LLNL-PRES-683261

Improving Density Functional Theory (for Warm Dense Matter)

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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 (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)

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- UC Irvine Chemistry Department and Electronic Structure Group
- Krell Institute and the DOE CSGF (DE-FG02-97ER25308)

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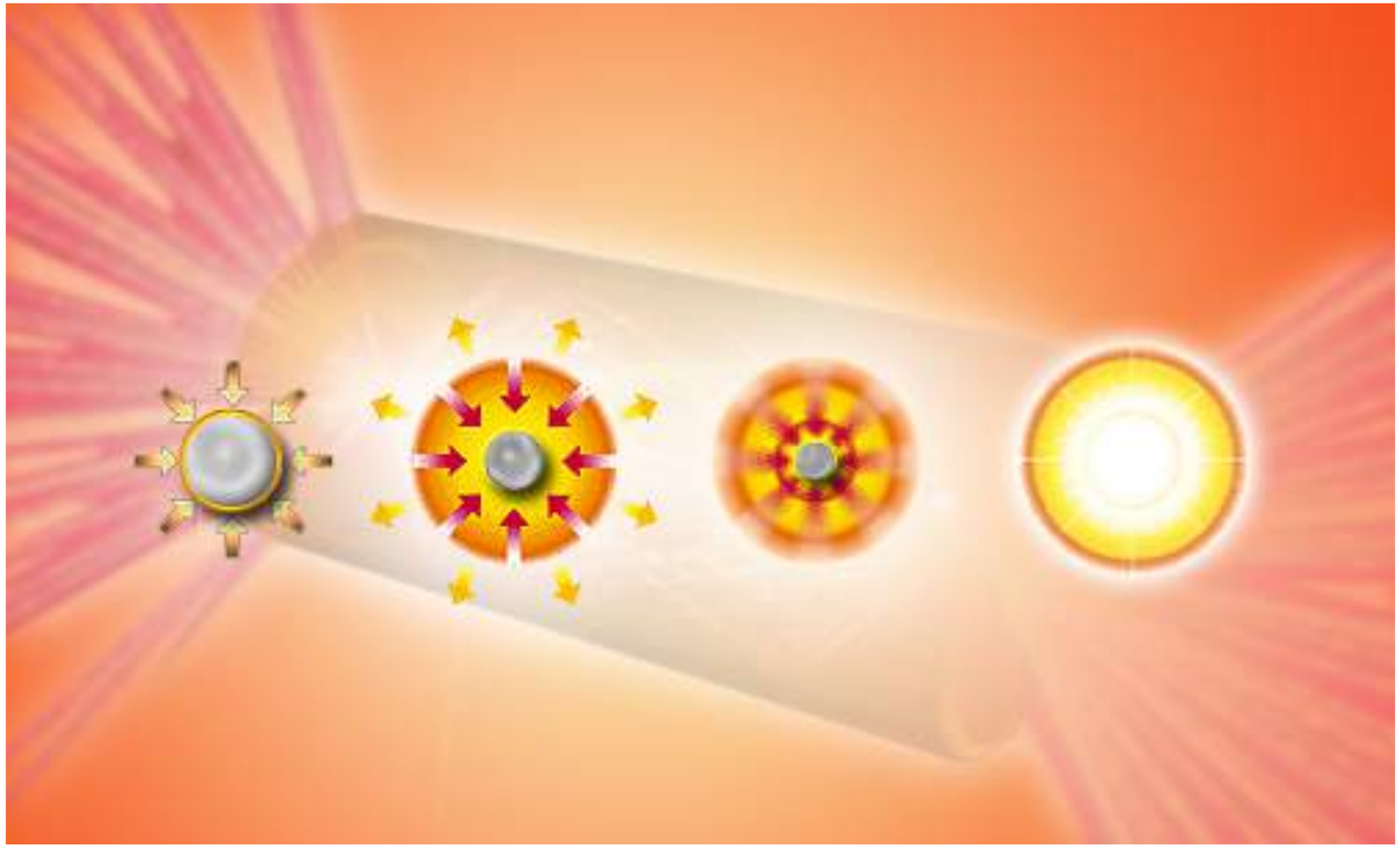
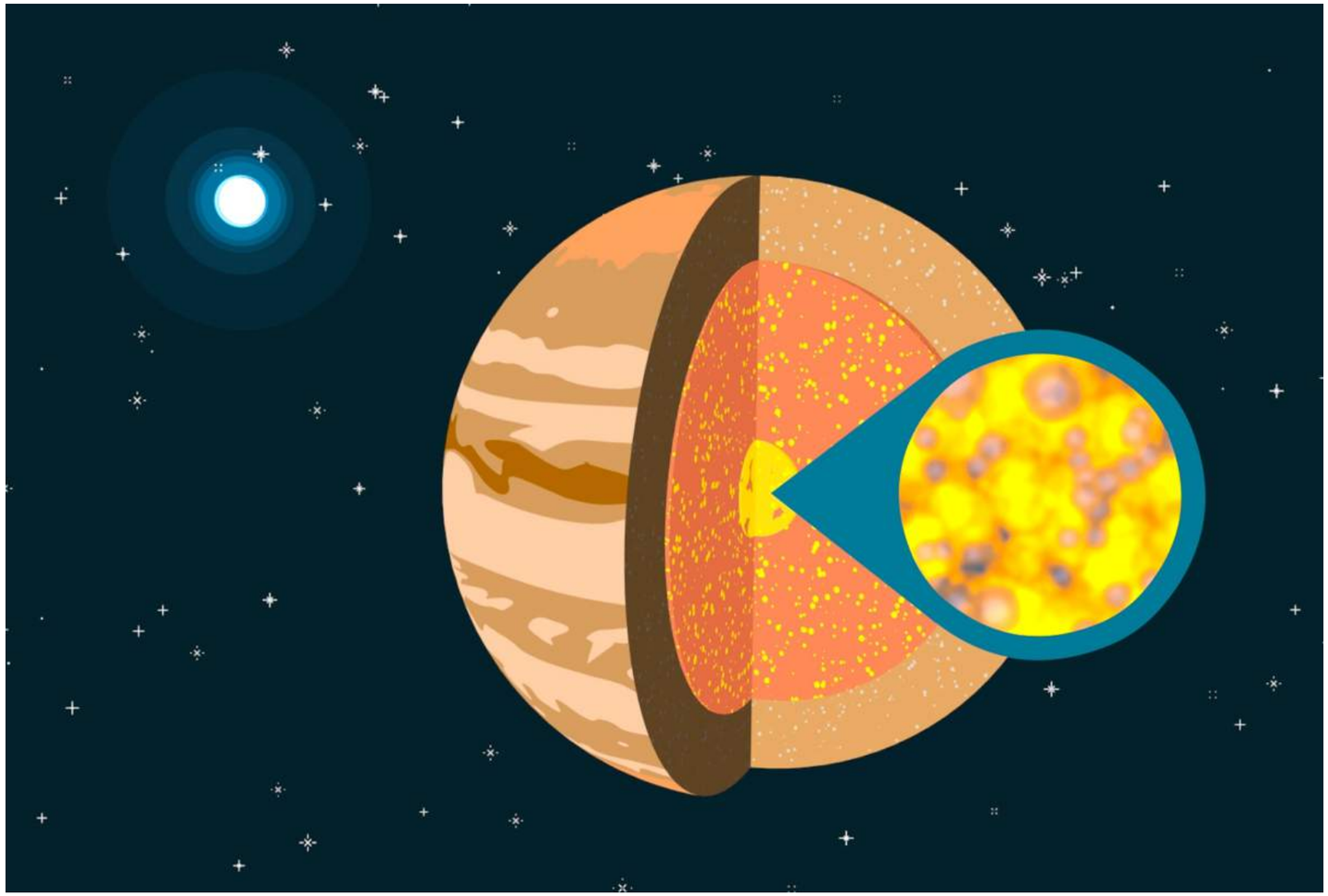
Inertial Confinement Fusion



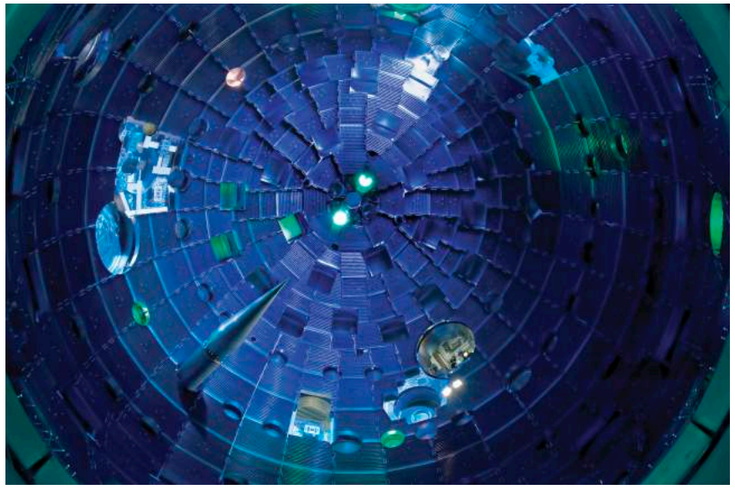
http://newscenter.lbl.gov/2011/10/19/part-i-energy-stars-earth/

