Dielectric function of six elemental metals

Maria K Pogodaeva¹, Sergey V Levchenko¹, Vladimir P Drachev¹,², Ildar R Gabitov¹,³

¹ Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, 3 Nobel Street, Moscow 121205, Russia
² Department of Physics and Advanced Materials and Mechanical Processing institute, University of North Texas, Denton, TX, 76203, USA.
³ Department of Mathematics, University of Arizona, 617 North Santa Rita Avenue, Tucson, Arizona 85721, USA
E-mail: mariia.pogodaeva@skoltech.ru

Abstract. We present an accurate first-principles study of the electronic structure and absorption spectrum of six elemental metals (aluminium, gold, silver, copper, palladium, platinum) using density functional theory in an all-electron full-potential framework. We calculate dielectric function spectra and plasma frequency, and compare with experimental data obtained from photo-emission, absorption, and electron energy loss spectra.

1. Introduction
Recent research in plasmonics have shown an inconsistency between theoretical predictions and experimental measurements of plasmon resonance for cobalt nanoparticles [1]. Imaginary part of dielectric function describes absorption spectrum of the material. By adopting a Drude-like form of the imaginary part of dielectric function, one can extract plasma frequency and relaxation lifetime from experimental results. However, this requires assumptions regarding the role of the surface and relative contribution of different spin channels. Ab initio simulations of dielectric properties can provide additional insight and validate the assumptions. Despite a significant progress in modeling optical properties of solids, it remains an outstanding challenge even for bulk materials, however there are some attempts to model dielectric properties of nanoparticles [2]. Here, we analyze effects of various approximations in density-functional theory (DFT) on the computed dielectric response properties of bulk nonmagnetic metals, and show that a good accuracy can be achieved without artificial tuning of model parameters.

Ground-state DFT is a powerful tool for calculating atomic and electronic structure of solids. Several papers have demonstrated that combining ground-state DFT with random-phase approximations is a computationally efficient way to model dielectric response of metals with an acceptable accuracy. However, a closer look at the existing literature reveals that special care must be taken to reach a good agreement with experiment. This includes careful selection of pseudopotentials that replace core electrons in the standard plane-wave calculations [3], and high k-point grid density [4]. Alternatively, GW approximation and Bethe-Salpeter equation can be used to obtain accurate optical properties of solids [5]. In GW method electronic self-energy is expressed in terms of the single-particle Green’s function G and the screened Coulomb interaction W, which results in very accurate quasiparticle energies. Bethe-Salpeter equation...
includes excitonic effects on top of $GW$. However, these methods are much more computationally expensive than DFT.

In this study, we use all-electron full-potential electronic-structure calculations to investigate the effects of exchange-correlation functional, pseudopotential approximation, and k-grid convergence on calculated optical properties for bulk aluminium, gold, silver, copper, palladium, and platinum.

2. Computational Approach

Plasma frequency and dielectric function of the six metals (Ag, Al, Au, Cu, Pt, Pd) is obtained using an approach detailed in [6]. DFT calculations are performed using the FHI-aims electronic-structure package [7]. This code employs the numeric atomic orbital basis sets, and therefore core electrons are explicitly included in the calculation, without the need for pseudopotential approximation. "Tight" settings are used to ensure convergence with respect to numerical settings. We employ the strongly constrained and appropriately normed (SCAN) exchange-correlation functional [8], [9]. Some convergence tests are performed using generalizzed gradient approximation (GGA) in the parametrization of Perdew, Burke and Ernzerhof (PBE) [10].

Crystal structure of all six metals is face-centered cubic (fcc). Calculations are done using primitive cells containing 1 atom. Lattice parameters are obtained from relaxation and compared to experimental values. Convergence of calculated plasma frequency $\omega_{pl}$ with respect to the k-point grid is tested for grids up to $100 \times 100 \times 100$ ($\Gamma$-centered). We also study convergence of relaxed geometry and density of states (DOS). During convergence studies we used k-point grids with equal number of points in each direction.

