U.S. DOE SciDAC Partnership

Predictive Computing for Condensed Matter

So Hirata (Chemistry)
Peter Abbamonte (Physics)
David Ceperley (Physics)
Shinsei Ryu (Physics)
Lucas Wagner (Physics)

Garnet Chan (Chemistry)
Bryan Clark (Physics)
Shiwei Zhang (Physics)
A DOE report on Computational Materials Science (2010): “We are at the threshold of a new era where the integrated synthesis, characterization, and modeling of complex materials and chemical processes will transform our ability to understand and design new materials and chemistries with predictive power.”

Materials Genome Initiative for Global Competitiveness (2011): “the development of advanced materials can be accelerated through advances in computational techniques”
The team

**So Hirata** (Chemistry, UIUC) - Lead PI

Hirata is a theoretical/computational chemist and an expert in electron-correlation theories for molecules and solids. He is the primary author of the computer-generated, high-rank electron-correlation modules in DOE’s massively parallel NWChem suite of software, implementing several of his original methods.

**Lucas Wagner** (Physics, UIUC) - Co-lead PI

Wagner is the principal author of the quantum Monte Carlo program, QWALK, with which he has performed predictively accurate calculations on strongly correlated systems.

**Peter Abbamonte** (Physics, UIUC)

Abbamonte, an experimental condensed-matter physicist, brings an invaluable experimental insight into the project. He is one of the originators of resonant soft x-ray scattering, with which he discovered a Wigner crystal in doped spin ladders and the charged stripes in copper-oxide superconductors.

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Ceperley is a theoretical/computational physicist and an authority of quantum Monte Carlo (QMC). He invented a number of QMC algorithms and is the author of massively parallel QMCPACK software.

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Chan is a recognized expert in strong correlation theories including density matrix renormalization group (DMRG), tensor networks, and density matrix functional theory. He has, in particular, established DMRG as a practical, powerful tool for strongly correlated molecular electronic structures.

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Ryu specializes in mathematical theories of strong correlation and other condensed phase electronic structures. Ryu is a pioneer in the use of entanglement entropy in classifying topological phases of matter and has predicted the fractional topological insulator in two dimension.

**Shiwei Zhang** (Physics, W&M)

Zhang specializes in computational condensed matter physics and materials science. Zhang is a pioneer in the use of quantum Monte Carlo (QMC) in the Hilbert space for strong correlation. He is the inventor of the phaseless auxiliary field QMC.
Project goals

Theories
(Finite-\(T\)) MP, CC, RPA, etc.; QMC; DMRG, TN; FCIQMC, AFQMC, MC-MP2; DMFT

Software
Algorithm redesign; massive parallelism; fast integrals

Applications – experimental verification
Metals; (copper oxide) superconductors; graphene; molecular crystals; Peierls systems and Luttinger liquid; Mott-Hubbard systems; spin liquid

Abbamonte
Schrödinger equation for water

10-particle, 30-dimensional partial differential equation

\[
\hat{H} = \left\{-\frac{\hbar^2}{2m_e} \sum_{i=1}^{10} \nabla_i^2 - \frac{\hbar^2}{2m_I} \sum_{i=1}^{3} \nabla_i^2 - \sum_{I=1}^{3} \sum_{i=1}^{10} \frac{Z_I e^2}{4\pi\varepsilon_0 r_{ii}} + \sum_{i=1}^{3} \sum_{j=i+1}^{10} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{I=1}^{2} \sum_{J=I+1}^{3} \frac{Z_I Z_J e^2}{4\pi\varepsilon_0 r_{IJ}} \right\} \Psi = E\Psi
\]

\[
\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} + \frac{1}{r_i^2} \left( \frac{1}{\sin^2 \theta_i} \frac{\partial^2}{\partial \phi_i^2} + \frac{1}{\sin \theta_i} \frac{\partial}{\partial \theta_i} \sin \theta_i \frac{\partial}{\partial \theta_i^2} \right)
\]

