Reduced Density Matrix Methods

for Quantum Chemistry and Physics

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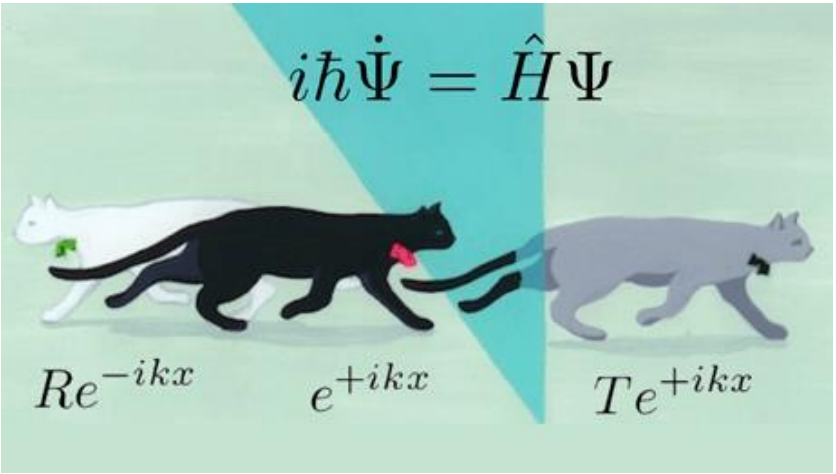
James Franck Institute
The University of Chicago

RDM Workshop, Oxford

13 April 2016

Quantum Chemistry

What is Quantum Chemistry?



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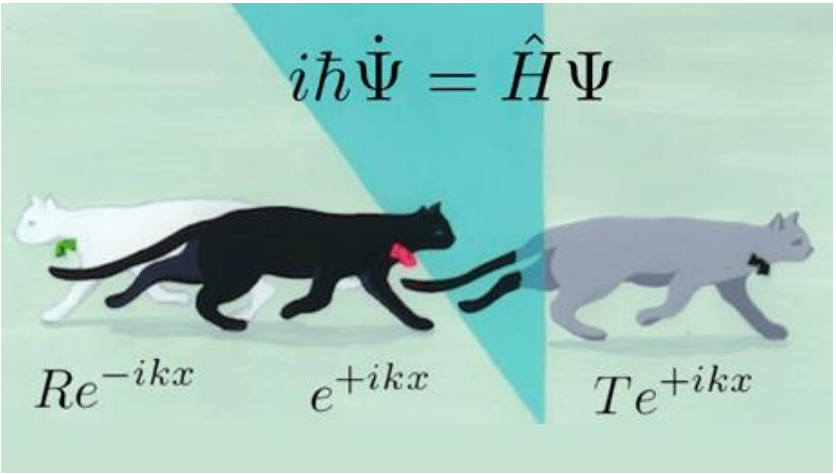

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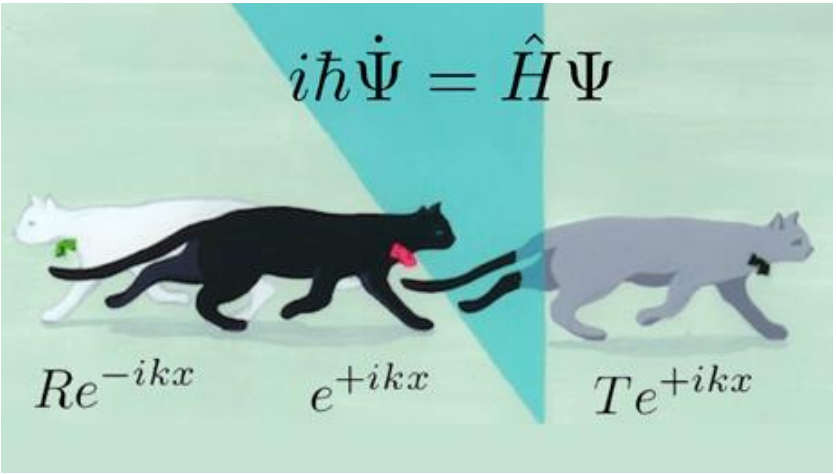

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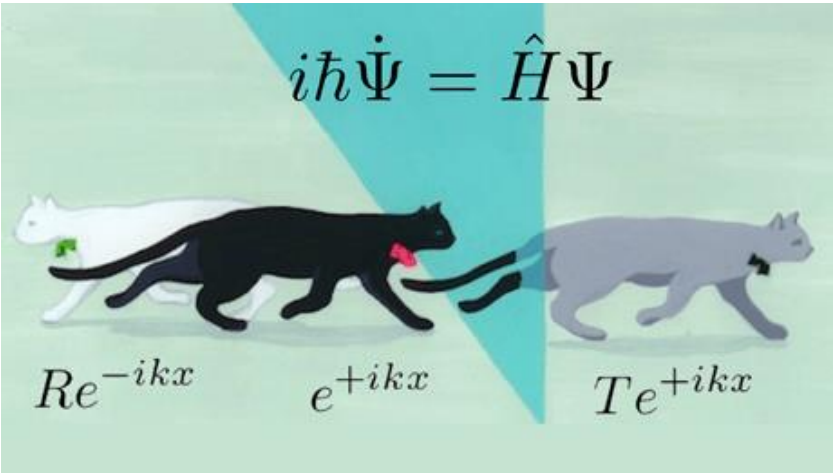

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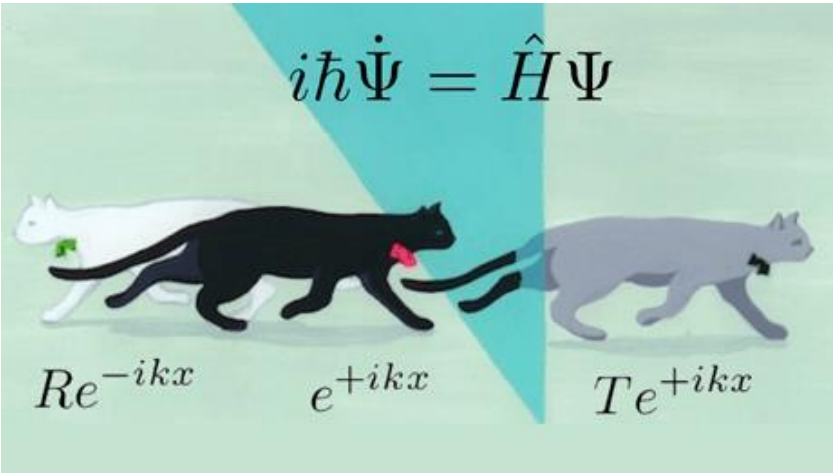

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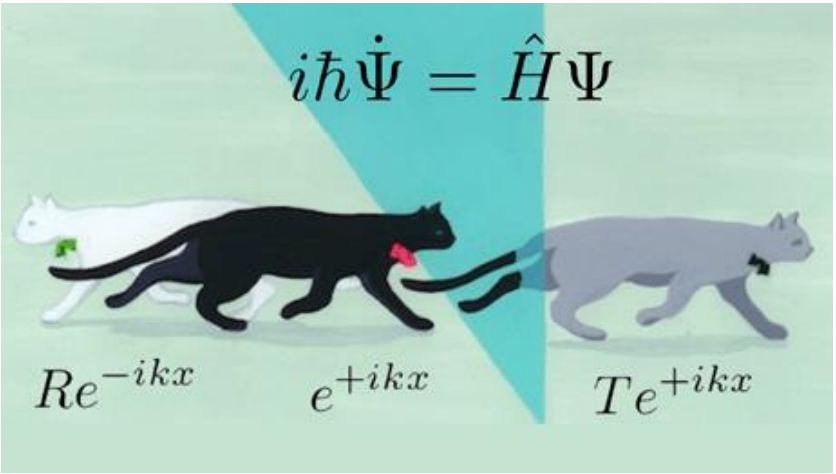

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What is Quantum Chemistry?

Advances in the 20th century have resulted in the ability to compute the electronic structure of *equilibrium* molecular systems of *modest size* with reasonable accuracy …

What is Quantum Chemistry?

But what about the rest of chemistry?

Chemistry is *Potential energy landscapes*

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Chemistry is *Potential energy landscapes*
Quantum molecular dynamics

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Chemistry is *Potential energy landscapes*

Quantum molecular dynamics

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Catalysts and enzymes

and much more …

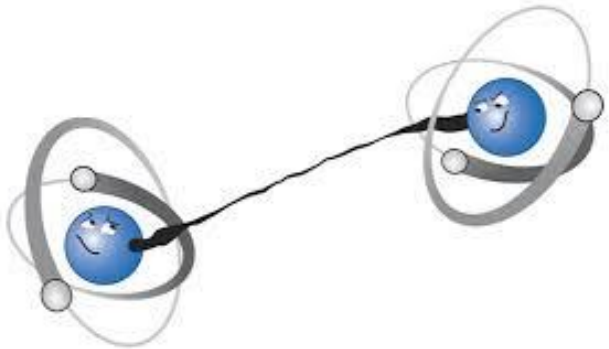
What is Quantum Chemistry?

What determines what we can and cannot do?

What is Quantum Chemistry?

What determines what we can and cannot do?

Quantum Entanglement



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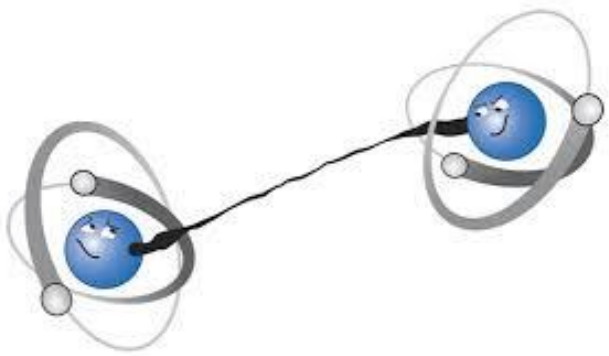
Quantum Entanglement

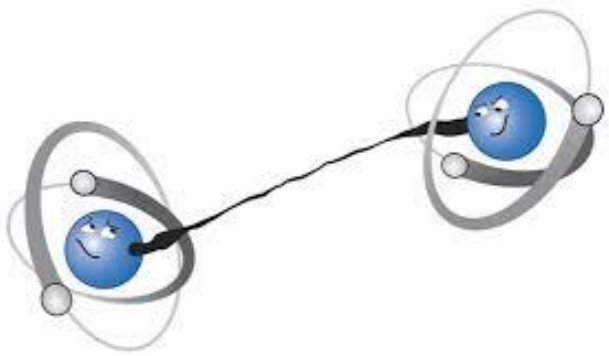


… a special kind of entanglement that we call electron correlation

What is Quantum Chemistry?

What determines what we can and cannot do?

Quantum Entanglement



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What is Quantum Chemistry?

Entanglement versus Correlation

What is Quantum Chemistry?

Entanglement versus Correlation

A *disentangled*, *uncorrelated* wave function has the form:

$$\Psi(1, 2, \ldots, N) = \phi_i(1) \otimes \phi_j(2) \otimes \ldots \otimes \phi_q(N)$$

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Entanglement versus Correlation

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which *breaks* the fermionic nature of the electrons.

What is Quantum Chemistry?

Entanglement versus Correlation

An *entangled*, *uncorrelated* wave function has the form:

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$$\Psi(1, 2, \ldots, N) = \phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$

which *satisfies* the fermionic nature of the electrons by the Grassmann wedge product.

What is Quantum Chemistry?

Entanglement versus Correlation

An *entangled*, *correlated* wave function has the form:

$$\Psi(1,2,\ldots,N) = \sum_{ij\ldots q} c_{ij\ldots q}\phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$

which coefficients *c* give the *probability amplitude* for being in each of the configurations in the sum.

What is Quantum Chemistry?

Weak versus Strong Correlation

What is Quantum Chemistry?

Weak versus Strong Correlation

Let us examine the *entangled*, *correlated* wave function:

$$\Psi(1,2,\ldots,N) = \sum_{ij\ldots q} c_{ij\ldots q}\phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$

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Weak versus Strong Correlation

Let us examine the *entangled*, *correlated* wave function:

$$\Psi(1,2,\ldots,N) = \sum_{ij\ldots q} c_{ij\ldots q}\phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$

When a single *c* dominates the sum, we have *weak correlation*, but when more than one *c* is similar in magnitude, we have *strong correlation*.

What is Quantum Chemistry?

Degrees of Strong Correlation

Let us examine the *entangled*, *correlated* wave function:

$$\Psi(1,2,\ldots,N) = \sum_{ij\ldots q} c_{ij\ldots q}\phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$

When a few *c*'s are large: → Not a big deal!

When *O(N!)* *c*'s are large: → We have a problem!

What is Quantum Chemistry?

Degrees of Strong Correlation

Let us examine the *entangled*, *correlated* wave function:

$$\Psi(1,2,\ldots,N) = \sum_{ij\ldots q} c_{ij\ldots q}\phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$

In the strong, strong correlation limit an ***exponential*** number of terms ***must be added*** to the wave function.

What is Quantum Chemistry?

Degrees of Strong Correlation

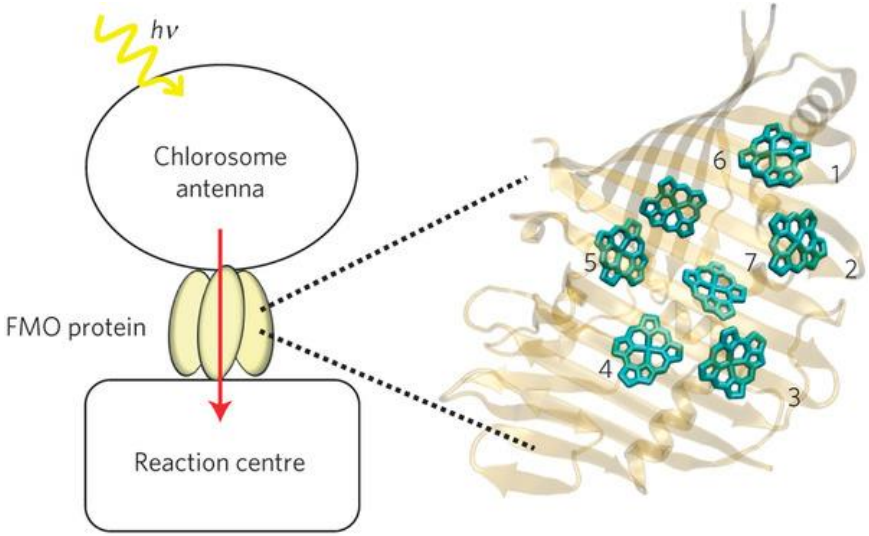
Let us examine the *entangled*, *correlated* wave function:

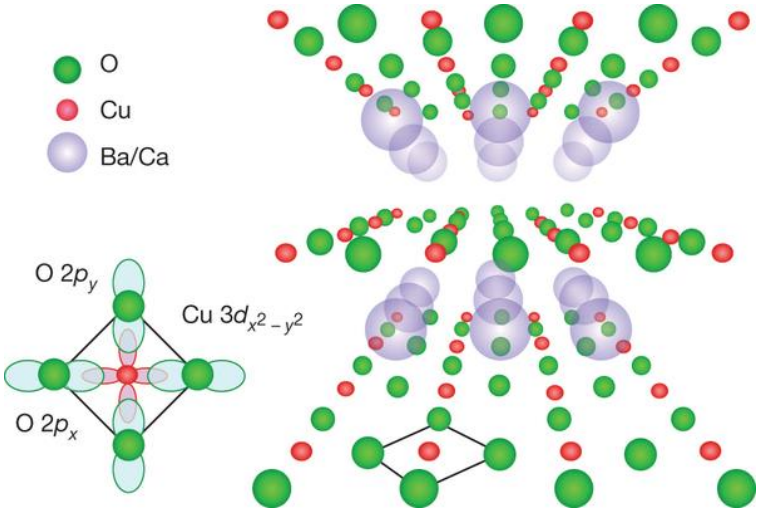
$$\Psi(1,2,\ldots,N) = \sum_{ij\ldots q} c_{ij\ldots q}\phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$

In the strong, strong correlation limit an ***exponential*** number of terms ***must be added*** to the wave function.

We can try to exploit structure in probability amplitudes, but in general, this can be challenging.

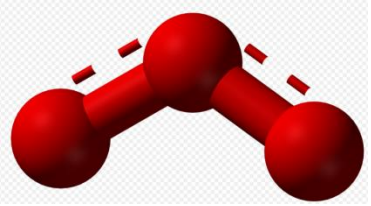
What is Quantum Chemistry?





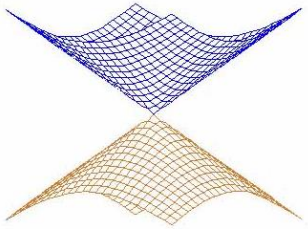
Such ***strong, strong correlation*** arises precisely in many of the molecules and materials that are most important in both 21st century *biology* and *materials*, and hence, further advances in the treatment of strong, strong correlation are needed.

What is Quantum Chemistry?

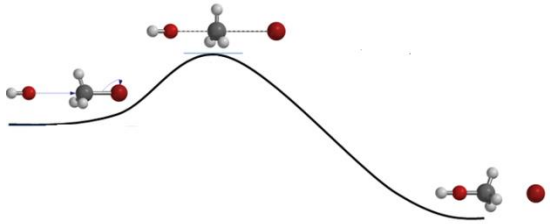


equilibrium

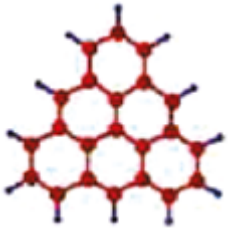
excited states



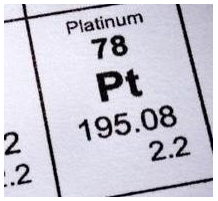
conical intersections



transition states



size



transition metals

Chemistry is about energy differences which require
a balanced treatment of moderate and strong electron correlation.