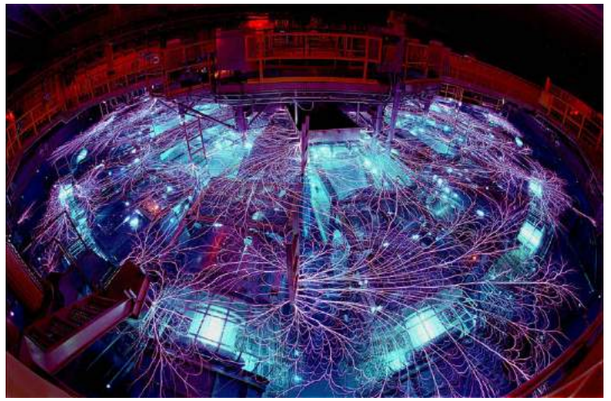
“Warm” Dense Planetary Cores

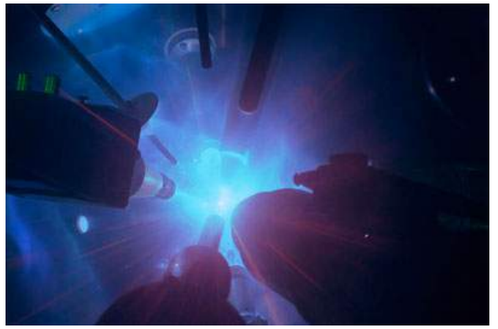


Promotional Materials, SLAC, Stanford University (2015)

Warm Dense Matter

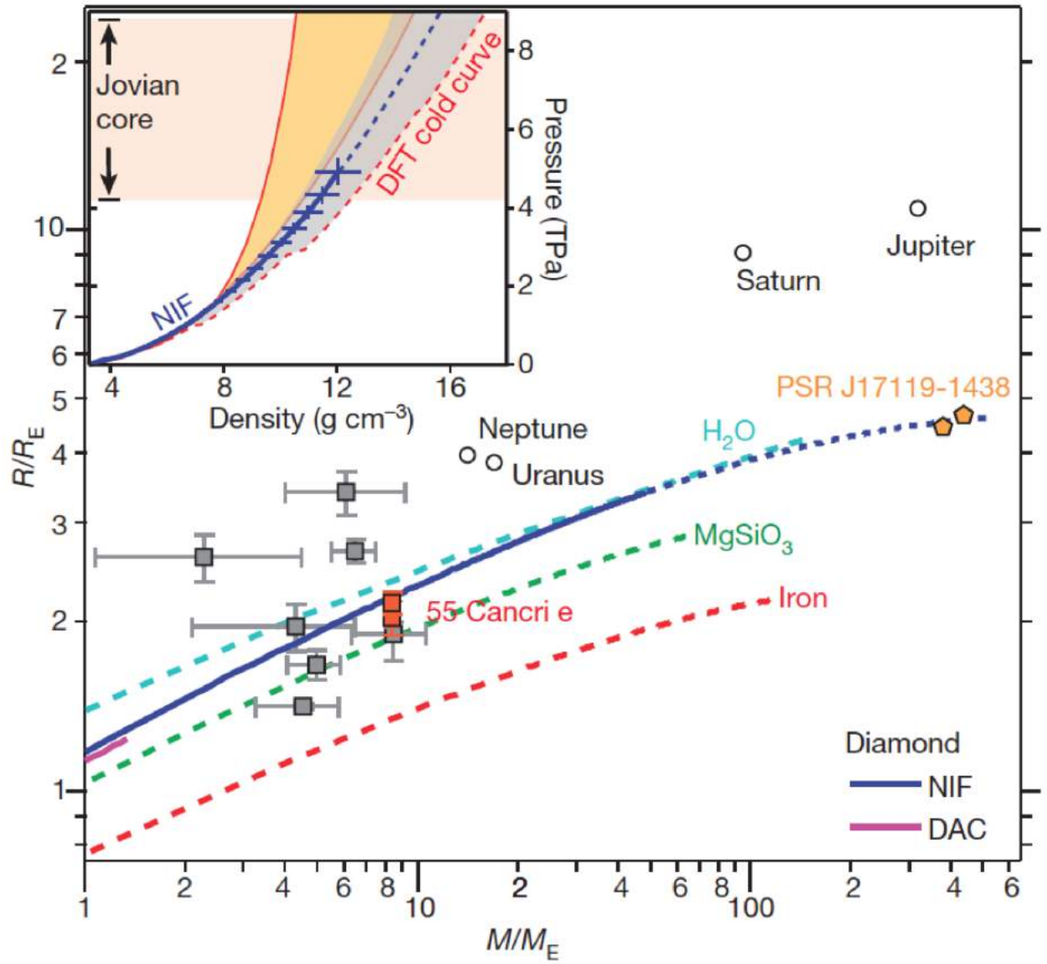






LLNL, SNL, LBL, Rochester U websites

Experimental Probes of Planetary Conditions



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

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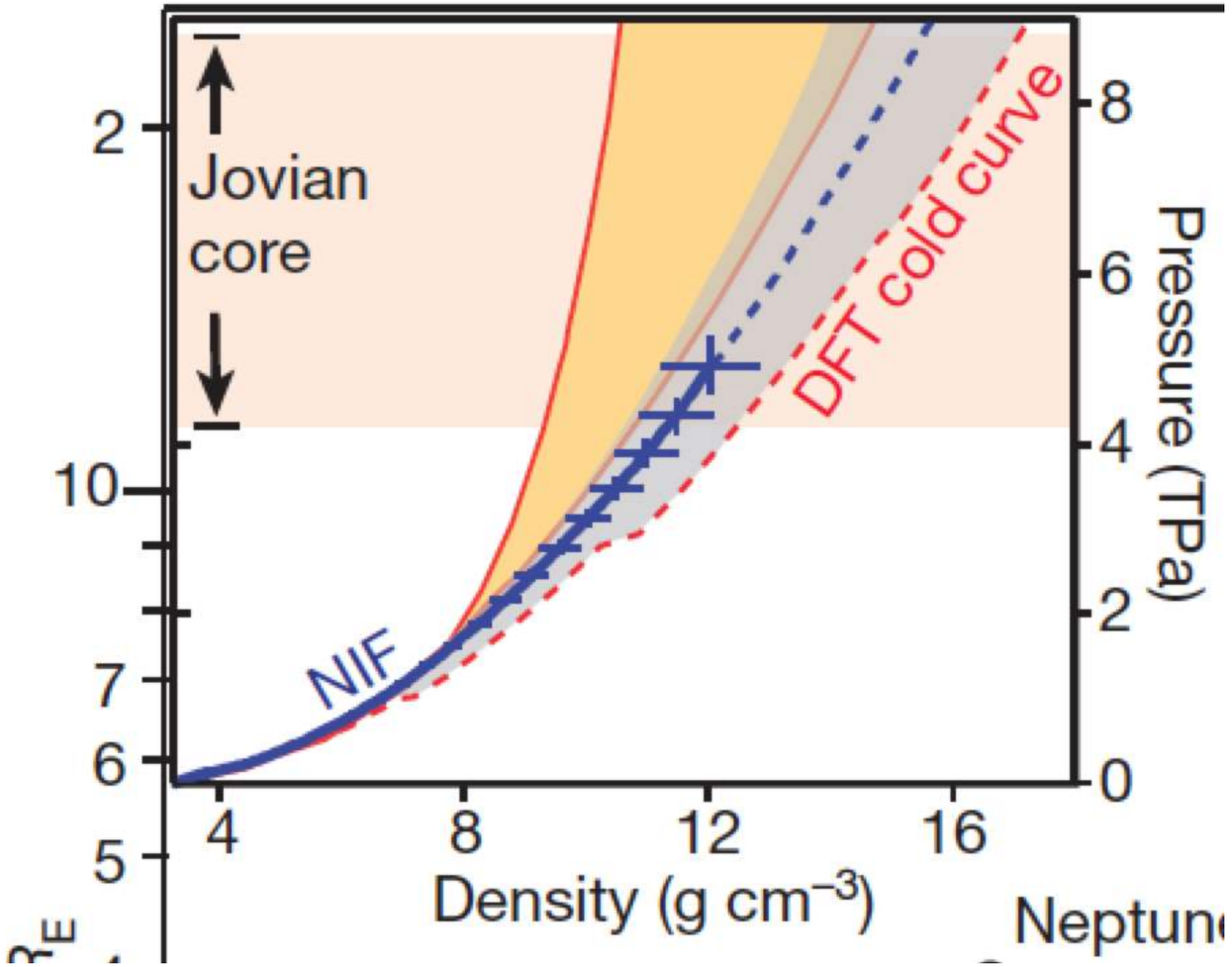
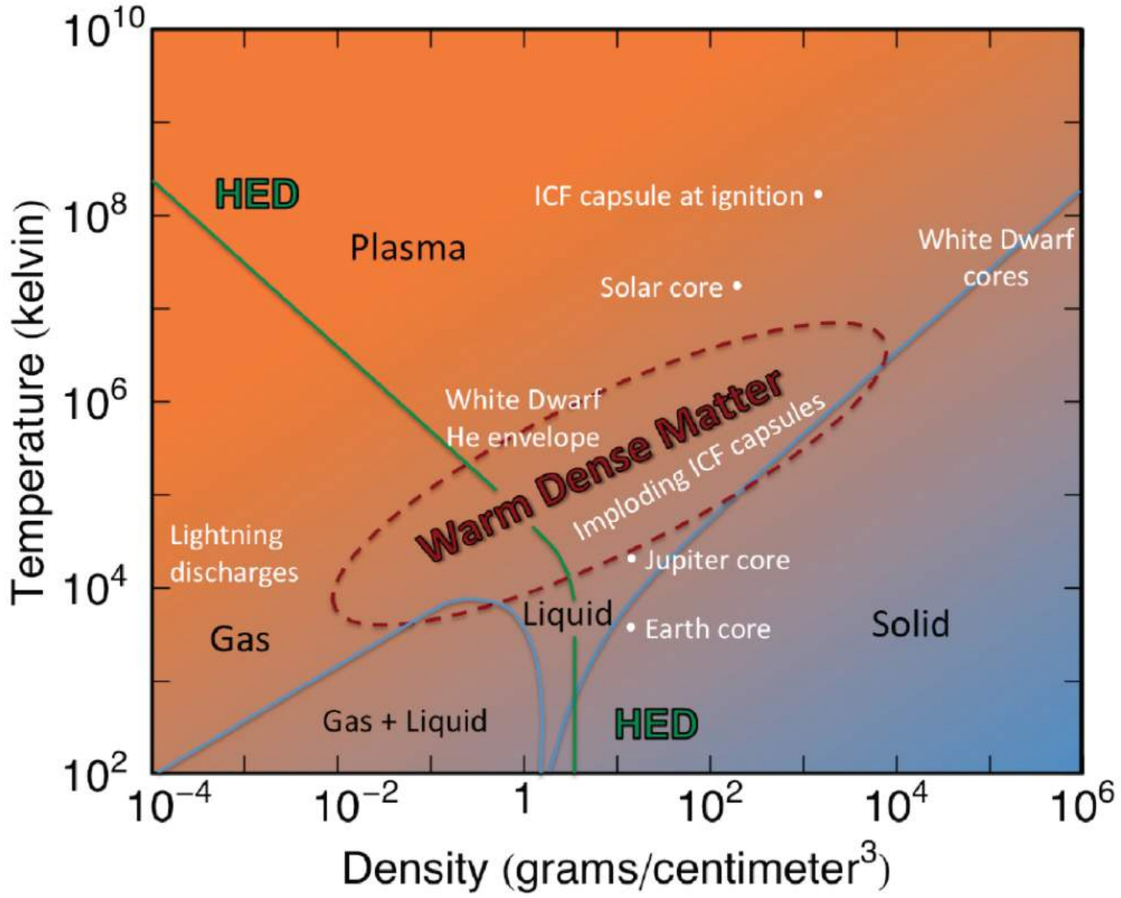


