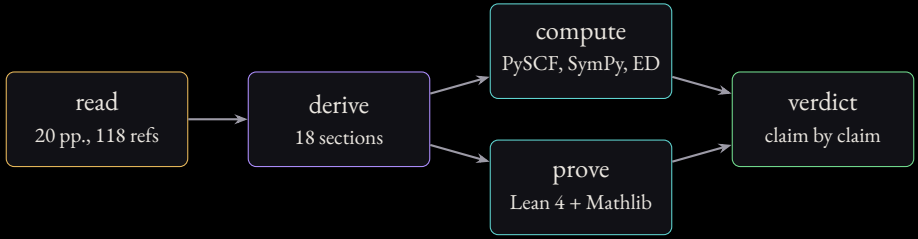
What we did with it



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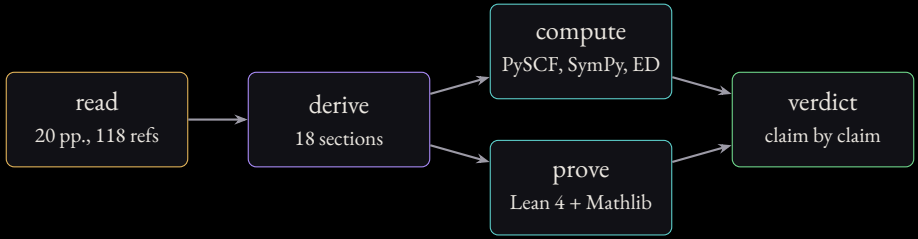
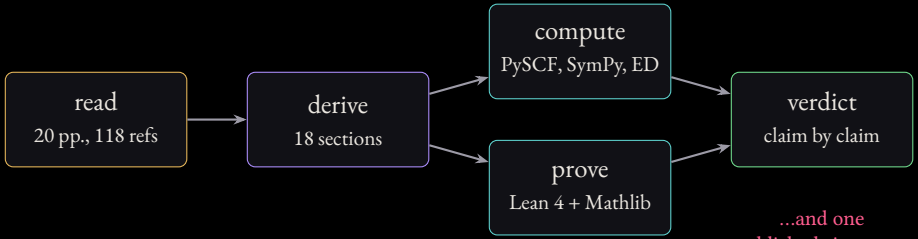


21 checks (T1–T17, with T1b, T9b, T11a–c)
17 machine-checked theorems

What we did with it



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

Part II

Foundations

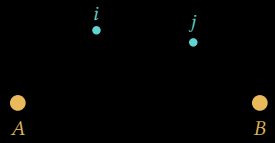
II

Where everything starts

the molecular Schrödinger equation

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

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



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 $\hbar = m_e = e = 1$

Where everything starts

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

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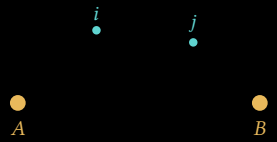

▸ *kinetic energy is $-\frac{1}{2}\nabla^2$ (second derivatives): curvature of Ψ costs energy*

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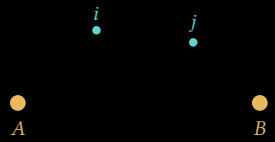

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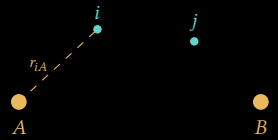

- *kinetic energy is $-\frac{1}{2}\nabla^2$ (second derivatives): curvature of Ψ costs energy*
- *attraction: every electron i to every nucleus A of charge Z_A, falling off as $1/r$*

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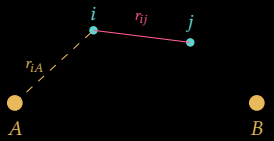

- *kinetic energy is $-\frac{1}{2}\nabla^2$ (second derivatives): curvature of Ψ costs energy*
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Where everything starts

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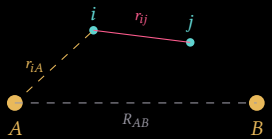

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$$\hat{H} = \sum_{i=1}^{N} \hat{h}(i) + \sum_{i<j} \frac{1}{r_{ij}}, \qquad \hat{h}(i) = -\tfrac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

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- $\hat{h}(i)$ = *everything that involves electron i alone;* $1/r_{ij}$ *couples electrons in pairs and is the hard part*

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The variational principle

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

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

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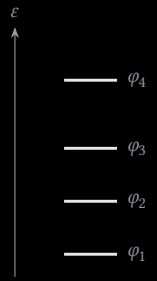
Orbitals: the independent-electron picture

Independent-particle model

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



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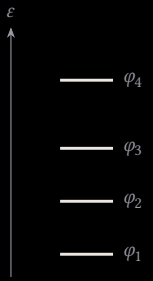

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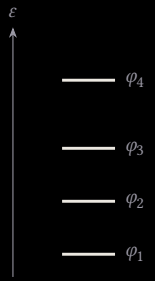

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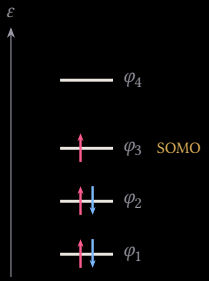

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Box 1: ``Much ado about orbitals''

The paper says

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

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

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Part III

Spin & antisymmetry

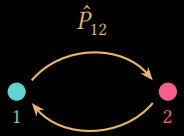
III

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*



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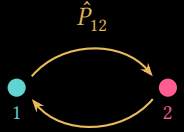

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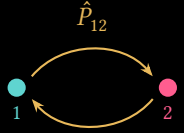

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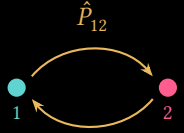

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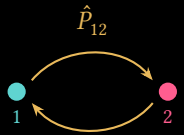

so eigenstates have definite λ; for electrons nature picks -1. The paper: "the wavefunction for a system of fermions must be antisymmetric with respect to the interchange of any two particles" (p. 441)

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Slater determinants

antisymmetry built in

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

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

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

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Two electrons: add each electron's operator

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

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A useful identity:

$$\hat{S}_-\hat{S}_+ = (\hat{S}_x - i\hat{S}_y)(\hat{S}_x + i\hat{S}_y) \qquad \textit{definition of } \hat{S}_\pm$$

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\end{aligned}$$

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

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

$\alpha_1\alpha_2$ (both up)

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

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 $\pm\frac{1}{2}$)

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

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

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$\hat{S}^2$ 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)

$$\hat{S}_+\alpha_1\beta_2 = \alpha_1\alpha_2$$

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

$\hat{S}^2$ *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)

$$\hat{S}_+\alpha_1\beta_2 = \alpha_1\alpha_2 \qquad \hat{S}_-\alpha_1\alpha_2 = \beta_1\alpha_2 + \alpha_1\beta_2$$

SYMBOLS $\hat{S}_\pm$ 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

$\hat{S}^2$ 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)

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

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

Add and subtract the two results:

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

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+: eigenvalue 2 $\Rightarrow S = 1$

−: eigenvalue 0 $\Rightarrow S = 0$

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Triplet and singlet spin functions

The four two-electron spin states

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

- $\frac{1}{\sqrt{2}}$: *the two products are orthonormal, so the sum has norm^2 2*

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

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- triplet spin functions are symmetric under $1 \leftrightarrow 2$

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- triplet spin functions are symmetric under $1 \leftrightarrow 2$
- the singlet is antisymmetric

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The four two-electron spin states

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

- $\frac{1}{\sqrt{2}}$: *the two products are orthonormal, so the sum has norm^2 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

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

Triplet and singlet spin functions

The four two-electron spin states

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✓ 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

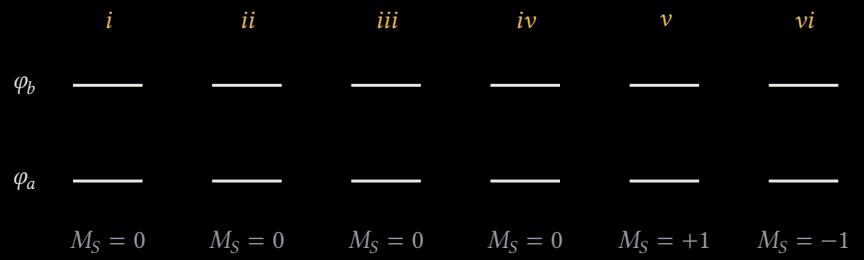
Part IV

Two electrons, two orbitals

IV

Six ways to place two electrons

Figure 1 of the review, rebuilt



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

Six ways to place two electrons

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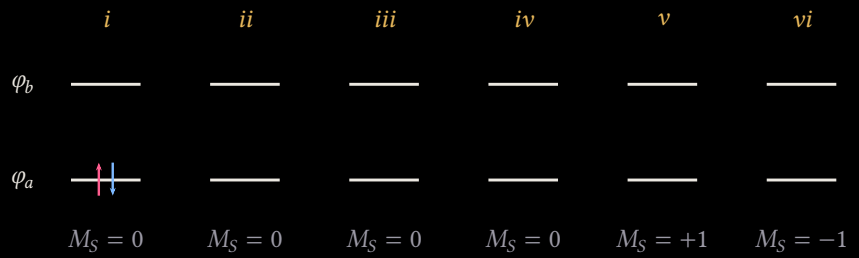

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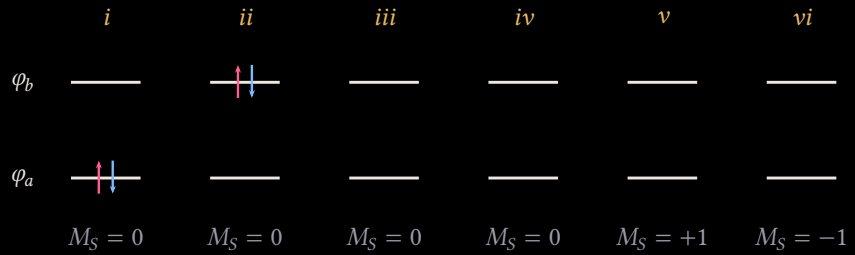

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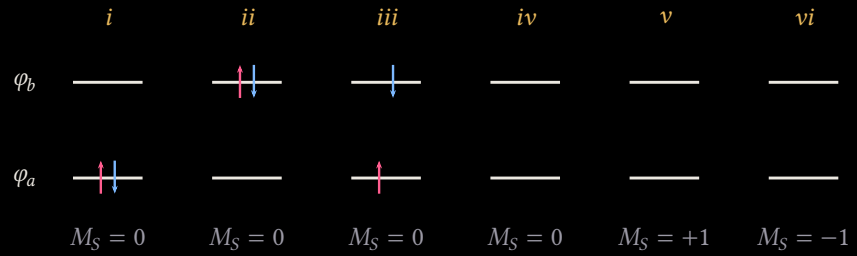

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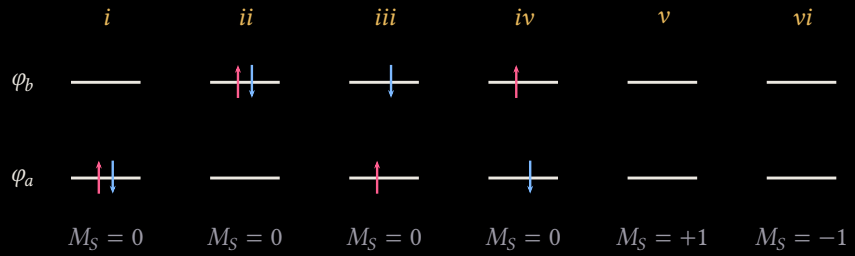

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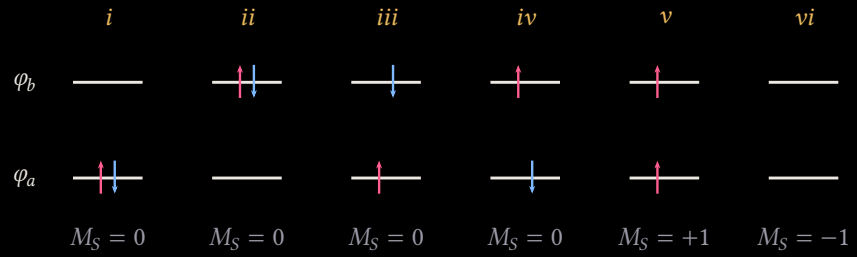

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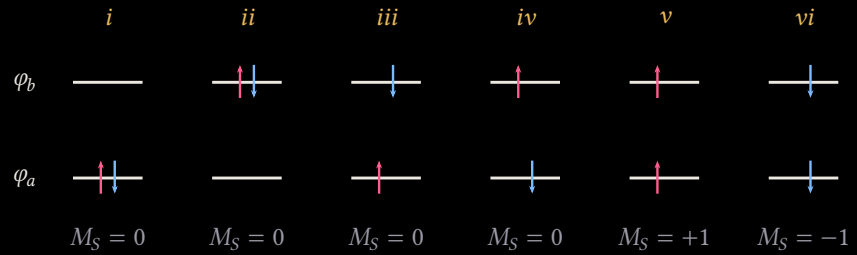