2-RDM Mechanics

A New Paradigm Beyond Wave Mechanics

	Wave Mechanics:	**2-RDM Mechanics:**
Variable:	Ψ	$\text{2-RDM} = \int \Psi\Psi^* d3 \ldots dN$
Number of e$^-$:	***N* electrons**	***2* electrons**
Complexity:	**Exponential**	**Polynomial**

Reduction in computational complexity with 2 electrons!

D. A. Mazziotti, Chemical Reviews **112**, 244 (2012).

Reduced-Density-Matrix Mechanics

Ingredients:

(1) only ***two-particle*** interactions in the Hamiltonian

(2) ***indistinguishability*** of the electrons in the wave function.

Wave Mechanics:

$$E = \int \Psi^* H \Psi d1 d2..dN$$

$$H = \sum_{i=1}^{N} h(i) + \frac{1}{2} \sum_{i \neq j=1}^{N} u(i, j)$$

RDM Mechanics:

$$E = \int \Psi^* {}^2K \Psi d1 d2..dN$$

$$= \int {}^2K (\int \Psi \Psi^* d3 d4..dN) d1 d2$$

$$= \int {}^2K {}^2D \; d1 d2$$

$${}^2K = \frac{N}{2} \sum_{i=1}^{2} h(i) + \frac{N(N-1)}{2} \sum_{i \neq j=1}^{2} u(i, j)$$

N-representability Constraints

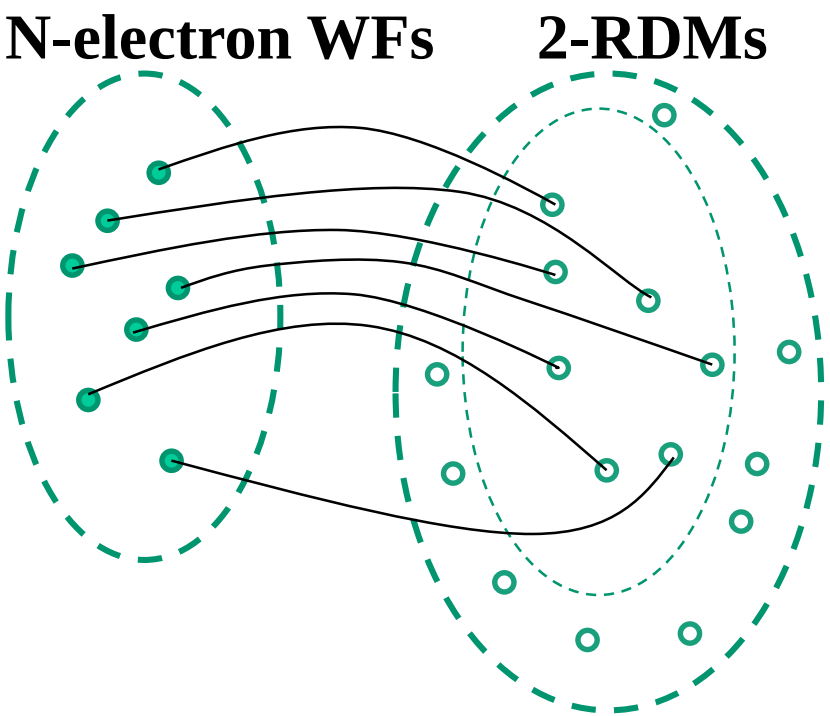
Beryllium as an Example:

	Wave Mechanics:	**RDM Mechanics:**
Number	4 electrons	2 quasi-electrons
Hamiltonian	$H = \sum_{i=1}^{4} h(i) + \frac{1}{2} \sum_{i \neq j=1}^{4} u(i, j)$	${}^2K = 2\sum_{i=1}^{2} h(i) + 6 \sum_{i \neq j=1}^{2} u(i, j)$
Energy	$E = \int \Psi H \Psi^* d1 d2..d4$	$E = \int {}^2K\, {}^2D\ d1 d2$
Correlation	E_{CE} = **-0.0944 au**	E_{CE} = **-0.7315 au**

Requirement: constraints for the 2-RDM to ensure that it corresponds to an *N*-particle wave function – *N*-representability constraints.

N-representability Problem

- Information lost by integration is relevant to the structure of overall wave function
- Not all 2-RDMs from physical *N*-particle wave function
- *N*-representability conditions



Picture by A. Rothman

2-RDM Mechanics: History

Electron Correlation

JOSEPH E. MAYER
Institute for Nuclear Studies, University of Chicago, Chicago, Illinois and The Rand Corporation, Santa Monica, California
(Received May 16, 1955)

"conditions employed by Mayer in this context are insufficient . . . The formulation of adequate conditions presents considerable difficulty . . ." - R. H. Tredgold

2-RDM Mechanics: History

"All the necessary information required for the energy and for calculating the properties of molecules is embodied in the first- and second-order density matrices. These may, of course, be obtained from the wave function by a process of integration. But this is aesthetically unpleasing . . ."

- C. A. Coulson (1959)

2-RDM Theory

Three complementary approaches to the direct calculation of the 2-RDM without the many-electron wavefunction:

(1) variational 2-RDM methods
(2) contracted Schrödinger equation (CSE) methods
(3) parametric 2-RDM methods

Two-electron Reduced-Density-Matrix Mechanics: With Application to Many-electron Atoms and Molecules, Advances in Chemical Physics Vol. 134 edited by D. A. Mazziotti (New York, John Wiley & Sons, 2007).

D. A. Mazziotti, Chemical Reviews **112**, 244 (2012).

Variational 2-RDM Theory

Variational 2-RDM Method

Minimize

$$E = \int {}^2K\, {}^2D \; d1\, d2$$

where the reduced Hamiltonian is

$${}^2K = \frac{N}{2}\sum_{i=1}^{2} h(i) + \frac{N(N-1)}{2}\sum_{i \neq j=1}^{2} u(i,j)$$

and *N*-representability conditions constrain the 2-RDM.

D. A. Mazziotti and R. M. Erdahl, Phys. Rev. A **63**, 042113 (2001);
M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda,
K. Nakata, and K. Fujisawa, J. Chem. Phys. **114**, 8282 (2001);
D. A. Mazziotti, Phys. Rev. A **65**, 062511 (2002).

N-representability Conditions

Early **known conditions**:

$$^2D \succeq 0 \qquad \bullet \quad \bullet$$

$$^2Q \succeq 0 \qquad \circ \quad \circ$$

$$^2G \succeq 0 \qquad \bullet \quad \circ$$

A. J. Coleman, Rev. Mod. Phys. **35** 668 (1963);
C. Garrod and J. Percus, J. Math. Phys. **5**, 1756 (1964).

Semidefinite Programming

RDM Mechanics:

Minimize energy

$$E = \int {}^2K\,{}^2D \;\; d1d2$$

such that

$${}^2D \geq 0$$
$${}^2Q \geq 0$$
$${}^2G \geq 0$$

and

$${}^2Q^{i,j}_{k,l} = 2\,{}^1I^i_j \wedge {}^1I^k_l - 4\,{}^1D^i_j \wedge {}^1I^k_l + {}^2D^{i,j}_{k,l}$$
$${}^2G^{i,j}_{k,l} = {}^1I^k_i\,{}^1D^j_l - {}^2D^{k,j}_{i,l}$$

Semidefinite Programming:

Minimize objective (linear function of X)

such that

$$X \geq 0$$

and

linear constraints

R. M. Erdahl, Reports Math. Phys. **15**, 147 (1979);
D. A. Mazziotti, Phys. Rev. A **65**, 062511 (2002).

Be Revisited:

A Variational 2-RDM Calculation

Method	E (a.u.)	% Correlation E
HF	-14.5034	0
MP2	-14.5273	45.5
MP3	-14.5417	72.7
MP4	-14.5496	87.8
D	-17.8973	6437.0
DQ	-14.5573	102.4
DQG	-14.5561	100.0
FCI	-14.5561	100.0

D. A. Mazziotti, Phys. Rev. A **65**, 062511 (2002).

Variational 2-RDM Method

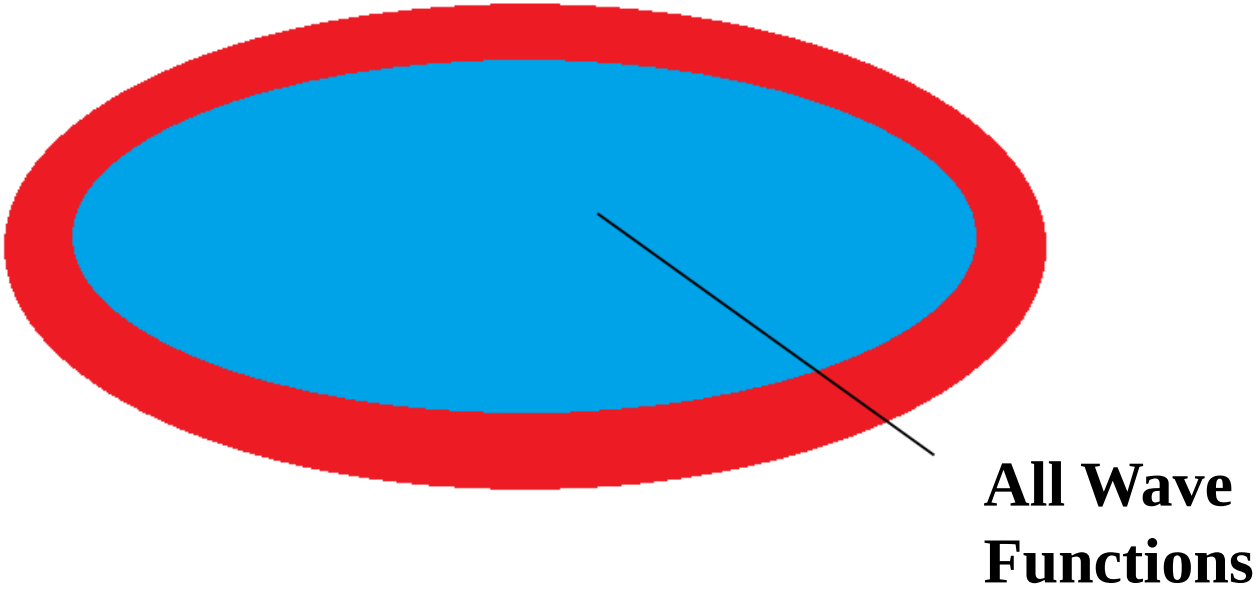
Characteristics:

1. variational *lower* bound
2. *systematic* hierarchy of 2-RDM constraints
3. *independence* from a reference wavefunction
4. *size consistent* and *size extensive*
5. *random* selection of initial 2-RDM
6. *global* minimum in semidefinite programming

D. A. Mazziotti, Acc. Chem. Res. **39**, 207 (2006).

2-RDM Set

The 2-RDM set contains *all wave functions* including the most strongly correlated wave functions that have an *exponentially* scaling number of large probability amplitudes:



Two Advances

Two Advances:

(1) Boundary-point SDP algorithm: 10-100x faster

(2) Systematic hierarchy of *N*-representability conditions

D. A. Mazziotti, Phys. Rev. Lett. **106**, 083001 (2011).

D. A. Mazziotti, Phys. Rev. Lett. **108**, 263002 (2012).

N-representability Conditions:

Positivity Conditions

1-Positivity Conditions (Pauli principle):

$$^{1}D \geq 0 \qquad ^{1}Q \geq 0$$

2-Positivity Conditions (Coleman '63; Garrod & Percus '64):

$$^{2}D \geq 0 \qquad ^{2}G \geq 0 \qquad ^{2}Q \geq 0$$

3-Positivity Conditions (Mazziotti & Erdahl '01):

$$^{3}D \geq 0 \qquad ^{3}E \geq 0 \qquad ^{3}F \geq 0 \qquad ^{3}Q \geq 0$$

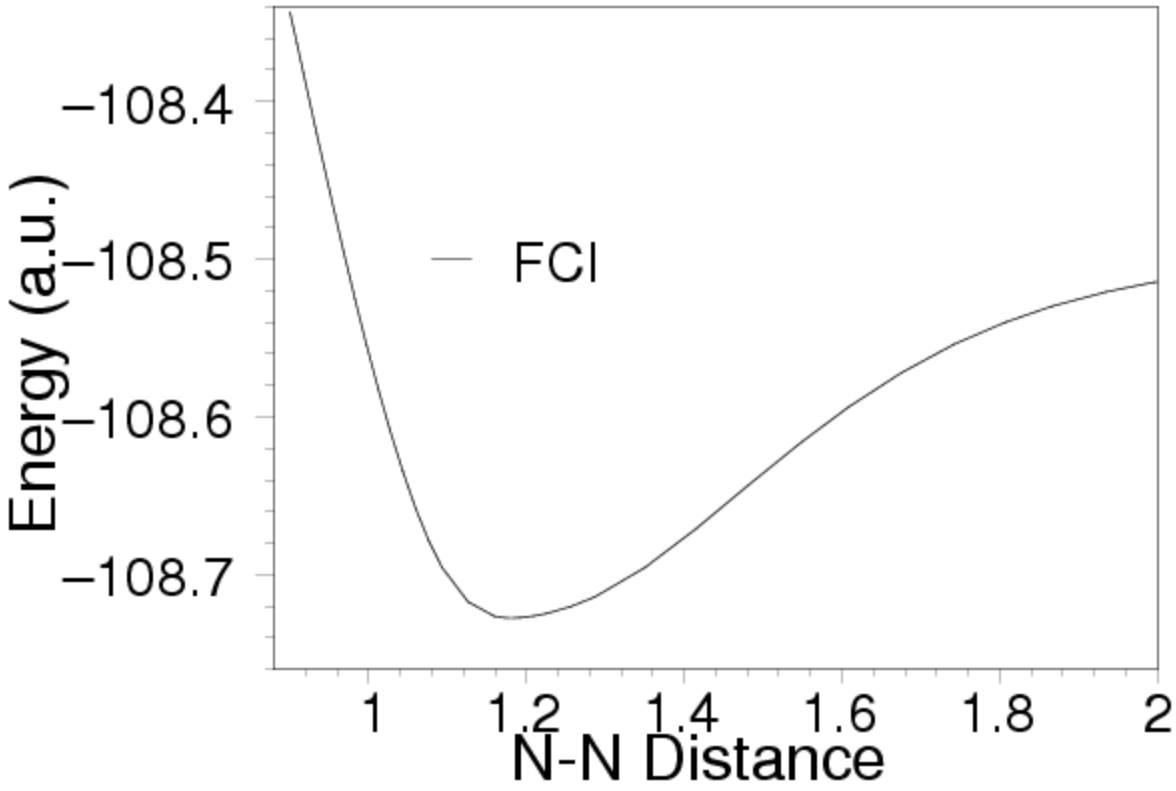
T_2 Condition (Erdahl '78; Zhao et al. '04; Mazziotti '05):

$$T_2 = {}^{3}E + {}^{3}F \geq 0$$

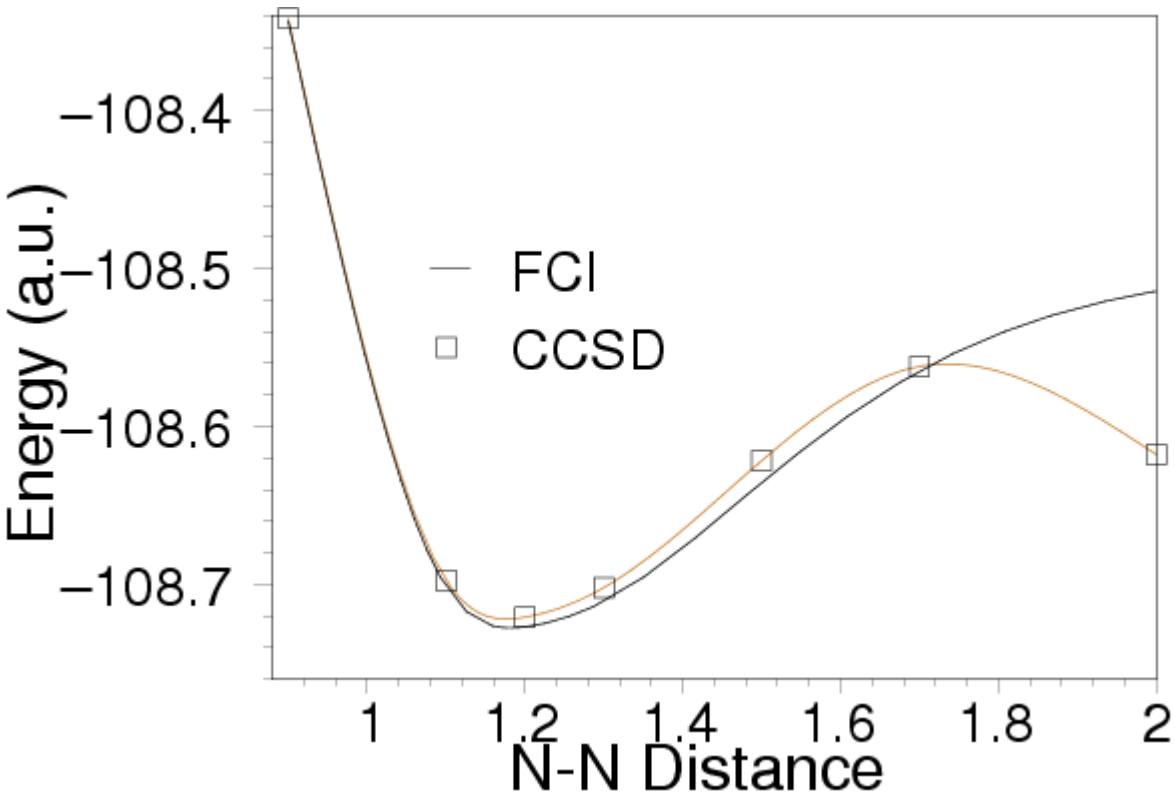
D. A. Mazziotti, Phys. Rev. Lett. **108**, 263002 (2012).

