An Efficient Formalism for Warm Dense Matter Electronic Structure

Aurora Pribram-Jones
University of California, Irvine

DOE CSGF Annual Program Review
July 29, 2015

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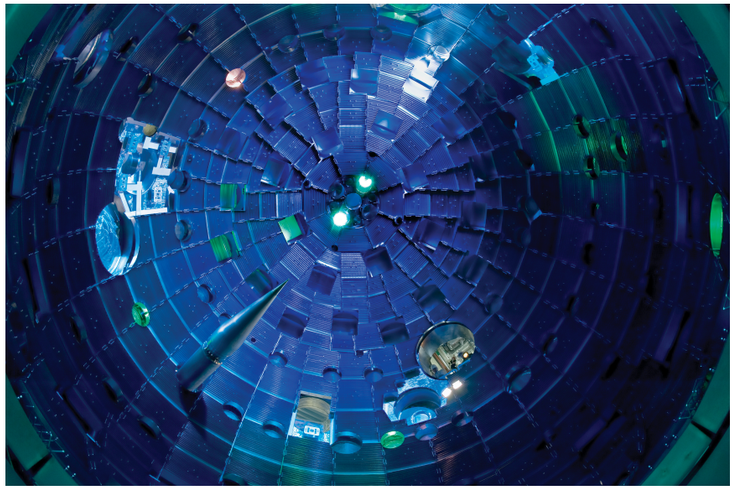
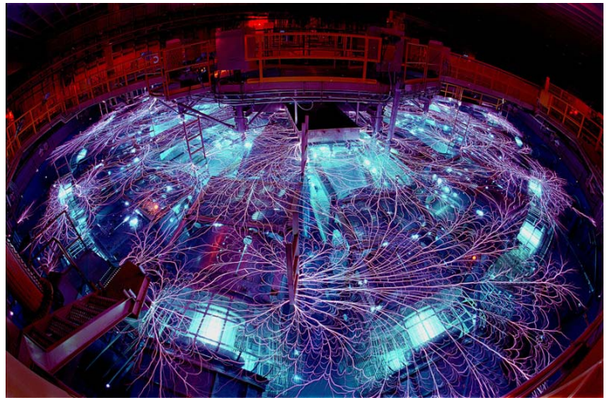
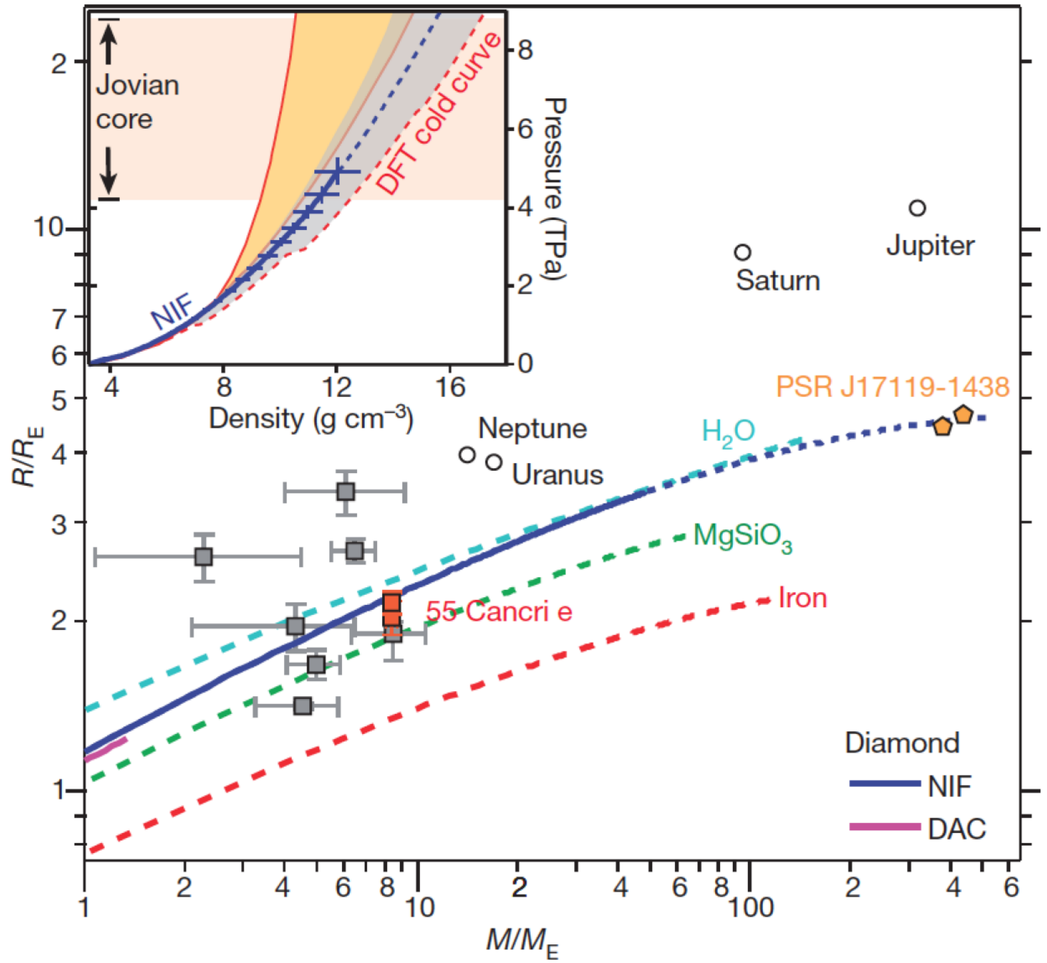
Warm Dense Matter





