Understanding Properties of Materials under Extreme Conditions with *First-Principles* Methods for ICF/HED Applications

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Seminar @ HEDS Center at LLNL  Feb 7th, 2019
A “startup” HEDP-theory group is being built recently at LLE

High-Energy-Density Physics (HEDP) Theory Group

Suxing Hu
Group Leader

Scientists
Valentin Karasiev

Contents
- What is HEDP/WDM?
- Why do we care about HEDP & WDM?
- Current Research Topics
  - First-Principles/Ab-Initio Methods for HEDP
- List of Selected Recent Publications and Preprints
- Opportunities & Contact information

Graduate Students
Yanhao Ding (~2021)
Maitrayee Ghosh (~2023)
Josh Hinz (~2022)
Reetam Paul (~2022)
Tian Tang (~2023)

Undergraduate/High School Interns
Barry Xu
(Columbia University, 2010)
Jesse Pan
(Case Western, 2012)
Nathan Xu
(Univ. Pennsylvania, 2014)
Xilin Zhou
(Harvard, 2015)
Ryan Gao
(Princeton, 2016)

We are currently looking for two more scientists to join us!
Outline

- **Introduction:** *Why do we care about high-energy-density physics (HEDP) as ICF scientists?*

- **What are our “first-principles toolkits” to understand HED matter as a quantum many-body system?**
  - Density-Functional-Theory (DFT)
  - Path-integral Monte-Carlo (PIMC)
  - Quantum Monte-Carlo (QMC)

- **First-principles-based and self-consistent material properties under extreme conditions for ICF/HED applications:**
  - What have we learned so far?
  - How do these knowledges impact on the ICF community?

- **Some recent focuses in a broad HEDS arena**

- **Conclusion & Outlook**
Why do we care about HEDP as ICF scientists?

How a rocket works?

How ICF works?

An ICF physicist is also a “rocket scientist”!
Accurate knowledge of *intrinsic* plasma properties (EOS,* opacity, thermal conductivity, and stopping power) of DT and ablators is required for ICF simulations.
ICF implosions routinely access the WDM regime,* which demands a better understanding of material properties.

1. The Coulomb coupling parameter:
   \[ \Gamma = \frac{q^2}{r_s k_B T}, \quad r_s = (3/4\pi n)^{1/3} \]

2. The electron-degeneracy parameter:
   \[ \theta = \frac{T}{T_F} \]

WDM: \( \Gamma \geq 1; \theta \leq 1 \)

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A view of an HEDP-theorist: Warm-dense matter (dense plasmas) as *quantum many-body systems*

Quantum many-body Schrödinger Equation

\[
\left[ -\frac{\hbar^2}{2m} \sum_i \nabla^2 + V(r_1, r_2, \ldots, r_n) \right] \Psi(r_1, r_2, \ldots, r_n) = E\Psi(r_1, r_2, \ldots, r_n)
\]
Quantum many-body Schrödinger Equation:
Well-defined equation, but no easy solution

Quantum Mechanics

Dirac (1929)

“ The general theory of quantum mechanics is now almost complete... The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. ”

How can we learn the many-body physics and chemistry from the Quantum Mechanics equations?
Our “first-principles toolkits” for quantum many-body systems

- Density-Functional-Theory (DFT)*
- Path-integral Monte-Carlo (PIMC)**
- Quantum Monte-Carlo (QMC)***

*** E. Fermi & R. D. Richtmyer (1948) and many papers afterwards [e.g., R. C. Clay, M. Holzmann, D. M. Ceperley, and M. A. Morales, Phys. Rev. B 93, 035121 (2016).]
DFT versus the Schrödinger Equation

Properties of the system

Hard problem to solve

“Easy” problem to solve

Schrödinger view

DFT view

Formally equivalent

\[ v_{\text{eff}}(r) = v(r) + \int \frac{n(r')}{|r-r'|} dr' + \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \]

All many-body effects are included in the effective potential via the Exchange-Correlation functional, \( E_{xc}[n(r)] \).