Conditions arising from the indistinguishability of electrons

\[\Psi(r_{e1}, r_{e2}, r_{e3}, r_{e4}, r_{e5}, r_{e6}, r_{e7}, r_{e8}, r_{e9}, r_{e10}, r_{H1}, r_{H2}, r_O) = \]
\[-\Psi(r_{e2}, r_{e1}, r_{e3}, r_{e4}, r_{e5}, r_{e6}, r_{e7}, r_{e8}, r_{e9}, r_{e10}, r_{H1}, r_{H2}, r_O) = \]
\[\Psi(r_{e3}, r_{e1}, r_{e2}, r_{e4}, r_{e5}, r_{e6}, r_{e7}, r_{e8}, r_{e9}, r_{e10}, r_{H1}, r_{H2}, r_O) = \]
\[-\Psi(r_{e3}, r_{e2}, r_{e1}, r_{e4}, r_{e5}, r_{e6}, r_{e7}, r_{e8}, r_{e9}, r_{e10}, r_{H1}, r_{H2}, r_O) = \ldots\]

3,628,800 terms!
Systematic many-body methods

Density Functional Theory
- Excited States
- Analytical Derivatives
- Local functional
- Gradient-corrected
- Hybrid HF functional

Molecular Orbital Theory
- Hartree-Fock Theory
- Analytical Derivatives
- CISD
- CISDT
- CISDTQ
- MP2
- MP3
- MP4
- CCSD
- CCSDT
- CCSDTQ

Exact solution of the Schrödinger equation
**MP2**

- A member of a systematic series of approximations converging toward exactness.
- Can describe covalent, ionic, hydrogen-bond, and dispersion interactions.
- Size consistent and thus applicable to solids.
- Accurate energy bands and band gaps.
- The operation cost grows as $O(n^5)$, where $n$ is the number of orbitals.
- The memory cost grows as $O(n^2)$ to $O(n^4)$.
- Parallelization is difficult.

\[
\langle ij | ab \rangle = \int \frac{\varphi_i^*(r_1) \varphi_j^*(r_2) \varphi_a(r_1) \varphi_b(r_2)}{|r_1 - r_2|} dr_1 dr_2
\]

\[
G_i(\tau_2, \tau_1) = \frac{1}{\tau_2 - \tau_1} \int_0^{\tau_2 - \tau_1} e^{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} d\tau
\]

\[
E^{(2)} = -\frac{1}{4} \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \langle ij | ab \rangle \langle ab | ij \rangle \int_0^{\infty} e^{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)\tau} d\tau = \frac{1}{4} \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{virt.}} \frac{\langle ij | ab \rangle \langle ab | ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}
\]
Systematic many-body methods

Density Functional Theory
- Local functional
- Gradient-corrected
- Hybrid HF functional

Molecular Orbital Theory
- Hartree-Fock Theory

Exact solution of the Schrödinger equation

QMC

Excited States
- Analytical Derivatives
- CISD
- CCSD
- MP2
- CCSDT
- CCSDTQ

Analytical Derivatives
- Excited States
Monte Carlo

\[ E = \int f(x) \, dx = \int \frac{f(x)}{g(x)} \, dx \cdot \sum_{x \in g(x)} \frac{f(x)}{g(x)} \cdot \int g(x) \, dx \]

**Requirement 1:** the weight function \( g \) is analytically integrable

\[ \int g(x) \, dx = N \]

**Requirement 2:** the weight function \( g \) behaves like the integrand \( f \)

\[ f(x) / g(x) \]
Quantum Monte Carlo

\[ \hat{H}\Psi = E\Psi \]

- Gives the best wave function and energy in the variational sense, which is usually nearly exact.
- Easily and efficiently parallelized.
- Nearly zero memory cost.
- Has statistical errors, which decay slowly as \( O(N^{-1/2}) \) with the number of MC steps \( (N) \).
- Calculations of structures and properties (including energy bands) and applications to excited states difficult.
Contents

• Research highlights of 2012-2013
  – QMC for copper oxide superconductors
  – Auxiliary field QMC for band gaps
  – Full CI QMC for excited states

