# Structure and X-Ray Scattering in Warm Dense Matter

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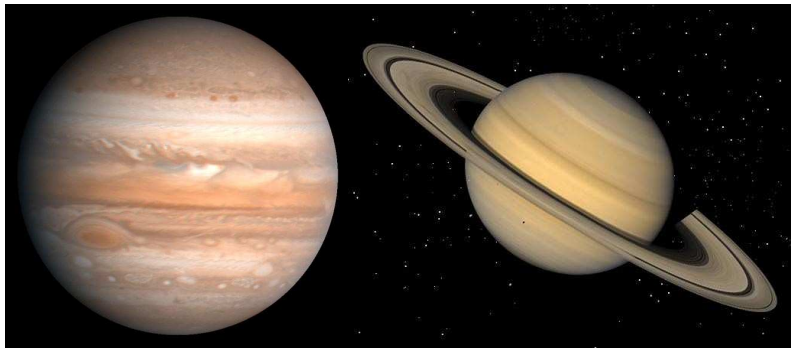
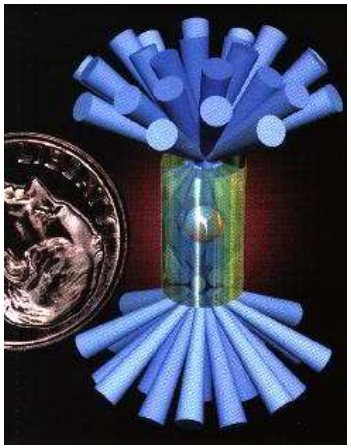
CFSA centre for fusion, space and astrophysics

THE UNIVERSITY OF WARWICK

# Introduction – Motivation for Dense Plasma Physics

- Mean density: $\varrho = 1.33\,\mathrm{g/cm^3}$
- Temperature: $T = 500 \ldots 10^4\,\mathrm{K}$

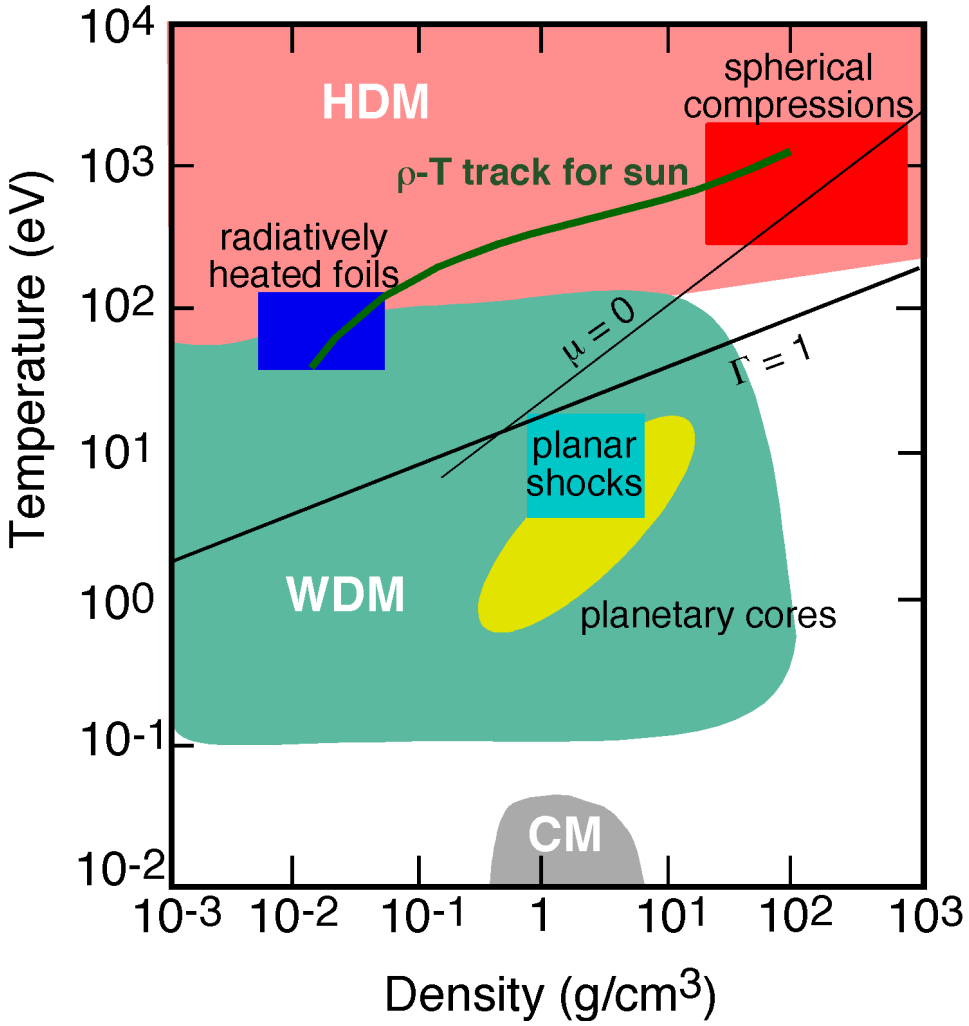




- Solid density to 1000 times compressed
- Temperature: $T = 14\,\mathrm{K}$ to $T = 2 \times 10^8\,\mathrm{K}$

- Solid density or slightly expanded
- Temperature: $T = 10^4\,\mathrm{K}$ to $T = 10^6\,\mathrm{K}$

# Introduction – Motivation for WDM Research




## WDM covers region that

- cannot be described as usual condensed matter, $T \approx 0$
- cannot be described as (hot) weakly coupled plasma with $T \gg T_F$ and $T \gg E_{cor}$

## Theoretical Issues

- degenerate electrons
- strongly coupled ions
- system is not fully ionised

! No expansion parameters

! Matter is fully coupled!

# X-Ray Scattering – Diagnostics & Theory Test Problem

## Light scattered from strongly coupled, partially ionized plasmas

$$P(\theta,\omega) \sim S_{ee}^{tot}(k,\omega) = \left|f_i(k) + q(k)\right|^2 S_{ii}(k,\omega) + Z_f S_{ee}^0(k,\omega) + Z_b \int d\omega' \, \tilde{S}^{ce}(k,\omega-\omega') S_s(k,\omega')$$

Chihara, 1987, 2000

$1^{\mathrm{st}}$ term: **Ion feature** (electrons co-moving with the ions)

- Static approximation possible: $S_{ii}(k,\omega) \sim S_{ii}(k)\delta(\omega)$
- Weak coupling treatment (RPA) fails; **strong correlations** important!
- Needed:
  1. Bound electron density – ion form factor $f(k)$
  2. Electron density in the screening cloud $q(k)$
  3. Ion structure factor $S_{ii}(k)$
- Term yields: ionization degree $Z$, (ion) temperature $T_i$

# X-Ray Scattering – Diagnostics & Theory Test Problem

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$1^{\text{st}}$ term: **Ion feature** (electrons co-moving with the ions)

$2^{\text{nd}}$ term: **Electron feature** (free electrons)

- Dynamic treatment needed (electron modes - plasmons)
- Weak coupling treatment (RPA) appropriate (+ weak collisions)
- Needed: response function for **degenerate** electron gas $\chi(k,\omega)$
- Term yields: electron density $n_e$, (electron) temperature $T_e$

$3^{\text{rd}}$ term: **Inelastic Raman scattering** (unimportant for light elements)

# X-Ray Scattering – Diagnostics & Theory Test Problem

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**DONE in RPA**

3$^{\text{rd}}$ term: **Inelastic Raman scattering** (unimportant for light elements)

**OFTEN NEGLECTED**

# Ionic Structure for Strong Coupling – HNC

## Ornstein-Zernicke relation (exact)

$$h_{ab}(\mathbf{r}) = c_{ab}(\mathbf{r}) + \sum_c n_c \int d\bar{\mathbf{r}}\, c_{ac}(\bar{\mathbf{r}})\, h_{cb}(|\mathbf{r} - \bar{\mathbf{r}}|)$$

Convolution! $\Rightarrow$ transformation in Fourier space (matrix notation)

$$\tilde{H}(k) = \tilde{C}(k) + \tilde{C}(k)\, \delta_{ab} n_a\, \tilde{H}(k)$$

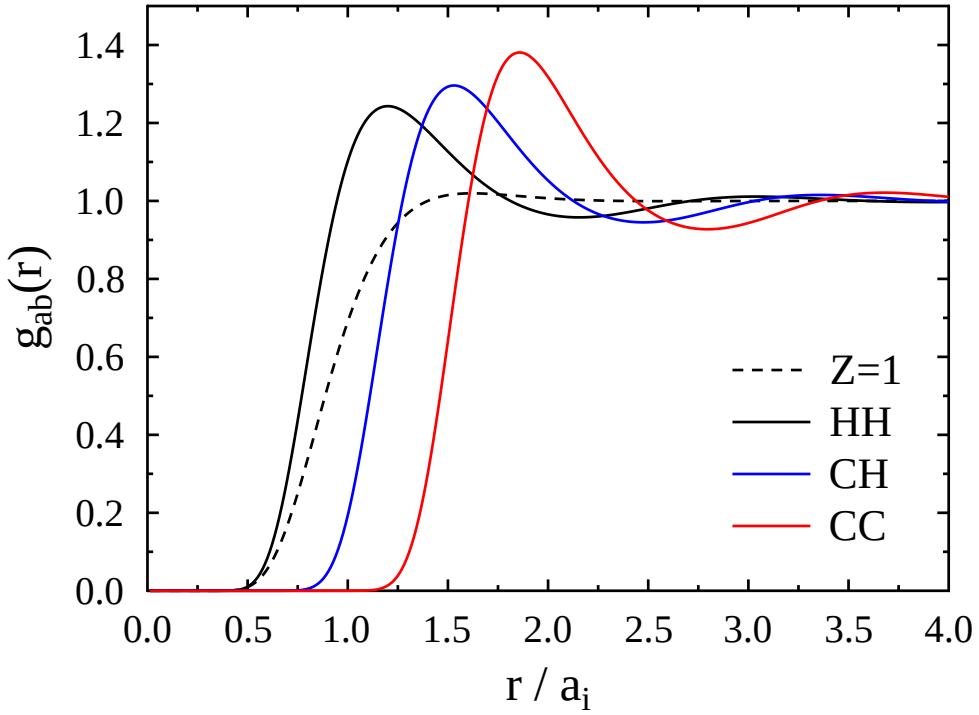
## Hypernetted Chain (HNC) closure relation (approximation)

$$g_{ab}(r) = \exp(-\beta V_{ab}(r) + h_{ab}(r) - c_{ab}(r))$$

- Approach uses **classical mechanics** only
- Approach **works well** for ions up to coupling strength of $\Gamma \leq 100$