*Courtesy of Ann Mattsson*
Kohn-Sham equations:

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right) \psi_\nu(\mathbf{r}) = \epsilon_\nu \psi_\nu(\mathbf{r}) \quad \nu = 1, 2, \ldots, N
\]

\[
n(\mathbf{r}) = \sum_{\nu=1}^{N} |\psi_\nu(\mathbf{r})|^2
\]

Seeking accurate ones for a long-time

\[
v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, dr' + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}
\]

If we had the divine exchange-correlation functional, self-consistently solving these equations would give exactly the same density as the Schrödinger Equation, and thus via the HK theorem, we should be able to extract all information about the system.
Finding the best exchange-correlation functional is the key to have made DFT practical.

LDA for $V_{xc}$

Alex Zunger
University of Colorado, Boulder, Colorado, Renewable and Sustainable Energy Institute
Physics
Material Science
nano science
photovoltaics

<table>
<thead>
<tr>
<th>TITLE</th>
<th>CITED BY</th>
<th>YEAR</th>
</tr>
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<tbody>
<tr>
<td>Self-interaction correction to density-functional approximations for many-electron systems</td>
<td>18405</td>
<td>1981</td>
</tr>
</tbody>
</table>

GGA for $V_{xc}$

John P. Perdew
Temple University
density functional theory
materials theory
quantum chemistry

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<tr>
<th>TITLE</th>
<th>CITED BY</th>
<th>YEAR</th>
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<tbody>
<tr>
<td>Generalized gradient approximation made simple</td>
<td>86940</td>
<td>1996</td>
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The journey of searching for more and more accurate XC-functionals still continues: Meta-GGA, Hybrid, temperature-dependent,......
Quantum Molecular Dynamics (QMD) method is based on the **thermal** density-functional theory (DFT)*

- The **thermal-DFT** is a “mean-field” theory of many-electron system at finite temperatures:

  \[
  \left\{-\frac{1}{2}\Delta + V_Z(r) + V_H[n](r) + V_{xc}[n](r)\right\}\psi_i = \epsilon_i\psi_i
  \]

  \[
  n(r) = \sum_{i=1}^{N} f_i |\psi_i(r)|^2, \quad V_H[n](r) = \int \frac{n(r')}{|r-r'|} dr'
  \]

- Since \(V_H\) and \(V_{xc}\) terms depend on electron density \(n(r)\), which depends on the \(\psi_i\), the thermal-DFT equation can be solved in a self-consistent (i.e., **iterative**) way, once the \(V_{xc}\) is known!

- The resulting electronic force together with ionic forces will drive the classical ions to move, through the Newton’s equation, in the MD simulations.

A variety of material properties can be self-consistently calculated from QMD simulations

- EOS are direct outputs from QMD simulations
- Transport properties can be calculated using the Kubo-Greenwood formalism:

\[ L_{ij}(\omega) = \frac{2\pi}{3Vm_e^2\omega} \sum_{mn} F_{mn} |D_{mn}|^2 \]

\[ \times \left( \frac{E_m + E_n - H}{2} \right)^{i+j-2} \delta(E_m - E_n - \hbar\omega), \]

- Thermal/Electrical conductivities and optical absorption coefficients can be derived from these Onsager coefficients \( L_{ij}(\omega) \):

\[ \sigma = L_{11}; \kappa = \frac{1}{T} (L_{22} - \frac{L_{12}^2}{L_{11}}); \]

\[ \alpha_m(\omega) = \frac{\alpha_K(\omega)}{\rho} = \frac{4\pi a_1(\omega)}{c\times n(\omega)} \times \frac{1}{\rho} \]
PIMC*, based on the convolution of density matrix, uses Monte-Carlo method to efficiently evaluate multi-dimensional integrations

- Density-matrix \( \rho(R, R'; T) \), introduced by John von Neumann in 1927, describes the statistical distribution of a quantum system in thermal equilibrium:

\[
\rho(R, R'; T) = \langle R \mid e^{-\frac{\mathcal{H}}{kT}} \mid R' \rangle = \sum_n \phi_n(R)\phi_n(R')e^{-E_n/kT}
\]

