LLNL-PRES-683261

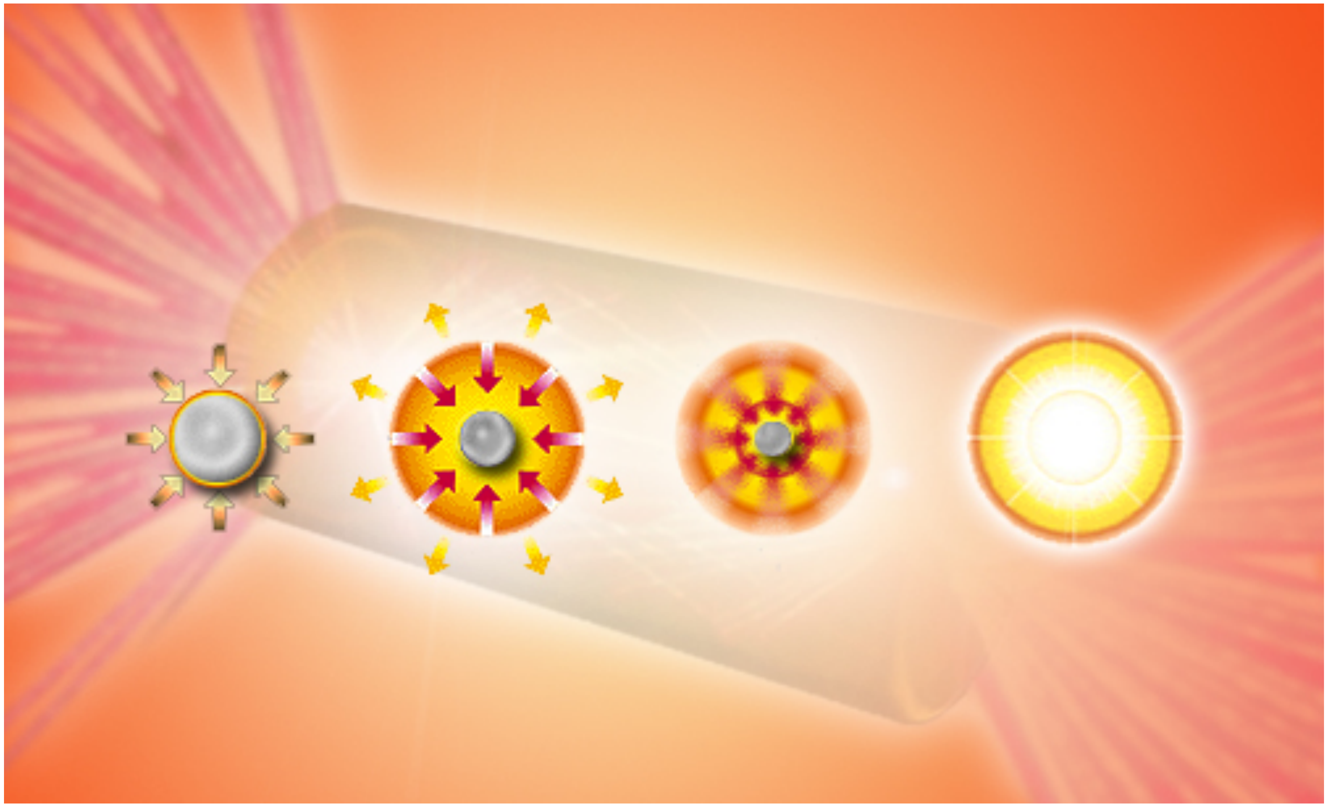
New XC free energy approximations from TDDFT

Aurora Pribram-Jones
Lawrence Livermore National Laboratory
UC Berkeley Department of Chemistry