# Ion Structure: Strongly Coupled, Multi-Ion Systems (HNC)

## Protons & Carbon Ions in a CH Plasma

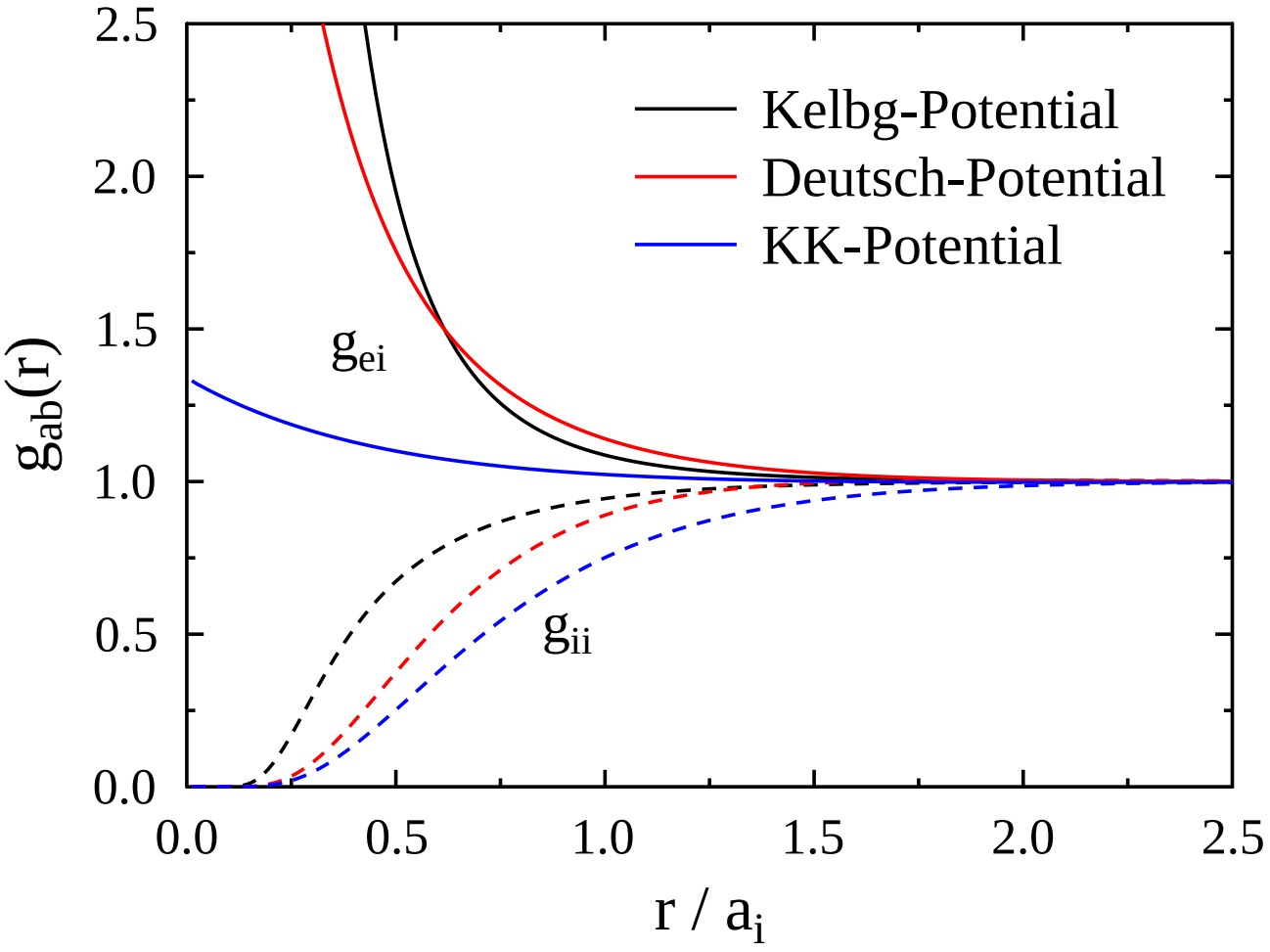



Partial pair distributions for a CH plasma with $n_H = n_C = 2.5 \times 10^{23}\,\mathrm{cm}^{-3}$ and $T = 2 \times 10^4\,\mathrm{K}$. The hydrogen and carbon ions are fully and 4-fold ionized, respectively Wünsch et al. (PRE, 2008).

**Strong Coupling Effects:**

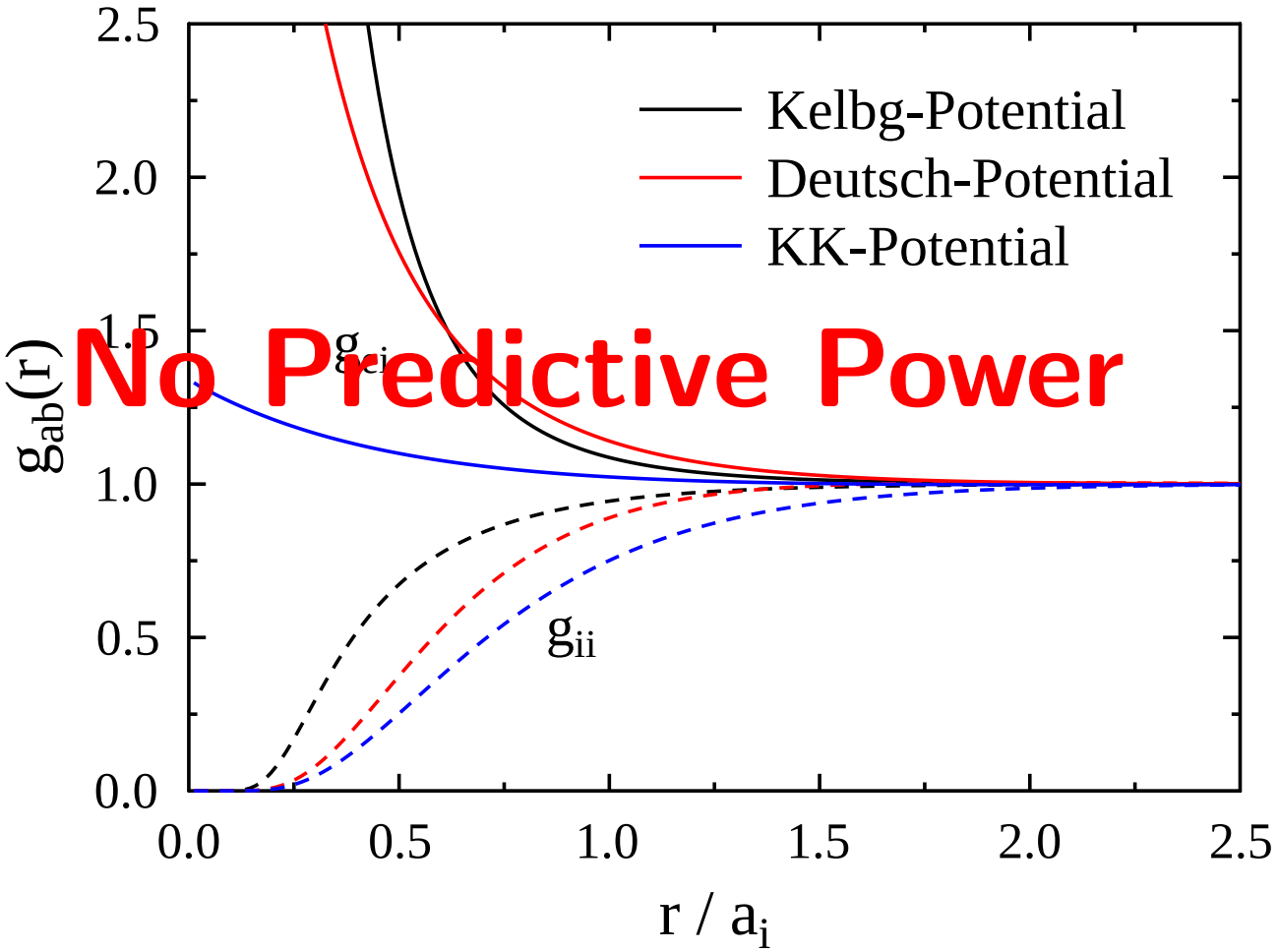
- Correlation holes at small distances
- Maxima / minima in $g(r)$ and $S(k)$
- Most pronounced structure in the carbon subsystem
- Carbon ions imprint their structure into the proton subsystem

# HNC for Electron-Ion Systems – Quantum Potentials




Electron-ion and ion-ion pair distributions for a plasma with $n = 10^{22}\,\mathrm{cm}^{-3}$, $Z = 1$, and $T = 4.5 \times 10^4\,\mathrm{K}$.

# HNC for Electron-Ion Systems – Quantum Potentials




Electron-ion and ion-ion pair distributions for a plasma with $n = 10^{22}\,\mathrm{cm}^{-3}$, $Z = 1$, and $T = 4.5 \times 10^4\,\mathrm{K}$.

