First-principles study of math xmlns="http://www.w3.org/1998/Math/MathML">mi>L/mi> /math>-shell iron and chromium opacity at stellar interior temperatures

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A *first-principles* study of L-shell iron and chromium opacity at stellar interior temperatures

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Recently developed free-energy density functional theory (DFT)-based methodology for optical property calculations of warm dense matter has been applied for studying L-shell opacity of iron and chromium at $T = 182$ eV. We use Mermin–Kohn–Sham density functional theory with a ground-state and a fully temperature-dependent generalized gradient approximation exchange-correlation (XC) functionals. It is demonstrated that the role of XC at such a high-T is negligible due to the total free-energy of interacting system being dominated by the noninteracting free-energy term in agreement with estimations for the homogeneous electron gas. Our DFT predictions are compared to the radiative emissivity and opacity of dense plasmas model, to the real-space Green's function method, and to experimental measurements. Good agreement is found between all three theoretical methods, and in the bound–continuum region for Cr when compared to the experiment, while the discrepancy between direct DFT calculations and the experiment for Fe remains essentially the same as for plasma-physics models.

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I. INTRODUCTION

Accurate prediction of optical properties of matter across a wide range of material densities and temperatures is of great importance in planetary science, astrophysics, and inertial confinement fusion (ICF) [1–4]. For example, uncertainties in calculations of solar interior opacities can potentially affect predictive capabilities of solar models. Building a reliable opacity model for materials under extreme condition is one of the grand challenges in high-energy-density physics (HEDP), especially across the most complicated warm-dense-matter (WDM) domain of thermodynamic conditions when both the Coulomb coupling parameter and the electron degeneracy are close to unity. The traditional opacity models based on isolated atomic physics when the important plasma density and temperature effects such as Stark broadening, ionization potential depression (IPD), and continuum lowering are incorporated via corrections [5–13], often become unreliable beyond the ideal plasma conditions [14–19].

A *first-principles* approach, based on finite-temperature density functional theory (DFT) [20], treats deeply bounded core and free electrons in an equal footing, provides a fully self-consistent calculation of screening effects, and as a consequence, allows a fully consistent calculation of the IPD and continuum lowering effects. Quasistatic pressure broadening due to interaction with neighboring ions and respective shift of energy on individual ions is taken into account in DFT-based *ab-initio* molecular dynamics (AIMD) simulations. Such simulations become prohibitively expensive, however, in the case of low material density (i.e., a large real-space size simulation cell) and explicit treatment of all electrons with bare Coulomb or an all-electron pseudopotential and huge number of thermally occupied bands required for optical calculations using the Kubo–Greenwood formalism [21, 22] at a wide range of x-ray photon energies. A method recently proposed in Ref. [23] drastically alleviates these computational challenges. The method combines the usual supercell molecular dynamics (MD) simulations with a *single-atom-in-a-cell* calculation at the same thermodynamic conditions with the same periodic boundary condition. The supercell MD results take into account effects due to interaction with neighboring ions required to describe x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). Since short-wavelength interactions mainly probe the local plasma environment, single-atom-in-a-cell calculations can give reasonably good results for high-energy photon absorptions in L- and K edge tail regions.

In this work we use this *first-principles* methodology to calculate optical properties (mass-absorption coefficient and opacity) of Cr and Fe at stellar interior temperatures corresponding to recent experiments [14, 19]. The purpose is to explore whether or not such *ab initio* calculations can resolve the reported disagreement between previous atomic physics calculations and measured data [14, 19]. The methods used in previous calculations in particular include an average atom model based on time-dependent DFT [24], and calculation of opacity from two-

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photon processes [25, 26]. Our DFT results are compared to the real-space Green's function (RSGF) method [27–29] and to the radiative emissivity and opacity of dense plasmas (REODP) atomistic model [30]. We found good agreement on Cr and Fe among all three theoretical predictions in the bound–continuum region corresponding to the L edge tail, and agreement in the same region on Cr when compared to the experiment. However, the difference between direct DFT calculations and the experiment for Fe remains essentially the same as for other plasma-physics models.

The paper is organized as follows: the next section introduces details of the DFT-based methodology including a simple way of computing the average ionization state from DFT data (Sec. II A). In Sec. II B we present orbital-free DFT simulations. Computational details and some convergence tests are presented in Sec. II C. Section III describes our main results for the opacity of low-density iron and chromium at stellar interior temperatures, and Sec. IV provides a short summary of this work.

II. METHOD

A free-energy DFT-based methodology for optical property calculations in the WDM domain presented in Ref. [23] handles deeply bounded core electrons in an equal footing with free electrons in the system and takes into account in a self-consistent way effects such as quasistatic pressure broadening due to interaction with neighboring ions (in case of calculations on MD multi-ion supercell snapshots), the ionization potential depression (IPD), continuum lowering, and Fermi surface rising. The methodology incorporates a combination of the Kubo–Greenwood (KG) optical data, evaluated on a set of the *ab initio* molecular dynamics (AIMD) snapshots, with a periodic *single-atom-in-a-cell* calculation at the same thermodynamic conditions. KG calculations on snapshots account for the influence of the local plasma environment, which is important for photon energies near the L and K edges. Kubo–Greenwood data from periodic calculations with single atom cover the tail regions beyond the L and K edges, closing the photon energy gap between the L and K edges and extending the K edge tail toward many-keV photon energies. This gap and short extension beyond the K edge arise in the standard scheme due to a prohibitively large number of bands required for the Kubo–Greenwood calculations with AIMD snapshots.