D. A. Mazziotti, Phys. Rev. A **74**, 032501 (2006).

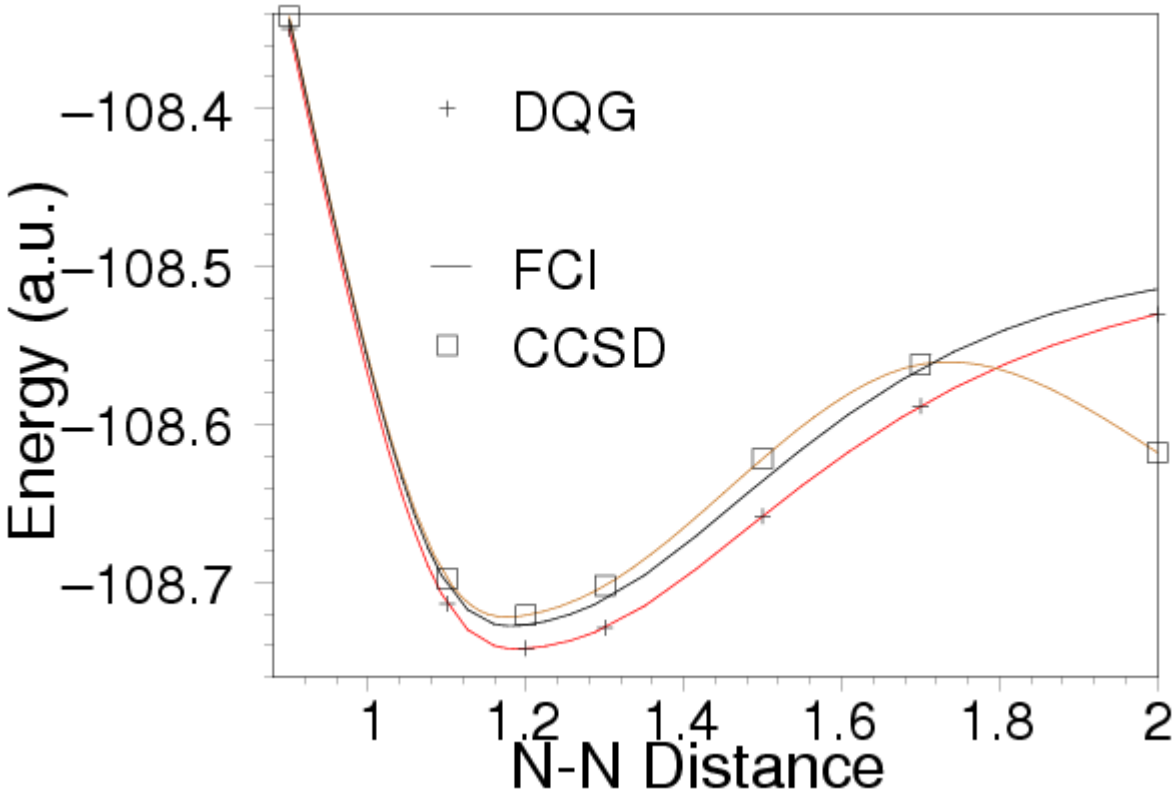
N_2 Molecule



N_2 Molecule


−108.4
−108.5
−108.6
−108.7
Energy (a.u.)
FCI
CCSD
1
1.2
1.4
1.6
1.8
2
N-N Distance

N_2 Molecule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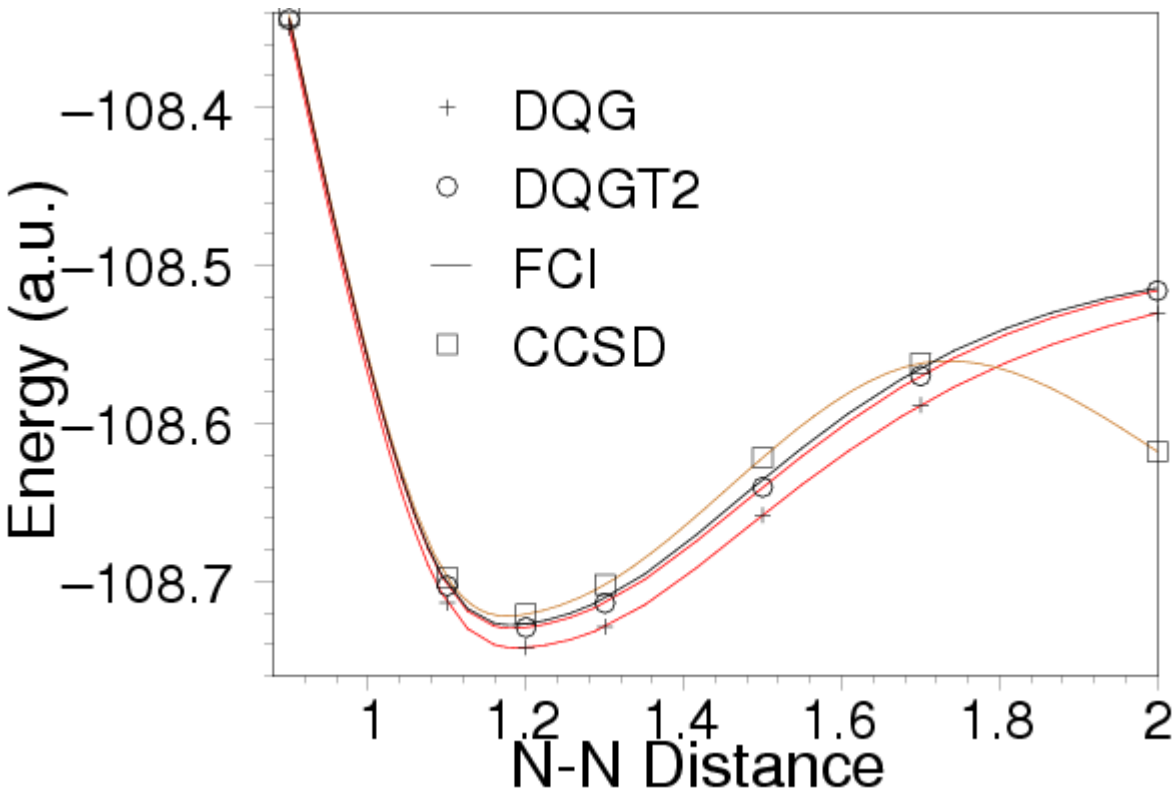
DQG
DQGT2
FCI
CCSD
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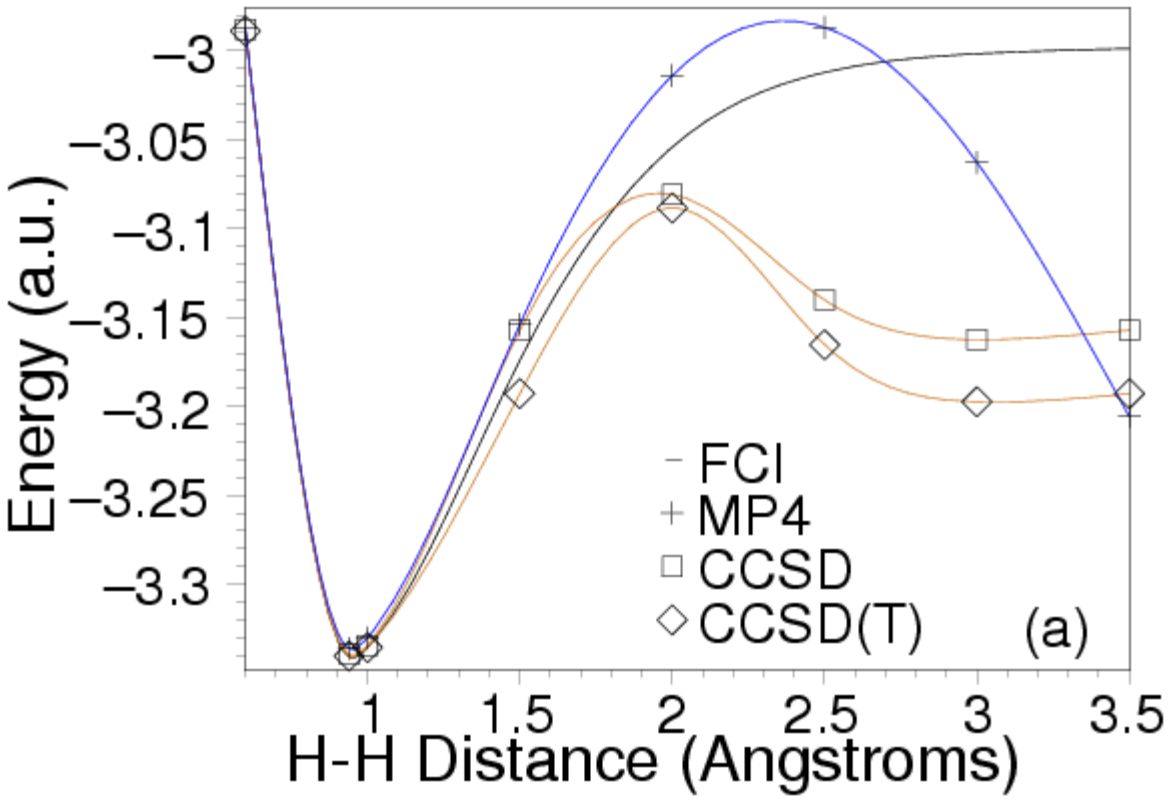
1
1.2
1.4
1.6
1.8
2
N-N Distance

Strong Electron Correlation:

Hydrogen Chains and Lattices

Bonding in a Hydrogen Chain:

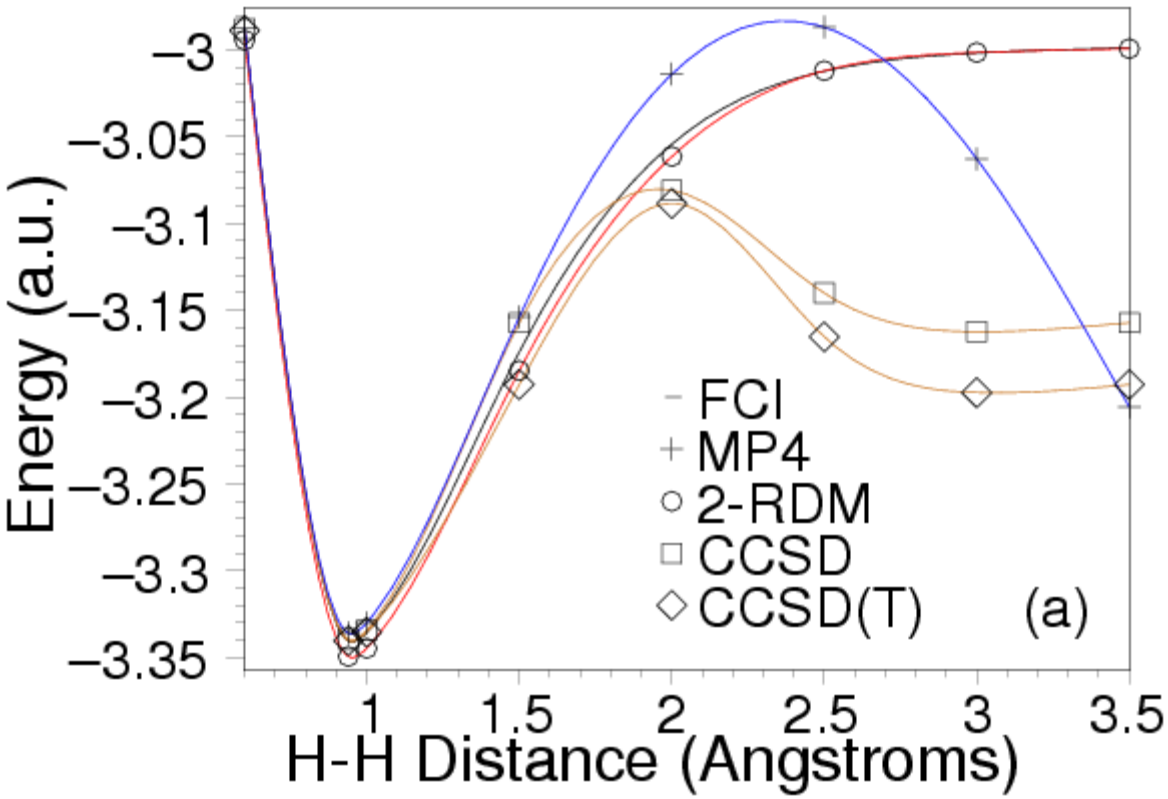
Stretched geometries



D. A. Mazziotti, Phys. Rev. Lett. **93**, 213001 (2004).

Bonding in a Hydrogen Chain:

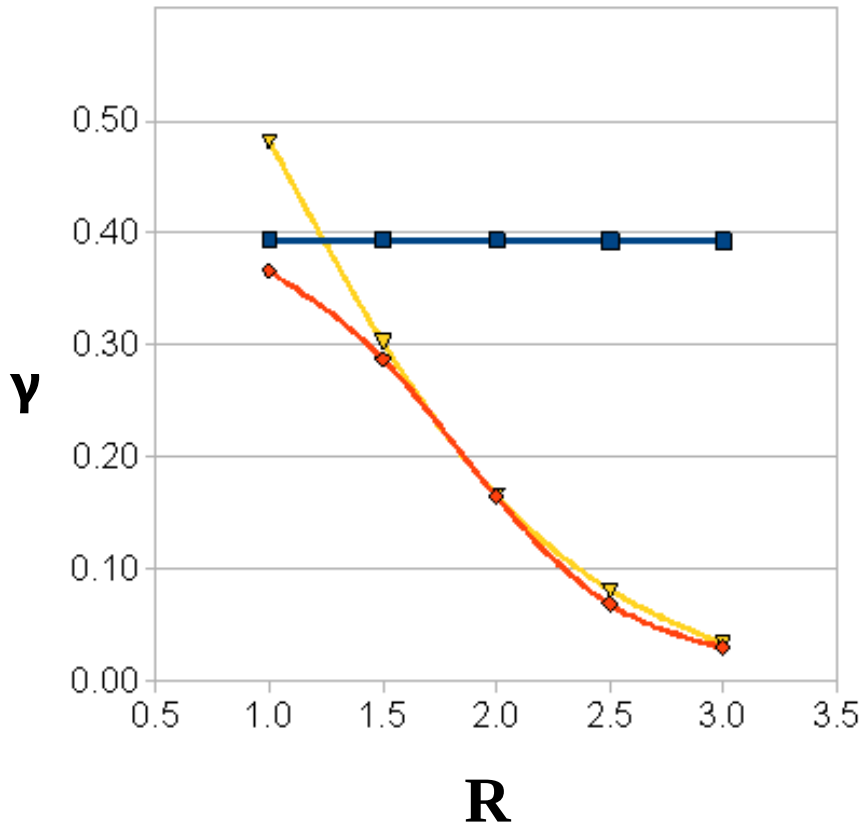
Stretched geometries



D. A. Mazziotti, Phys. Rev. Lett. **93**, 213001 (2004).

Bonding in a Hydrogen Chain:

Metal-to-Insulator Transition



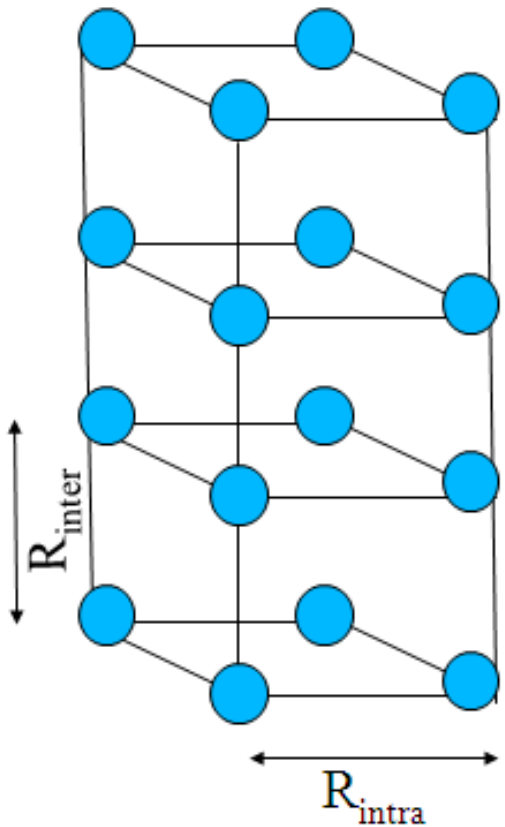
where

$$\gamma \propto \sqrt{\sum_{i \neq j} \left({}^{1}D_{ij} \right)^{2}}$$

A. Sinitskiy, L. Greenman, and D. A. Mazziotti, J. Chem. Phys. **133**, 014104 (2010).

Bonding in a Hydrogen Lattice:

Computational Cost of 4 x 4 x 4 Lattice



Wave Functions:

Number of Important Configurations:

10^{18} determinants!

