LA-UR-16-23345

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Title: Dense Quantum Plasma Simulation

Author(s): Sjostrom, Travis

Intended for: LANL T-5 Seminar.

Issued: 2016-05-11

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Dense Quantum Plasma Simulation

Density functional theory algorithms and bottlenecks

Travis Sjostrom
T-1 LANL

T-5 Seminar, April 27, 2016

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Acknowledgements

- Jérôme Daligault, T-5
 - Charlie Starrett, XCP-5
 - Didier Saumon, XCP-5
 - Scott Crockett, T-1
 - Sam Trickey, U. Florida
 - Jim Dufty, U. Florida
-
- Funding: Office of Science, FES; Equation of State project, PEM

Outline

- **Dense Quantum Plasma / Warm Dense Matter**
 - Physical regime and theoretic approaches
- **Kohn-Sham Density Functional Theory Quantum Molecular Dynamics**
 - State of the art approaches and issues
- **Orbital-Free (Pure) DFT QMD**
 - Scalable alternative to Kohn-Sham method
- **Beyond QMD**

Dense Quantum Plasmas

Parameters of WDM

$$\theta = \frac{k_B T}{\varepsilon_F}$$

Electron degeneracy

$$\Gamma = \frac{Z^2 e^2}{r_{ws} k_B T}$$

Ion Coupling

Computational approaches to WDM

Emerged standards

Path Integral Monte Carlo

- Computationally expensive to begin
- More expensive as temperature is lowered
- More expensive as Z increases

Kohn-Sham Density Functional Theory MD

- Pseudopotential approximation (transferability)
- Exchange-correlation approximation
- Scaling with orbitals cubed
- More expensive as temperature increases (Kohn-Sham)

Alternatives

Average atom models

- Model dependent
 - Boundary conditions
 - Ion-ion correlations
- Mixtures

Orbital-free Density Functional Theory MD

- Local pseudopotential approximation
- Exchange-correlation approximation
- *Kinetic Energy functional approximation*

Quantum Molecular Dynamics

- Classical MD for nuclei with forces derived from quantum mechanical electrons.
- Born-Oppenheimer approximation, non-dynamic electrons.
 - Kohn-Sham DFT:
Computationally prohibitive for large systems or high temperature.
 - Orbital-free DFT:
Requires approximate kinetic energy functional.

Time for single density optimization for hydrogen at 2 g/cc.

Orbital-free Density Functional Theory

Total free energy functional for the electrons:

$$F[n, T] = F_S[n, T] + F_H[n] + F_{xc}[n, T] + F_{ei}[n]$$

$$\left. \begin{array}{l} F_{xc}[n, T] \\ F_S[n, T] \end{array} \right\} \begin{array}{l} \text{Unknown exact form.} \\ \text{Requires approximate} \\ \text{functionals.} \end{array}$$

Minimize free energy with respect to density.

Solved by Euler-Lagrange eq. with constraint
for conserved number of electrons, N
(additionally $n(r) > 0$ must be enforced)

$$\frac{\delta F}{\delta n} - \mu = 0$$

Ion forces for QMD:

$$\begin{aligned} \vec{F}_I &= -\nabla_{\vec{R}_I} F[n, T] \\ &= -\frac{\partial}{\partial \vec{R}_I} (F_{ei} + F_{ii}) \end{aligned}$$

Kohn-Sham Density Functional Theory

Total free energy functional for the electrons:

$$F[n, T] = F_S[n, T] + F_H[n] + F_{xc}[n, T] + F_{ei}[n]$$

Minimize free energy with respect to orbitals,
Kohn-Sham equations:

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

Kohn-Sham:

$$F_s = -\frac{1}{2} \sum_i f_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i^*(\mathbf{r}) \\ - k_B \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)]$$

$$n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2$$

$$f_i = \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}} , \quad N_e = \sum_i f_i$$

Kohn-Sham eigenvalue problem

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

Hamiltonian must be diagonalized, here in a plane wave basis.

Iterative techniques to get lowest eigenstates (Lanczos, Davidson, CG)

Costly orthonormalization. Preconditioning?

Electronic Structure: Basic Theory and Practical Methods,
Richard M. Martin, (Cambridge University Press, 2004).

Alternative diagonalization is residual minimization method – direct inversion of the iterative subspace (RMM-DIIS).
Parallelizable, with technical issues.
PRB 54, 11169 (1996)

Linear scaling methods have been developed.
Problems with extended orbitals.

