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Title: An average atom model with self-consistent ion-distribution

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# **An average atom model with self-consistent ion distribution**

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**Charles Starrett**  
**LANL**

# Overview

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- **Modeling warm and hot dense matter**
  - Brief introduction
- **The new model**
  - General overview of approach
  - Key equations
- **First numerical results**
  - Pair distribution functions for Al, Fe and H
- **Summary and outlook**

# Warm and hot dense matter

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- **Typical temperatures and densities:**

- few eV, few times solid density

- **Important physics:**

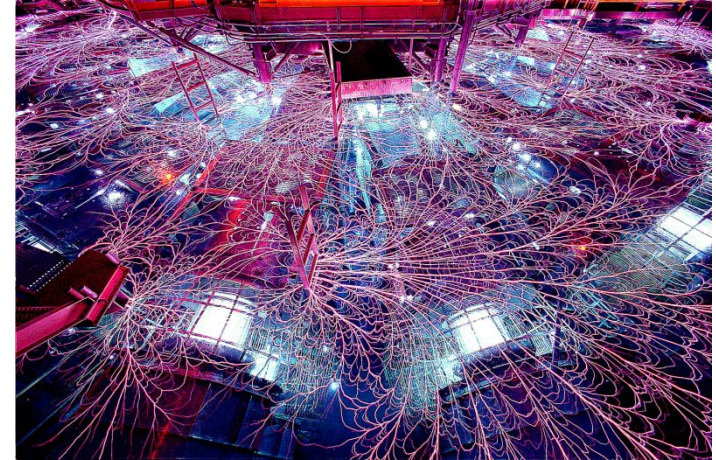
- Electron-ion coupling
- ion-ion coupling
- electron-electron coupling
- quantum or semi-classical electrons
- classical ions

- **Applications**

- Interiors of Jupiter-like planets
- Outer layers of white dwarfs
- Inertial confinement fusion (NIF)

- **Experiments**

- XANES (e.g. Mancic *et al*, PRL (2010))
- XRTS (Glenzer & Redmer, RMP (2009))
- Shock compression (Z-machine, OMEGA, LULI)



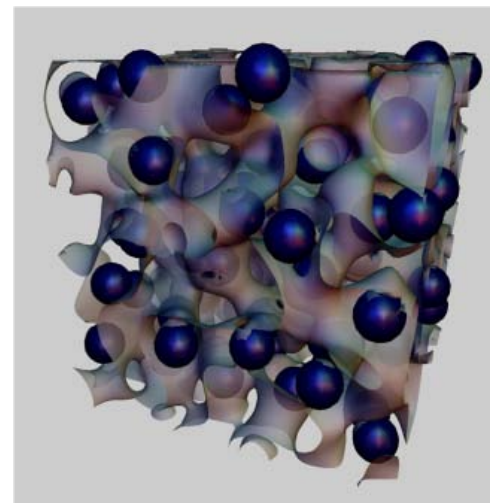
[www.sandia.gov](http://www.sandia.gov): Z-machine

# Current models

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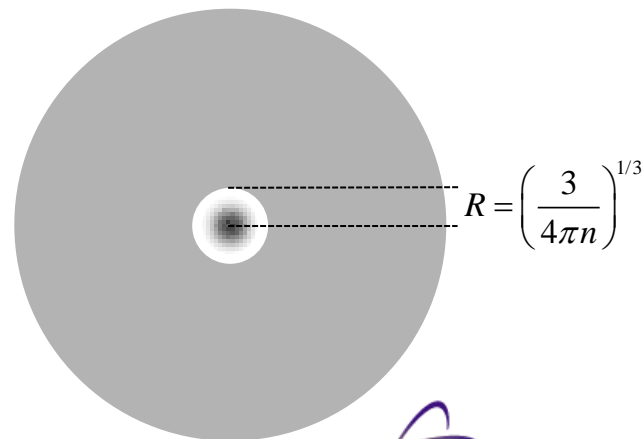
- **Molecular dynamics (Classical nuclei):**
  - Quantum electrons (Schrodinger equation)
  - Semi-Classical electrons (Thomas Fermi equation)

**Powerful but expensive with some limitations**



- **Average atom: atom in a spherically averaged plasma**
  - Quantum or semi-classical (Thomas-Fermi model)
  - Many variations
  - Often ion structure is imposed

**More approximate but inexpensive**

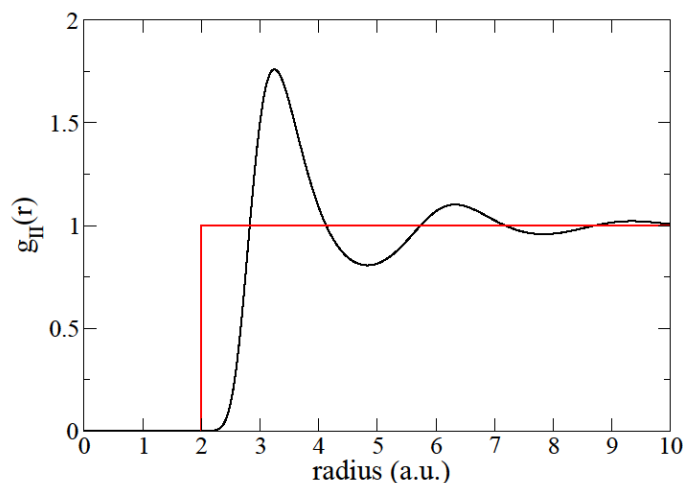


# Our Goal

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- Fill the gap between *ab initio* methods and Average atom
  - Determine electronic and ionic structure simultaneously
  - Relatively inexpensive model  
(spherical symmetry about a central ion)

Single model from melting temperature to very high temperatures : EOS, Transport properties