IPAM DFT Workshop
August 23, 2016

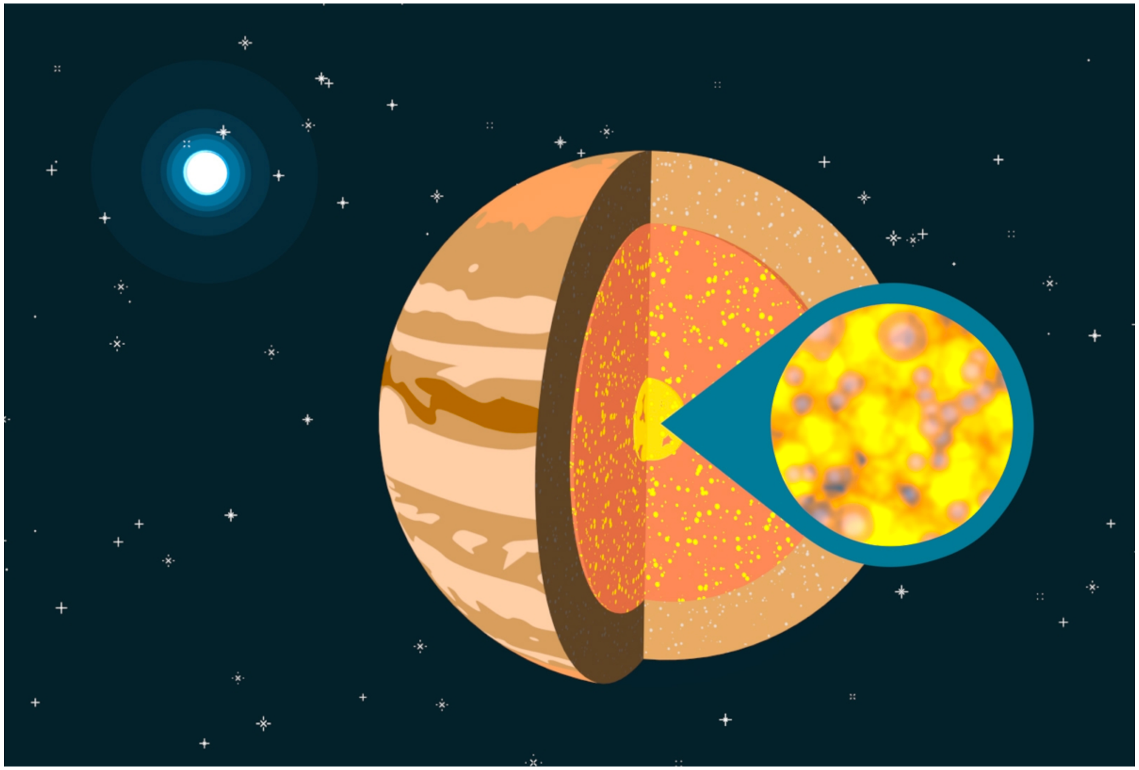
Part of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Inertial Confinement Fusion



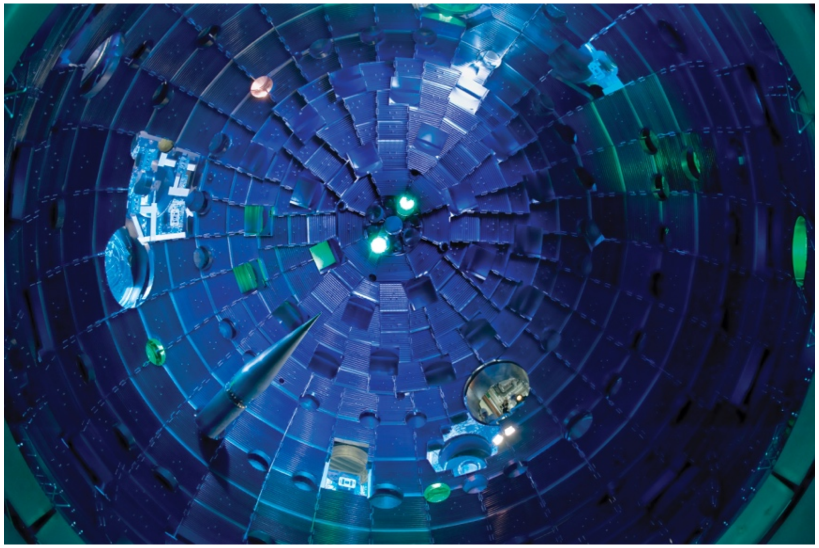
http://newscenter.lbl.gov/2011/10/19/part-i-energy-stars-earth/