- The convolution property of \( \rho(R, R'; \beta) \) can be written as:

\[
\rho(R, R'; \beta_1 + \beta_2) = \langle R \mid e^{-(\beta_1 + \beta_2)\mathcal{H}} \mid R' \rangle = \int dR_1 \rho(R, R_1; \beta_1)\rho(R_1, R'; \beta_2)
\]

with \( \beta_1 = 1/kT_1 \) and \( \beta_2 = 1/kT_2 \).

Difficult (if not impossible) to obtain transport and optical properties

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- Conclusion & Outlook
We studied the properties of deuterium* in a wide range of conditions by combining PIMC and QMD methods.

Significant differences have been identified for warm dense deuterium when FPEOS, $^{*} \kappa_{QMD}$, $^{**}$ and FPOT$^{†}$ are compared with traditional models.


New experiments continue to challenge our understanding of the behavior of deuterium at WDM conditions

2011

2018: more surprises for the double-shock data

The QMD-predicted reflectivity* along the Hugoniot of deuterium agreed with NOVA and OMEGA experiments**

\[
\sigma_1(\omega) = L_{11}(\omega), \quad \sigma_2(\omega) = -\frac{2}{\pi} P \left( \frac{\omega \sigma_1(\omega')}{\omega' - \omega} \right) d\omega' \\
\epsilon_1(\omega) = 1 - \frac{4\pi}{\omega} \sigma_2(\omega), \quad \epsilon_2(\omega) = \frac{4\pi}{\omega} \sigma_1(\omega) \\
n(\omega) = \sqrt{\frac{\epsilon_1(\omega) + \epsilon_2(\omega)}{2}}, \quad k(\omega) = \sqrt{\frac{\epsilon_1(\omega) - \epsilon_2(\omega)}{2}} \\
R(\omega) = \frac{[n(\omega) - n_0]^2 + k(\omega)^2}{[n(\omega) + n_0]^2 + k(\omega)^2} \\
\alpha_m(\omega) = \frac{\alpha_K(\omega)}{\rho} = \frac{4\pi \bar{\sigma}_1(\omega)}{c \times \bar{n}(\omega)} \times \frac{1}{\rho}
\]

** V. V. Karasiev et al., Phys. Rev. B (to be submitted)
A wide range of material conditions of ICF-relevant ablators* has also been studied by KSMD+OFMD calculations in their liquid phase.

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The calculated principal Hugoniot* of CH from FPEOS has been well compared with experiments.
Recent EOS measurements at high pressures on NIF are in better agreement with FPEOS than SESAME-7592

PHYSICAL REVIEW LETTERS 121, 025001 (2018)

Absolute Equation-of-State Measurement for Polystyrene from 25 to 60 Mbar Using a Spherically Converging Shock Wave

T. Döppner,1,6 D. C. Swift,1 A. L. Kritcher,1 B. Bachmann,1 G. W. Collins,1,2 D. A. Chapman,1 J. Hawreliak,1 D. Kraus,3,4 J. Nilsen,1 S. Rothman,3 L. X. Benedict,1 E. Dewald,1 D. E. Fratanduono,1 J. A. Gaffney,1 S. H. Glenzer,6 S. Hamel,1 O. L. Landen,1 H. J. Lee,6 S. LePape,1 T. Ma,1 M. J. MacDonald,4 A. G. MacPhee,1 D. Milatichianaki,6 M. Millot,1 P. Neumayer,1 P. A. Sterne,1 R. Tommasini,1 and R. W. Falcone4

PHYSICAL REVIEW E 89, 063104 (2014)

Properties of warm dense polystyrene plasmas along the principal Hugoniot

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1Laboratory for Laser Energetics, University of Rochester, 250 East River Road, Rochester, New York 14623, USA
2Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
(Received 13 March 2014; published 30 June 2014)