# General approach and key concepts

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- **General formulation:**

- Write down formally exact expression for Grand Potential  $\Omega$ :  
non-interacting + interacting terms
- Use functional Taylor expansion of interacting terms
- Introduce **Average Atom** approximation  $\rightarrow$  **spherical symmetry**
- **Minimize  $\Omega$**  w.r.t. particle densities (electron and ion): **Density functional theory**

- **For input of  $Z$ ,  $n_i^0$  and  $T$ , get the plasma properties by**

- Solving SE or TF for electronic structure
- Solving the (quantum) Ornstein-Zernike equations for ionic structure

# The Grand potential and DFT

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$$\Omega = f^{id} + f^{ex} - \int d\vec{r} n_I(\vec{r}) (\mu_I - V_I(\vec{r})) - \int d\vec{r} n_e(\vec{r}) (\mu_e - V_e(\vec{r}))$$

**DFT condition:**

$$\frac{\delta\Omega}{\delta n_e(\vec{r})} = 0$$

$$\frac{\delta\Omega}{\delta n_I(\vec{r})} = 0$$

$\mu$  : Chemical potential

$V(r)$  : External potential that couples to species  $I$  or  $e$

$f$  : Intrinsic free energy (non-interacting 'id' and interacting 'ex')



# Ideal terms: electrons

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$$f^{id} = f_e^{id} + f_I^{id}$$

Separate into electronic and ionic contributions

$$f_e^{id} = \int d\vec{r} \sum_{s \in \text{Bound}} \left[ g_s \psi_s^*(\vec{r}) \hat{T} \psi_s(\vec{r}) - TS(g_s) |\psi_s(\vec{r})|^2 \right]$$

Sum over Bound states

$$+ \int d\vec{r} \frac{2}{(2\pi)^3} \int d\vec{k} \left[ g_k \left( \psi_k^*(\vec{r}) \hat{T} \psi_k(\vec{r}) \right) - TS(g_k) \left( |\psi_k(\vec{r})|^2 \right) \right]$$

Integral over Continuum states

## Formally correct

- Ensures that all electrons are treated in the same way: essential to avoid problems with pressure ionization

# Ideal terms: ions

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$$f^{id} = f_e^{id} + f_I^{id}$$

Separate into electronic and ionic contributions

$$f_I^{id} = \frac{1}{\beta} \int d\vec{r} n_I(\vec{r}) \left( \ln \left| \Lambda^3 n_I(\vec{r}) \right| - 1 \right)$$

$\Lambda$  - Thermal wavelength of ions

**Formally correct**

- Easy to calculate

# Functional Taylor expansion of excess free energy

$$\begin{aligned} f^{ex} = & \mu_e^{ex} \int d\vec{r} \Delta n_e(r) + \mu_I^{ex} \int d\vec{r} \Delta n_I(r) \\ & - \frac{1}{\beta} \iint d\vec{r} d\vec{r}' C_{Ie}(|\vec{r} - \vec{r}'|) \Delta n_e(\vec{r}) \Delta n_I(\vec{r}') \quad \text{e}^- - \text{ion coupling} \\ & - \frac{1}{2\beta} \iint d\vec{r} d\vec{r}' C_{ee}(|\vec{r} - \vec{r}'|) \Delta n_e(\vec{r}) \Delta n_e(\vec{r}') \quad \text{e}^- - \text{e}^- \text{ coupling} \\ & - \frac{1}{2\beta} \iint d\vec{r} d\vec{r}' C_{II}(|\vec{r} - \vec{r}'|) \Delta n_I(\vec{r}) \Delta n_I(\vec{r}') \quad \text{ion} - \text{ion coupling} \\ & + \text{higher order terms} \end{aligned}$$

$$\Delta n_e(r) = n_e(r) - n_e^0$$

$$\Delta n_I(r) = n_I(r) - n_I^0$$

$(n_e^0, n_I^0)$  Reference state with no external potential

# Functional Taylor expansion of excess free energy

$$f^{ex} = \mu_e^{ex} \int d\vec{r} \Delta n_e(r) + \mu_I^{ex} \int d\vec{r} \Delta n_I(r)$$

$$- \frac{1}{\beta} \iint d\vec{r} d\vec{r}' C_{Ie}(|\vec{r} - \vec{r}'|) \Delta n_e(\vec{r}) \Delta n_I(\vec{r}') \quad \text{e}^- - \text{ion coupling}$$

$$- \frac{1}{2\beta} \iint d\vec{r} d\vec{r}' C_{ee}(|\vec{r} - \vec{r}'|) \Delta n_e(\vec{r}) \Delta n_e(\vec{r}') \quad \text{e}^- - \text{e}^- \text{ coupling}$$

$$- \frac{1}{2\beta} \iint d\vec{r} d\vec{r}' C_{II}(|\vec{r} - \vec{r}'|) \Delta n_I(\vec{r}) \Delta n_I(\vec{r}') \quad \text{ion} - \text{ion coupling}$$

$C_{ij}$  **Direct correlation functions:** Can be written in terms of Coulomb interaction + exchange and correlations

$$C_{ij}(k) = -\beta V_{ij}^C(k) (1 - G_{ij}(k))$$

↑  
**Coulomb**

↑  
**Local field correction (LFC)**

# Average atom approximation

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Fix a nucleus of charge  $Z$  at the origin

- With  $C_{ij}$ 's  $\rightarrow$  spherical symmetry

$$V_I(\vec{r}) \rightarrow \frac{ZZ^*}{r}$$

$$V_e(\vec{r}) \rightarrow -\frac{Z}{r}$$

Non-central ions are treated in an spherically averaged sense through the functional Taylor expansion

# Minimization → potentials

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$$\frac{\delta\Omega}{\delta n_e(\vec{r})} = 0 \quad \rightarrow \text{Nucleus-electron interaction potential}$$

$$\frac{\delta\Omega}{\delta n_I(\vec{r})} = 0 \quad \rightarrow \text{Nucleus-ion interaction potential}$$