The Kubo–Greenwood formulation implemented in post-processing code named KGEC ([K]ubo [G]reenwood [E]lectronic [C]onductivity) for use with Quantum-Espresso large-scale DFT-based simulation package, KGEC@Quantum-Espresso [31, 32], calculates the frequency-dependent real and imaginary parts of electric conductivity, $\sigma_1(\omega)$ and $\sigma_2(\omega)$, the real part of the index of refraction, $n(\omega)$, the absorption coefficient, $\alpha(\omega) = \sigma_1(\omega)\frac{4\pi}{n(\omega)c}$, and the mass absorption coefficient $\alpha_{\rm m}(\omega) = \alpha(\omega)/\rho$ (where c is the speed of light, ρ is the material density, and the photon energy is $\hbar\omega = h\nu$). See Appendix for further details. The optical properties were calculated for a single-atom-in-a-cell and as an average over a selected set of uncorrelated two-atom MD snapshots. Eventually the grouped Rosseland mean opacities for a narrow group of photon energies between $\hbar\omega_1$ and $\hbar\omega_2 = \hbar\omega_1 + \hbar\Delta\omega$ (with $\hbar\Delta\omega = 4$ eV) in the range between 0 and 3 keV are calculated as follows

$$\kappa_{\rm R}(\omega_1:\omega_2) = \frac{\int_{\omega_1}^{\omega_2} n^2(\omega)\frac{\partial B(\omega,T)}{\partial T}{\rm d}\omega}{\int_{\omega_1}^{\omega_2} n^2(\omega)\alpha_{\rm m}^{-1}(\omega)\frac{\partial B(\omega,T)}{\partial T}{\rm d}\omega}\,, \quad (1)$$

where the Planck black-body radiation energy density distribution $B(\omega,T) = (\hbar\omega^3/4\pi^3c^2)/(e^{\hbar\omega/k_{\rm B}T}-1)$ depends on the photon frequency and the plasma temperature. Rosseland mean opacity, Eq. (1), uses a temperature derivative of the Planck function, $\partial B(\omega,T)/\partial T$, as the weighting function, and represents one of the commonly used ways to define the average opacity [33, 34].

Accuracy of the methodology was confirmed by comparison to NIST reference data for silicon at near-ambient conditions [23]. Recently, a good agreement was found between the DFT predictions and RSGF method for Si at selected warm, dense thermodynamic conditions [29].

Our DFT predictions for the chromium and iron opacity are compared to two recently developed methods: the radiative emissivity and opacity of dense plasmas model and the real-space Green's function method. The REODP model [30] is comprised of two linked sub-models: 1) the post Hartree-Fock-Slater (HFS) and Hartree-Fock (HF) models accounting for the near-degenerate states (multi-configuration method) and correlations of electronic motions with respect to each other (Configuration Interaction method); and 2) Collisional-Radiative Steady-State (CRSS) model. The inclusion of static and dynamic electron correlations allows to go beyond the "mean field" approximation of the electron interactions used in HFS/HF as well as DFT methods [35].

In the REODP code there are two implementations of the effects of dense plasma environment. In the first approach the atomic data (wavefunctions, energy levels, etc.) are calculated for the isolated (free) atoms and then the plasma density effects such as the ionization potential depression using the Stewart and Pyatt model [36, 37], continuum lowering, and shift in positions of spectral lines and their broadening are taken into account within the CRSS model [30]. This approach is used in the present calculations of Fe and Cr opacities. In the second approach, the HFS/HF quantum models initially developed for isolated atoms are modified using the ion-sphere approximation to include the effects of a dense plasma on wavefunctions and energy levels of atoms and ions. A hard wall potential is added to the Hamiltonian in order to force the wavefunctions to zero on the outer boundary of atom for radial distances greater than the radius of ion sphere [35]. With the decrease of a sphere radius corresponding to the increase of plasma density, the outer-shell wavefunctions are perturbed, the energies of outermost atomic levels increase, and the electrons become unbounded within a spherical volume. The "distorted" HFS/HF wavefunctions and modified orbital energies are used to calculate the atomic data such as transition probabilities, ionization potentials, oscillator strengths, broadening constants, photo-ionization cross-sections, etc. These atomic data are then used in the CRSS plasma model. This second approach, however is not well stable when the treatment of multiply-ionized ions is required.

The non local thermodynamic equilibrium CRSS model solves the system of kinetic rate equations for collisional and radiative processes in a plasma in order to determine populations of atomic levels in ions that are used for calculating the number density of different ionic species and free electrons. The concentrations of different type of ions and free electrons are used to calculate the thermodynamic and optical properties of high energy density plasmas. Thus, in either of two ways the REODP model accounts for the effects of dense plasma environment on the wavefunctions and energy levels of ions that affect the continuum lowering, pressure ionization, shifts of spectral lines, broadening of lines and change of their shapes.