# Full Quantum Simulations (DFT-MD)

**The goal is to include**

- **Full quantum mechanics** (diffraction/exchange) for the electrons
- **All correlations** in the target (especially ionic structure)

**Method applied: Density Functional Theory + MD (DFT-MD)**

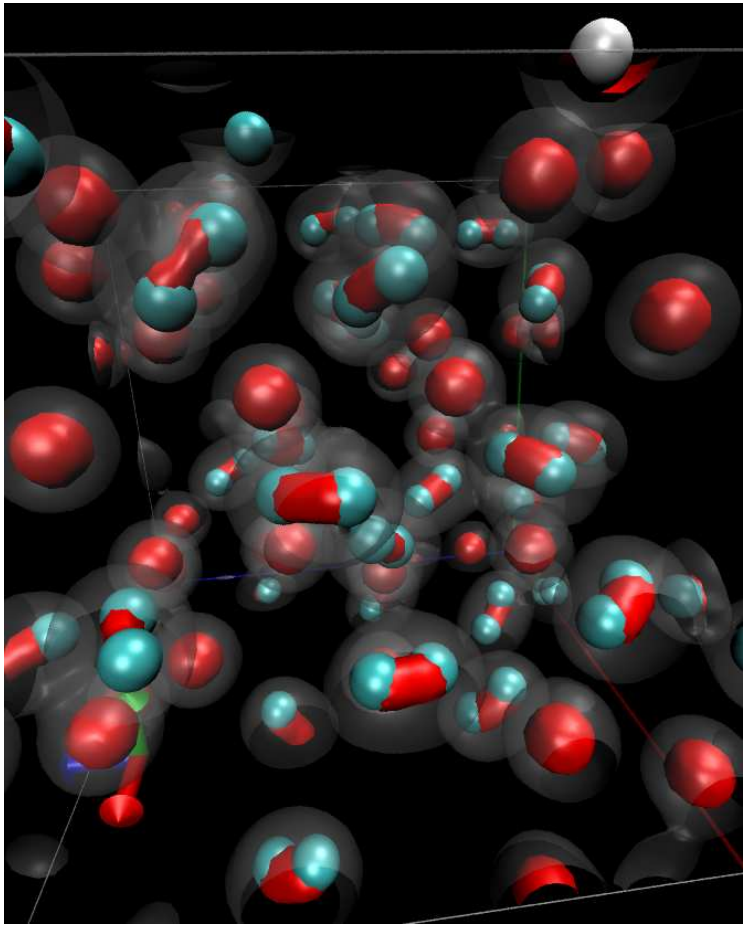
1. Solve Kohn-Sham equations for given ion positions (effective Schrödinger equation $\Rightarrow$ states and energy levels)
2. Populate energy levels according to Fermi-distribution
3. Calculate forces (i-i and i-e) on ions $\Rightarrow$ Move ions; $\Rightarrow$ **Start again!**
4. After initial time, equilibrium properties follow: $g_{ii}(r)$, $g_{ei}(r)$, $p$, $E_{cor}$

**Problems:**

- Very long run times for DFT-MD (weeks) $\Rightarrow$ Switch to MC
- Box size and noise make Fourier transformation hard

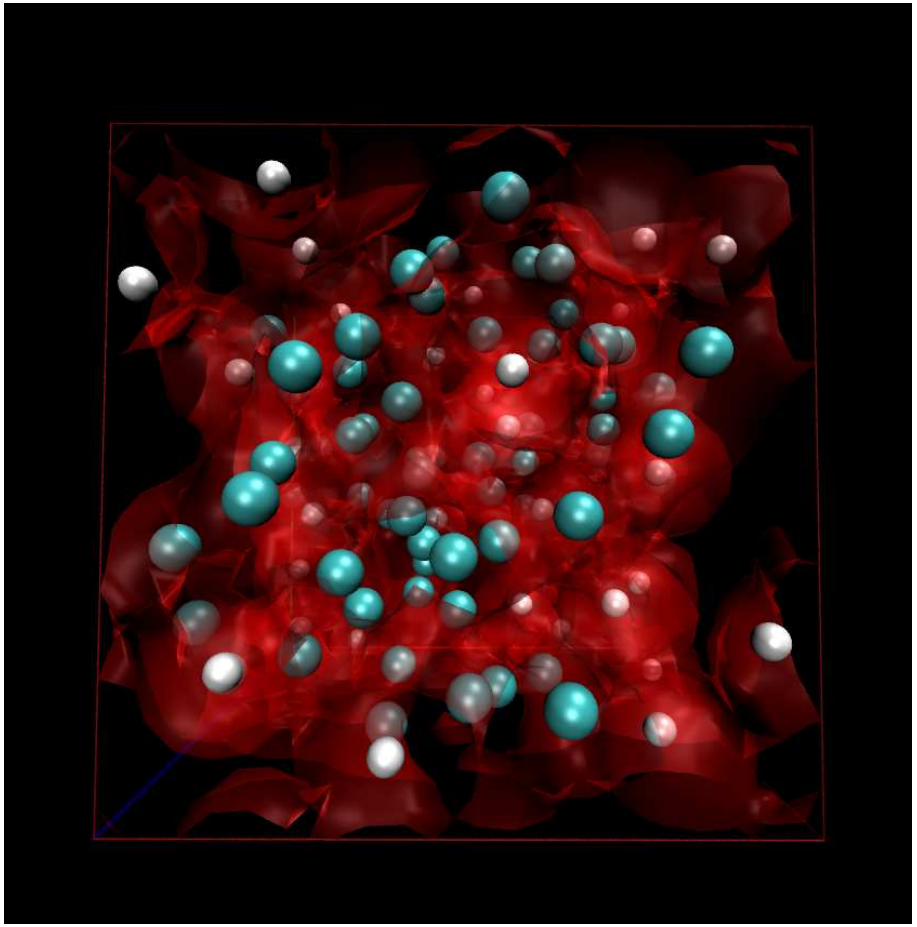
# Results from DFT-MD Simulations using VASP

**Molecular Hydrogen**



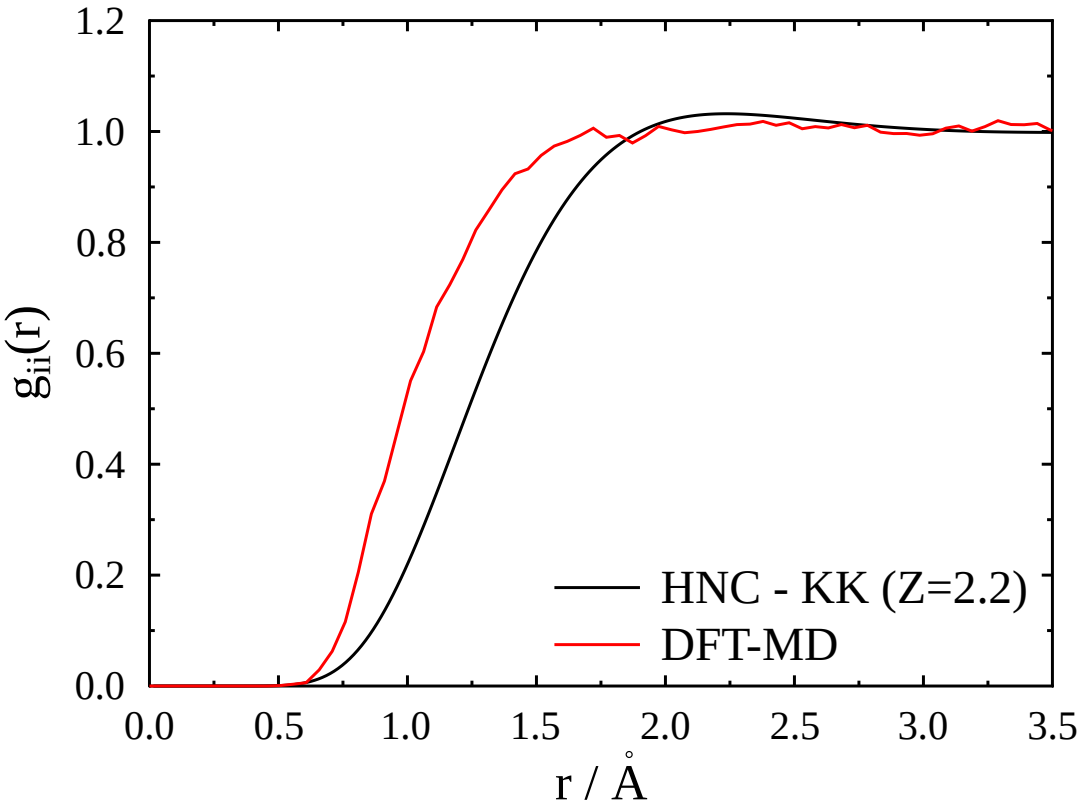
$\varrho = 0.2\,\mathrm{gcm}^{-3}$ and $T = 4 \times 10^3\,\mathrm{K}$.

**Metallic Hydrogen**



$\varrho = 3.7\,\mathrm{gcm}^{-3}$ and $T = 4 \times 10^3\,\mathrm{K}$.

# Ionic Structure: HNC versus DFT-MD




Warm Beryllium with:

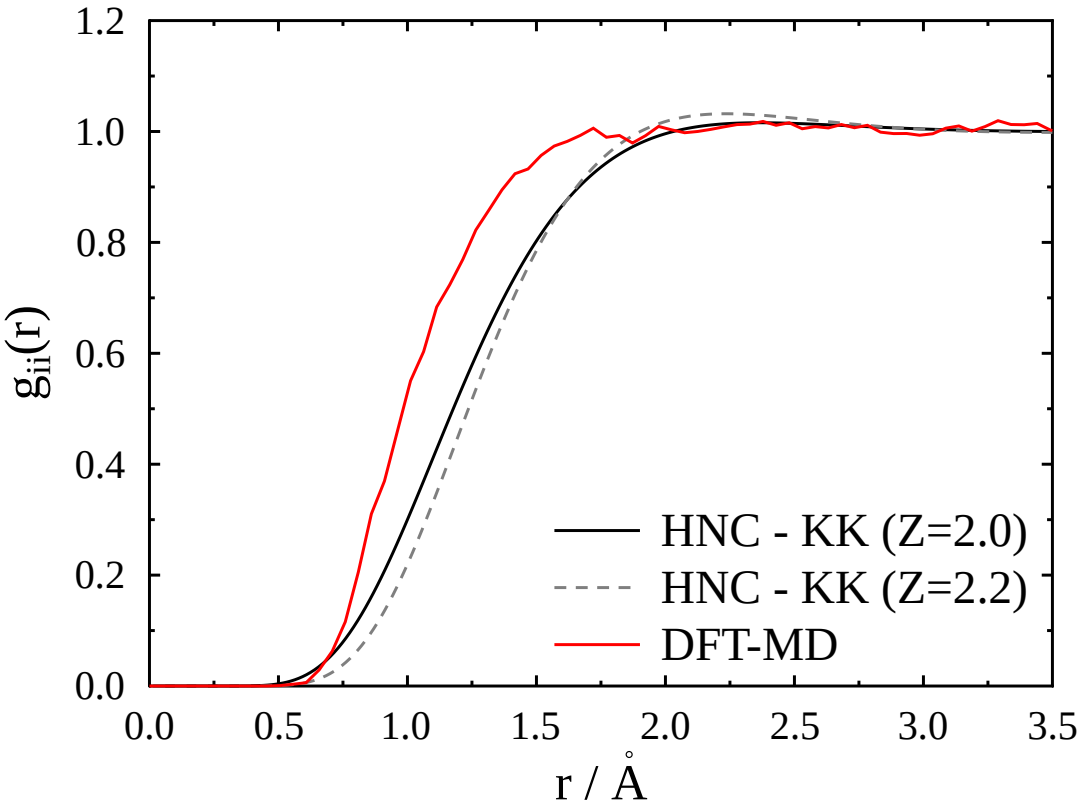
$$n_i = 1.23 \times 10^{23}\,\mathrm{cm}^{-3}$$

$$T = 1.39 \times 10^{5}\,\mathrm{K}$$

(isochorically heated)

