Sandia National Laboratories

First-principles predictions of novel features in XRTS spectra of warm dense matter

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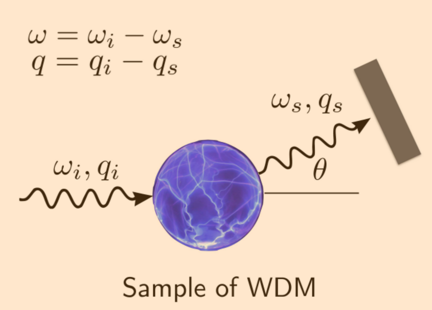
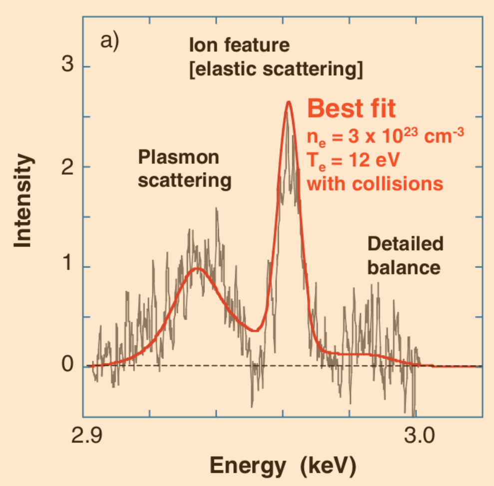
Background

- Warm dense matter (WDM) occurs in planetary cores and on the way to inertial confinement fusion
- X-ray Thomson scattering (XRTS) reveals laboratory sample conditions
  - typically extract T_e from detailed balance of plasmon features
  - limited sensitivity for $kT_e \gtrsim \hbar\omega_p$

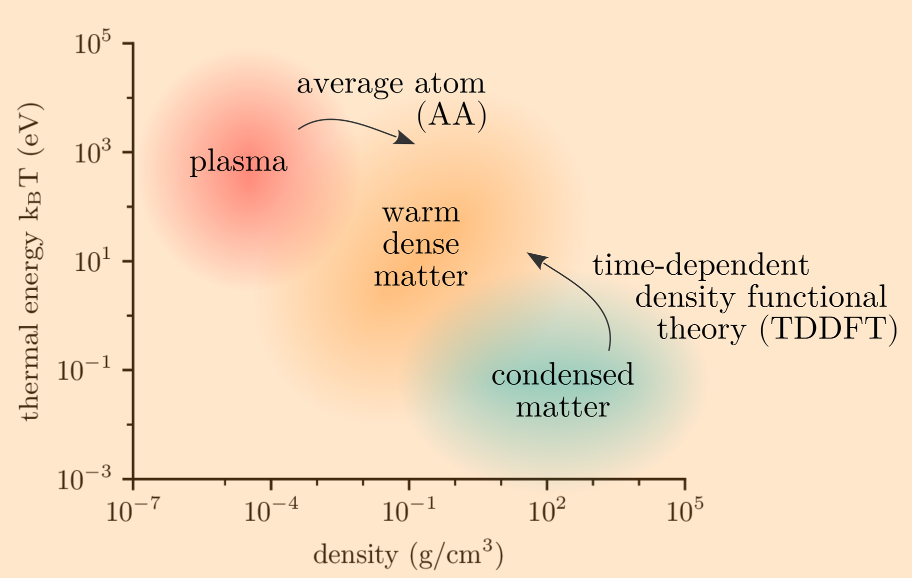


$$\frac{S(\mathbf{q},\omega)}{S(\mathbf{q},-\omega)} = e^{\hbar\omega/(k_B T)}$$



Glenzer et al., PRL 98 (2007)

- Interpretation of experimental data relies on accurate models
- WDM regime is challenging to model
  - AA assumptions break down at high density
  - TDDFT expensive at high temperature