The RSGF method described in [29] uses a multi-center expansion to solve the electronic structure problem. Each atom is assigned to a polyhedral zone in which the DFT potential is treated in a muffin-tin approximation, similar to an average atom (AA) model [38]. Corrections to the electronic structure due to scattering between zones is negligible for hot dense plasmas, making RSGF useful for efficient DFT-based opacity calculations. Being a multi-center approach, the continuum lowering and ionization potential depression are naturally included. Some broadening is also accounted for, due to variations in the electronic structure from atom to atom. In this way, the RSGF method may be viewed as introducing multi-center corrections to AA opacities based on a single center [39].

A. Ionization state from DFT simulations

The L-shell iron opacity measured at Sandia National Laboratories [14] corresponds to the inferred temperature and free-electron density values of $T = 2.11$ MK ($\sim$182 eV) and $n_\mathrm{e} = 3.1 \cdot 10^{22}$ cm^{-3}. Later measurements on chromium and nickel were performed at similar conditions [19]. The density of free-electrons in a system is determined by the average ionization state. The Mermin–Kohn–Sham (MKS) DFT calculates the one-electron states and corresponding Fermi–Dirac (FD) occupations, thereby making it possible to predict the number of free electrons in the continuum and free-electron density for each thermodynamic condition. At finite T, the density of states (DOS) consists of a nearly discrete part corresponding to bound electrons followed by a densely distributed quasi-continuous part corresponding to free-electron (continuum) states. The energy of the continuum edge, E_c, can be readily identified from calculated DOS data: bound levels merge the continuum at E_c when DOS as a function of energy, $g(E)$, changes behavior to the typical homogeneous electron gas (HEG) result

$$g(E) \propto \sqrt{E - E_\mathrm{c}}\,. \tag{2}$$

The number of free electrons in the simulation box can be found by integrating the DOS multiplied by Fermi–Dirac occupations

$$N_\mathrm{free} = \int_{E_\mathrm{c}}^{\infty} g(E) f_\mathrm{FD}(E) \mathrm{d}E\,, \tag{3}$$

where

$$f_\mathrm{FD}(E) = \frac{1}{e^{\beta(E-E_\mathrm{F})}+1}\,, \tag{4}$$

with $\beta = 1/k_\mathrm{B}T$, and E_F is the Fermi level energy. The free-electron density is calculated by dividing the number of free electrons by the simulation cell volume, $n_\mathrm{free} = N_\mathrm{free}/\Omega$, and the average ionization state is equal to $Z = N_\mathrm{free}/N_\mathrm{ions}$, where N_ions is the total number of ions in a simulation.

Application of the approach to calculating the ionization state of cold rarefied hydrocarbon (CH) plasmas was reported in Ref. [40]. These calculations were cross-validated by comparisons between DFT-based results and the Saha–Fermi–Debye–Hückel (SFDH) ones based on the free-energy minimization approach (see details in Ref. [40]). After this cross-validation, we use the method to calculate the free-electron density reported in experimental measurements on Fe and Cr ($n_\mathrm{free} = 3 \cdot 10^{22}$ cm^{-3} at $T = 182$ eV) to infer corresponding material density conditions. We performed single-atom-in-a-cell calculations for Fe and Cr at $T = 182$ eV with the corresponding material densities, calculated the average ionization state and free-electron density. These results gave material densities of $\rho_\mathrm{Fe} = 0.165$ g/cm^3 and $\rho_\mathrm{Cr} = 0.161$ g/cm^3 corresponding to the free-electron density reported in experiments. Figure 1 illustrates calculation of the average ionization state. DOS behavior changes to the HEG form in Eq. (2) at $E_\mathrm{c} \approx 0$. We also emphasize that the inte-

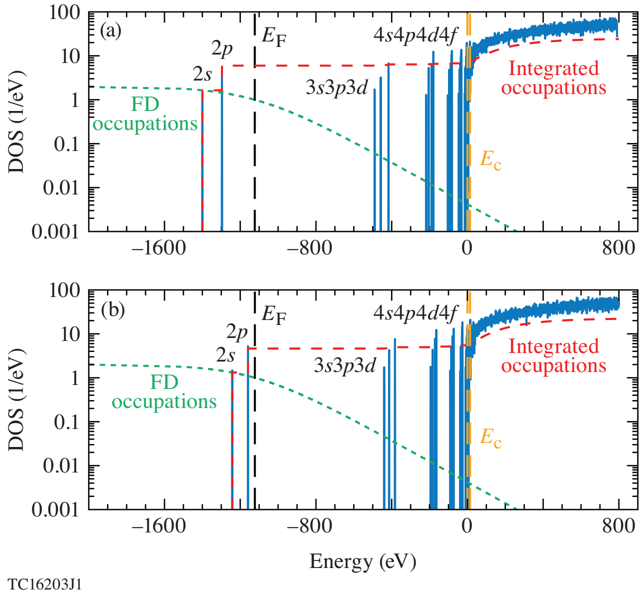

FIG. 1: (a) DOS of Fe at $\rho_{\text{Fe}} = 0.165$ g/cm^3 and $T = 2.11$ MK; (b) DOS of Cr at $\rho_{\text{Cr}} = 0.161$ g/cm^3 and $T = 2.11$ MK. The solid green line shows Fermi-Dirac occupations (Eq. (4)), the solid red line corresponds to the integrated occupation (integrated number of electrons), $N(E)$ defined by Eq. (5), vertical dashed lines indicate locations of the Fermi level, E_{F} (dashed black) and of the continuum edge, E_{F} (dashed orange).