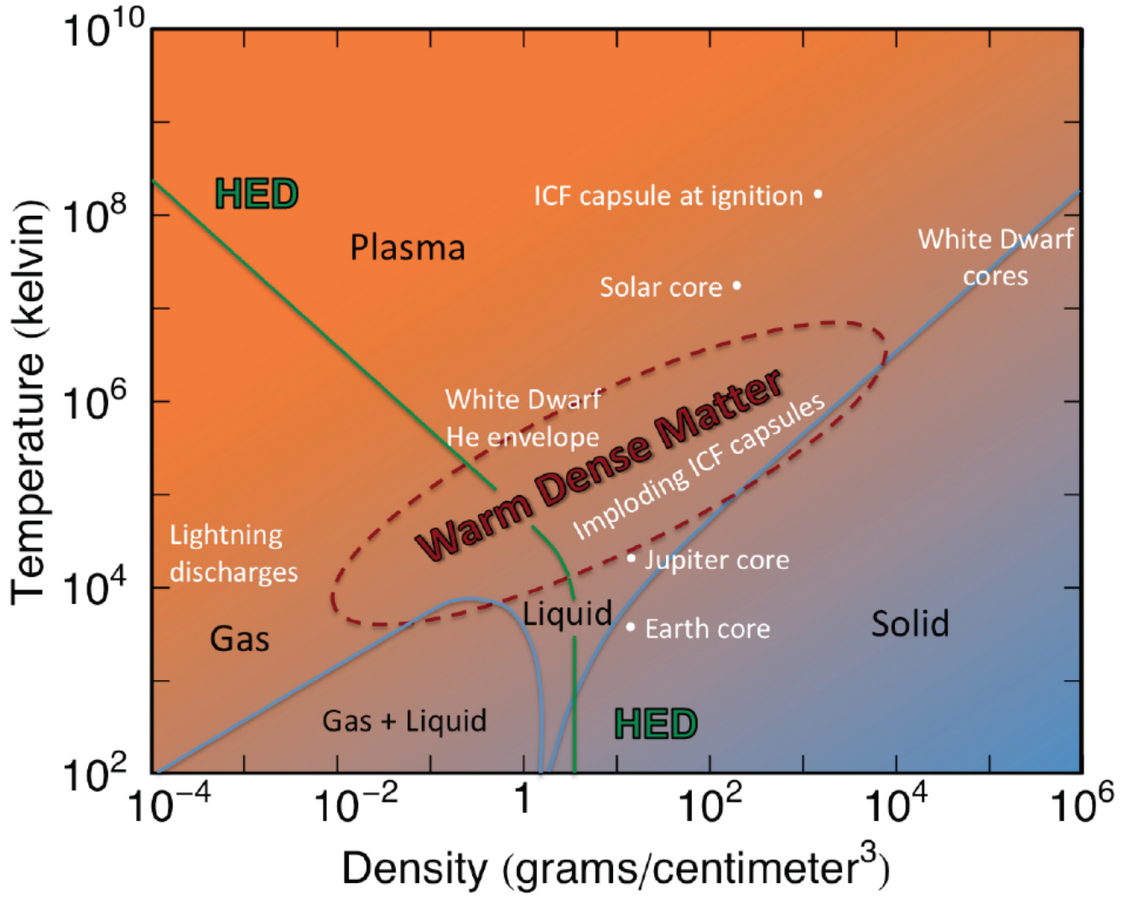
LLNL, SNL, LBL, Rochester U websites

Experimental Probes of Planetary Conditions



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

The Malfunction Junction



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

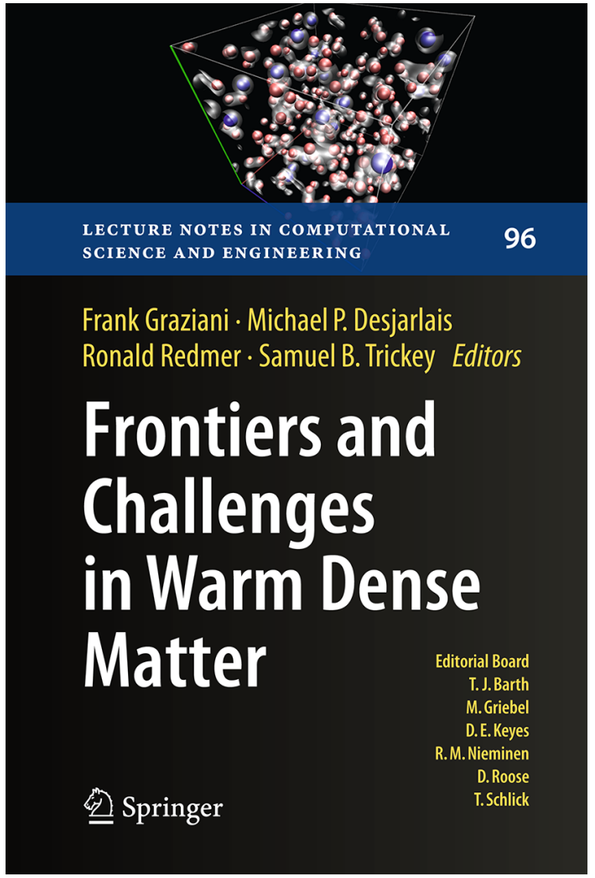
Quantum and Classical

Simulations are difficult!

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

Simulations are important!

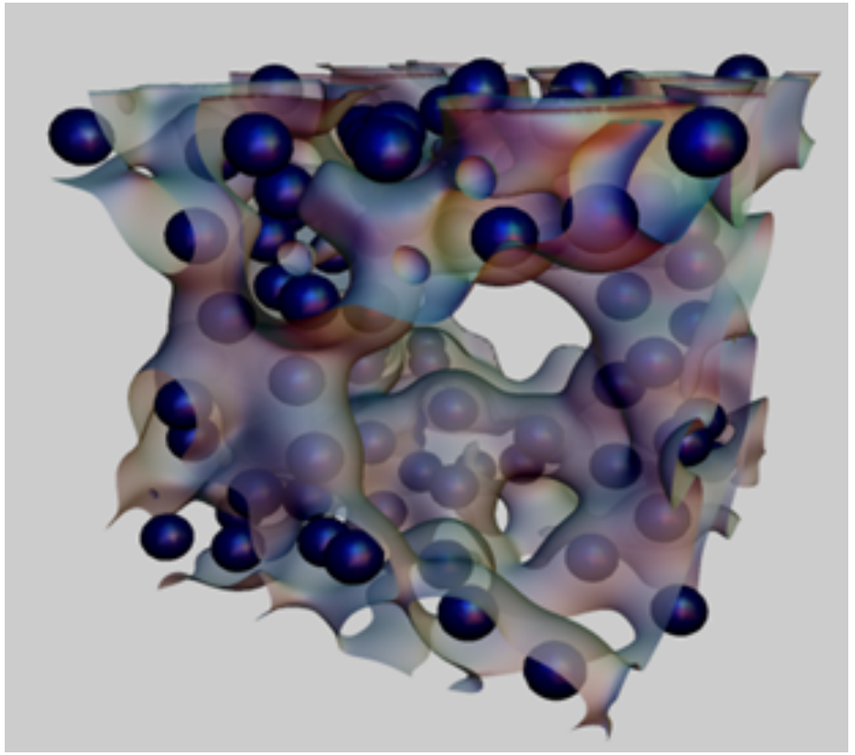
- Data used in core structure modeling, experimental design
- Experiments hard, expensive, limited