Wünsch et al., PRE (2009)

# Ionic Structure: HNC versus DFT-MD

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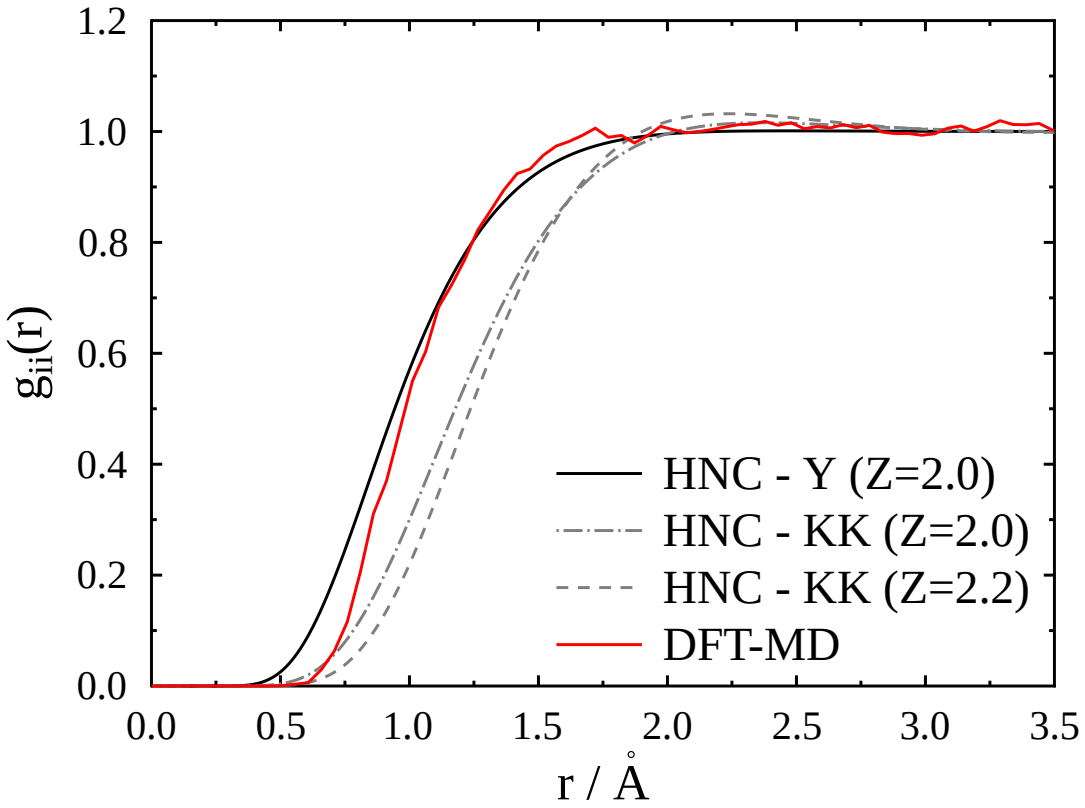


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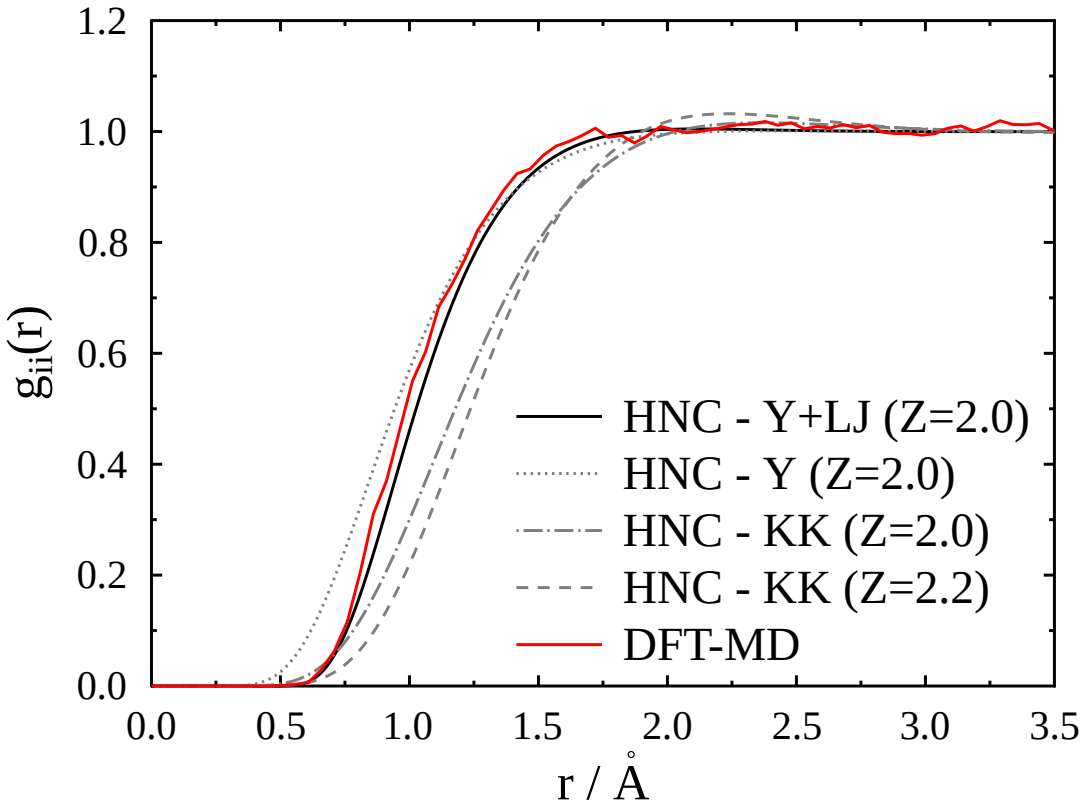


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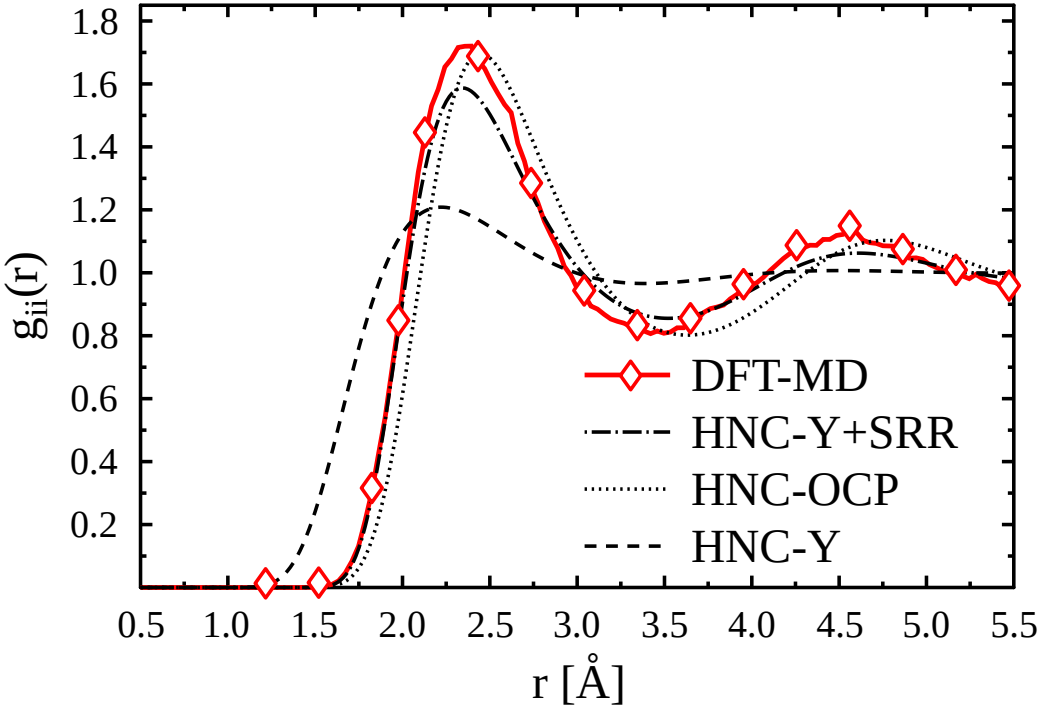
(isochorically heated)

Wünsch et al., PRE (2009)

$\Rightarrow$ **good agreement with Yukawa+SSR (Y-LS) model**

- Yukawa model: linearly screened interaction potential (deg. electrons)
- 1s shell results additional repulsion at small distances $\sim 1/r^4$ (LJ part)
- 1s shell must be intact! $\Rightarrow$ Possibility to obtain charge state: $Z = 2$

# Ionic Structure: HNC versus DFT-MD




Warm Aluminium with:

$$n_i = 2.7 \times 10^{22}\,\mathrm{cm}^{-3}$$

$$T = 1.2 \times 10^{4}\,\mathrm{K}$$

(isochorically heated)

