Reduced Density Matrix Methods
for Quantum Chemistry and Physics

David A. Mazziotti
Department of Chemistry
James Franck Institute
The University of Chicago

RDM Workshop, Oxford
13 April 2016
Quantum Chemistry
What is Quantum Chemistry?

\[ i\hbar \dot{\Psi} = \hat{H} \Psi \]

\[ \text{Re} e^{-ikx} \quad e^{ikx} \quad T e^{ikx} \]
What is Quantum Chemistry?

\[ i\hbar \dot{\Psi} = \hat{H} \Psi \]

\[ Re^{-ikx} \quad e^{ikx} \quad Te^{ikx} \]

+
What is Quantum Chemistry?

\[ i\hbar \dot{\Psi} = \hat{H} \Psi \]

\[ \text{Re}^{-ikx} \quad e^{ikx} \quad T e^{ikx} \]
What is Quantum Chemistry?

\[ i\hbar \dot{\Psi} = \hat{H} \Psi \]

\[ \text{Re}^{-ikx} \quad e^{ikx} \quad T e^{ikx} \]
What is Quantum Chemistry?

\[ i\hbar \dot{\Psi} = \hat{H} \Psi \]

\[ Re^{-ikx} \quad e^{ikx} \quad Te^{ikx} \]
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*
What is Quantum Chemistry?

But what about the rest of chemistry?

Chemistry is *Potential energy landscapes*

*Quantum molecular dynamics*
What is Quantum Chemistry?

But what about the rest of chemistry?

Chemistry is *Potential energy landscapes*
*Quantum molecular dynamics*
*Organometallic chemistry*
What is Quantum Chemistry?

But what about the rest of chemistry?

Chemistry is  
*Potential energy landscapes*  
*Quantum molecular dynamics*  
*Organometallic chemistry*  
*Semi-metals and conductance*
What is Quantum Chemistry?

But what about the rest of chemistry?

Chemistry is  *Potential energy landscapes*

*Quantum molecular dynamics*

*Organometallic chemistry*

*Semi-metals and conductance*

*Photochemistry*
What is Quantum Chemistry?

But what about the rest of chemistry?

Chemistry is  *Potential energy landscapes*
*Quantum molecular dynamics*
*Organometallic chemistry*
*Semi-metals and conductance*
*Photochemistry*
*Catalysts and enzymes*
What is Quantum Chemistry?

But what about the rest of chemistry?

Chemistry is  
*Potential energy landscapes*  
*Quantum molecular dynamics*  
*Organometallic chemistry*  
*Semi-metals and conductance*  
*Photochemistry*  
*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
What is Quantum Chemistry?

What determines what we can and cannot do?

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

… a special kind of entanglement that we call electron correlation
What is Quantum Chemistry?

Entanglement versus Correlation
What is Quantum Chemistry?

Entanglement versus Correlation

A disentangled, uncorrelated wave function has the form:

$$\Psi(1, 2, \ldots, N) = \phi_i(1) \otimes \phi_j(2) \otimes \ldots \otimes \phi_q(N)$$
What is Quantum Chemistry?

Entanglement versus Correlation

A disentangled, uncorrelated wave function has the form:

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

which breaks the fermionic nature of the electrons.
What is Quantum Chemistry?

Entanglement versus Correlation

An entangled, uncorrelated wave function has the form:

$$\Psi(1, 2, \ldots, N) = \phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$
What is Quantum Chemistry?

Entanglement versus Correlation

An entangled, uncorrelated wave function has the form:

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

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:

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

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:

$$\Psi(1, 2, \ldots, N) = \sum_{i,j\ldots q} c_{ij\ldots q} \phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N)$$
What is Quantum Chemistry?

Weak versus Strong Correlation

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

\[ \Psi(1, 2, \ldots, N) = \sum_{i,j\ldots q} c_{i,j\ldots q} \phi_i(1) \land \phi_j(2) \land \ldots \land \phi_q(N) \]

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:

\[ \Psi(1, 2, \ldots, N) = \sum_{i,j\ldots q} c_{i,j\ldots q} \phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N) \]

- 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:

\[ \Psi(1, 2, \ldots, N) = \sum_{i,j \ldots q} c_{i,j \ldots q} \phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N) \]

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:

\[ \Psi(1, 2, \ldots, N) = \sum_{i,j\ldots q} c_{i,j\ldots q} \phi_i(1) \wedge \phi_j(2) \wedge \ldots \wedge \phi_q(N) \]

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?