Thanks to Phil Sterne for file-format conversion, the FPEOS tables can now be accessed by HYDRA!
One more example: Our QMD study* has predicted a much softer Hugoniot of Si, which is proven to be true by recent experiments** on OMEGA-EP

**B. Henderson et al., talk at APS-DPP (2017).
Thermal conductivity models ($\kappa_{\text{QMD}}$) based on QMD calculations* has also been developed for D$_2$ and ablator materials [adopted into LANL’s code: \textit{Xrage}**]

\begin{itemize}
  \item The Coulomb-logarithm for electron-ion collisions is reduced in WDM condition
  \begin{itemize}
    \item *S. X. Hu \textit{et al.}, Phys. Plasmas 23, 042704 (2016).
    \item ** B. M. Haines \textit{et al.}, Phys. Plasmas 26, 012707 (2019).
  \end{itemize}
\end{itemize}
QMD calculations can also give us self-consistent optical properties of materials under HED conditions: *K-edge shifting as an example*
Both continuum-lowering and Fermi-surface-rising effects can be naturally included in QMD simulations.
The continuum-lowering and Fermi-surface-rising (Pauli-blocking) can explain the K-edge up-shifting in strongly-coupled and degenerate dense plasmas.
How our physics understanding may evolve for high-Z materials is waiting to be seen from our ExtremeDFT LBS campaigns.

Experiments on iron K-edge shifting are proposed to test our DFT calculations.
In addition, some existing experimental data* also indicated that traditional plasma-physics models do not catch all essential physics in HED conditions.

Kα-emission from OMEGA-EP-heated solid-Cu targets

*P. M. Nilson et al., APS-DPP Talk (2018).
Preliminary DFT calculations show the red-shifts of Kα emission observed in experiment* when the target passes through warm-dense matter (WDM) regime.

DFT-predicted Kα-line shifts in OMEGA-EP-heated solid-Cu target

*P. M. Nilson et al., APS-DPP Talk (2018).
Another challenge for traditional physics models is how to handle the mixture in dense plasmas (e.g., CH).

**CH plasma at $T = 10.77$ eV**

$$\rho = 50 \text{ g/cm}^3 \text{ and } T = 10.77 \text{ eV}$$

![Graph showing the K edge of carbon vs. density and absorption coefficient vs. photon energy.](image)

- Stewart–Pyatt
- Ecker–Kroell
- Modified ion sphere
- Crowley
- ATOMIC
- QMD (this work)
- SMIAB model (this work)

![Graph showing the absorption coefficient vs. photon energy.](image)

- QMD
- ATOMIC

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*S. X. Hu et al., Phys. Rev. B 96, 144203 (2017).*

**N. R. Shaffer et al., High Energy Density Phys. 23, 31 (2017).*
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Several different experimental observables show better agreement with FPEOS than SESAME EOS for CH.

*P. B. Radha et al., “Shock Velocity Measurements at the National Ignition Facility,” to be submitted to Physical Review E.
How did these first-principles properties of HED plasmas affect ICF target designs?

The major differences are due to: DT-EOS, DT-Opacity, and CH-EOS.
Significant variations have been seen in direct-drive ICF target designs with first-principles plasma properties.

1-D target gain:

- $G = 31$ (SESAME/AOT/$\kappa_{\text{Lee-More}}$)
- $G = 8$ (FPEOS/FPOT/$\kappa_{\text{QMD}}$)

*S. X. Hu et al., Phys. Plasmas 25, 056306 (2018).*
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What are the current limits of DFT? How can we improve it for better understanding HEDS?

- Most of the current exchange-correlation functionals underestimate band-gaps of materials*
- Current exchange-correlation functionals do NOT have temperature dependence*
- Current DFT implementations are using plane-wave basis and pseudopotentials, which have frozen core-electrons.

These efforts are also supported by an NSF grant.
Time-Dependent Orbital-Free DFT (TD-OF-DFT) code has been developed in our group to understand stopping-power of warm-dense plasmas.

proton stopping in warm-dense Be (solid @ kT=32-eV)

The TD-OF-DFT-calculated proton stopping power in high velocities in comparison with three stopping-power models.

