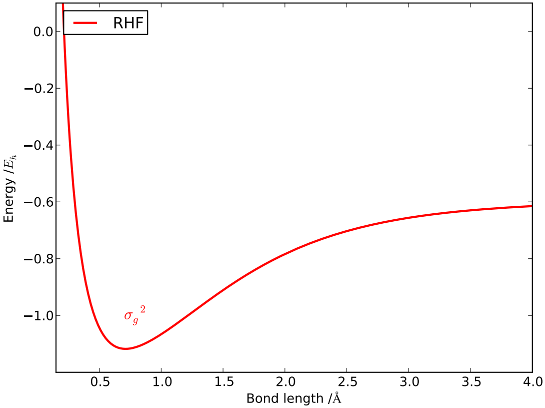
Holomorphic HF and NOCI

Alex Thom, Hamish Hiscock, James Farrell, Hugh Burton

CECAM VB/NonorCI Workshop, Institut Henri Poincaré, Paris

SCF Solutions of H_2



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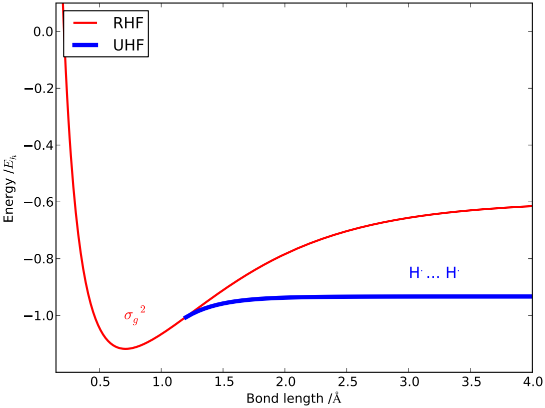

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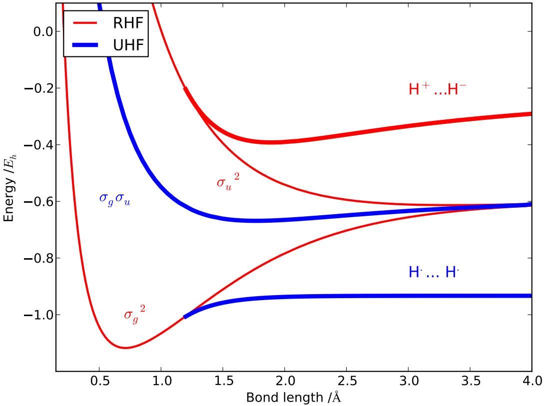


AJWT, M. Head-Gordon *Phys. Rev. Lett.* **101**, 193001 (2008)

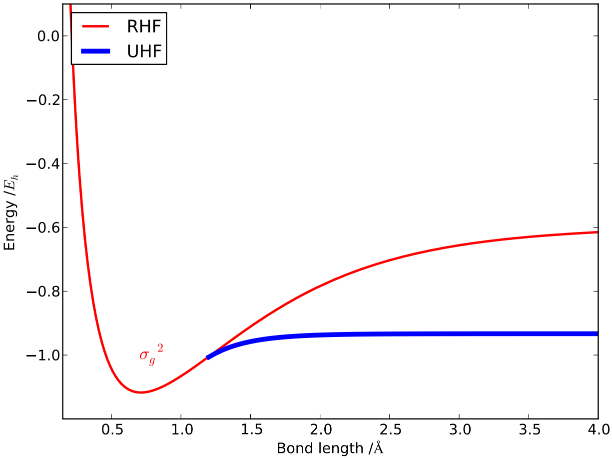
Non-orthogonal Configuration Interaction

Different SCF solutions (${}^x\Psi$ and ${}^y\Psi$) are not orthogonal, nor are their orbitals.

- We can still evaluate matrix elements $H_{xy} = \langle {}^x\Psi | \hat{H} | {}^y\Psi \rangle$
- Need overlap matrix elements $S_{xy} = \langle {}^x\Psi | {}^y\Psi \rangle$
- Solve generalized eigenvalue problem $\mathbf{Hv} = E\mathbf{Sv}$ to get energies.
- Scaling: $\mathcal{O}(n_s^2 \max\{N^3, M^2\})$ much like an SCF step per pair of solutions.

