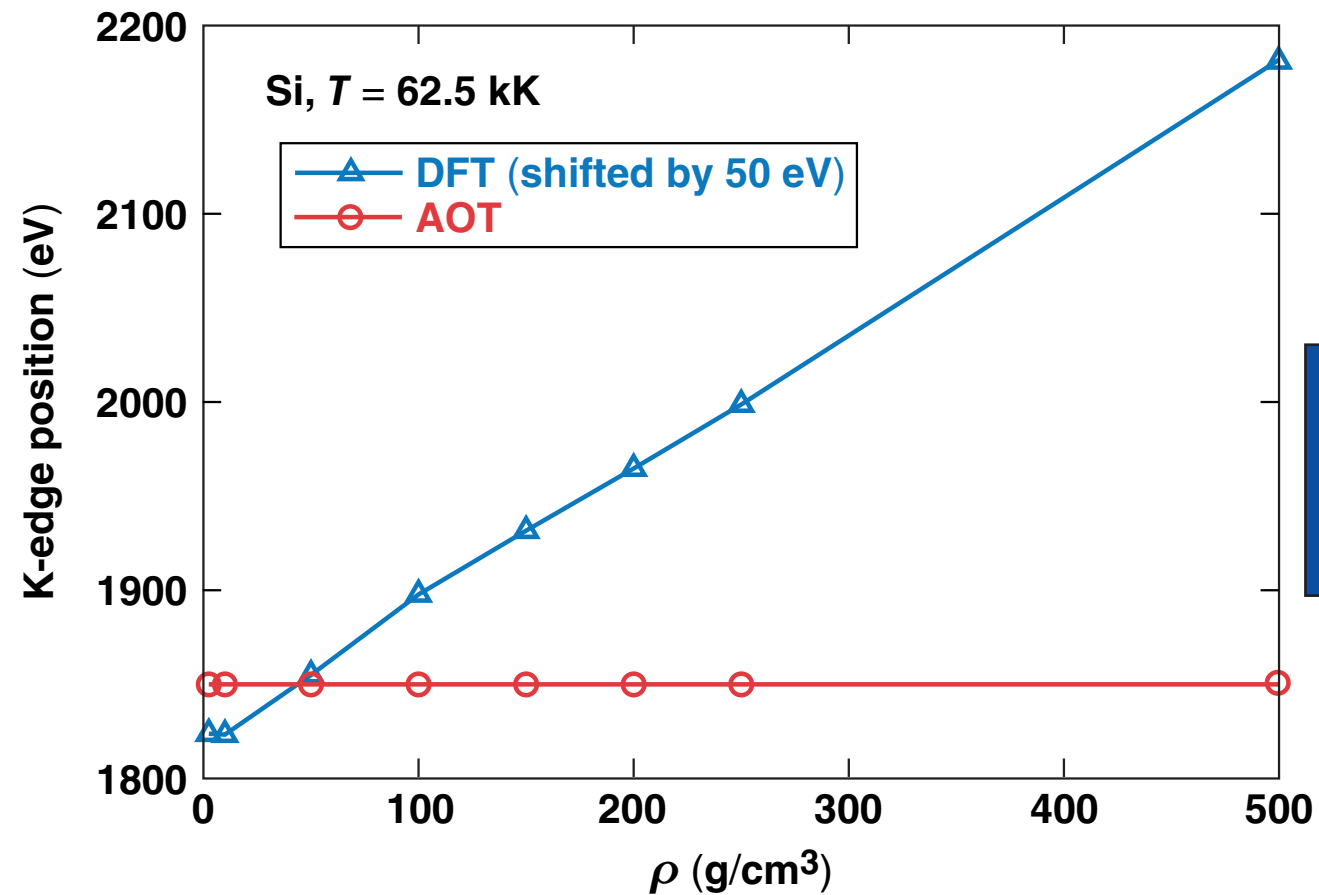# Density Functional Theory Methods for Transport and Optical Properties: Application to Warm Dense Silicon

- Significant K-edge shift in dense silicon is predicted
- Astrophysics opacity table (AOT) data fail to predict it

V. V. Karasiev
University of Rochester
Laboratory for Laser Energetics

Summary

Finite-temperature density functional theory (DFT) is a powerful tool to accurately predict properties of matter at a wide range of densities across temperature regimes [warm-dense-matter (WDM) conditions]

UR
LLE

- Exchange-correlation (XC) thermal effects in simulations of WDM are taken into account via use of a temperature-dependent XC functional

- A set of accurate all-electron pseudo-potentials for the calculation of x-ray absorption near edge structure (XANES) spectra has been constructed

- Absorption coefficients and opacities of silicon (densities between 0.1 and 500 g/cm^3 and temperature between 0.5 and 1000 eV) have been calculated