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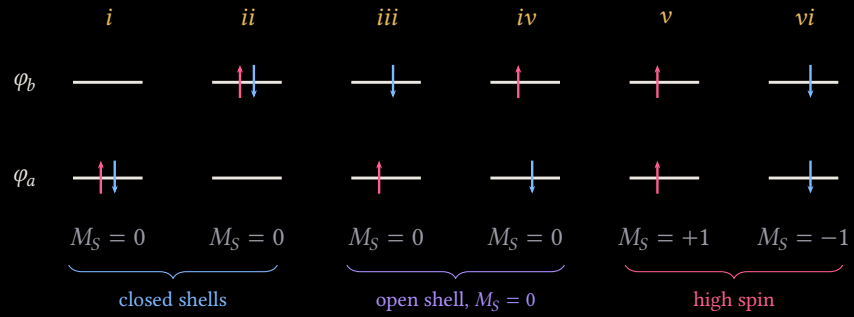
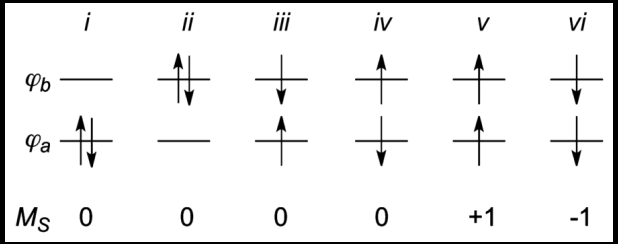


four spin orbitals $\varphi_a\alpha, \varphi_a\beta, \varphi_b\alpha, \varphi_b\beta$; choose 2 of 4 $\Rightarrow \binom{4}{2} = 6$ determinants

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

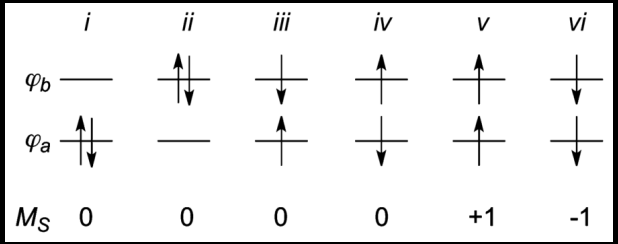


The paper says

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

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

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	$\varphi_b\alpha,\ \varphi_b\beta$	$\varphi_b(1)\varphi_b(2)\,(\alpha_1\beta_2 - \beta_1\alpha_2)$

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

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iii	$\varphi_a\alpha,\ \varphi_b\beta$	$A\,\alpha_1\beta_2 - B\,\beta_1\alpha_2$

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*

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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	$\varphi_a\beta,\ \varphi_b\beta$	$(A - B)\,\beta_1\beta_2$

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$M_S = \pm 1$: *one determinant each*

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

row v: $(A - B)\,\alpha_1\alpha_2$

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 $\langle A - B | A - B \rangle = 2$

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row v: $(A - B)\,\alpha_1\alpha_2$

$$\frac{1}{\sqrt{2}} D_{\mathrm{vi}} = \frac{1}{\sqrt{2}}\big[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)\big]\ \beta_1\beta_2$$

same space, both spins down

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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 $\beta_1\beta_2$)

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 $\langle A - B | A - B \rangle = 2$

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

The paper says

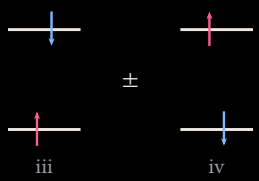
"${}^3\Psi(M_s = +1) = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)][\alpha_1\alpha_2]$" … "i.e., they can be represented as single determinants v and vi" (p. 441; $M_s = -1$ analogous with $\beta_1\beta_2$)

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*

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



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

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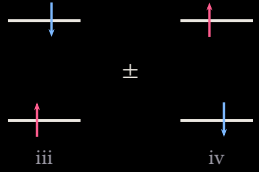
$$D_{\text{iii}} = A \underbrace{\alpha_1\beta_2}_{\text{not }\Theta} - B \underbrace{\beta_1\alpha_2}_{\text{not }\Theta}$$

From the spin slides:

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



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

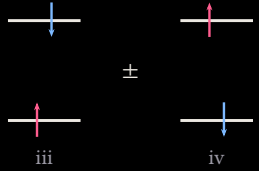
From the spin slides:

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

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)*



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

$$D_{\mathrm{iii}} + D_{\mathrm{iv}} = A\,\alpha_1\beta_2 - B\,\beta_1\alpha_2 + A\,\beta_1\alpha_2 - B\,\alpha_1\beta_2$$

rows iii, iv

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

$$
\begin{aligned}
D_{\mathrm{iii}} + D_{\mathrm{iv}} &= A\,\alpha_1\beta_2 - B\,\beta_1\alpha_2 + A\,\beta_1\alpha_2 - B\,\alpha_1\beta_2 && \textit{rows iii, iv} \\
&= A\,(\alpha_1\beta_2 + \beta_1\alpha_2) - B\,(\beta_1\alpha_2 + \alpha_1\beta_2) && \textit{collect } A, B
\end{aligned}
$$

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, $M_S = 0$

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&= (A - B)\,(\alpha_1\beta_2 + \beta_1\alpha_2) && \textit{same bracket}
\end{aligned}
$$

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, $M_S = 0$

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

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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}\\
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&= (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 $D_{iv} - D_{iii}$

$$D_{\mathrm{iv}} - D_{\mathrm{iii}} = A\,\beta_1\alpha_2 - B\,\alpha_1\beta_2 - A\,\alpha_1\beta_2 + B\,\beta_1\alpha_2$$ *iv minus iii*

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Result

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

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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*:

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Erratum

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

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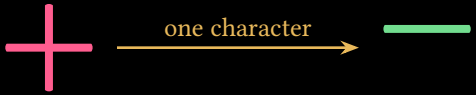
Fluctuating multiplicity, live in print



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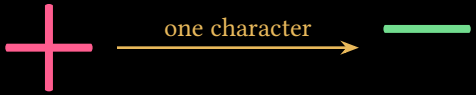

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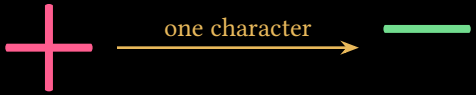

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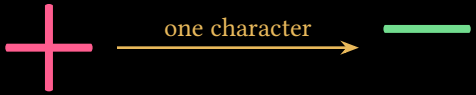

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(It survived peer review and typesetting. Two referees with parallel spins, presumably: the Fermi hole kept them from ever meeting the error.)

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

SymPy (T1): symbolic expansion

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3Psi(0)  = (iii+iv)/2          : True
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paper's (iii+iv)/2 == OSS ?    : False
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$\hat{S}^2$ as an operator (T1b): the paper's matrices on a grid

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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
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- three singlets: i, ii, OSS

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VERIFIED conclusion right, despite the typo

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Part V

Energies: J and K



The integrals we need

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

one electron

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

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

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

- $(pq|rs)$: *electron 1 sits in the "charge" $\varphi_p\varphi_q$, electron 2 in $\varphi_r\varphi_s$; they repel as $1/r_{12}$*

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

The integrals we need

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

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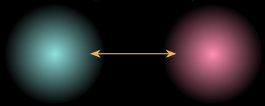
$$J_{pq} = (pp|qq) \qquad \textit{Coulomb}$$

J: $|\varphi_a|^2$ repels $|\varphi_b|^2$



- $(pq|rs)$: *electron 1 sits in the "charge" $\varphi_p\varphi_q$, electron 2 in $\varphi_r\varphi_s$; they repel as $1/r_{12}$*
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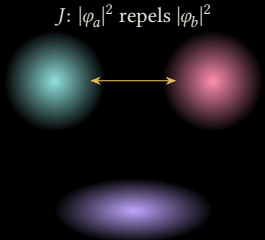

- $(pq|rs)$: *electron 1 sits in the "charge" $\varphi_p\varphi_q$, electron 2 in $\varphi_r\varphi_s$; they repel as $1/r_{12}$*
- *J: two ordinary charge clouds $|\varphi_a|^2$ and $|\varphi_b|^2$ repelling: classical electrostatics*
- *K: no classical analogue; it comes from antisymmetry (the swapped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

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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*

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

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

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

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Triplet energy, step by step (1/2)

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

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

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

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 $M = 0, \pm 1$

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

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Triplet energy, step by step (2/2)

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

$$\langle A|r_{12}^{-1}|A\rangle = (aa|bb) = J_{ab}$$

$p, r = a; q, s = b$: two charge clouds

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

Triplet energy, step by step (2/2)

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

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Result

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

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 +

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

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$$
\begin{aligned}
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&= h_a + h_b + J_{ab} + K_{ab} \\
E_{\mathrm{OSS}} - E_T &= (J_{ab} + K_{ab}) - (J_{ab} - K_{ab}) = \boxed{2K_{ab}} && \textit{h and J cancel}
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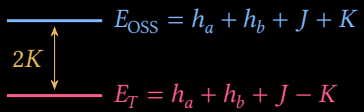

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The closed shells and their couplings

Diagonal (both electrons in one orbital)

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

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

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*

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

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$$\Rightarrow \quad = \sqrt{2}\,\big(h_{ab} + (aa|ab)\big)$$

▸ *$\hat{h}(1)$ 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)*

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

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T2: BRUTE FORCE

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

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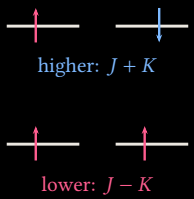
Hund's rule at frozen orbitals

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"



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

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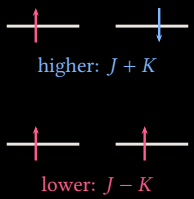

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$$E_T - E_{\mathrm{OSS}} = -2K_{ab} < 0 \quad \text{if } K_{ab} > 0$$

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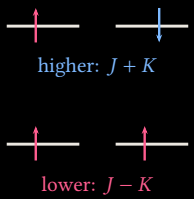

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Two things to prove: $K \geq 0$ (next part), and whether "same orbitals" is legitimate (it is not).

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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 $\mathbf{r}_2$"*

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

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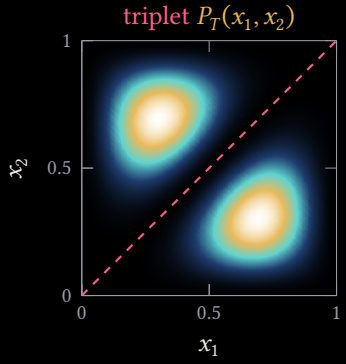
Seeing the Fermi hole

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

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)

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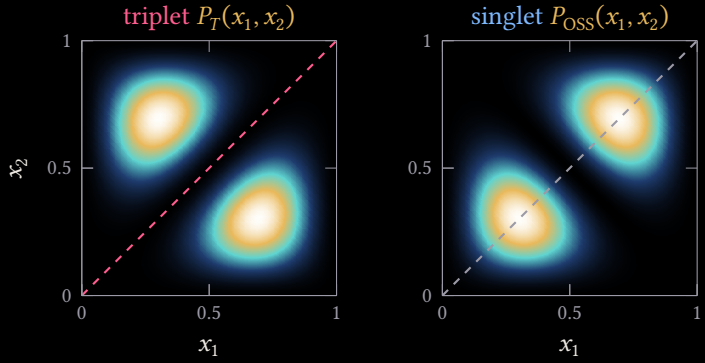

dashed line $x_1 = x_2$: dark all along for the triplet, bright for the singlet

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$K_{ab} \geq 0$: *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) $\quad \dfrac{1}{|\mathbf{r}|} = \displaystyle\int \frac{\mathrm{d}^3k}{(2\pi)^3}\,\frac{4\pi}{k^2}\,e^{i\mathbf{k}\cdot\mathbf{r}}$

$1/r$ as a sum of plane waves, all with positive weight $4\pi/k^2$

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

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

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&\qquad = 2(J_{ab} - K_{ab})
\end{aligned}
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$$\boxed{J_{ab} \geq K_{ab} \geq 0}$$

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

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

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

(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.

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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)

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

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

triplet wins by lower repulsion

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Less screening (relaxed orbitals)

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

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

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The virial theorem by scaling (1/2)

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

---

$$\Psi_\eta(\mathbf{r}_1, \dots, \mathbf{r}_N) = \eta^{3N/2}\, \Psi(\eta\mathbf{r}_1, \dots, \eta\mathbf{r}_N) \tag{1}$$

squeeze ($\eta > 1$) or stretch ($\eta < 1$) the whole cloud

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

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

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

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

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- *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)

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

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

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

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$$E(\eta) = \eta^2 \langle T\rangle + \eta \langle V\rangle \qquad \text{(5)}$$

add them

$$\left.\frac{\mathrm{d}E}{\mathrm{d}\eta}\right|_{\eta=1} = 2\langle T\rangle + \langle V\rangle = 0 \qquad \text{(6)}$$

exact state: stationary under any variation

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

Result

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

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Frozen orbitals cannot be the mechanism

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

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

SYMBOLS same orbitals ⇒ 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 $\langle T\rangle$

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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)

(1) $\Delta T = -\Delta E > 0$ *virial: $E = -T$; electrons more compressed*

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

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

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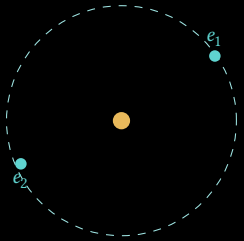
The physical picture



singlet: electrons may overlap,
each screens the nucleus

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

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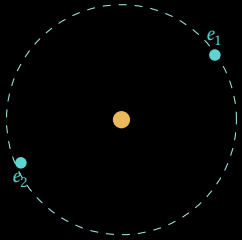

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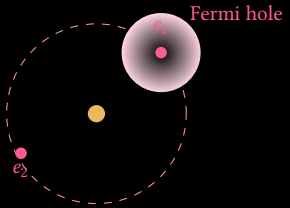

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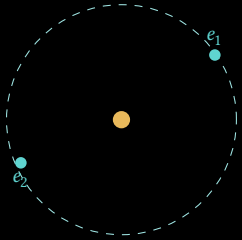

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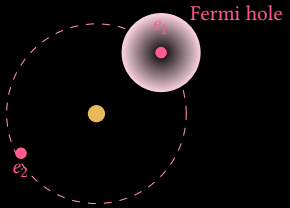