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

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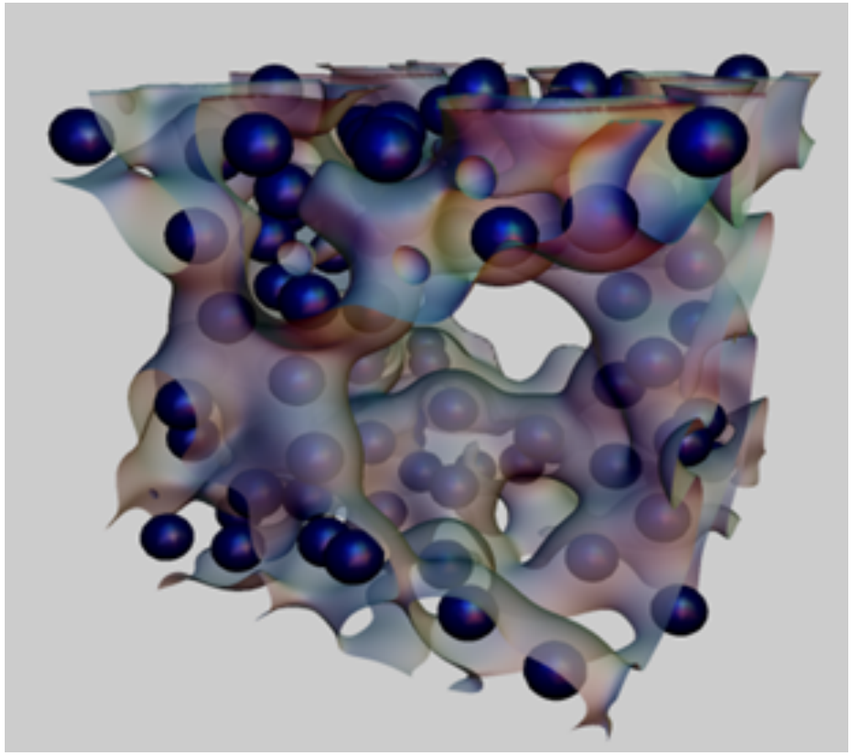
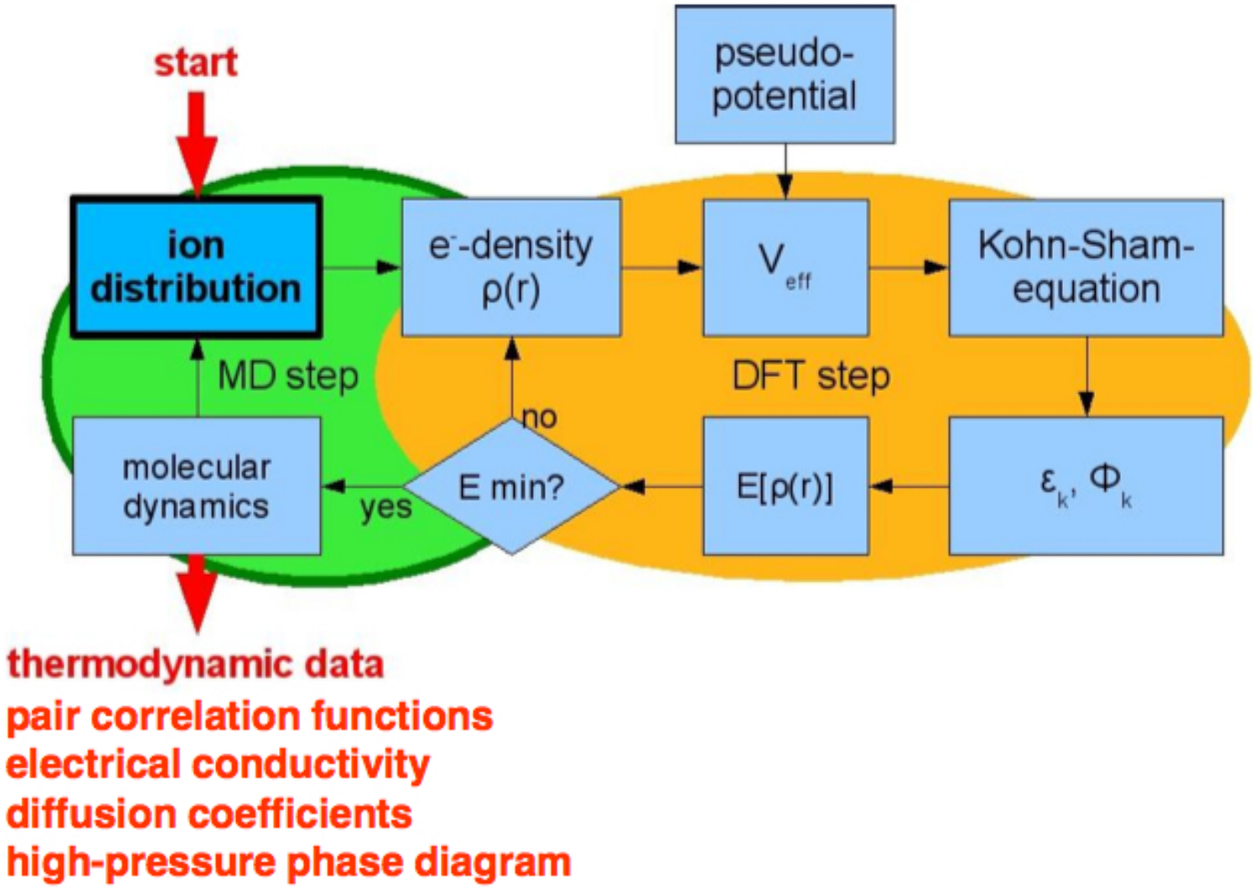