Computational Approach

- Real-time time-dependent density functional theory
- Initial condition: ground state from Mermin-DFT
- Probe represents momentum transferred q by scattered x-ray

$$V_{\text{probe}}(\mathbf{r},t) = V_0\, e^{i\mathbf{q}\cdot\mathbf{r}} f(t)$$

- Evolve response to probe in real time

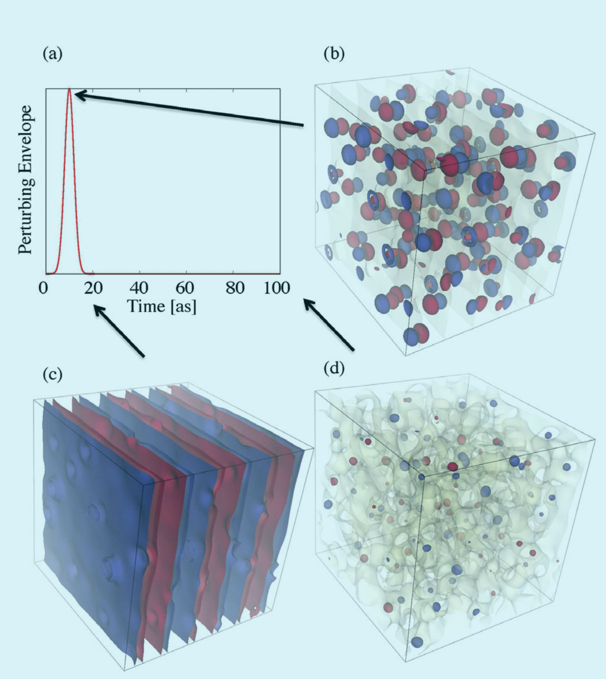
$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r},t) = \hat{H}[n(\mathbf{r},t)]\phi_j(\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_j f_j(T)|\phi_j(\mathbf{r},t)|^2$$

- Dynamic structure factor related to Fourier transform of density response

$$\delta\tilde{n}(\mathbf{q},\omega) = V_0 \tilde{f}(\omega)\tilde{\chi}(\mathbf{q},-\mathbf{q},\omega)$$

$$S(\mathbf{q},\omega) = -\frac{1}{\pi}\frac{\text{Im}\,[\tilde{\chi}(\mathbf{q},-\mathbf{q},\omega)]}{1-e^{-\omega/(k_B T)}}$$

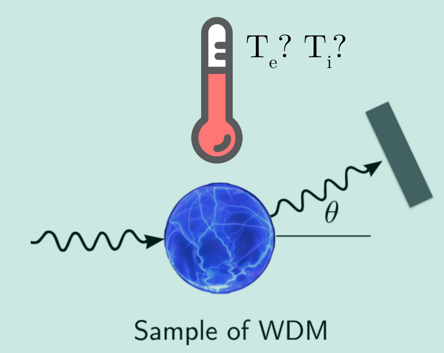


Baczewski et al., PRL 116 (2016)

Modified VASP

Objectives

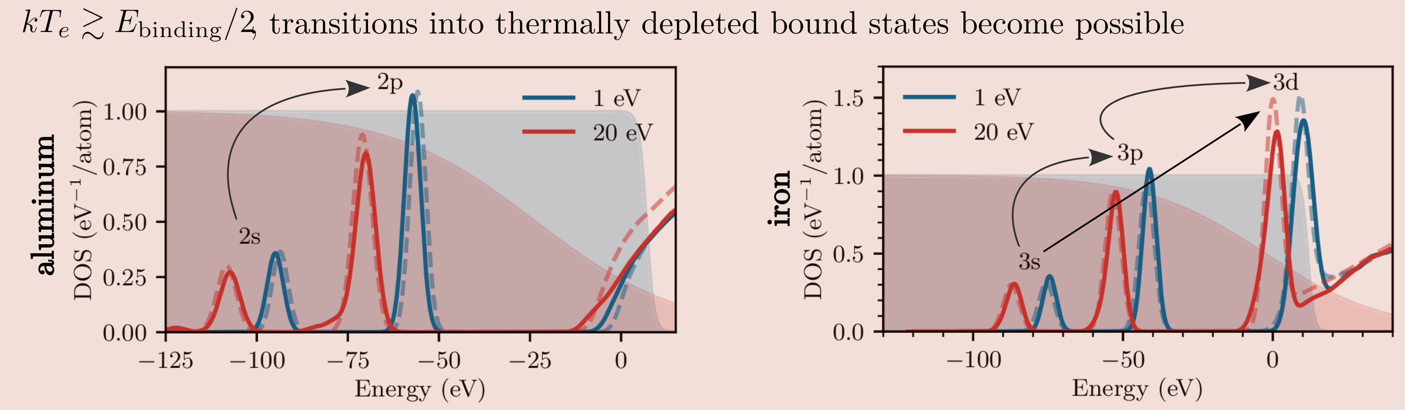
- Benchmark and improve AA using TDDFT
  - continuity of XRTS features with respect to sample conditions
  - inclusion of accurate electron-ion collisions for free-free response
- Study other XRTS features potentially useful for thermometry
  - signatures of bound-bound transitions
  - evolution of band structure effects as lattice melts