Kohn-Sham SCF

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$v_{KS}(\mathbf{r}) = v_{ei}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta F_{xc}[n]}{\delta n(\mathbf{r})}$$

The potential depends on the solution, and requires iteration to self-consistency.

Typically 10-20 iterations for SCF. Mixing scheme is crucial for efficiency (Linear, Pulay, Broyden).

Alternative to extrapolation/mixing for MD is integrated coupling of ions and electrons via extended Lagrangian method.

PRL 100, 123004 (2008)

Hybrid method using KS corrected OF method may speed up SCF.

Direct minimization of the Kohn-Sham functional?

Kohn-Sham pseudopotential

Bcc iron T=0

T = 15, 10, 5, 1 eV

Plane wave basis requires coulomb regularization near nucleus.
Compression testing is straightforward, temperature validation is difficult.

Non-interacting F_s

Total free energy functional for the electrons:

$$F[n, T] = F_s[n, T] + F_H[n] + F_{xc}[n, T] + F_{ei}[n]$$

At finite-T both kinetic and entropic contributions are needed:

$$F_s = T_s[n, T] - TS_s[n, T]$$

Single Euler equation

$$\frac{\delta F}{\delta n} - \mu = 0$$

Kohn-Sham:

$$F_s = -\frac{1}{2} \sum_i f_i \int d\mathbf{r} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i^*(\mathbf{r}) \\ - k_B \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)]$$

$$f_i = \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}} , \quad N_e = \sum_i f_i$$

Local orbital-free functionals

$$F_{TF}[n, T] = \int f_{TF}(n(\vec{r}), T) d\vec{r}$$

$$f_{TF}(n, T) = (F_{UEG} / V) |_{n, T}$$

- Thomas-Fermi is LDA for free energy
- Exact in uniform electron gas limit
- Moderate improvement with gradient expansion, GE2. (Perrot, Brack)

$$F_{GE2}[n, T] = F_{TF}[n, T] + \frac{\hbar^2}{m_e} \int \zeta(n, T) \frac{|\nabla n(\vec{r})|^2}{8n(\vec{r})} d\vec{r}$$

$$\zeta(n, T) : \left(\frac{1}{9}, \frac{1}{3} \right)$$

$$F_{vW}[n] = \frac{\hbar^2}{m_e} \int \frac{|\nabla n(\vec{r})|^2}{8n(\vec{r})} d\vec{r}$$

$$F_{TFW}[n, T] = F_{TF}[n, T] + F_{vW}[n]$$

- von Weizsäcker is lower bound for the kinetic energy
- Exact for single orbital systems
- Same form as gradient expansion

Local functional response

In the noninteracting
uniform electron gas limit:

$$\chi(\vec{r} - \vec{r}'; n_0, T) = - \left(\frac{\delta^2 F_s[n, T]}{\delta n(\vec{r}) \delta n(\vec{r}') \Big|_{n_0}} \right)^{-1}$$

$$-\frac{1}{\chi(q)} = \hat{F} \left(\frac{\delta^2 F_s}{\delta n(\vec{r}) \delta n(\vec{r}') \Big|_{n_0}} \right)$$

Should reproduce the Lindhard function,
But all functionals shown so far do not.

An Accurate Orbital-Free DFT (sometimes)

$$F_S = F_{TF} + F_{vW} + F_{NL}$$

$$F_{TF} = \int f^{HEG}(n(\vec{r})) d\vec{r}$$

$$F_{vW} = \frac{\hbar^2}{m_e} \int \frac{|\nabla n(\vec{r})|^2}{8n(\vec{r})} d\vec{r}$$

$$F_{NL} = \iint n^{5/6}(\vec{r}) w_1(\vec{r} - \vec{r}') n^{5/6}(\vec{r}') d\vec{r}' d\vec{r} \\ + \iint \nabla n^{1/2}(\vec{r}) w_2(\vec{r} - \vec{r}') \nabla n^{1/2}(\vec{r}') d\vec{r}' d\vec{r}$$

- Kernels $\mathbf{W}_1$ and $\mathbf{W}_2$ determined by enforcing exact density-density response for HEG.

$$\chi(\vec{r} - \vec{r}'; n_0, T) = - \left(\frac{\delta^2 F_S[n, T]}{\delta n(\vec{r}) \delta n(\vec{r}') \Big|_{n_0}} \right)^{-1}$$

$$w_1(k) = f(k) w(k)$$

$$f(k) = \exp(-k^2 / 4^2 k_F^2)$$

Phys. Rev. Lett. 113, 155006 (2014)

An Accurate Orbital-Free DFT - Kernels

FFT scaling

Recall: $\frac{\delta F}{\delta n} - \mu = 0$ Evaluated many times in conjugate gradient method.