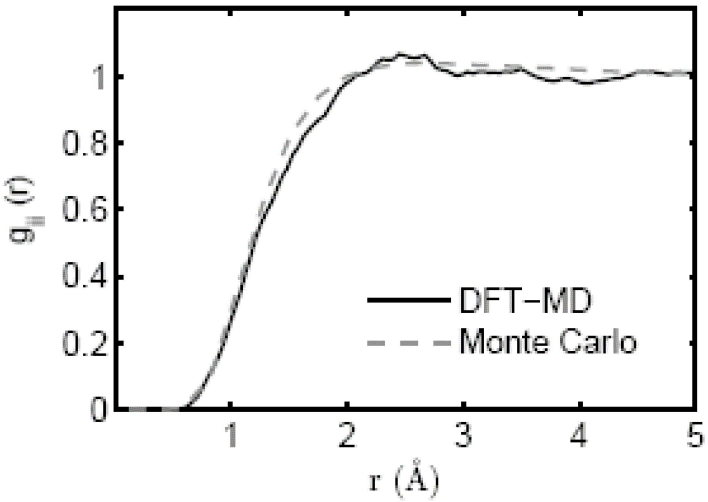
Wünsch et al., PRE (2009)

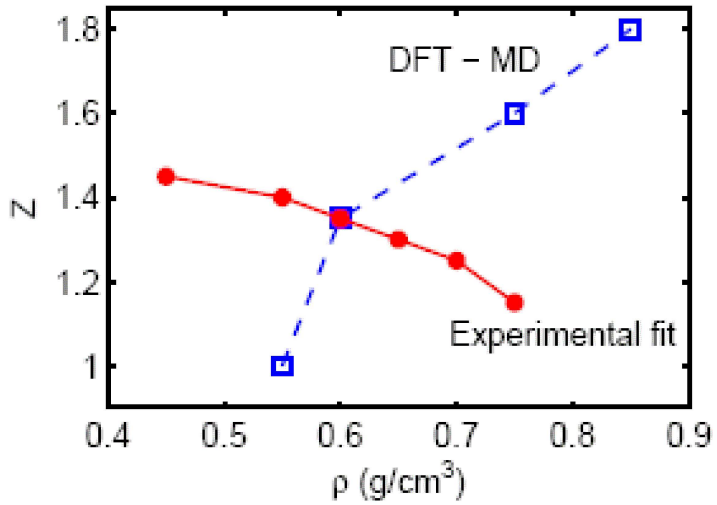
$\Rightarrow$ **good agreement with Yukawa+SSR model**

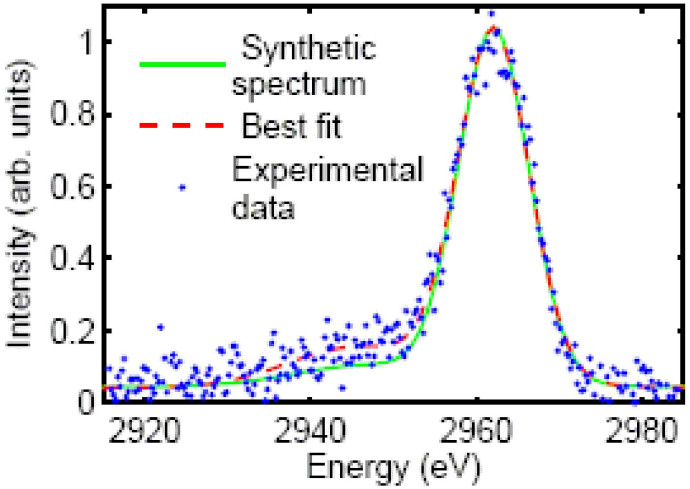
- Yukawa model: linearly screened interaction potential (deg. electrons)
- Full shells results additional repulsion at small distances $\sim 1/r^4$ (SRR part)
- Y-SRR Model works for heavier elements as well !

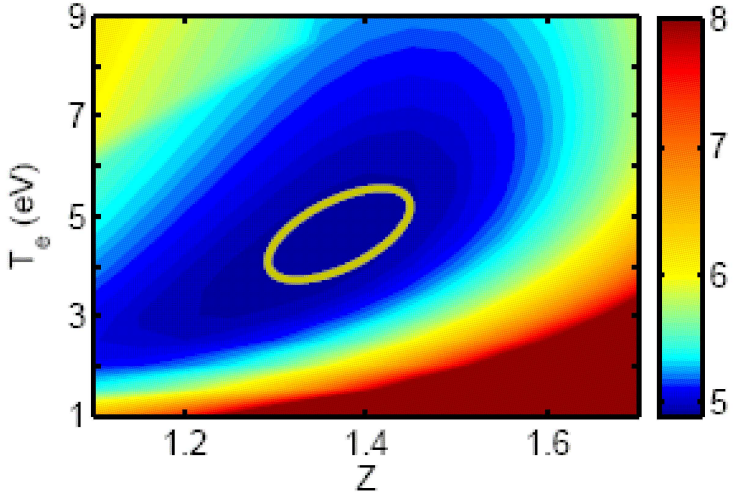
# Experimental Verification: Ionic Structure in Lithium

How can the mass density be fixed? Combine Experiments and DFT-MD!



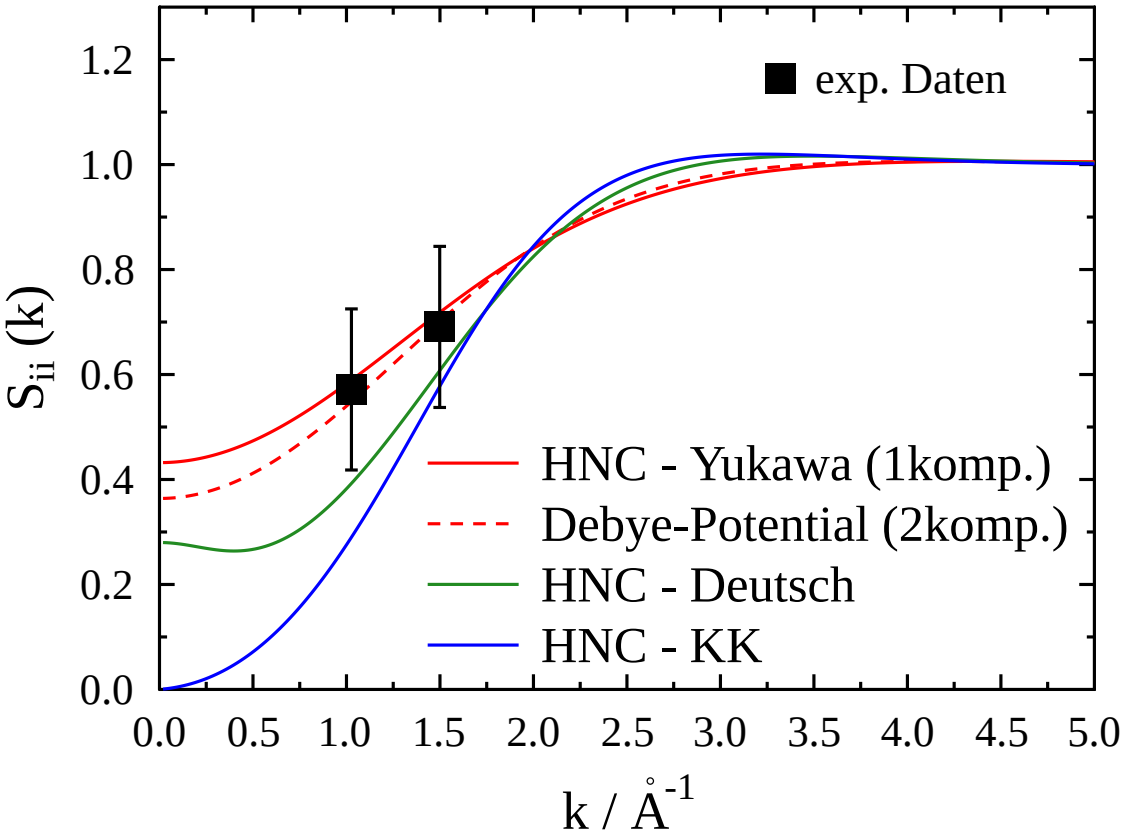




García Saiz et al., Nature Physics (2008)

# Experimental Verification: Ionic Structure in Lithium

## Structure in compressed Lithium




Static structure factor for a lithium plasma with $n_i = 5.2 \times 10^{22}\,\mathrm{cm}^{-3}$, $T = 4.5\,\mathrm{eV}$, $\bar{Z} = 1.35$.

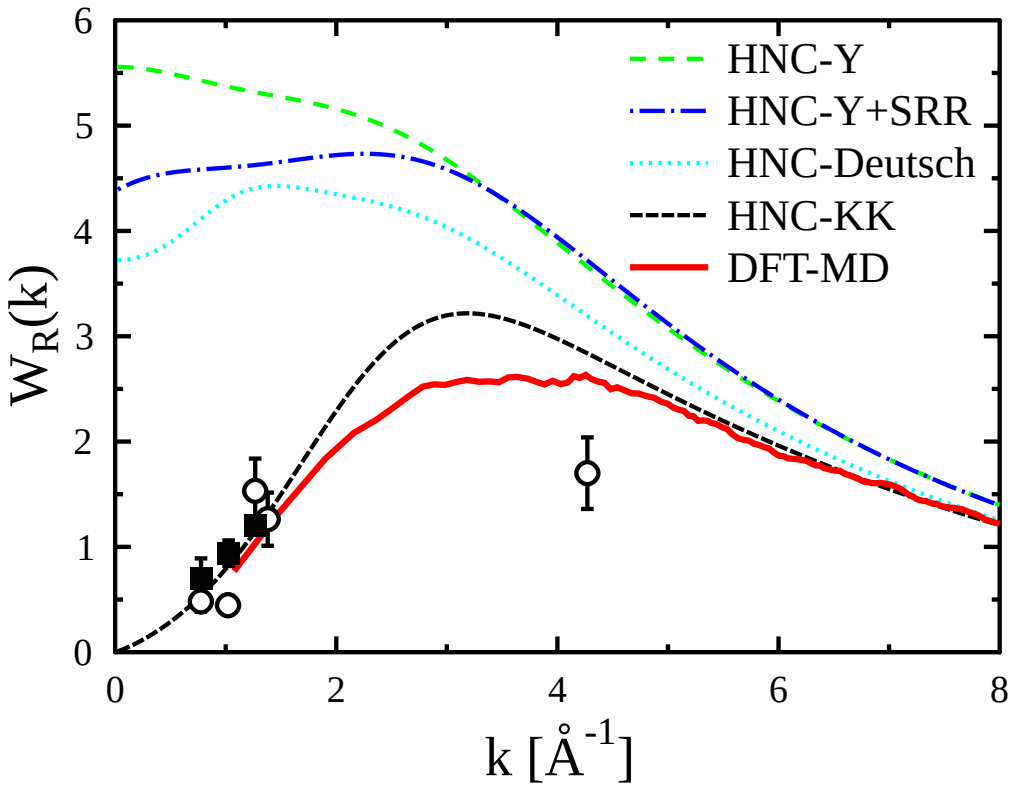
García Saiz et al., Nature Physics (2009)