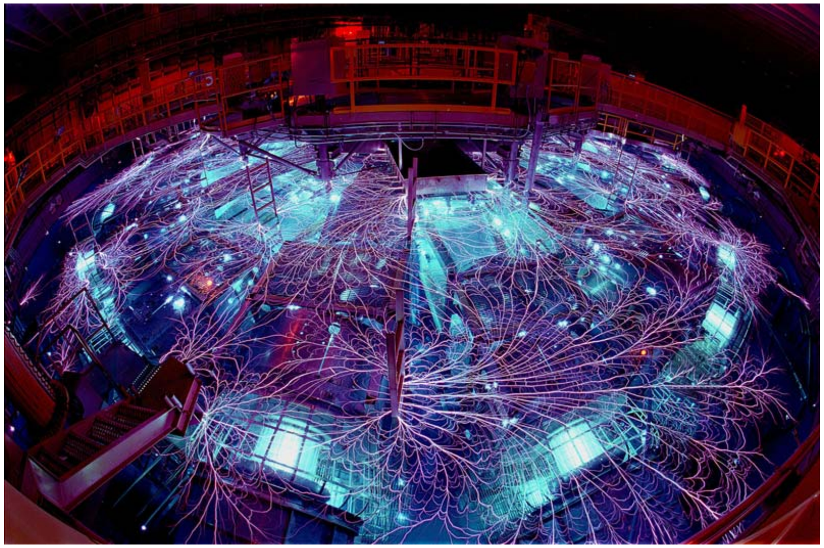
"Warm" Dense Planetary Cores



Promotional Materials, SLAC, Stanford University (2015)