grated occupation (solid red line in Fig. 1) defined as

$$N(E) = \int_{-\infty}^{E} g(E) f_{\text{FD}}(E) \text{d}E \,, \tag{5}$$

increases with discrete increments for $E < E_{\text{c}}$, changes the slope, and starts to behave as $N(E) \propto \text{erf}(E - E_{\text{c}})$ at $E \geq E_{\text{c}}$ approaching the total number of electrons limit at high energy. These calculations were performed for a single atom in a cubic cell, Baldereschi's mean value k-point (BMVP) [41], and the ground-state Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation (XC) density functional [42]. See Sec. II B for discussion of finite-size and XC thermal effects. Further computational details are reported in Sec. II C.

B. Equation of state and pair correlation function

Thermodynamic conditions in experiments on Fe and Cr correspond to high reduced temperature [temperature in terms of the Fermi temperature, $T_{\text{F}} = (3\pi^2 n_{\text{free}})^{2/3}/(2k_{\text{B}})$], $t = T/T_{\text{F}} \approx 52$ and weak Coulomb coupling, $\Gamma = 2\lambda^2 r_{\text{s}}/t \approx 0.04$, where $\lambda = (4/9\pi)^{1/3}$ and $r_{\text{s}} = (3/(4\pi n_{\text{free}}))^{1/3} \approx 3.8$ bohr is the Wigner–Seitz radius. To investigate equation of states and some structural properties such as pair correlation function (PCF) of Fe and Cr under these conditions, we performed AIMD simulations driven by orbital-free DFT forces. Computational details are reported in Sec. II C.

First, we studied the finite-size effects performing AIMD simulations with the number of atoms in the simulation cell ranging between 2 and 32, the Thomas–Fermi (TF) noninteracting free-energy [43], and ground-state local density approximation (LDA) for exchange-correlation [44]. The total pressure as a function of the number of atoms is shown in Fig. 2(a). Pressure variation within 0.1% for both elements indicates negligible finite-size effects. Pressure predicted by the TF average atom model shown in Fig. 2(a) as $N_{\text{atoms}} = 1$ data, is also very accurate, underestimating the AIMD value by about only 0.5%. To investigate the importance of the nonhomogeneity and thermal exchange-correlation effects, we additionally performed AIMD simulations employing the ground-state GGA PBE and finite-temperature Karasiev-Dufty-Trickey (KDT16) GGA [45] exchange correlation functionals. The nonhomogeneity XC effects taken into account at the GGA level by the PBE functional and the combined nonhomogeneity and thermal XC effects taken into account by the thermal GGA KDT16 density functional increase pressure by less than 0.5% within statistical errors. In the latter case, when the ground-state LDA XC is replaced with the thermal KDT16 GGA, the total pressure increases from 9.12 Mbar to 9.16 Mbar for Fe and from 9.15 Mbar to 9.19 Mbar for Cr. This result is expected. Analysis performed in Ref. [46] for the HEG at finite-temperature suggests that at given thermodynamic conditions ($t \approx 52$, $r_{\text{s}} \approx 3.8$ bohr), the XC contribution is almost three orders of magnitude smaller as compared to the noninteracting or total free energy: at such high temperatures and moderate values of r_{s}, the XC contribution to the free-energy ($\mathcal{F}_{\text{xc}}$) is negligible as compared to the noninteracting free-energy term: $\mathcal{F}_{\text{xc}} << \mathcal{F}_{\text{s}}$.

Ion–ion pair correlation functions for Fe and Cr as predicted by AIMD simulations with 32 atoms in simulation cell are shown in Fig. 2(b). PCF's at these conditions do not exhibit any structure except a weak correlation peak near 14 bohr. The closest ion–ion approach distance of about 5 bohr is large enough to reduce interaction between neighboring ions and expect small finite-size effects. This is true for pressure calculations [Fig. 2(a)] and for bound–free absorption, but not for the location of bound–bound absorption peaks (see Fig. 4 in next subsection).

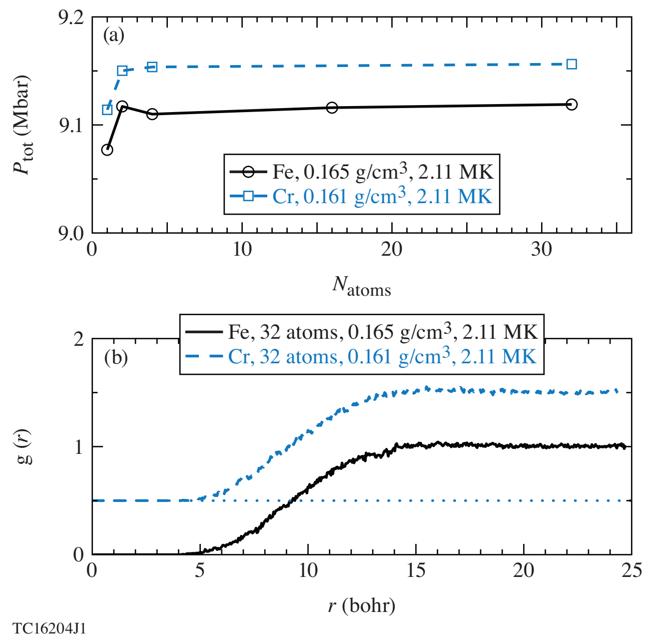

FIG. 2: (a) Convergence of the total pressure with respect to the number of atoms in the OFDFT-MD simulation cell for Fe at $\rho_{\rm Fe}$ = 0.165 g/cm^3, and T = 2.11 MK and Cr at $\rho_{\rm Cr}$ = 0.161 g/cm^3, and T = 2.11 MK; (b) The ion pair-correlation function from OFDFT-MD simulations for Fe with 32 atoms and for Cr with 32 atoms (shifted by 0.5).