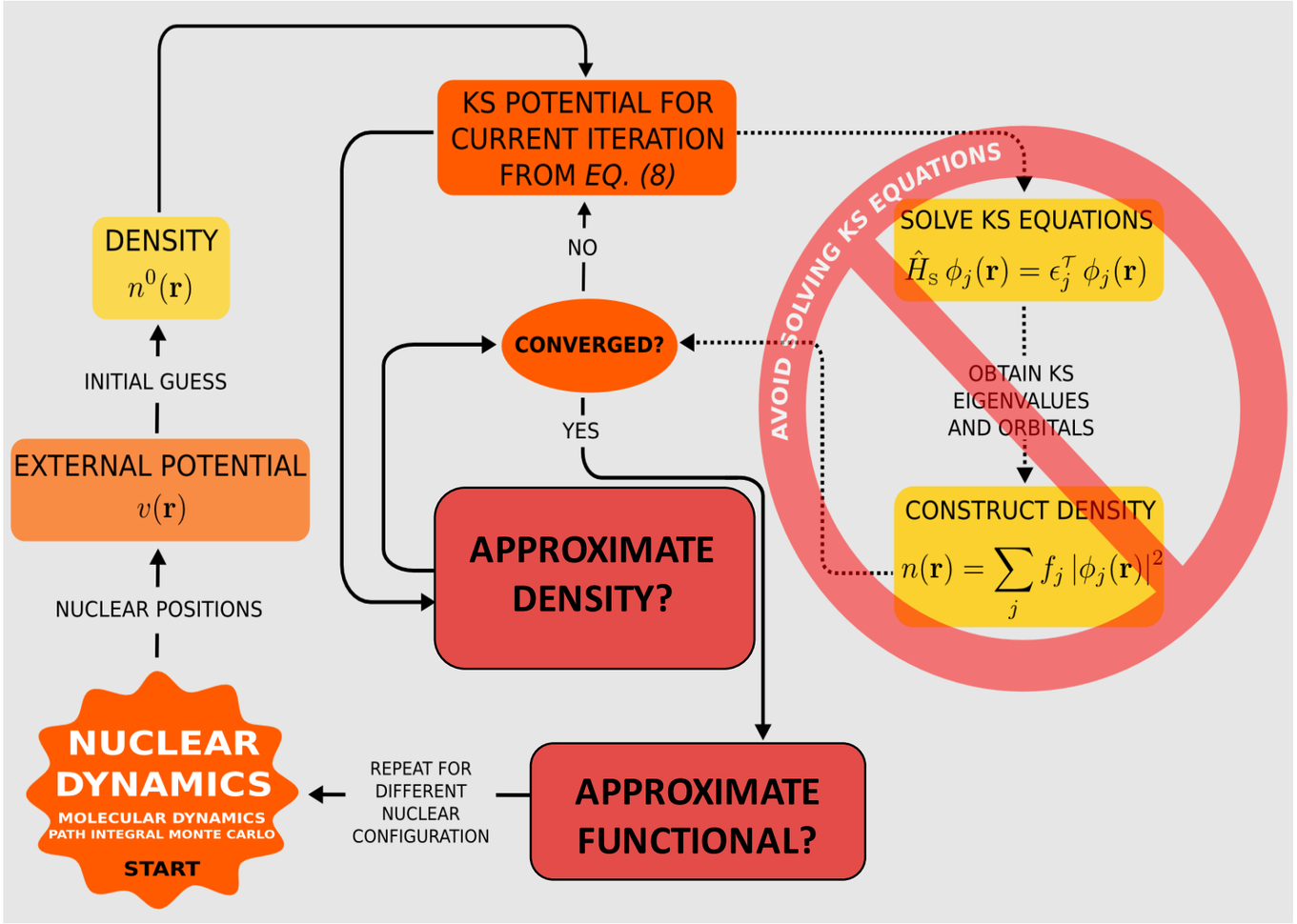
IPAM, UCLA

The Bottleneck



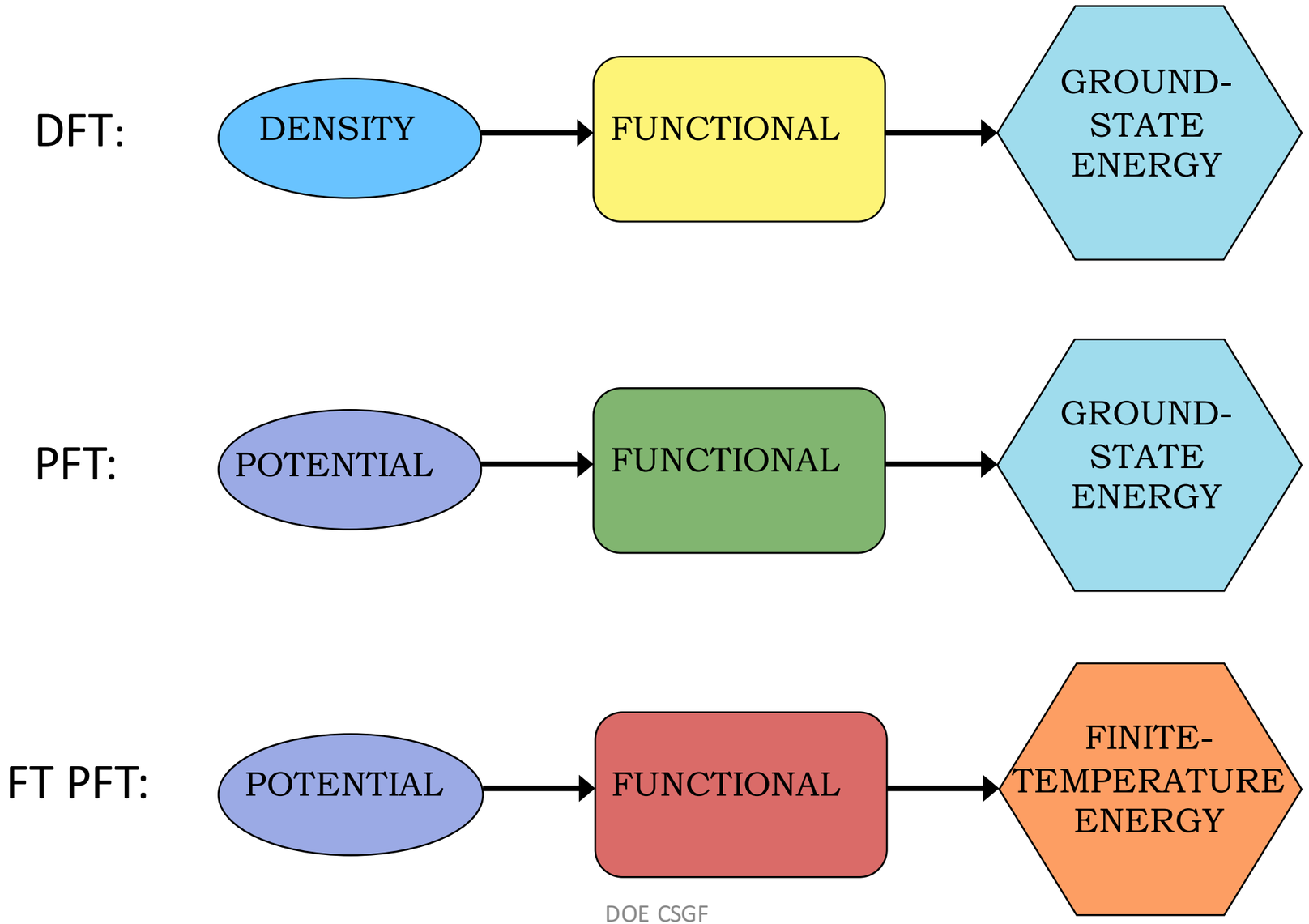
Adapted from http://hifweb.lbl.gov/public/BeamHEDP2010, original by W. Lorenzen

Zoom in on electronic step…



A. Cangi and A. Pribram-Jones, arxiv:1411.1532

PFT: An Exact Formulation



Exact Expression for Kentropy

$$K_{\mathrm{S}}^{\tau}[v_{\mathrm{S}}] = \int d^3r \;\; \{\bar{n}_{\mathrm{S}}^{\tau}(\mathbf{r}) - n_{\mathrm{S}}^{\tau}[v_{\mathrm{S}}](\mathbf{r})\}\, v_{\mathrm{S}}(\mathbf{r})$$

K_s : "universal" part of thermal electrons' free energy

τ : temperature

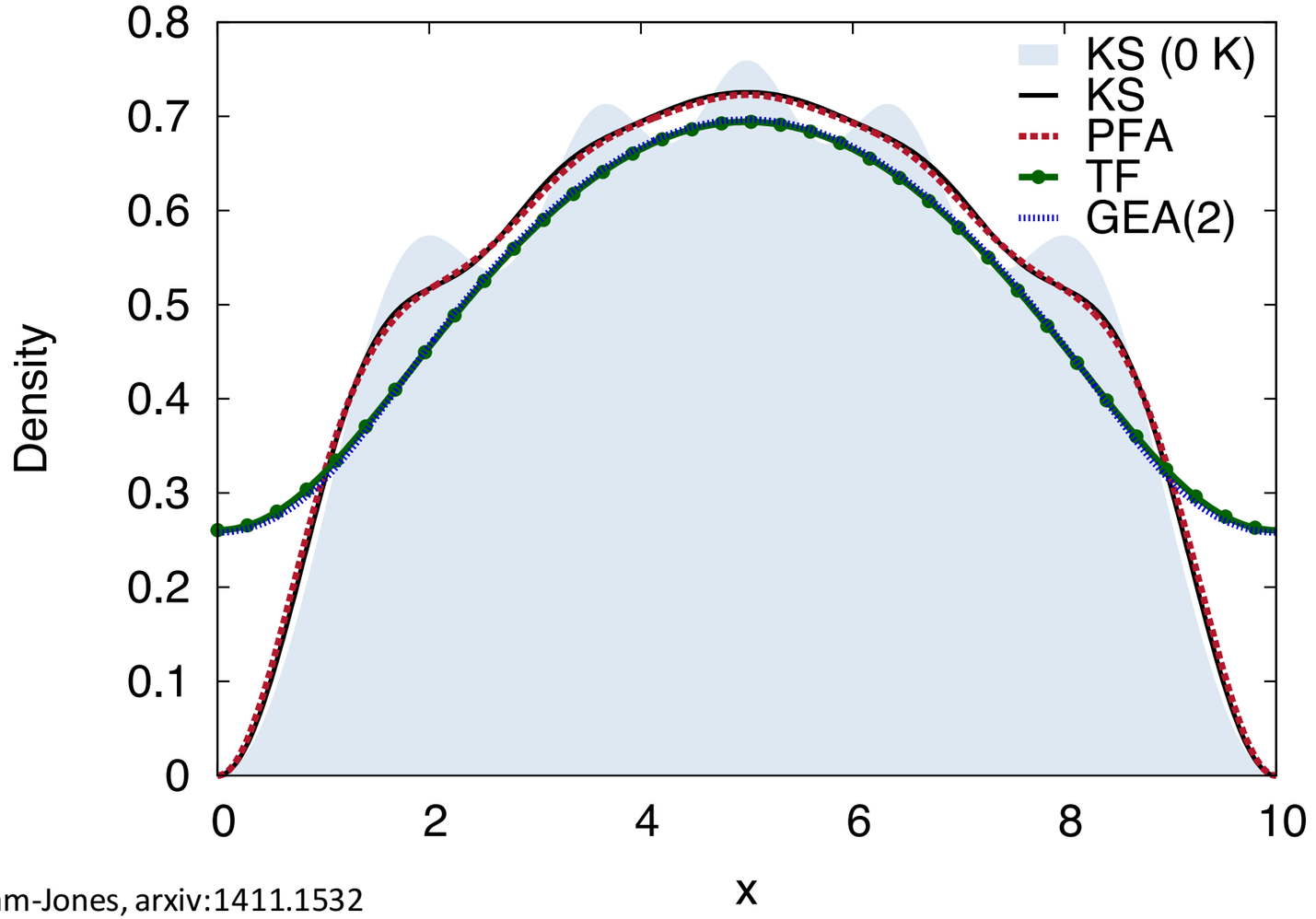
v_s : external potential of non-interacting system