Probability of Each Configuration:

10^{-18}

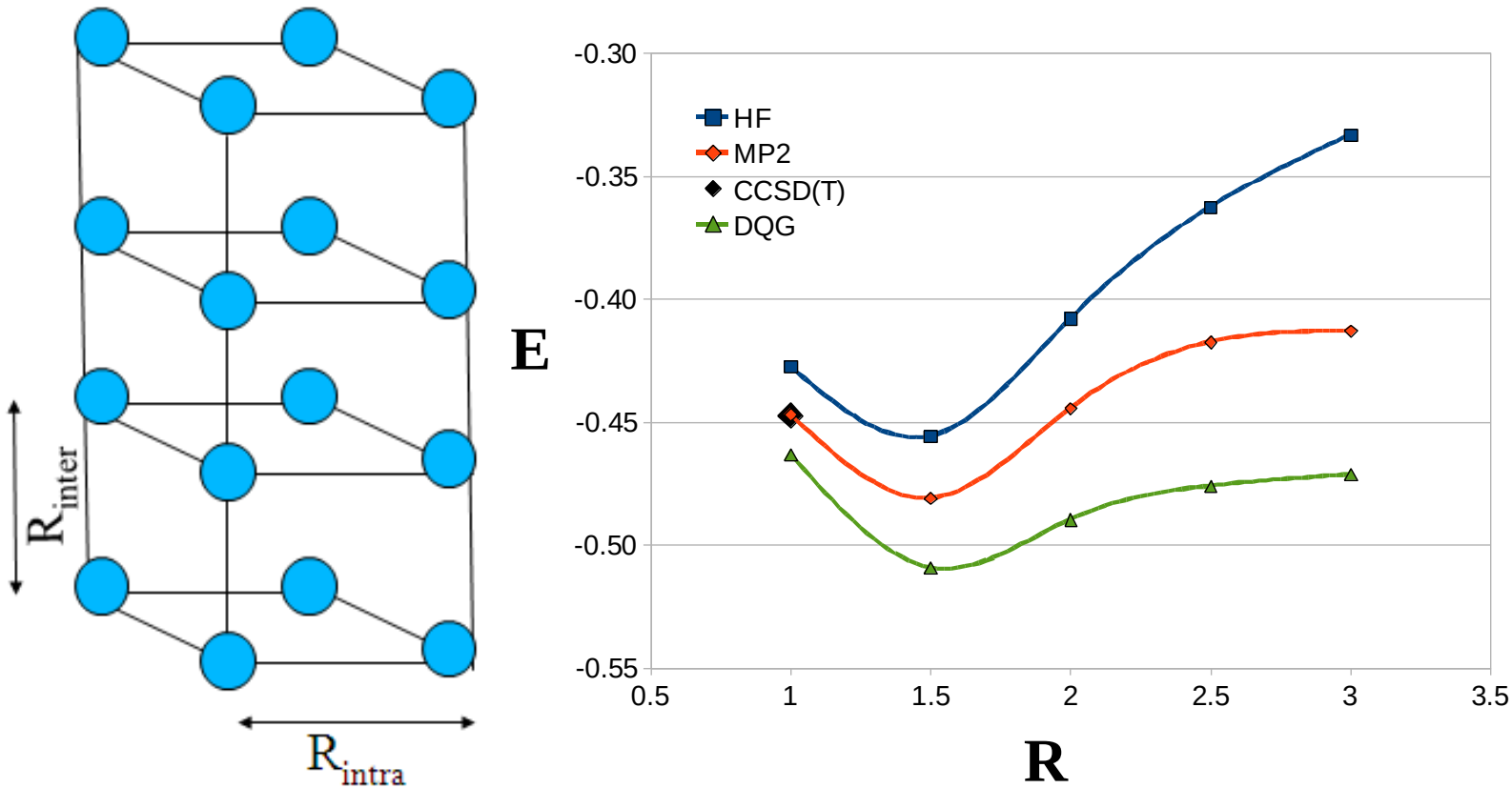
Can this calculation be done?

No.

A. Sinitskiy, L. Greenman, and D. A. Mazziotti, J. Chem. Phys. **133**, 014104 (2010).

Bonding in a Hydrogen Lattice:

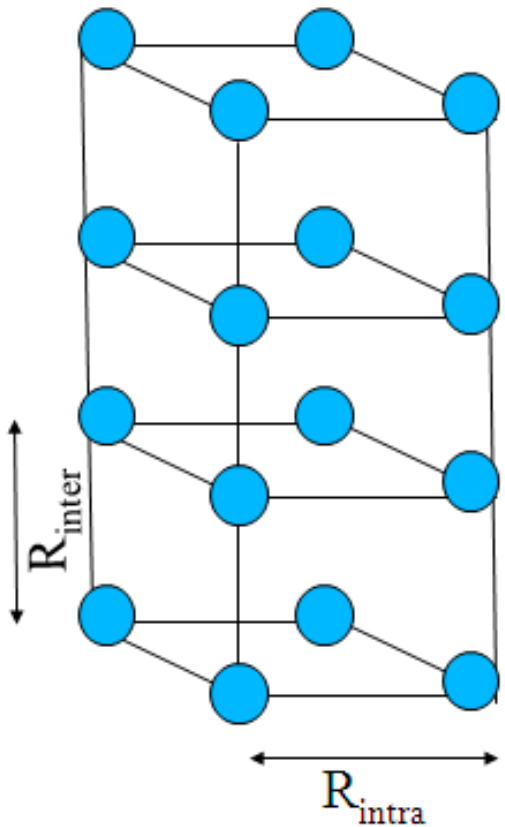
Stretched geometries



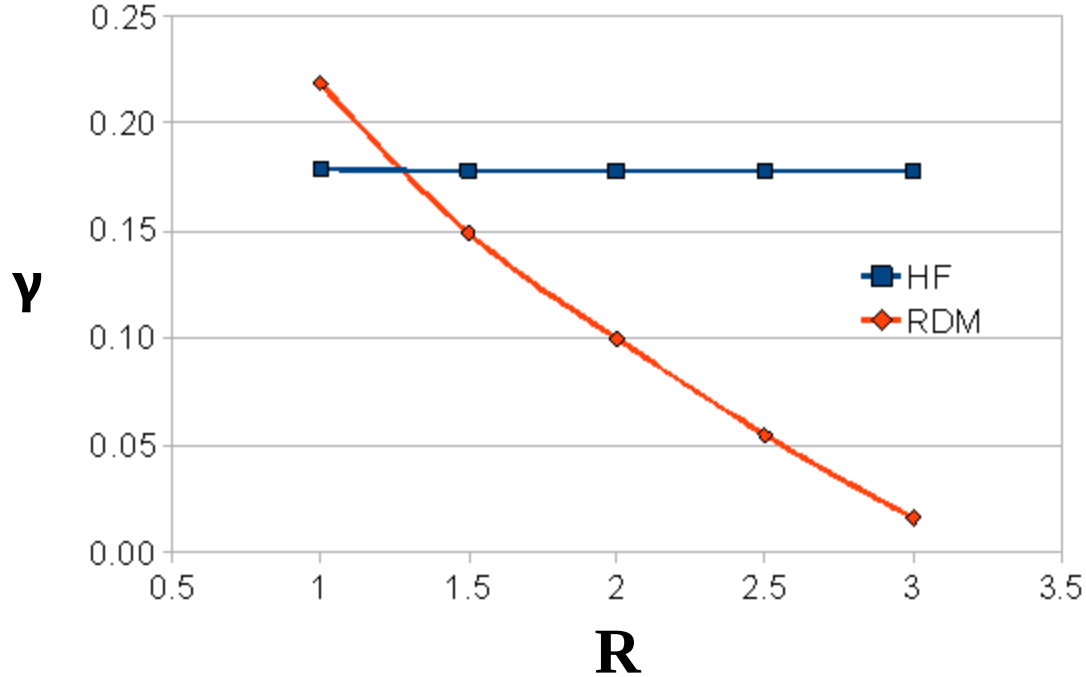
A. Sinitskiy, L. Greenman, and D. A. Mazziotti, J. Chem. Phys. **133**, 014104 (2010).

Bonding in a Hydrogen Lattice:

Metal-to-Insulator Transition



$$\gamma \propto \sqrt{\sum_{i \neq j} \left({}^{1}D_{ij} \right)^2}$$



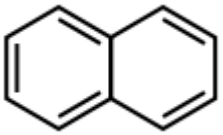
A. Sinitskiy, L. Greenman, and D. A. Mazziotti, J. Chem. Phys. **133**, 014104 (2010).

Strong Electron Correlation:

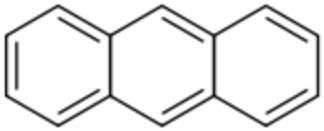
Polyaromatic Hydrocarbons

n-Acenes: Polyaromatic Hydrocarbons

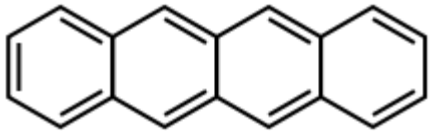
Napthalene (2-acene):



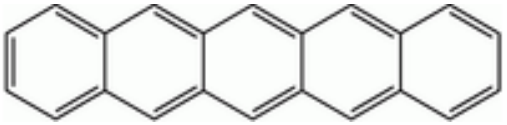
Anthracene (3-acene):



Tetracene (4-acene):

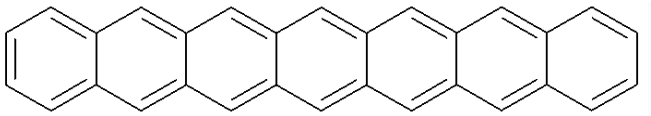


Pentacene (5-acene):



Hexacene (6-acene):

Heptacene (7-acene):



G. Gidofalvi and D. A. Mazziotti, J. Chem. Phys. **129**, 134108 (2008).

n-Acenes:

Molecule	Number of Variables in CI
2-acene	4936
3-acene	69116
4-acene	112298248
5-acene	19870984112
6-acene	3725330089248
7-acene	728422684135920
8-acene	147068001734374624

5- and higher-acenes cannot be treated by traditional CAS-SCF.
8-acene has 1.5×10^{17} configuration state functions (CSFs).

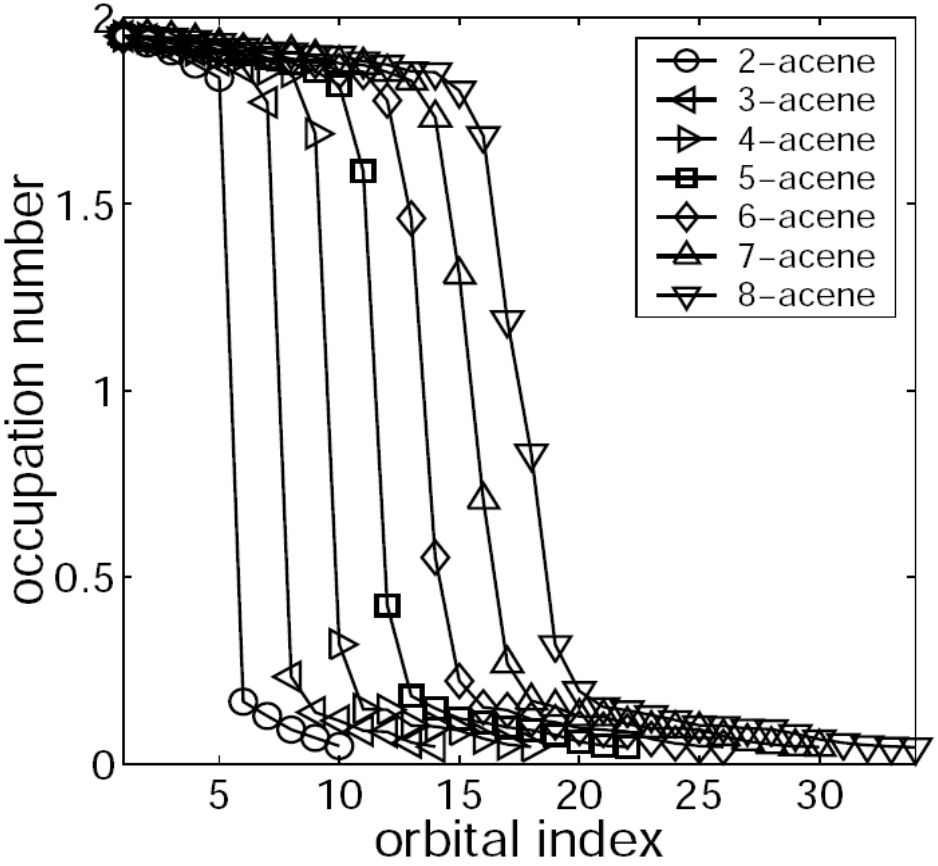
G. Gidofalvi and D. A. Mazziotti, J. Chem. Phys. **129**, 134108 (2008).

Acenes: Memory and Timings

	CI-CASSCF	CI-CASSCF	2-RDM CASSCF	2-RDM CASSCF
molecule	Memory	Time	Memory	Time
2-acene	0.2 MB	0.02 min	12.6 MB	1.1 min
3-acene	44.9 MB	2.2 min	15.8 MB	4.0 min
4-acene	9.0 GB	25.4 hr	23.3 MB	30 min

G. Gidofalvi and D. A. Mazziotti, J. Chem. Phys. **129**, 134108 (2008).

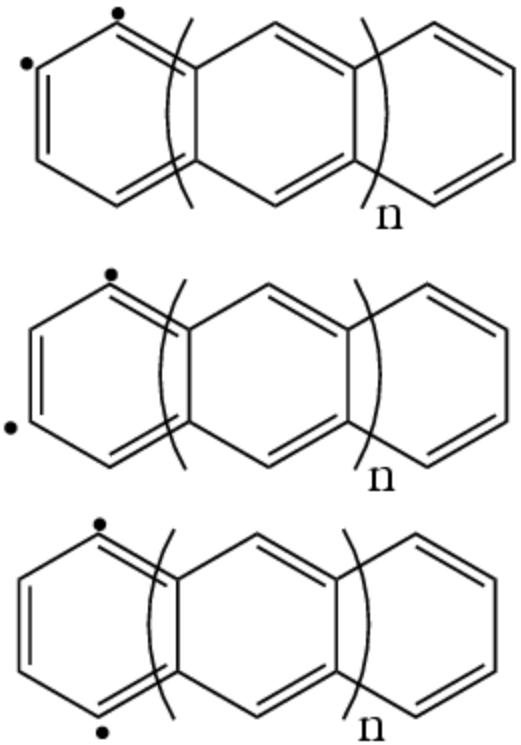
Active-space
Variational 2-RDM Method



The occupation numbers of the HOMO and LUMO *spatial* orbitals approaches one as the length of the acene increases.

G. Gidofalvi and D. A. Mazziotti, J. Chem. Phys. **129**, 134108 (2008).

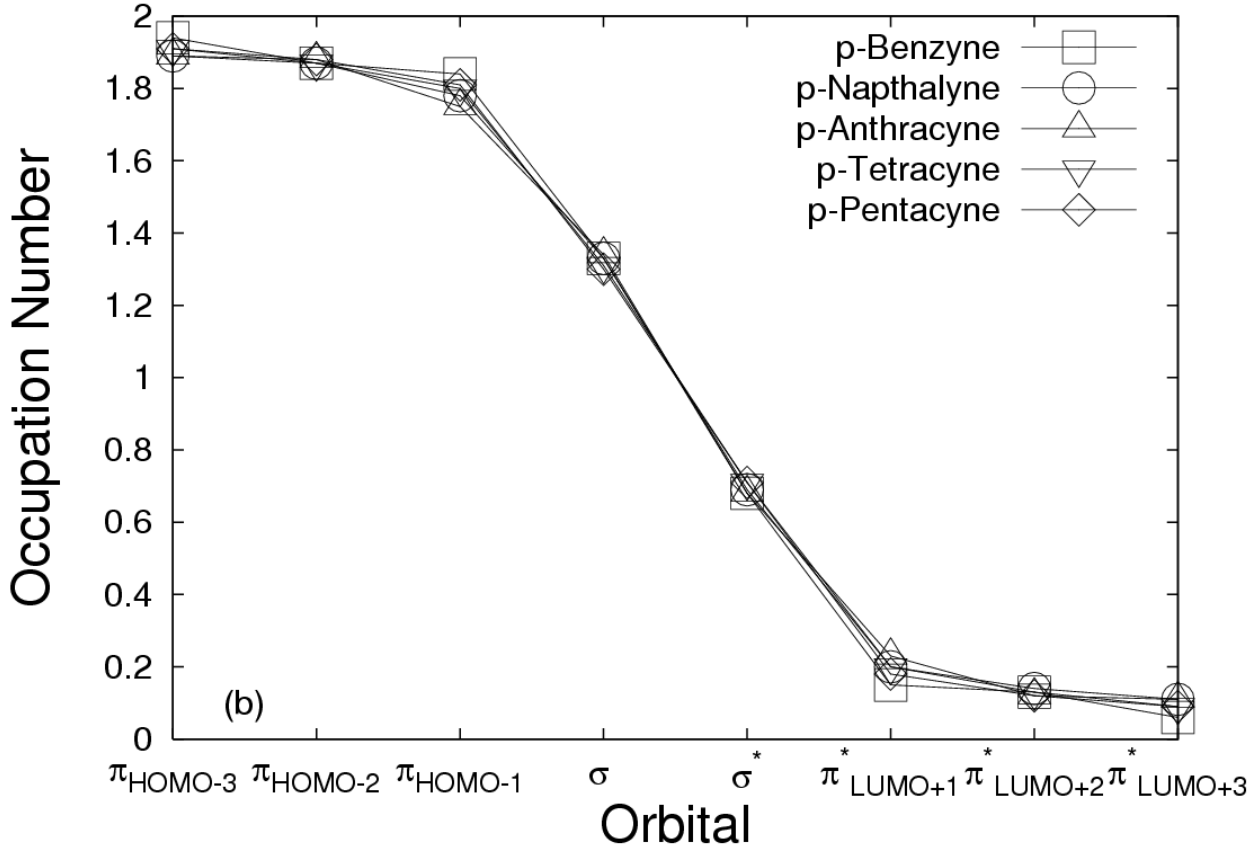
n-Arynes:



L. Greenman and D. A. Mazziotti, J. Chem. Phys. **130**, 184101 (2009) .

n-Arynes:

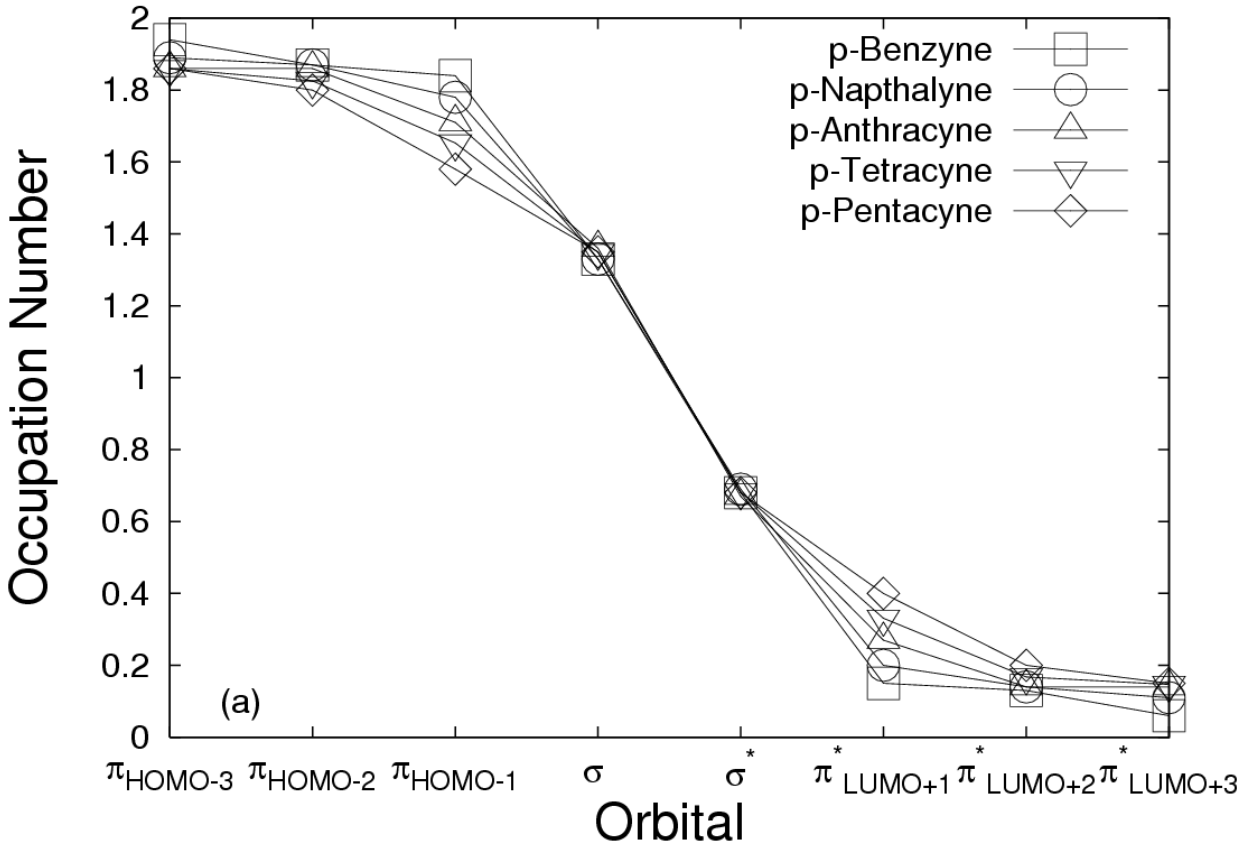
(12,12) 2-RDM Calculation



L. Greenman and D. A. Mazziotti, J. Chem. Phys. **130**, 184101 (2009) .

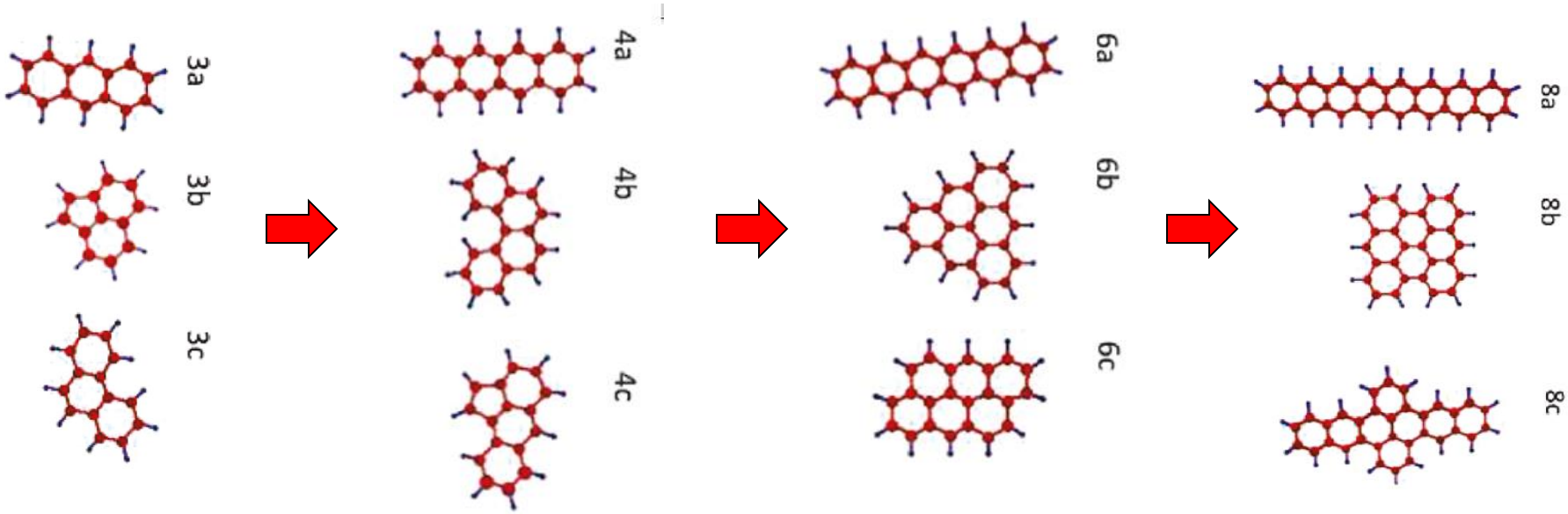
n-Arynes:

(n_C+2,n_C+2) 2-RDM Calculation



L. Greenman and D. A. Mazziotti, J. Chem. Phys. **130**, 184101 (2009) .

Planar Acenes: Size



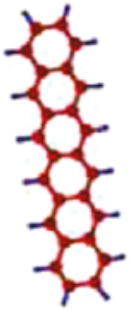
We also observe the ***emergence of polyradical character with system size*** in planar acenes.

K. Pelzer, L. Greenman, G. Gidofalvi and D. A. Mazziotti, JPC A **114**, 583 (2011).

Planar Acenes: Geometry

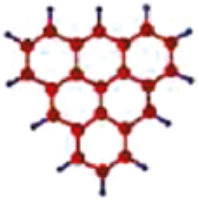
Which of these molecules is most strongly correlated?

6a



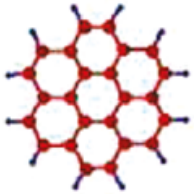
linear

6b



triangular

6f



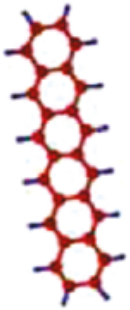
superbenzene

K. Pelzer, L. Greenman, G. Gidofalvi and D. A. Mazziotti, JPC A **114**, 583 (2011).

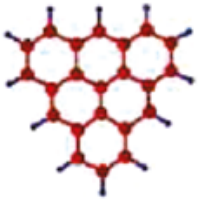
Planar Acenes: Geometry

Which of these molecules is most strongly correlated?

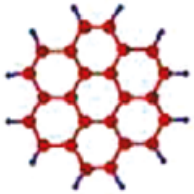
6a



6b



6f



linear triangular superbenzene

Answer: triangular > linear > superbenzene

K. Pelzer, L. Greenman, G. Gidofalvi and D. A. Mazziotti, JPC A **114**, 583 (2011).

Strongly Correlated Periodic Systems

Basis for Polymers and Molecular Crystals

Bloch orbitals composed of atomic orbitals:

$$\phi_i(r) = \sum_{\mu} c_{i,\mu} b_{\mu}^{k}(r) \qquad b_{\mu}^{k}(r) = \sum_{m} e^{ikm} \chi_{\mathrm{AO}}^{m}(r)$$

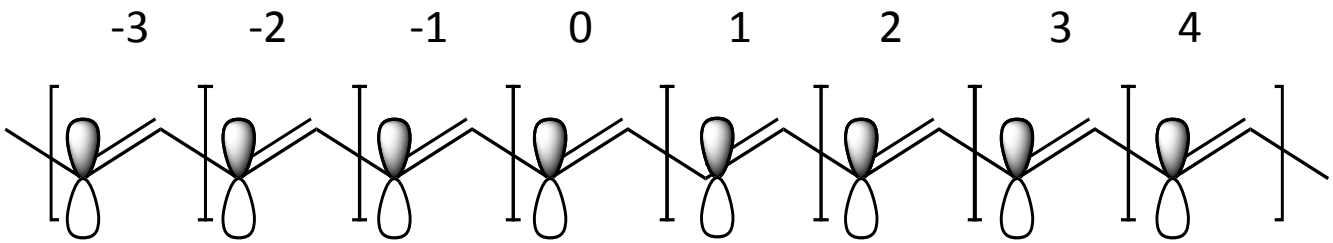
Use non-orthogonal Bloch functions instead of plane waves for a basis representing the crystal.

Allows us to use the quantum chemical basis set technologies—correlation consistent, polarizability, etc...

Payne, et. Al. *Rev. Mod. Phys.* 64 1045 (1992); Pisani, *Lec. Notes. Chem.* Springer, (1996)

Crystalline-Orbital Hartree-Fock

The momentum space representation of an operator is related to its position space representation by a Fourier transform.



$$\psi_{pk_q}(r) = K^{-1/2} \sum_{\mu} \sum_{m} c_{pk_q}^{\mu k_q} e^{(imk_q a)} \chi_\mu(r - m\mathbf{a})$$

$$\langle pk_p | \hat{O} | qk_p \rangle = \sum_{m} e^{ik_p m} \int \chi_p^*(r - \mathbf{0a}) \hat{O} \chi_q(r - (m)\mathbf{a})$$

Fourier transform formally involves an infinite number of cells. We need to employ a cut off to discretize k-space.

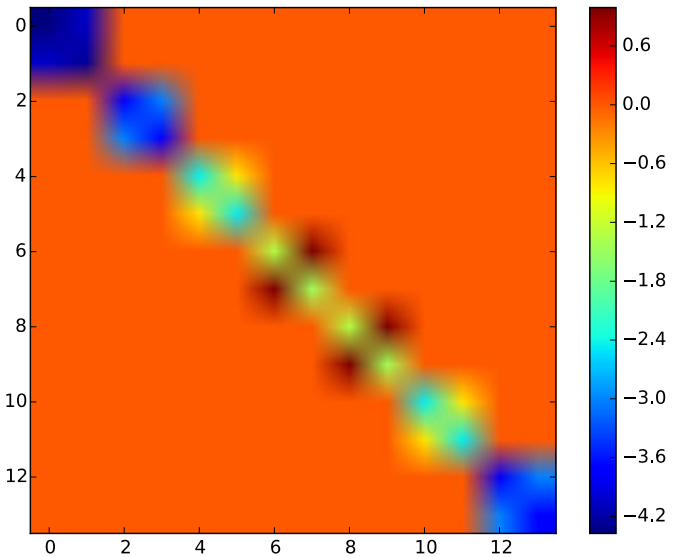
Pisani, *Lec. Notes. Chem.* Springer, (1996); J. M. André *et. al*. J. Com. Chem. (1984)

k-space advantage for Hartree-Fock equations

The Fock operator is diagonalized in each irreducible representation of the translational group:

$$f^{\mu k_q}_{\nu k_q} = \sum_{m_1=-S}^{+S} f^{\nu(0)}_{\mu(m_1)} \exp(i m_1 k_q a)$$

$$s^{\mu k_q}_{\nu k_q} = \sum_{m_1=-S}^{+S} s^{\nu(0)}_{\mu(m_1)} \exp(i m_1 k_q a)$$

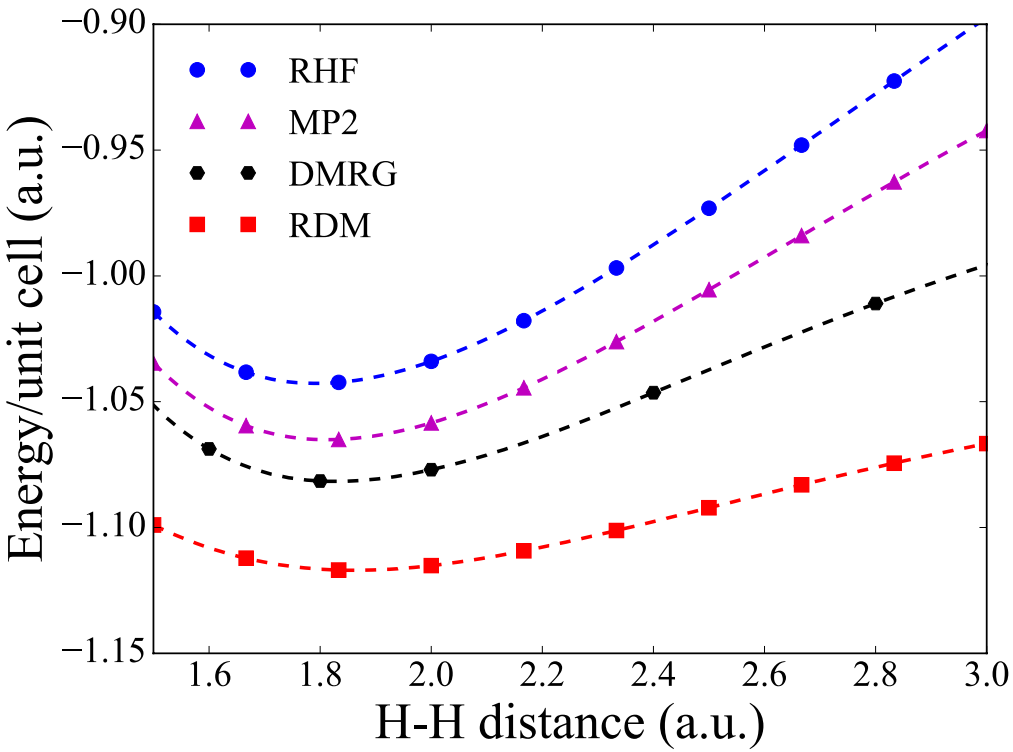


CO-HF gives us a set of orbitals (a representation) of the crystal that obeys the correct symmetry.

Electron correlation in an infinite Hydrogen chain calculated by variational 2-RDM (DQG)

- Infinite chain of Hydrogen atoms
- 2 Hydrogen atoms/cell, 10 neighboring cells
- > 10^{24} determinants in active space if traditional electronic structure is used.

- 1-RDM $\mathcal{O}(n^2) \times K$
- 2-RDM $\mathcal{O}((n \times n \times K)^2) \times K$



But RDM has failed? Why are we below the ground state by 50 mhartrees?

Symmetries in quantum mechanics and time-reversal symmetry operator in a spin-orbital basis

$$[g, \hat{O}] = 0 \quad g\hat{O}g^{-1} = \hat{O}$$

$$e^{i\hat{S}}\hat{O}e^{-i\hat{S}} = \hat{O} + [\hat{O}, i\hat{S}] + \frac{1}{2!}[[\hat{O}, i\hat{S}], i\hat{S}] + \cdots$$

$$[\hat{O}, i\hat{S}] = 0$$

Time-reversal symmetry can be even or odd after operation

$$\langle\psi|\Theta\hat{O}\Theta^{-1}|\psi\rangle = \pm\langle\tilde{\psi}|\hat{O}|\tilde{\psi}\rangle$$

$$\langle\psi|\Theta\hat{X}\Theta^{-1}|\psi\rangle = \langle\tilde{\psi}|\hat{X}|\tilde{\psi}\rangle$$

$$\langle\psi|\Theta\hat{P}\Theta^{-1}|\psi\rangle = -\langle\tilde{\psi}|\hat{P}|\tilde{\psi}\rangle$$

Time-reversal also rotates spin-momenta

$$\Theta|\alpha>=|\beta>$$

$$\Theta|\beta>=-|\alpha>$$

$$\hat{U} = e^{-i\frac{\pi}{2}\sigma_y}$$

$$\boxed{\Theta = \hat{U}\hat{K}}$$

Time reversal symmetry on one-body operators dictates symmetry between (k,-k) Kramers pairs

Position space constraints for TR symmetry:

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} K \begin{pmatrix} O_{\vec{r},\alpha,\alpha} & 0 \\ 0 & \hat{O}_{\vec{r},\beta,\beta} \end{pmatrix} K^\dagger \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}^{-1} = \begin{pmatrix} O^*_{\vec{r},\beta,\beta} & 0 \\ 0 & O^*_{\vec{r},\alpha,\alpha} \end{pmatrix} = \begin{pmatrix} O^*_{\vec{-k},\alpha,\alpha} & 0 \\ 0 & O^*_{\vec{-k},\beta,\beta} \end{pmatrix}$$

Momentum space space constraints for TR symmetry:

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} K \begin{pmatrix} O_{\vec{k},\alpha,\alpha} & 0 \\ 0 & \hat{O}_{\vec{k},\beta,\beta} \end{pmatrix} K^\dagger \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}^{-1} = \begin{pmatrix} O^*_{\vec{-k},\beta,\beta} & 0 \\ 0 & O^*_{\vec{-k},\alpha,\alpha} \end{pmatrix} = \begin{pmatrix} O^*_{\vec{-k},\alpha,\alpha} & 0 \\ 0 & O^*_{\vec{-k},\beta,\beta} \end{pmatrix}$$

Equality constraints on the 1-particle and 2-particle density matrices

$${}^1D(k) = {}^1D(-k)^* \qquad {}^2M_{i\alpha,j\beta;k\alpha,l\beta}(k) = \left[{}^2M_{i\beta,j\alpha;,k\beta,l\alpha}(-k)\right]^*$$

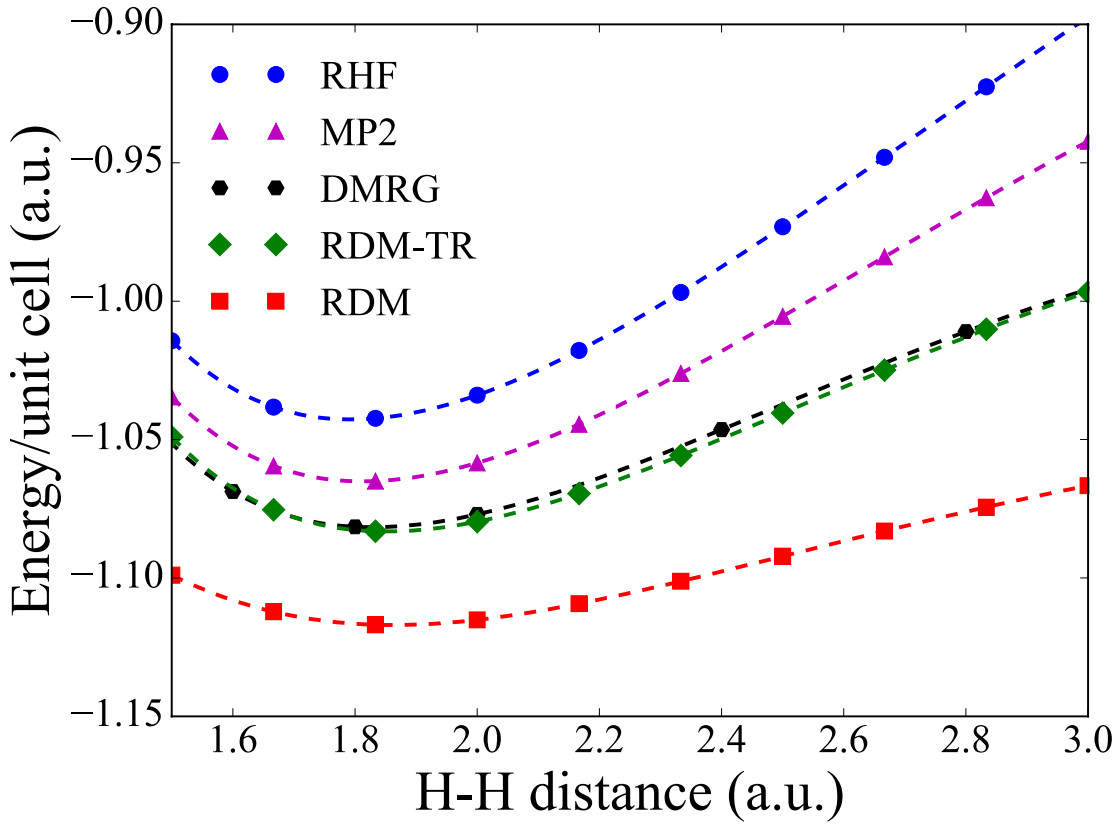
$${}^1Q(k) = {}^1Q(-k)^* \qquad M = D, Q, G$$

Constraints are explicitly included in the SDP

Variational 2-RDM with time-reversal equalities included in the constraints on the 2-RDM

Infinite Hydrogen chain revisited

- Time-reversal constraints are added to the SDP as equality constraints
- Still lower bound!