C. Computational details and convergence tests

We used AIMD simulations driven by the orbital-free (OF) DFT forces. The singularity of the Coulomb electron–ion interaction was regularized via local pseudopotential (LPP) generated at a corresponding thermodynamic condition as described in Ref. [47] by employing the Thomas–Fermi noninteracting free-energy density functional [43] in combination with the ground-state LDA. For consistency, the same combination of the noninteracting free-energy and exchange-correlation density functionals was used in our OF-AIMD simulations performed with the PROFESS@QUANTUM-ESPRESSO computational package [48]. Employing a more accurate finite-temperature KDT16 GGA exchange-correlation [45] affects results essentially within very small statistical uncertainties ($\sim$ 0.5% or so, see Sec. II B). The Thomas–Fermi approximation for noninteracting free-energy is also very accurate at high temperatures. Two advanced GGA-level noninteracting free-energy density functionals, VT84F [49] and LKTF [50], at high T reduce to the Thomas–Fermi approximation by construction and yield virtually identical results.

In this study we are focused on the L-shell absorption and opacity calculations at temperatures when the deep 1s bands remain fully populated. Therefore 1s frozen-core projector augmented wave (PAW) data sets for Fe and Cr are generated using the ATOMPAW code [51]. A small augmentation sphere radius $r_{\rm PAW}$ = 0.35 bohr requires a relatively high cutoff energy of $E_{\rm cut}$ = 800 Ry to converge electronic pressure. The optical properties are calculated using the Kubo–Greenwood formulation implemented within the PAW formalism in KGEC@QUANTUM-ESPRESSO [31, 32, 48] packages. The Gaussian broadening was done with relatively large δ = 15 eV due to the sparsity of states in the case of the single-atom-in-a-cell calculations. Tests comparing the ground-state PBE and finite-T KSDT XC functionals provided virtually identical results for the mass absorption coefficients, demonstrating again that the role of the XC functional at these thermodynamic conditions is negligible. Figure 3(a) shows that the mass absorption coefficient (and other optical properties) converges at lower $E_{\rm cut}$ value (as compared to the converged value of $E_{\rm cut}$ for pressure) of 400 Ry.

Convergence of the mass absorption coefficient with respect to the number of thermally occupied bands included in calculation is shown in Fig. 3(b). Calculation with $N_{\rm b}$ = 4096 covers a range of photon energies up to 1500 eV. Increase of $N_{\rm b}$ between 4096 and 28672 gradually increases the absorption photon energy range up to 2500 eV. In order to analyze the importance of free–free contributions and to find out which bound–free transitions contribute into the mass absorption coefficient, we compare the DOS calculated for two values of $N_{\rm b}$ = 4096 and 28672 shown in Fig. 3(c). Contribution of the L-shell bound–free transitions starts at photon energies around 1200 eV, given by a difference between the continuum edge location ($E_{\rm c} \approx 0$ eV) and L-shell 2p bound level location ($E_{2p} \approx -1200$ eV); for the $N_{\rm b}$ = 4096 calculation, these transitions contribute into the mass absorption coefficient for photon energies up to 1500 eV [shown in Fig. 3(b)]. This value can be estimated as the difference between the highest free-electron state energy ($\approx$ 350 eV) and E_{2p} bound state location (≈ -1200 eV). The same considerations for the M-shell bound–free transitions lead us to the conclusion that for the $N_{\rm b}$ = 4096 calculation these transitions contribute in the range of photon energies between $\approx$ 400 eV and $\approx$ 750 eV, i.e., for calculations with $N_{\rm b}$ = 4096, the M-shell bound–free transitions are not taken into account for the mass absorption in the range of photon energies above 1200 eV. Calculations with $N_{\rm b}$ = 28672 account for the M-shell bound–free transitions contribution into the mass absorption in the range of photon energies between $\approx$ 400 eV and $\approx$ 1650 eV (estimated as a difference between the highest free-electron state energy ($\approx$ 1250 eV) and the M-shell bound states location (≈ -400 eV). Taking into account that the mass absorption coefficients for photon energies between 1200 eV and 1500 eV for calculations with $N_{\rm b}$ = 28672 (with the M-shell bound–free transitions taken into account) and with $N_{\rm b}$ = 4096 (the M-