To determine e<sup>-</sup> chemical potential:  $\mu_e^{id}$

Require model to be thermodynamically consistent:

$$P_{\text{Virial}} = P_{\text{Thermo}}$$

# Summary: closed set of equations

Potentials:

$$V_{Ne}(r) = -\frac{Z}{r} - \frac{1}{\beta} \int d\vec{r}' C_{Ie}(|\vec{r} - \vec{r}'|) \Delta n_I(r') - \frac{1}{\beta} \int d\vec{r}' C_{ee}(|\vec{r} - \vec{r}'|) \Delta n_e(r')$$

$$V_{NI}(r) = \frac{ZZ^*}{r} - \frac{1}{\beta} \int d\vec{r}' C_{Ie}(|\vec{r} - \vec{r}'|) \Delta n_e(r') - \frac{1}{\beta} \int d\vec{r}' C_{II}(|\vec{r} - \vec{r}'|) \Delta n_I(r')$$

Particle densities:

$$n_I(r) = n_I^0 \exp(-\beta V_{NI}(r))$$

Schrodinger equation →

$$n_e(r) = \sum_{s \in \text{Bound}} g_s(\mu_e^{id}) |\psi_s(\vec{r})|^2 + \frac{2}{(2\pi)^3} \int d\vec{k} g_k(\mu_e^{id}) |\psi_k(\vec{r})|^2$$

Chemical potential:

$$\int d\vec{r} [n_I(r) V_{NI}(r)] = 0$$

Recovers **TF**, **TFD** and **VAAQP** upon application of some simplifications

Full model requires  
**Local Field Corrections**

# Local Field Corrections

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$$C_{ij}(k) = -\beta V_{ij}^C(k) (1 - G_{ij}(k))$$

  
Coulomb

  
Local field correction (LFC)



# Two component plasma model

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- **Mixture of classical ions and quantum electrons**

- Analog of classical one-component plasma (OCP), but electrons and ions interact

- **Quantum Ornstein-Zernike relations (Chihara (1991))**

$$h_{II}(k) = C_{II}(k) + n_I^0 C_{II}(k) h_{II}(k) + n_e^0 C_{Ie}(k) h_{Ie}(k)$$
$$h_{Ie}(k) = -\frac{\chi_{ee}^{id}}{n_e^0 \beta} \left[ C_{Ie}(k) + n_I^0 C_{Ie}(k) h_{II}(k) + n_e^0 C_{ee}(k) h_{Ie}(k) \right]$$

To Solve: need three closure relations

1. ***Electron-electron: closed with the jellium model***
2. ***Ion-ion: closed in the HNC approximation (or with bridge function)***
3. ***Electron-ion: use Perrot's neutral pseudo-atom (Perrot 1990)***

# Perrot's neutral pseudo-atom

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Get full electron density for the full average atom model potential

$$V_{Ne}(r) = -\frac{Z}{r} - \frac{1}{\beta} \int d\vec{r}' C_{Ie}(|\vec{r} - \vec{r}'|) \Delta n_I(r') - \frac{1}{\beta} \int d\vec{r}' C_{ee}(|\vec{r} - \vec{r}'|) \Delta n_e(r')$$

→  $n_e(r)$

Get electron density for the same potential but without the central nucleus term

$$V_{Ne}^{ext}(r) = -\frac{1}{\beta} \int d\vec{r}' C_{Ie}(|\vec{r} - \vec{r}'|) \Delta n_I(r') - \frac{1}{\beta} \int d\vec{r}' C_{ee}(|\vec{r} - \vec{r}'|) \Delta n_e^{ext}(r')$$

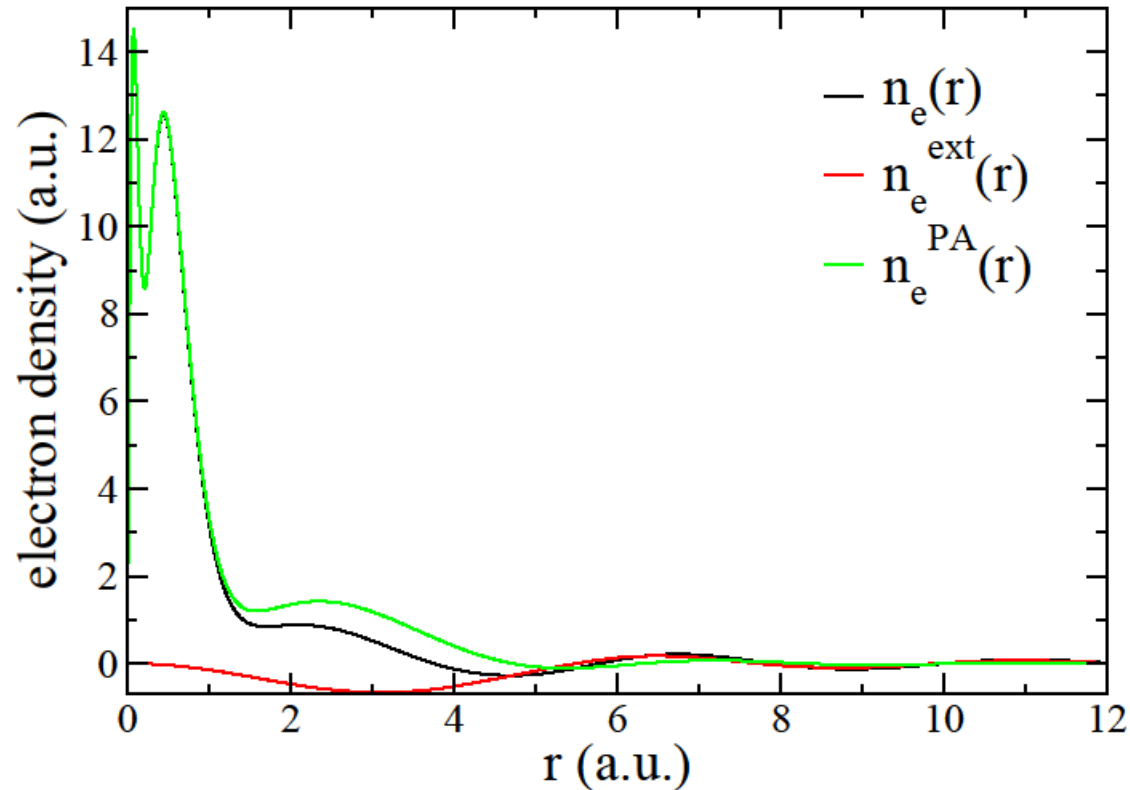
→  $n_e^{ext}(r)$

Define e<sup>-</sup> density of the  
Pseudo-Atom:

$$n_e^{PA}(r) = n_e(r) - n_e^{ext}(r)$$

# Neutral pseudo-atom example

Aluminum at solid density (2.7g/cm<sup>3</sup>) and 1eV



# Electron-ion closure relation

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Use pseudo-atom density to define a screening charge by removing “bound states”

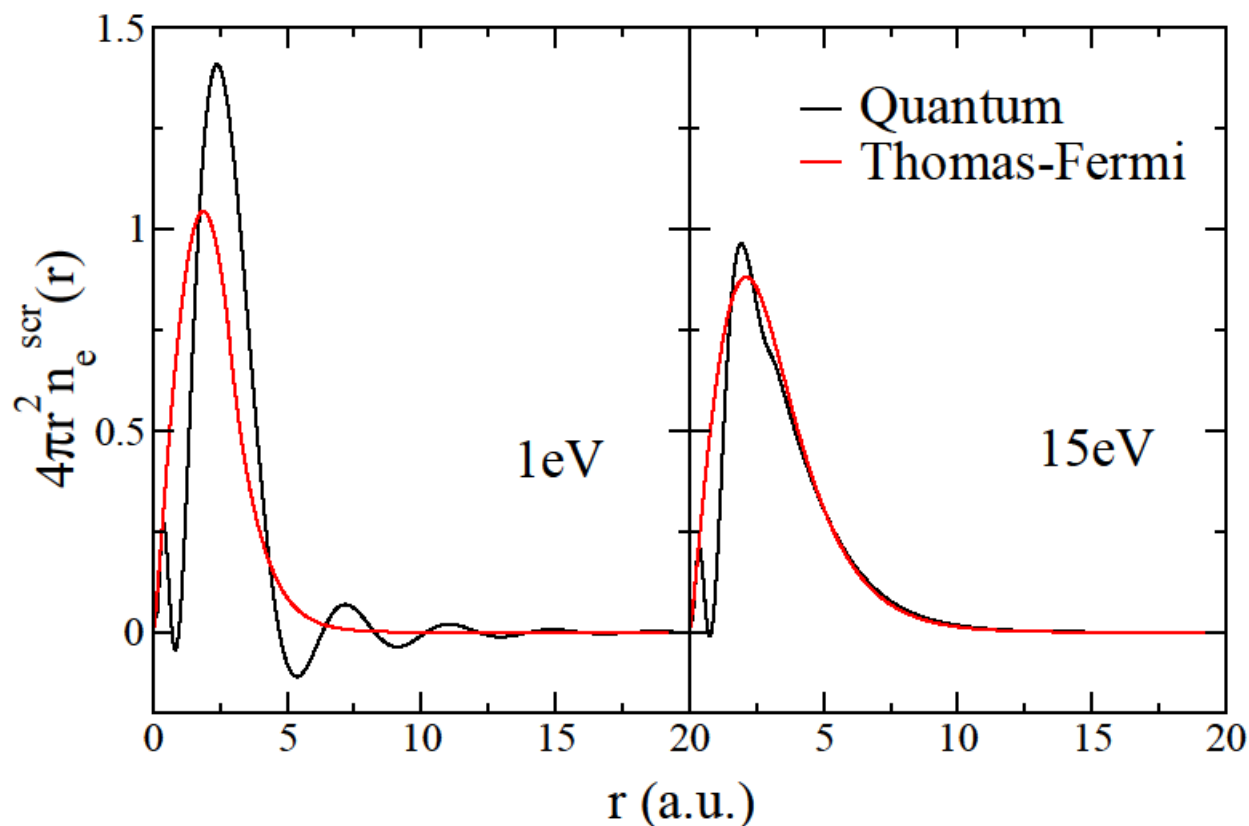
$$n_e^{scr}(r) = n_e^{PA}(r) - n_e^{bound}(r)$$

Close quantum Ornstein-Zernike relations:

