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Holomorphic Hartree Fock Theory: Beyond the Coulson–Fischer point

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There are many solutions to the SCF equations

SCF solutions are stationary points of the Hartree–Fock energy with respect to occupied-virtual orbital rotations:

- Many local maxima, minima and saddle points exist.
- Local stationary points correspond loosely to excited electronic states.
- SCF solutions are quasidiabatic states.

Stationary points may disappear as geometry changes:

- States coalesce and vanish at instability thresholds.
- Often related to emergence of symmetry broken solutions. • Leads to discontinuous energies when used as a basis for NOCI.

States of H₂ vanish as geometry changes





UHF energy as a function of θ_{α} and θ_{β} . 8 stationary points exist at 4.00 Å (left) but only 4 at 0.75 Å (right).

The UHF orbitals for H_2 (STO-3G) can be

 $\psi^{\alpha} = \cos(\theta_{\alpha})\sigma_q + \sin(\theta_{\alpha})\sigma_u$ $\psi^{\beta} = \cos(\theta_{\beta})\sigma_q + \sin(\theta_{\beta})\sigma_u.$

represented by two angles θ_{α} and θ_{β} .

Holomorphic Hartree–Fock prevents states from disappearing

SCF orbitals are a linear combination of basis orbitals,

 $\psi_i = \sum c_{\alpha i} \chi_{\alpha}.$

The Hartree-Fock energy depends on the coefficients $c_{\alpha i}$ and their complex conjugates $c^*_{\alpha i}$

 $E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$

Hartree-Fock states can disappear because the dependence of E on c_i^* means its gradient is not welldefined for complex coefficients.

Remove the complex conjugate to define the Holomorphic Hartree–Fock energy

$$\widetilde{E}[\Psi] = \frac{\langle \Psi^* | H | \Psi \rangle}{\langle \Psi^* | \Psi \rangle}.$$

E is analytic for $c_{\alpha i}$ and where UHF solutions disappear, the h-UHF coefficients become complex.

 $E[\Psi_{\rm hUHF}]$ is real and the h-UHF states can be used as a basis for NOCI.

h-UHF solutions for H_2 (STO-3G). Where UHF states disappear, their h-UHF counterparts continue with complex coefficients.



Holomorphic states provide a basis for NOCI

SCF states are not mutually orthogonal so we must solve the generalised eigenvalue equation

 $\mathbf{H}\mathbf{v} = E\mathbf{S}\mathbf{v},$

The number of holomorphic states is constant

Algebraic geometry shows the number of h-RHF states for two electron systems with n basis functions is

where $H_{wx} = \langle {}^{w}\Psi | H | {}^{x}\Psi \rangle$ and $S_{wx} = \langle {}^{w}\Psi | {}^{x}\Psi \rangle$.

- Energies are size-consistent and scaling is similar to SCF.
- NOCI states provide excited state trial wavefunctions for DMC.

DMC energies of H_2 at 2.5 Å using NOCI trial wave-	1
functions in 6-31G. Lowest cc-pV5Z FCI energies are	
$-1.00552 \ E_{h}$, $-0.99783 \ E_{h}$ and $-0.71396 \ E_{h}$.	1

Ψ_{T}	E_{NOCI}	$E_{\text{NOCI-DMC}}$	Abs. Error
1_+	/ Ľh	/ E _h	/ me _h
$^{1}\Sigma_{g}^{+}$	-0.9967	-1.00532(9)	0.2
$^{3}\Sigma_{u}^{+}$	-0.9902	-0.99775 (5)	0.1
${}^{1}\Sigma_{u}^{+}$	-0.6078	-0.7070(4)	6.9

Is F₂ charge-shift bound?

Valence bond theory results suggest bonding in F_2 arises from fluctuations of the electron pair density between Ψ_{cov} and $\Psi_{F^+F^-}$ / $\Psi_{F^-F^+}$ structures, creating a "charge-shift" bond.

NOCI using only ground state RHF and diradical h-UHF states can also yield a bound wavefunction.



Covalent bonding achieved without ionic states.

- $|\Phi_{\rm NOCI}\rangle = c_{\rm RHF} |\Psi_{\rm RHF}\rangle$ $+c_{\mathrm{F}^{\uparrow}\mathrm{F}^{\downarrow}}|\Psi_{\mathrm{F}^{\uparrow}\mathrm{F}^{\downarrow}}\rangle+c_{\mathrm{F}^{\downarrow}\mathrm{F}^{\uparrow}}|\Psi_{\mathrm{F}^{\downarrow}\mathrm{F}^{\uparrow}}\rangle$
- Suggests static correlation gives



- Must exist for all geometries and all atomic charges
- Provides a rigorous upper bound on number of real RHF solutions.
- States can be complex across all geometries.

HZ in STO-3G provides a model for symmetric and asymmetric diatomics.



Acknowledgements and References



NOCI energies of F_2 (6-31G) using basis of ground

RHF state and diradical h-UHF states.

key contribution to bonding.

NOCI mirrors Pauling description

where bonding arises from electrons

interchanging between two AOs.

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[3] H. G. A. Burton and A. J. W. Thom, J. Chem. Theory Comput. 12, 167 (2016), arXiv:1509.01179.