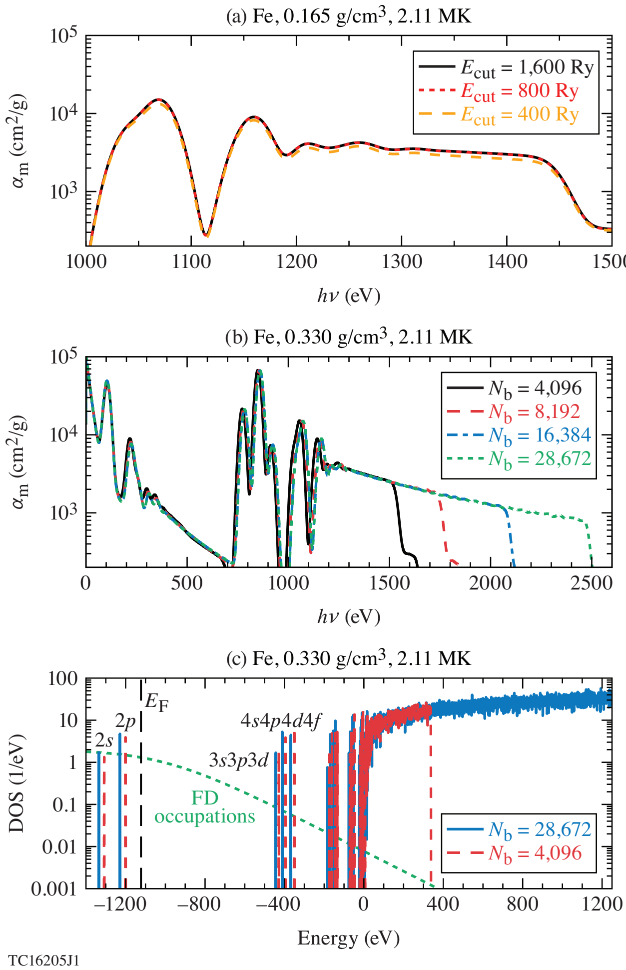

FIG. 3: (a) Convergence of the mass absorption coefficient of Fe with respect to the energy cutoff for a $1s^2$ frozen-core PAW data set with $r_{\rm PAW} = 0.35$ bohr performed for a single-atom-in-a-cell at $\rho_{\rm Fe} = 0.165$ g/cm^3 and $T = 2.11$ MK; calculations performed with a small number of bands $N_{\rm b}$=4096. (b) Convergence of the mass absorption coefficient of Fe with respect to the number of bands included in calculation performed for a single-atom-in-a-cell at $\rho_{\rm Fe} = 0.330$ g/cm^3 and $T = 2.11$ MK; calculations performed with converged value of $E_{\rm cut} = 800$ Ry; (c) DOS of Fe at $\rho_{\rm Fe} = 0.330$ g/cm^3, and $T = 2.11$ MK calculated for two number of thermally occupied bands, $N_{\rm b} = 28672$ (solid blue curve) and $N_{\rm b} = 4096$ (dashed red curve).

shell bound–free transitions are not accounted) are identical, we conclude that the contribution of the M-shell bound–free transitions into the mass absorption coefficient is negligible.

The range of the photon energies for the free–free absorption for calculations with two number of bands (4096 and 28672) included in calculation can be estimated from the DOS exactly on the same way. These two calculations lead to the same value of the absorption coefficient for photon energies up to 1250 eV (when the free–free transitions are taken into account for calculations with

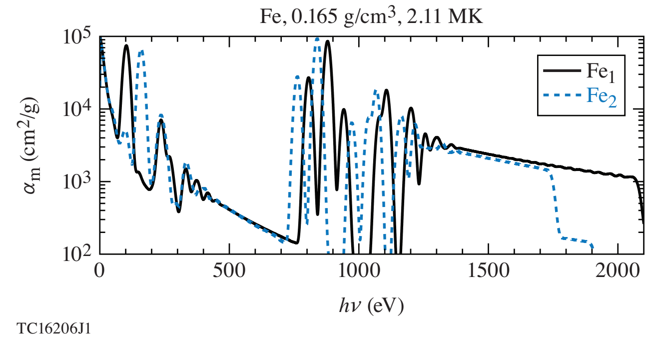

FIG. 4: The mass absorption coefficient of Fe calculated for a single-atom-in-a-cell (Fe_1), and a two-atom MD snapshot (Fe_2) at $\rho_{\rm Fe} = 0.165$ g/cm^3 and $T = 2.11$ MK.

$N_{\rm b} = 28672$); thus we conclude that the free–free transitions are also negligible for the L-shell mass absorption (and opacity) calculations.

Lastly, Fig. 4 compares the mass absorption coefficient of Fe calculated for a single-atom-in-a-cell, and for a two-atom MD snapshot. A calculation based on the MD snapshot changes the location of bound–bound absorption peaks for photon energies below 1300 eV. The bound–free absorption above 1300 eV is almost identical for the two calculations, except that the single-atom-in-a-cell results cover larger photon energy range because the number of bands per atom included in this calculation is larger compared to the MD snapshot calculation.

At such weakly degenerate and weakly coupled plasma conditions ($t \approx 52$, $\Gamma \approx 0.04$) one may expect that much simpler approaches, based essentially on semi-classical plasma-screening models [52–54], should be reasonably accurate. However, opacity calculations based on these approaches would represent limiting cases of average-atom models, which are already known not to agree with the Sandia experiments [24, 55].