• Monte Carlo MP2 and MP3

• MP2 for molecular crystals: solid-solid phase transition in CO₂
**QMC for copper oxide superconductors**

Wagner and Abbamonte, to be published (2013)

**Table:**

<table>
<thead>
<tr>
<th>Method</th>
<th>$J / \text{eV}$</th>
<th>Magnetic moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT (LDA)</td>
<td>0.82</td>
<td>0.3</td>
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<tr>
<td>DFT (GGA)</td>
<td>0.6</td>
<td>0.5</td>
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<tr>
<td>QMC</td>
<td>0.15</td>
<td>0.62</td>
</tr>
<tr>
<td>Expt</td>
<td>0.13</td>
<td>0.6</td>
</tr>
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</table>

For more details, please visit the poster by Lucas Wagner
## Auxiliary field QMC for band gaps

*Zhang et al., to be published (2013)*

<table>
<thead>
<tr>
<th>Method</th>
<th>Band gap / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT (LDA)</td>
<td>0.67</td>
</tr>
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<td>GW</td>
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<td>QMC</td>
<td>3.97</td>
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<tr>
<td>Expt</td>
<td>3.7, 3.87, 4.0, 4.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>Band gap / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT (LDA)</td>
<td>1.0</td>
</tr>
<tr>
<td>GW</td>
<td>2.4, 2.6, 2.8</td>
</tr>
<tr>
<td>QMC</td>
<td>3.26</td>
</tr>
<tr>
<td>Expt</td>
<td>3.3 – 3.57</td>
</tr>
</tbody>
</table>
Full CI QMC for excited states
Booth and Chan, JCP Comm (2012)

\[ \exp[-\beta(H - E)] \]

Standard propagator:
max at ground-state

\[ \exp[-\beta(H - \omega)^2] \]

Gaussian propagator:
max at specified omega
Monte Carlo MP

Wave function theory

MP2, MP3, CCSD, CCSD(T)
Monte Carlo MP
AFQMC

Quantum Monte Carlo

Strong correlation

FCIQMC

DMC, VMC
Monte Carlo MP2
Willow, Kim and Hirata, JCP (2012)

Very long $O(n^4)$ summation of products of 2 x 6-dimensional integrals

$$E^{(2)} = \sum_{i,j} \sum_{a,b} \frac{\langle ab | ij \rangle \langle ij | ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

Explicit two-electron integrals

$$E^{(2)} = \sum_{i,j} \sum_{a,b} \int \varphi_i(r_1) \varphi_j(r_2) \frac{1}{r_{12}} \varphi_a(r_1) \varphi_b(r_2) dr_1 dr_2 \int \varphi_i(r_3) \varphi_j(r_4) \frac{1}{r_{34}} \varphi_a(r_3) \varphi_b(r_4) dr_3 dr_4$$

Laplace transformation of the denominator

$$E^{(2)} = -\sum_{i,j} \sum_{a,b} \int \varphi_i(r_1) \varphi_j(r_2) \frac{1}{r_{12}} \varphi_a(r_1) \varphi_b(r_2) dr_1 dr_2 \int \varphi_i(r_3) \varphi_j(r_4) \frac{1}{r_{34}} \varphi_a(r_3) \varphi_b(r_4) dr_3 dr_4 \int_0^{\infty} e^{(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)\tau} d\tau$$

Change of orders of summations and integrations

$$E^{(2)} = -\int \cdots \int_0^{\infty} \sum_{i} \varphi_i(r_1) \varphi_i(r_3) e^{\varepsilon_i \tau} \sum_{j} \varphi_j(r_2) \varphi_j(r_4) e^{\varepsilon_j \tau} \sum_{a} \varphi_a(r_1) \varphi_a(r_3) e^{-\varepsilon_a \tau} \sum_{b} \varphi_b(r_2) \varphi_b(r_4) e^{-\varepsilon_b \tau}$$