$$n_e^0 h_{Ie}(k) = n_e^{scr}(k) S_{II}(k)$$

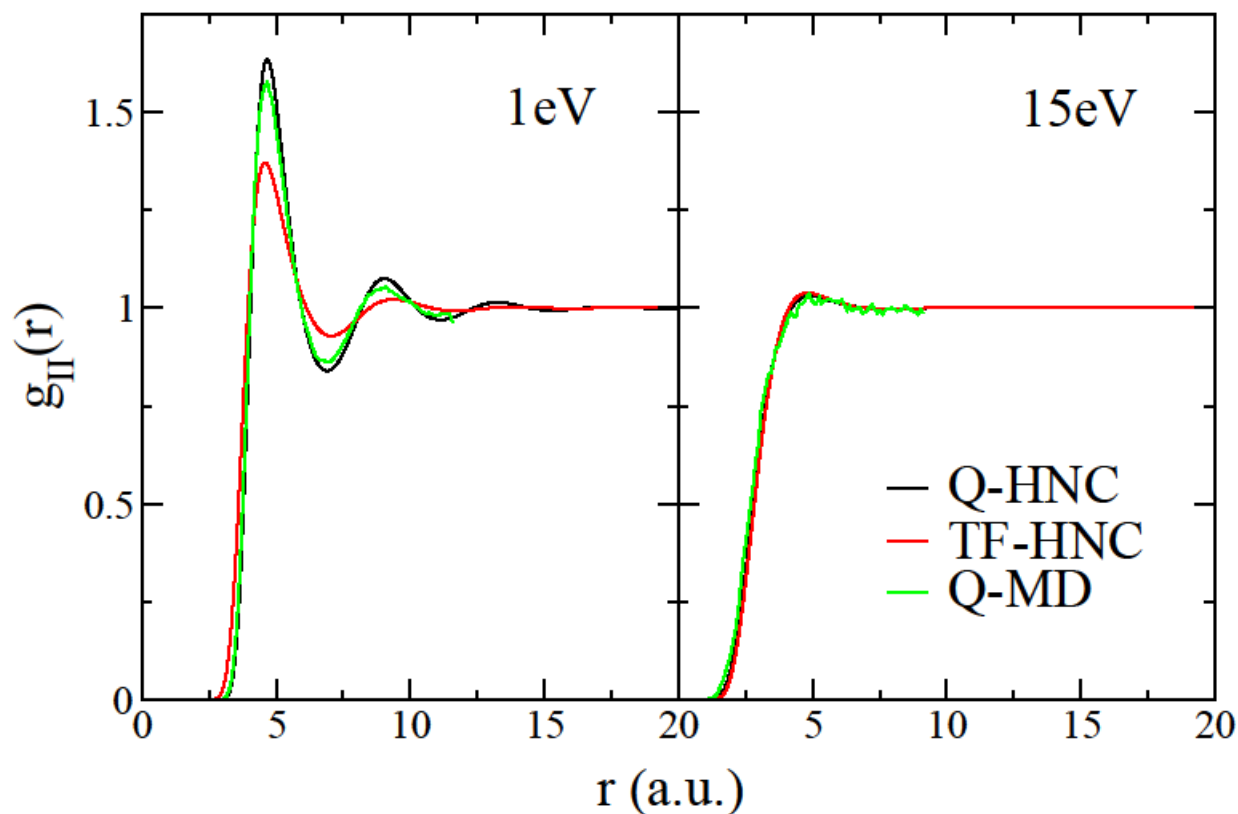
# Screening density example

Aluminum at solid density (2.7g/cm<sup>3</sup>)



# Ion-ion pair distribution functions

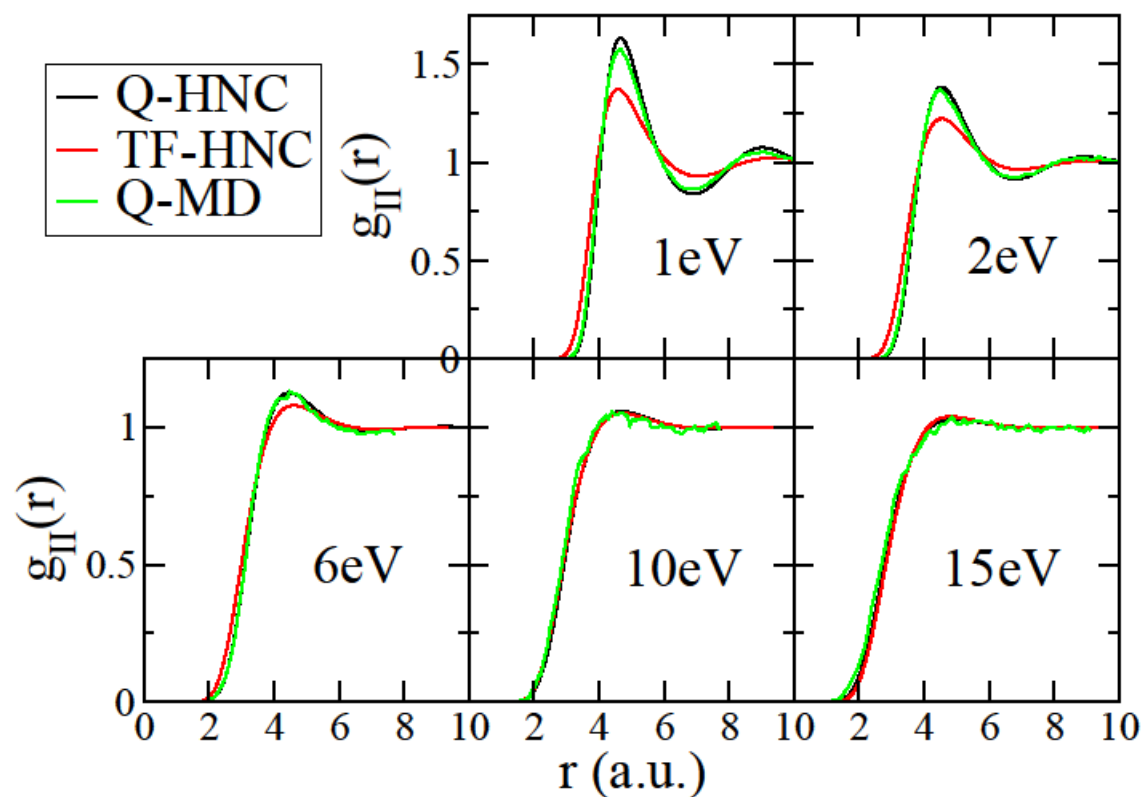
Aluminum at solid density (2.7g/cm<sup>3</sup>)



QMD courtesy of J. Kress & L. A. Collins (LANL)