III. RESULTS

In this section we present our results on the free-electron density and the L-shell opacity of chromium and iron as predicted by the DFT, REODP, and RSGF methods and provide a comparison to the pulse-power experimental opacity measurements [14, 19].

Table I shows free-electron densities of chromium and iron calculated at $T = 182$ eV and $\rho = 0.161$ g/cm^3 and 0.165 g/cm^3, respectively. Theoretical predictions by all three methods are in very good agreement; relative differences of the REODP and RSGF values with respect to the DFT data do not exceed 2% and 4%, respectively, matching the experimental value of $3{\cdot}10^{22}$ cm^{-3} from measurements for Cr and Fe.

Figure 5 shows our main results for opacity of

TABLE I: Free-electron density (in cm^{-3} units) for chromium and iron at $T = 182$ eV and $\rho_{Cr} = 0.161$ g/cm^3, $\rho_{Fe} = 0.165$, respectively, as predicted by the DFT, REODP and RSGF methods.

System	DFT	REODP	RSGF
Cr	$3.00 \cdot 10^{22}$	$2.95 \cdot 10^{22}$	$3.12 \cdot 10^{22}$
Fe	$3.00 \cdot 10^{22}$ $(2.98 \cdot 10^{22})$	$2.95 \cdot 10^{22}$	$3.12 \cdot 10^{22}$

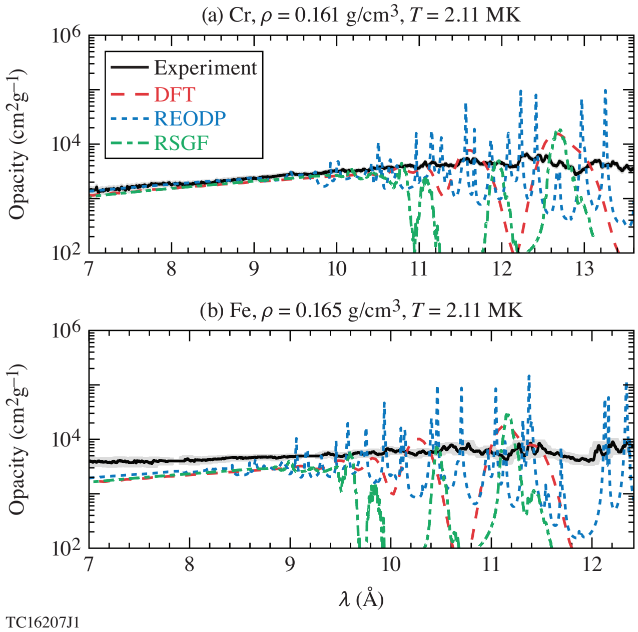

FIG. 5: Opacity of iron and chromium at 0.165 g/cm^3, and 0.165 g/cm^3, respectively. Comparison is made between the experimental measurements (solid black curve, grey shaded area corresponds to the experimental measurements error) and three theoretical predictions done at $T = 182$ eV.

chromium and iron calculated at $T = 182$ eV and material density of 0.161 g/cm^3 and 0.165 g/cm^3, respectively, alongside with experimental measurements. At short wavelengths below ~ 9.5 $\mathring{A}$ [the L-shell bound–continuum region for photon energies above ~ 1.2 keV], the agreement between all three theoretical data and experiments is very good for chromium: the REODP curve goes straight through the experimental data, while the DFT and RSGF data are located slightly below, touching the shaded grey experimental error bars. The situation for iron is different; opacity predicted by theoretical methods in the L-shell bound–continuum region is underestimated by about 50% as compared to the experimental data. The REODP curve is slightly closer to the experimental data as compared to the DFT single-atom-in-a-cell and RSGF simulations.

In the wavelength range above 9.5 $\mathring{A}$ opacity is dominated mostly by the bound–bound absorption lines. The DFT and RSGF calculations predict a small set of smooth and strong discrete lines separated by deep windows. The REODP method predicts a richer spectrum of sharp peaks. The REODP-calculated opacities represent the detailed all-line spectra without any kind of averaging into spectral groups. The peaks and wings of lines are resolved with a high accuracy. The spectral lines are roughly centered on the experimental opacity curves. However, none of our theoretical predictions is close to the measured bound–bound opacity in that range. The DFT predictions for the bound–bound absorption can be improved by performing the Kubo–Greenwood optical calculations on top of the AIMD snapshots for larger supercells including more than two atoms, by considering more realistic charge state distributions. However, such demanded calculations, on both memory and time, are currently out of reach.

IV. SUMMARY

Recently proposed DFT-based methodology for optical property predictions of matter in the warm dense regime has been used for calculations of L-shell opacity of iron and chromium with a hope to resolve the previously reported discrepancy between atomic physics code calculations and experimental measurements for Fe in the bound–free range [14, 19, 29]. First, we estimated the average ionization state and free-electron density from the DFT density of state data and found the iron and chromium material densities corresponding to experimental conditions. Next, the AIMD simulations driven by orbital-free DFT forces were performed to investigate finite-size effects, equation of state and PCF. Eventually, the Kubo–Greenwood optical calculations were performed and the DFT opacity data were compared to the REODP and RSGF models. Good agreement was found between all three theoretical methods in the range of photon energies corresponding to transitions between the L-shell-bound and free-electron states. Theoretical predictions also agree with experimental measurements in that quasi-continuum range for Cr, while the difference between the direct DFT calculations and the experiment for Fe remains close to 50%, very similar to existing calculations from other atomic physics models.