TC14292

Collaborators

S. X. Hu

**University of Rochester
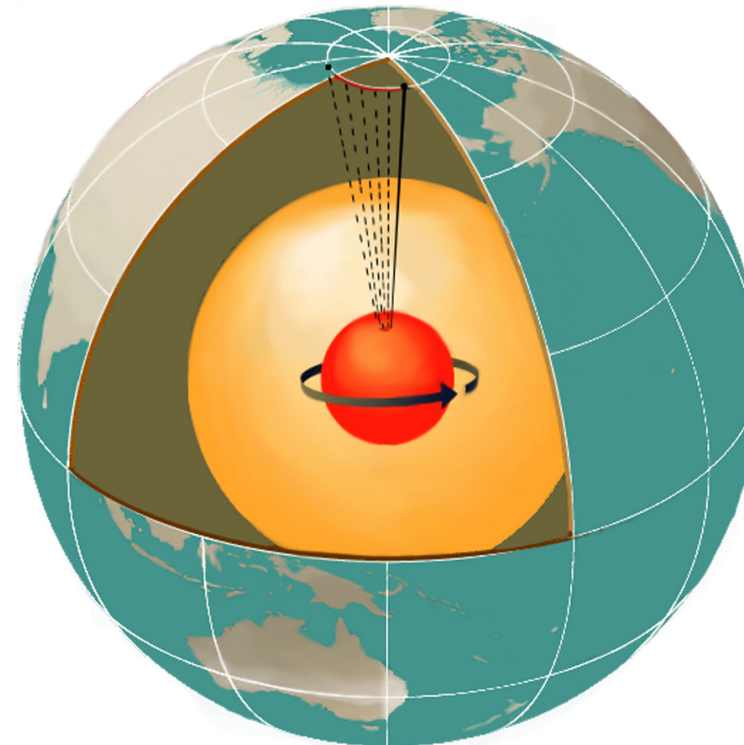Laboratory for Laser Energetics**

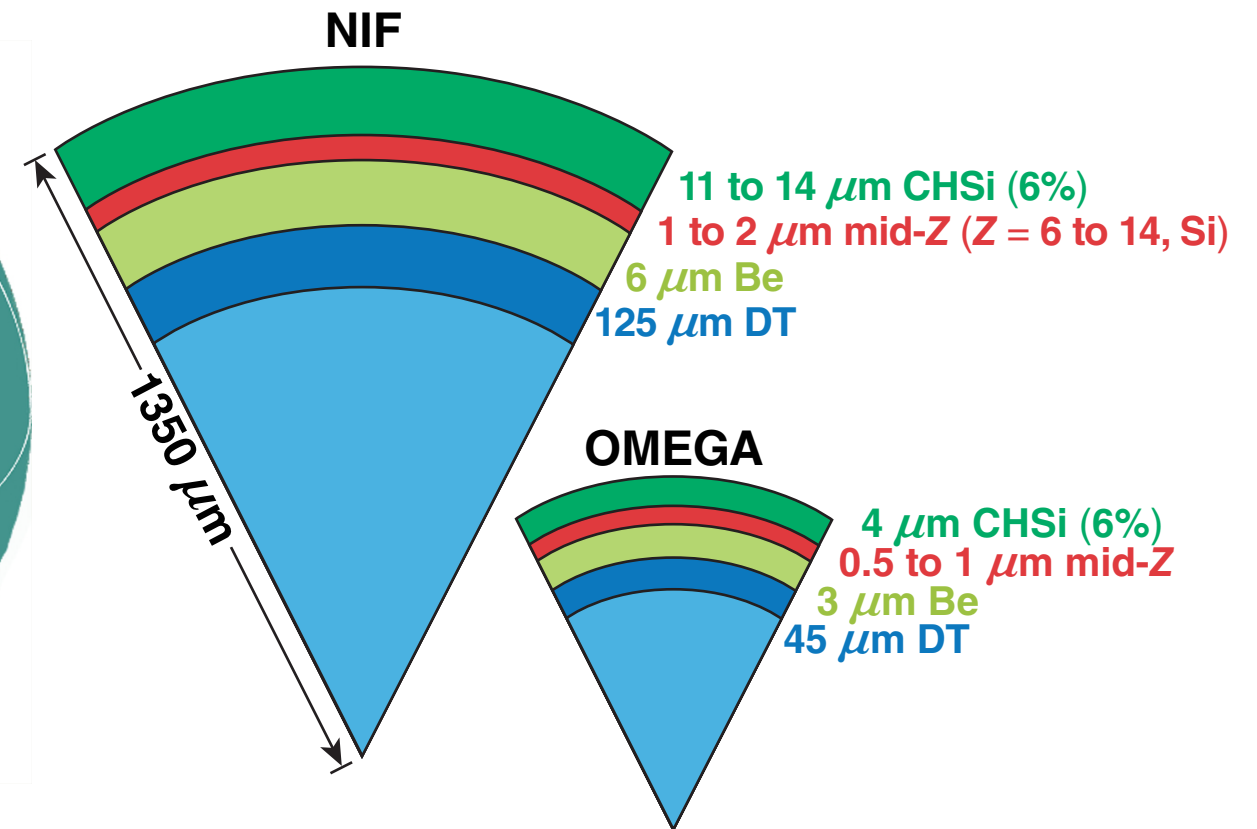## L. Calderin

University of Arizona

Silicon is important to HED physics, such as planetary science and ICF capsules

- **The high-pressure silicon equation of state (EOS) is crucial to understanding the dynamics of silicon-rich planets (i.e., Earth)**

- **Silicon is used in ICF capsules to reduce fuel preheat and laser–plasma instability (LPI) effects**

Planetary science*

ICF capsule**

NIF

11 to 14 μm CHSi (6%)
1 to 2 μm mid-Z (Z = 6 to 14, Si)
6 μm Be
125 μm DT

1350 μm

OMEGA

4 μm CHSi (6%)
0.5 to 1 μm mid-Z
3 μm Be
45 μm DT

E25548c

Warm dense matter is of interest in planetary science, astrophysics, and ICF
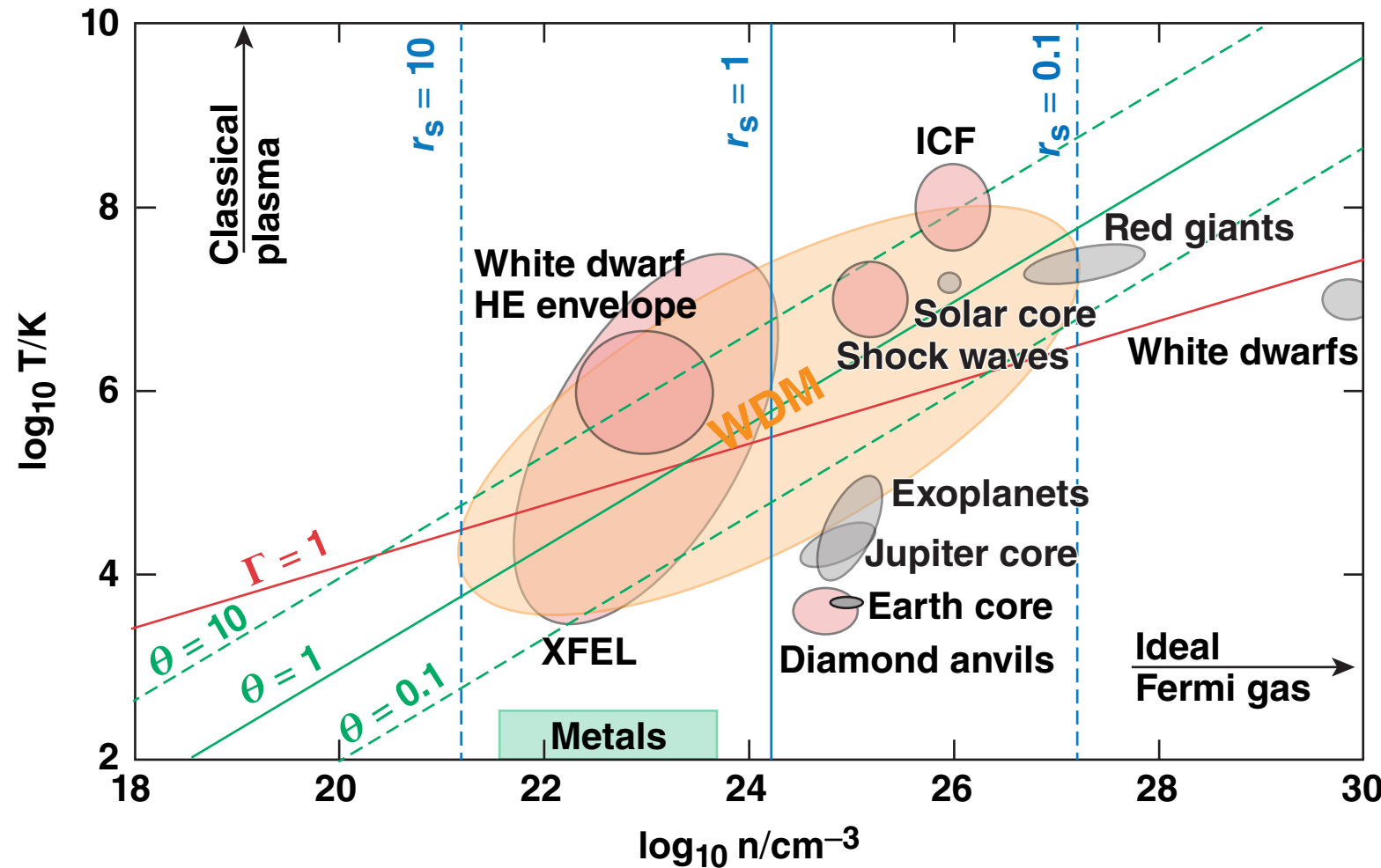
Schematic temp.-density diagram (PR 744, 1 (2018))

$\Gamma = e^2 / r_s k_B T \geq 1$: the Couloumb coupling parameter

$\theta = t = T/T_F \approx 1$: reduced temperature

T_F: Fermi temperature

- Classical plasma approaches work only for weakly coupled nondegenerate systems ($\Gamma \ll 1$: low density, very high temperature)

- All regions except left-upper corner require quantum treatment of electronic degrees of freedom
- Most of (semi-) classical models are inaccurate or fail

HE: high energy
XFEL: X-ray free-electron laser

TC14293

Thermal DFT coupled with *ab initio* molecular dynamics (AIMD) has become a standard tool in high-energy-density physics (HEDP)