R.F. Smith et al., Nature **511** (2014) 330-333

The Malfunction Junction



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

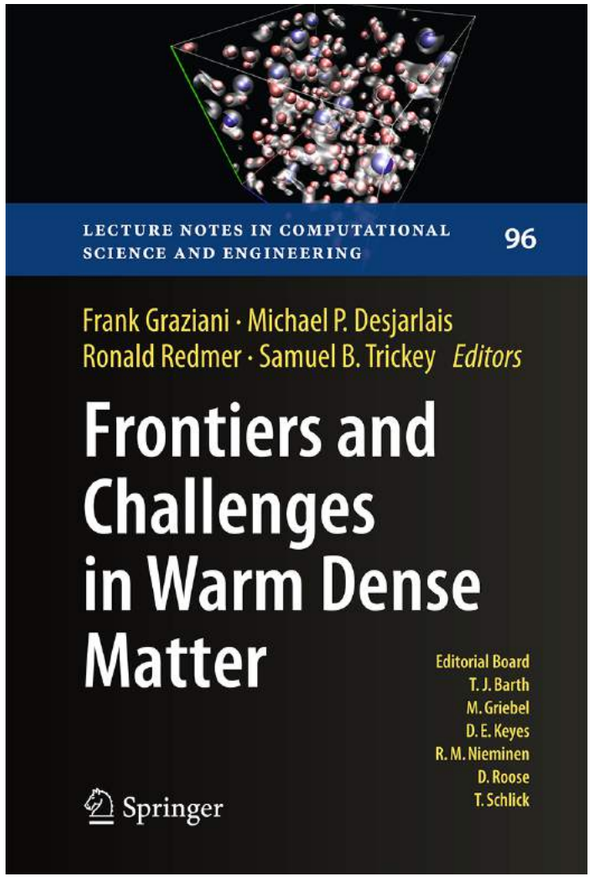
Quantum and Classical

Simulations are difficult!

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

Simulations are important!

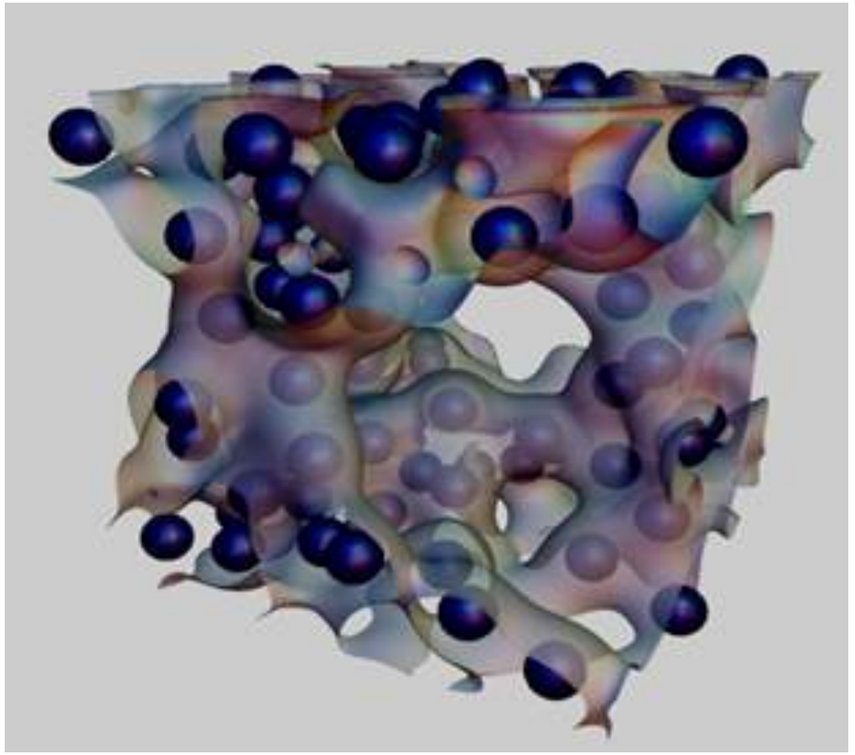
- Data used in core structure modeling, experimental design
- Experiments hard, expensive, limited



Quantum Molecular Dynamics

Popular, but...