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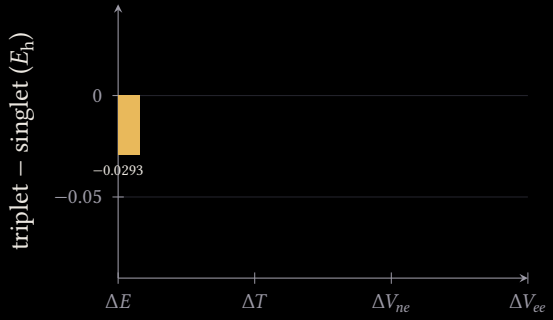
contraction lowers V_{ne} • raises T • also raises V_{ee} (closer on average)

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

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

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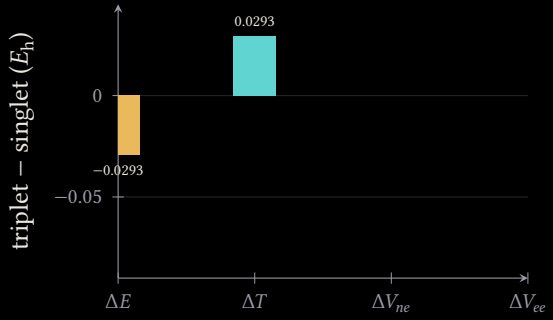

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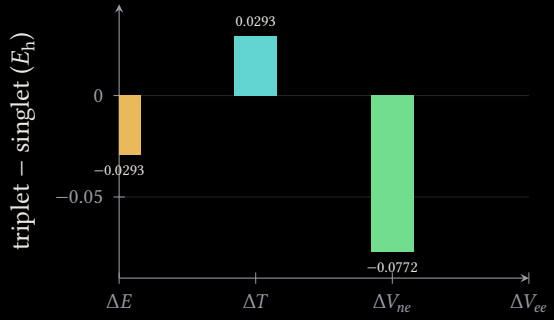

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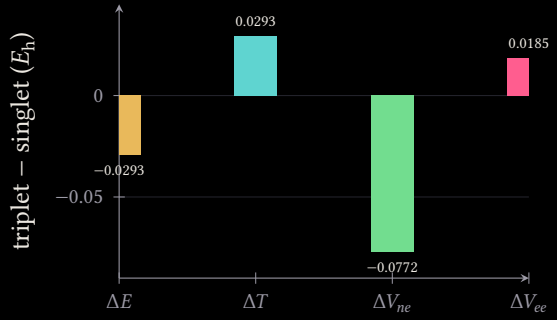

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$\Delta V_{ee} > 0$: Slater's mechanism fails; ΔV_{ne} pays for everything.

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

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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

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

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

Result

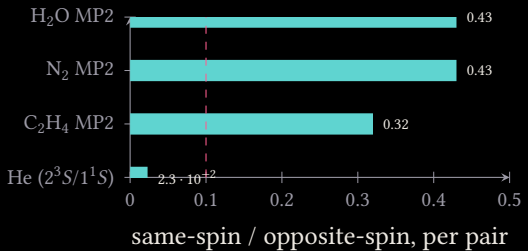
The review's account (less screening, V_{ee} *greater* in the high-spin state) agrees with He (ours) and C (Hongo). VERIFIED

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)



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

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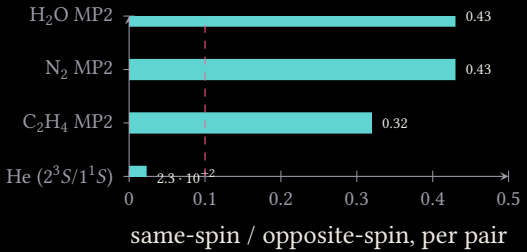

dashed: "order of magnitude" (0.1)

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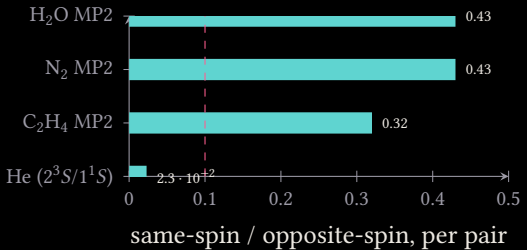

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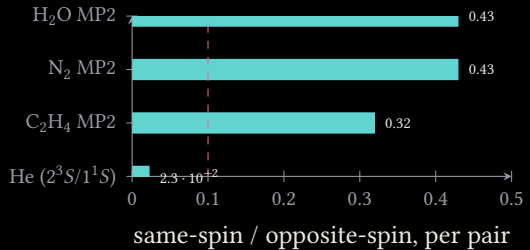

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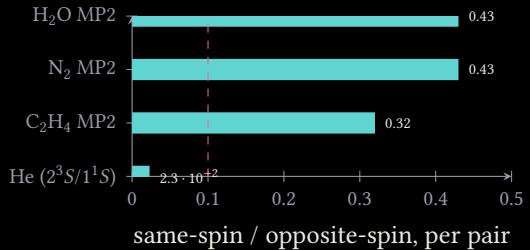

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OVERSTATED true for compact two-electron systems, overstated in general (T15)

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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)

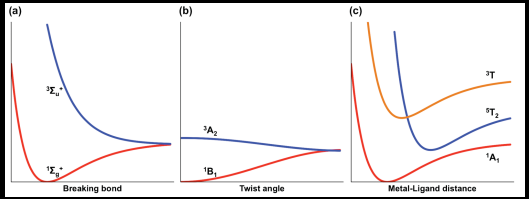

Fig. 2: (a) H_2 bond breaking (b) ethylene twist (c) metal–ligand distance

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

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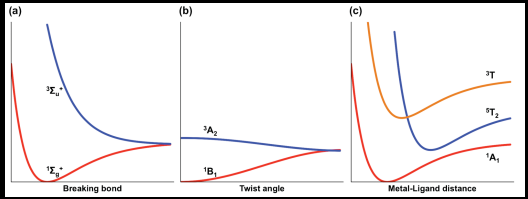
dynamic: electrons dodging each other within one configuration

static: several configurations of comparable weight



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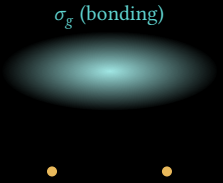
$\mathcal{H}_2$ in a minimal basis

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

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

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



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

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

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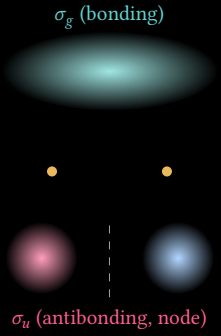

- $\sqrt{2(1 \pm S)}$: $\langle \chi_A \pm \chi_B | \chi_A \pm \chi_B \rangle = 1 + 1 \pm 2S$

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*

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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 $\langle \Phi_i | \hat{H} | \Phi_{\bar{i}i} \rangle$ derived in Part V*

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 $\sigma_g^1\sigma_u^1$

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

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

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

$$\varphi_1^2 = \frac{1}{2}(\chi_A^2 + \chi_B^2 + 2\chi_A\chi_B) \to \frac{1}{2}(\chi_A^2 + \chi_B^2)$$

the atoms no longer overlap

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

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$$\varphi_2^2 \to \frac{1}{2}(\chi_A^2 + \chi_B^2)$$

same, minus sign gone

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

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

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

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

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- *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*

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

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

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

CI: purely covalent
Heitler–London H· ·H

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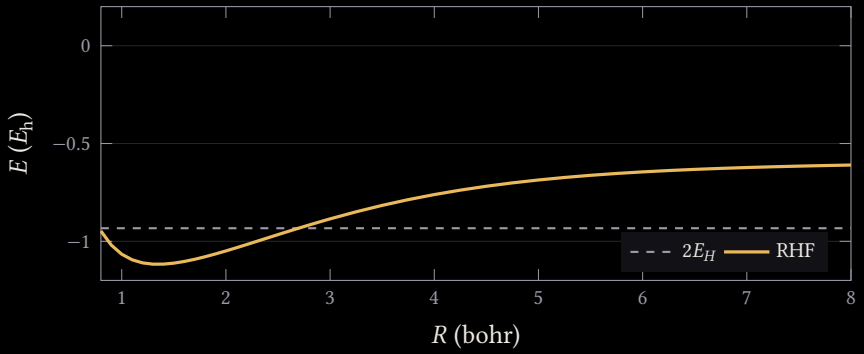
H_2 curves from our calculation

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



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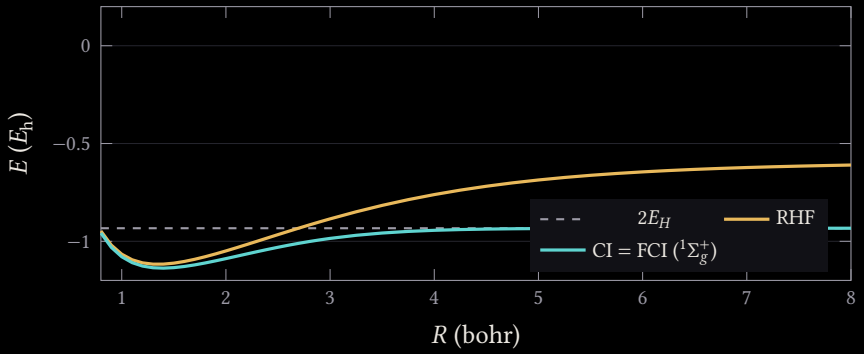

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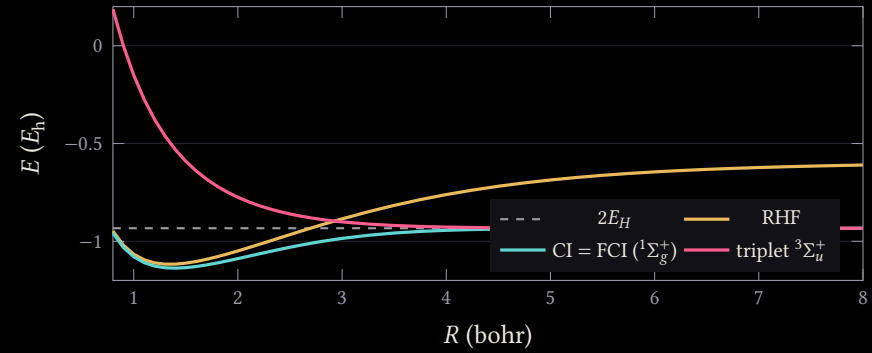

CI and triplet converge on $2E_H$; RHF does not (T5: still $0.362\ E_\mathrm{h} = K_{12}$ too high at $R = 20$ bohr)

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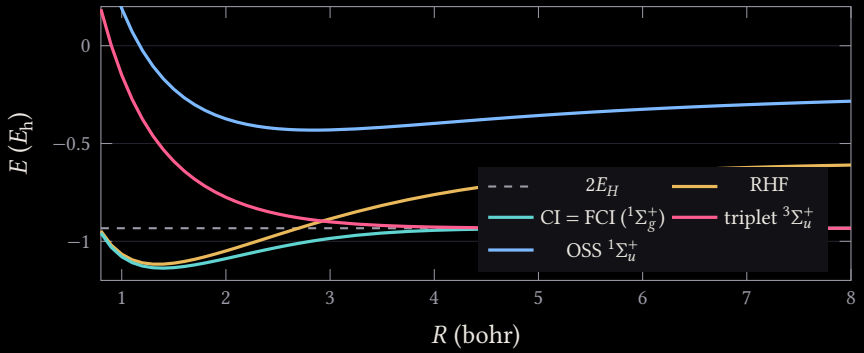

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The general rule: orbital gap versus exchange

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

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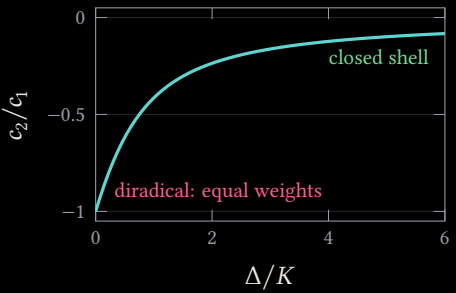

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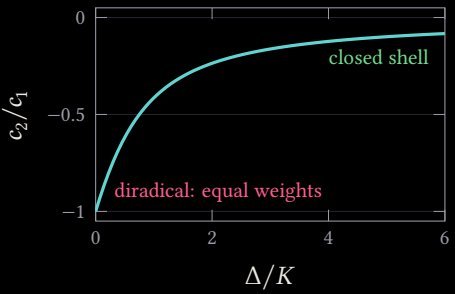

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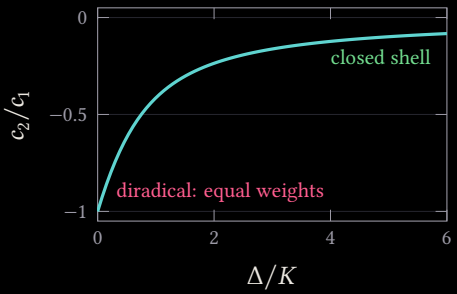

VERIFIED weak interaction ⇒ strong static correlation (T6)

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Part IX

Kinetic exchange

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The Hubbard picture

The paper says

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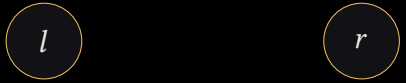

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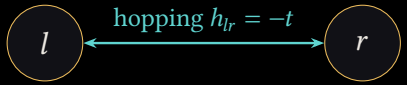

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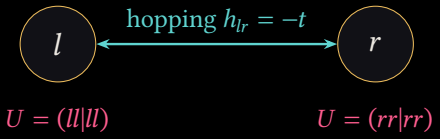