Flagship Facilities



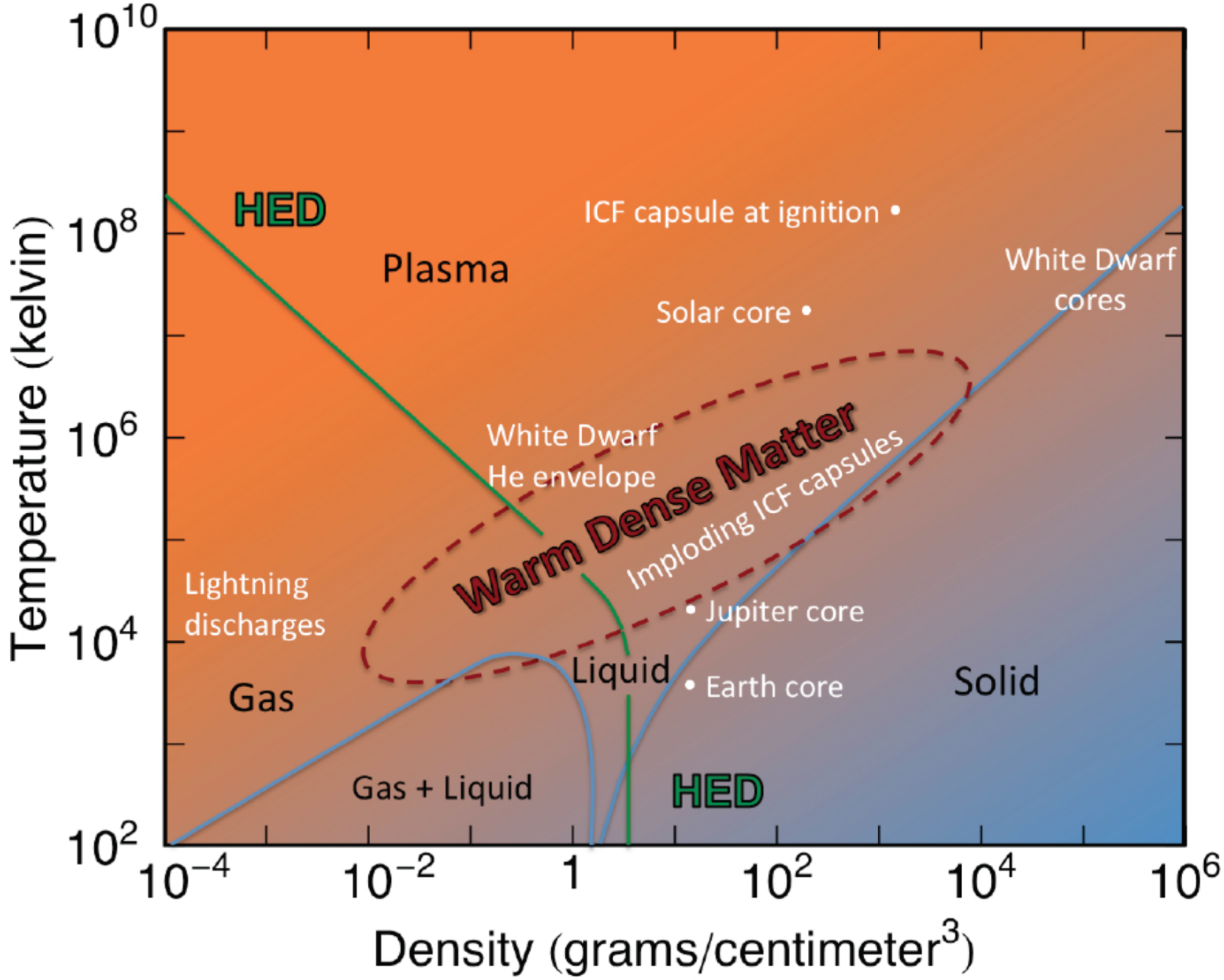


LLNL, SNL, LBL websites

Real world equivalents

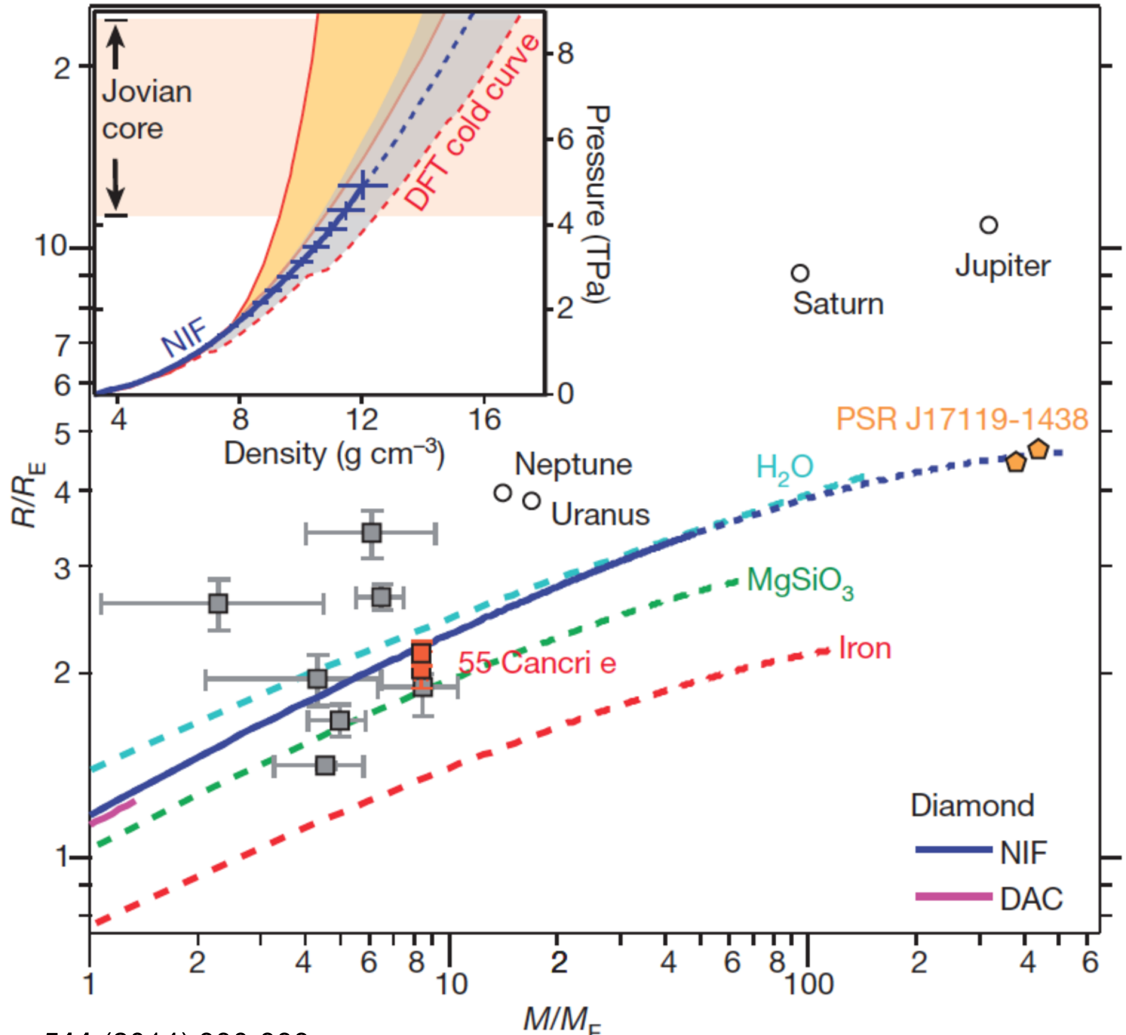
- Magnetic pressure of half a billion refrigerator magnets
- 1 million times atmospheric pressure
- Power >2000 lightning bolts
- 2.5 sticks of dynamite
  - in 1 cc
  - over a few ns