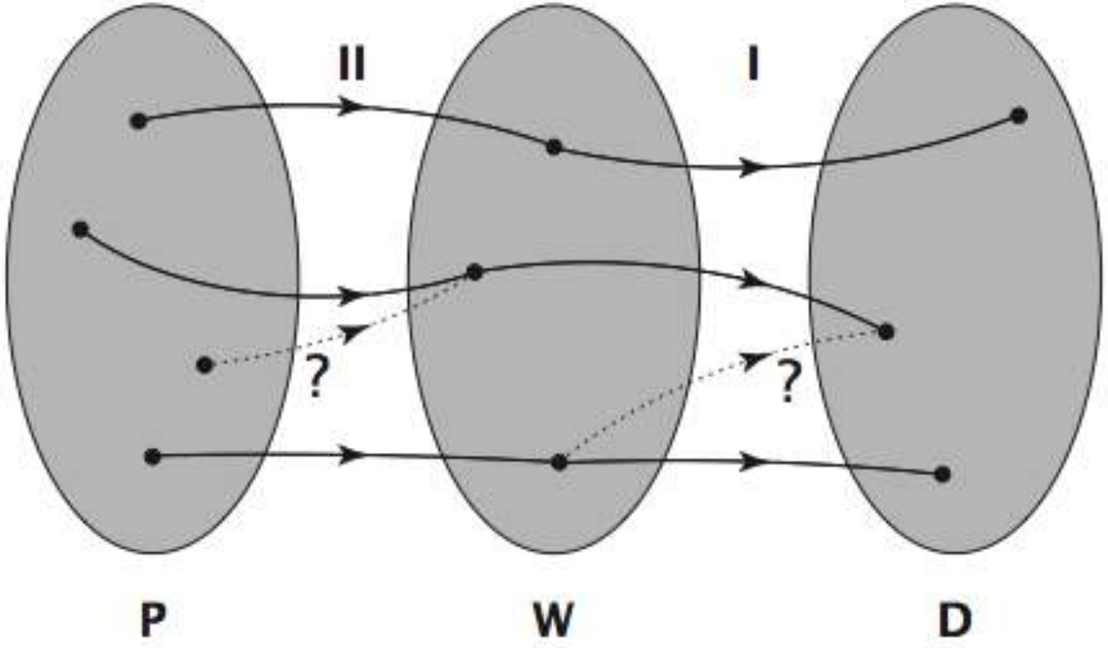
- no explicit temperature dependence in electrons
- computationally expensive
- need TD electrons for response
- no energy transfer between electrons and ions



IPAM, UCLA

Hohenberg-Kohn (1964)

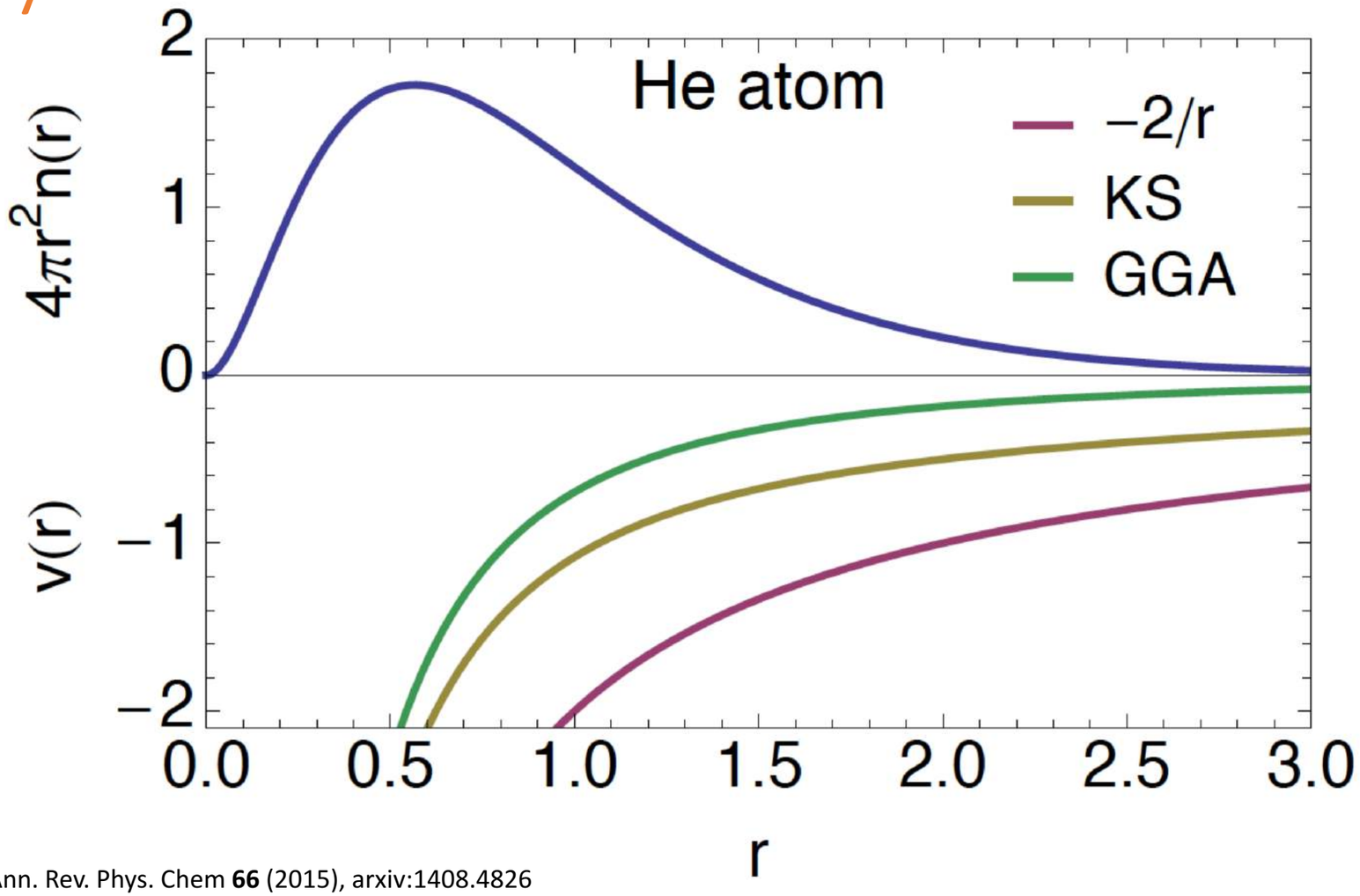
1. One-to-one correspondence between potential and density



2. Energy is a functional of the density; universal piece and system-specific piece

P. Hohenberg and W. Kohn, Phys. Rev., 136, 3B (1964)
Pribram-Jones et al., “Thermal DFT in Context,” *Frontiers and Challenges in Warm Dense Matter*, Springer Publishing (2014) 25-60

Non-interacting electrons replicate interacting density



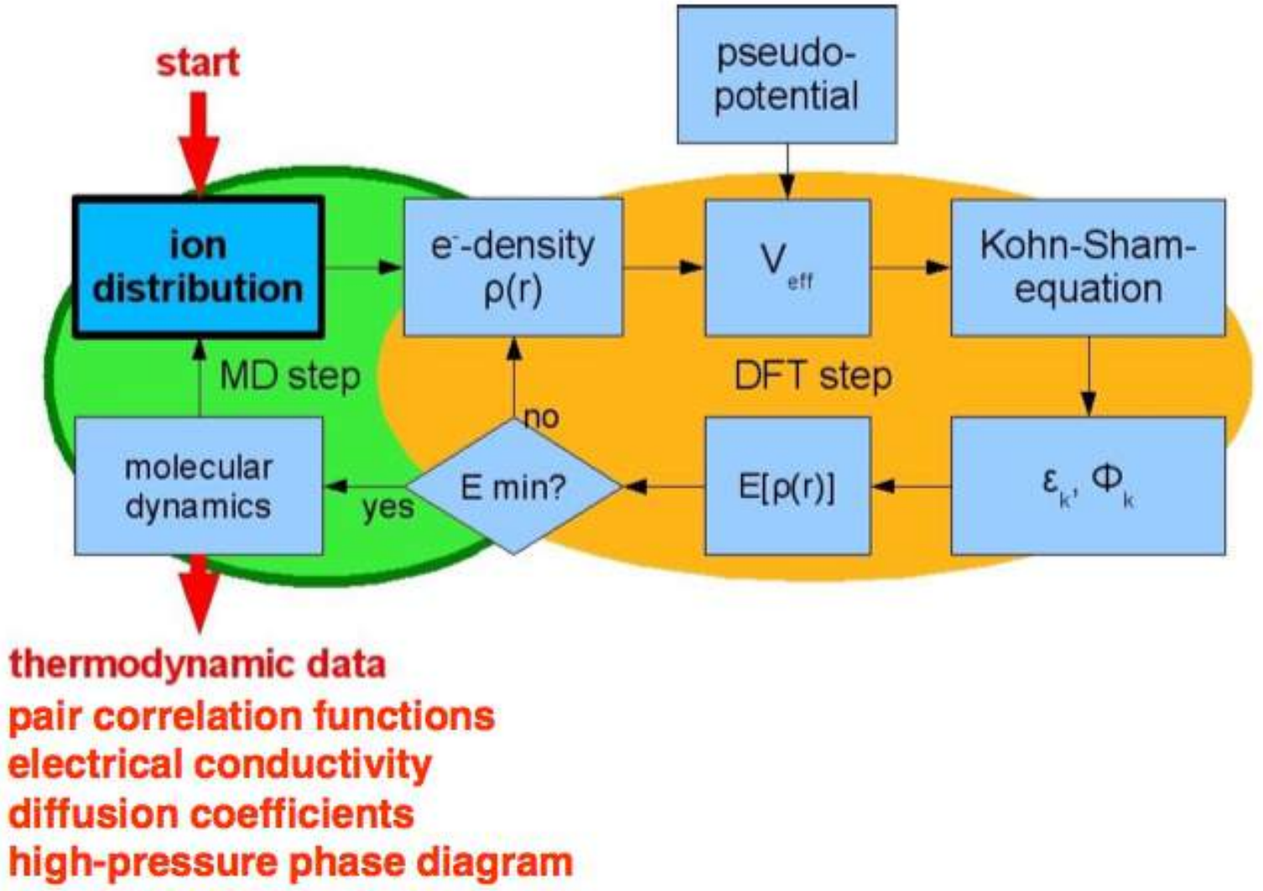
Pribram-Jones et al., Ann. Rev. Phys. Chem **66** (2015), arxiv:1408.4826

Kohn-Sham and Mermin (1965)

- **Mapping:** KS maps interacting system to non-interacting system
- **Approximations:** KS writes down local density approximation (LDA) and its finite-temperature version
- **Thermal ensembles:** Mermin showed HK holds for finite temperatures

W. Kohn and L. Sham, Phys. Rev. **140** 4A (1965).

The Bottleneck



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

How can DFT for WDM be improved?