Start

Ion distribution

Electron density $\rho(r)$

Pseudo-potential

V_{eff}

Kohn–Sham equation

MD step

DFT step

Molecular dynamics

Yes **E min?** **No**

$E[\rho(r)]$

$\varepsilon_k - \phi_k$

Thermodynamic data
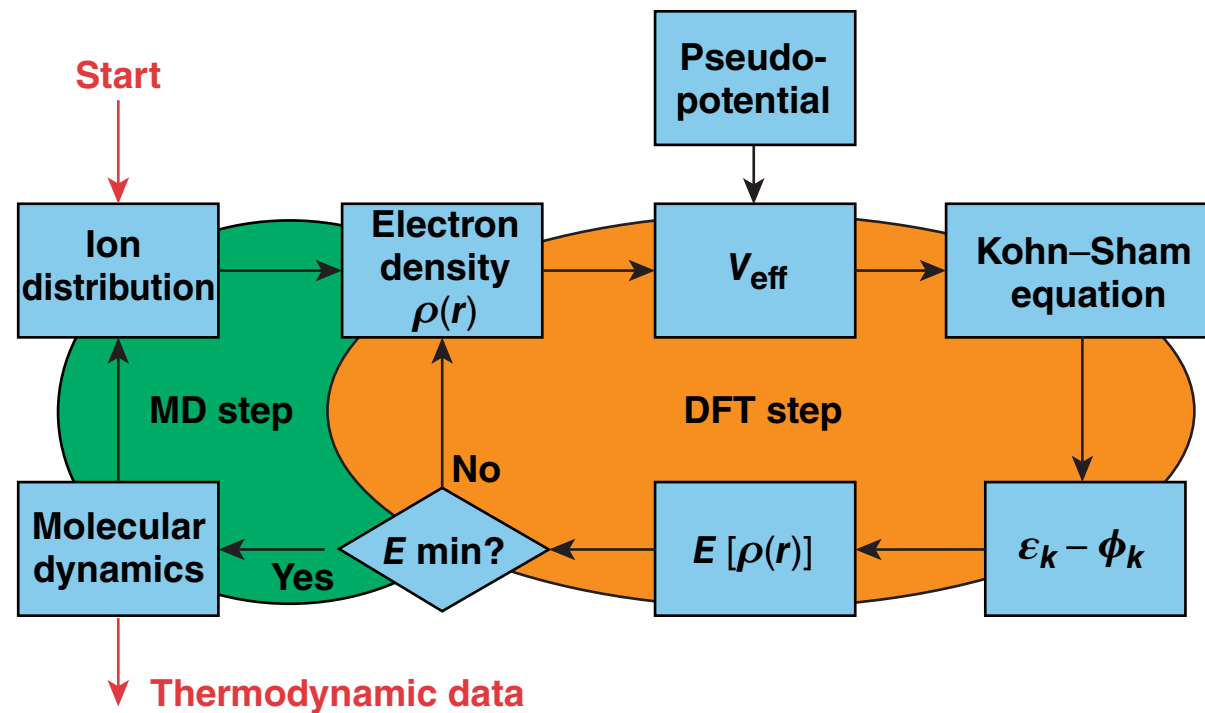
Molecular dynamics $\quad m_I \ddot{R}_I = -\vec{\nabla}_I V(R_1, R_2, ..., R_N)$

Born–Oppenheimer energy surface: $V(\{R\}) = \Omega(\{R\}) + E_{\text{ion–ion}}\{(R)\}$

The current best practice uses free-energy DFT with one-electron Kohn–Sham orbitals

The Kohn–Sham scheme replaces the $(3N_e)$-dimensional problem by N_e-coupled 3-D problems

Free-energy density functionals:

$\Omega(n) = \mathcal{F}(n) + \int \vec{d}r \left[v_{\text{ext}}(\vec{r}) - \mu \right] n(\vec{r})$: **grand potential**

$\mathcal{F}(n) = \mathcal{F}_s(n) + \mathcal{F}_H(n) + \mathcal{F}_{xc}(n)$: **free-energy functional**

$\mathcal{F}_H(n)$: **Hartee energy**

$\mathcal{F}_{xc}(n)$: **XC energy**

$\mathcal{F}_s(n)$: **non-interacting (Kohn–Sham) free energy**

MD: molecular dynamics

DFT-based AIMD makes it possible to calculate many material properties required for simulations of ICF implosions and provides predictions for HEDP experiments

Some of material properties accessible from DFT-based AIMD simulations

- **Equation of state**

- **Thermal conductivity**

- **Electrical conductivity**

- **Reflectivity**

- **Absorption coefficients → Rosseland and Planck mean opacities**

HEDP requires development of new methods and functionals to accurately predict matter properties

- Temperature-dependent exchange-correlation functionals are required to take into account the XC thermal effects

- All-electron (i.e., with active 1s-core electrons) pseudo-potentials are needed for x-ray absorption calculations

TC14295

A framework for temperature-dependent XC functionals has been developed to address the issue of thermal effects

Generalized gradient approximation (GGA)

Exchange

$$F_x^{GGA}[n,T] = \int n\, f_x^{LDA}(n,T) F_x[s_{2x}(T)]\, d\vec{r}$$

$$s_{2x}(n,\nabla n,T) \equiv s^2(n,\nabla n)\tilde{B}_x(t);$$

$$f_x^{LDA}(n,T) = \varepsilon_x^{LDA}(n)\tilde{A}_x(t); \; t = T/T_F$$

Constraints

- **Reproduce finite-temperature gradient expansion**

- **Satisfy Lieb–Oxford bound at $T = 0$**

- **Reduce to correct $T = 0$ limit**

- **Reduce to correct high-temperature limit**

Correlation

$$F_c^{GGA}[n,T] = \int n\, f_c^{GGA}(n,\nabla n,T)\, d\vec{r}$$

GGA correlation energy per particle:

$$f_c^{GGA}(n,\nabla n,T) = f_c^{LDA}(n,T) + H\left[f_c^{LDA}, q_c(T)\right]$$

$$q_c(n,\nabla n,T) \equiv q(n,\nabla n)\sqrt{\tilde{B}_c(n,t)}$$

Constraints

- **Reproduce finite-temperature gradient expansion**

- **Reduce to correct $T = 0$ limit**

- **Reduce to correct high-temperature limit**

*V. V. Karasiev, J. W. Dufty, and S. B. Trickey, "Non-Empirical Semi-Local Free-Energy Density Functional for Matter Under Extreme Conditions." Phys. Rev. Lett. 120, 076401 (2018).

TC13730

Electronic transport coefficients are calculated from *ab initio* simulations within the framework of the Kubo–Greenwood approach (linear response theory)

- The real part of electrical conductivity σ_1 and thermal conductivity κ are given in terms of the Onsager coefficients L_{mn}

$$\sigma = \sigma_1 + i\sigma_2; \sigma_1 = L_{11}; \kappa = \frac{1}{T}\left(L_{22} - \frac{L_{12}^2}{L_{11}}\right)$$

- The frequency-dependent Onsager coefficients are defined in terms of the velocity operator matrix elements:

$$\left|\left\langle \psi_{\bar{k}i}\left|\nabla_\alpha\right|\psi_{\bar{k}j}\right\rangle\right|^2$$

- The imaginary part σ_2 could be calculated via Kubo Greenwood formula in terms of the velocity operator matrix elements or alternatively from the principal value integral

The dielectric function and index of refraction (Re and Im parts, *n* and *k*):

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = [n(\omega) + ik(\omega)]^2$$

$$\varepsilon_1(\omega) = 1 - \frac{4\pi}{\omega}\sigma_2(\omega); \varepsilon_2(\omega) = \frac{4\pi}{\omega}\sigma_1(\omega)$$

$$n(\omega) = \sqrt{\frac{|\varepsilon(\omega)| \cap \varepsilon_1(\omega)}{2}}; k(\omega) = \sqrt{\frac{|\varepsilon(\omega)| - \varepsilon_1(\omega)}{2}}$$

The reflectivity absorption coefficient and grouped Rosseland mean opacity:

$$r(\omega) = \frac{[1 - n(\omega)]^2 + k^2(\omega)}{[1 + n(\omega)]^2 + k^2(\omega)} \qquad \alpha(\omega) = \frac{4\pi}{n(\omega)c}\sigma_1(\omega)$$

$$K_R(\omega_1 : \omega_2) = \frac{\displaystyle\int_{\omega_1}^{\omega_2} n^2(\omega)\frac{\partial B(\omega, T)}{\partial T}d\omega}{\displaystyle\int_{\omega_1}^{\omega_2} n^2(\omega)\frac{1}{\alpha_m(\omega)}\frac{\partial B(\omega, T)}{\partial T}d\omega}$$