The Malfunction Junction



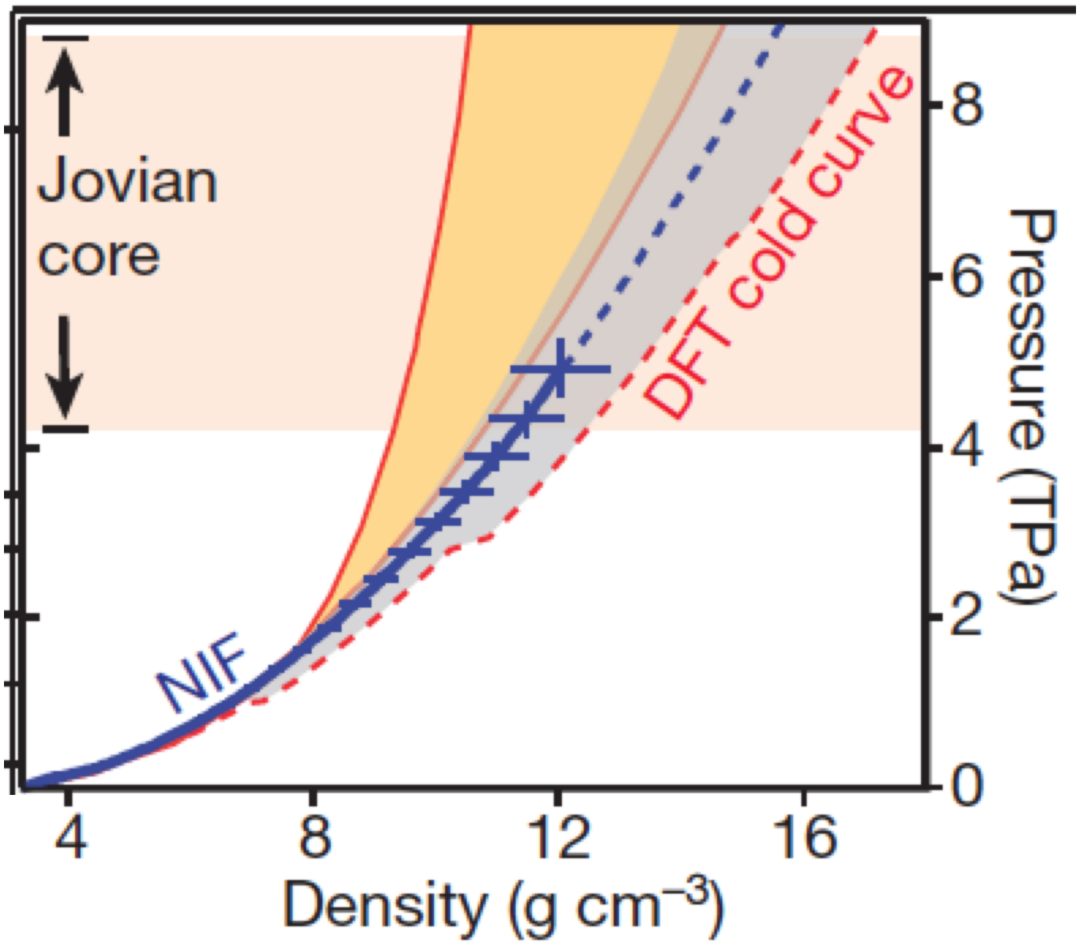
Basic Research Needs for HEDLP: Report of the Workshop on HEDLP Research, DOE (2009)

Probing Planetary Conditions



R.F. Smith et al., Nature **511** (2014) 330-333

Probing Planetary Conditions



R.F. Smith et al., Nature **511** (2014) 330-333

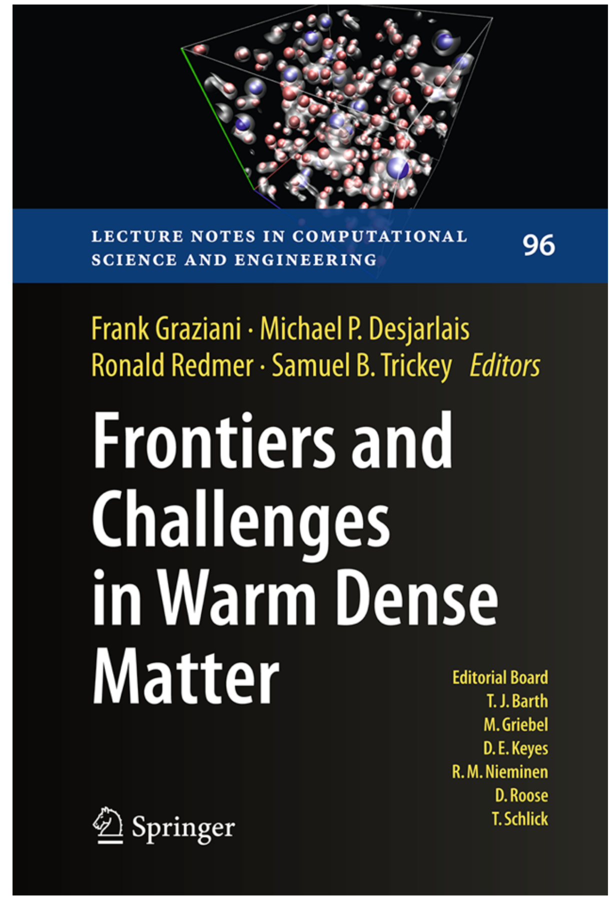
Quantum and Classical

Simulations are difficult!