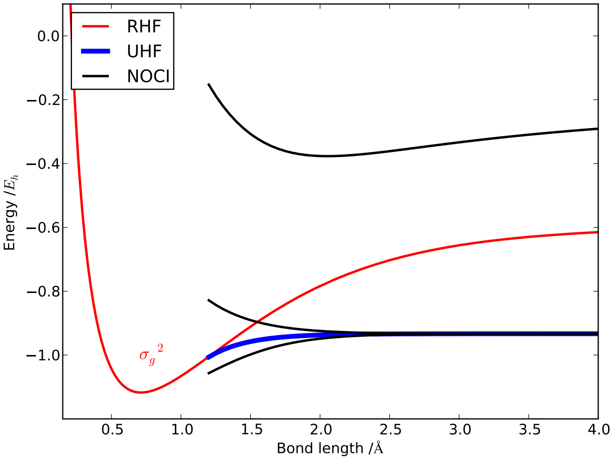
AJWT and M. Head-Gordon, *J. Chem. Phys.* **131** 124113-1–5, (2009)

H_2 UHF NOCI



RHF
UHF
0.0
−0.2
−0.4
−0.6
−0.8
−1.0
Energy /E_h
$\sigma_g{}^2$
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Bond length /Å

H_2 UHF NOCI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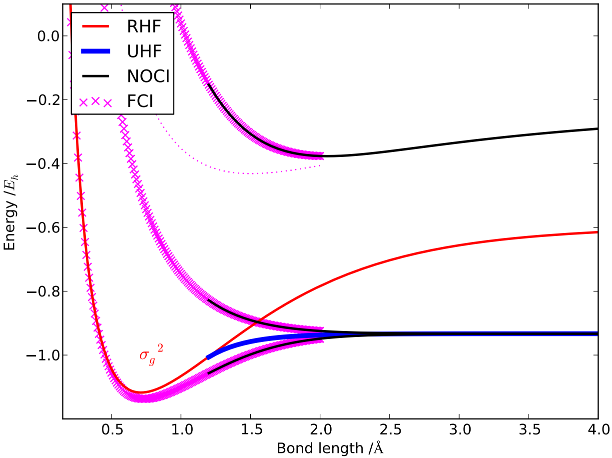

RHF
UHF
NOCI
FCI
$\sigma_g{}^2$
Energy $/E_h$
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0.5
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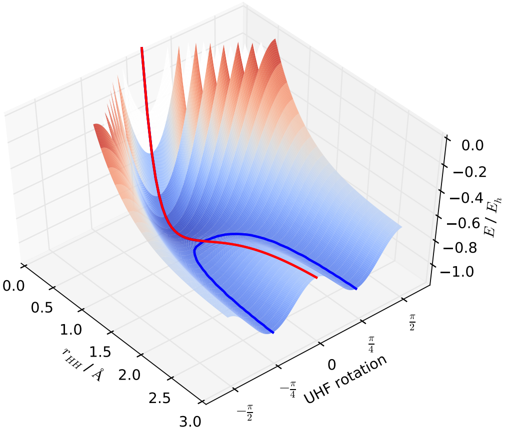
4.0

H_2 UHF Energy Surface



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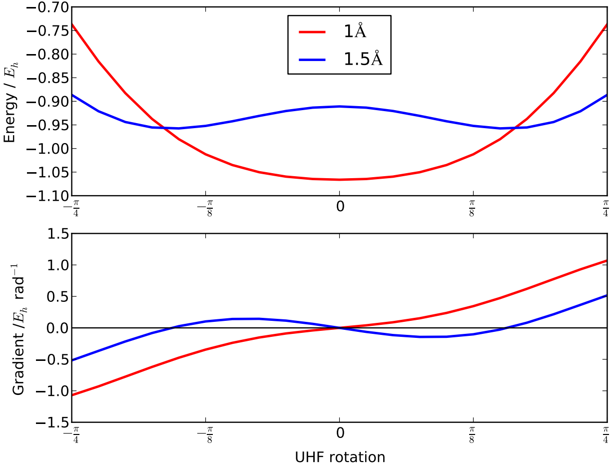

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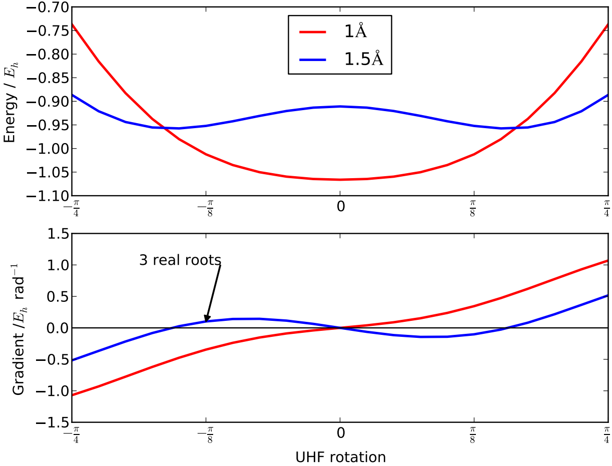