- **Path I:** **Temperature-dependent approximations** with predictable errors and correct limiting behaviors (equilibrium and response properties)

- **Path II:** Rigorous framework for **temperature-dependent, time-dependent DFT** (response properties)

- **Path III:** **Improved computational efficiency** for the DFT steps in WDM simulations (equilibrium properties, possibly response)

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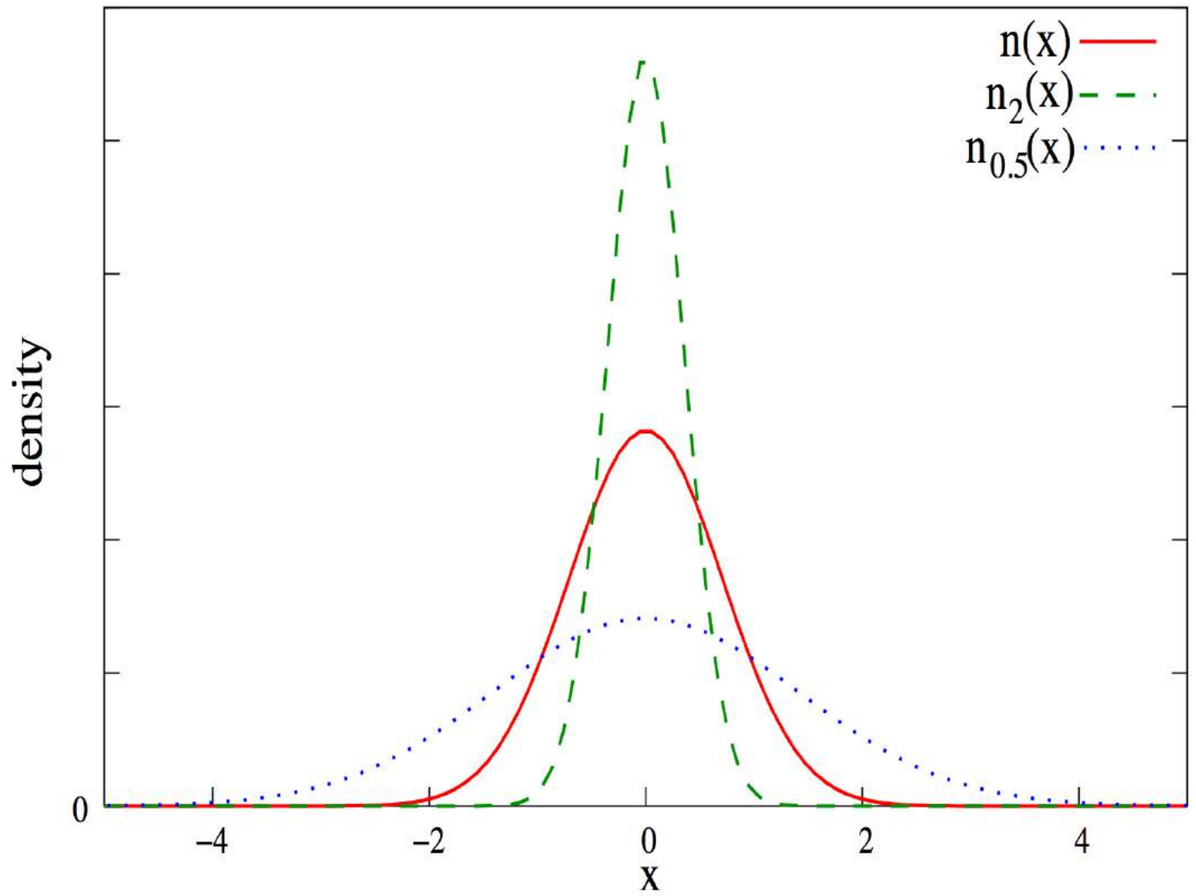
Pribram-Jones et al., “Thermal DFT in Context,” *Frontiers and Challenges in Warm Dense Matter*, Springer Publishing (2014) 25-60

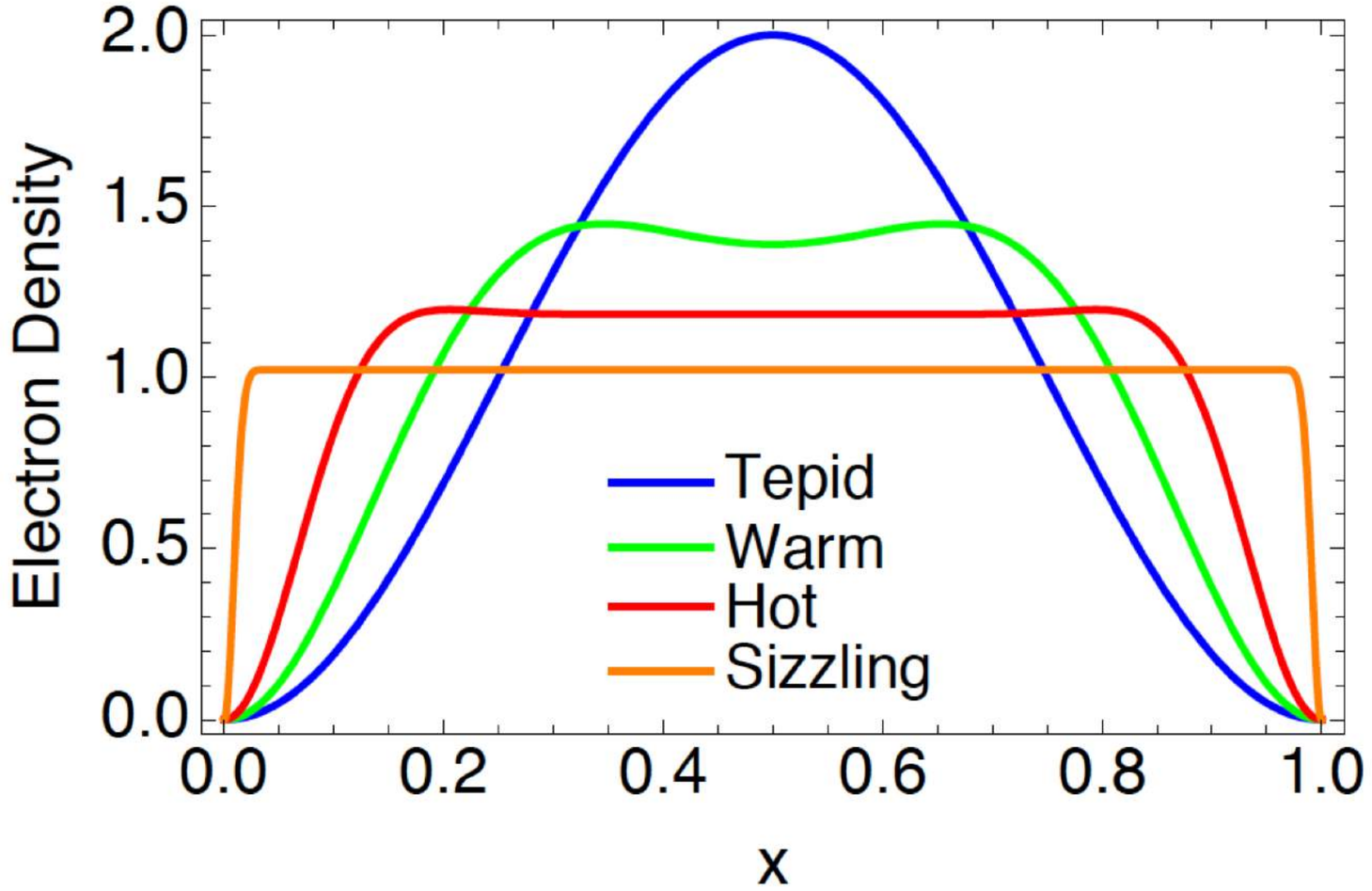
Building Temperature-Dependent DFT Approximations from TDDFT