**Insights gained:**

- Good agreement: DFT-MD simulations and experiments
- Good agreement: linearly screened HNC and experiments
- HNC with quantum potentials yields too strongly coupled ions (screening too weak)

# Experimental Verification: Ionic Feature for Beryllium

## Weight of the Ion Feature in Isochorically Heated Beryllium




**Ion peak using HNC**

$$W_R(k) = |f_i(k) + q(k)|^2 \, S_{ii}(k)$$

**Ion peak using DFT-MD**

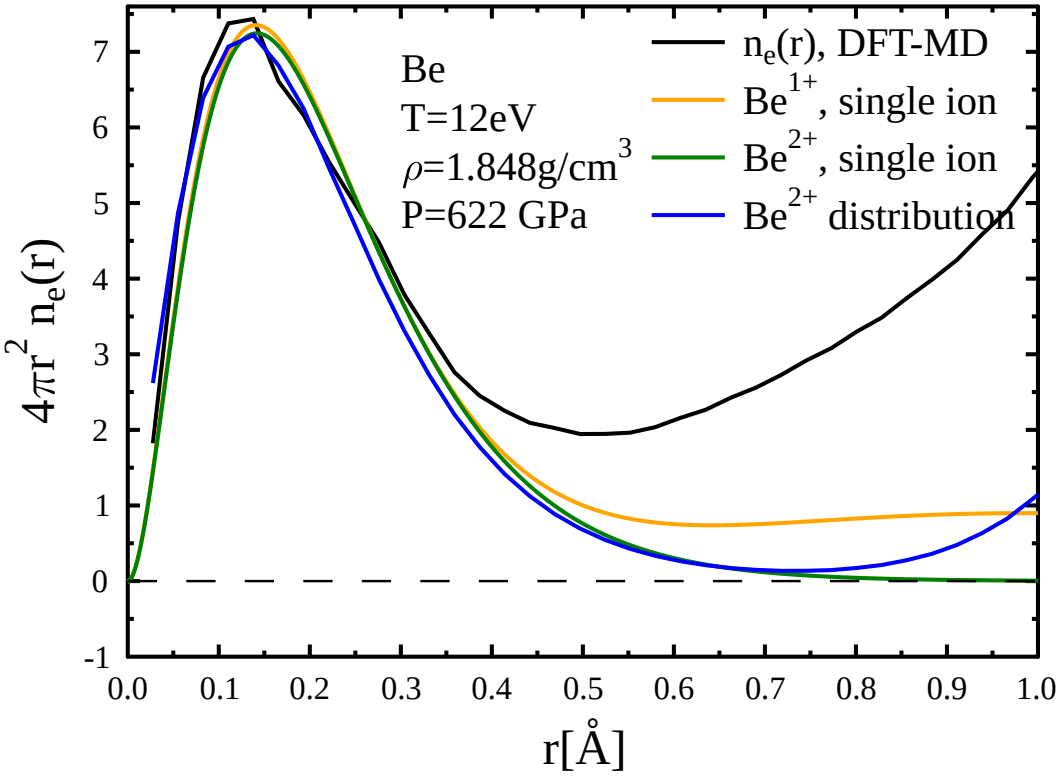
$$W_R(k) = n_e^2(k) S_{ii}(k)$$

plasma parameters:
$n_i = 1.23 \times 10^{23}\,\mathrm{cm}^{-3}$,
$T = 12\,\mathrm{eV}$, $Z = 2$

⇒ **Good agreement: DFT-MD simulations and experiments**
⇒ **Good agreement: DFT-MD and HNC using KK-potential**

Experimental data from: Glenzer et al., PRL (2003 / 2007) and new data

# Electronic Structure in Be from DFT-MD: Charge State




Warm Beryllium with:

$$n_i = 1.23 \times 10^{23}\,\mathrm{cm}^{-3}$$

$$T = 1.39 \times 10^{5}\,\mathrm{K}$$

(isochorically heated)

⇒ **Many bands needed!**
**energy cutoff >4000 eV**

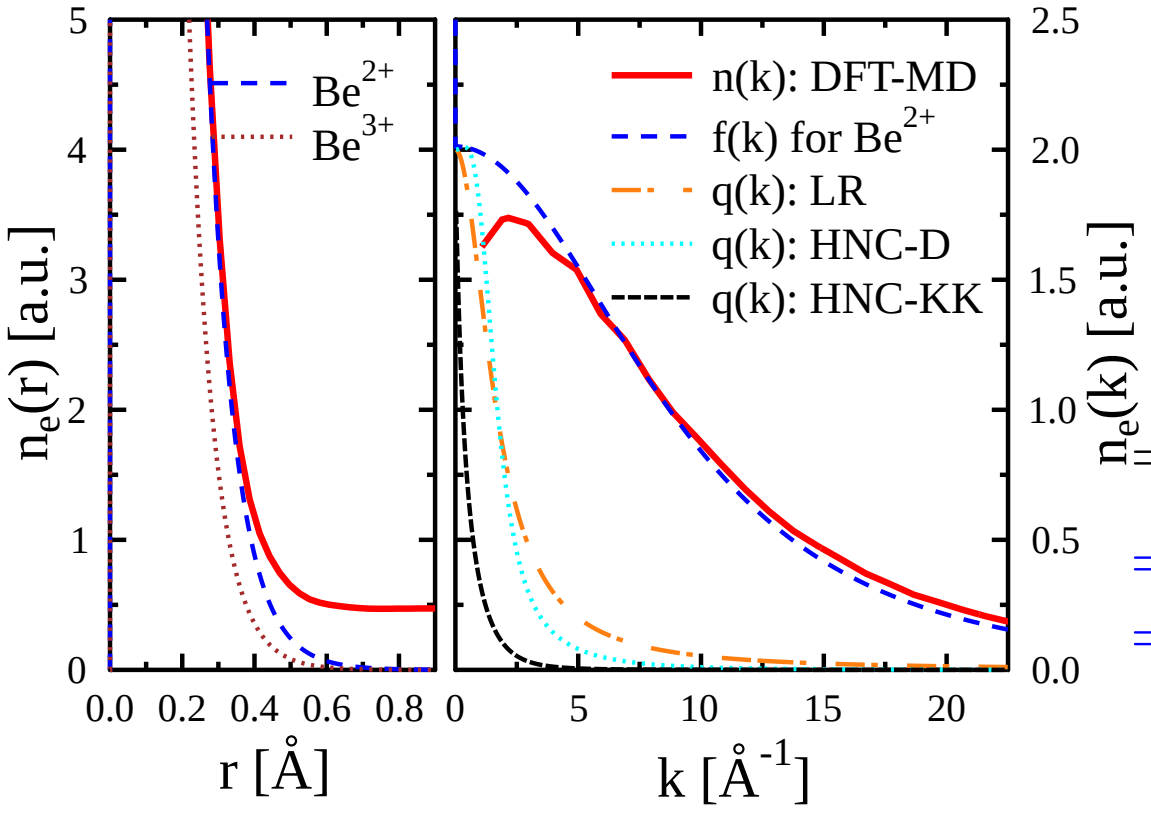
⇒ **Core structure resolved!**

⇒ **Charge state of $Z = 2$**

⇒ **Core structure yield valuable information:**

- Electron densities for small distances unchanged from isolated ions
- Correlations / overlap with other ions at larger distances

# Electronic Structure in Be: DFT vs. Reduced Models




Warm Beryllium with:

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⇒ **Single Snapshot DFT**

⇒ **Already $n_e(k) > f(k)$ !**

⇒ **Blurred bound states for larger distances**

⇒ **Improved electronic structure important to describe data**

- Agreement DFT-MD with experiments due to better description of $n(k)$
- Match of HNC-KK and Exp. due compensation of errors in $n_e(k)$ and $S_{ii}(k)$

