Putting a spin on time dependent electronic structure theory

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General Exam

Thursday, May 14, 10:00am CHB 339
Thank you to General Exam Committee

Xiaosong Li (chair)
Jim Pfaendtner (GSR)
Matthew Bush
David Masiello
Stefan Stoll
How can we predict and understand the electronic and magnetic responses of molecules and nano-materials?
Research Directions (2014—2015)

Quantum Dots

Excited States

Magnetic Materials


Research Directions (2014—2015)

Excited States


Quantum Dots


Magnetic Materials


Other

Research Directions (2014—2015)

- Quantum Dots
- Excited States
- Magnetic Materials
Research Directions (2014—2015)

- Quantum Dots
- Excited States
- Magnetic Materials
Excited States

Balancing Cost + Accuracy of Electronic Excited State Methods

LR-TDDFT
- $O(N^4)$
- Unpredictable
- No excited state exchange kernel
- Limited to single electron phenomena

Balance cost + accuracy
(P)-EOM-MBPT2, CC2, etc.

EOM-CCSD
- $O(N^6)$
- Systematically improvable
- Excited state electron correlation
- Multi-electron phenomena

Excited States

Balancing Cost + Accuracy of Electronic Excited State Methods

- Applied perturbation theory to coupled cluster (CC) equations
- Reduced computational time of CC equations by an order of magnitude
- Accuracy generally outperforms density functional theory

Research Directions (2014—2015)

- Quantum Dots
- Excited States
- Magnetic Materials
Understanding Dopant Influence on Excitations in n-type Quantum Dots

Al$^{3+}$:ZnO
extra conduction band electron
tough to oxidize

e-$:ZnO
extra conduction band electron
easy to oxidize

Understanding Dopant Influence on Excitations in n-type Quantum Dots

- n-type ZnO QDs
- UV-Vis spectra from aluminum doped and photodoped QDs
- Rationalized theoretical/experimental results in terms of particle-in-a-sphere

• n-type ZnO QDs

• UV-Vis spectra from aluminum doped and photodoped QDs

• Rationalized theoretical/experimental results in terms of particle-in-a-sphere

Research Directions (2014—2015)

Quantum Dots

Excited States

Magnetic Materials
Exploring spin-frustrated molecules with the generalized Hartree Fock (GHF) method

Take a three site lattice
Now add two electrons
(assume antiferromagnetism is favored)
Now add the third electron. No orientation simultaneously favors all anti-ferromagnetic interactions.
Magnetic Materials

Conventional methods force you to pick a collinear configuration. Few methods can give you non-collinear state.
Magnetic Materials

Magnetic Materials
Can we describe this with Hartree Fock (HF)?
Hartree-Fock (HF): minimize the energy of a single Slater Determinant

\[ E \leq \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \]

The solution is \textit{variational}; an upper bound to the exact energy.

This is an independent particle model (IPM). It is the quantitative basis of molecular orbital theory.
# Magnetic Materials

## Types of Hartree-Fock

<table>
<thead>
<tr>
<th></th>
<th>Restricted (RHF)</th>
<th>Unrestricted (UHF)</th>
<th>General (GHF)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>orbital</strong></td>
<td>spatial</td>
<td>$\phi(r)\alpha(\omega); \phi(r)\beta(\omega)$</td>
<td>$\phi(r)\alpha(\omega) + \phi(r)\beta(\omega)$</td>
</tr>
<tr>
<td>$\hat{S}^2$</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>$\hat{S}_z$</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td><strong>system</strong></td>
<td>closed shell</td>
<td>open shell</td>
<td>spin frustrated</td>
</tr>
</tbody>
</table>
Generalized Hartree Fock (GHF)

- GHF allows you to change spin smoothly
Generalized Hartree Fock (GHF)

• GHF allows you to change spin smoothly
• Lowest energy HF solution possible
Magnetic Materials

**Generalized Hartree Fock (GHF)**

- GHF allows you to change spin smoothly
- Lowest energy HF solution possible
- Largely insensitive to guess multiplicity
Generalized Hartree Fock (GHF)

- GHF allows you to change spin smoothly
- Lowest energy HF solution possible
- Largely insensitive to guess multiplicity
- Only HF method to treat spin frustration
Problem:
Just because you *can* get the lowest energy solution, doesn’t mean you will.
How to obtain GHF local minima?

stable

unstable

How to obtain GHF local minima?

We want stable electronic solutions to the GHF model.