Scaling in DFT

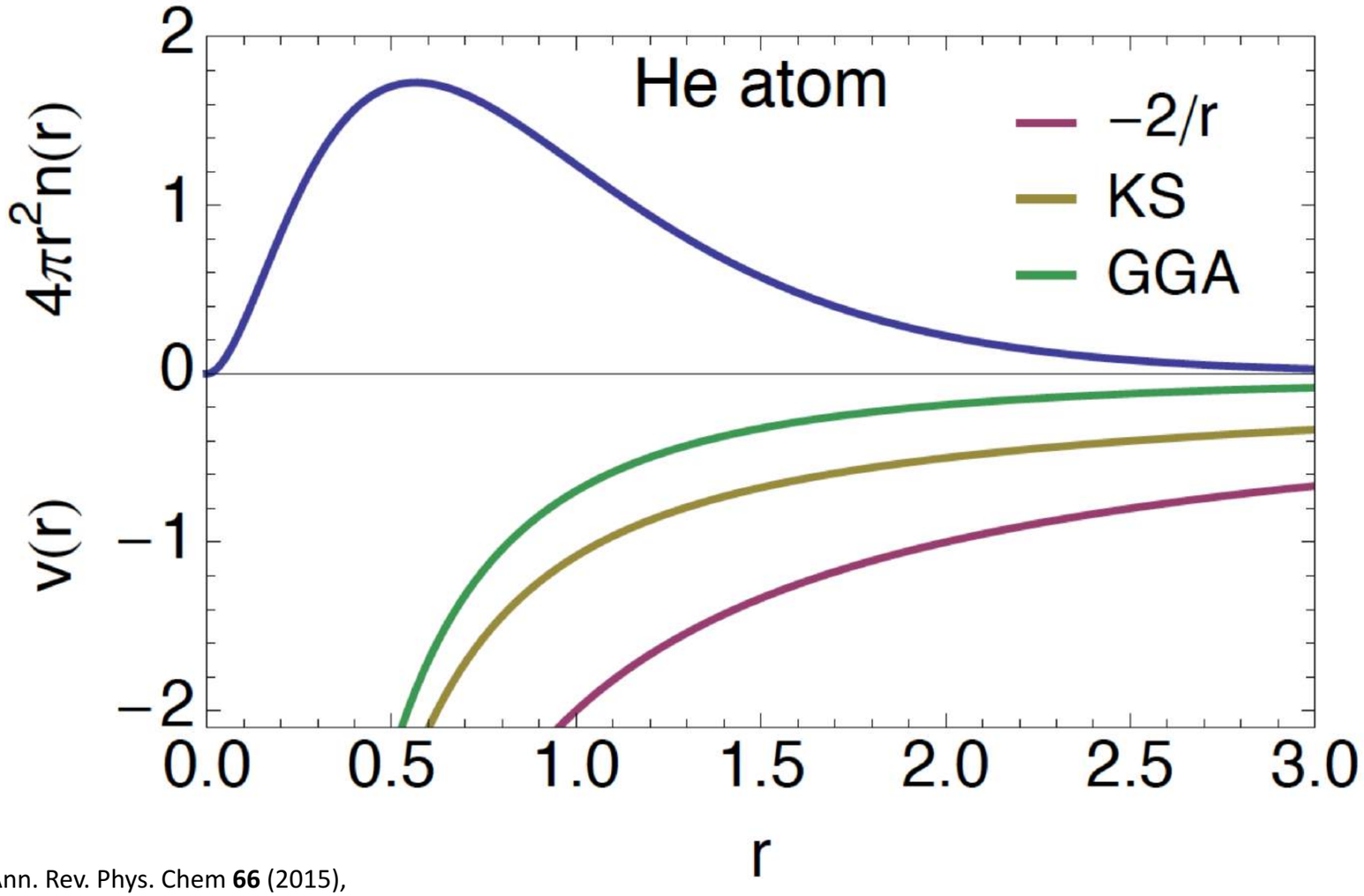


Takeyce K. Whittingham, Dissertation, Rutgers, The State University of New Jersey (2004)

Heating Things Up in DFT



Turn the Knob



Pribram-Jones et al., Ann. Rev. Phys. Chem **66** (2015),

Coordinate, Interaction, Temperature Scaling

Combine finite-temperature ACF…

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

…with coupling constant-coordinate-temperature scaling.

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

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

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

- 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)

TDDFT for WDM

- Runge-Gross (1984): one-to-one mapping between time-dependent density and potential (given initial state)
- KS still maps interacting to non-interacting system
- Common: linear response and ground-state approximations
- Stopping power and optical response calculations at Sandia, Lawrence Livermore, and Los Alamos
- New proof derived for linear response of thermal ensembles, thermal fluctuation-dissipation theorem…

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

An "Application"

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

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

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

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)

Exchange-Correlation Approximations

Exact expression, as long as exact thermal kernel is used:

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

Approximations to thermal XC kernel:

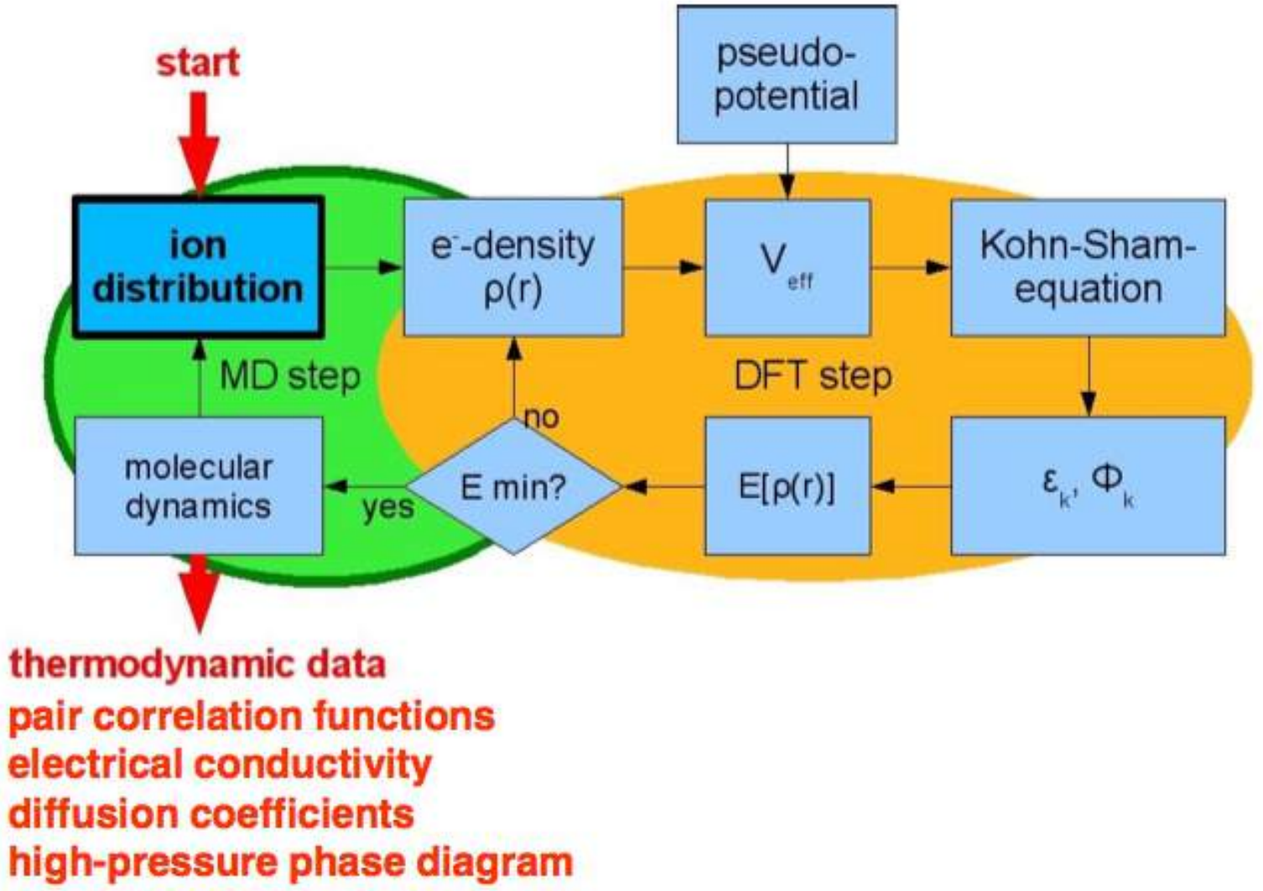
- $f_{\mathrm{XC}}^{\tau}(12)$ = 0 → thermal RPA
- $f_{\mathrm{XC}}^{\tau,\mathrm{thALDA}}[n](\mathbf{r},\mathbf{r}',\omega)=\left.\frac{d^2 a_{\mathrm{XC}}^{\tau,\mathrm{unif}}(n)}{d^2 n}\right|_{n(\mathbf{r})}\delta(\mathbf{r}-\mathbf{r}')$