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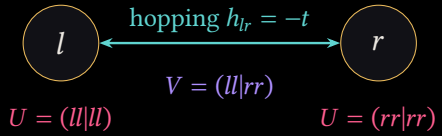

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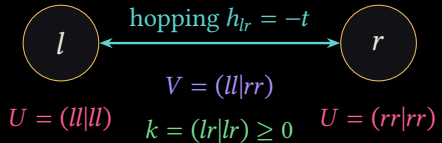

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Step 1: ionic configurations are pure singlets

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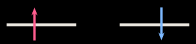

covalent



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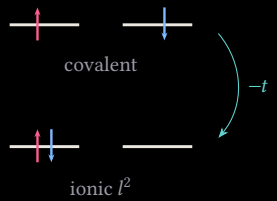

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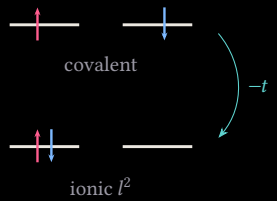
2. that spatial part is symmetric: swapping 1 and 2 changes nothing
3. antisymmetry $\Rightarrow$ its spin part must be the antisymmetric singlet $\Theta_{0,0}$
4. $\hat{H}$ is spin-free, so $\langle \text{ionic}|\hat{H}|\text{triplet}\rangle \propto \langle \Theta_{0,0}|\Theta_{1,M}\rangle = 0$



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* $\sqrt{2}(h_{lr} + (ll|lr)) = -\sqrt{2}t$

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

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

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

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

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Hubbard dimer: exact versus kinetic exchange

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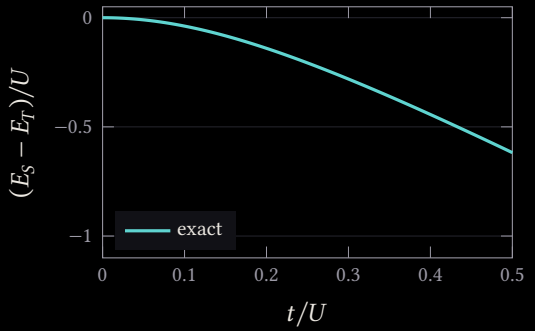

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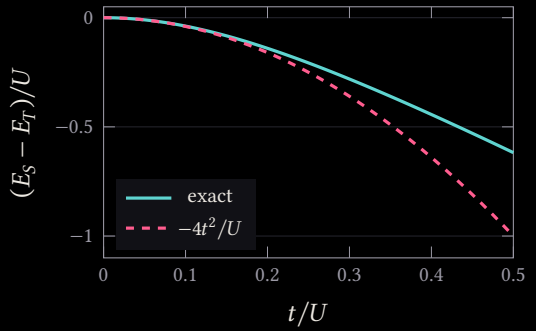

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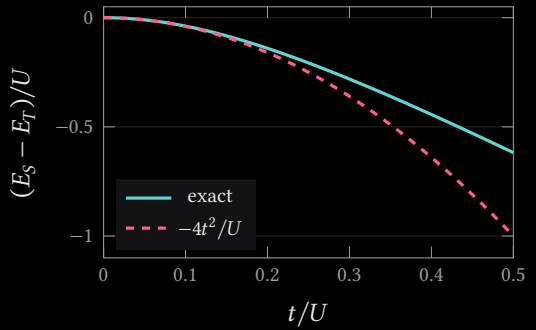

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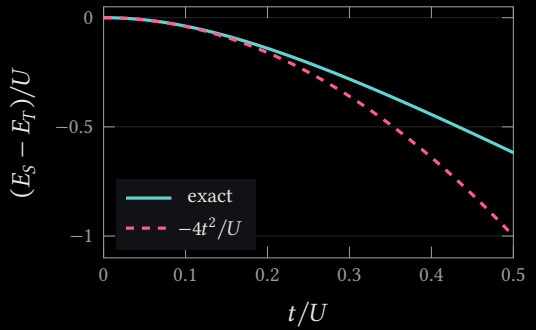

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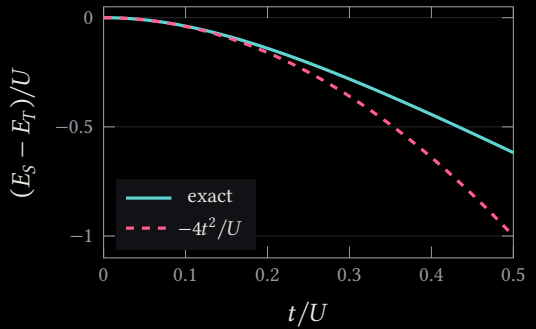

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✓ T7: symbolic + PySCF FCI (t=1, U=6, V=1.5, k=0.2)

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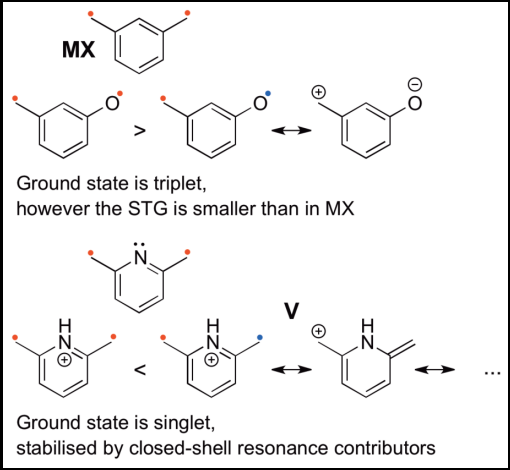
Ionic resonance reverses a spin state (Figure 6)



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)

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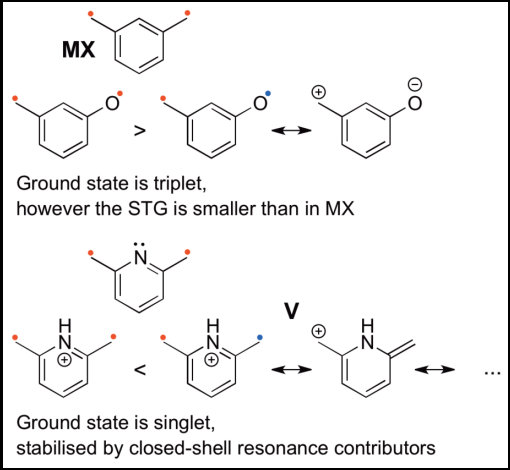

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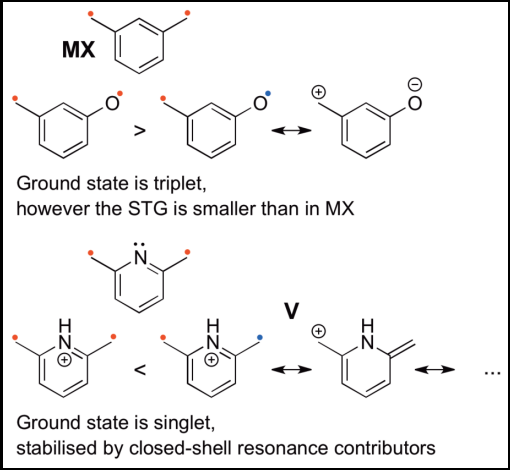

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Delocalised and localised: two views of one state

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

- *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

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

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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)

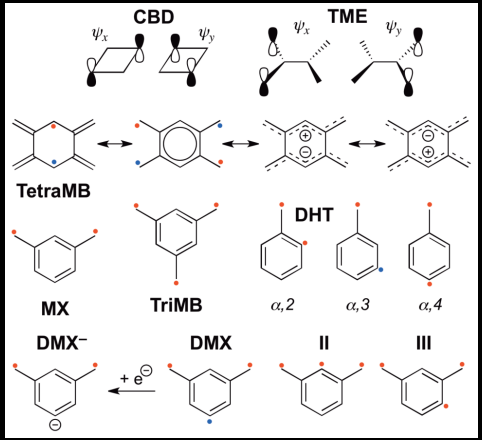

Fig. 3: high- and low-spin polyradicals

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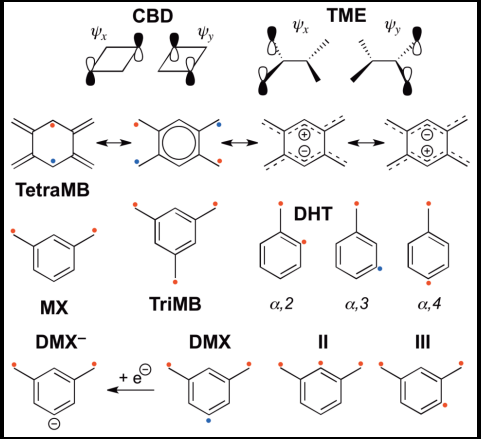
three things to derive: (1) how to find NBMOs, (2) when they can be disjoint, (3) why disjoint means $K \approx 0$



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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

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

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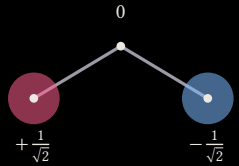

allyl NBMO: centre sees $c_1 + c_3 = 0$

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Alternant hydrocarbons: the pairing theorem

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

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

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

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

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flip the sign on one set

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flip the sign on one set

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

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How many NBMOs?

$$\operatorname{rank} \mathbf{A} = 2 \operatorname{rank} \mathbf{B}$$

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

How many NBMOs?

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

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

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Careful: only a bound

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



perfect matching

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T8 caught our own wrong assumption here.

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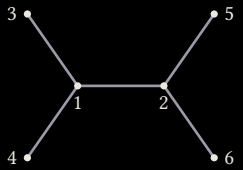
Tetramethyleneethane: solving the zero-sum equations

atom 3: $c_1 = 0$



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

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) ⇒ two NBMOs $\frac{1}{\sqrt{2}}$: normalisation

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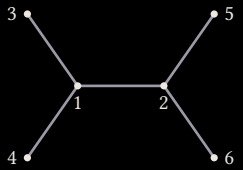

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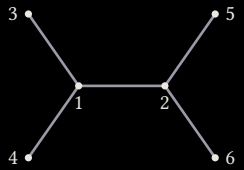

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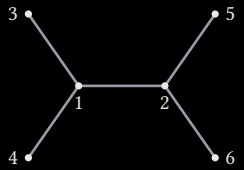

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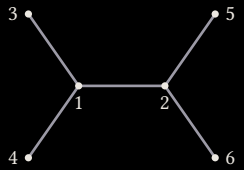

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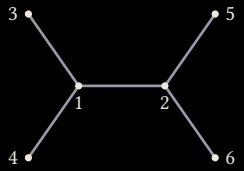

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no common atom: disjoint

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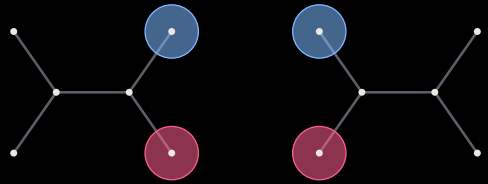
Disjoint pairs, drawn by our JavaScript

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

tetramethyleneethane

φ_a φ_b



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

cyclobutadiene (D_4h)

φ_a φ_b



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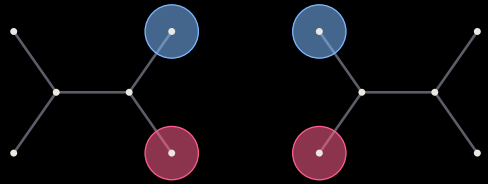

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JS code: Hückel matrix → Jacobi diagonalisation → rotate the degenerate pair to minimise $\sum_i a_i^2 b_i^2$ → SVG → PDF

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Trimethylenemethane cannot be made disjoint

1. zero-sum at a terminal $\Rightarrow c_0 = 0$

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

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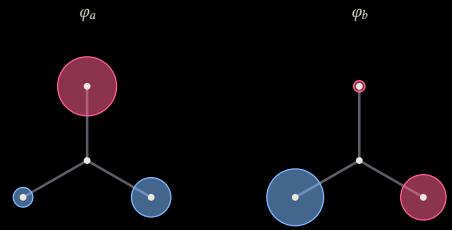

nondisjoint: min $\Sigma\, a_i^2\, b_i^2 = 0.1667 \Rightarrow K_{ab} > 0$

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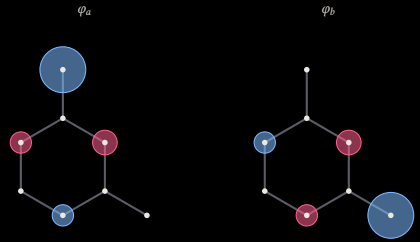
m-xylylene



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

m-xylylene: also nondisjoint

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Why disjoint means $K_{ab} = 0$

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

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

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 $\Rightarrow K_{ab} > 0$

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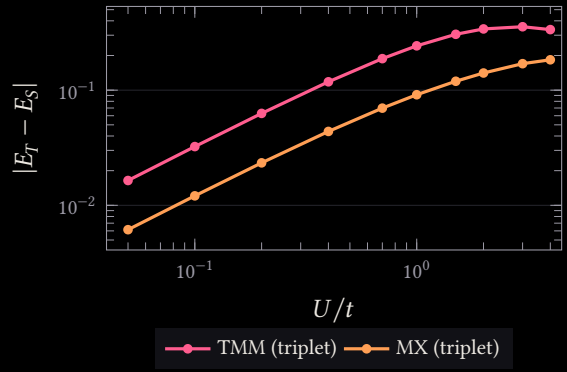
TMM: $\min \sum a^2 b^2 = \frac{1}{6}$ MX: $\frac{1}{16}$ (Python *and* JavaScript agree)