$n_s[v_s]$: density ***written in terms of the potential***

bar: integral over the coupling constant

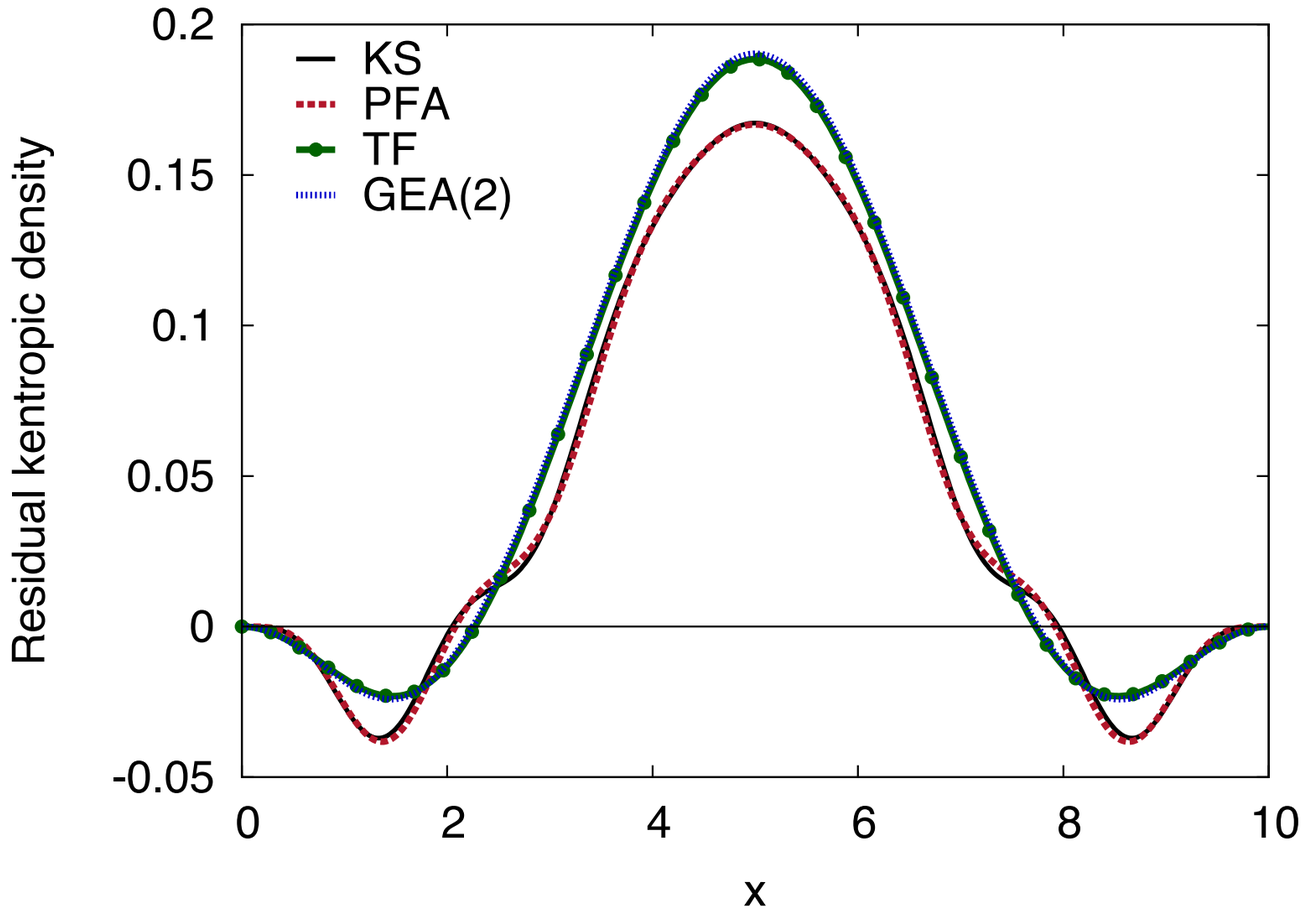
A. Cangi and A. Pribram-Jones, arxiv:1411.1532

Highly Accurate Density



A. Cangi and A. Pribram-Jones, arxiv:1411.1532

Not Reliant on Error Cancellations



A. Cangi and A. Pribram-Jones, arxiv:1411.1532

Accurate Across Regimes

Λ	$K^{\tau}_{\mathrm{S},0}$	$\Delta K^{\tau}_{\mathrm{S}}$	error $\times$ 10^2		
			TF	GEA(2)	PFA
0.16	3.94	0.462	6.39	8.93	−0.32
0.31	3.87	0.461	7.16	9.85	−0.28
0.47	3.76	0.459	7.91	10.11	−0.31
0.62	3.64	0.456	8.39	10.01	−0.29
0.78	3.50	0.452	8.61	9.78	−0.30
0.93	3.34	0.448	8.65	9.52	−0.37
1.09	3.16	0.444	8.58	9.24	−0.50
1.40	2.77	0.435	8.21	8.63	−0.87
1.71	2.36	0.425	7.69	7.99	−1.27
2.02	1.92	0.414	7.13	7.35	−1.61
2.48	1.25	0.396	6.34	6.46	−1.86
2.94	0.58	0.378	5.64	5.69	−1.80
3.41	−0.10	0.360	5.04	5.04	−1.45
4.03	−0.99	0.338	4.37	4.33	−0.63

A. Cangi and A. Pribram-Jones, arxiv:1411.1532

Proposed FT PFT Development

Year 1

- Test different classes of potentials
- New density approximations: boundary layer theory, contour integration

Year 2

- Test density approximations in various potential classes
- Extend semiclassical nearly-exact exchange method to our approximate density matrix and combine with FT PFT

Year 3

- Extend to realistic systems; implement PFT-MD method?
- Compare to VASP DFT-MD simulations, if warranted

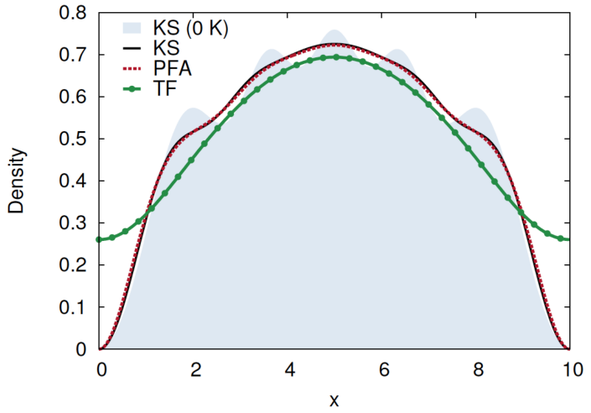
FT PFT: Promising New Approach

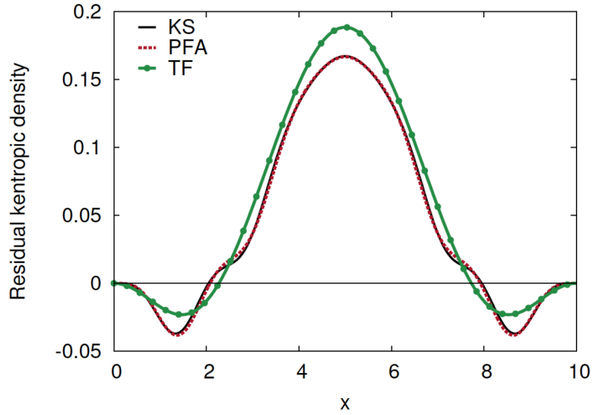
Exact formulation of coupling constant non-interacting kentropy

- Orbital-free (i.e., computationally efficient)
- Takes advantage of decades of DFT research

Demonstration using semiclassical density approximation

- Connects condensed matter and plasma regimes
- Leverages “unreasonable” accuracy of asymptotic expansions





Acknowledgments

- Advisor and collaborators: K. Burke (UCI), A. Cangi (MPI), Z.-Y. Yang (Temple), C.A. Ullrich (UMC), 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)

- Electronic Structure Group and the UCI Chemistry Department

- Krell and the DOE CSGF (DE-FG02-97ER25308)