→ approximate $A_{\mathrm{XC}}^{\tau}[n]$

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

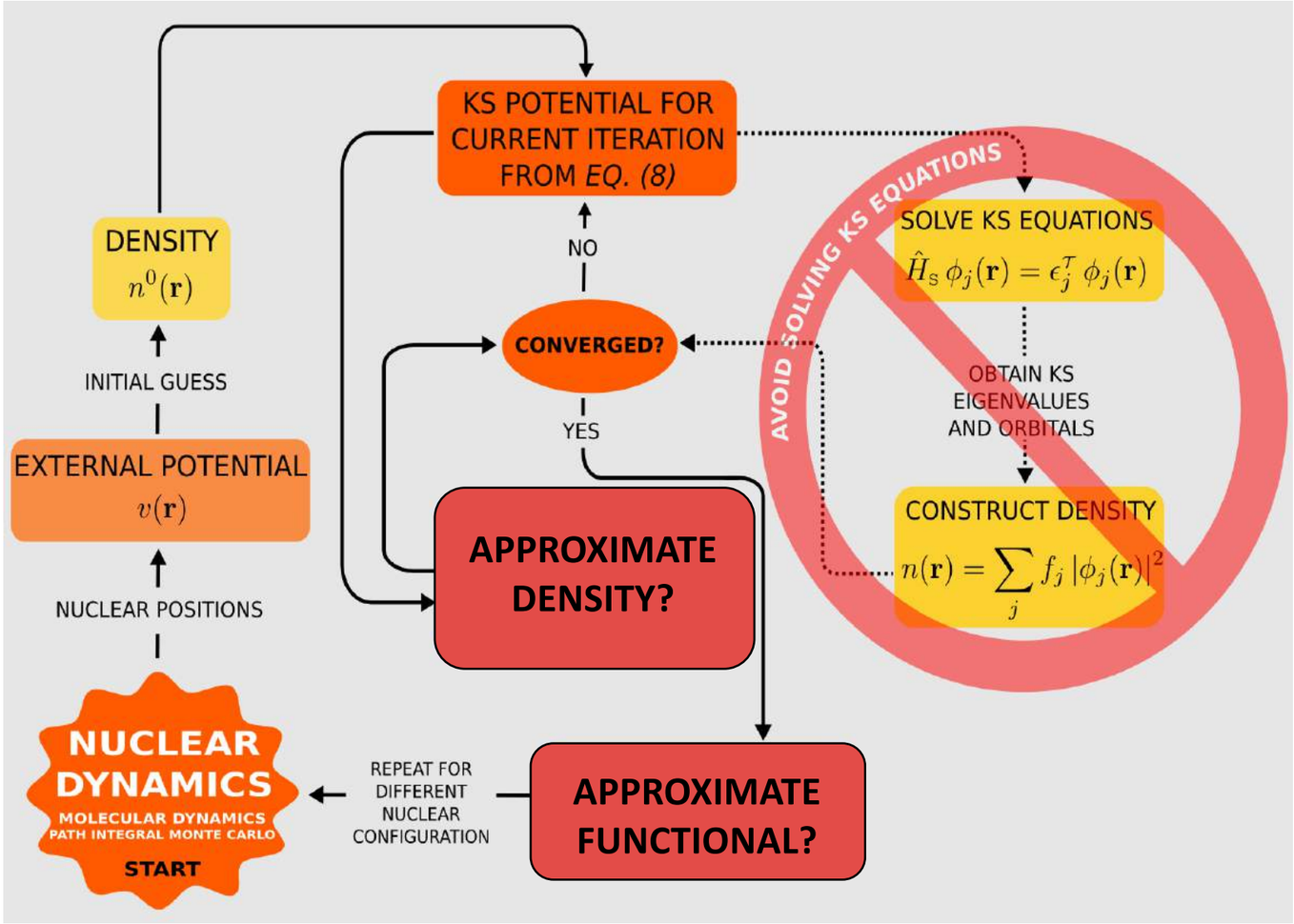
Avoiding Mermin-Kohn-Sham in WDM Simulations

The Bottleneck



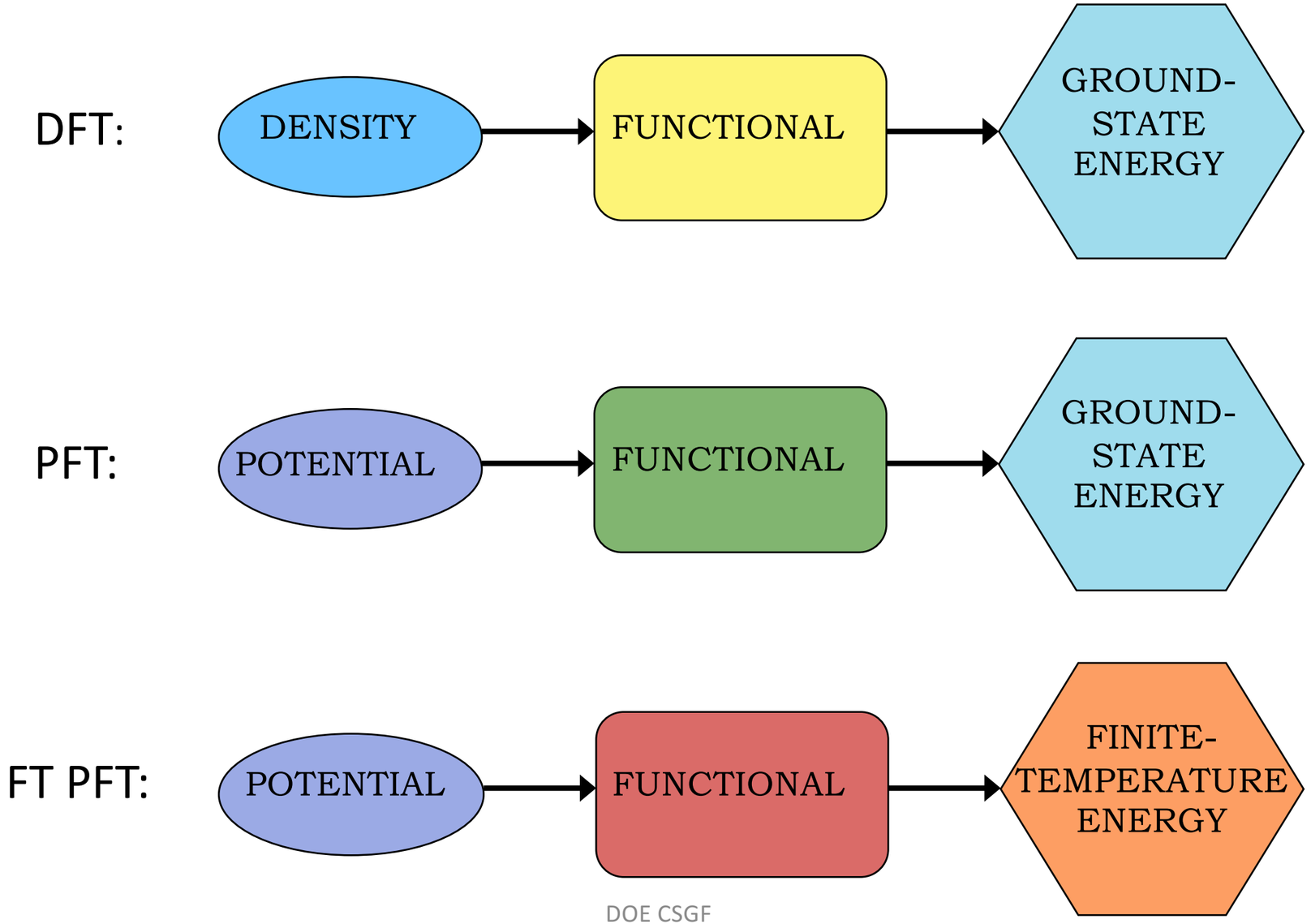
Adapted from http://hifweb.lbl.gov/public/BeamHEDP2010, original by W. Lorenzen

Zoom in on electronic step…



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

PFT: An Exact Formulation



The PFT Idea

For zero or finite temperature:

Step 1 Derive exact F[v].

Step 2 Approximate n[v].

Step 3 Join steps 1 and 2, so that approximating density *automatically* generates F[n[v]].

This scheme introduces no additional approximations beyond that in the density approximation.