Single 13-dimensional integral evaluated by Monte Carlo

$$E^{(2)} = -\int \cdots \int_0^{\infty} \frac{G^{-}(r_1, r_3, \tau) G^{-}(r_2, r_4, \tau) G^{+}(r_1, r_3, \tau) G^{+}(r_2, r_4, \tau)}{r_{12} r_{34}} dr_1 \cdots dr_4 d\tau$$
Monte Carlo MP2
Willow, Kim and Hirata, JCP (2012)

\[ E = \int f(x) \, dx = \int \frac{f(x)}{g(x)} \, g(x) \, dx = \sum_{x \in g} \frac{f(x)}{g(x)} \cdot \int g(x) \, dx \]

Requirement 1: **analytically integrable** \[ \int g(x) \, dx = N \]
Requirement 2: **cancellation of singularities** \[ \frac{f(x)}{g(x)} \]

\[ E^{(2)} = -\int \cdots \int_{r_{12}^{r_{34}}} G^{-}(r_{1}, r_{2}, r_{3}, \tau) G^{-}(r_{2}, r_{3}, r_{4}, \tau) G^{+}(r_{1}, r_{3}, \tau) G^{+}(r_{2}, r_{4}, \tau) dr_{1} \cdots dr_{4} d\tau \]

\[ g(r_{1}, r_{2}, r_{3}, r_{4}) = \frac{\rho(r_{1}) \rho(r_{2})}{r_{12}} \frac{\rho(r_{3}) \rho(r_{4})}{r_{34}} \]

\[ \int g(r_{1}, r_{2}, r_{3}, r_{4}) \, dr_{1} \, dr_{2} \, dr_{3} \, dr_{4} = 4 E_{\text{Coulomb}}^{2} \]
Monte Carlo MP2
Willow, Kim and Hirata, JCP (2012)

Nitrogen 6-31G**

Water monomer, dimer, trimer 6-31G**
Monte Carlo MP2 for self-energies

Willow, Kim and Hirata, JCP (2013)

HOMO & HOMO−1 of H₂O

Dyson self-energies (quasiparticle energies) for multiple states obtainable from a single MC run

Efficiency

Dyson self-energies (quasiparticle energies) for multiple states obtainable from a single MC run
Real-space Green’s function
Willow, Kim and Hirata, to be published (2013)

\[ E^{(2)} = -\int \cdots \int_{0}^{\infty} \frac{G^{-}(r_1, r_3, \tau) G^{-}(r_2, r_4, \tau) G^{+}(r_1, r_3, \tau) G^{+}(r_2, r_4, \tau)}{r_{12} r_{34}} \, dr_1 \cdots dr_4 \, d\tau \]
Monte Carlo MP3
Willow, Kim and Hirata, to be published (2013)

Water 6-31G**

![Graphs and diagrams showing Monte Carlo simulation results for Water 6-31G**.](image-url)
Redundant-walker MC-MP2
Willow, Hermes, Kim and Hirata, under review by JCTC (2013)

Benzene 6-31G**

![Graphs showing errors in $E^{(2)}$/m$E_h$ against MC steps (10^7).](image)

$m = 2$: 2 electron walker pairs

\[ E^{(2)} = \int \int \int_0^\infty G^-(r_1, r_3, \tau) G^-(r_2, r_4, \tau) G^+(r_1, r_3, \tau) G^+(r_2, r_4, \tau) \, dr_1 \, dr_2 \, dr_3 \, dr_4 \, d\tau \]

$m = 10$: 10 electron walker pairs

**Cost:** 5 times

**Benefit:** $10 \times 9 / 2 = 45$ times MC steps
Massively parallel MC-MP2
Willow, Hermes, Kim and Hirata, under review by JCTC (2013)

C_{60} cc-pVDZ on 320 processors of Blue Waters

\( m = 120: 120 \text{ electron walker pairs} \)

Cost: \textbf{60 times}

Benefit: \( 120 \times 119 / 2 = \textbf{7140 times} \) MC steps
MP2 for molecular crystals

[Graphs showing IR, Raman, and INS intensity spectra with frequency in cm\(^{-1}\) and pressure in GPa.]
Embedded-fragment approach