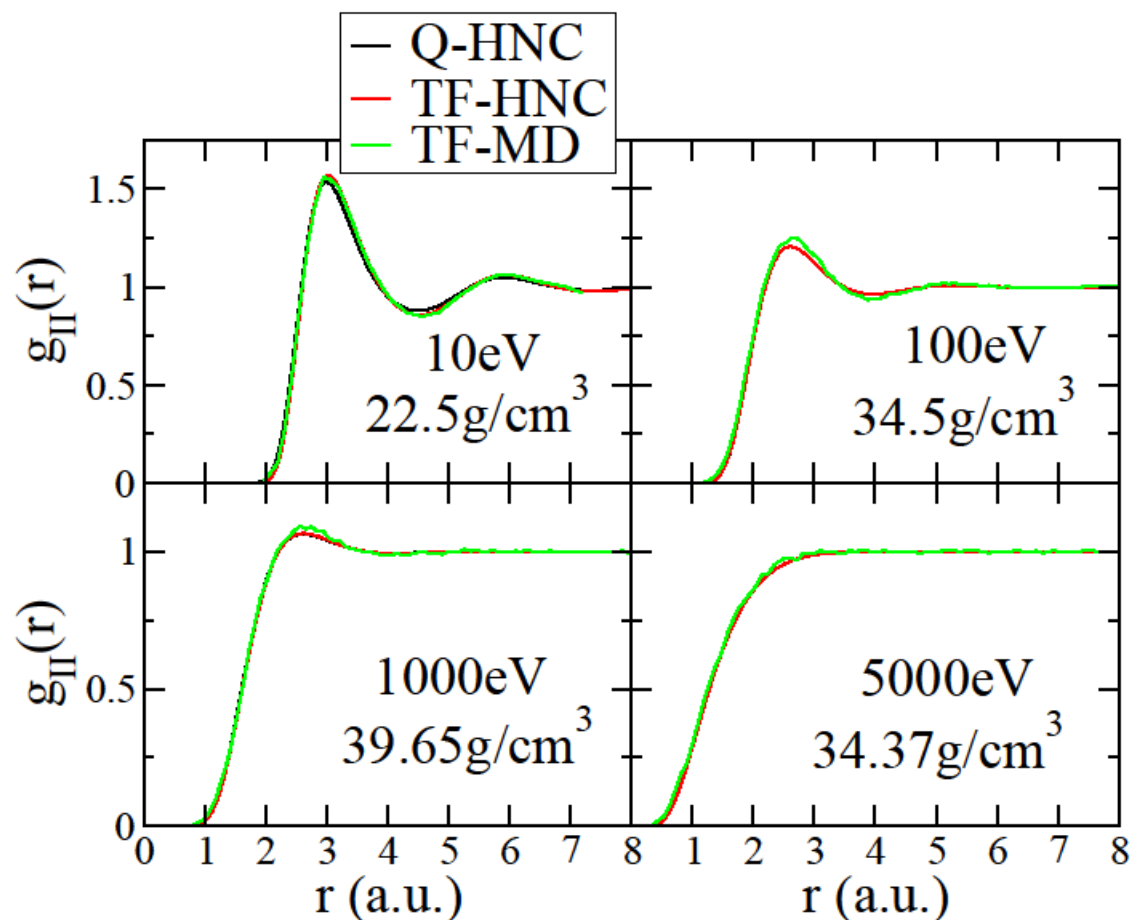
# Ion-ion pair distribution functions

Aluminum at solid density (2.7g/cm<sup>3</sup>)



QMD courtesy of J. Kress & L. A. Collins (LANL)