Frequency-dependent linear macroscopic dielectric tensor [6] includes inter- (equation 2) and intraband (equation 1) contributions:

$$
\epsilon_{i,j}(\omega) = \delta_{i,j} - \frac{4\pi}{V_{\text{cell}}\omega^2} \sum_{n,k} \left( -\frac{\partial f_0}{\partial \epsilon} \right) \varepsilon_{n,k} p_{i;n,n,k} p_{j;n,n,k},
$$

$$
+ \frac{4\pi}{V_{\text{cell}}} \sum_k \sum_{c,v} p_{i,c,c,k} p_{j,c,c,k} \frac{(\varepsilon_{c,k} - \varepsilon_{v,k} - \omega)(\varepsilon_{c,k} - \varepsilon_{v,k})^2}{(\varepsilon_{c,k} - \varepsilon_{v,k})^2}. 
$$

Here $f$ is Fermi function, $V_{\text{cell}}$ is unit cell volume, $\delta_{i,j}$ is vacuum contribution. $p_{n,l,k}$ is momentum matrix elements between states of bands $n$ and $l$ with crystal momentum $k$. $\varepsilon_k$ is Kohn-Sham energy; $c,v$ runs over the empty states and occupied states respectively.
Figure 3: Calculated projected density of states (DOS) for Cu. Black line shows total DOS, blue line - s-electrons, green - p-electrons, red - d-electrons.

Figure 4: Calculated projected density of states (DOS) for Al. Black line shows total DOS, blue line - hybridised sp-electrons, red - d-electrons.

Figure 5: Calculated projected density of states (DOS) for Pd. Black line shows total DOS, blue line - s-electrons, green - p-electrons, red - d-electrons.

Figure 6: Calculated projected density of states (DOS) for Pt. Black line shows total DOS, blue line - s-electrons, green - p-electrons, red - d-electrons.

Figure 7: Dielectric function for aluminium
The plasma frequency is evaluated using the following formula:

$$\omega_{pl}^2;_{ij} = \frac{1}{\pi} \sum_n \int \vec{k} p_{i;n,n,k} p_{j;n,n,k} \delta (\epsilon_{n,k} - \epsilon_F).$$

(3)

By adopting Drude-like shape for the intraband contribution a lifetime broadening $\Gamma$ is introduced and $\epsilon_{ij}^{\text{intra}}(\omega)$ becomes

$$\text{Im} (\epsilon_{ij}^{\text{intra}}(\omega)) = \frac{\Gamma \omega_{pl}^2;_{ij}}{\omega (\omega^2 + \Gamma^2)},$$

(4)

$$\text{Re} (\epsilon_{ij}^{\text{intra}}(\omega)) = 1 - \frac{\omega_{pl}^2;_{ij}}{\omega^2 + \Gamma^2}.$$  

(5)

3. Results and Discussion

Table 1 summarizes calculated properties compared to the reference values (calculated and/or experimental). As one can see, the deviation of calculated lattice constants from experimental values is < 1% for all studied metals. Figures 1-6 show projected DOS for all considered metals. Our DOS for all metals reproduces in general the shape and all main peaks reported in literature [17]. We note that some peaks have slightly different relative heights and some very
Table 1: Calculated lattice constants and dielectric properties for metals compared to experimental values. Zero-point vibrational effects are removed from experimental results for lattice constants for a direct comparison with the calculated values [11]. Experimental values for plasma frequency are reported in [12].

| Element | Lattice constant | \( \omega_{pl}, \text{eV} \) | \( \Gamma, \text{meV} \) |
|---------|-----------------|-----------------|-----------------|
| Al      | 4.012           | 15.2            | 15.4 [6]        |
| Ag      | 4.082           | 11.34           | 12.6 [5]        |
| Au      | 4.084           | 11.04           | 9.01 [4]        |
| Cu      | 3.556           | 11.14           | 9.03 [3]        |
| Pd      | 3.888           | 9.1             | 9.72 [2]        |
| Pt      | 3.912           | 10.1            | 9.59 [1]        |

Figure 10: Dielectric function for copper

narrow peaks are absent in our calculations. This is explained mainly by a denser k-point grid in our calculations. Figures 7 - 12 show calculated dielectric function spectra compared with experimental results (from [14] for Au, Ag, and Cu, from [13] for Al, from [15] for Pd, from [16] for Pt). Plasma frequency is calculated by formula 3 using obtained results for electronic structure. The relaxation constant \( \Gamma \) is taken from literature. As one can see, there is a good qualitative agreement between theory and experiment. In particular, major peaks for imaginary part and general shape of the dielectric function are reproduced for all metals. Interestingly, this is achieved without any special tuning of pseudo-potentials or the lattice constants for very tightly converged k-grids. This demonstrates a high sensitivity of the calculated optical properties of metals with respect to common approximations in electronic-structure calculations.

The calculated plasma frequency of aluminum is about 15.2 eV, which is in excellent agreement with the experimental value of 15.4 eV. This is a significant improvement over a previously reported value of 12.6 eV [6], which uses LDA exchange-correlation functional and less dense k-point grid. Our tests show that major improvement of plasma frequency in our case is due to SCAN exchange-correlation functional. Indeed, according to our calculations, the PBE exchange-correlation functional for aluminium converges to the value of 12.8 eV as it is shown.
Figure 11: Dielectric function for palladium

Figure 12: Dielectric function for platinum

in figure 13).