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
  $2U \cdot \frac{1}{6} = 0.0167$

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

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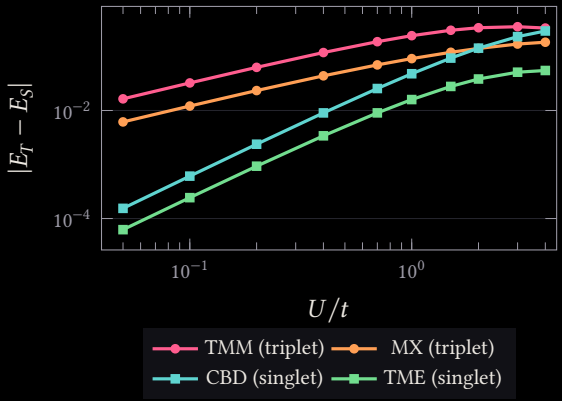

- nondisjoint: slope ≈ 1; at $U = 0.05$: TMM 0.0164 vs $2U \cdot \frac{1}{6} = 0.0167$
- disjoint: slope ≈ 2 (fit 1.97, 1.95), singlet below triplet

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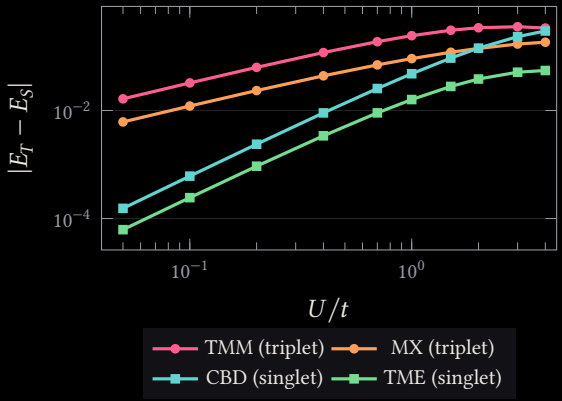
T9b: exact Hubbard diagonalisation, $t = 1$



- 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

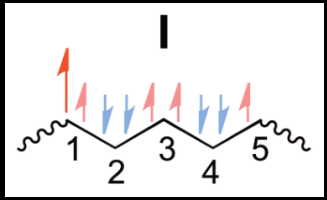
Spin polarisation

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

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

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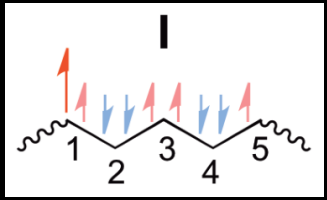

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1. Hückel: the unpaired electron sits in the NBMO, which is zero on unstarred atoms

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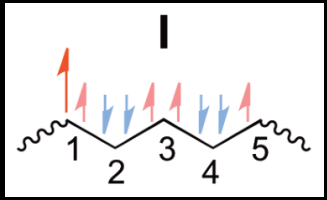

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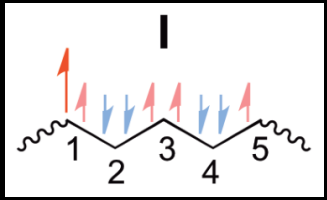

Scheme 1

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

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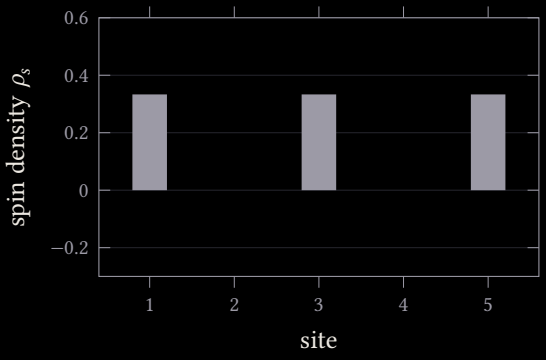
Measured on the pentadienyl radical

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



$U = 0$ (Hückel):
unstarred sites exactly 0

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

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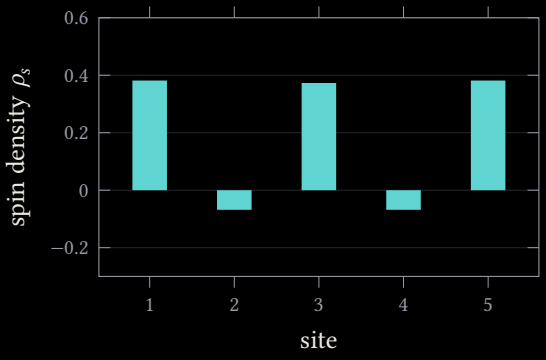

$U = t$: small negative dips

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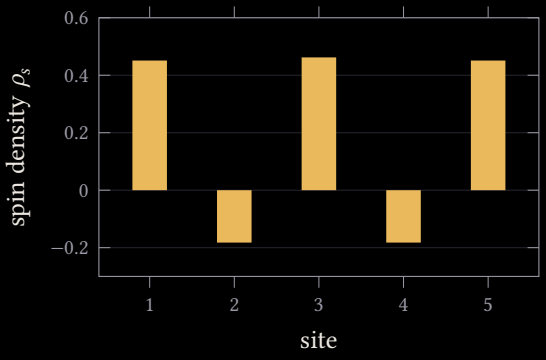

$U = 3t$: -0.18 on sites 2, 4

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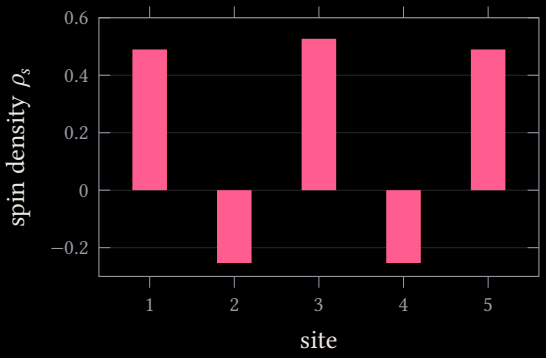

$U = 6t$: -0.25; the "damped spin wave"

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

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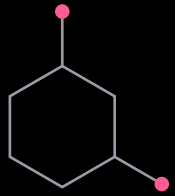

meta: 3 atoms between
parallel, triplet

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

From bonds to topology

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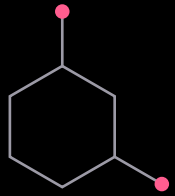

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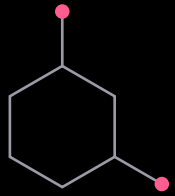

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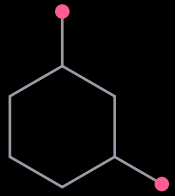

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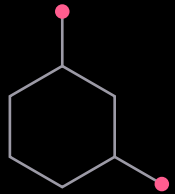
same set: parallel; different sets: antiparallel



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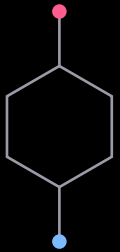

para: 4 atoms between
antiparallel, singlet

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

count the Néel arrangement: n_A up, n_B down

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

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

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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

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

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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)

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

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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)

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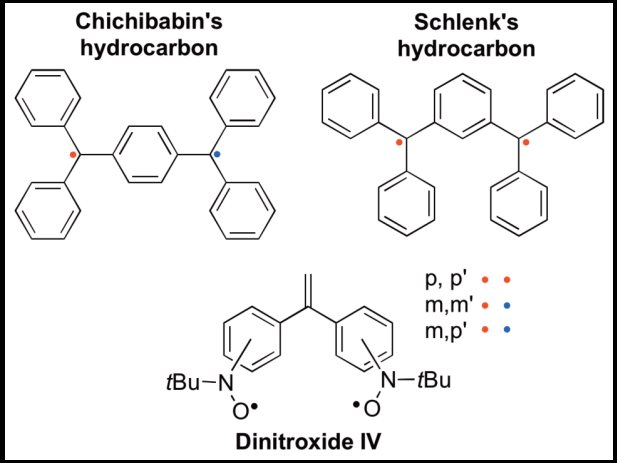
Topology in the paper: Figure 4



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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)

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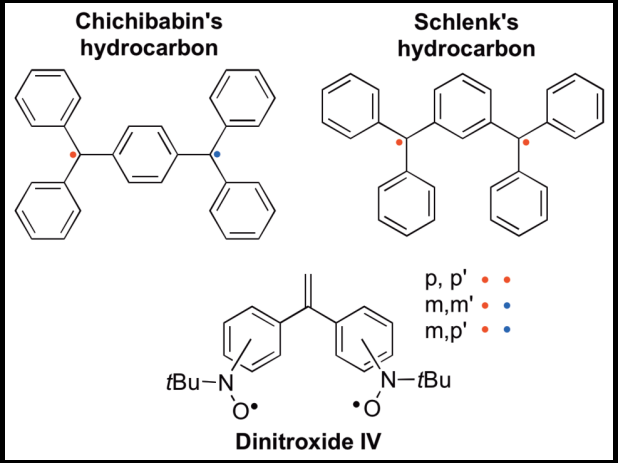

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in Fig. 4, IV with p, p' links: parallel spins; m, m' and m, p': antiparallel. Same atoms, different topology.

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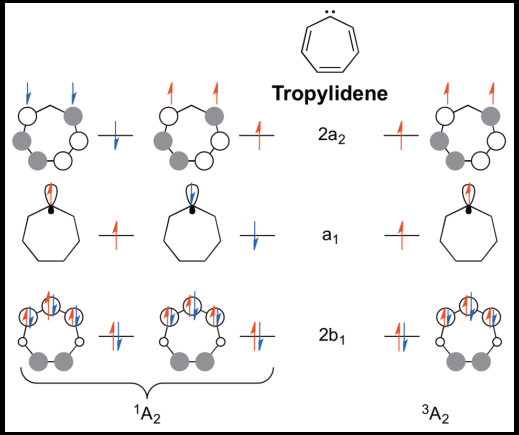
Tropylidene: a singlet from spin polarisation (Figure 5)



1. unpaired electron in the $2a_2$ π orbital

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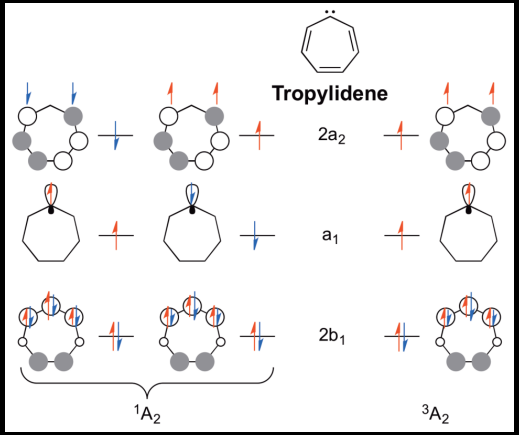

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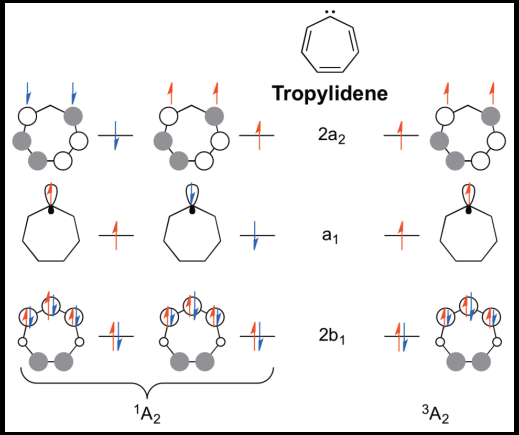

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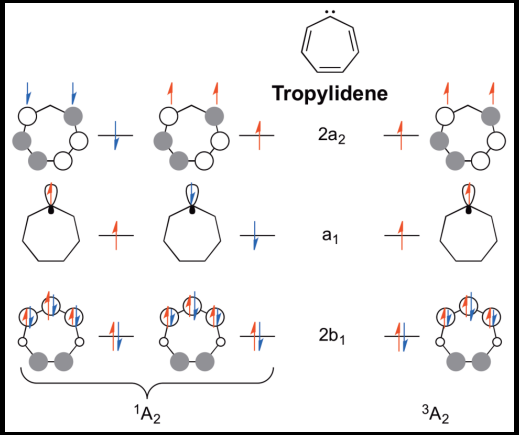

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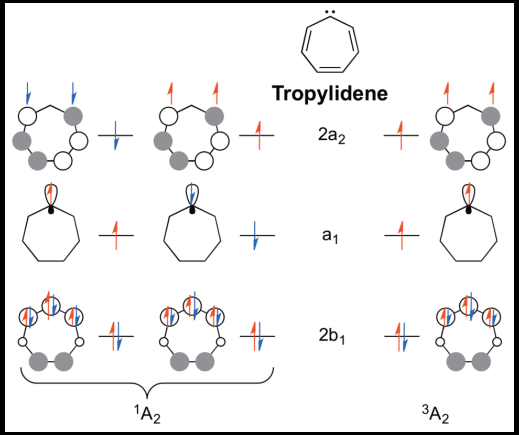

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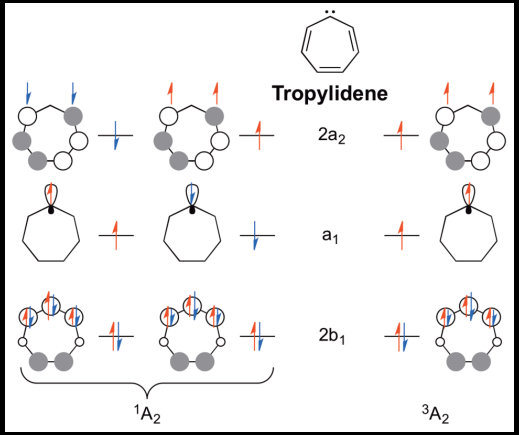