- Ion-ion and ion-electron implemented via particle-particle particle-mesh (P³M) and particle-mesh-Ewald (PME), and so require 3D FFT.
- Other terms then utilize 3D FTT.

$$\phi^2(r) = n(r) \quad \frac{\delta F}{\delta n} = \frac{\delta F}{\delta \phi} \frac{\delta \phi}{\delta n}$$

$$\frac{\delta F_{vw}}{\delta \phi} = -\hat{F}^{-1} \left[(iq)^2 \hat{F}[\phi] \right]$$

$$\frac{\delta F_{a,b}}{\delta n} = an^{a-1}(\vec{r}) \int w(\vec{r} - \vec{r}'; n_0, T) n^b(\vec{r}') d\vec{r}' +$$

$$bn^{b-1}(\vec{r}) \int w(\vec{r} - \vec{r}'; n_0, T) n^a(\vec{r}') d\vec{r}'$$

$$= an^{a-1}(\vec{r}) \hat{F}^{-1} \left[w(q) n_b(q) \right] +$$

$$bn^{b-1}(\vec{r}) \hat{F}^{-1} \left[w(q) n_a(q) \right]$$

Caveat: Prohibitive parallel scaling issues.

Amelioration possible in SmallBox FFT, divide and conquer.

CPC 184, 2693 (2013)

An Accurate Orbital-Free DFT - Tests

Simple-cubic hydrogen at 2 g/cc and elevated temperatures shows excellent agreement between KS and non-local OF.

Ion-electron pair distribution function for aluminum (3e) shows electron density is the same in non-local OF and KS calculations. Random configuration at 2.8 g/cc and 100 K.

An Accurate Orbital-Free DFT - Results

Pressure for hydrogen at 4.04 g/cc, showing very good agreement with Kohn-Sham and PIMC calculations

Pair distribution function for aluminum at 2.7 g/cc and 5 eV, and 2.35 g/cc and 1025 K.

Local pseudopotentials

- Significant issues of construction and transferability properties of accurate local pseudopotentials. Eliminating pseudopotentials would be ideal through real-space multigrid method.
- Functional breaks down at large density gradients.
Resolution: Design better functionals, i.e. density decomposed, hybrid with Kohn-Sham.

Thomas-Fermi-Weizsäcker DFT Matching

Non-interacting free energy:

$$F_S[n, T] = F_{TF}[n, T] + \lambda F_{vW}[n]$$

$$F_{TF}[n, T] = \int \frac{F^{HEG}(n(\mathbf{r}), T)}{V} d\mathbf{r}$$

$$F_{vW}[n] = \int \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})} d\mathbf{r}$$

λ

- determined by matching Kohn-Sham isochore (n_0) pressure curves at a temperature between 5 and 10 eV
- mostly material dependent, only moderately density dependent, $\sim 1/5$

Phys. Rev. B 92 115104 (2015)

A norm-conserving pseudopotential is available by simple prescriptive average atom method, *Phys. Rev. E 73, 016403 (2006)*.

Orbital-free matching for SiO2

Results at 6.9 g/cc, shows correct high and low temperature limits.

11-5.5 g/cc, match is at 6 eV
slope with temperature validates method

$$\lambda = 0.288 - 0.0114\rho$$

Ionic transport – self-diffusion

$$D = \frac{1}{3N} \sum_{i=1}^N \int_0^\infty \langle \mathbf{V}_i(t) \cdot \mathbf{V}_i(0) \rangle dt$$

Green-Kubo formalism

Phys. Rev. E 92, 063304 (2015)

Ionic transport – shear viscosity

$$\eta = \frac{1}{6\Omega k_B T} \sum_{\alpha \neq \beta}^3 \int_0^\infty \langle \sigma_{\alpha,\beta}(t) \sigma_{\alpha,\beta}(0) \rangle dt$$

$$\sigma = \sum_{i=1}^N m \mathbf{V}_i \mathbf{V}_i + \sigma^{II} + \sigma^{IE}$$

Good agreement for hydrogen viscosity compared with KS at low temperatures.