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: \( \Psi \) 2-RDM: \( \int \Psi \Psi^* d^3 \ldots dN \)

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:**

\[ E = \int \Psi^* H \Psi \, d1d2..dN \]
\[ H = \sum_{i=1}^{N} h(i) + \frac{1}{2} \sum_{i \neq j=1}^{N} u(i, j) \]

**RDM Mechanics:**

\[ E = \int \Psi^* K \Psi \, d1d2..dN \]
\[ = \int 2K(\int \Psi \Psi^* \, d3d4..dN) \, d1d2 \]
\[ = \int 2K^2D \, d1d2 \]
\[ 2K = \frac{N}{2} \sum_{i=1}^{2} h(i) + \frac{N(N-1)}{2} \sum_{i \neq j=1}^{2} u(i, j) \]
# N-representability Constraints

**Beryllium as an Example:**

<table>
<thead>
<tr>
<th>Wave Mechanics:</th>
<th>RDM Mechanics:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Number</strong></td>
<td>4 electrons</td>
</tr>
<tr>
<td><strong>Hamiltonian</strong></td>
<td>$H = \sum_{i=1}^{4} h(i) + \frac{1}{2} \sum_{i \neq j=1}^{4} u(i, j)$</td>
</tr>
<tr>
<td><strong>Energy</strong></td>
<td>$E = \int \Psi H \Psi^* d\mathbf{1} d\mathbf{2} \ldots d\mathbf{4}$</td>
</tr>
<tr>
<td><strong>Correlation</strong></td>
<td>$E_{CE} = -0.0944 \ \text{au}$</td>
</tr>
</tbody>
</table>

**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
“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


D. A. Mazziotti, Chemical Reviews 112, 244 (2012).
Variational 2-RDM Theory
Variational 2-RDM Method

Minimize

\[ E = \int 2K^2 D \ d1d2 \]

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.

Early known conditions:

\[ 2D \geq 0 \]

\[ 2Q \geq 0 \]

\[ 2G \geq 0 \]

A. J. Coleman, Rev. Mod. Phys. 35 668 (1963);
Semidefinite Programming

RDM Mechanics:

Minimize energy

\[ E = \int 2K^2D \, d1d2 \]

such that

\[ 2D \geq 0 \]
\[ 2Q \geq 0 \]
\[ 2G \geq 0 \]

and

\[ 2Q^{i,j}_{k,l} = 21I_j^i \wedge I_l^k - 41D_j^i \wedge I_l^k + 2D_{k,l}^{i,j} \]
\[ 2G^{i,j}_{k,l} = 1I_i^k D_j^l - 2D_{i,l}^{k,j} \]

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);
Be Revisited:
A Variational 2-RDM Calculation

<table>
<thead>
<tr>
<th>Method</th>
<th>E (a.u.)</th>
<th>% Correlation E</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>-14.5034</td>
<td>0</td>
</tr>
<tr>
<td>MP2</td>
<td>-14.5273</td>
<td>45.5</td>
</tr>
<tr>
<td>MP3</td>
<td>-14.5417</td>
<td>72.7</td>
</tr>
<tr>
<td>MP4</td>
<td>-14.5496</td>
<td>87.8</td>
</tr>
<tr>
<td>D</td>
<td>-17.8973</td>
<td>6437.0</td>
</tr>
<tr>
<td>DQ</td>
<td>-14.5573</td>
<td>102.4</td>
</tr>
<tr>
<td>DQG</td>
<td>-14.5561</td>
<td>100.0</td>
</tr>
<tr>
<td>FCI</td>
<td>-14.5561</td>
<td>100.0</td>
</tr>
</tbody>
</table>

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

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

$N$-representability Conditions:

Positivity Conditions

1-Positivity Conditions (Pauli principle):
\[ ^1D \geq 0 \quad ^1Q \geq 0 \]

2-Positivity Conditions (Coleman ’63; Garrod & Percus ’64):
\[ ^2D \geq 0 \quad ^2G \geq 0 \quad ^2Q \geq 0 \]