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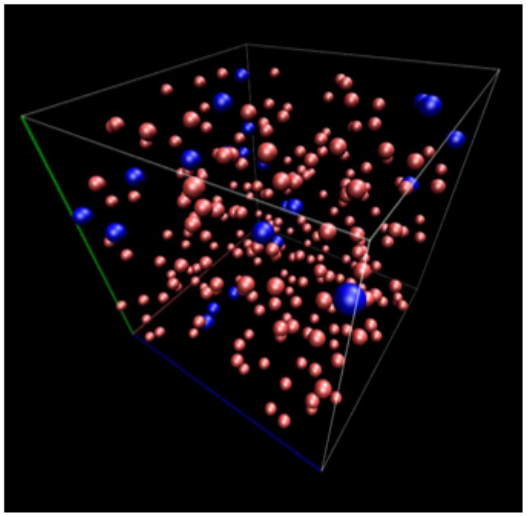
Bypassing the malfunction junction

Aurora Pribram-Jones
with Attila Cangi (MPI Halle)
arXiv:1411.1532

Department of Chemistry
University of California, Irvine

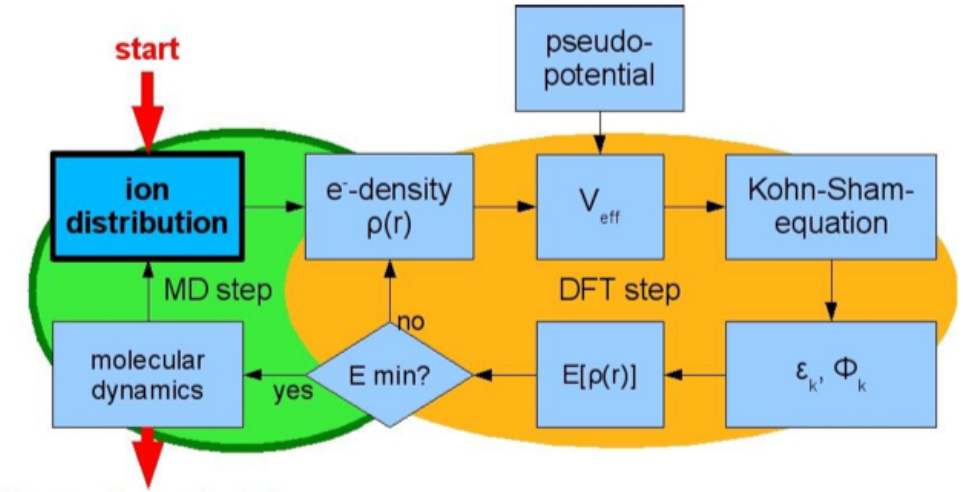
IPAM Reunion #2, Lake Arrowhead
December 9, 2014

Quantum Molecular Dynamics

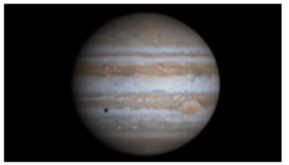


H-He (8.6%) @ 1 Mbar, 4000 K

box length ~ 10^{-9} m



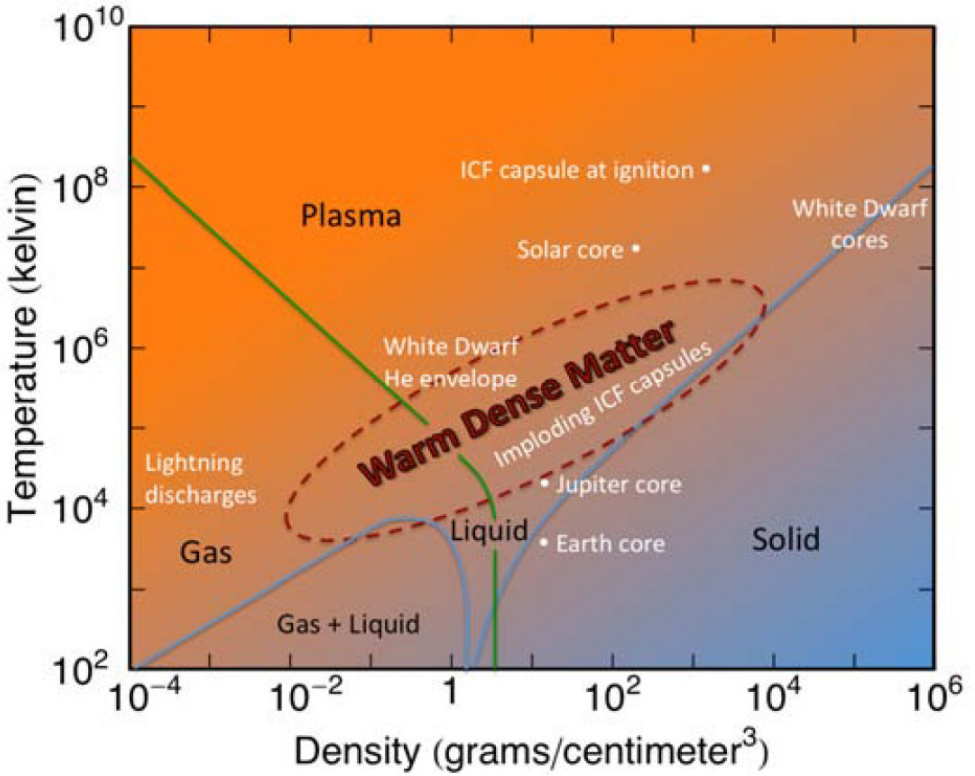
thermodynamic data
pair correlation functions
electrical conductivity
diffusion coefficients
high-pressure phase diagram



GP size ~ 10^{8} m

Adapted from http://hifweb.lbl.gov/public/BeamHEDP2010, original by W. Lorenzen

What's the malfunction junction?



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

Outline

Theory
- Background
- Finite-Temperature Potential Functional Theory
- Connecting Density and Potential

Demonstration
- Density Approximation
- Numerical Example

Theory

Hohenberg-Kohn (1964)

Hohenberg-Kohn Theorem (1964)

- ground-state energy depends on density
- one-to-one correspondence between density and external potential

$$\begin{aligned} E &= T + V_{\mathrm{ee}} + V \\ &= F[n] + \int d^3r \; n(\mathbf{r})(v(\mathbf{r}) - \mu) \end{aligned}$$

Kohn-Sham (1965)

- maps interacting system to non-interacting system
- defines exchange-correlation:

$$F[n] = T_{\mathrm{S}}[n] + U[n] + E_{\mathrm{XC}}[n]$$

- Kohn-Sham equations:

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\mathrm{S}}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi(\mathbf{r})$$

Orbital-Free DF Approach

Needs: approximate non-interacting kinetic energy density functional.

$$F[n] = T_{\mathrm{S}}[n] + U[n] + E_{\mathrm{XC}}[n]$$

OF-DFT challenge: T_{S} approximations on par with KS accuracy

Orbital-Free PF Approach

Needs: approximate non-interacting kinetic energy potential functional.

$$\begin{aligned} F[v] &= T_{\mathrm{S}}[v] + U[v] + E_{\mathrm{XC}}[v] \\ &= T_{\mathrm{S}}[n[v]] + U[n[v]] + E_{\mathrm{XC}}[n[v]] \end{aligned}$$

PFT challenge: T_{S} & $n(\mathbf{r})$ approximations on par with KS accuracy

Cangi et al., PRA **88**, 062505 (2013).

The PFT Idea

For zero or finite temperature:

- Step 1: get $F[v]$
- Step 2: approximate $n[v]$
- Step 3: join Steps 1 and 2, so that approximating the density generates $F[n[v]]$ automatically

This scheme introduces no additional errors beyond those from the density approximation.

Cangi et al., PRA **88**, 062505 (2013); PRL **106**, 236404 (2011); PRB **81**, 235128 (2010).

Elliott et al. PRL **100**, 256406 (2008).

Heating Things Up

Grand canonical operator:

$$\hat{\Omega} = \hat{H} - \frac{1}{\beta}\hat{S} - \mu\hat{N}$$

Electronic Hamiltonian:

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

Mermin, N.D. *Phys. Rev.*, 137:A: 1441, 1965.

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

Entropy and the Statistical Operator

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.