- Quantum effects, strong correlation, partial ionization…
- Approximations affect calculated material properties

Simulations are important!

- Data used in core structure modeling, experimental design
- Experiments hard, expensive, limited



Quantum Molecular Dynamics

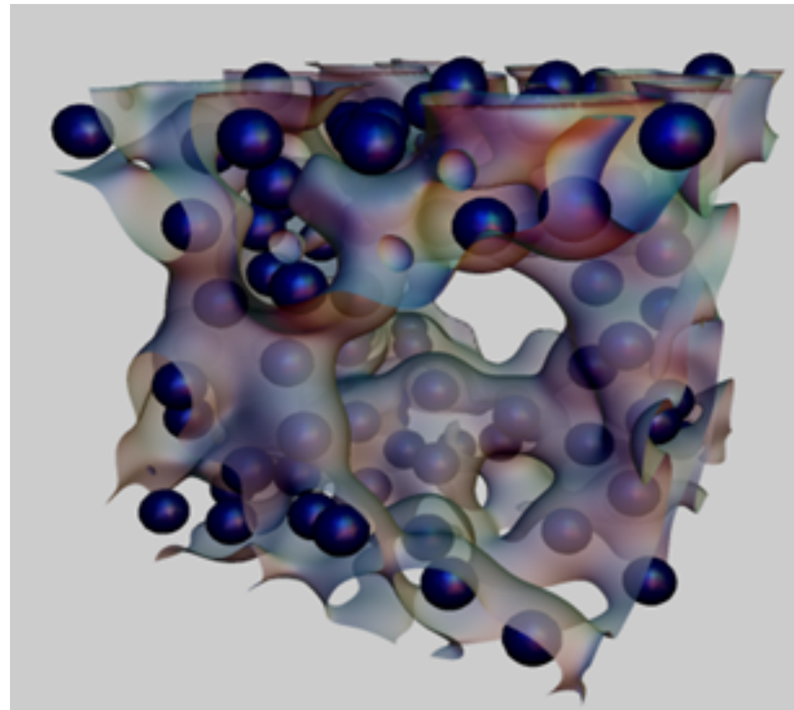
Popular, but...

•no explicit temperature dependence in electrons

•computationally expensive

•need TD electrons for response

•no energy transfer between electrons and ions



IPAM, UCLA

Quantum Molecular Dynamics

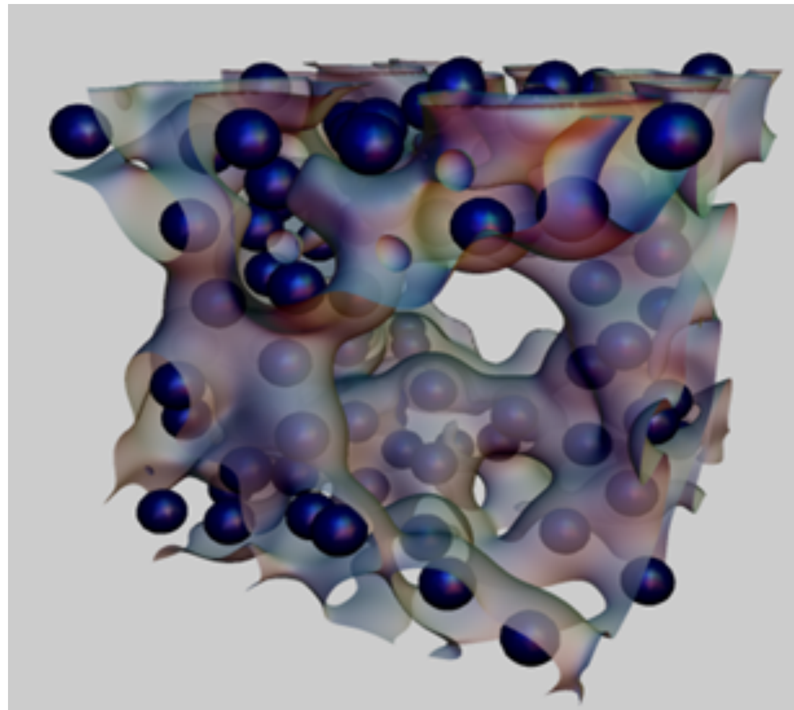
…some **progress**:

•building "math toolbox" for approximations

•novel orbital-free method

•derived new linear response proof for thermal ensembles

•no energy transfer between electrons and ions



IPAM, UCLA

Heating Things Up

Grand canonical potential operator

$$\hat{\Omega} = \hat{H} - \tau \hat{S} - \mu \hat{N}$$

Electronic Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{\mathrm{ee}} + \hat{V}$$

Mermin, N.D. *Phys. Rev. A,* 137: 1441 (1965).
Pittalis, S. et al. *Phys. Rev. Lett.*, 107: 163001 (2011).

Entropy and Statistics

Entropy operator:

$$\hat{S} = -\, k_B \ln \hat{\Gamma}$$

Statistical operator:

$$\hat{\Gamma} = \sum_{N,i} w_{N,i} |\Psi_{N,i}\rangle\langle\Psi_{N,i}|$$

Observables:

$$O[\hat{\Gamma}] = \mathrm{Tr}\,\{\hat{\Gamma}\hat{O}\} = \sum_{N}\sum_{i} w_{N,i}\langle\Psi_{N,i}|\hat{O}|\Psi_{N,i}\rangle$$

Pittalis, S. et al. *Phys. Rev. Lett.,* 107: 163001 (2011).
Pribram-Jones et al., "Thermal DFT in Context," *Frontiers and Challenges in Warm Dense Matter*, Springer Publishing (2014), p 25-60.

Finite-temperature Kohn-Sham

Map interacting system to non-interacting system with same density.

$$\left[-\frac{1}{2}\nabla^2 + v_{\rm S}^{\tau}(\mathbf{r})\right]\phi_i^{\tau}(\mathbf{r}) = \epsilon_i^{\tau}\phi_i^{\tau}(\mathbf{r})$$

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

$$f_i^{\tau} = \left(1 + e^{(\epsilon_i^{\tau}-\mu)/\tau}\right)^{-1}$$

Kohn and Sham, 1965.

Free energies: Helmholtz and XC

Temperature-dependent free energy:

$$A^{\tau}[n] = T[n] + V_{\text{ee}}[n] + V[n] - \tau S[n]$$
$$= T_{\text{S}}[n] + U[n] + V[n] - \tau S_{\text{S}}[n] + A_{\text{XC}}[n]$$

Kinetic, potential, entropic exchange-correlation:

$$A_{\text{XC}}[n] = T_{\text{XC}}[n] + U_{\text{XC}}[n] - \tau S_{\text{XC}}[n]$$

Pittalis, S. et al. *Phys. Rev. Lett.,* 107: 163001 (2011).

Pribram-Jones et al., "Thermal DFT in Context," *Frontiers and Challenges in Warm Dense Matter*, Springer Publishing (2014), p 25-60.

Correlation Relations

Correlation free energy: kentropic, potential, kinetic, entropic

$$A_{\mathrm{C}}^{\tau}[n] = K_{\mathrm{C}}^{\tau}[n] + U_{\mathrm{C}}^{\tau}[n]$$

$$K_{\mathrm{C}}^{\tau}[n] = T_{\mathrm{C}}^{\tau}[n] - \tau\, S_{\mathrm{C}}^{\tau}[n]$$

Combine with ACF to get a set of relations, such as:

$$A_{\mathrm{C}}^{\tau}[n] = -\int_0^1 \frac{d\lambda}{\lambda^2}\, K_{\mathrm{C}}^{\tau,\lambda}[n]$$

APJ and K. Burke, Phys. Rev. B **93**, 205140 (2016)

ACF via scaled density/temperature

Combine finite-temperature ACF (Pittalis, et al., 2011)

$$A_{\mathrm{C}}^{\tau}[n] = \int_0^1 \frac{d\lambda}{\lambda}\, U_{\mathrm{C}}^{\tau,\lambda}[n]$$

with coupling constant-coordinate-temperature scaling (Pittalis, et al., 2011)

$$A_{\mathrm{XC}}^{\tau,\lambda}[n] = \lambda^2\, A_{\mathrm{XC}}^{\tau/\lambda^2}[n_{1/\lambda}]$$