L. Calderín, V. V. Karasiev, and S. B. Trickey, Comput. Phys. Commun. **221**, 118 (2017).
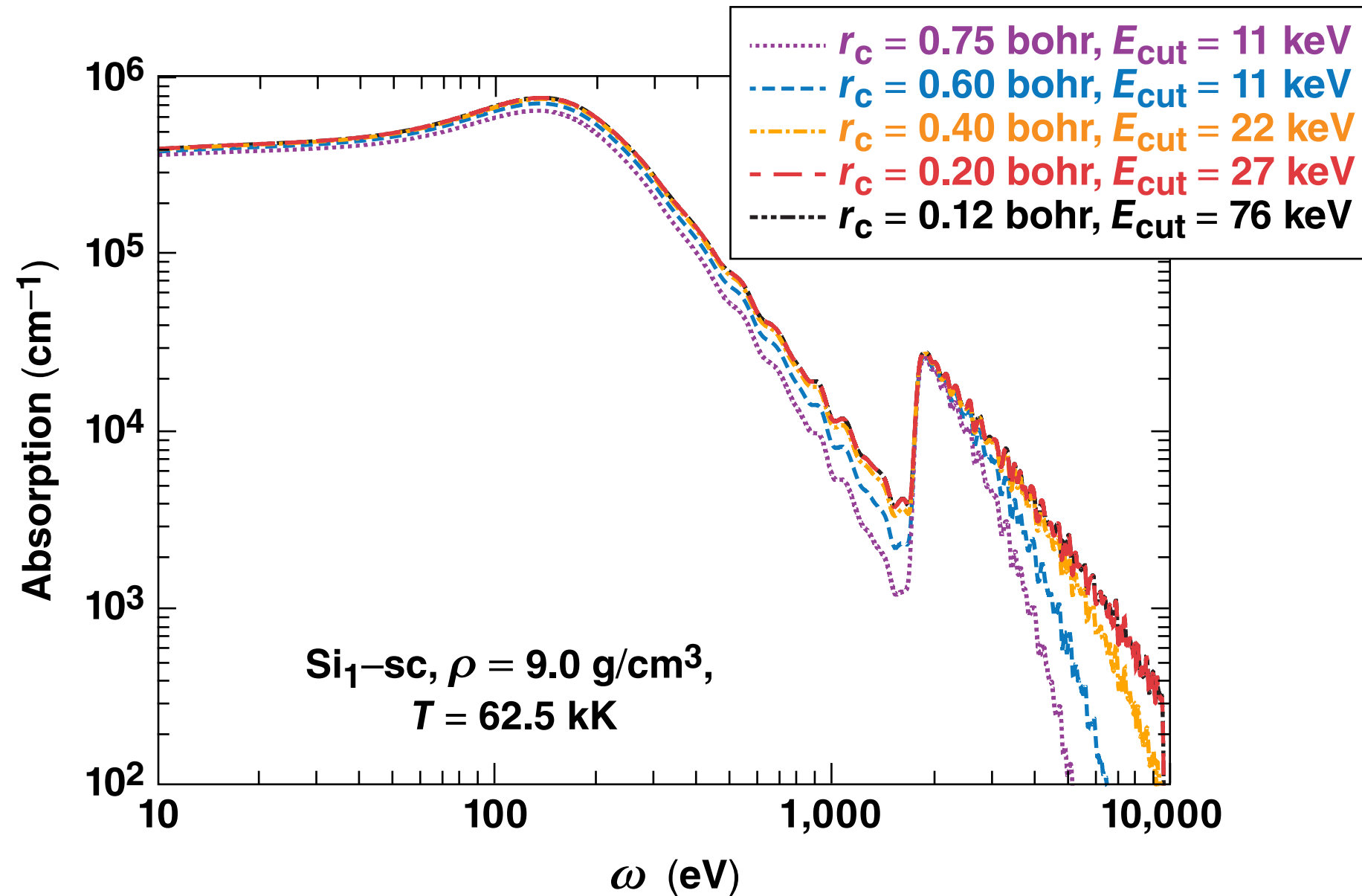
Calculation of optical properties within the x-ray range involves transitions from core states → explicit treatment of 1s electrons in electronic structure calculations is required
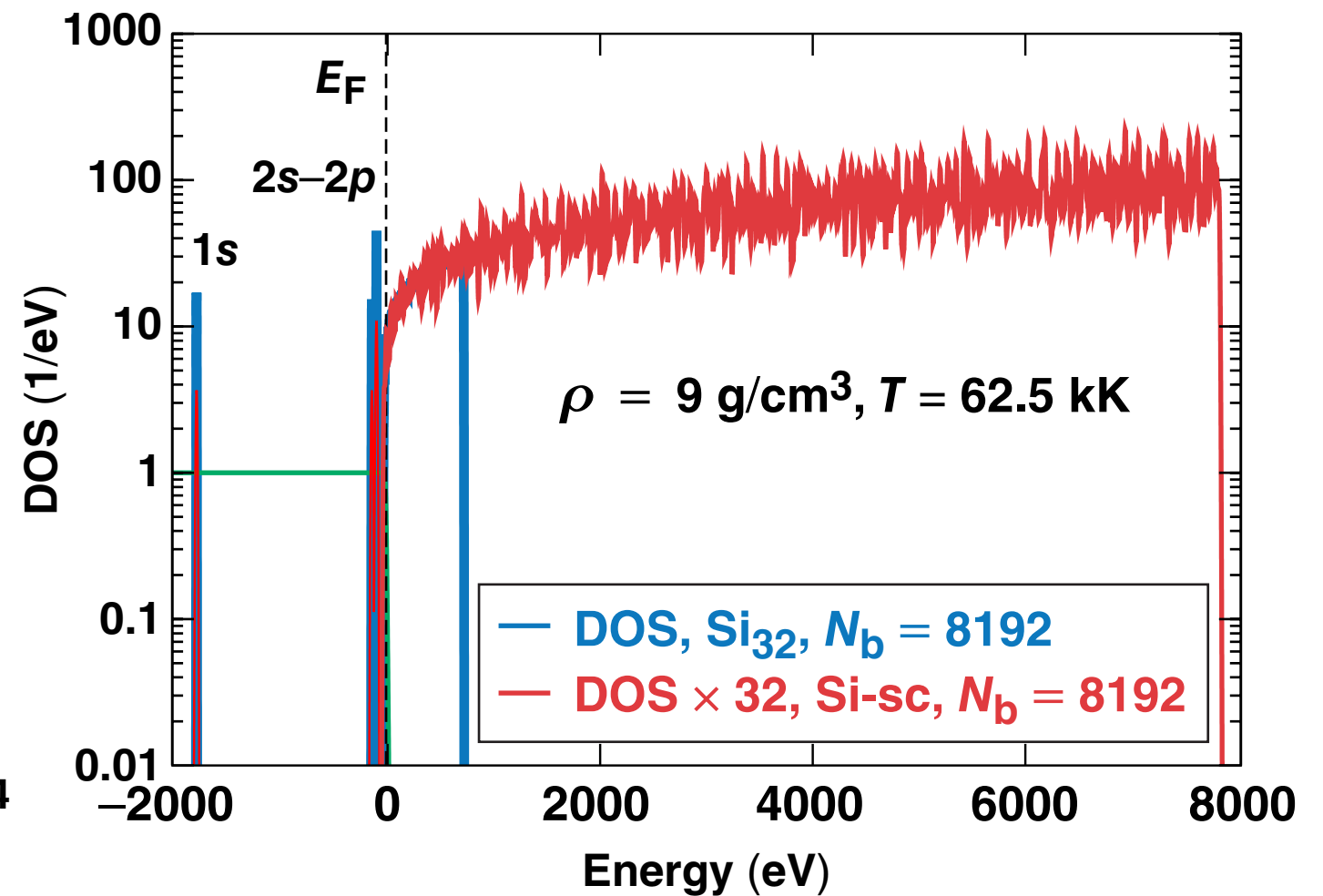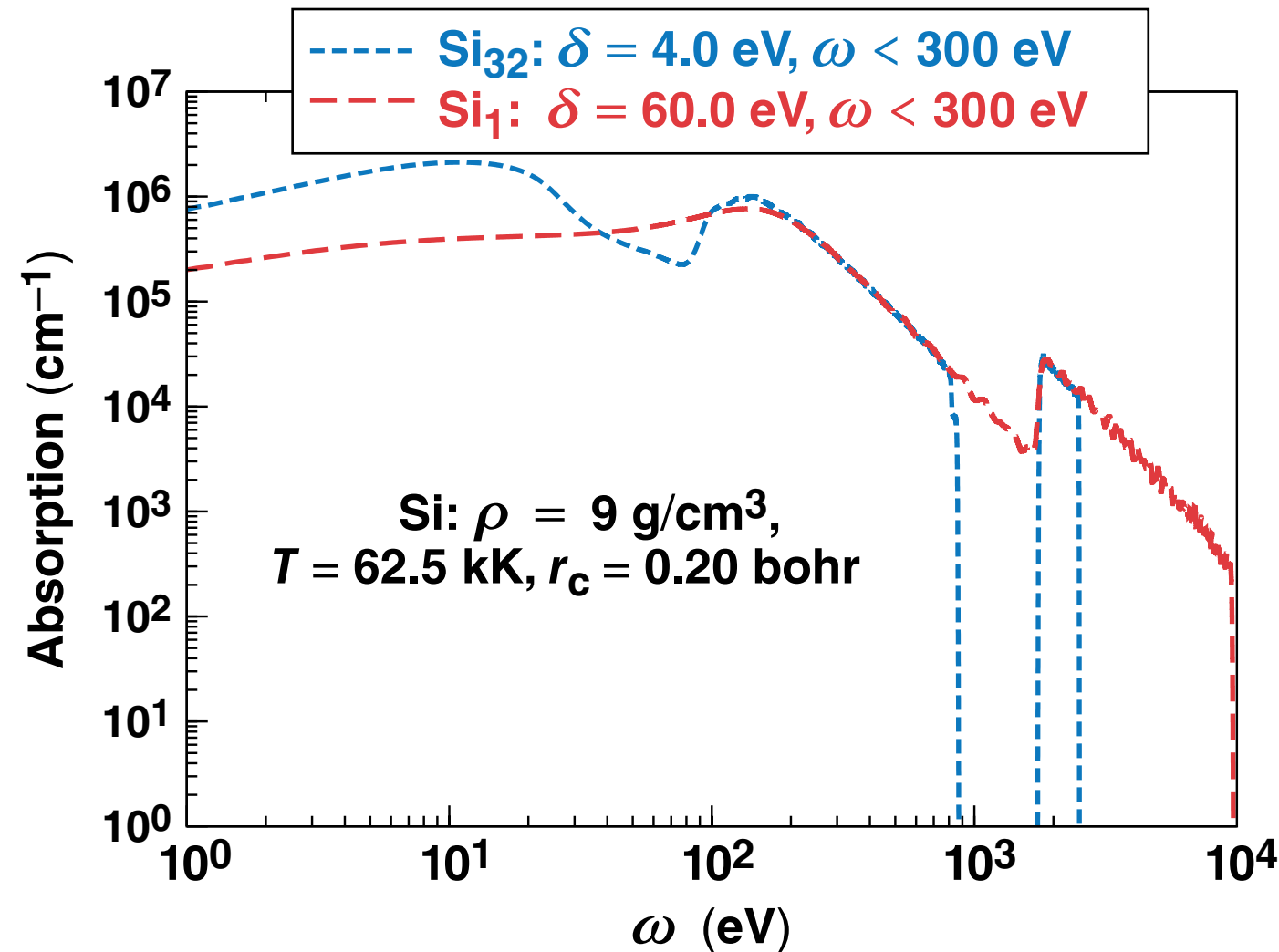
E_{cut} = 5.4 keV