APJ et al., *Thermal DFT in Context*, Springer, 2014.

FT Potential Functionals

Grand canonical potential in terms of potential functionals:

$$\Omega^{\beta}_{v-\mu} = F^{\beta}[v] + \int d^3r \; n^{\beta}[v](\mathbf{r})(v(\mathbf{r}) - \mu)$$

with

$$F^{\beta}[v] = F^{\beta}[\hat{\Gamma}^0_{v-\mu}] = T[\hat{\Gamma}^0_{v-\mu}] + V_{ee}[\hat{\Gamma}^0_{v-\mu}] - \frac{1}{\beta} S[\hat{\Gamma}^0_{v-\mu}].$$

Coupling Constant

Connect potential of interest to reference potential:

$$v^\lambda(\mathbf{r}) = (1-\lambda)v_0(\mathbf{r}) + \lambda v(\mathbf{r})$$

Via Hellmann-Feynman:

$$\Omega^\beta_{v-\mu} = \Omega^\beta_0 + \int d\lambda \int d^3r\ n^\beta[v^\lambda](\mathbf{r})\Delta v(\mathbf{r}),$$

where $\Delta v(\mathbf{r}) = v(\mathbf{r}) - v_0(\mathbf{r})$.
Set $v_0 = 0$ and define $\bar{n}^\beta[v](\mathbf{r}) = \int_0^1 d\lambda\, n^\beta[v^\lambda](\mathbf{r})$:

$$F^{\beta,\mathrm{cc}}_{n^\beta}[v] = \int d^3r\ \left\{\bar{n}^\beta[v](\mathbf{r}) - n^\beta[v](\mathbf{r})\right\} v(\mathbf{r}).$$

Coupling-Constant Kohn-Sham

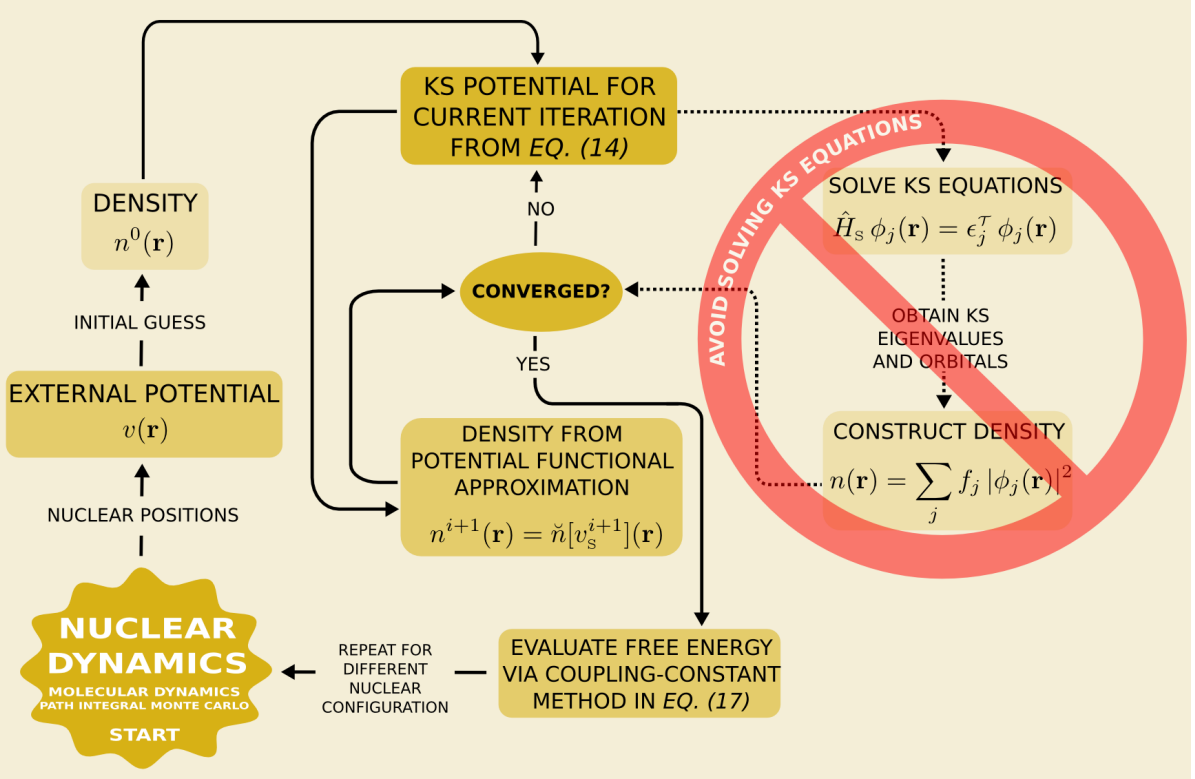
FT universal density functional:

$$F_{\mathrm{s}}^{\beta}[n] := \min_{\hat{\Gamma}\to n} K^{\beta}[\hat{\Gamma}] = K^{\beta}[\hat{\Gamma}_{\mathrm{s}}^{\beta}[n]] = K_{\mathrm{s}}^{\beta}[n]$$

FT Kohn-Sham potential:

$$v_{\mathrm{S}}(\mathbf{r}) = v(\mathbf{r}) + \tilde{v}_{\mathrm{H}}[n_{\mathrm{S}}^{\beta}[v_{\mathrm{S}}]](\mathbf{r}) + \tilde{v}_{\mathrm{XC}}[n_{\mathrm{S}}^{\beta}[v_{\mathrm{S}}]](\mathbf{r})$$

Avoiding KS Eigenstates



Cangi, A. and APJ, arxiv:1411.1532

Coupling-constant Non-Interacting Kentropy

Once potential is found, apply earlier equation:

$$K^{\beta,\mathrm{cc}}_{\mathrm{S},n^{\beta}_{\mathrm{S}}}[v_{\mathrm{S}}] = \int d^3r \ \left\{\bar{n}^{\beta}_{\mathrm{S}}(\mathbf{r}) - n^{\beta}_{\mathrm{S}}[v_{\mathrm{S}}](\mathbf{r})\right\} v_{\mathrm{S}}(\mathbf{r})$$

Demonstration

General Density Approximation

Density approximation:

$$n_{\mathrm{S}}^{\beta}[v_{\mathrm{S}}](\mathbf{r}) \approx \lim_{\mathbf{r}'\to\mathbf{r}} \frac{1}{2\pi i} \int_{\eta-\infty}^{\eta+\infty} d\alpha \, \frac{e^{\mu\alpha}}{\alpha} \, G_{\mathrm{sc}}^{\beta}[v_{\mathrm{S}}](\mathbf{r},\mathbf{r}';\alpha) \ ,$$

where $\eta \geq 0$.
Generated by inverse Laplace transform of

$$G_{\mathrm{sc}}^{\beta}(\mathbf{r},\mathbf{r}';\alpha) = G_{\mathrm{sc}}^{0}(\mathbf{r},\mathbf{r}';\alpha)\, f^{\beta}(\alpha)$$

with $f^{\beta}(\alpha) = \pi\alpha/[\beta \sin(\pi\alpha/\beta)]$.

