Communications in Physics, Vol. 27, No. 1 (2017), pp. 65-70
DOI:10.15625/0868-3166/27/1/9201

ENERGY-LOSS FUNCTION FOR LEAD

HIEU T. NGUYEN-TRUONG[1,†], TAN-TIEN PHAM[2], NAM H. VU[2], DANG H. NGO[2] AND HUNG M. LE[3]

[1]*Theoretical Physics Research Group & Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam*

[2]*Faculty of Materials Science, University of Science, Vietnam National University, Ho Chi Minh City, Vietnam*

[3]*Computational Chemistry Research Group & Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam*

[†]*E-mail:* nguyentruongthanhhieu@tdt.edu.vn

Received 7 February 2017
Accepted for publication 30 March 2017

Abstract. *We study the energy-loss function for lead in the framework of the time-dependent density functional theory, using the full-potential linearized augmented plane-wave plus local orbitals method. The ab initio calculations are performed in the adiabatic local density approximation. The comparison between the obtained energy-loss function for zero momentum transfer with those from reflection electron energy loss spectroscopy measurements and from first-principles calculations shows good agreement.*

Keywords: energy-loss function, local field effect, adiabatic local density approximation.

Classification numbers: 72.15.Lh, 34.80.Dp, 79.20.Uv, 77.22.Ch.

I. INTRODUCTION

The energy-loss function (ELF) represents the probability that an incident electron loses an energy and transfers a momentum per unit path length traveled in a solid. The ELF is directly related to the dielectric function, and hence many dielectric properties of materials can be extracted from the determination of the ELF. Unfortunately, experimental data for the ELF is not always available because it is difficult to determine experimentally. The ELF for zero momentum transfer is usually obtained from optical reflection and transmission measurements on thin film [1]. The ELF for finite momentum transfer is then determined with extrapolation algorithms [2–6]. However, the accuracy of the extrapolated ELF is questionable due to the lack of experimental

data for evaluations. An approach of the extrapolation algorithms is to use a linear combination of Drude/Lindhard/Mermin ELF [2, 4] with fitting parameters for oscillators. Another approach is based on the Penn algorithm [3] without any fitting parameters. An advantage of the fitting approach is to take into account plasmon damping. This quantity is, however, neglected in the Penn algorithm due to the use of the Lindhard dielectric function [7] without damping. Plasmons in the Lindhard theory are treated as undamped electron excitations (i.e. infinite lifetime or zero linewidth). An implementation of damping is necessary due to the finite plasmon lifetime (inverse of plasmon damping) in real materials. The shortcoming of the Lindhard dielectric function is solved in the Mermin dielectric function [8], which is a phenomenological modification of the Lindhard dielectric function with including plasmon damping in a consistent manner for the finite plasmon lifetime. Recently, the drawback of the Penn algorithm has been addressed in the Mermin–Penn algorithm [6] by using the Mermin dielectric function instead of the Lindhard dielectric function to take plasmon damping into account. The ELF can also be determined with the self-consistent coupled-plasmon model [5]. In this model, the Lindhard dielectric function is used to estimate an initial damping value, which is then updated iteratively by employing the Mermin dielectric function until the ELF is converged. Although the self-consistent ELF is determined in both a physical and uniquely constrained way, its accuracy remains unknown.

Here we determine the ELF for lead in the framework of the time-dependent density functional theory (TDDFT), using the full-potential linearized augmented plane-wave (FP-LAPW) plus local orbitals (LO) method. In this method, the unit cell is divided into non-overlapping muffin-tin spheres centered on the atoms and an interstitial region. Within a muffin-tin sphere, the basic functions are represented as a sum of products of radial functions and spherical harmonics. Outside the sphere, the basic functions are represented as plane-waves. The wave function must be continuous and smooth at the boundary between two regions to satisfy the variational principle. Local orbitals are introduced as additional basis functions to improve the description of semicore states. The *ab initio* calculations were performed in the adiabatic local density approximation (ALDA). The ELF for lead in the limit of zero momentum transfer have been determined both experimentally [9, 10] and theoretically [10]. These results are also included here for comparisons.

This paper is organized as follows. In Sec. II, the methodology to calculate the ELF is outlined. In Sec. III, the ELF for zero momentum transfer is analyzed and compared with other results; then the ELF for finite momentum transfers is presented and analyzed. In particular, the plasmon dispersion line and width are determined and compared with experimental data. The main results are summarized in Sec. IV.