Si_{64}, 2.57 g/cm^3, 2 kK
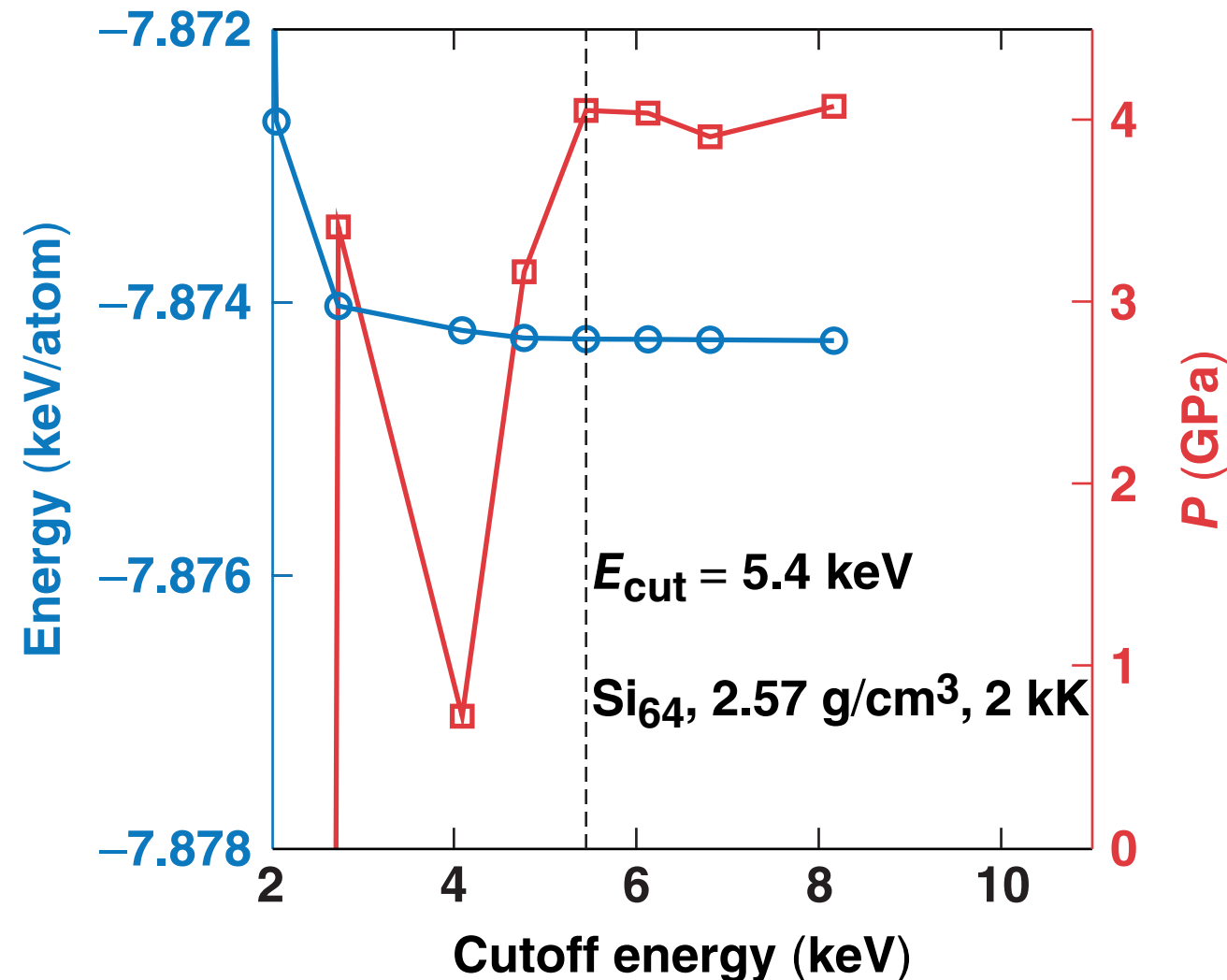
- There is a need for an "all-electron" pseudo-potential (PP) to treat 1s states

- We constructed an all-electron PP for Si, r_c = 0.75 bohr

- Converged cutoff energy: E_{cut} = 400 Ry = 5.4 keV

← Convergence study of the total energy and pressure with regard to E_{cut} for all-electron PP for Si_{64} atoms molecular-dynamics snapshot (ρ = 2.57 g/cm^3, T = 2000 K)

TC14300

Convergence study of absorption with regard to pseudopotential cutoff radius for Si_1, $\rho = 9.0$ g/cm^3, and $T = 62{,}500$ K

Legend:
- $r_c = 0.75$ bohr, $E_{cut} = 11$ keV
- $r_c = 0.60$ bohr, $E_{cut} = 11$ keV
- $r_c = 0.40$ bohr, $E_{cut} = 22$ keV
- $r_c = 0.20$ bohr, $E_{cut} = 27$ keV
- $r_c = 0.12$ bohr, $E_{cut} = 76$ keV