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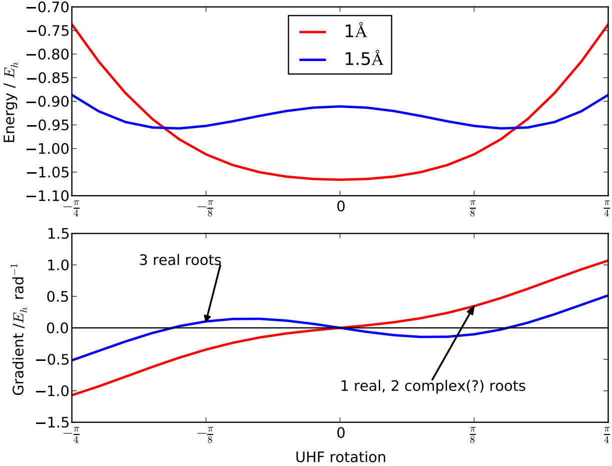

The Fundamental Theorem of Algebra

Every non-zero, single-variable, degree n polynomial with complex coefficients has, counted with multiplicity, exactly n roots.

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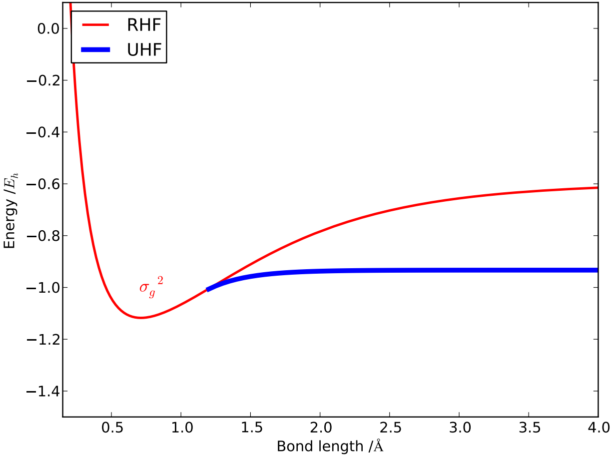
- For RHF→UHF symmetry breaking, we can parameterize with a single parameter, z, and just remove the complex conjugates. $\tilde{E} = \langle\Psi^*|\hat{H}|\Psi\rangle$.
- Search for stationary points of holomorphic energy, $\tilde{E}$.

Holomorphic H_2 UHF



H. G. Hiscock, AJWT *J. Comput. Theor. Chem.* **10**, 4795 (2014)

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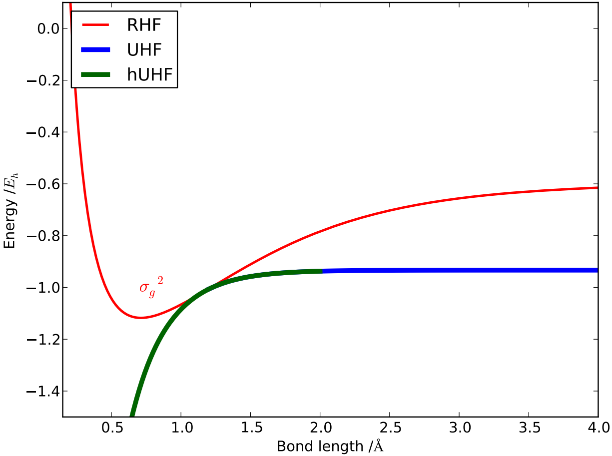

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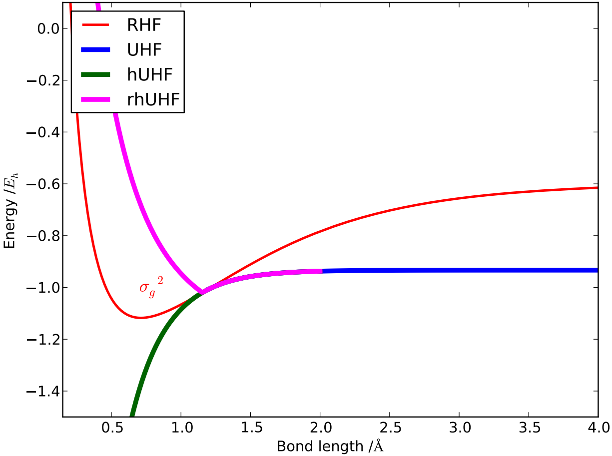