3-Positivity Conditions (Mazziotti & Erdahl ’01):
\[ ^3D \geq 0 \quad ^3E \geq 0 \quad ^3F \geq 0 \quad ^3Q \geq 0 \]

$T_2$ Condition (Erdahl ’78; Zhao et al. ’04; Mazziotti ’05):
\[ T_2 = ^3E + ^3F \geq 0 \]

\( \text{N}_2 \text{ Molecule} \)
$\textbf{N}_2$ Molecule
$N_2$ Molecule
N$_2$ Molecule

![Graph showing energy vs. N-N distance for different methods: DQG, DQGT2, FCI, CCSD.](image)
Strong Electron Correlation:
Hydrogen Chains and Lattices
Bonding in a Hydrogen Chain:  
*Stretched geometries*

Bonding in a Hydrogen Chain: 

Stretched geometries

Bonding in a Hydrogen Chain: 
*Metal-to-Insulator Transition*

where

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

Bonding in a Hydrogen Lattice:

Computational Cost of $4 \times 4 \times 4$ Lattice

Wave Functions:

Number of Important Configurations:

$10^{18}$ determinants!

Probability of Each Configuration:

$10^{-18}$

Can this calculation be done?

No.

Bonding in a Hydrogen Lattice: 

Stretched geometries

Bonding in a Hydrogen Lattice: *Metal-to-Insulator Transition*

\[ \gamma \propto \sqrt{\sum_{i \neq j} (\frac{1}{2} D_{ij})^2} \]

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):

n-Acenes:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Number of Variables in CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-acene</td>
<td>4936</td>
</tr>
<tr>
<td>3-acene</td>
<td>69116</td>
</tr>
<tr>
<td>4-acene</td>
<td>112298248</td>
</tr>
<tr>
<td>5-acene</td>
<td>19870984112</td>
</tr>
<tr>
<td>6-acene</td>
<td>3725330089248</td>
</tr>
<tr>
<td>7-acene</td>
<td>728422684135920</td>
</tr>
<tr>
<td>8-acene</td>
<td>147068001734374624</td>
</tr>
</tbody>
</table>

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

### Acenes: Memory and Timings

<table>
<thead>
<tr>
<th>molecule</th>
<th>Memory</th>
<th>Time</th>
<th>Memory</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-acene</td>
<td>0.2 MB</td>
<td>0.02 min</td>
<td>12.6 MB</td>
<td>1.1 min</td>
</tr>
<tr>
<td>3-acene</td>
<td>44.9 MB</td>
<td>2.2 min</td>
<td>15.8 MB</td>
<td>4.0 min</td>
</tr>
<tr>
<td>4-acene</td>
<td>9.0 GB</td>
<td>25.4 hr</td>
<td>23.3 MB</td>
<td>30 min</td>
</tr>
</tbody>
</table>

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.

n-Arynes:

n-Arynes:

(12,12) 2-RDM Calculation

n-Arynes:

\[(n_{C}+2,n_{C}+2)\] 2-RDM Calculation

Planar Acenes: Size

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

Planar Acenes: Geometry

Which of these molecules is most strongly correlated?

6a 6b 6f
linear triangular superbenzene

Planar Acenes: Geometry

Which of these molecules is most strongly correlated?

linear  
triangular  
superbenzene

Answer: triangular > linear > superbenzene

Strongly Correlated Periodic Systems
Basis for Polymers and Molecular Crystals

Bloch orbitals composed of atomic orbitals:

\[ \phi_i(r) = \sum_{\mu} c_{i,\mu} b^{k}_{\mu}(r) \quad b^{k}_{\mu}(r) = \sum_{m} e^{ikm} \chi^m_{\text{AO}}(r) \]

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...