Issues: Long run time even for OFMD, lack of electron contribution.

Effective Potential Theory + Average Atom

EPT – kinetic theory based on interacting potentials, requiring input pair distribution function.
 AA-TCP – AA model with coupling between ions found through integral fluid equations, providing $g(r)$.

Phys. Rev. Lett. 116, 075002 (2016)

Electronic Transport

Kubo-Greenwood formalism requires orbitals.

$$\sigma = |L_{11}|, \quad \kappa = \frac{1}{T} \left(L_{22} - \frac{L_{12}^2}{L_{11}} \right)$$

$$L_{mn}(\omega) = \frac{2\pi e^{4-m-n}}{3V m_e^2 \omega} \sum_{\mathbf{k}\nu\mu} |\langle \mathbf{k}\nu | \hat{\mathbf{p}} | \mathbf{k}\mu \rangle|^2 (f_{\mathbf{k}\nu} - f_{\mathbf{k}\mu})$$

$$\left(\frac{\varepsilon_{\mathbf{k}\nu} + \varepsilon_{\mathbf{k}\mu}}{2} - \hbar\omega \right)^{m+n-2} \delta(\varepsilon_{\mathbf{k}\mu} - \varepsilon_{\mathbf{k}\nu} - \hbar\omega)$$

Here we use both the ion positions and the electron density to determine the KS orbital by a **single** diagonalization.

This saves an order of magnitude or more in computation time.

Still requires memory of KS calculation. Dynamic electrons in the form of TDDFT particularly in OF DFT can allow direct calculation.

PRL 116, 115004 (2016)

Electrical and thermal conductivity, Al

Electrical conductivity Al

Summary

- **Diagonalization is the Kohn-Sham bottleneck.**
- **FFT is the orbital-free bottleneck.**
 - Relatively general problems, that have seen significant work, but major improvements would have substantial impact.
 - Exascale?
- **More reasonable improvements likely**
 - i.e. limiting KS SCF iterations, and possible near linear scaling
- **Orbital-Free DFT remains a promising alternative**
 - Efforts to design more advanced functionals including hybrid KS efforts.

Pseudopotential / Coulomb regularization

A norm-conserving pseudopotential is available by simple prescriptive average atom method, *Phys. Rev. E* 73, 016403 (2006), and allows for OFMD on regular grid.

Finite temperature Lindhard

...or density-density response of the noninteracting uniform electron gas.

$$\chi_0(\vec{q}, \omega = 0; n_0, T) = \frac{2}{(2\pi)^3} \int \frac{f_{\vec{k}} - f_{\vec{k}+\vec{q}}}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}+\vec{q}}} d\vec{k}$$

$$\chi_0(q; T = 0) = \frac{m_e}{\hbar^2} \frac{k_F}{\pi^2} \left\{ 1 + \frac{1-\eta^2}{2\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right\}$$

$$\eta = \frac{q}{2k_F} \quad k_F = (3\pi^2 n)^{1/3}$$

A nonlocal orbital-free functional

$$F_S^{a,b} = F_{TF} + F_{vW} + F_{ab} \quad F_{ab}[n, T] = \iint n^a(\vec{r}) w(\vec{r} - \vec{r}', T) n^b(\vec{r}') d\vec{r}' d\vec{r}$$

For the nonlocal functional, the correct linear response is enforced:

$$-\frac{1}{\chi_0} \equiv \hat{F} \left(\frac{\delta^2 F_S^{a,b}}{\delta n(\vec{r}) \delta n(\vec{r}') \Big|_{n_0}} \right) = -\frac{1}{\chi_{TF}} - \frac{1}{\chi_{vW}} - \frac{1}{\chi_{ab}}$$

$$\hat{F} w(\vec{r} - \vec{r}', T) = w(\vec{q}) = \frac{\chi_{TF}^{-1} + \chi_{vW}^{-1} - \chi_0^{-1}}{2abn_0^{(a+b-2)}}$$

a and b chosen by considering small variations from the UEG in both the large and small q limit. A judicious choice is used here.

$$a = b = 5/6$$

Phys. Rev. B 88, 195103 (2013)