Si_1–sc, $\rho = 9.0$ g/cm^3, $T = 62.5$ kK

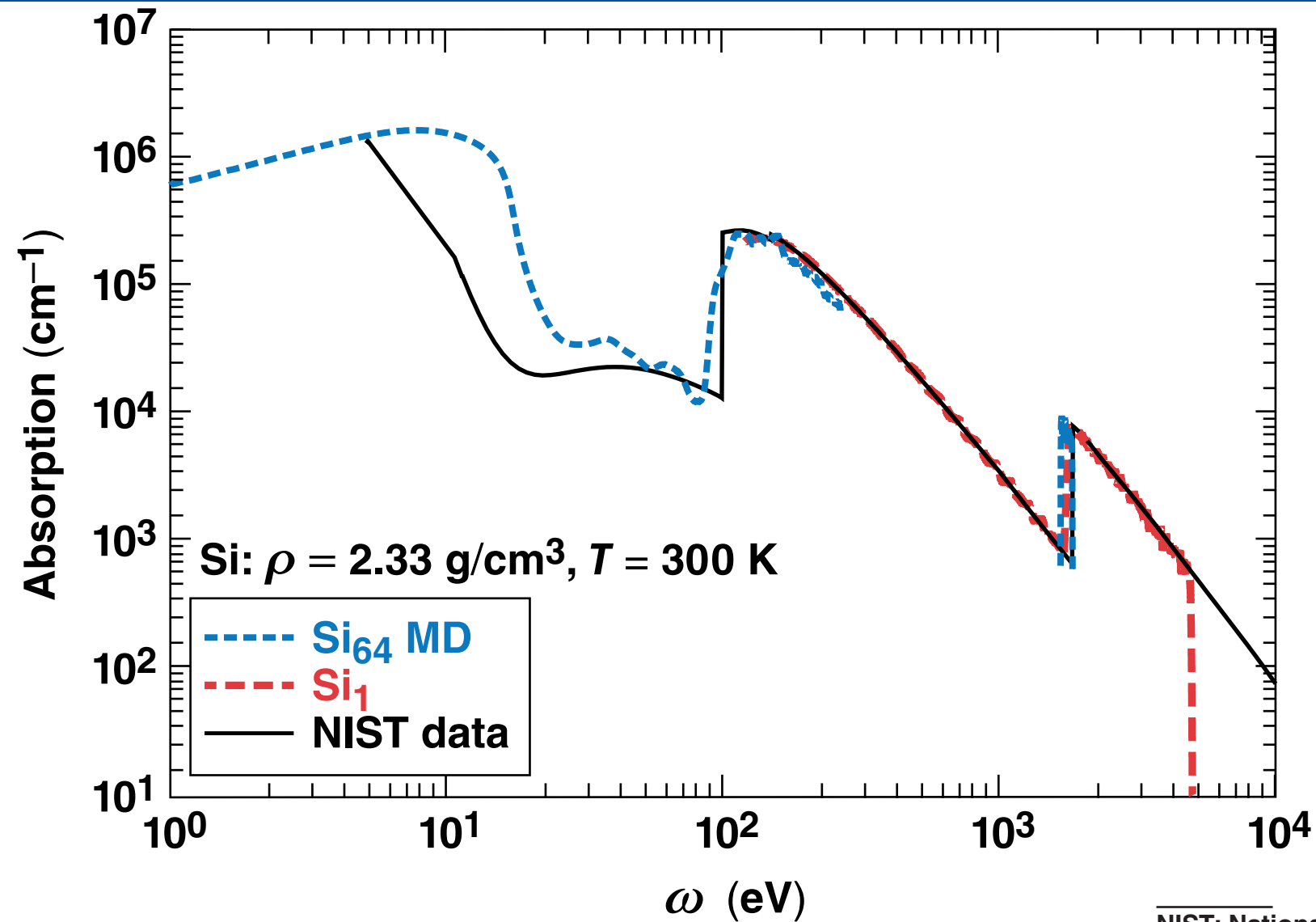Absorption (cm^{-1}) vs ω (eV)

A novel method of extending calculations to the x-ray range was proposed: combine the MD snapshot (Si$_{32}$) and single-atom (Si$_1$) data for absorption: Si$_{32}$ data at $\omega < 300$ eV and Si$_1$ data at $\omega > 300$ eV
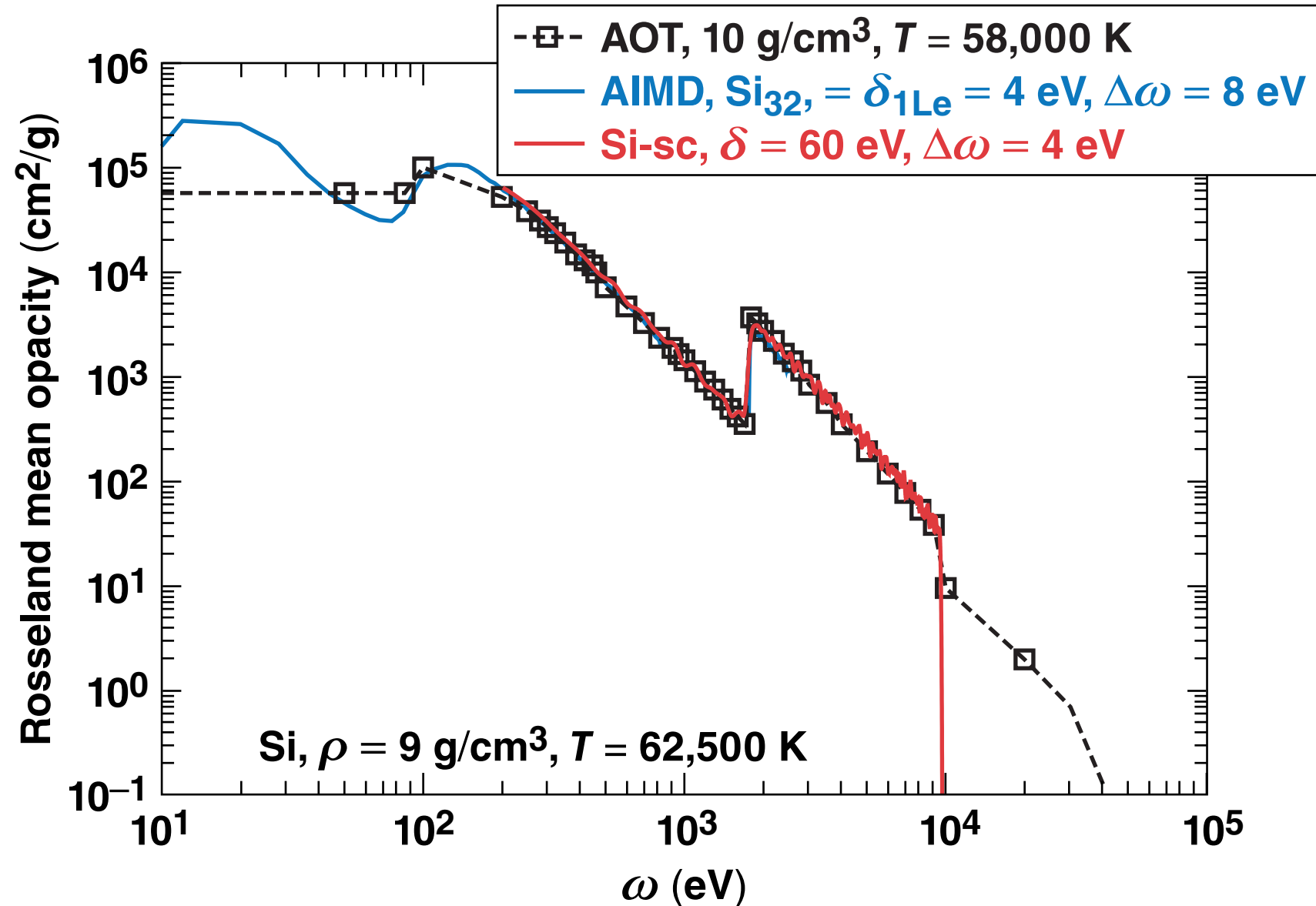
Left panel legend:
- - - - Si$_{32}$: $\delta = 4.0$ eV, $\omega < 300$ eV
- - - - Si$_1$: $\delta = 60.0$ eV, $\omega < 300$ eV

Si: $\rho = 9$ g/cm^3, $T = 62.5$ kK, $r_c = 0.20$ bohr

Left axis: Absorption (cm^{-1})
Bottom axis: ω (eV)

Right panel:
E_F
2s–2p
1s

$\rho = 9$ g/cm^3, $T = 62.5$ kK

- —— DOS, Si$_{32}$, $N_b = 8192$
- —— DOS $\times$ 32, Si-sc, $N_b = 8192$

Left axis: DOS (1/eV)
Bottom axis: Energy (eV)

MD: molecular dynamics
DOS: density of states

TC14303

UNIVERSITY of ROCHESTER

12

Comparison to the NIST reference data for Si absorption, $\rho = 2.33$ g/cm^3, $T = 300$ K confirms accuracy of the method; some discrepancies are observed at low ω

Si: $\rho = 2.33$ g/cm^3, $T = 300$ K

- - - - Si$_{64}$ MD
- - - - Si$_1$
—— NIST data

Absorption (cm^{-1})

ω (eV)

NIST: National Institute of Standards and Technology

Comparison between the AOT and DFT data for opacity, silicon, ρ = 9.0 g/cm^3, T = 62,500 K shows good agreement only at some conditions

Legend:
- AOT, 10 g/cm^3, T = 58,000 K
- AIMD, Si$_{32}$, = δ_{1Le} = 4 eV, $\Delta\omega$ = 8 eV
- Si-sc, δ = 60 eV, $\Delta\omega$ = 4 eV

Si, ρ = 9 g/cm^3, T = 62,500 K

y-axis: Rosseland mean opacity (cm^2/g)

x-axis: ω (eV)