# Iron along principal Hugoniot

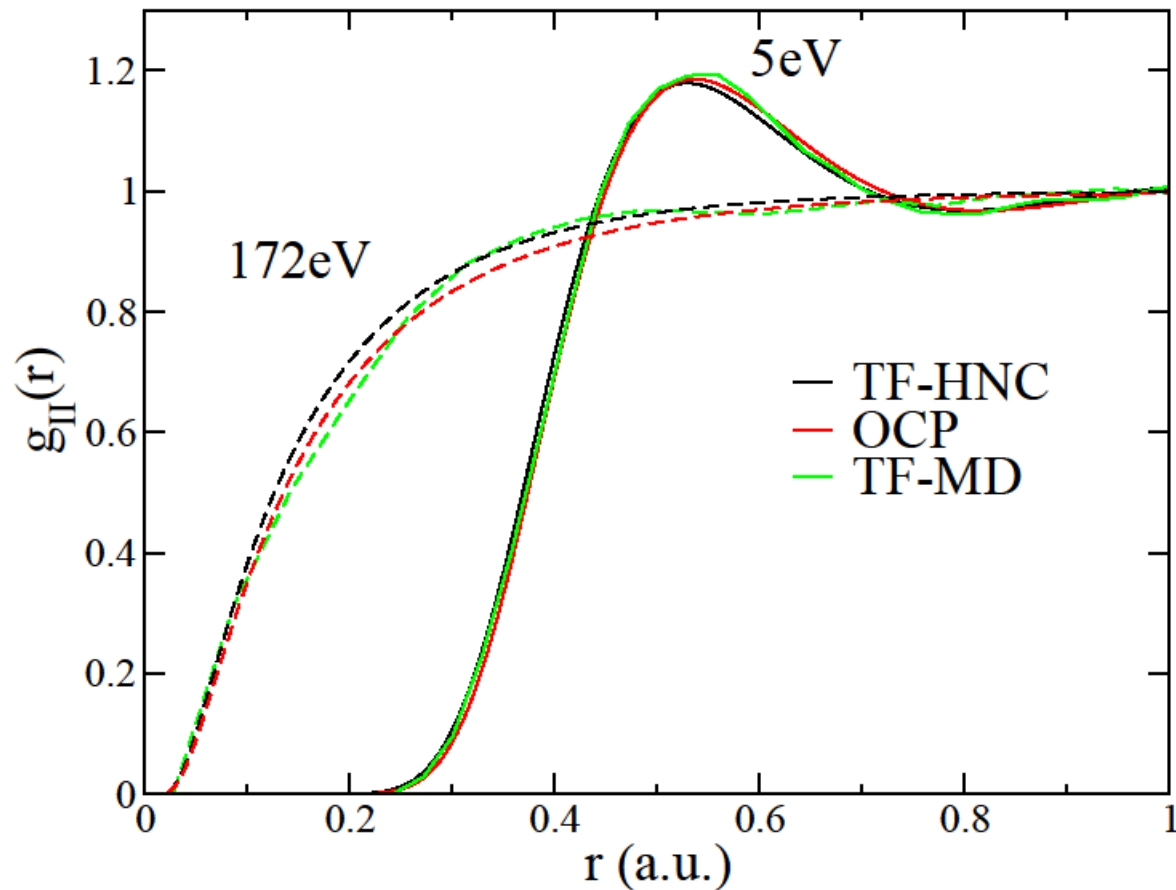


TF-MD: 10eV, with exchange and correlation (Kress & Collins)

TF-MD: 100-5000eV, no exchange and correlation (Lambert, PRE (2006))



# Dense Hydrogen: 80g/cm<sup>3</sup>



TF-MD: Recoules *et al*/ PRL (2009)

# Summary

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## First principles derivation of an average atom model with ion-correlations

- Thomas-Fermi or quantum mechanical electrons
- Classical ions

## Numerically solved the quantum Ornstein-Zernike equations

- Electron-ion closure by coupling to average atom model
- Electronic and ionic structure, local field corrections
- A difficult numerical problem
- Thomas-Fermi case works (in contrast to Ofer *et al*)
- Quantum case works in warm/hot dense matter regime (in contrast to Chihara's QHNC model)
- Overlap of Thomas-Fermi and Quantum results
- Test accuracy of widely used OCP

# Outlook

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## Thermo-dynamics from average atom model

- Simple pressure formula
- Thermo-dynamic consistency is required (guaranteed)
- Also have internal energy, entropy, free energy etc.

## Applications and extensions

- EOS tables
- Conductivities (Quantum and Thomas-Fermi)
- Opacities
- diffusion coefficients
- Modeling experiments: XRTS, XANES
- Mixtures – in principle the model is extendable to mixtures with no additional assumptions (LDRD-ER)
- Different electron-ion temperatures

# Evaluation time and limitations

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## Evaluation time for single density-temperature point

- Thomas-Fermi ~ 1-3 minutes
- Schrodinger ~ 30-60 minutes
- Output gives thermodynamics, fluid structure

## Limitations

- Liquids to hot dense matter (not solids)
- Molecular bonding is (probably) poorly represented
- Angular effects washed out

# Acknowledgements

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- **Didier Saumon**
- William Daughton
- Joel Kress & Lee Collins
- Jérôme Daligault

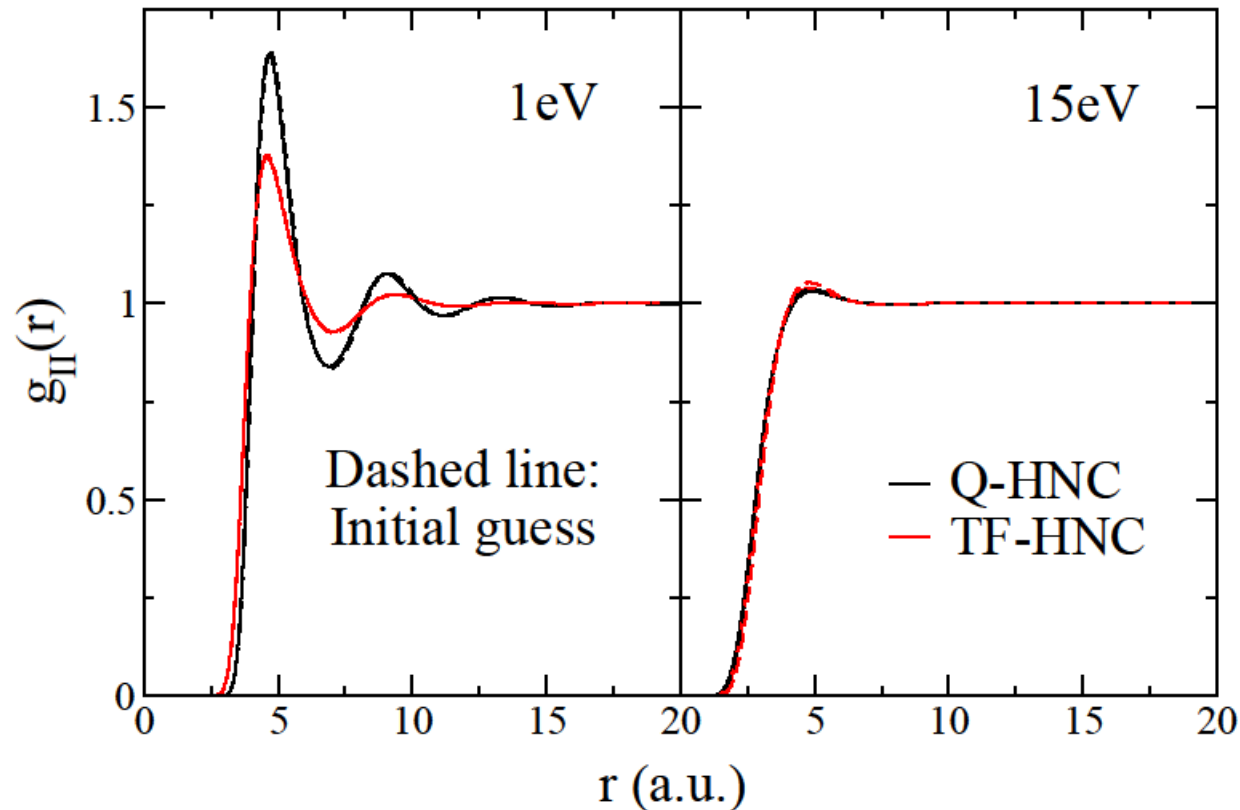
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# Extra slides