J. Bartel, M. Brack, and M. Durand, it Nuclear Physics A **445**, 263 (1985).

S. Golden, *Rev. Mod. Phys.* **32**, 322 (1960).

A Useful Example

- non-interacting, spinless fermions
- arbitrary potential confined to a box of size L
- Dirichlet boundary conditions

Applied to Example

Extend zero-temperature method:

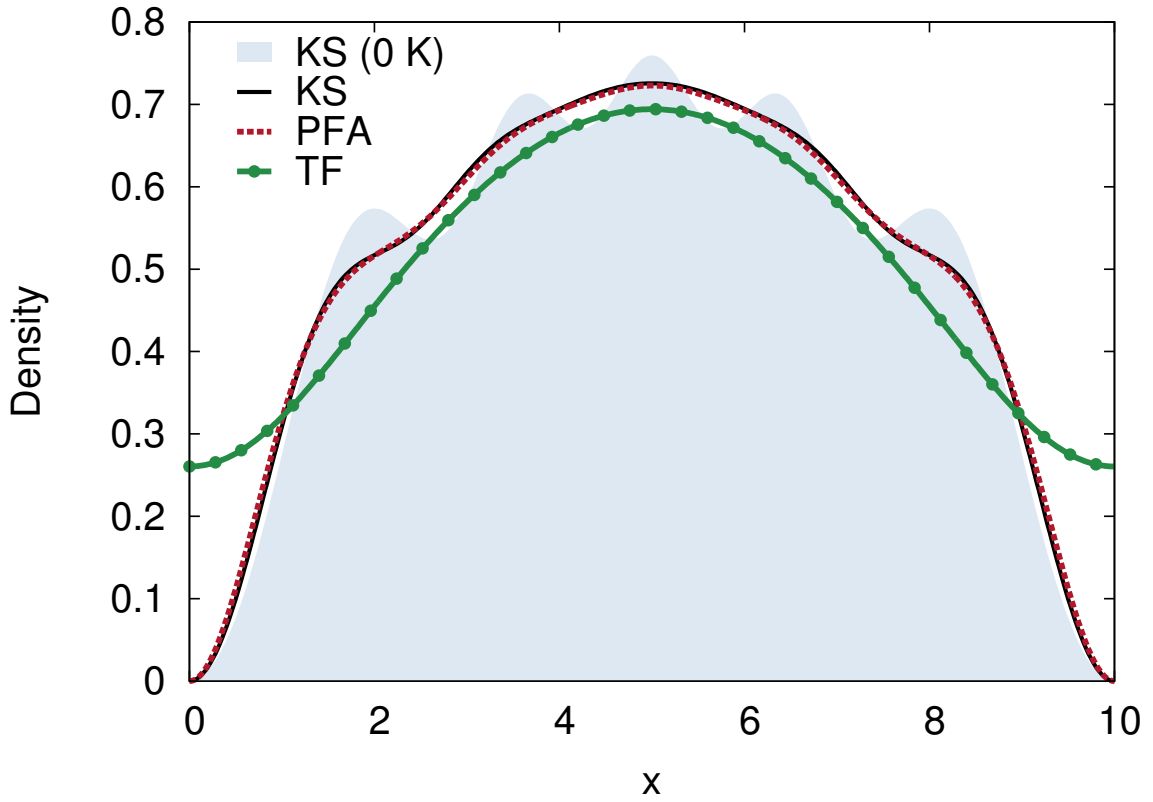
- uses path integral formalism and semiclassical method
- assumes stationary phase approximation
- breaks infinite number of classical paths into four primitive classes
- first primitive generates Thomas-Fermi
- all others produce quantum density oscillations

A. Cangi, E. Sim, and K. Burke, in preparation (2014).

Enforcing limits and boundary conditions

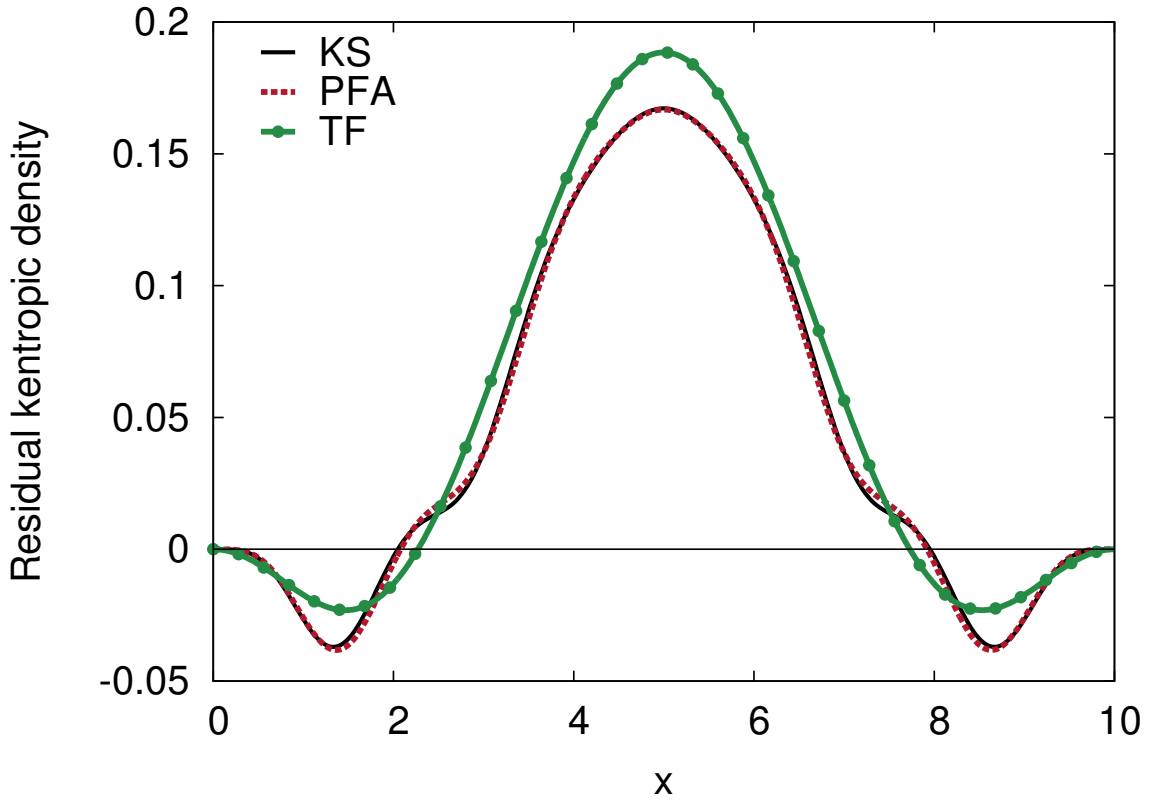
- infinite sum converges faster at higher temperatures
- only first term needed at WDM conditions
- two regions: edges and center
- use Gaussian interpolation between ZT and FT TF for first primitive
- ad hoc stitching $\approx$ boundary-layer theory

Density PFA Captures Density Oscillations



Density of five particles in $v(x) = -2\sin^2(\pi x/10)$, $L = 10$, $\Lambda = 1/(\beta\mu) = 0.93$. Exact (solid black curve), PFA (dashed red curve), TF (dotted green curve).

Residual kentropic density



Residual kentropic density of five particles in $v(x) = -2\sin^2(\pi x/10)$, $L = 10$, $\Lambda = 1/(\beta\mu) = 0.93$. Exact (solid black curve), PFA (dashed red curve), TF (dotted green curve).

Residual Kentropy

Λ	$K^{\beta}_{\mathrm{S},0}$	$\Delta K^{\beta}_{\mathrm{S}}$	error $\times 10^2$	
			TF	PFA
0.31	3.87	0.461	7.16	-0.28
0.47	3.76	0.459	7.91	-0.31
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0.78	3.50	0.452	8.61	-0.30
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2.02	1.92	0.414	7.13	-1.61
2.48	1.25	0.396	6.34	-1.86
2.94	0.58	0.378	5.64	-1.80
3.41	-0.10	0.360	5.04	-1.45

Future Work

- boundary-layer theory for density approximation
- reconcile complex integration with path integral approximation
- extension to realistic systems
- investigate classes of potentials
- classical continuum limit

Summary

- derived PFT for thermal ensembles
- equation for the kentropy solely dependent on finite-temperature density
- derived and implemented a highly accurate density approximation in one dimension
- performed PFT calculations in the WDM regime

Advantages:

- highly accurate
- orbital free
- systematic
- converges more quickly as temperatures rise
- maintains accuracy at low temperatures

Acknowledgments

- Kieron
- Attila Cangi
- U.S. Department of Energy Computational Science Graduate Fellowship and The Krell Institute