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Appendix: Details of Kubo-Greenwood optical calculations

Kubo-Greenwood formalism [21, 22] is based on the linear response theory and one-electron approximation. In practice, and in our implementation, the one-electron states and corresponding eigenvalues are from a Mermin-Kohn-Sham DFT calculation. Kubo-Greenwood data calculated on a set of statistically independent "snapshots" (a set of fixed ionic configurations) along an AIMD trajectory provide a reliable description of optical properties of matter at wide range of thermodynamic conditions including warm-dense regime. These calculations with KGEC@QUANTUM-ESPRESSO [31, 32] include two steps: solution of Mermin-Kohn-Sham equations and the Kubo-Greenwood post-processing. Within the MKS formalism, for each lattice configuration snapshot at lattice coordinates $\{\mathbf{R}\}_I$, we obtain N_b thermally occupied states $\psi_{i,\mathbf{k},I}$ and corresponding band energies $\varepsilon_{i,\mathbf{k},I}$ for a given $\mathbf{k}$-point by solving the following system of coupled differential equations

$$\{-\frac{1}{2}\nabla^2 + v_\mathrm{ext} + v_\mathrm{H} + v_\mathrm{xc}\}\psi_{i,\mathbf{k},I} = \varepsilon_{i,\mathbf{k},I}\psi_{i,\mathbf{k},I}\,. \quad (6)$$

Here v_ext is the external (electron-ion) potential, v_H and v_xc are functional derivatives with respect to the electron density of the Hartree energy and the exchange-correlation term respectively. The real and imaginary parts of the KG frequency dependent electrical conductivity are (see details in Ref. [31])

$$\sigma_1(\omega;\{\mathbf{R}\}_I) = \frac{2\pi}{3\omega\Omega}\sum_{\mathbf{k}} \mathrm{w}_\mathbf{k} \sum_{i,j}^{N_b}\sum_{\nu=1}^{3}(f_\mathrm{FD}(\varepsilon_{i,\mathbf{k},I}) - f_\mathrm{FD}(\varepsilon_{j,\mathbf{k},I}))|\langle\psi_{j,\mathbf{k},I}|\nabla_\nu|\psi_{i,\mathbf{k},I}\rangle|^2 \frac{\delta/2}{(\epsilon_{j,\mathbf{k},I} - \epsilon_{i,\mathbf{k},I} - \omega)^2 + \delta^2/4}\,, \quad (7)$$

and

$$\sigma_2(\omega;\{\mathbf{R}\}_I) = \frac{2\pi}{3\omega\Omega}\sum_{\mathbf{k}} \mathrm{w}_\mathbf{k} \sum_{i,j}^{N_b}\sum_{\nu=1}^{3}\frac{f_\mathrm{FD}(\varepsilon_{i,\mathbf{k},I}) - f_\mathrm{FD}(\varepsilon_{j,\mathbf{k},I})}{\varepsilon_{i,\mathbf{k},I} - \varepsilon_{j,\mathbf{k},I}}|\langle\psi_{j,\mathbf{k},I}|\nabla_\nu|\psi_{i,\mathbf{k},I}\rangle|^2 \frac{\epsilon_{j,\mathbf{k},I} - \epsilon_{i,\mathbf{k},I} - \omega}{(\epsilon_{j,\mathbf{k},I} - \epsilon_{i,\mathbf{k},I} - \omega)^2 + \delta^2/4}\,, \quad (8)$$

where Ω is the system volume, $\mathrm{w}_\mathbf{k}$ is the weight of Brillouin zone point $\mathbf{k}$, and $f_\mathrm{FD}(\varepsilon_{i,\mathbf{k},I})$ are Fermi-Dirac occupations Eq. (4) of MKS bands $\psi_{i,\mathbf{k},I}$. The $\delta/2$ in Eqs. (7) and (8) is magnitude of an imaginary factor related to damping or relaxation effects. The Lorentzian in Eq. (7) can be replaced by a Gaussian with δ-width; both functions behave like a Dirac delta function in the limit of the δ-width going to zero.

Other properties are calculated directly from the frequency dependent real and imaginary parts of the electrical conductivity. The dielectric function (omitting the ionic configuration dependence)

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)\,, \quad (9)$$

where

$$\epsilon_1(\omega) = 1 - \frac{4\pi}{\omega}\sigma_2(\omega)\,, \quad (10)$$

and

$$\epsilon_2(\omega) = \frac{4\pi}{\omega}\sigma_1(\omega)\,. \tag{11}$$

The real and imaginary parts of the index of refraction are related to the dielectric function

$$n(\omega) = \sqrt{\frac{1}{2}\{|\epsilon(\omega)| + \epsilon_1(\omega)\}}\,, \tag{12}$$

and

$$k(\omega) = \sqrt{\frac{1}{2}\{|\epsilon(\omega)| - \epsilon_1(\omega)\}}\,, \tag{13}$$

Eventually the absorption coefficient is calculated as

$$\alpha(\omega) = \sigma_1(\omega)\frac{4\pi}{n(\omega)c}\,, \tag{14}$$

where c is the speed of light. Final answers are given by the average of each property of interest over all snapshots.

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