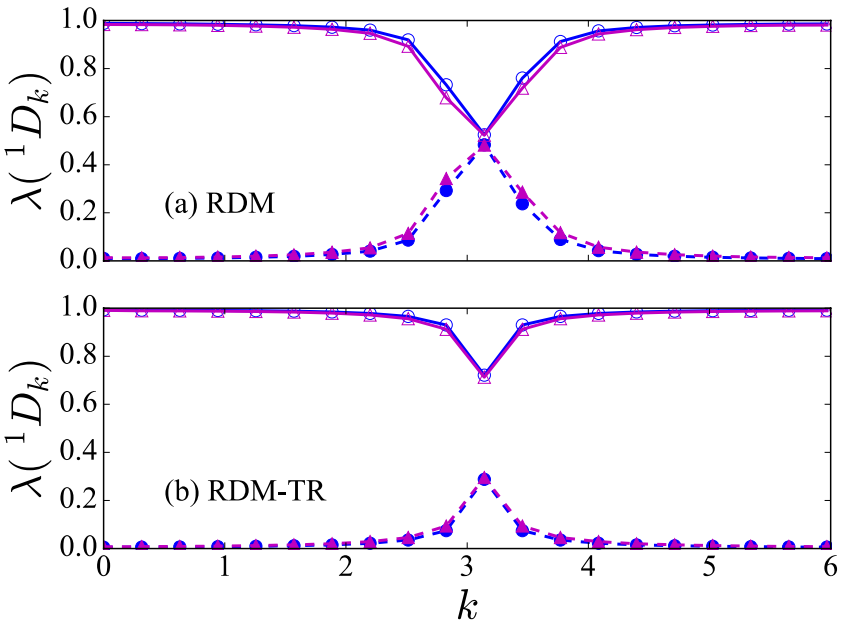


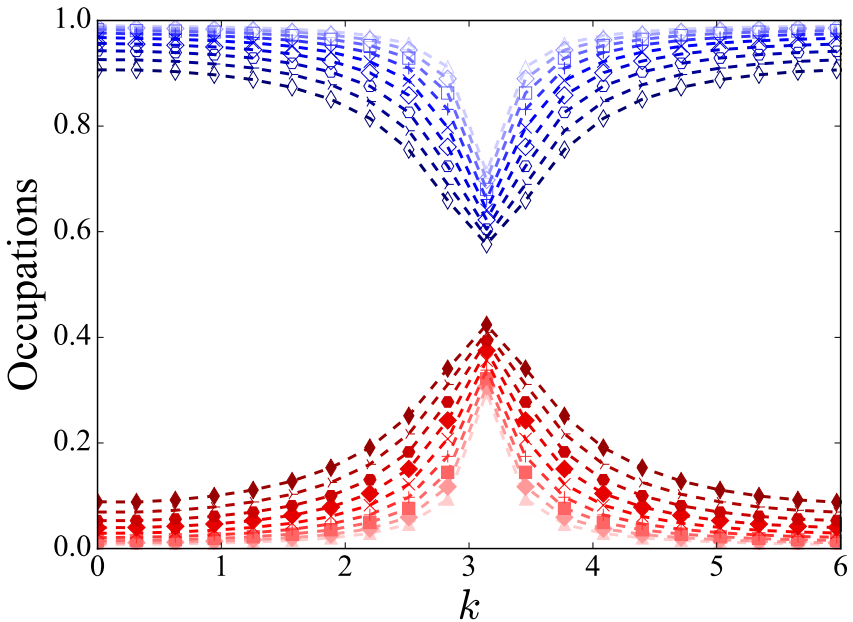
Time-reversal symmetry constraints restore accuracy of DQG constraints!

N. C. Rubin, D. A. Mazziotti, *in preparation* (2016).

Time-reversal fixes occupation number symmetry

Occupation numbers of an infinite H-chain indexed by k-point:



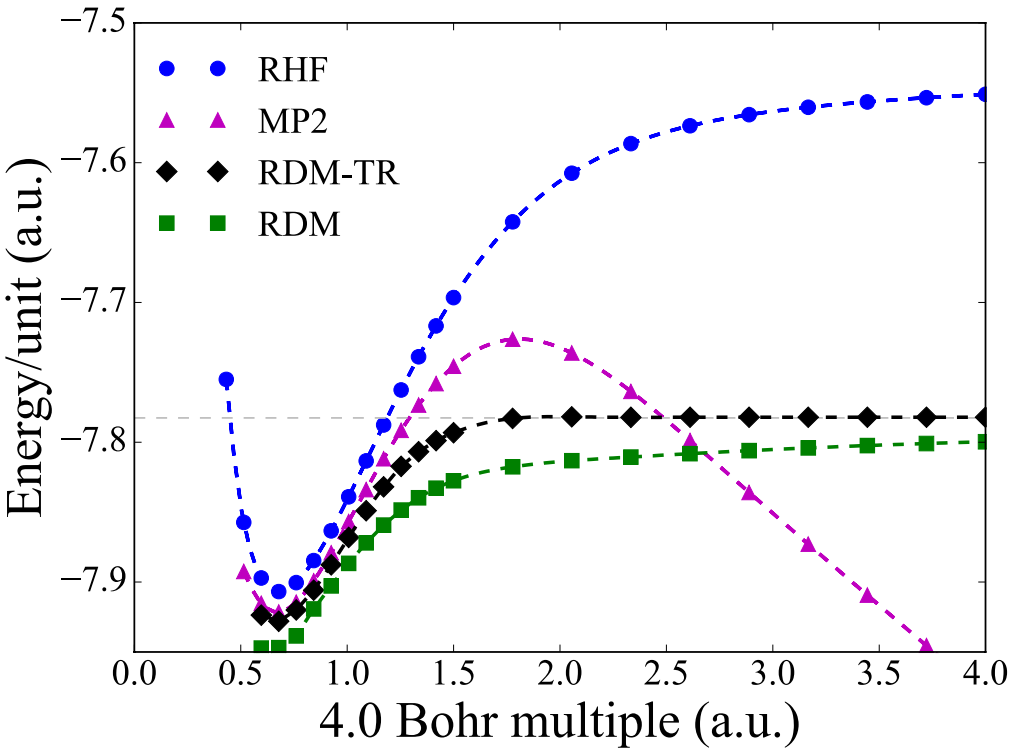


Symmetry broken solution is fixed automatically by constraining D(k) = D(-k)*

N. C. Rubin, D. A. Mazziotti, *in preparation* (2016).

Active space treatment of LiH crystal

- LiH crystal with 5 unit cells in CO-HF summation
- 10^7 determinants on active space
- Core treated at the mean-field level by creating new effective one-electron operators
- RDM without TR fails

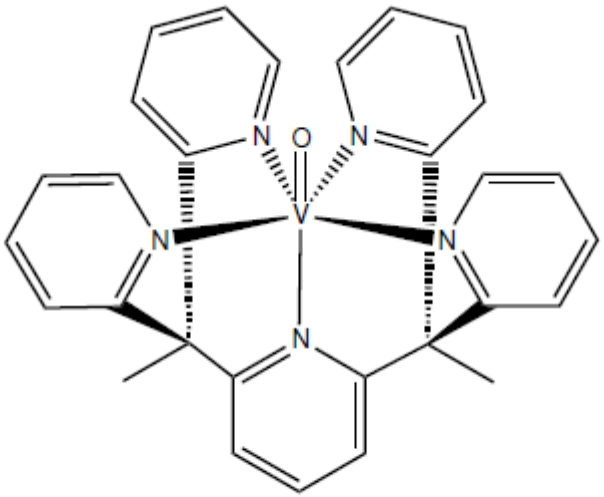


N. C. Rubin, D. A. Mazziotti, *in preparation* (2016).

To Reduce or Not to Reduce:

A Story of a Transition Metal Complex

Main Character



(1) Vanadium oxo 2,6-bis[1,1-bis(2-pyridyl)ethyl]pyridine.

A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

The Facts

- The synthesis of a vanadium oxo complex with low-valent vanadium (III) has been elusive.

- Both ligand-field theory and computationally feasible wave function calculations predict a metal-centered reduction of V (IV) to V (III) in the complex through the addition of an electron to the d_{xy} molecular orbital.

A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

The Experiment

The recent reduction of vanadium (IV) oxo 2,6-bis[1,1-bis(2-pyridyl)ethyl]pyridine to a dark blue substance suggested the potential *first synthesis* of low-valent vanadium (III) in a vanadium oxo complex.

King, A. *et al*. Inorg. Chem. **53,** 11388-11395 (2014).

What's Been Done Before

[12,10] CASSCF Calculations:

- active space = 12 electrons and 10 orbitals
- active orbitals on V and O
- 10,000 quantum degrees of freedom!

King, A. *et al*. Inorg. Chem. **53,** 11388-11395 (2014).

What Was Found Before

[12,10] CASSCF Calculations:

Metal-centered reduction of the vanadium from V (IV) to V (III) in the vanadium oxo complex in agreement with ligand-field theory.

King, A. *et al*. Inorg. Chem. **53,** 11388-11395 (2014).

A 2-RDM Calculation

[42,40] 2-RDM Calculations:

- active space = 42 electrons and 40 orbitals
- active orbitals on V and O and pyridine ligands
- 10^{21} quantum degrees of freedom!

A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

Natural-orbital Occupations

CASSCF[12,10]:

HOMO = 1.97

LUMO = 0.03

A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

Natural-orbital Occupations

CASSCF[12,10]:

HOMO = 1.97

LUMO = 0.03

2-RDM[12,10]:

HOMO = 1.97

LUMO = 0.03

A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

Natural-orbital Occupations

CASSCF[12,10]:

HOMO = 1.97

LUMO = 0.03

2-RDM[12,10]:

HOMO = 1.97

LUMO = 0.03

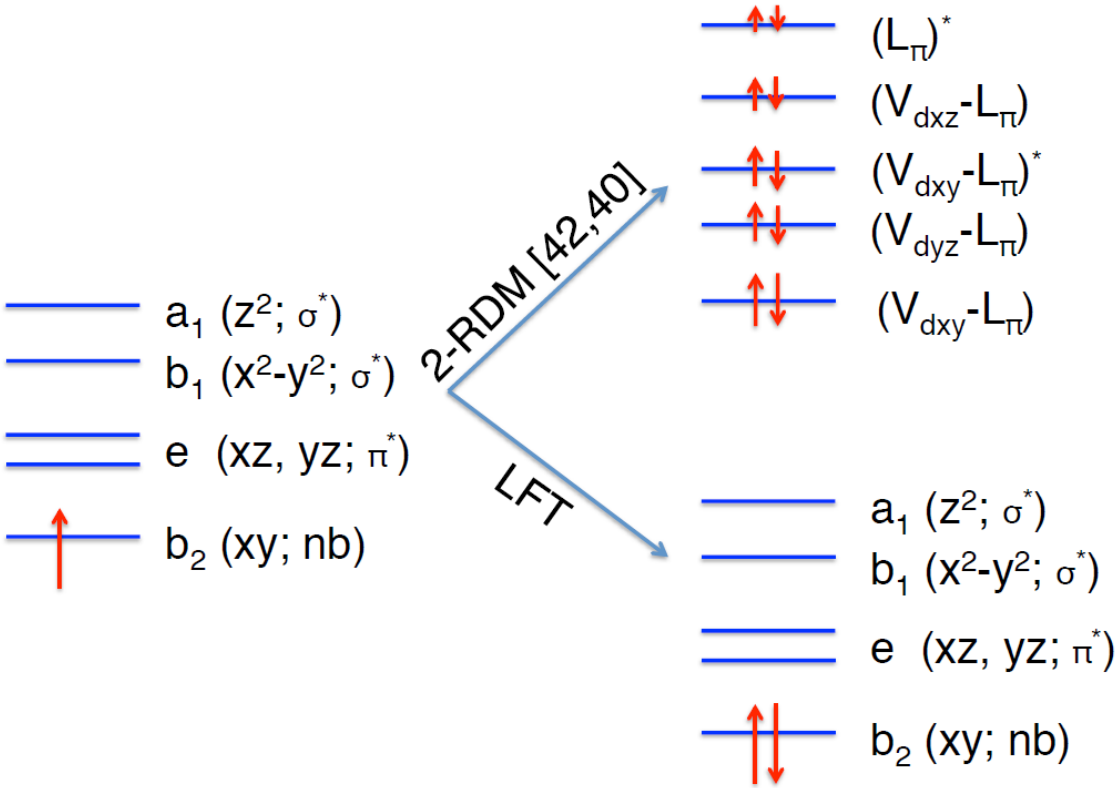
2-RDM[42,40]:

HOMO = **1.37**

LUMO = **0.26**

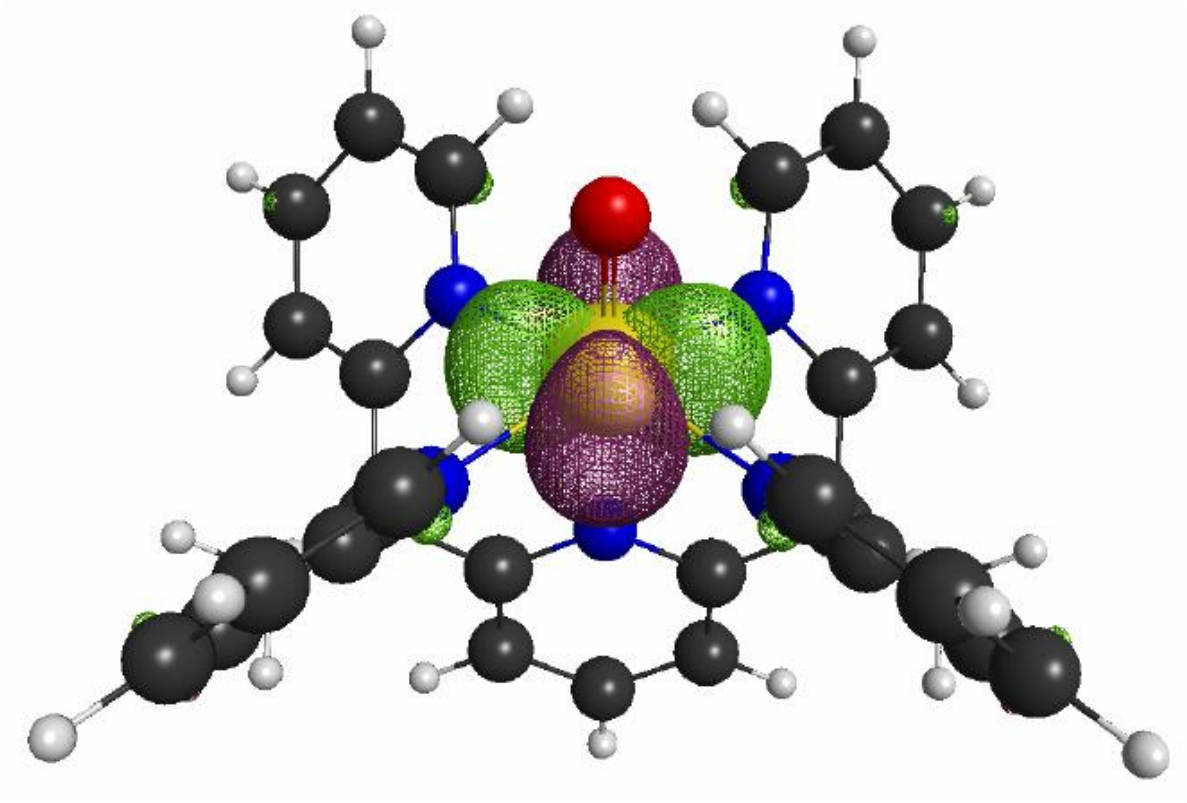
A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