Bound-Bound Transitions

arXiv:2109.09576

- For $kT_e \gtrsim E_{\text{binding}}/2$ transitions into thermally depleted bound states become possible



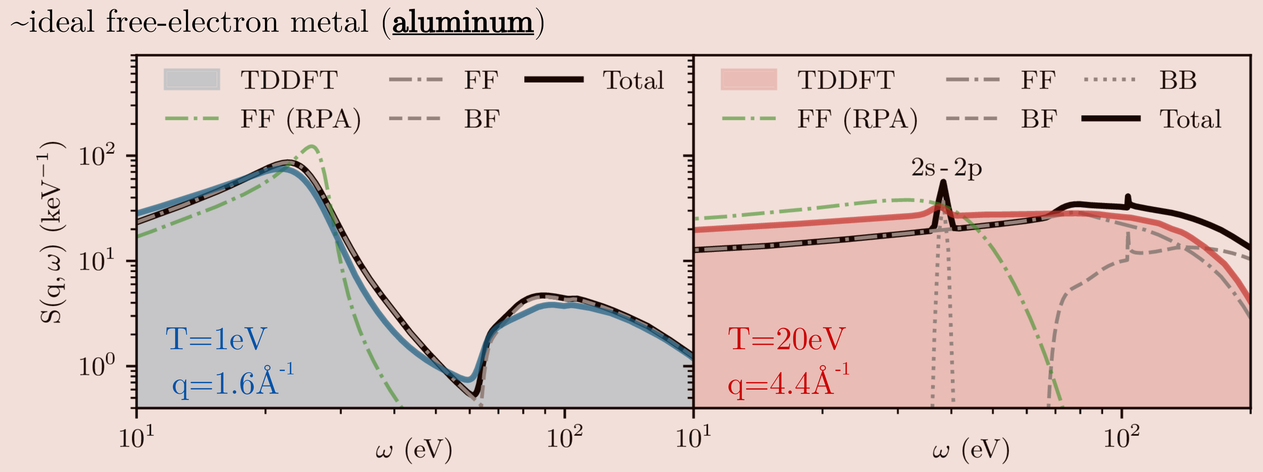
- Modified AA to capture bound-bound features and achieve continuity w.r.t. sample conditions

$$S(q,\omega) = S_{ii}(q,\omega) + S_{FF}(q,\omega) + S_{BF}(q,\omega) + S_{BB}(q,\omega)$$