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5. net result: the $^1A_2$ singlet is lower

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

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

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

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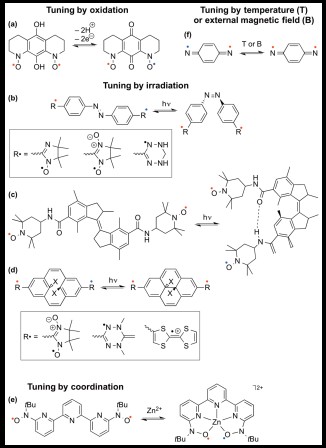
Part XII

Switching spin states

XII

Spin-state crossover by external stimuli (Figure 7)



- (a) oxidation: quinone coupler switches two nitroxides between ferro- and antiferromagnetic coupling

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

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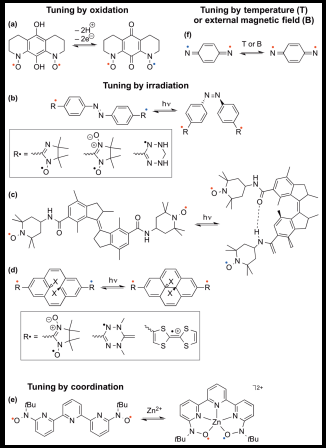

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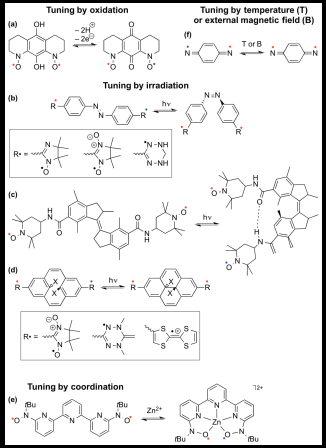

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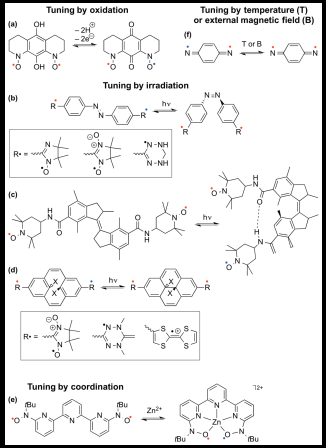

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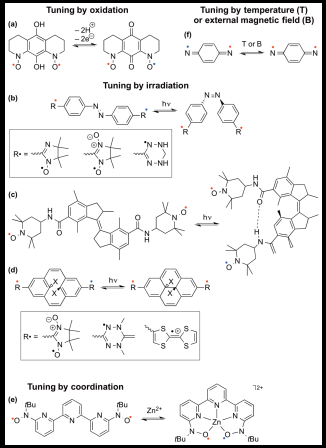

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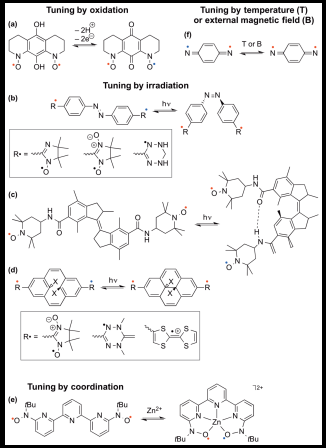

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- (f) *T* or *B*: 1,4-phenylenedinitrene, open-shell singlet → triplet

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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)

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

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Panel (f), quantitatively: temperature

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

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

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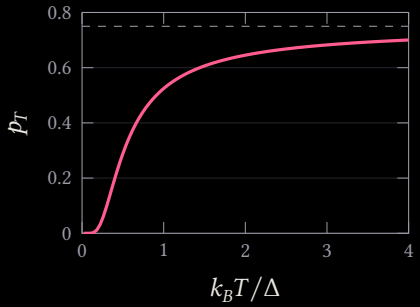

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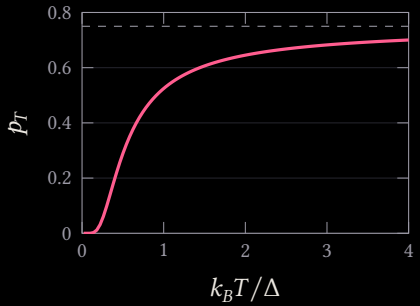

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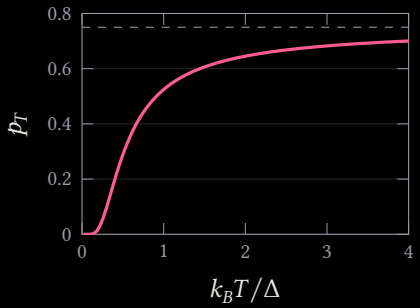

"increased temperature … promotes electrons to populate the triplet state" (p. 445) VERIFIED

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

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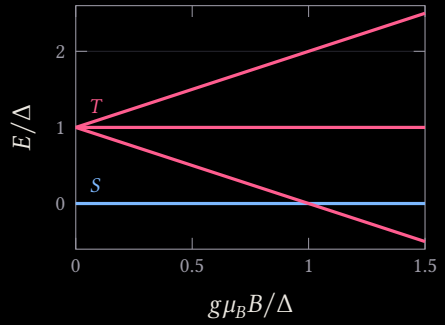

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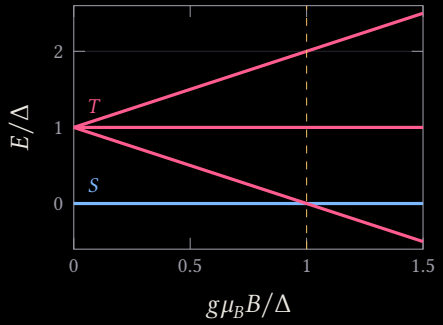

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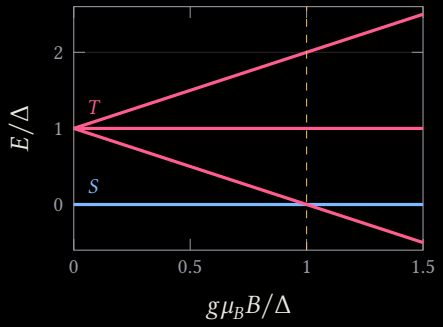
"external magnetic field that splits the triplet into microstates, one of which approaches the energy of the ground-state singlet" (p. 445) VERIFIED



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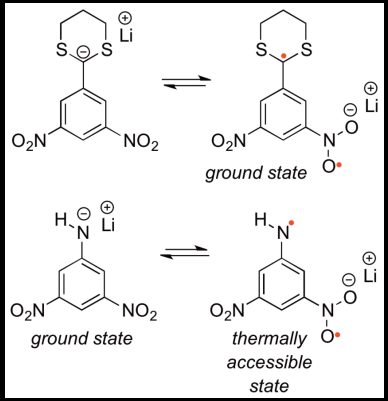
Closed shell or diradical? (Figures 8 and 9)



- 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

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

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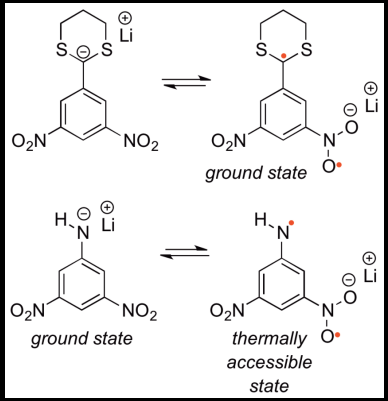

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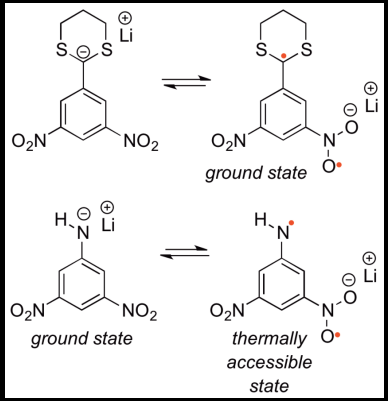

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- singlet fission: one excited singlet shares its excitation with a neighbour; both end in a low triplet

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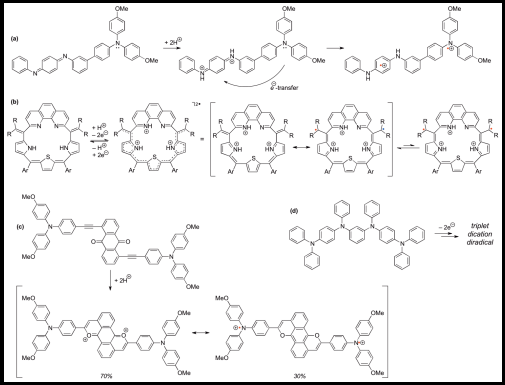
Protonation-induced magnetisation (Figure 9)



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)

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"

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

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Koopmans' theorem

Assumptions

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

$$E_N = \sum_i \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{i,j}\big([ii|jj] - [ij|ji]\big) \qquad \textit{Slater--Condon rules}$$

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

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$$= \varepsilon_k \qquad \textit{definition of the Fock eigenvalue}$$

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

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

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

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

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

n_i enters ρ linearly; chain rule

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

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

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

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

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

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The gap as a HOMO difference

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

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

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$$\varepsilon_b^T = E_T - E_{\text{ion}} = h_b + J_{ab} - K_{ab}$$

$E_T = h_a + h_b + J - K$ (Part V)

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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)

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 $\hat{H}$

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Exhibit A

one-electron quantum numbers are not conserved

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Exhibit B

the adiabatic argument behind "building up"

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one-electron quantum numbers are not conserved

Exhibit B
the adiabatic argument behind "building up"

Exhibit C
the 3d/4s paradox

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

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

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insert both derivatives

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&= -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*

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Result

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

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$\hat{\mathbf{L}}$ 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

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Exhibit B: the adiabatic theorem

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)

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 ($m \neq n$)

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

expand in snapshot eigenstates

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

insert in $i\dot{\Psi} = \hat{H}\Psi$, project on ψ_m

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slow $\dot{\hat{H}}$, finite gaps $\Rightarrow$ 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.

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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

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

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: the algebra

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

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Result

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

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3d/4s: reading the identity

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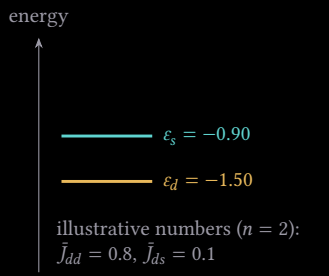

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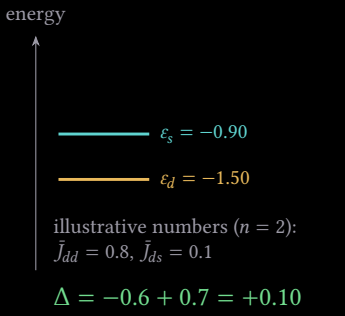

orbital energies belong to a *configuration*: the building-up and removal orders need not agree

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Verdict on the aufbau critique

right

- one-electron quantum numbers are model labels (Exhibit A)

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

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- orbital energies depend on the configuration (Exhibit C)

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OVERSTATED

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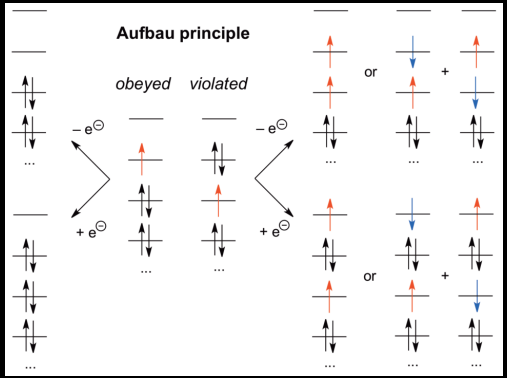
Part XV

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)

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)

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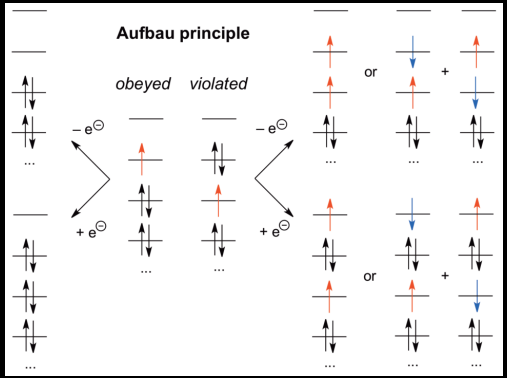

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the fingerprint is redox: products are polyradicals (diradicals in the simplest case), not closed shells

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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; $\varepsilon_k = E_N - E_{N-1}^{(k)}$ (Koopmans)

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

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

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

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

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

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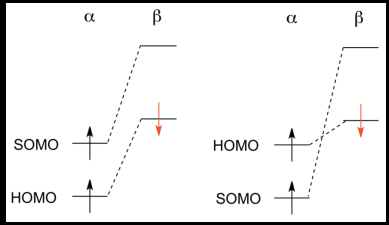
Scheme 3, derived

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



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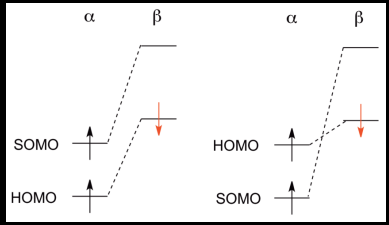

✓ T2: all four checked against determinant energies

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When does the SOMO drop below the HOMO?

compare within the α manifold:

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insert the two α energies

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)