Fractional Occupation Numbers



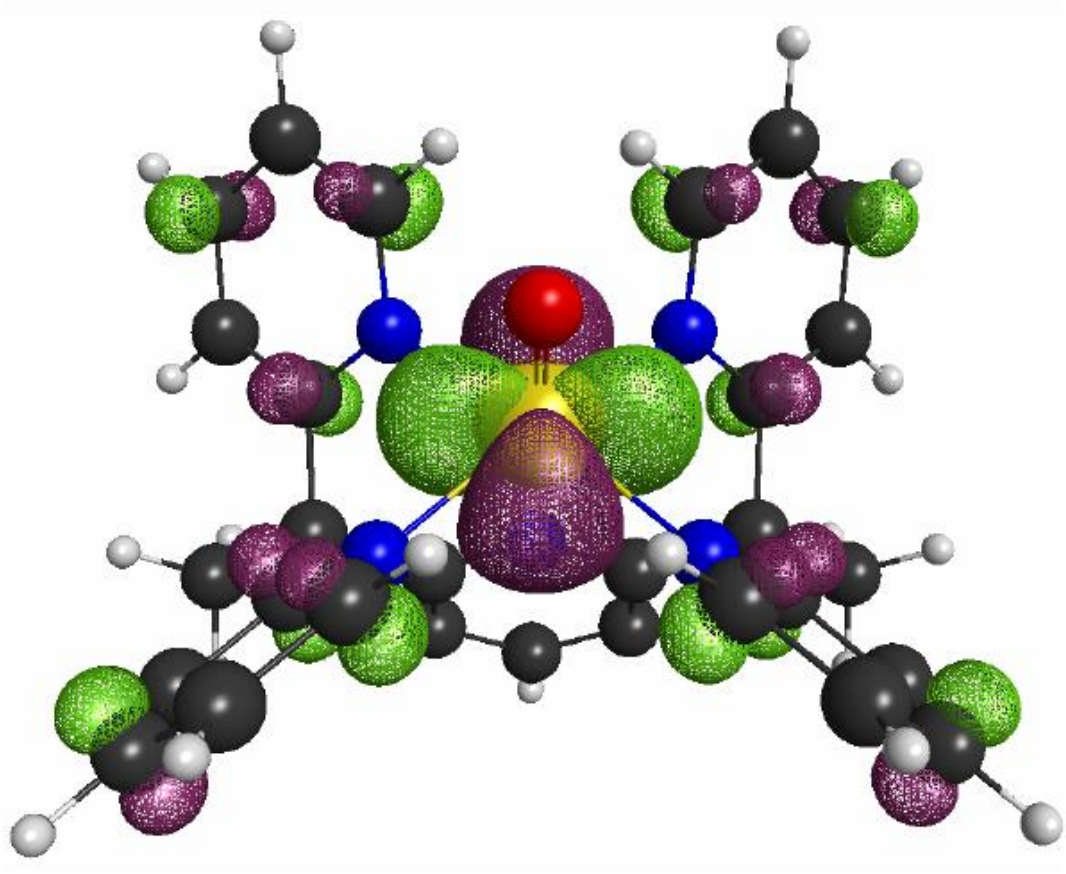
A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

CASSCF [12,10] HOMO Orbital



A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

2-RDM [42,40] HOMO Orbital



A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

2-RDM [42,40]
Mulliken Populations and Charges

	2-RDM [42,40]		
	V(IV)	V(III)	Δ
Vanadium	1.684	1.721	+0.037
Oxygen	-0.455	-0.479	-0.024
Pyridine $_{ax}$	0.209	0.058	-0.151
Pyridine $_{eq}$	0.872	0.046	-0.826
Ethyl	-0.311	-0.346	-0.036

A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

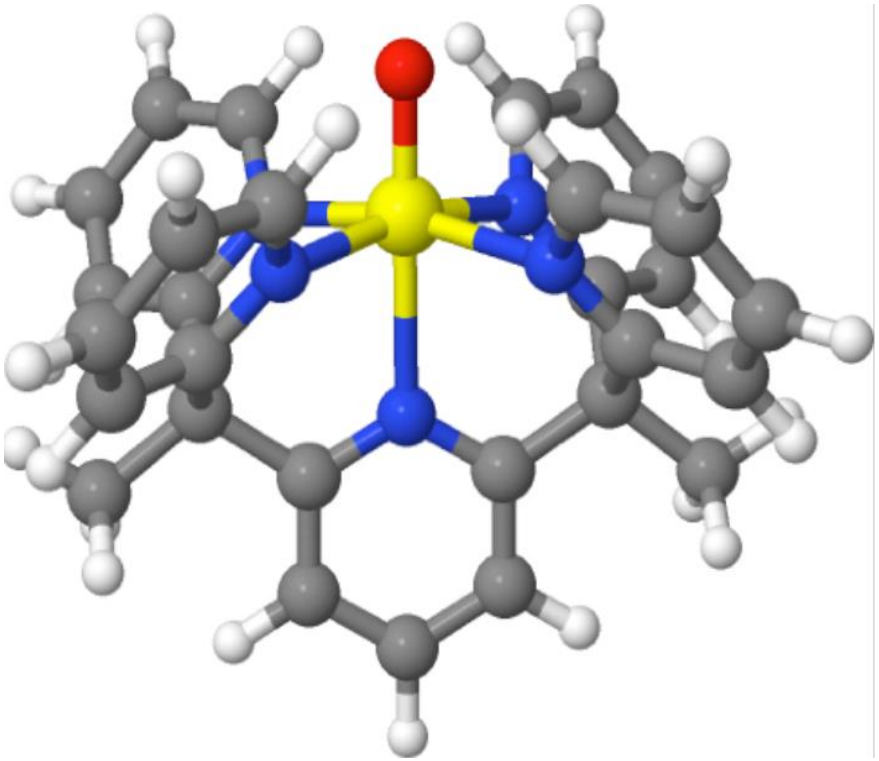
Pyridine Reduction

But pyridine is NOT a great reducing agent!

A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

Entangled Electrons!

- 5 pyridine ligands
- electrons become entangled among the 5 pyridine ligands!



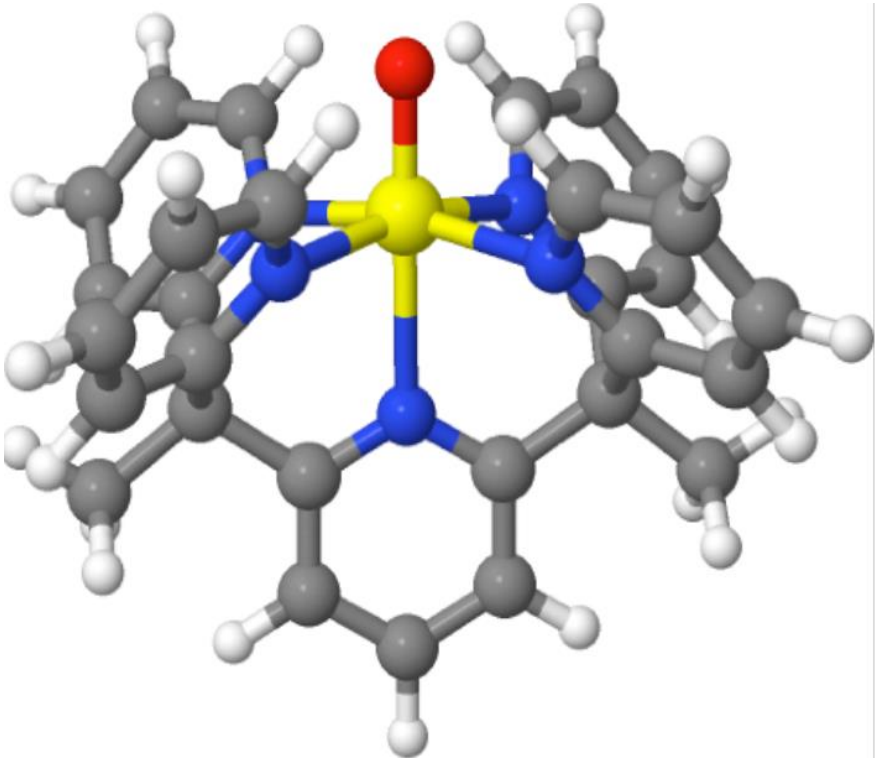
A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

Some Conclusions

- The elusive V (III) oxo complex has *NOT yet been formed*.

- Ligand-centered reduction is stabilized by *strong electron correlation*.

- Significant difference between the [12,10] and [42,40] active spaces with the latter space having 10^{21} quantum variables.



A. Schlimgen, C. Heaps, and D. A. Mazziotti, *J. Phys. Chem. Lett.* **2016**, 7, 627−631.

Strong “Classical” Correlation

Classical Limit of Quantum Many-particle Systems

I. General Classical Limit:

$$\lim_{m\to\infty} \text{Quantum Mechanics} \Rightarrow \text{Classical Mechanics}$$

II. Classical Limit of Many-particle Systems:

$$\lim_{m\to\infty} {}^{2}D(1,2;\bar{1},\bar{2}) \Rightarrow {}^{2}\rho(1,2)$$

$$\lim_{m\to\infty} \text{Quantum } N\text{-rep} \Rightarrow \text{Classical } N\text{-rep}$$

E. Kamarchik and D. A. Mazziotti, Phys. Rev. Lett **99**, 243002 (2007).

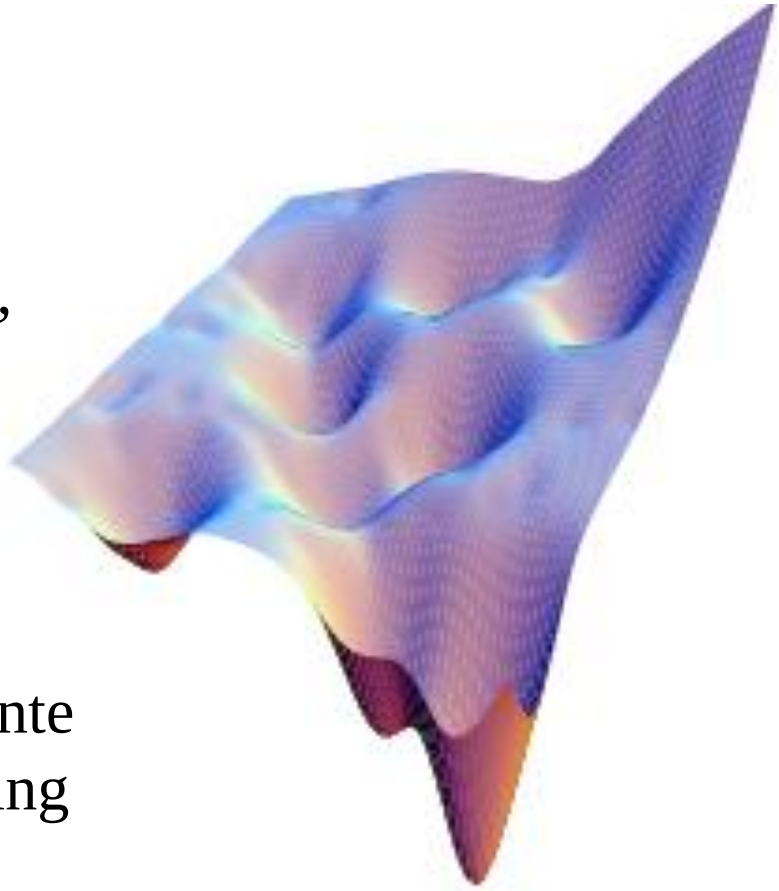
Potential Energy Landscapes

Problem: Determining the global minimum of a complicated PES

Applications: Bio-molecules (protein-folding), atomic clusters, liquids, and glasses

Difficult: Large numbers of local minima

How to: stochastic sampling, Monte Carlo methods, simulated annealing

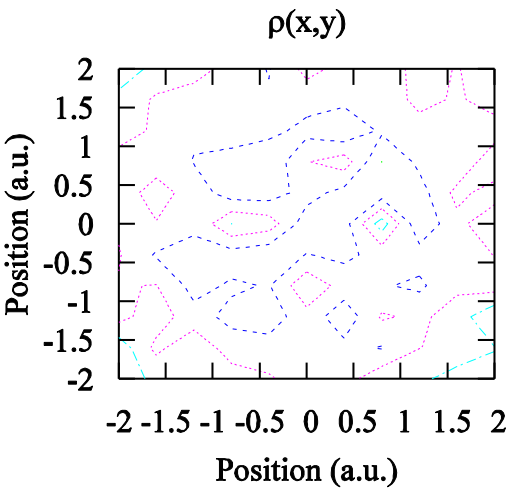


D. Wales, *Energy Landscapes* (Cambridge: Cambridge Univ. Press, 2004).

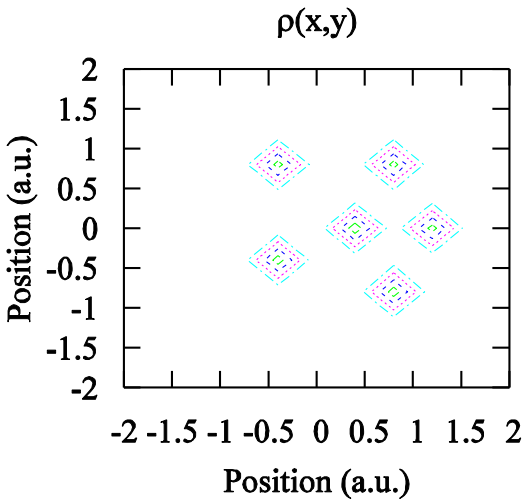
Global Energy Minima of Clusters

Computed in Polynomial Time via SDP

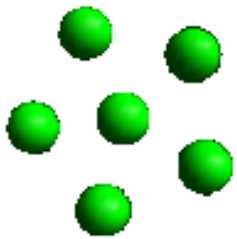
Initial Guess:



Intermediate:



Final Result:



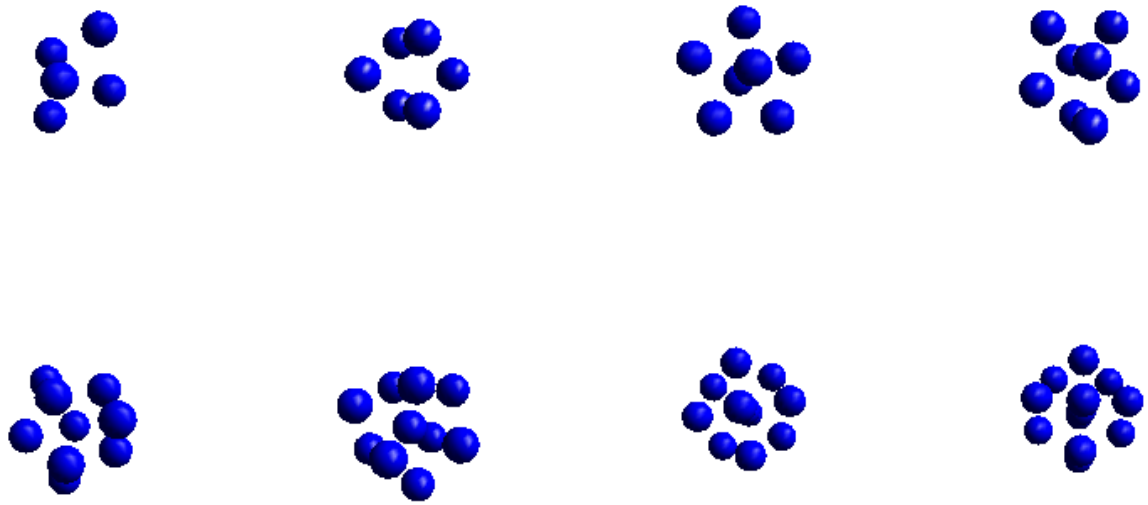
E. Kamarchik and D. A. Mazziotti, Phys. Rev. Lett **99**, 243002 (2007).

Global Energy Minima of Clusters

N	SDP MIN	Global MIN	Found MIN?
5	-9.543323	-9.543323	Yes
6	-14.133584	-14.133584	Yes
7	-18.826786	-18.826786	Yes
8	-24.288527	-24.288527	Yes
9	-30.308254	-30.308254	Yes
10	-36.816641	-36.816641	Yes
11	-44.296619	-44.296619	Yes
12	-51.979131	-51.979131	Yes

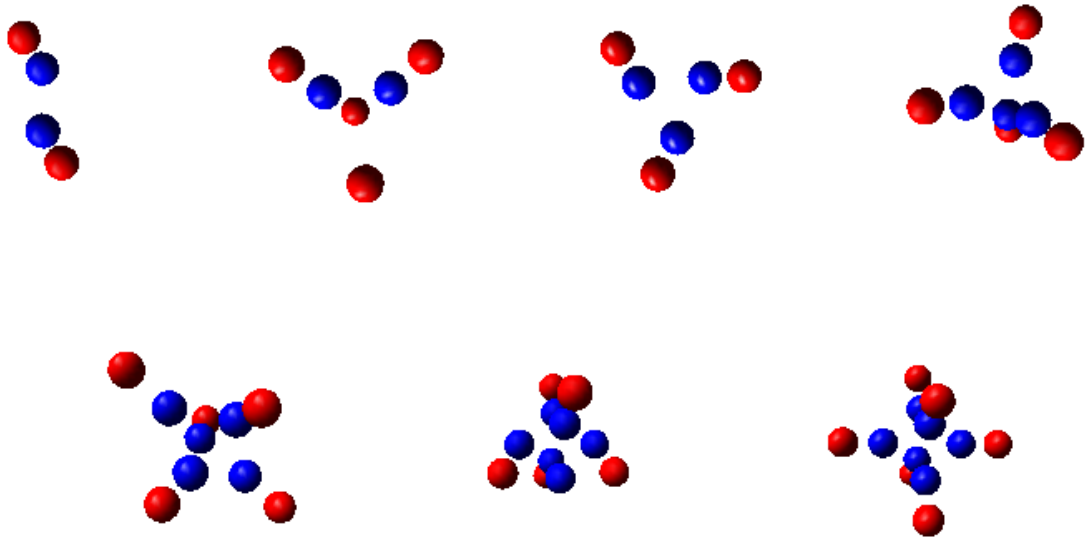
E. Kamarchik and D. A. Mazziotti, Phys. Rev. Lett **99**, 243002 (2007).