AOT: astrophysics opacity table

Comparison between the AOT and DFT data for total opacity, silicon $\rho = 50$ g/cm^3 K shows discrepancy at $T < 30$ eV
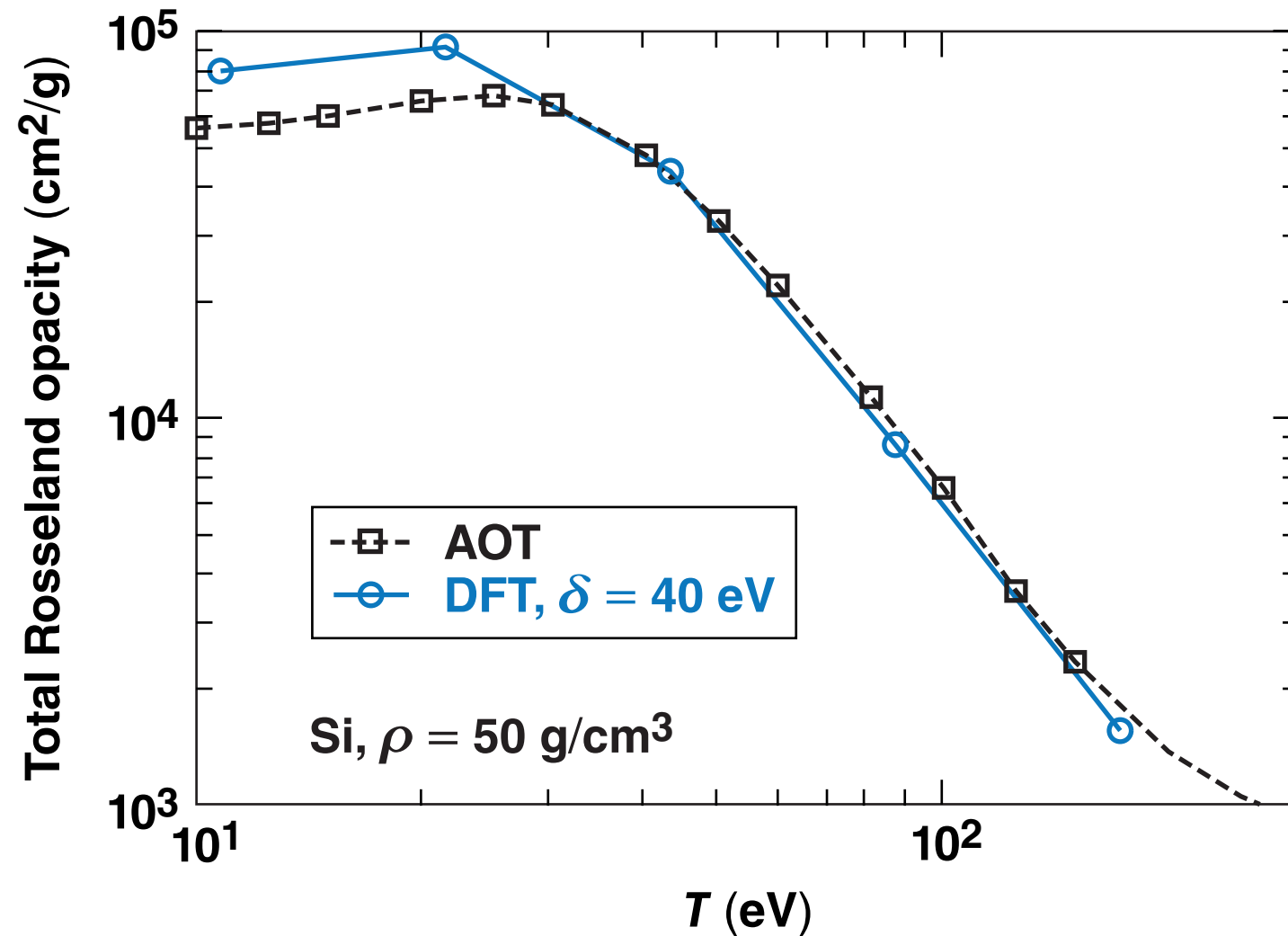
- AOT data are not accurate at low temperatures
- The same trend previously was observed in AOT data for other materials D$_2$ and CH*

S. X. Hu *et al.*, Phys. Rev. E **90**, 033111 (2014);
S. X. Hu *et al.*, Phys. Rev. B **96**, 144203 (2017).

UNIVERSITY of ROCHESTER

We predicted the K-edge shift of the x-ray absorption spectra in dense silicon as a result of continuum lowering and Fermi surface rising effects*