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

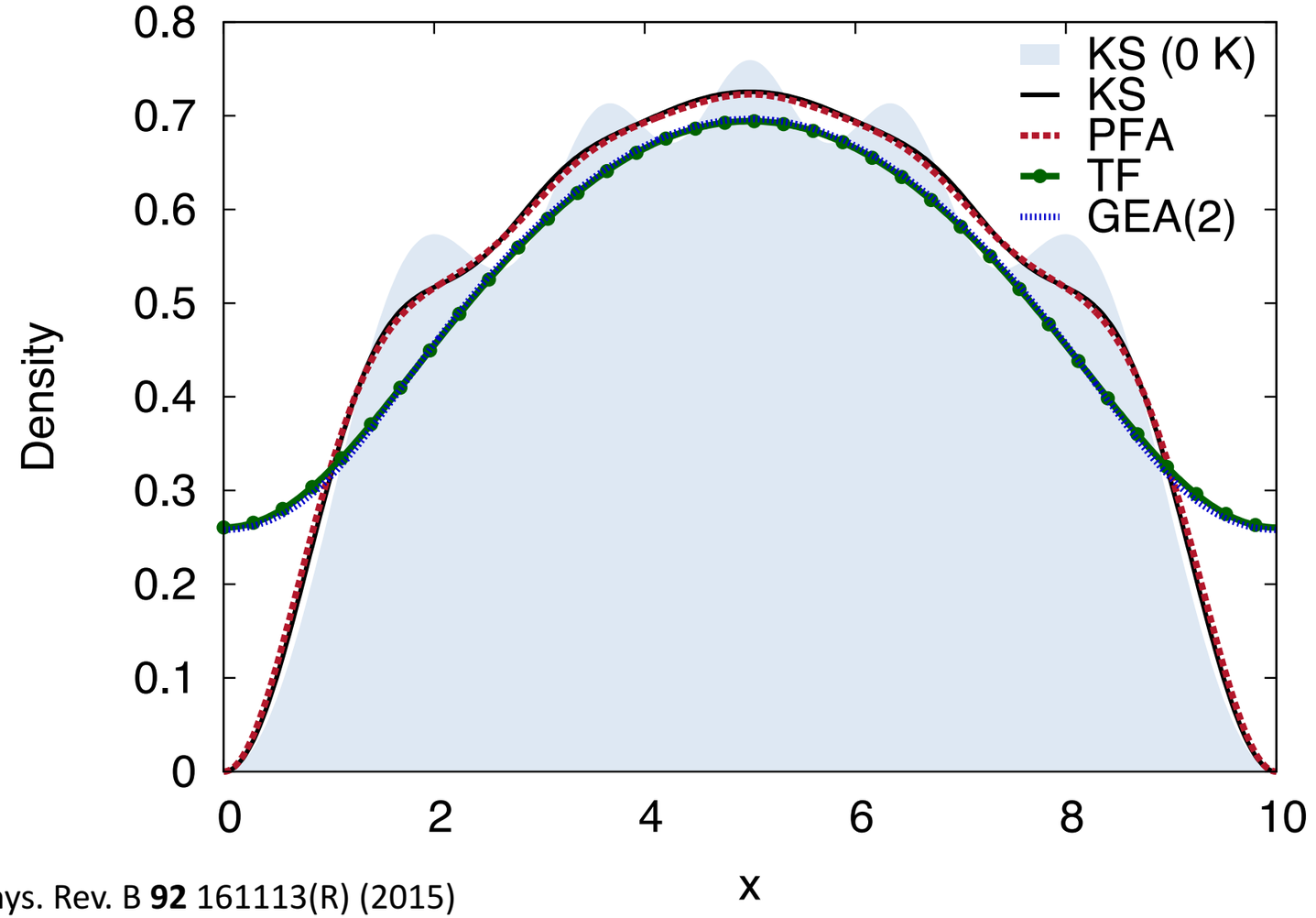
v_s : external potential of non-interacting system

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

bar: integral over the coupling constant

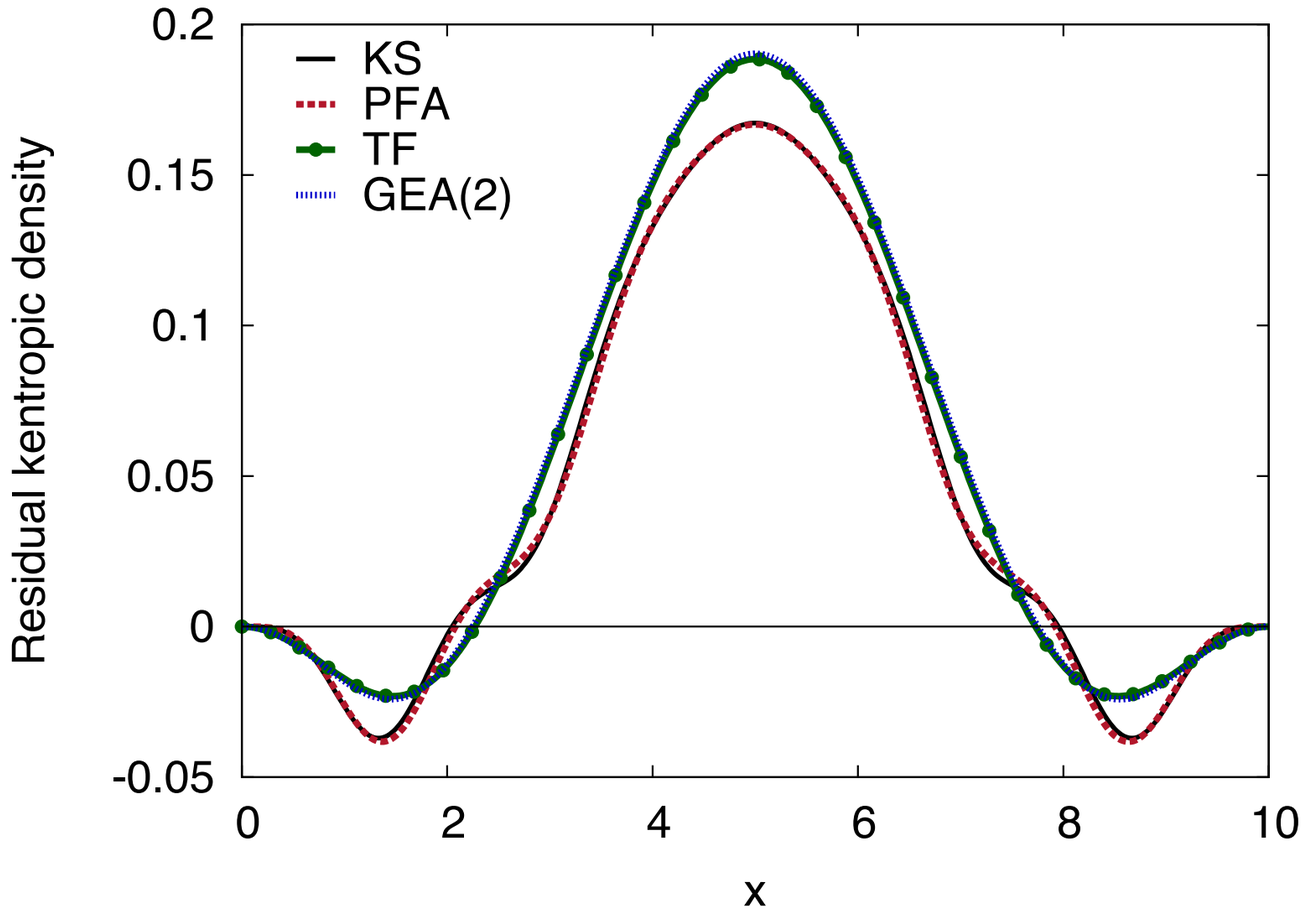
A. Cangi and APJ, Phys. Rev. B **92** 161113(R) (2015)

Highly Accurate Density



A. Cangi and APJ, Phys. Rev. B **92** 161113(R) (2015)

Not Reliant on Error Cancellations



A. Cangi and APJ, Phys. Rev. B **92** 161113(R) (2015)

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 APJ, Phys. Rev. B **92** 161113(R) (2015)

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A. Cangi and APJ, Phys. Rev. B **92** 161113(R) (2015)

Continuing and Future Work

FT PFT:

- Test demonstration approximation with more complicated potentials
- Extend approximations to realistic systems (turning points, 3d)
- Implement in combination with molecular dynamics
- Asymptotic analysis of finite-temperature electronic systems
- Use semiclassical methods for time-dependent systems

Thermal DFT and TDDFT:

- Use thermal kernel to generate FT XC approximations
- Derive finite-temperature exact conditions
- Extend linear response proof to vector potentials
- Examine accuracy of adiabatic and ground-state approximations

Origin Stories

Origin Stories

BE BOLD

Personal Acknowledgments

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Summary

- Exact conditions relate components of the correlation free energy
- Thermal connection formula: adiabatic connection via temperature
- XC free energy approximations can be generated from thermal kernel
- Exact formulation of coupling constant non-interacting kentropy
- Demonstration of FT-PFT using semiclassical density approximation

For further information

1. FT TDDFT: APJ, P.E. Grabowski, and K. Burke, Phys. Rev. Lett. **116**, 233001 (2016)
2. TCF: APJ and K. Burke, Phys. Rev. B **93**, 205140 (2016)
3. FT PFT: A. Cangi and APJ, Phys. Rev. B **92** 161113(R) (2015)

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