Cluster Geometries at Global Energy Minima



E. Kamarchik and D. A. Mazziotti, Phys. Rev. Lett **99**, 243002 (2007).

Binary Cluster Geometries at Global Energy Minima



E. Kamarchik and D. A. Mazziotti, Phys. Rev. Lett **99**, 243002 (2007).

Generalized Pauli Constraints

Ensemble *N*-representability

Ensemble *N*-representability of the 1-RDM:

Theorem 1 (Coleman): A 1-RDM is derivable from the the integration of at least one ensemble *N*-electron density matrix if and only if its eigenvalues lie between 0 and 1, that is obey the Pauli exclusion principle.

A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).

Pure *N*-representability

Pure *N*-representability of the 1-RDM:

Theorem 1 (Klyachko): A 1-RDM is derivable from the the integration of at least one pure *N*-electron density matrix if and only if its eigenvalues obey a generalized Pauli exclusion principle.

A. Klyachko, J, Phys. Conf. Ser. **36**, 72 (2006).

Pure Conditions for 3 Electrons

Pure *N*-representability Conditions for 3 electrons:

$$\lambda_i \geqslant \lambda_{i+1}$$

$$0 \leq \lambda_i \leq 1$$

$$\lambda_1 + \lambda_6 = \lambda_2 + \lambda_5 = \lambda_3 + \lambda_4 = 1$$

$$\lambda_5 + \lambda_6 - \lambda_4 \geqslant 0$$

R. E. Borland and K. Dennis, J. Phys. B 5, 7 (1972).

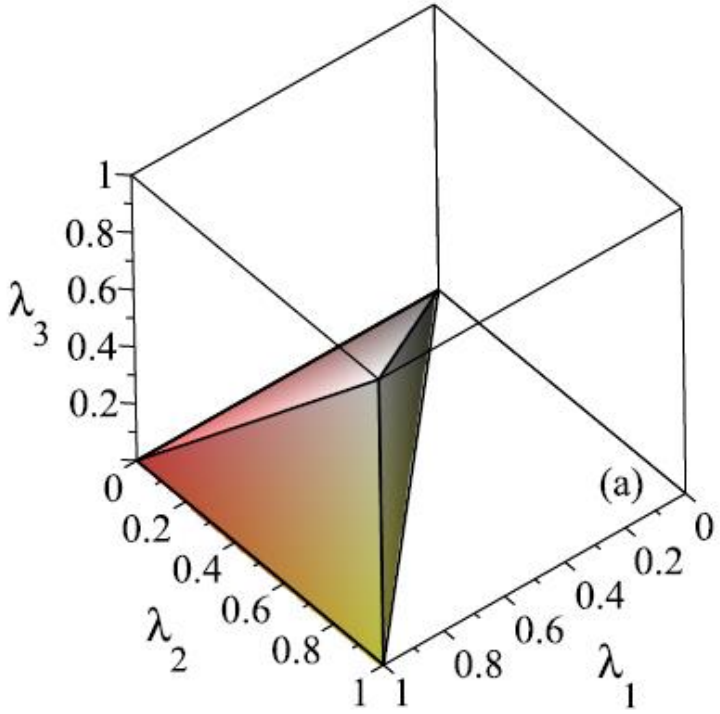
Ensemble N-representable Set

Consider the 3-electron Case:

$$0 \leq \lambda_i \leq 1$$

$$+$$

$$\lambda_i \geqslant \lambda_{i+1}$$



R. Chakraborty and D. A. Mazziotti, Phys. Rev A **89**, 042505 (2014).

Pure N-representable Set

Consider the 3-electron Case:

$$0 \leq \lambda_i \leq 1$$

+

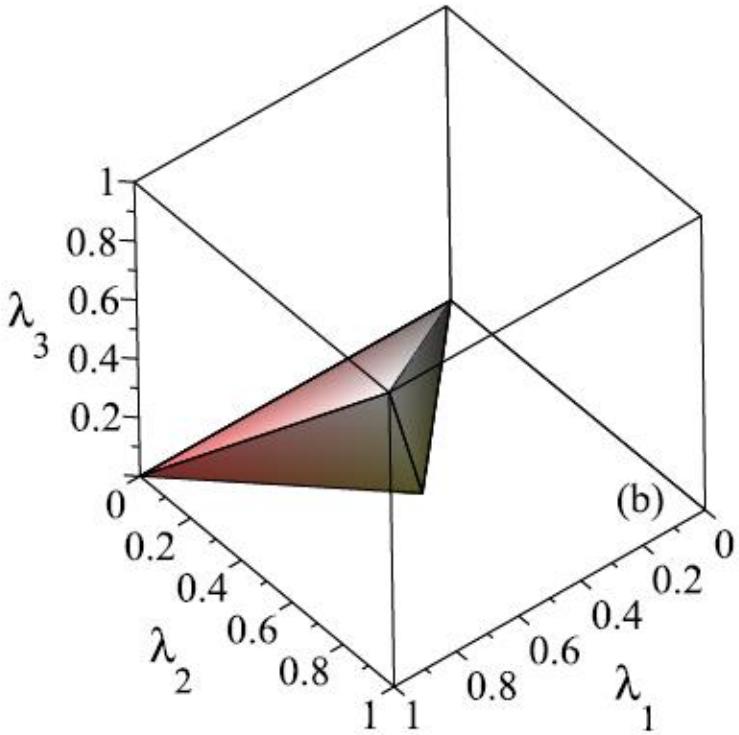
$$\lambda_i \geqslant \lambda_{i+1}$$

+

$$\lambda_5 + \lambda_6 - \lambda_4 \geqslant 0$$

+

$$\lambda_1 + \lambda_6 = \lambda_2 + \lambda_5 = \lambda_3 + \lambda_4 = 1$$



R. Chakraborty and D. A. Mazziotti, Phys. Rev A **89**, 042505 (2014).

Pinning and Quasi-Pinning

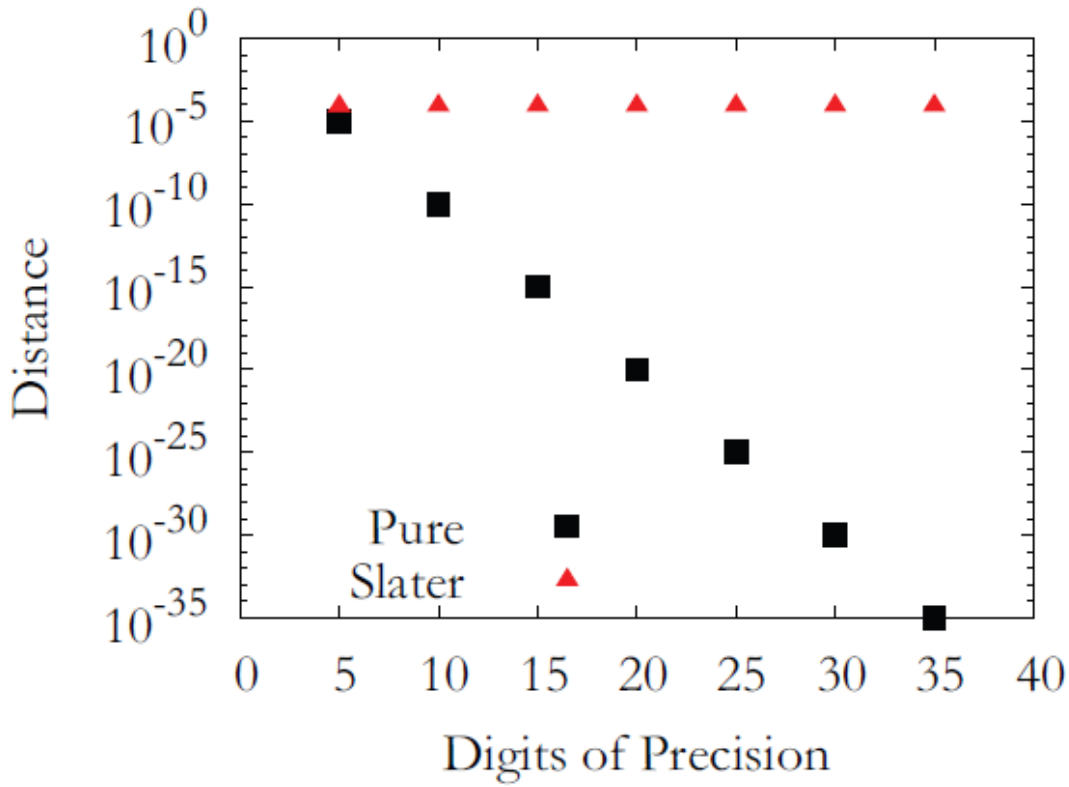
Is the 1-RDM of a ground state or excited state pinned or quasi-pinned to the boundary of the pure set?

Schilling, Gross, and Christandl, PRL (2013).

Theorem: The 1-RDM is pinned only if the 2-RDM is pinned to the boundary of the pure set. Furthermore, the ground-state 2-RDM is always pinned to the boundary of the pure set (hence, the 1-RDM might be pinned), but the excited-state 2-RDM is generally not pinned.

R. Chakraborty and D. A. Mazziotti, Phys. Rev A **89**, 042505 (2014).

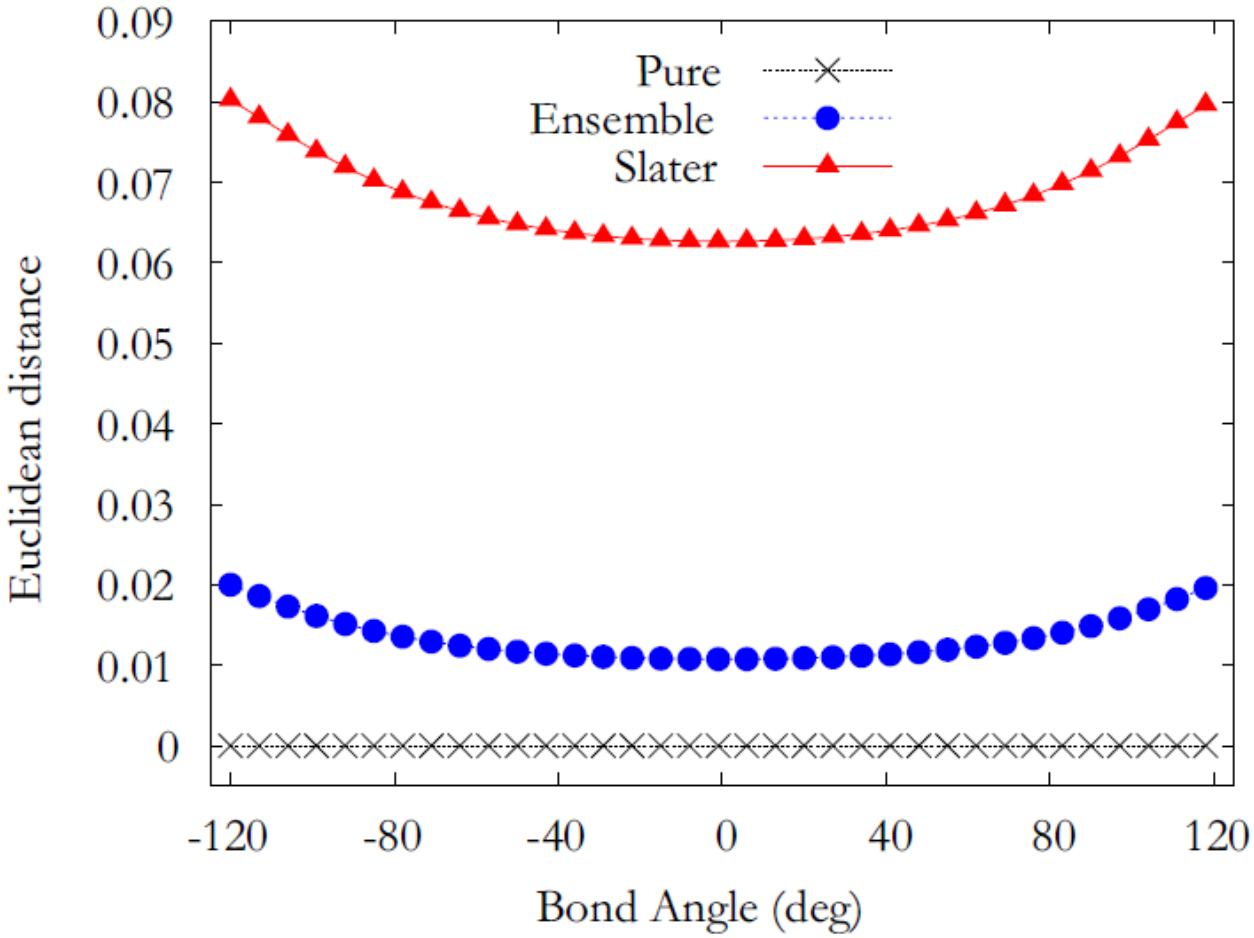
Li Ground State - Pinned!



Pinned to limit of numerical precision!

R. Chakraborty and D. A. Mazziotti, Phys. Rev A **89**, 042505 (2014).

H_3 Ground-state – Pinned!



R. Chakraborty and D. A. Mazziotti, Phys. Rev A **89**, 042505 (2014).

Excited States – Not Necessarily Pinned!

			Euclidean distance		
State	S_z	Energy (a.u.)	Pure	Ensemble	Slater
0	0.5	−7.316	1.00×10^{-30}	1.00×10^{-30}	8.53×10^{-5}
1		−7.230	1.00×10^{-30}	4.10×10^{-5}	1.41×10^{-4}
2		−5.264	1.00×10^{-30}	1.00×10^{-30}	1.75×10^{-1}
3		−5.244	2.72×10^{-1}	3.65×10^{-1}	8.16×10^{-1}
4	1.5	−5.244	1.00×10^{-30}	1.00×10^{-30}	1.00×10^{-30}

R. Chakraborty and D. A. Mazziotti, Phys. Rev A **89**, 042505 (2014).

5-e Ground/Excited States – Not Pinned!

Molecule	State		Means of Pure distance				
			Harmonic	Geometric	Arithmetic	Std dev.	Minimum
C_5H_5	Ground		0.0037	0.0103	0.0907	0.2566	0.0001
	Excited	1	0.0044	0.0303	0.1014	0.2366	0.0001
$^2B_1$, C_{2v}		2	0.0206	0.0516	0.1157	0.2425	0.0005
		3	0.0023	0.2178	0.3119	0.0952	0.0001

R. Chakraborty and D. A. Mazziotti, Int. J. Quantum Chem. **116**, 784 (2016).

2-RDM Mechanics

Opportunities and Challenges:

A New Paradigm:

- *variational 2-RDM method* – systematic *N*-representability conditions for lower bound on the ground-state energy
- *contracted Schrödinger equation* – anti-Hermitian part with 3-RDM reconstruction

Chemistry, Mathematics, & Physics:

- *potential energy surfaces*
- *transition states and kinetics*
- *radical and open-shell chemistry*
- *large-scale semidefinite programming*
- *strong correlation phenomena*

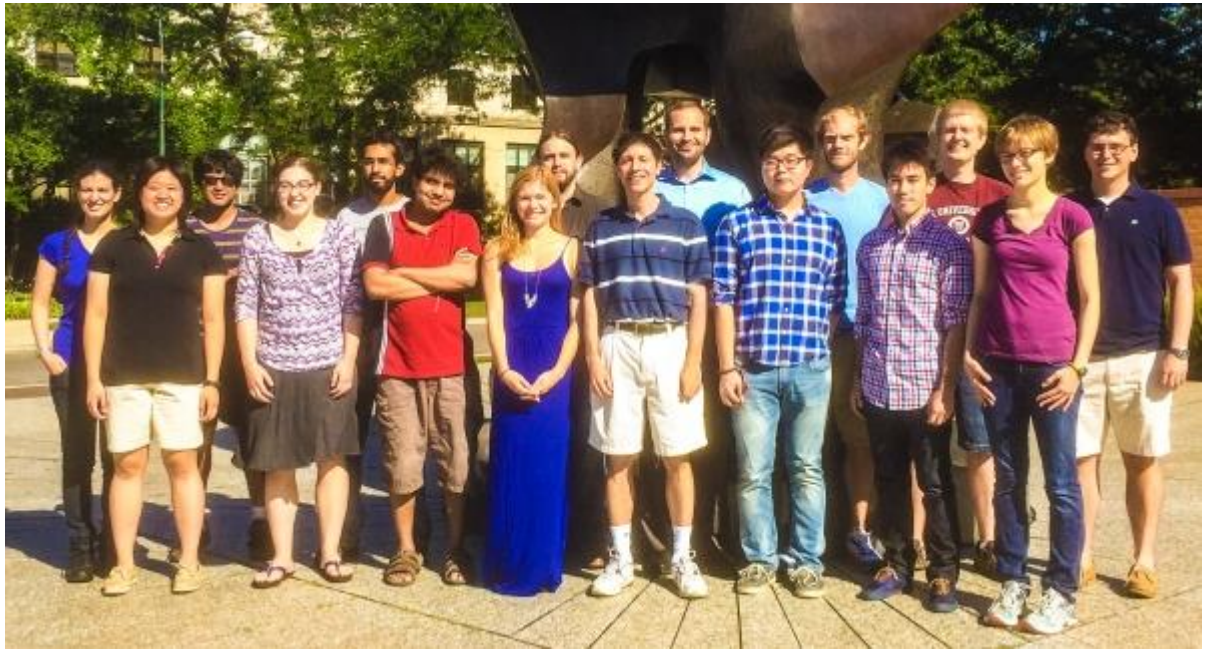
"All the necessary information required for the energy and for calculating the properties of molecules is embodied in the first- and second-order density matrices. These may, of course, be obtained from the wave function by a process of integration. But this is aesthetically unpleasing . . ."

- C. A. Coulson (1959)

Acknowledgments

Current Group Members:

- Chad Heaps
- Nicholas Rubin
- Andrew Valentine
- Charles Forgy
- Romit Chakraborty
- Erica Sturm
- Manas Sajjan
- Anthony Schlimgen
- Kade Head-Marsden
- Ali Raeber
- Alison McManus
- Claire Liu
- Lexie McIsaac



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