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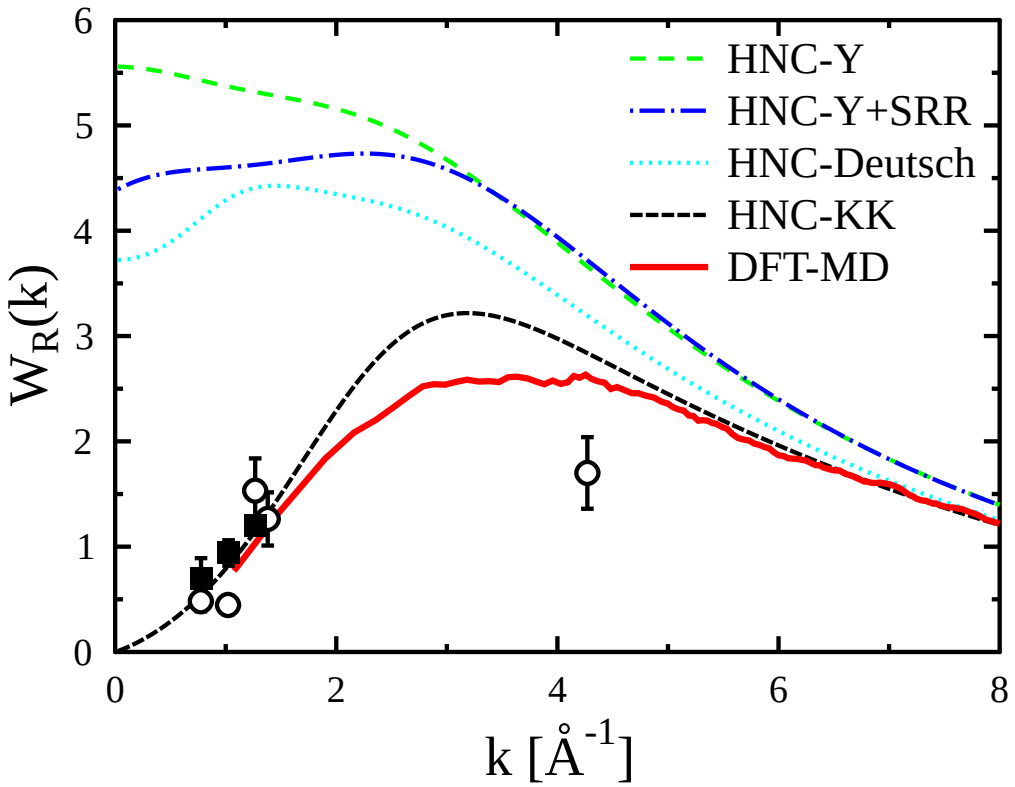



**Ion peak using HNC**

$$W_R(k) = |f_i(k) + q(k)|^2 \, S_{ii}(k)$$

**Ion peak using DFT-MD**

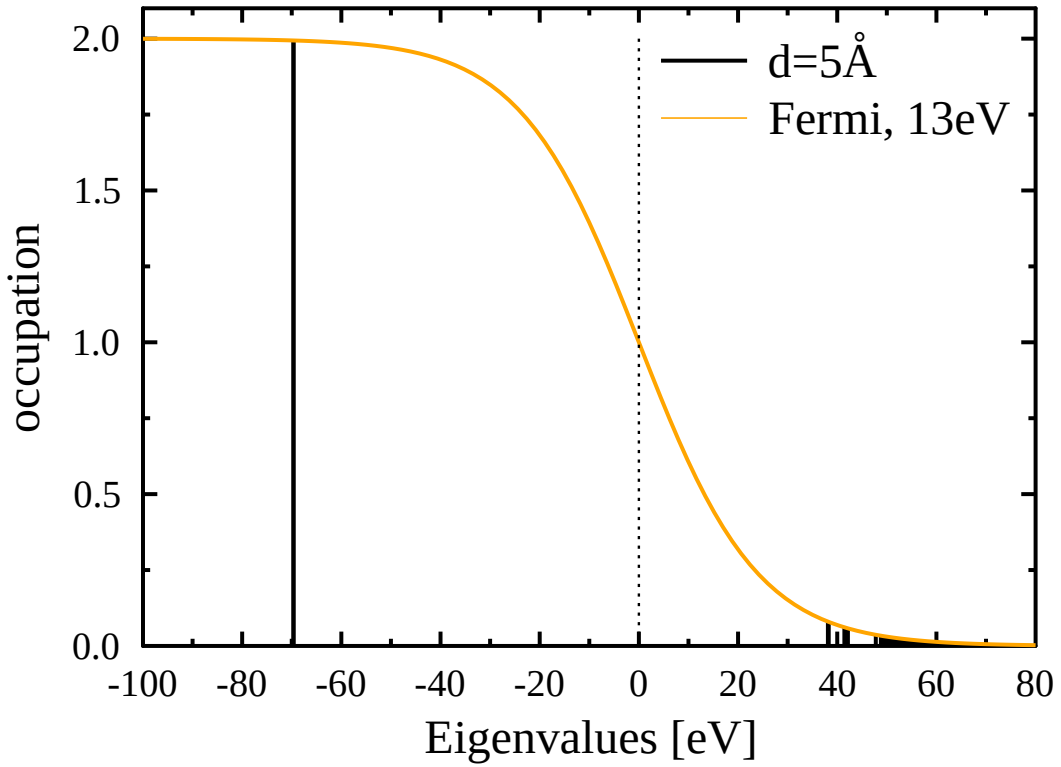
$$W_R(k) = n_e^2(k) S_{ii}(k)$$

plasma parameters:
$n_i = 1.23 \times 10^{23}\,\mathrm{cm}^{-3}$,
$T = 12\,\mathrm{eV}$, $Z = 2$

$\Rightarrow$ **Agreement of DFT-MD – KK is due to compensating errors!**

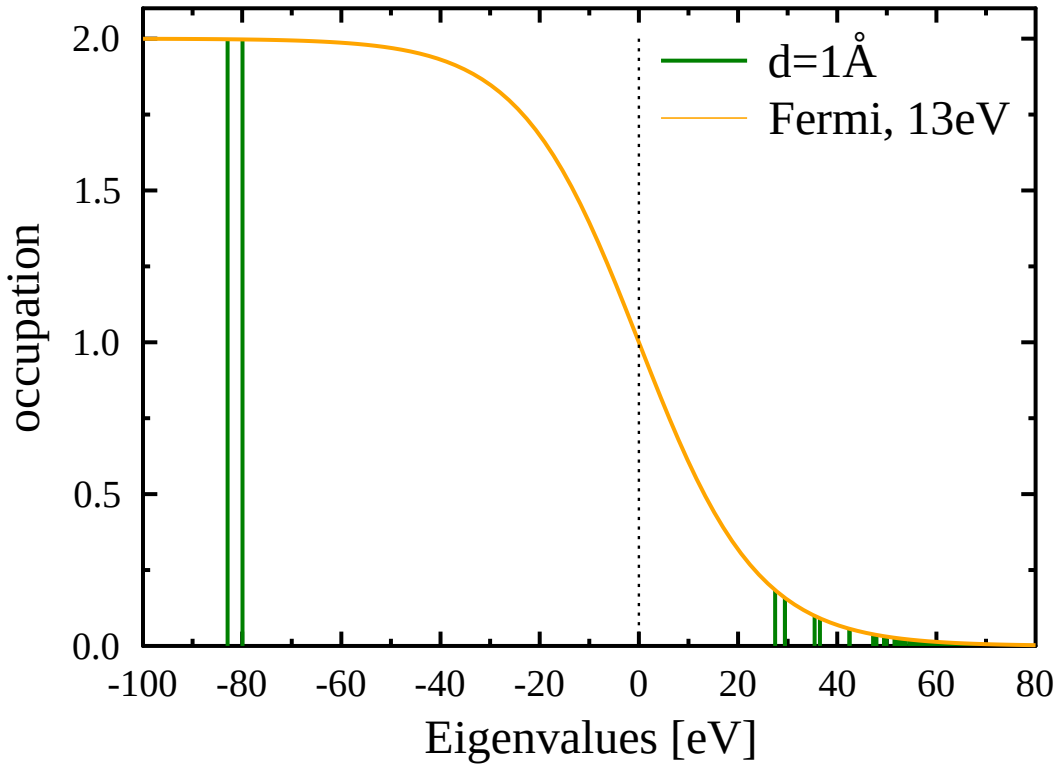
Experimental data from: Glenzer et al., PRL (2003 / 2007) and new data

# Are Internal Excitations Possible?



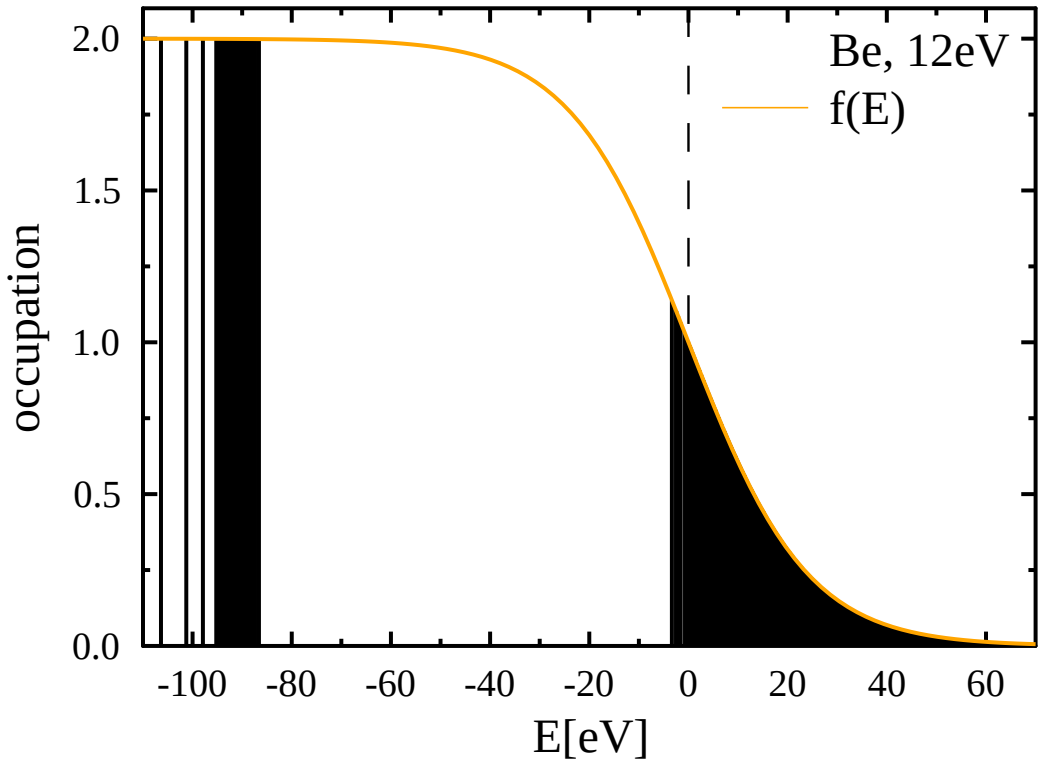

Pair of atoms at a distance of 5 Å

# Are Internal Excitations Possible?




Pair of atoms at a distance of 1 Å

# Are Internal Excitations Possible?




Full system Beryllium:

$$n_i = 1.23 \times 10^{23}\,\mathrm{cm}^{-3}$$

$$T = 1.39 \times 10^{5}\,\mathrm{K}$$

(isochorically heated)