*S. X. Hu, Phys. Rev. Lett. 119, 065001 (2017).
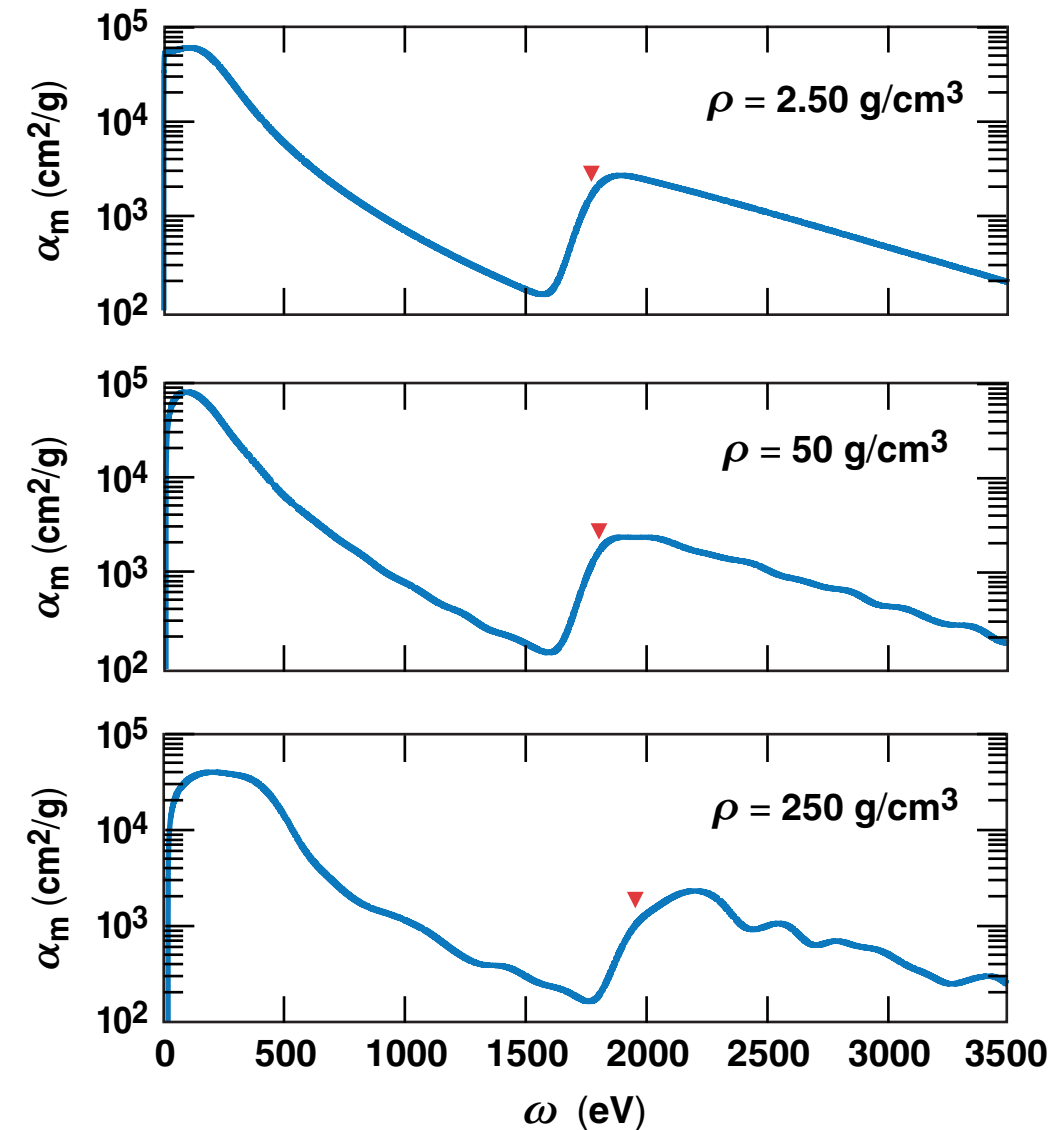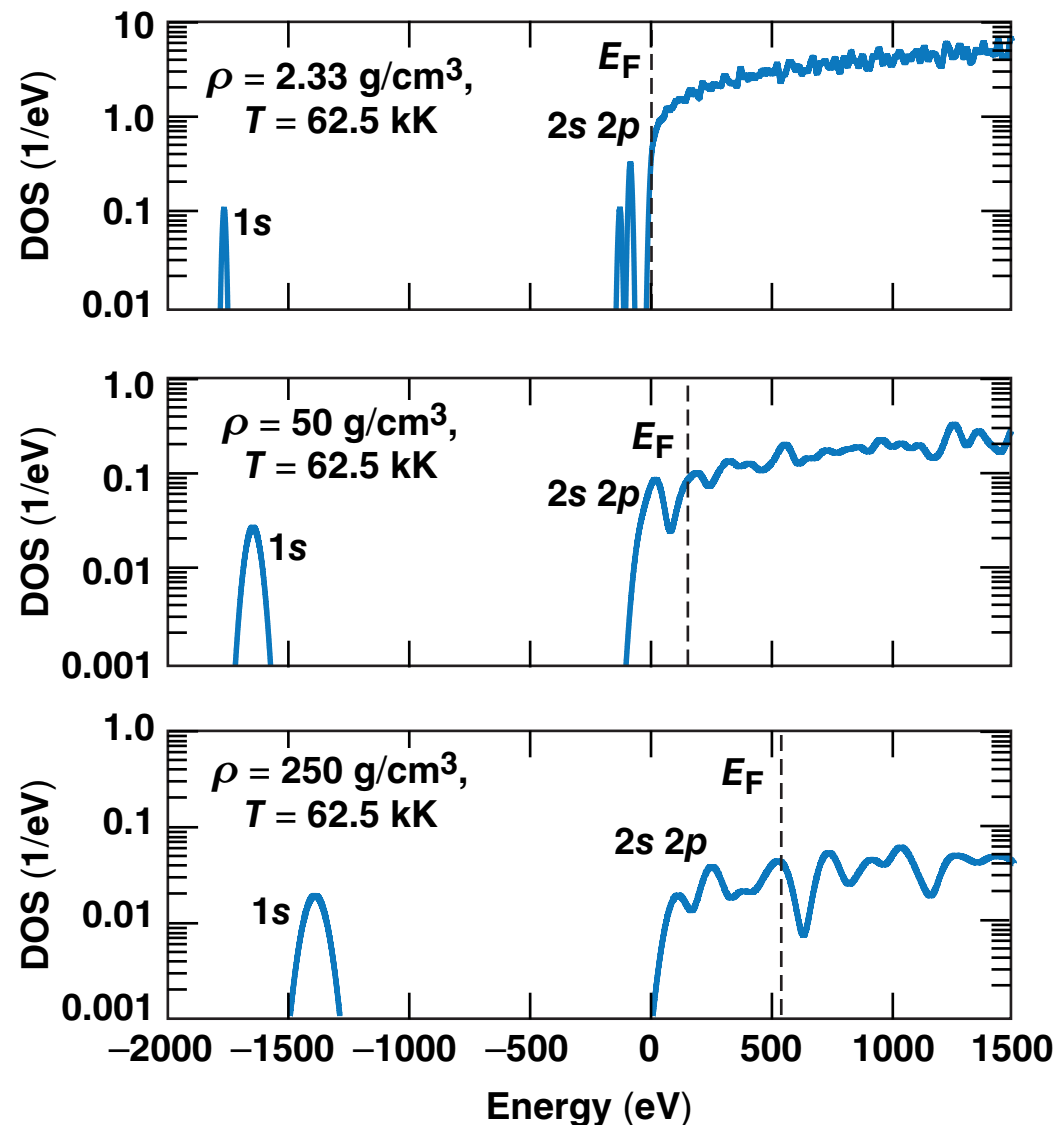
K-edge shift in dense silicon is significant; AOT data fail to predict the shift
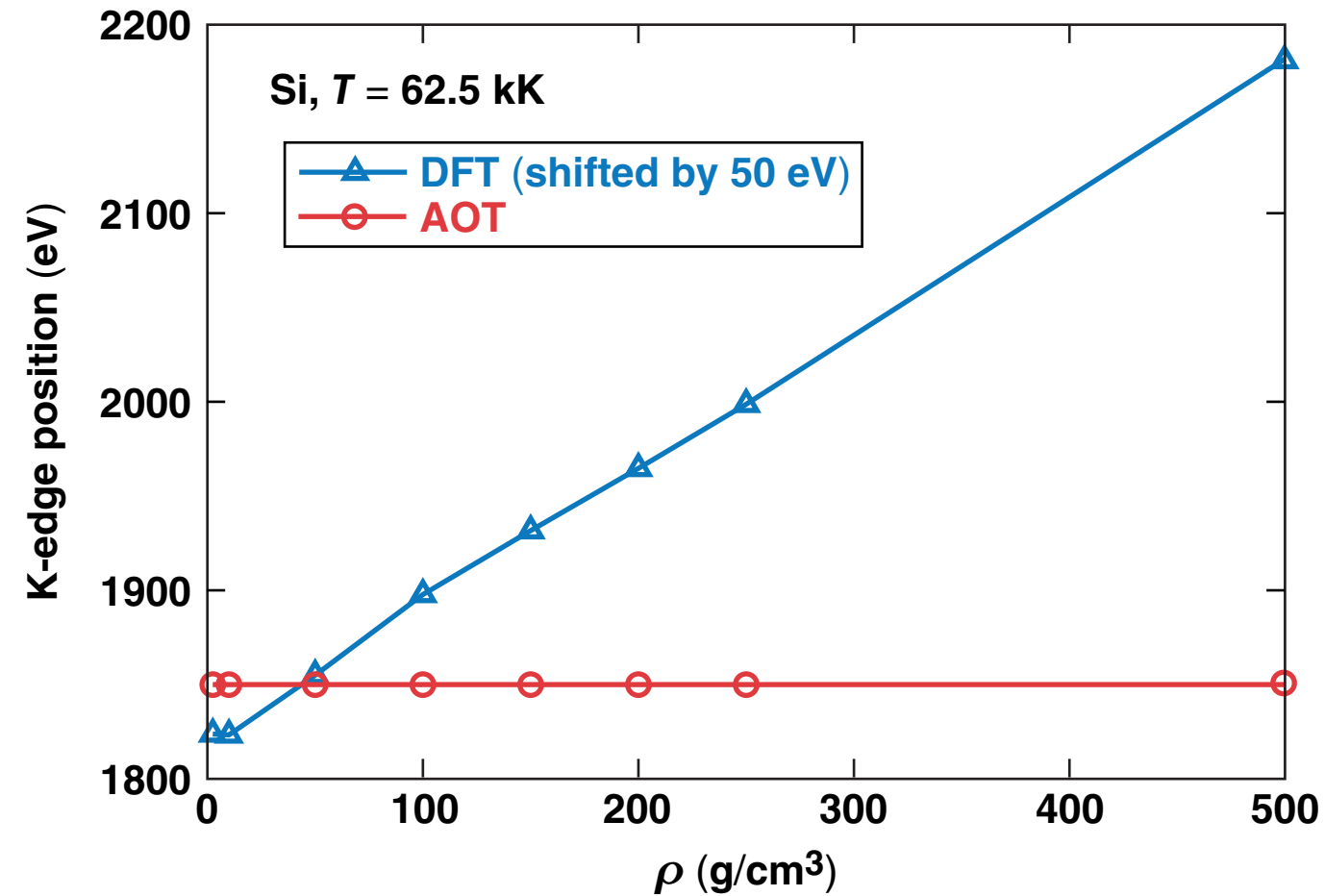
- LLE is planning experiments on OMEGA for experimental measurements of the K-edge shift

Finite-temperature density functional theory (DFT) is a powerful tool to accurately predict properties of matter at a wide range of densities across temperature regimes [warm-dense-matter (WDM) conditions]

UR
LLE

- Exchange-correlation (XC) thermal effects in simulations of WDM are taken into account via use of a temperature-dependent XC functional

- A set of accurate all-electron pseudo-potentials for the calculation of x-ray absorption near edge structure (XANES) spectra has been constructed

- Absorption coefficients and opacities of silicon (densities between 0.1 and 500 g/cm^3 and temperature between 0.5 and 1000 eV) have been calculated

UNIVERSITY of ROCHESTER