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# A Simple model

Aluminum at solid density (2.7g/cm<sup>3</sup>)



Initial guess of  $n_e^{scr}(r)$  from average atom model with step function  $g_{II}(r)$



# Examples of Average Atom models

## Thomas-Fermi (-Dirac) model (semi-classical, no wave functions)

(Feynman, Metropolis & Teller 1949)

Electron density

$$n(r) = \frac{\sqrt{2}}{\pi^2} \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon + V(r) - \mu_e)} + 1}$$

Thomas-Fermi potential (spherically symmetric)

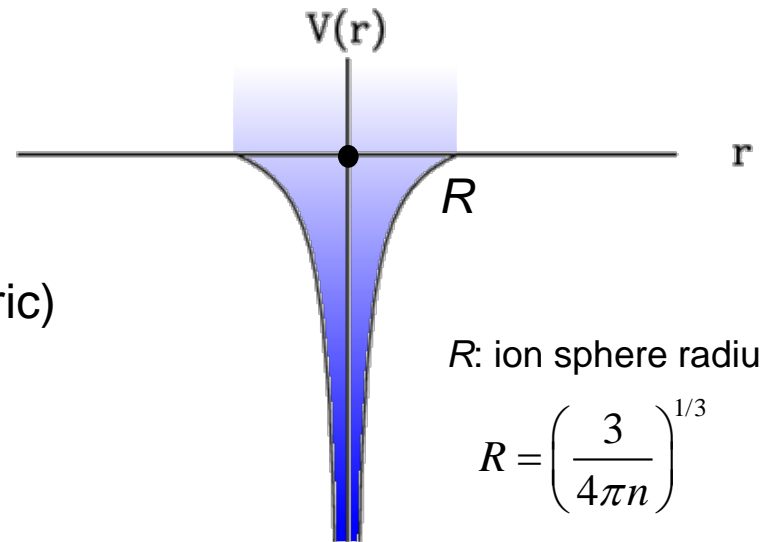
$$V(r) = \frac{-Z}{r} + \int \frac{n(r') d^3r'}{|\vec{r} - \vec{r}'|} + V_{xc}(n(r))$$

Dirac exchange potential

$$V_{xc}(r) = -\left(\frac{3n(r)}{\pi}\right)^{1/3}$$

Charge neutrality of ion sphere (gives  $\mu_e$ )

$$\int_0^R n(r) d^3r = Z$$



$R$ : ion sphere radius

$$R = \left(\frac{3}{4\pi n}\right)^{1/3}$$

# Examples of Average Atom models

## INFERNO/PURGATORIO model (quantum mechanical, with wave functions)

(Lieberman 1979, Wilson et al. 2006)

Electron density

$$n(r) = \frac{1}{4\pi} \sum_{\substack{n,l \\ \text{bound}}} \frac{2(2l+1) |\psi_{nl}(r)|^2}{e^{\beta(\varepsilon_{nl} - \mu_e)} + 1} + \frac{1}{4\pi} \int_0^\infty \frac{d\varepsilon}{e^{\beta(\varepsilon - \mu_e)} + 1} \sum_{l=0}^\infty 2(2l+1) |\psi_{\varepsilon l}(r)|^2$$

The wave functions  $\psi(r)$  are solutions of the Dirac or Schrödinger equation (Kohn-Sham formulation)

$$u_{nl}(r) = r\psi_{nl}(r)$$

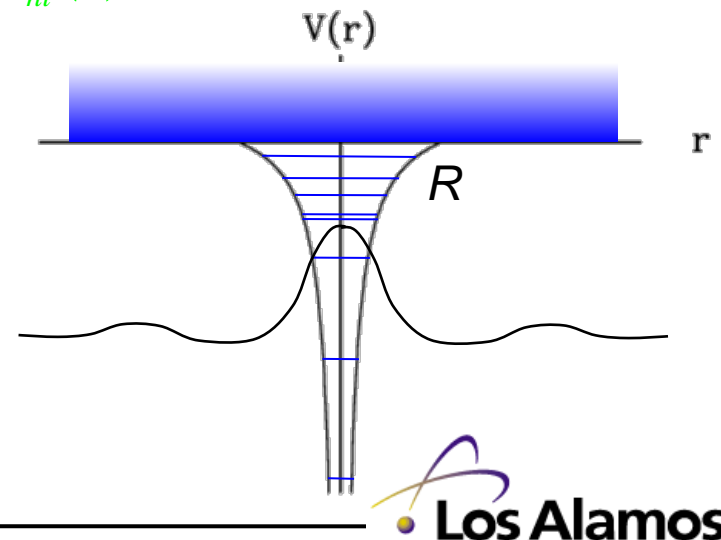
$$\left[ -\frac{1}{2} \left( \frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} \right) + V_{ie}(r) \right] u_{nl}(r) = \varepsilon_{nl} u_{nl}(r)$$

With the potential

$$V_{ie}(r) = \frac{-Z}{r} + \int_0^\infty \frac{n(r') d^3r'}{|\vec{r} - \vec{r}'|} + V_{xc}(n(r))$$

Charge neutrality of ion sphere (gives  $\mu_e$ )

$$\int_0^R n(r) d^3r = Z$$



---

Get  $C_{Ie}$  from QOZ, with  $N_e^{scr}$  defined using Perrot's trick

$$C_{Ie}(k) = -\beta n_e^{scr}(k) \left( \frac{\beta}{\chi_{ee}^{(0)}(k)} - C_{ee}(k) \right)$$

Solve effective one-component system with potential given by:

$$\beta V_{II}(k) = \beta V_{II}^C(k) - n_e^{scr}(k) C_{Ie}(k)$$