Figure 13: Plasma frequency convergence for PBE exchange-correlation functional for aluminium. On x-axis there is a number of k-points in each direction, y-axis represents calculated plasma frequency in eV.

Note, that for aluminium, a convergence of plasma frequency is reached at k-point grid around $60 \times 60 \times 60$. At this point the oscillations become less than 0.1 eV. For all the materials except
copper the convergence is reached at the same or even less dense k-point grid. However, for Copper at k-point grid $70 \times 70 \times 70$ the oscillations of plasma frequency are still around 1 eV.

Plasma frequencies for copper, palladium and platinum are within 10% of corresponding experimental values. In contrast, the calculated plasma frequencies for gold and silver are overestimated compared to experimentally measured values by about 2 eV. Further studies are in progress to explain this discrepancy.

References

[1] Hari L Bhatta, Ali E Aliev, and Vladimir P Drachev. New mechanism of plasmons specific for spin-polarized nanoparticles. Sci. Rep., 9(1):1–8, 2019.
[2] Yi He and Taofang Zeng. First-principles study and model of dielectric functions of silver nanoparticles. J. Phys. Chem. C, 114(42):18023–18030, 2010.
[3] Andrea Marini, Giovanni Onida, and Rodolfo Del Sole. Plane-wave dft-lda calculation of the electronic structure and absorption spectrum of copper. Phys. Rev. B, 64(19):195125, 2001.
[4] Slimane Laref, Jianguo Caop, Abu Asaduzzaman, Keith Runge, Pierre Deyniki, Richard W Ziolkowski, Mamoru Miyawaki, and Krishna Muralidharan. Size-dependent permittivity and intrinsic optical anisotropy of nanometric gold thin films: a density functional theory study. Opt. Express, 21(10):11827–11838, 2013.
[5] Andrea Marini, Rodolfo Del Sole, and Giovanni Onida. First-principles calculation of the plasmon resonance and of the reflectance spectrum of silver in the gw approximation. Phys. Rev. B, 66(11):115101, 2002.
[6] Claudia Ambrosch-Draxl and Jorge O Sofo. Linear optical properties of solids within the full-potential linearized augmented plane-wave method. Comput. Phys. Commun., 175(1):1–14, 2006.
[7] Volker Blum, Ralf Gehrke, Felix Hanke, Paula Havu, Ville Havu, Xinguo Ren, Karsten Reuter, and Matthias Scheffler. Ab initio molecular simulations with numeric atom-centered orbitals. Comput. Phys. Commun., 180(11):2175–2196, 2009.
[8] R Strange, FR Manby, and PJ Knowles. Automatic code generation in density functional theory. Comput. Phys. Commun., 136(3):310–318, 2001.
[9] Jianwei Sun, Adrienn Ruzsinszky, and John P Perdew. Strongly constrained and appropriately normed semilocal density functional. Phys. Rev. Lett., 115(3):036402, 2015.
[10] John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. Phys. Rev. Lett., 77(18):3865, 1996.
[11] Pan Hao, Yuan Fang, Jianwei Sun, Gábor I Csonka, Pier HT Philipsen, and John P Perdew. Lattice constants from semilocal density functionals with zero-point phonon correction. Phys. Rev. B, 85(1):014111, 2012.
[12] Aleksandar D Rakić, Aleksandra B Djurišić, Jovan M Elazar, and Marian L Majewski. Optical properties of metallic films for vertical-cavity optoelectronic devices. Appl. Opt., 37(22):5271–5283, 1998.
[13] H Ehrenreich, HR Philipp, and B Segall. Optical properties of aluminum. Phys. Rev., 132(5):1918, 1963.
[14] Peter B Johnson and RW Christy. Optical constants of the noble metals. Phys. Rev. B, 6(12):4370, 1972.
[15] PB Johnson and RW Christy. Optical constants of transition metals: Ti, v, cr, mn, fe, co, ni, and pd. Phys. Rev. B, 9(12):5056, 1974.
[16] JH Weaver. Optical properties of rh, pd, ir, and pt. Phys. Rev. B, 11(4):1416, 1975.
[17] Zhbin Lin, Leonid V Zhigilei, and Vittorio Celli. Electron-phonon coupling and electron heat capacity of metals under conditions of strong electron-phonon nonequilibrium. Phys. Rev. B, 77(7):075133, 2008.