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

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The paper says

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

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oxidation

- Koopmans: $\mathrm{IP}(h) = -\varepsilon_h < \mathrm{IP}(s)$

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

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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; $\quad \mathbf{D}^{\alpha} = \mathbf{D}_c + \mathbf{D}_o,\ \mathbf{D}^{\beta} = \mathbf{D}_c$

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

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

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✓ 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

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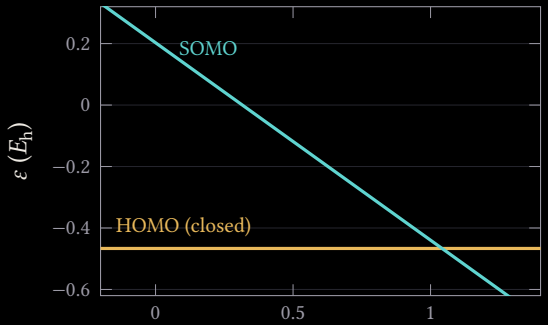
How arbitrary? H_2NO, ROHF/6-31G*



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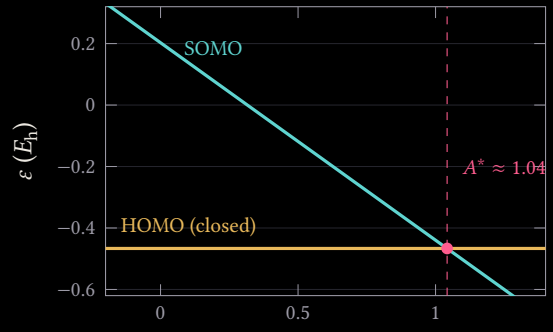

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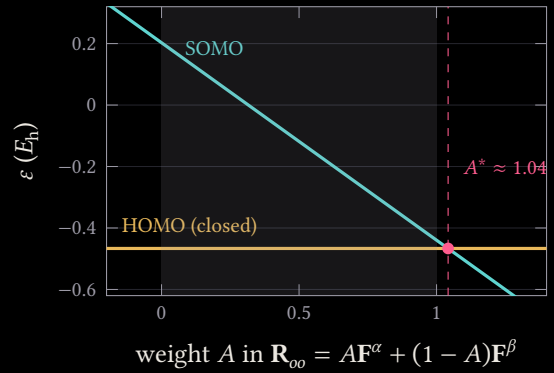

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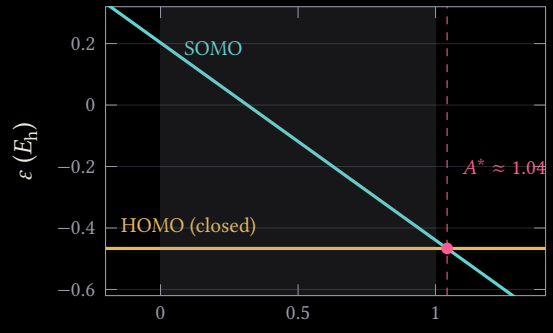

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OVERSTATED the review is right in principle; for ordinary radicals the standard choices do not flip

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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)

orbital ordering
convention-dependent

E(diradical) vs E(closed shell)
invariant

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

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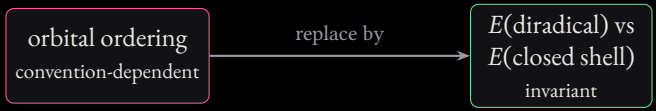

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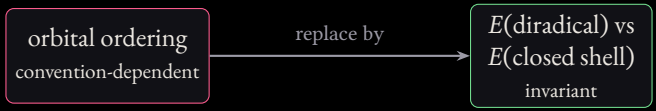

this is exactly the test we ran on a distonic radical anion (a few slides ahead)

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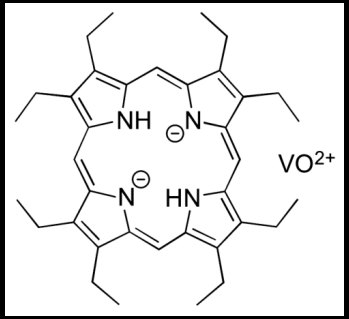
Inorganic precedents (Scheme 2)



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- unpaired electron localised on vanadium

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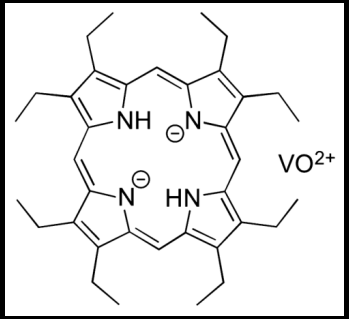

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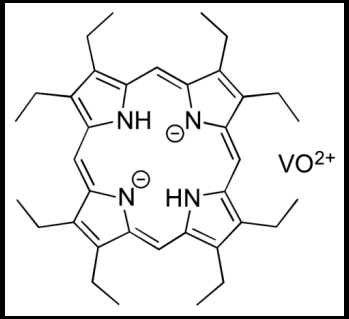

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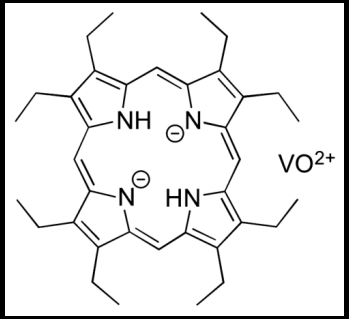

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also reported: quantum dots, the LiF dissociation curve

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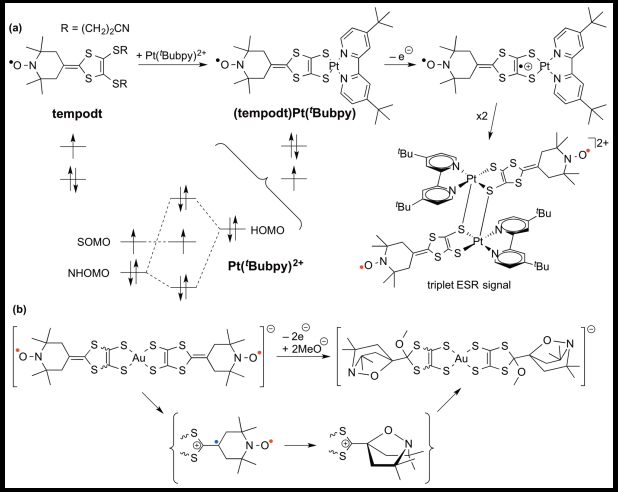
A TEMPO-dithiolate on platinum (Figure 11)



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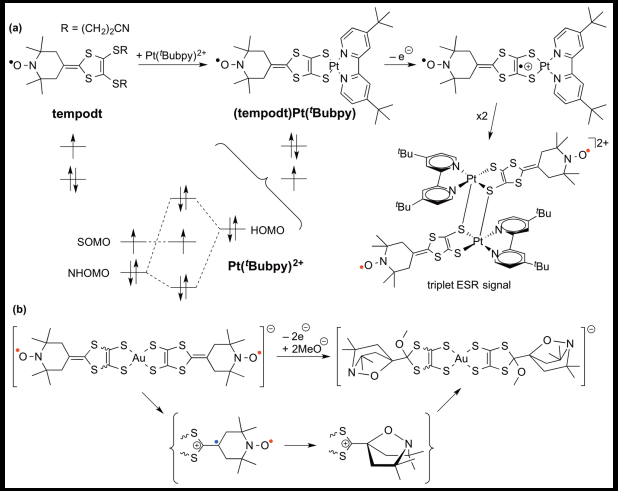

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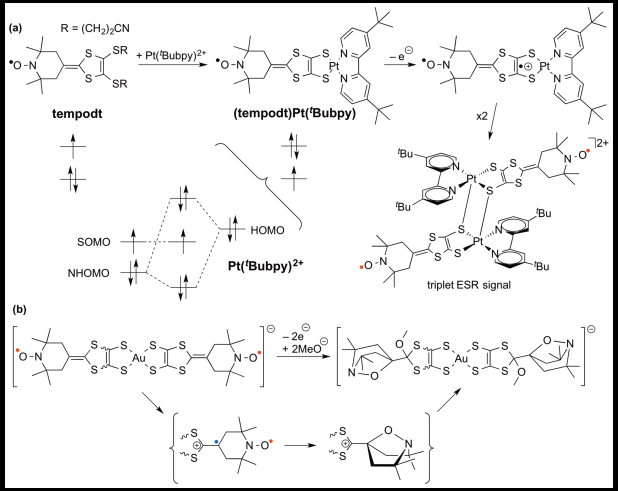

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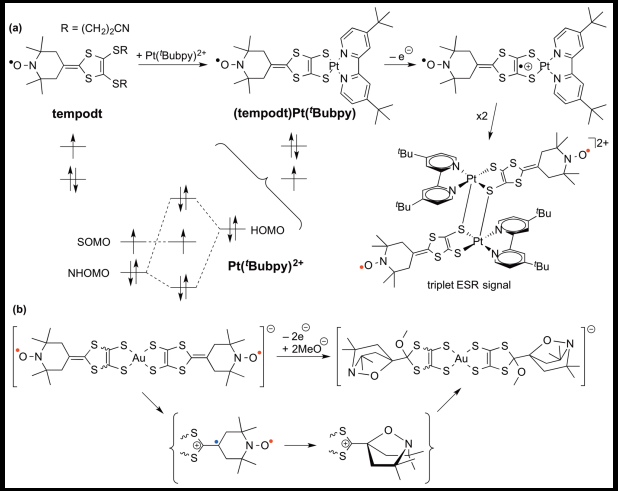

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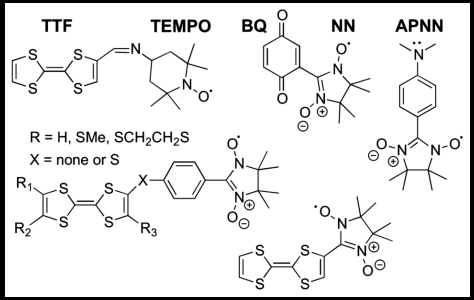
Spin-polarised donors (Figures 12, 13)



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

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

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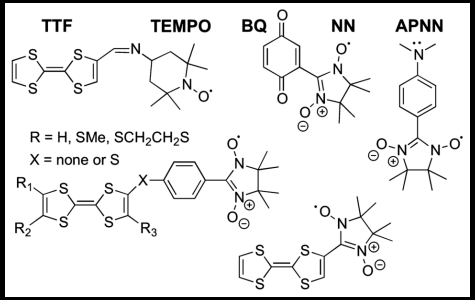

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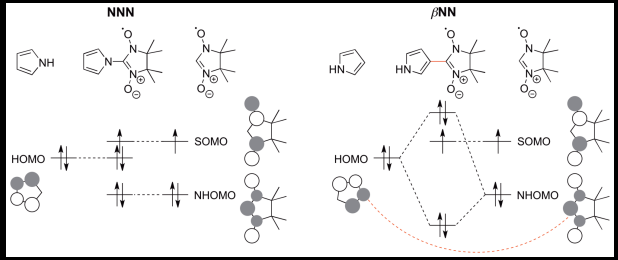

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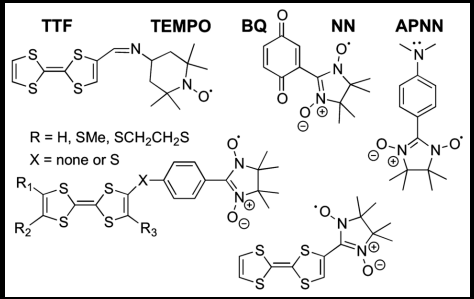

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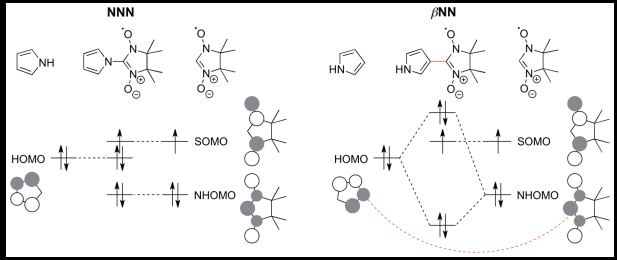

NNN (1-pyrrolyl): donor HOMO disjoint from SOMO/NHOMO. *β*NN (3-pyrrolyl): donor HOMO and NHOMO nondisjoint; their combination rises above the SOMO.