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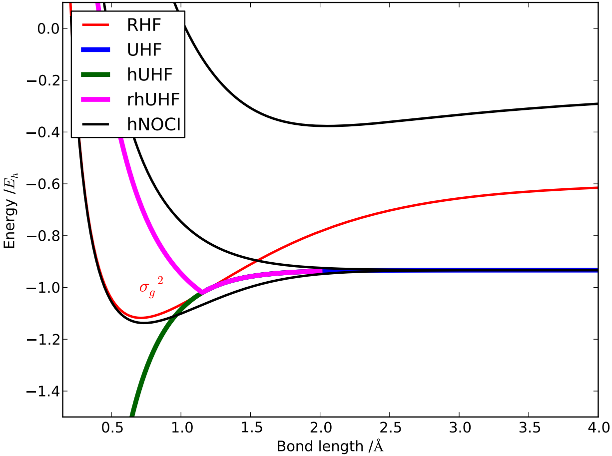

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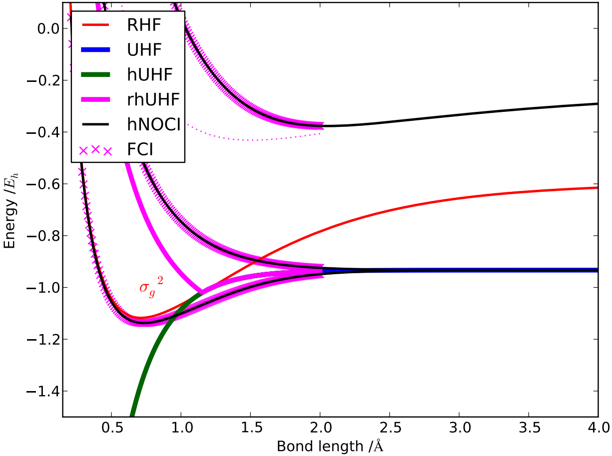

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SCF Energy

- Conventional:

$$E_{\text{SCF}} = v_{\text{nuc}} + \sum_{\mu\nu}^{2m} h_{\mu\nu} P_{\nu\mu} + \sum_{\mu\nu\sigma\tau}^{2m} P_{\nu\mu} (\mu\nu||\sigma\tau) P_{\tau\sigma}.$$

$P_{\mu\nu} = \sum_i^n C_{\mu i} C^*_{\nu i}$. Constrain $\langle \phi_i | \phi_j \rangle = \sum_\mu C^*_{\mu i} C_{\mu j} = \delta_{ij}$

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$$\tilde{E}_{\text{SCF}} = v_{\text{nuc}} + \sum_{\mu\nu}^{2m} h_{\mu\nu} \tilde{P}_{\mu\nu} + \sum_{\mu\nu\sigma\tau}^{2m} \tilde{P}_{\mu\nu} (\mu\nu||\sigma\tau) \tilde{P}_{\sigma\tau}.$$

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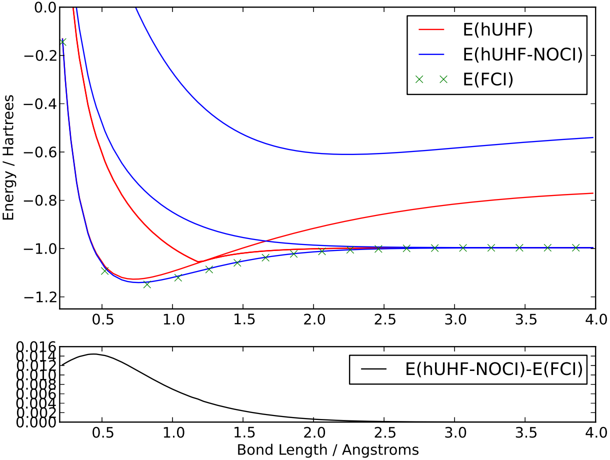
$\tilde{P}_{\mu\nu} = \sum_i^n C_{\mu i} C_{\nu i}$. Constrain $\sum_\mu C_{\mu i} C_{\mu j} = \delta_{ij}$