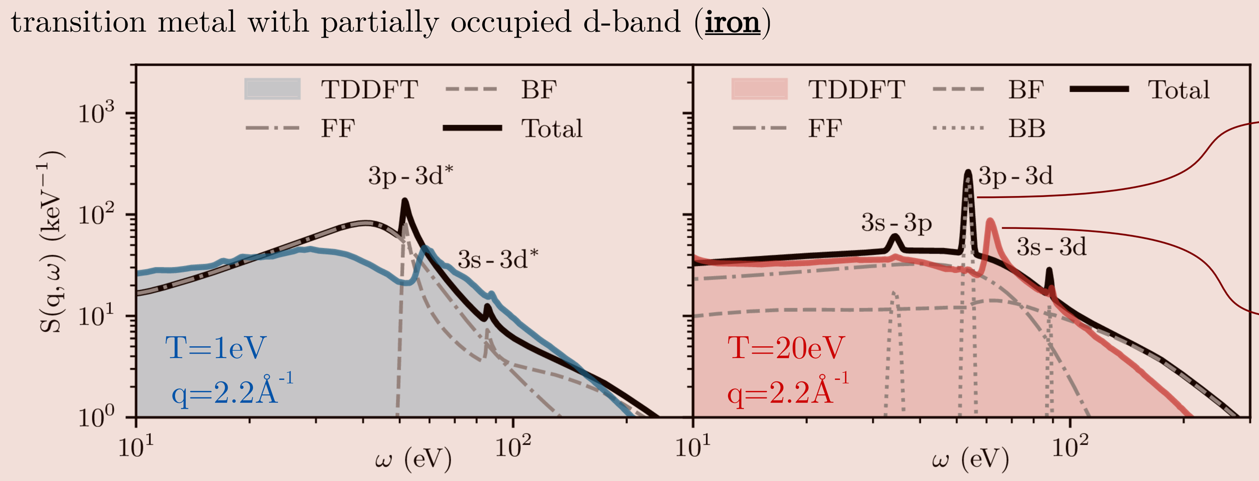
$S_{FF}(q,\omega)$ uses Mermin dielectric function with non-ideal DOS and T-matrix elastic collisions + inelastic processes

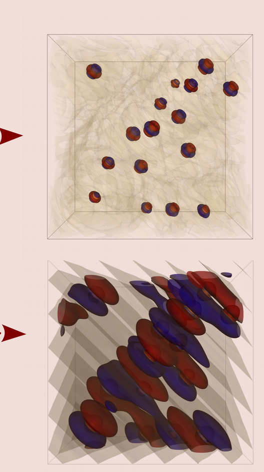
$S_{BB}(q,\omega)$ is similar to standard $S_{BF}(q,\omega)$; accounts for partial occupancy/vacancy of all initial/final bound states

- Modified AA is much closer to TDDFT than standard AA for:
  - ~ideal free-electron metal (**aluminum**)

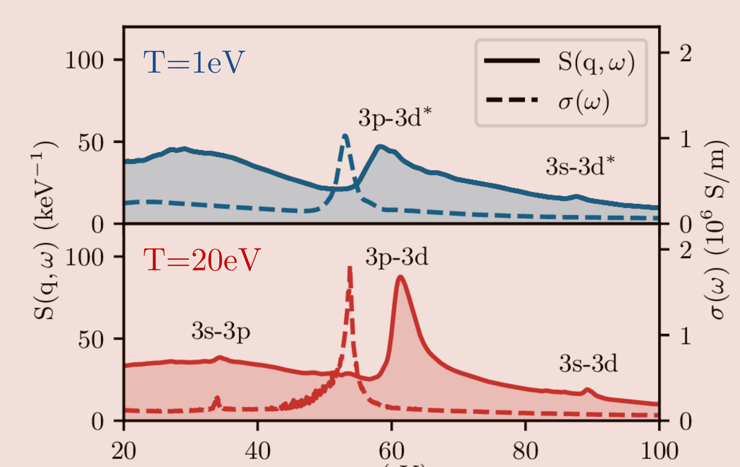


  - transition metal with partially occupied d-band (**iron**)