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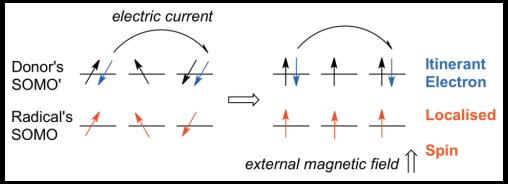
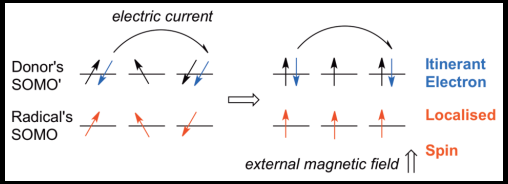
Conducting magnets (Scheme 4, Figure 14, Scheme 5)

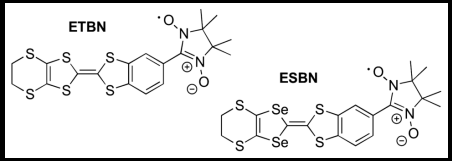


- two nondegenerate SOMOs: the donor's (higher) carries an itinerant electron, the radical's (lower) a localised spin

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

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"

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

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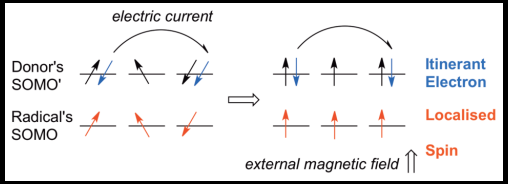

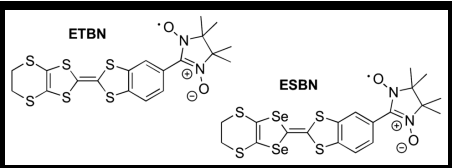

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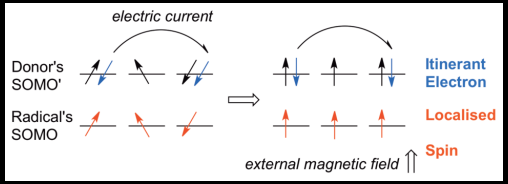

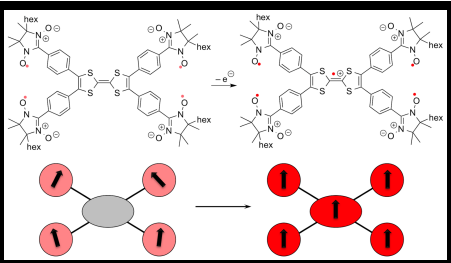

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- ETBN, ESBN perchlorate salts: "first genuine paramagnetic conductors"
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- Fig. 14: several radicals on one donor; oxidation gives a strongly ferromagnetic high-spin system

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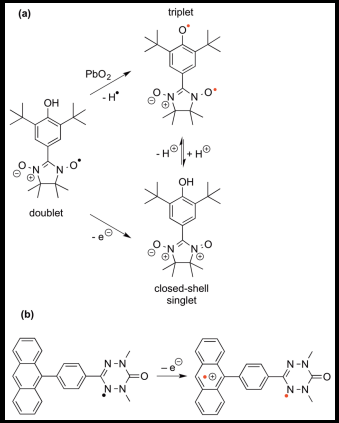
Other radicals, and a pH sensor (Figure 15)



- (a) NN with a phenol-based donor: (de)protonation switches between *triplet* and *closed-shell singlet*: a pH sensor

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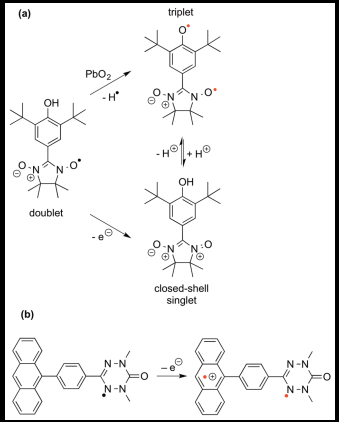

- (a) NN with a phenol-based donor: (de)protonation switches between *triplet* and *closed-shell singlet*: a pH sensor
- (b) anthracene–*p*-phenylene–oxoverdazyl (AnOV): high-spin oxidation products

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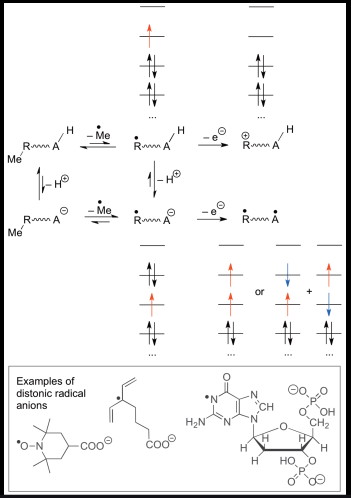
Distonic radical anions (Figure 16)



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)

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

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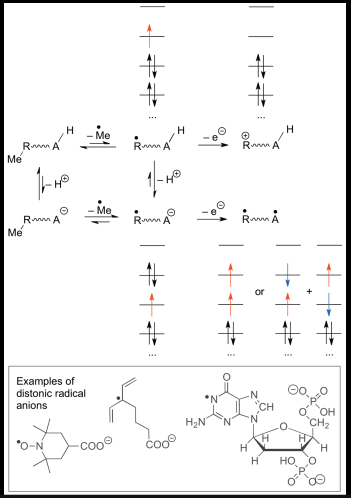

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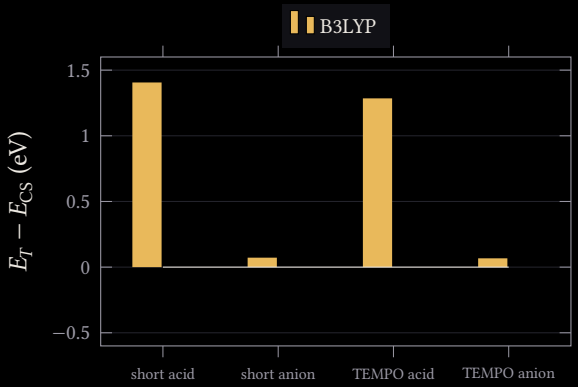
testable (and so far computational): compute both oxidised states, with and without the proton

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

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)

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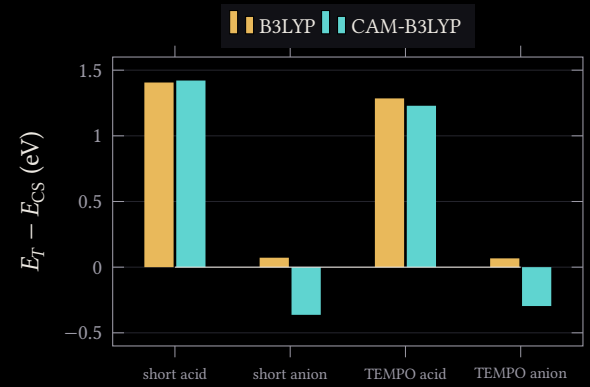

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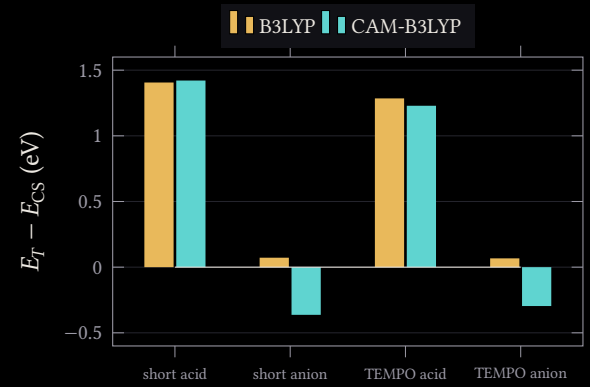

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- anions, B3LYP: misses by 0.06–0.07 eV

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What the test says

reproduced

- SOMO 2–3 levels below the HOMO in the anions; equal to the HOMO in the acids

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

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- SOMO 2–3 levels below the HOMO in the anions; equal to the HOMO in the acids
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- verdict flips at $\sim$ 0.07 eV: a functional-sensitive claim
- delocalisation error is a plausible cause (not tested)

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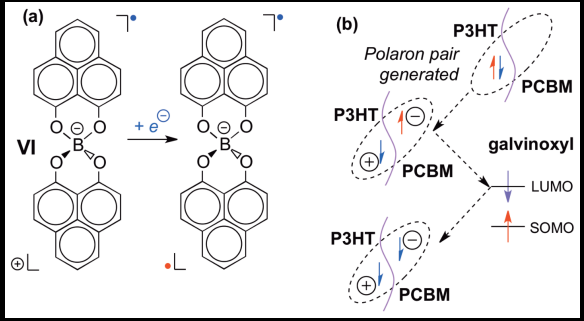
Non-aufbau by electron addition (Figure 17)



- (a) spirobiphenalenyl VI is reduced to an open-shell singlet; it crystallises without dimerising: an intrinsic molecular metal

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

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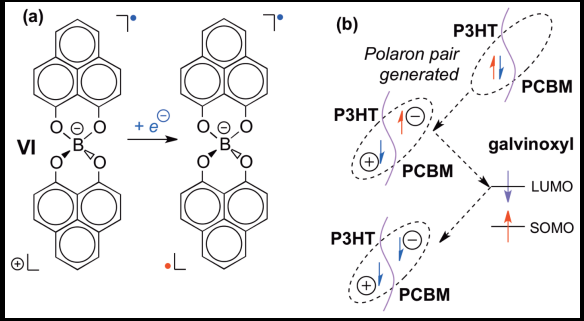

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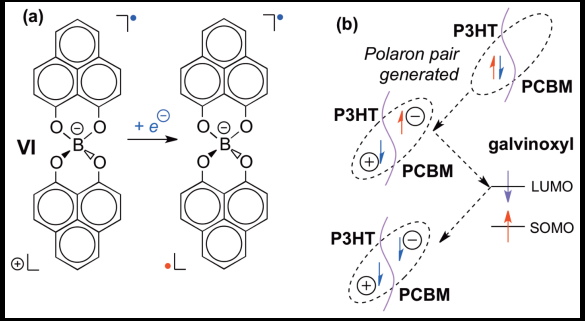

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- self-doping: in $TTFCOO^{-}NH_4^{+}$ the SOMO of the $TTF^{+\bullet}$ unit is not the highest occupied orbital, according to calculations on a model tetramer

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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, $s = \langle a'|b'\rangle$

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

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

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a single determinant cannot be the open-shell singlet (Part IV)

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Yamaguchi's projection, derived

Assumptions

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

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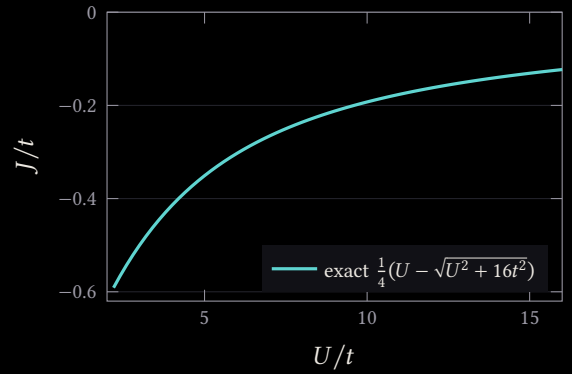
Lean: `yamaguchi`; sign conventions differ between sources, here $J < 0$ is antiferromagnetic

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



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

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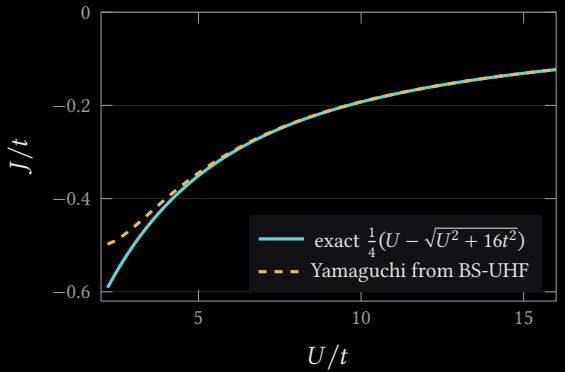

- $U = 3t$: error -7.7%

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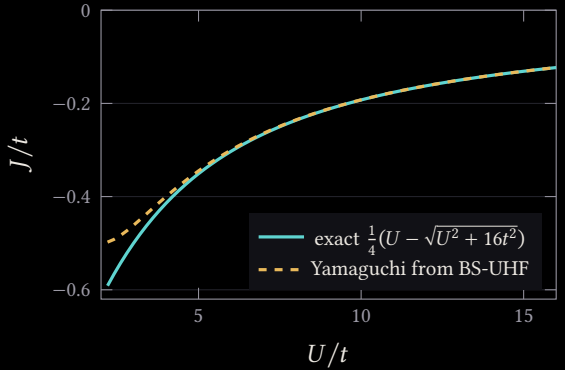

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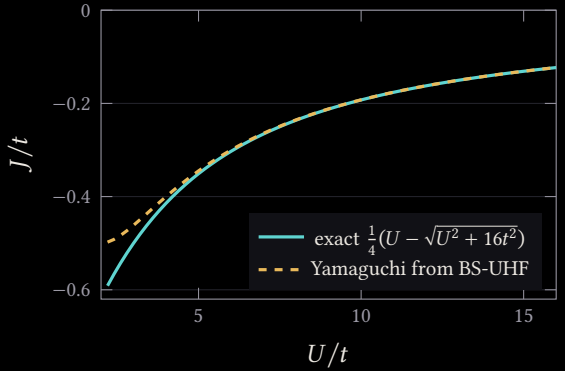

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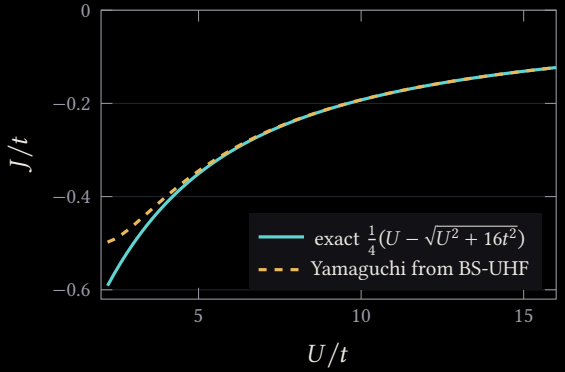

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VERIFIED "serious drawbacks" is fair

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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
```

The repository

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

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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)

```
# 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
```

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

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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

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

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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

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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

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

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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 $\frac{1}{2}(D_{\mathrm{iv}} - D_{\mathrm{iii}})$

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Possible slip, p. 445

“triplet ground state, predicted on the basis of disjoint NBMOs” contradicts the review’s own disjoint/nondisjoint rule

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

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Even the open-shell singlet in print can fluctuate.

Key references

- G. Gryn'ova, M. L. Coote, C. Corminboeuf, *WIREs Comput. Mol. Sci.* **5**, 440 (2015)
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Thank you

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