II. COMPUTATION

The ELF is defined as the imaginary part of the reciprocal complex dielectric function $\varepsilon(\boldsymbol{k},\omega)$, i.e. $\mathrm{Im}[-1/\varepsilon(\boldsymbol{k},\omega)]$, where $\hbar\boldsymbol{k}$ is the momentum transfer vector, and $\hbar\omega$ is the energy loss. There are two excitation modes with respect to the critical momentum transfer vector $\hbar\boldsymbol{k}_{\mathrm{c}}$: (i) the collective excitation for $k < k_{\mathrm{c}}$, and (ii) the single-particle excitation for $k > k_{\mathrm{c}}$. At $k = k_{\mathrm{c}}$, the collective excitation decays into the single-particle excitation via the Landau damping process. Many electronic properties of materials can be described in terms of the complex dielectric function $\varepsilon(\boldsymbol{k},\omega)$, which is given by

$$1/\varepsilon(\boldsymbol{k},\omega) = 1 + v(\boldsymbol{k})\chi(\boldsymbol{k},\omega), \tag{1}$$

where $v(\boldsymbol{k}) = 4\pi e^2/k^2$ is the Fourier transform of the bare Coulomb interaction, and χ is the density response function of the interacting many-electron system. Within the linear-response formulation of TDDFT, the density-response function χ of the interacting many-electron system is related to the density-response function χ_0 of the corresponding noninteracting Kohn-Sham system through the Dyson-like equation

$$\chi = \chi_0 + \chi_0(v + f_{\mathrm{xc}})\chi, \tag{2}$$

where f_{xc} is the exchange-correlation kernel that accounts for all many-body effect. Setting $f_{\mathrm{xc}} = 0$ corresponds to the random phase approximation (RPA). Within the RPA theory, plasmons are undamped (i.e. they have infinite lifetime). However, this situation is not observed in real materials. Beyond the RPA, the ALDA is known as the most common and simplest approximation, which also referred to as time-dependent local-density approximation in connection with TDDFT.

Here, the ALDA kernel was used for calculations *with* and *without* local-field effects (LFE). The calculations were performed with the EXCITING code [11], which is based on the FP-LAPW + LO method. The product of the muffin-tin radius and the largest reciprocal lattice vector in the interstitial region was set to 9. The Brillouin zone was sampled with an off-center $30\times30\times30$ k-point mesh. A lifetime broadening of 0.1 eV was employed. The generalized gradient approximation [12] was used for the exchange-correlation potential. The calculations were performed for momentum transfers along the crystal symmetry direction [111]. A possible anisotropy effect was not investigated here. This effect is expected to be small in lead due to its face centered cubic symmetry.

III. RESULTS AND DISCUSSION

Figure 1 shows the ELF of lead for zero momentum transfer. Such an ELF is typical for simple metals like aluminum, which has a single sharp plasmon peak in its ELF. Here, the plasmon peak for lead locates at 12.3 eV, with a full-width at half maximum (FWHM) of 2 and 3 eV for the ALDA-ELFs *with* and *without* LFE, respectively. This peak originates from interband transitions and corresponds to the bulk plasmon, whereas the less pronounced peak near 8 eV is responsible for the surface plasmon excitation [9].

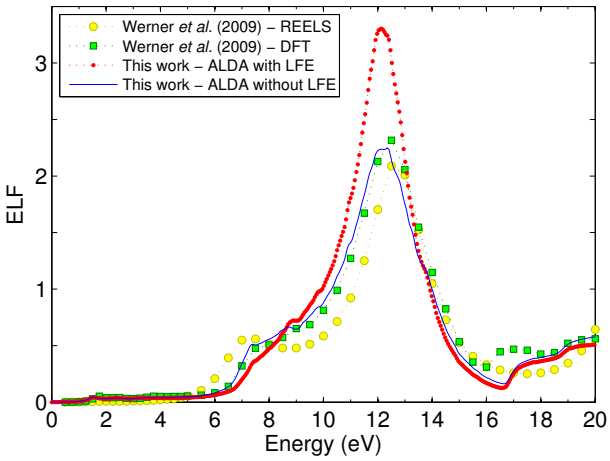

Fig. 1. Energy-loss function for zero momentum transfer.