Be: $\rho = 1.78 \text{ g/cm}^3 \ T = 32 \text{ eV}$

The stopping power calculated by TD-OF-DFT is slightly lower than predictions of the LP and BPS models by \~5% and \~11%, respectively, and higher than predicted by DF by 20%.
Ab-initio TD-OF-DFT calculations* indicated up to ~25% lower $\alpha$-particle stopping-power in warm-dense DT than current models.

$\alpha$-particle stopping in warm-dense DT (solid @ $kT=10$-eV)

High-pressure phase diagram of silicon up to ~4-TPa has been charted from *first-principles* DFT + Phonon-dynamics calculations*

- Anharmonic behavior of Si in the *cd* phase is important for properly predicting the shock Hugoniot at low pressures
- Two new phase transitions are predicted at ~2.8-/3.5-TPa: *fcc-to-bcc* & *bcc-to-sc*

* R. Paul, S. X. Hu, V. V. Karasiev, Phys. Rev. Lett. (submitted)
The phonon spectra (of ion vibration modes), a characteristic of different phases, can be picked up by Raman scattering measurements.
Under high pressures up to ~4-Tpa, silicon is still a metallic system even though interstitial electron localization appears (hydride-like)

Reetam Paul
How can diamond be formed in polystyrene (CH), methane (CH₄), and other hydro-carbons under dynamic compression?

Formation of diamonds in laser-compressed hydrocarbons at planetary interior conditions

Questions remain: How did this happen? where are the hydrogen atoms? …
Where are the hydrogen atoms when diamond is formed?

Diamond+H \rightarrow CH-mixture @ ~150-Gpa?

Case-1: Hydrogen sitting side-by-side with diamond

Case-2: Hydrogen randomly distributed in diamond
Back to the simplest element --- Hydrogen: The understanding of its optical property is still not complete ➔ better xc-functional? quantum-p?

It looks like there is a winning xc-functional for hydrogen!
Conclusion & Outlook

- First-principles methods developed for quantum many-body systems provide predictive capabilities for HED sciences (although limits exist);
- Significant improvements to current quantum many-body methods will be continuously made from our HEDS community;
- The HED-community efforts on seeking better understanding of the fundamental physics and chemistry at extreme conditions will make a difference to ICF, planetary science, astrophysics,…

- There are some urgent questions needed to be answered for communities of ICF and planetary science (my personal list):
  - What’s the microphysics of non-uniform shock transition from ablator to DT? “spall and ejecta” mixing at the ablator/DT interface in ICF
  - What are the true $\alpha$-particle stopping-power in ICF hot-spot and extremely-dense DT-shell?
  - Are there any “excessive” thermal conduction in ICF hot-spot?
  - What drives phase separation in hydrogen-helium mixture and hydrocarbons under WDM conditions?
  - …
Acknowledge to collaborators


Laboratory for Laser Energetics
University of Rochester

L. A. Collins, J. D. Kress, A. J. White, O. Certik
Theoretical Division, Los Alamos National Laboratory

B. Militzer
Department of Earth and Planetary Science and Astronomy
University of California – Berkeley
Thank you
There is no free lunch!

DFT versus the Schrödinger Equation

We have moved our problem from here ...

Properties of the system

Hard problem to solve

"Easy" problem to solve

Schrödinger view

Formally equivalent

DFT view

Kohn-Sham particle (non-interacting) effective potential

\[ v_{eff}(r) = v(r) + \int \frac{n(r')}{\|r-r'\|} \, dr' + \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \]

All many-body effects are included in the effective potential via the Exchange-Correlation functional, \( E_{xc}[n(r)] \).
Walter Kohn awarded the Nobel Prize in Chemistry 1998 for Density Functional Theory


The effect of Fermi-surface-rising on K-edge shifting can be naturally accounted in QMD simulations.

CH plasma at $T = 10.77$ eV