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

$$\psi_{pk_q}(r) = K^{-1/2} \sum_{\mu} \sum_{m} c_{pk_q}^{\mu} e^{imk_qa} \chi_{\mu}(r - ma)$$

$$\langle pk_p|\hat{O}|qk_q \rangle = \sum_{m} e^{ik_pm} \int \chi_{p}^{*}(r - 0a)\hat{O}\chi_{q}(r - (m)a)$$

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

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

\[ f_{\mu k q} = \sum_{m_1 = -S}^{+S} f^{0}_{\mu (m_1)} \exp \left( i m_1 k_q a \right) \]

\[ s_{\nu k q} = \sum_{m_1 = -S}^{+S} s^{0}_{\nu (m_1)} \exp \left( i m_1 k_q a \right) \]

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 $O(n^2) \times K$
- 2-RDM $O((n \times n \times K)^2) \times K$

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

\[
\Theta |\alpha \rangle = |\beta \rangle
\]

\[
\Theta |\beta \rangle = -|\alpha \rangle
\]

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

\[
\Theta = \hat{U} \hat{K}
\]
Time reversal symmetry on one-body operators dictates symmetry between (k,-k) Kramers pairs

Position space constraints for TR symmetry:
\[
\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} K \begin{pmatrix} O_{\tau^+,\alpha,\alpha} & 0 \\ 0 & \hat{O}_{\tau^+,\beta,\beta} \end{pmatrix} K^\dagger \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}^{-1} = \begin{pmatrix} O_{\tau^+,\beta,\beta}^* & 0 \\ 0 & O_{\tau^+,\alpha,\alpha}^* \end{pmatrix} = \begin{pmatrix} O_{-k,\alpha,\alpha}^* & 0 \\ 0 & O_{-k,\beta,\beta}^* \end{pmatrix}
\]

Momentum space space constraints for TR symmetry:
\[
\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} K \begin{pmatrix} O_{\tau^-,\alpha,\alpha} & 0 \\ 0 & \hat{O}_{\tau^-,\beta,\beta} \end{pmatrix} K^\dagger \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}^{-1} = \begin{pmatrix} O_{-k,\beta,\beta}^* & 0 \\ 0 & O_{-k,\alpha,\alpha}^* \end{pmatrix} = \begin{pmatrix} O_{-k,\alpha,\alpha}^* & 0 \\ 0 & O_{-k,\beta,\beta}^* \end{pmatrix}
\]

Equality constraints on the 1-particle and 2-particle density matrices
\[
1^D(k) = 1^D(-k)^* \quad 2^M_{i\alpha,j\beta;k\alpha,l\beta}(k) = \left[ 2^M_{i\beta,j\alpha;k\beta,l\alpha}(-k) \right]^*
\]
\[
1^Q(k) = 1^Q(-k)^* \quad M = D, Q, G
\]

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!

Time-reversal fixes occupation number symmetry

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

\[ \lambda(1D_k) \]

(a) RDM

(b) RDM-TR

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

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

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.

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.

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.

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!

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.

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!

Natural-orbital Occupations

CASSCF[12,10]:
  HOMO = 1.97
  LUMO = 0.03

Natural-orbital Occupations

CASSCF[12,10]:
    HOMO = 1.97
    LUMO = 0.03

2-RDM[12,10]:
    HOMO = 1.97
    LUMO = 0.03

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

Fractional Occupation Numbers

CASSCF [12,10] HOMO Orbital

2-RDM [42,40] HOMO Orbital

### 2-RDM [42,40]

Mulliken Populations and Charges

<table>
<thead>
<tr>
<th></th>
<th>2-RDM [42,40]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V(IV)</td>
</tr>
<tr>
<td>Vanadium</td>
<td>1.684</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-0.455</td>
</tr>
<tr>
<td>Pyridine (_{ax})</td>
<td>0.209</td>
</tr>
<tr>
<td>Pyridine (_{eq})</td>
<td>0.872</td>
</tr>
<tr>
<td>Ethyl</td>
<td>-0.311</td>
</tr>
</tbody>
</table>

Pyridine Reduction

But pyridine is NOT a great reducing agent!

Entangled Electrons!

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

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.

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:

\[
\lim_{m \to \infty} 2^D(1,2;\bar{1},\bar{2}) \rightarrow 2^\rho(1,2)
\]

\[
\lim_{m \to \infty} \text{Quantum } N\text{-rep} \rightarrow \text{Classical } N\text{-rep}
\]

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

Global Energy Minima of Clusters
Computed in Polynomial Time via SDP

Initial Guess:

Intermediate:

Final Result:

## Global Energy Minima of Clusters

<table>
<thead>
<tr>
<th>N</th>
<th>SDP MIN</th>
<th>Global MIN</th>
<th>Found MIN?</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-9.543323</td>
<td>-9.543323</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>-14.133584</td>
<td>-14.133584</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>-18.826786</td>
<td>-18.826786</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td>-24.288527</td>
<td>-24.288527</td>
<td>Yes</td>
</tr>
<tr>
<td>9</td>
<td>-30.308254</td>
<td>-30.308254</td>
<td>Yes</td>
</tr>
<tr>
<td>10</td>
<td>-36.816641</td>
<td>-36.816641</td>
<td>Yes</td>
</tr>
<tr>
<td>11</td>
<td>-44.296619</td>
<td>-44.296619</td>
<td>Yes</td>
</tr>
<tr>
<td>12</td>
<td>-51.979131</td>
<td>-51.979131</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Cluster Geometries at Global Energy Minima

Binary Cluster Geometries at Global Energy Minima

Generalized Pauli Constraints
Ensemble $N$-representability

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

**Theorem 1 (Coleman):** A 1-RDM is derivable from 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.

Pure $N$-representability

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

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

Pure $N$-representability Conditions for 3 electrons:

\[ \lambda_i \geq \lambda_{i+1} \]

\[ 0 \leq \lambda_i \leq 1 \]

\[ \lambda_1 + \lambda_6 = \lambda_2 + \lambda_5 = \lambda_3 + \lambda_4 = 1 \]

\[ \lambda_5 + \lambda_6 - \lambda_4 \geq 0 \]

Consider the 3-electron Case:

\[ 0 \leq \lambda_i \leq 1 \]

\[ + \]

\[ \lambda_i \geq \lambda_{i+1} \]

Pure N-representable Set

Consider the 3-electron Case:

\[ 0 \leq \lambda_i \leq 1 \]
\[ + \]
\[ \lambda_i \geq \lambda_{i+1} \]
\[ + \]
\[ \lambda_5 + \lambda_6 - \lambda_4 \geq 0 \]
\[ + \]
\[ \lambda_1 + \lambda_6 = \lambda_2 + \lambda_5 = \lambda_3 + \lambda_4 = 1 \]

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


**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.

Li Ground State - Pinned!

Pinned to limit of numerical precision!

H$_3$ Ground-state – Pinned!

Excited States – Not Necessarily Pinned!

<table>
<thead>
<tr>
<th>State</th>
<th>$S_z$</th>
<th>Energy (a.u.)</th>
<th>Pure</th>
<th>Ensemble</th>
<th>Slater</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5</td>
<td>-7.316</td>
<td>$1.00 \times 10^{-30}$</td>
<td>$1.00 \times 10^{-30}$</td>
<td>$8.53 \times 10^{-5}$</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>-7.230</td>
<td>$1.00 \times 10^{-30}$</td>
<td>$4.10 \times 10^{-5}$</td>
<td>$1.41 \times 10^{-4}$</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>-5.264</td>
<td>$1.00 \times 10^{-30}$</td>
<td>$1.00 \times 10^{-30}$</td>
<td>$1.75 \times 10^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>-5.244</td>
<td>$2.72 \times 10^{-1}$</td>
<td>$3.65 \times 10^{-1}$</td>
<td>$8.16 \times 10^{-1}$</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>-5.244</td>
<td>$1.00 \times 10^{-30}$</td>
<td>$1.00 \times 10^{-30}$</td>
<td>$1.00 \times 10^{-30}$</td>
</tr>
</tbody>
</table>

### 5-e Ground/Excited States – Not Pinned!

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Harmonic</th>
<th>Geometric</th>
<th>Arithmetic</th>
<th>Std dev.</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅H₅</td>
<td>Ground</td>
<td>0.0037</td>
<td>0.0103</td>
<td>0.0907</td>
<td>0.2566</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>Excited 1</td>
<td>0.0044</td>
<td>0.0303</td>
<td>0.1014</td>
<td>0.2366</td>
<td>0.0001</td>
</tr>
<tr>
<td>²B₁, C₂ᵥ</td>
<td>2</td>
<td>0.0206</td>
<td>0.0516</td>
<td>0.1157</td>
<td>0.2425</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.0023</td>
<td>0.2178</td>
<td>0.3119</td>
<td>0.0952</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

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

Funding:
National Science Foundation,
Army Research Office, Air Force Office of Scientific Research, Keck Foundation,
Microsoft Corporation