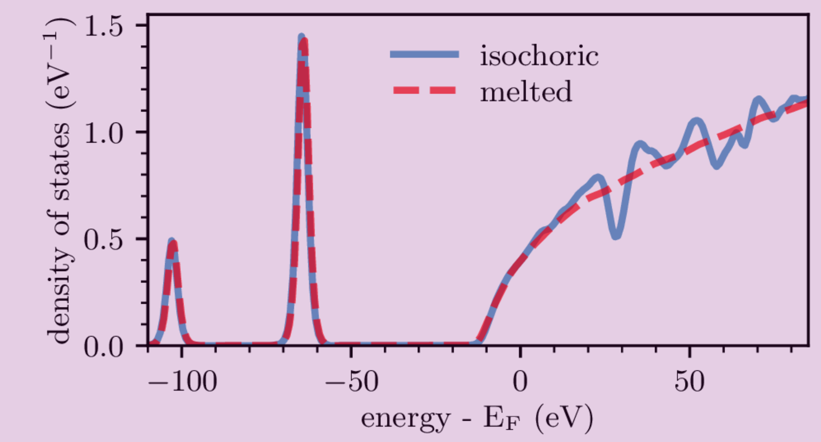


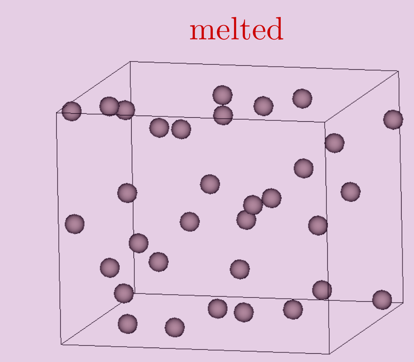
- Novel collective effect in 3p-3d transitions
  - TDDFT XRTS feature ~5eV higher energy than predicted by theories relying on single-particle picture:
    - DFT eigenvalue difference
    - AA XRTS spectra
    - Kubo-Greenwood dynamic conductivity
  - verified through visualization of density response
- Existence and strength of bound-bound transitions should be sensitive to T via occupancy of involved states
  - promising alternative to plasmon-based thermometry

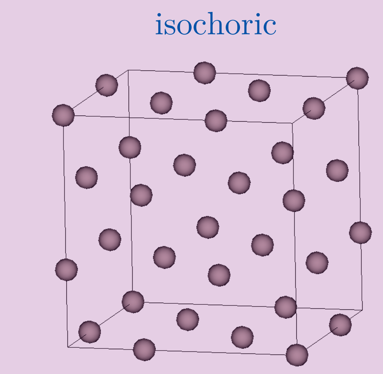


Band Structure Effects and Ion Temperature

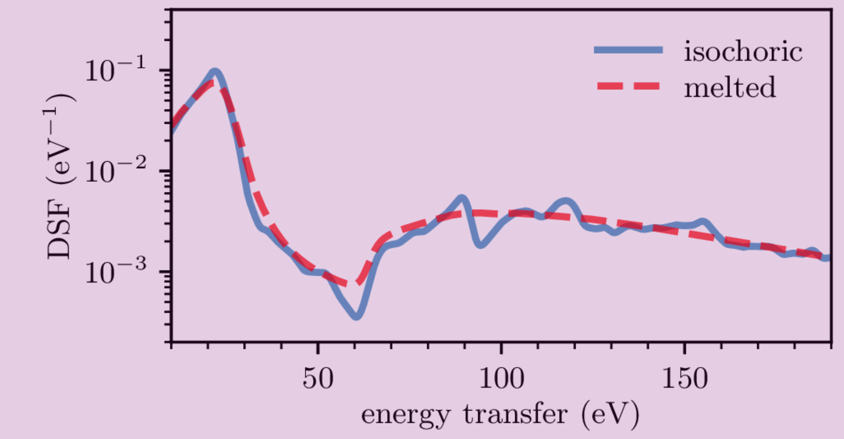
- Melted Al ($T_i = T_e$ = 1eV) forms ~ideal free-electron gas
- Isochorically heated Al ($T_i \approx 0$, T_e = 1eV) has gaps among high-energy conduction bands







- XRTS spectra reflect details of band structure
  - smooth for melted material
  - features in bound-free portion for isochorically heated crystal



- May allow simultaneous inference of T_i and T_e

Conclusions

- Achieve generally good agreement between TDDFT and AA
- Predict prominent bound-bound features in XRTS spectra at high T_e
  - need to be included in Chihara-based theories like AA
  - novel collective behavior for narrow bands near E_F
- Predict subtle band structure effects in XRTS spectra depending on T_i
- New features promising for temperature diagnostics

Outlook

- Further improve AA to capture subtle collective effects in bound-bound features
- Study temperature (both T_e and T_i) dependence of isochoric effects
- Look for similar bound-bound and isochoric features in TDDFT conductivities
- Apply framework to other materials and conditions of interest
  - e.g., ultrafast melting in copper
- Interested in exploring collaboration opportunities!

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