$\Rightarrow$ **Correlation effects / build up of bands in many-body system**

- Possible energies states are shifted downwards (Stark effect)
- Degeneracy is lifted for close pairs/clusters: energies split into bands
- Effectively, we have much smaller energy gap to bridge for excitations (here: shift of energy gap from 107 eV $\Rightarrow$ 80 eV)

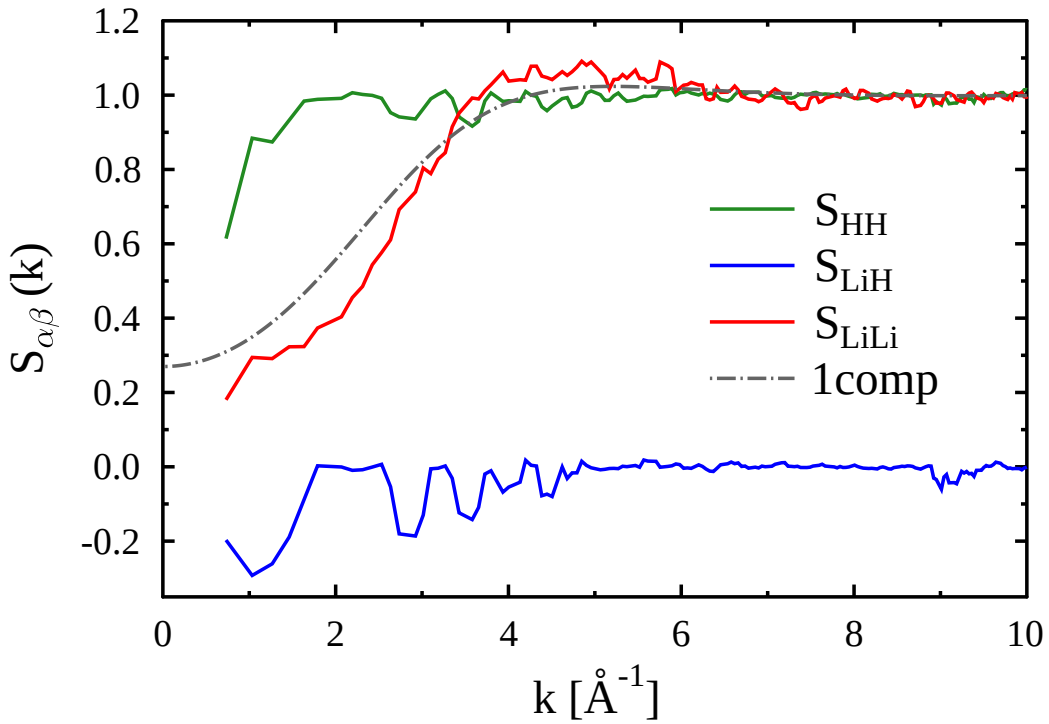
# Generalisation: Structure of Dense Mixtures

Structure in shock-compressed and heated Lithium Hydrate

see Kritcher et al., Science 2008

- 3x compressed LiH
- Charge states: $Z_{Li} = 1$ and $Z_H \approx 0$

**Partial ionic structure factors**



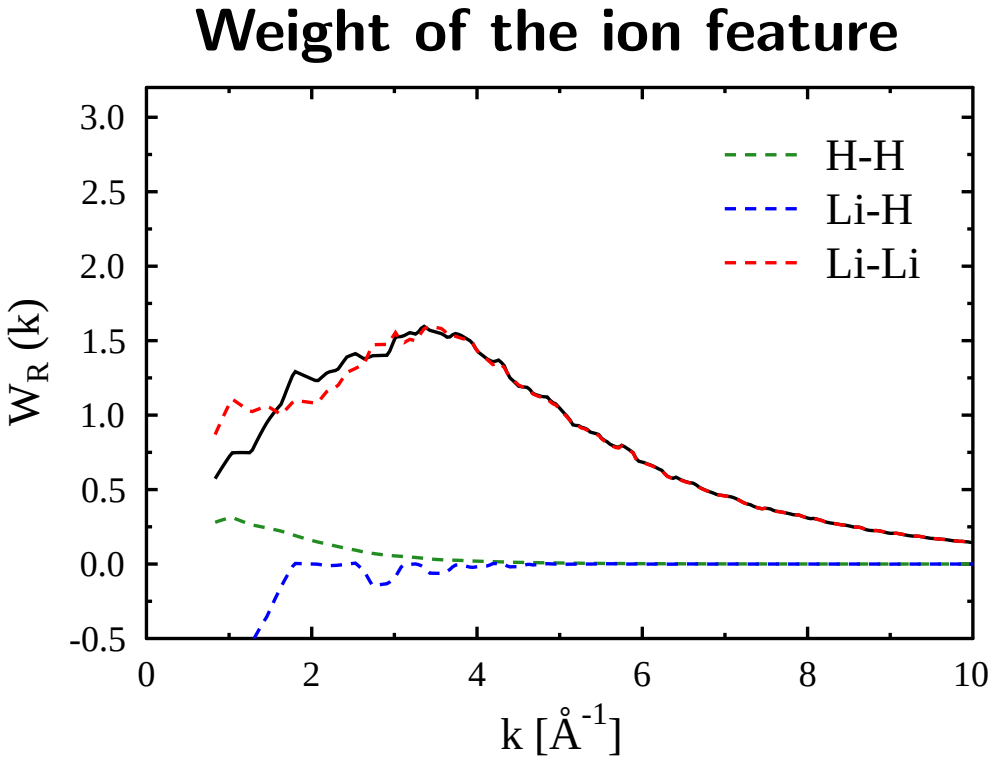

⇒ **DFT-MD yields structure w/o assumptions of charge states**

⇒ Quiet different structure from 2 component HNC (not shown)

! 1C-HNC calculations for screened $Li^+$ ions agree roughly

Vorberger, Wünsch and Gericke

# Ion Feature (Rayleigh Peak) for Warm Dense LiH




- DFT-MD + 2 component Chihara formula yields similar results than experiments
- Ion feature is dominated by scattering from $Li^+$ ions

## Weight of the Rayleigh Peak for Plasmas with 2 Ion Species

$$W_R(k) = \frac{n_\alpha}{n_\alpha + n_\beta}\left[f_\alpha + q_\alpha\right]^2 S_{\alpha\alpha}(k) + \frac{n_\beta}{n_\alpha + n_\beta}\left[f_\beta + q_\beta\right]^2 S_{\beta\beta}(k)$$
$$+ 2\,\frac{\sqrt{n_\alpha n_\beta}}{n_\alpha + n_\beta}\left[f_\alpha f_\beta + q_\alpha q_\beta + f_\alpha q_\beta + f_\beta q_\alpha\right] S_{\alpha\beta}(k)$$

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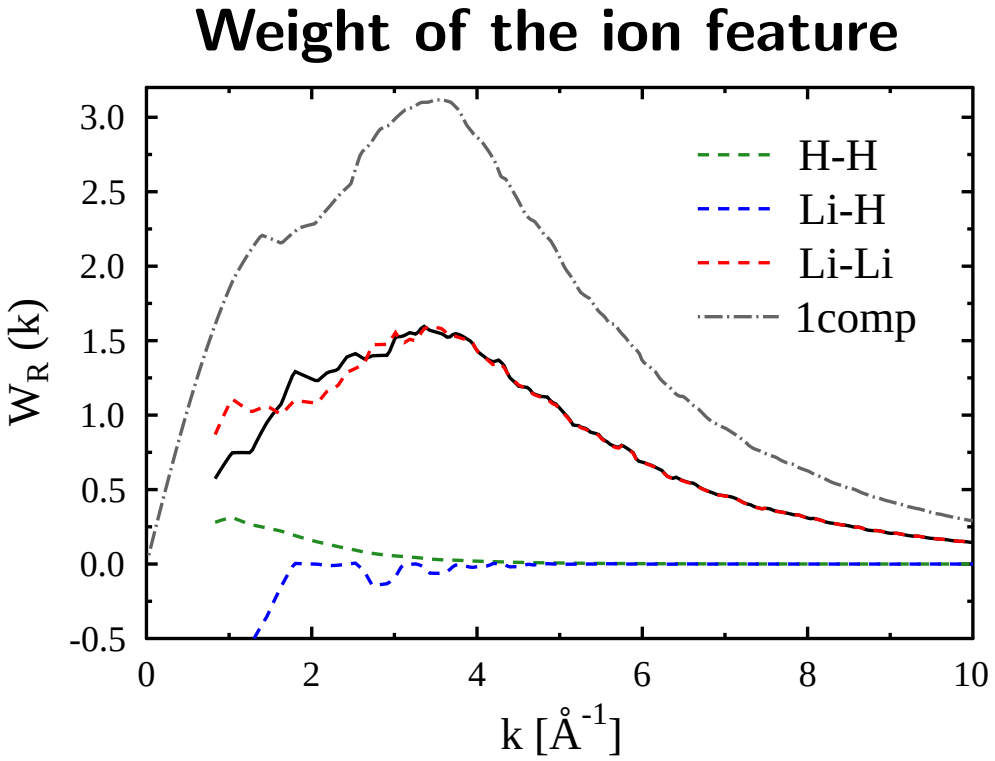


- DFT-MD + 2 component Chihara formula yields similar results than experiments
- Ion feature is dominated by scattering from $Li^+$ ions
- 1 component treatment uses wrong statistic factor in $W_R$

## Weight of the Rayleigh Peak for Plasmas with 2 Ion Species

$$W_R(k) = \frac{n_\alpha}{n_\alpha + n_\beta}\left[f_\alpha + q_\alpha\right]^2 S_{\alpha\alpha}(k) + \frac{n_\beta}{n_\alpha + n_\beta}\left[f_\beta + q_\beta\right]^2 S_{\beta\beta}(k)$$
$$+ 2\,\frac{\sqrt{n_\alpha n_\beta}}{n_\alpha + n_\beta}\left[f_\alpha f_\beta + q_\alpha q_\beta + f_\alpha q_\beta + f_\beta q_\alpha\right] S_{\alpha\beta}(k)$$

# Thank you!