Local minima:

(a) First variation equal to zero
(b) Second variation greater than zero

Differentiate $E$ with respect to wave function coefficients

$$\frac{\partial E}{\partial q_i^a} = \left( \begin{array}{c} \langle \phi_i^a | \hat{H} | 0 \rangle \\ \langle 0 | \hat{H} | \phi_i^a \rangle \end{array} \right) = \left( \begin{array}{c} f_{ai} \\ f_{ia} \end{array} \right)$$

This must equal zero, known as Brillouin’s theorem.

(Trivially satisfied as long as HF converges to something)
Second derivative of energy with respect to wave function coefficients

$$\frac{\partial^2 E}{\partial q_i^a \partial q_j^b} = \begin{pmatrix} \langle \phi_i^a | \hat{H} | \phi_j^b \rangle & \langle \phi_{ij}^{ab} | \hat{H} | 0 \rangle \\ \langle 0 | \hat{H} | \phi_{ij}^{ab} \rangle & \langle \phi_j^b | \hat{H} | \phi_i^a \rangle \end{pmatrix}$$

The Hessian, which must be **positive definite** if our solution is to be a minimum.
Magnetic Materials

\[
\text{Hessian} = \begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}
\]

\[A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle aj||ib\rangle, \quad B_{ia,jb} = \langle ab||ij\rangle\]

Compute eigenpairs of Hessian matrix.

If all eigenvalues are positive, we are at minima.

If any eigenvalues are negative, lower energy solution exists.
What if we run into instability?

**Steepest Descent Method**

1. Take the most negative eigenvalue and eigenvector
2. Step wave function in direction of eigenvector
3. Re-optimize GHF solution.
Magnetic Materials

Full details and working equations in the paper!
Looking for lowest energy solutions in spin frustrated rings

Cr$_3$ : high-spin solutions unstable. Lower energy non-collinear solution exists.
<table>
<thead>
<tr>
<th>Magnetic Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen rings for odd-member rings, GHF lowest energy solution</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>n</th>
<th>Ring</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td><img src="triangle.png" alt="Triangle" /></td>
</tr>
<tr>
<td>4</td>
<td><img src="square.png" alt="Square" /></td>
</tr>
<tr>
<td>5</td>
<td><img src="pentagon.png" alt="Pentagon" /></td>
</tr>
<tr>
<td>6</td>
<td><img src="hexagon.png" alt="Hexagon" /></td>
</tr>
<tr>
<td>7</td>
<td><img src="heptagon.png" alt="Heptagon" /></td>
</tr>
<tr>
<td>8</td>
<td><img src="octagon.png" alt="Octagon" /></td>
</tr>
<tr>
<td>9</td>
<td><img src="nonagon.png" alt="Nonagon" /></td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>GHF</th>
<th>UHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetization</td>
<td>Spin density</td>
</tr>
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In summary:

GHF allows for the **lowest-energy HF solution**

Can **determine multiplicity** without user input

Can **handle spin frustrated** systems

Loses all good **spin quantum numbers**
Future outlook

GHF can handle spin transitions, but lacks any spin operators (only Coulomb exchange interaction)
Including Arbitrary Magnetic Fields into *Ab Initio* Electron Dynamics

**RT-TD-GHF**

- Arbitrary magnetic field
- Magnetic moments precess with field
- No spin coupling!

Neutral Li$_3$ trimer, 20T field perpendicular to plane

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Observation: TD-GHF allows smooth evolution of spin states, but **lacks spin coupling** operators.

Can we extend this description by **adding explicit spin operators** to the TD-GHF description?
Spin is a non-classical effect. It arises from relativistic quantum mechanics.

One electron, Dirac equation:

\[
\begin{bmatrix}
V & c\sigma \cdot \Pi \\
\sigma \cdot \Pi & V - 2c^2
\end{bmatrix}
\begin{bmatrix}
\Psi^L \\
\Psi^S
\end{bmatrix}
= E
\begin{bmatrix}
\Psi^L \\
\Psi^S
\end{bmatrix}
\]

This replaces the one electron operators in GHF

Note four components:
\[
\Psi^L = \begin{bmatrix}
\Psi^{L\alpha} \\
\Psi^{L\beta}
\end{bmatrix}, \quad \Psi^S = \begin{bmatrix}
\Psi^{S\alpha} \\
\Psi^{S\beta}
\end{bmatrix}
\]
For multiple electrons, we have the approximate interaction operator—\textit{the Breit operator}

\[
\hat{V}_{12} = \frac{q_1 q_2}{r_{12}} - \frac{q_1 q_2}{2} \left[ \frac{\alpha_1 \cdot \alpha_2}{r_{12}} + \frac{(r_{12} \cdot \alpha_1) (r_{12} \cdot \alpha_2)}{r_{12}^3} \right]
\]