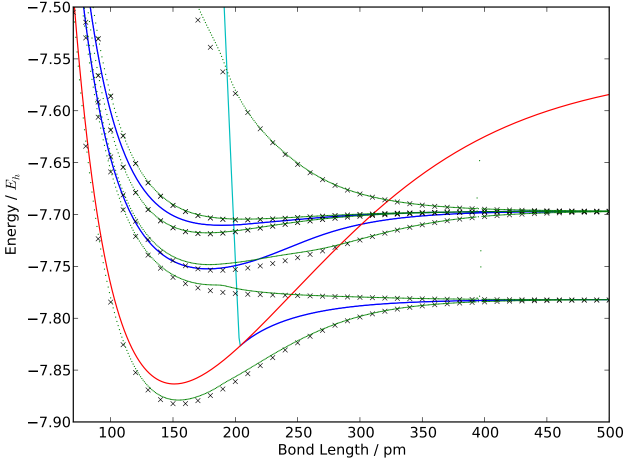
- $\tilde{E}$ not variational, but has constant number of stationary points.
- $\tilde{E} = E$ for real coefficients.

H_2 6-31G



E(hUHF)
E(hUHF-NOCI)
E(FCI)
Energy / Hartrees
0.0
−0.2
−0.4
−0.6
−0.8
−1.0
−1.2
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
E(hUHF-NOCI)-E(FCI)
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
Bond Length / Angstroms

LiH STO-3G



−7.50
−7.55
−7.60
−7.65
−7.70
−7.75
−7.80
−7.85
−7.90
Energy / E_h
100
150
200
250
300
350
400
450
500
Bond Length / pm

Algebraic Geometry

- Bézout's Theorem generalizes the Fundamental Theorem of Algebra to the intersection of polynomials of several variables.

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- e.g. RHF 2e in 2 orbitals:

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$$\mathbf{C}_\perp^T \frac{\partial E}{\partial \mathbf{C}} = 0$$

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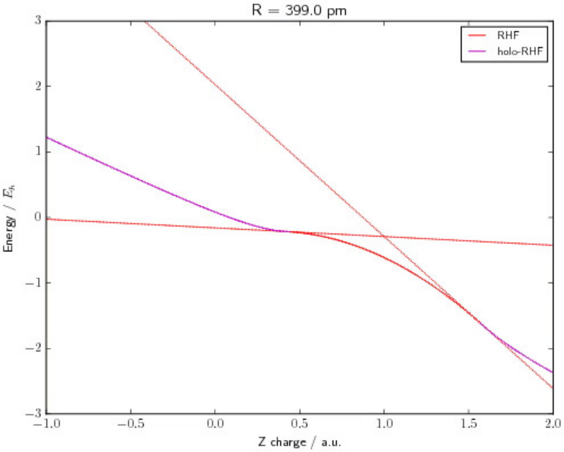
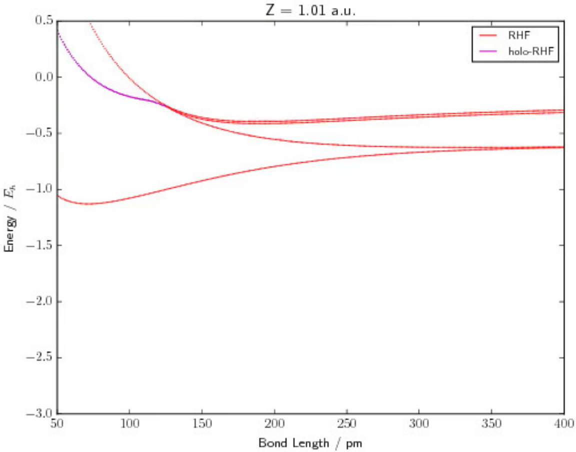
  with the orthogonality constraint is $c_1^2 + c_2^2 = c_0^2$ where c_0=1
- Overall the intersection of a 2nd order and 4th order polynomial give $2 \times 4 = 8$ solutions.
  Considering $\pm(c_1, c_2)$ equivalent, that is the 4 RHF solutions for all 2-orbital 2-electron systems.

HZ



R = 399.0 pm
RHF
holo-RHF
Energy / E_h
Z charge / a.u.
3
2
1
0
−1
−2
−3
−1.0
−0.5
0.0
0.5
1.0
1.5
2.0

HZ


Z = 1.01 a.u.
RHF
holo-RHF
Energy / E_h
Bond Length / pm
0.5
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
−3.0
50
100
150
200
250
300
350
400

Directions

- Understand solutions.
- Bigger systems - Modify real QC code.
- Complex basis functions.
- SCF Solutions vs VB states?
- Dynamic correlation.
- Extend Bézout.

Funding

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