\(N\)-body \((N > 2)\) Coulomb in point-charge or dipole approximation

1 and 2-body Coulomb
Exchange
Correlation

\[ E = \sum_{i=1}^{n} E'_i + \sum_{i<j}^{n} \left( E'_{ij} - E'_i - E'_j \right) + \Box \]
Molecular crystals
Hirata, JCP (2008)

Energy per unit cell

\[
E = \sum_i E_i(0) + \sum_{i<j} \left\{ E_{i(0)j(0)} - E_i(0) - E_j(0) \right\} + \frac{1}{2} \sum_{m=-L}^{+L} \left( 1 - \delta_{m0} \right) \sum_{i,j} \left\{ E_{i(0)j(m)} - E_i(0) - E_j(m) \right\}
\]

Energy gradients

\[
\frac{\partial E}{\partial x} \approx \sum_i \frac{\partial E_i(0)}{\partial x} + \sum_{i<j} \left\{ \frac{\partial E_{i(0)j(0)}}{\partial x} - \frac{\partial E_i(0)}{\partial x} - \frac{\partial E_j(0)}{\partial x} \right\} + \frac{1}{2} \sum_{m=-L}^{+L} \left( 1 - \delta_{m0} \right) \sum_{i,j} \left\{ \frac{\partial E_{i(0)j(m)}}{\partial x} - \frac{\partial E_i(0)}{\partial x} - \frac{\partial E_j(m)}{\partial x} \right\}
\]

\[
\frac{\partial E}{\partial a} \approx \frac{1}{2} \sum_{m=-L}^{+L} \sum_{i,j} \left\{ \frac{\partial E_{i(0)j(m)}}{\partial z_i^{j(m)}} - \frac{\partial E_{j(m)}}{\partial z_i^{j(m)}} \right\} + \frac{\partial E_{LR}}{\partial a}
\]

Linear scaling regardless of gradients algorithms (analytical vs. numerical)
Long-range electrostatic correction essential for cell gradients

Energy Hessian

\[
\frac{\partial^2 E}{\partial x \partial y} \approx \sum_i \frac{\partial^2 E_i(0)}{\partial x \partial y} + \sum_{i<j} \left\{ \frac{\partial^2 E_{i(0)j(0)}}{\partial x \partial y} - \frac{\partial^2 E_i(0)}{\partial x \partial y} - \frac{\partial^2 E_j(0)}{\partial x \partial y} \right\} + \frac{1}{2} \sum_{m=-L}^{+L} \left( 1 - \delta_{m0} \right) \sum_{i,j} \left\{ \frac{\partial^2 E_{i(0)j(m)}}{\partial x \partial y} - \frac{\partial^2 E_i(0)}{\partial x \partial y} - \frac{\partial^2 E_j(m)}{\partial x \partial y} \right\}
\]

\[x\text{ and } y\text{ need not be in-phase coordinates: phonon dispersions can be obtained}\]
Finite pressures and temperatures
Li, Sode, Voth and Hirata, under review by Nature Comm (2013)

Gibbs free energy per unit cell

\[ G = E + E_{zp} + P(abc) - TS \]

For an orthorhombic unit cell

Partition function

\[ Z = \prod_i \prod_{\mathbf{k}} \frac{\exp\left(-\omega_{\mathbf{k}_i} / 2k_B T\right)}{1 - \exp\left(-\omega_{\mathbf{k}_i} / k_B T\right)} \]

Zero-point energy, entropy, and heat capacity

\[ E_{zp} = k_B T^2 \frac{\partial \ln Z}{\partial T} \quad S = -\frac{\partial (k_B T \ln Z)}{\partial T} \quad C_V = \frac{\partial (E + E_{zp})}{\partial T} \]
Phase transition in solid CO$_2$

Li, Sode, Voth and Hirata, under review by *Nature Comm* (2013)

296 K
Phase transition in solid CO$_2$

Li, Sode, Voth and Hirata, under review by *Nature Comm* (2013)
Phase transition in solid CO\textsubscript{2}  
Li, Sode, Voth and Hirata, under review by *Nature Comm* (2013)
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For more information, please visit http://www.predictive-scidac.org