This replaces the two electron Coulomb operator

\[
\alpha = \begin{pmatrix} 0_2 & \sigma \\ \sigma & 0_2 \end{pmatrix}
\]
For multiple electrons, we have the approximate interaction operator—**the Breit operator**

\[
\hat{V}_{12} = \frac{q_1 q_2}{r_{12}}\left( \frac{\alpha_1 \cdot \alpha_2}{r_{12}} + \frac{(r_{12} \cdot \alpha_1)(r_{12} \cdot \alpha_2)}{r_{12}^3} \right)
\]

(Coulomb) (Breit correction, note spin-dependence)

This replaces the two electron Coulomb operator

\[
\alpha = \begin{pmatrix}
0_2 & \sigma \\
\sigma & 0_2
\end{pmatrix}
\]
We can reduce to two component form

\[
\begin{bmatrix}
H_{LL} & H_{LS} \\
H_{SL} & H_{SS}
\end{bmatrix}
\begin{bmatrix}
\Psi^L \\
\Psi^S
\end{bmatrix}
\]

\[U \left[
\begin{array}{cc}
H_{LL} & H_{LS} \\
H_{SL} & H_{SS}
\end{array}
\right] U^{-1} \rightarrow \left[
\begin{array}{cc}
\tilde{H}_{LL} & 0 \\
0 & \tilde{H}_{SS}
\end{array}
\right]\]

Usually approximate

Off diagonal terms zero to some order

Order 1/c gives Breit-Pauli

Order V gives Douglas-Kroll-Hess
Uncertain best way to include these operators into the TDSE

<table>
<thead>
<tr>
<th></th>
<th>Four Component</th>
<th>Breit-Pauli (two component, 1/c)</th>
<th>Douglas-Kroll-Hess (two component, V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naive cost?</td>
<td>$2(4N)^4$</td>
<td>$2(2N)^4$</td>
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</tr>
<tr>
<td>Variational?</td>
<td>No (yes, in practice)</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Interpretation?</td>
<td>Must account for positron-like component</td>
<td>Clear relation to spin-Hamiltonian</td>
<td>Spin-terms mixed</td>
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</table>
Future Roadmap

DKH

Property Transf.

Breit

4c

cheaper, harder to code

picture-change

expensive, simpler

Spin-dependent electronic dynamics

Heavy-element response properties

response properties, physical observables

Time Domain

 retardation effects

spin-spin
How can we predict and understand the electronic and magnetic responses of molecules and nano-materials?
Maybe settle for atoms at the moment?

TD-DKH

Sodium D-lines (daug-cc-pVTZ)

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<tr>
<th>[eV]</th>
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<th>2c-TD-DKH</th>
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<tr>
<td>(^2S_{1/2} \rightarrow ^2P_{1/2})</td>
<td>1.9733</td>
<td>1.9730</td>
<td>2.1023</td>
</tr>
<tr>
<td>(^2S_{1/2} \rightarrow ^2P_{3/2})</td>
<td>1.9733</td>
<td>1.9736</td>
<td>2.1044</td>
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<tr>
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<td>0.0000</td>
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A lot more more more needs to be done!

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Future work

Spin-dependent dynamics and response theory
Future work

Spin in Time-Dependent Theory

Spin-dependent dynamics and response theory
Thank you!

Li Group
Exam Committee
Ernest Davidson

Excited States
Quantum Dots
Magnetic Materials
Spin in Time-Dependent Theory
Coupling between charge carriers and Mn$^{2+}$ in ZnO QDs

holes in p-type dopants couple with Mn$^{2+}$ dimer

exciton couples to Mn$^{2+}$ in ZnO QDs
It seems reasonable that excess CB electrons would couple to Mn$^{3+}$:ZnO QDs; no evidence excess electrons couple with Mn.

Data courtesy Dr. Alina Schimpf

Al$^{3+}$:ZnO QDs; no evidence excess electrons couple with Mn.
Of course, similar story with photodoped e⁻:ZnO

All systems studied so far are heavily doped

Currently, Gamelin group looking at low-carrier concentrations

Can we help explain this with spin dependent electronic structure theory?