Change of variables yields thermal connection formula:

$$A_{\mathrm{XC}}^{\tau}[n] = \frac{\tau}{2} \lim_{\tau''\to\infty} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^2}\, U_{\mathrm{XC}}^{\tau'}[n_{\sqrt{\tau'/\tau}}]$$

APJ and K. Burke, Phys. Rev. B **93**, 205140 (2016)

Thermal Connection Formula

$$A^{\tau}_{\rm XC}[n] = \frac{\tau}{2} \lim_{\tau''\to\infty} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^2} U^{\tau'}_{\rm XC}[n_{\sqrt{\tau'/\tau}}]$$

- Relates exact XC free energy to high temperature, high density limit
- Need knowledge of XC potential energy at scaled densities, ***not*** at scaled interaction strengths
- Reduces to plasma physics coupling-constant relation for uniform systems
- Generalization of plasma physics formula to density functionals and inhomogeneous systems

APJ and K. Burke, Phys. Rev. B **93**, 205140 (2016)

An Application

Using finite-temperature fluctuation-dissipation theorem for the correlation free energy in terms of the thermal density-density response function:

$$A_{\rm C}^{\tau}[n] =$$

$$\lim_{\tau''\to\infty} \frac{\tau}{2} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^2} \int d\mathbf{r} \int d\mathbf{r}' \int \frac{d\omega}{2\pi} \coth\left(\frac{\omega}{2\tau}\right) \frac{\Im \Delta\chi^{\tau'}[n_\gamma](\mathbf{r},\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|}$$

Useful for computation and theory:

- Generates ***new*** XC approximations for FT DFT
- Provides link between finite-temperature and infinite-temperature limit

APJ, P.E. Grabowski, and K. Burke, Phys. Rev. Lett. **116**, 233001 (2016)

XC Approximations

<u>*Exact expression*</u>, as long as exact thermal kernel is used:

$$\left(\chi_{\rm S}^{\tau}\right)^{-1}(12) = \left(\chi^{\tau}\right)^{-1}(12) + f_{\rm H}(12) + f_{\rm XC}^{\tau}(12)$$

Approximations to thermal XC kernel:

- $f_{\rm XC}^{\tau}(12)$ = 0 → thermal RPA
- $f_{\rm XC}^{\tau,{\rm thALDA}}[n](\mathbf{r},\mathbf{r}',\omega) = \left.\frac{d^2 a_{\rm XC}^{\tau,{\rm unif}}(n)}{d^2 n}\right|_{n(\mathbf{r})} \delta(\mathbf{r}-\mathbf{r}')$

→ Approximate $A_{\rm XC}^{\tau}[n]$

APJ, P.E. Grabowski, and K. Burke, Phys. Rev. Lett. **116**, 233001 (2016)

Acknowledgments

Mentors and Collaborators

- F. Graziani (LLNL), E. Schwegler (LLNL), M. Head-Gordon (UCB), **K. Burke (UCI)**, **A. Cangi (MPI),** Z.-Y. Yang (Temple), C.A. Ullrich (UMC), **J.C. Smith (UCI), D. Feinblum (UCI**), **S. Pittalis (CNR-NANO)**, **E.K.U. Gross (MPI), P.E. Grabowski (UCI/LLNL)**, R.J. Needs (Cambridge), J.R. Trail (Cambridge), D.A. Gross (UCI), M.P. Desjarlais (SNL), K.R. Cochrane (SNL), M.D. Knudson (SNL)

Funding Sources

- Lawrence Fellowship, Lawrence Livermore National Laboratory
- UC President's Postdoctoral Fellowship, UC Berkeley Chemistry
- Quantum Simulation Group and WCI, LLNL
- Krell Institute and the DOE CSGF (DE-FG02-97ER25308)

Summary

- Exact conditions relating components of correlation free energy
- Thermal connection formula: adiabatic connection via temperature integral
- Can generate XC free energy approximations from thermal kernel

<u>For further information</u>

- **Linear response of thermal ensembles:** A. Pribram-Jones, P.E. Grabowski, and K. Burke, Phys. Rev. Lett. **116**, 233001 (2016).
- **Thermal connection formula and exact conditions:** A. Pribram-Jones and K. Burke, Phys. Rev. B **93**, 205140 (2016).
- **Thermal DFT:** A. Pribram-Jones, S. Pittalis, E.K.U. Gross, K. Burke, *Frontiers and Challenges in Warm Dense Matter*, Springer Publishing (2014), p 25-60.
- **Quirky overview of DFT:** A. Pribram-Jones, D.A. Gross, K. Burke, Ann. Rev. Phys. Chem **66** (2015).