The ALDA-ELFs *with* and *without* LFE have the same peak position at 12.3 eV but differ significantly in peak amplitude. This is because the most-outer subshell $6p^2$ of lead is still unfilled (up to 4 empty p-states), and hence it is very sensitive to external perturbations. The LFE is responsible for the appearance of dipoles and inhomogeneous electron subsystems caused by external perturbations in the a solid. The significant discrepancy in peak amplitude is mainly due to the LFE and less

likely to be influenced by the core polarization effect [9], which is usually described in terms of an energy- and momentum-independent background dielectric constant. The edge-like feature at 16.7 eV corresponding to the core excitation is rather far from the plasmon peak at 12.3 eV.

The ALDA-ELF *without* LFE agrees well with those from measurements of reflection electron energy loss spectroscopy (REELS) and calculations in the framework of the density-functional theory (DFT) [10]. The REELS data were processed with a procedure eliminating multiple scattering from measured spectra to retrieve a single-scattering loss distribution in an inelastic collision. The DFT calculations were performed in the RPA with the WIEN2k code [13], which is also based on the FP-LAPW + LO method like the EXCITING code.

Entering into the region of finite momentum transfer (Fig. 2), the plasmon peak of both ALDA-ELFs goes along the same plasmon dispersion (Fig. 3), the corresponding FWHM is shown in Fig. 4. However, there is a difference in the change of peak high between two ALDA-ELFs. Moving along the dispersion line, the peak high of the ALDA-ELF *without* LFE (Fig. 2b) is lowered slowly and suddenly falls to minimum at the critical momentum transfer of 0.5 bohr^{-1}, where a plasmon excitation decays to a single-electron excitation via the Landau damping process [14]. Meanwhile, the peak high of the ALDA-ELF *with* LFE (Fig. 2a) experiences two sudden changes at the momentum transfer of 0.28 bohr^{-1} and at the critical momentum transfer. The LFE is responsible for this discrepancy.

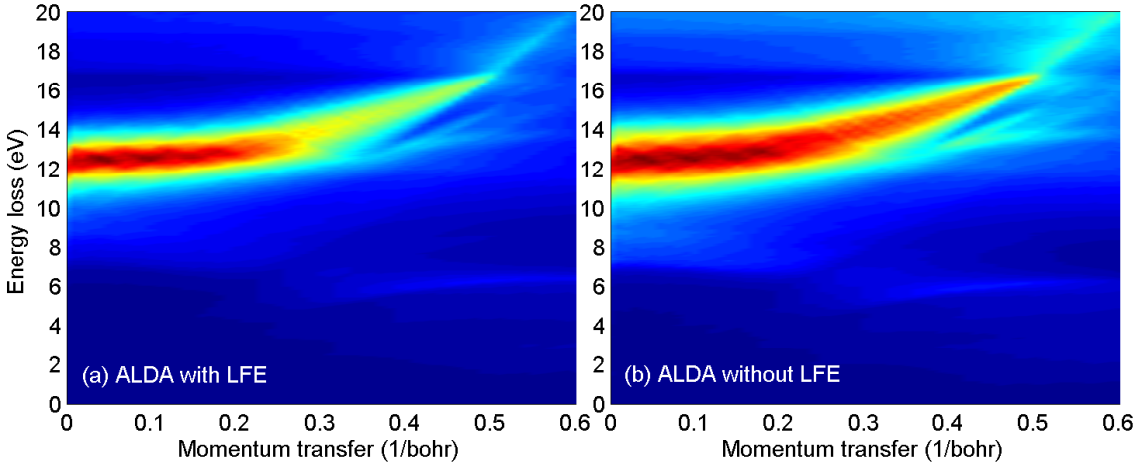

Fig. 2. Energy-loss function for finite momentum transfer.

Both ALDA-ELFs have the same plasmon dispersion relation (solid line in Fig. 3)

$$\hbar\Omega_{\rm pl}(\hbar k) = \hbar\Omega_{\rm pl}(0) + E_{\rm H}\alpha(\hbar k)^2, \tag{3}$$

where $\hbar\Omega_{\rm pl}(\hbar k)$ is the plasmon energy (eV) as a function of momentum transfer $\hbar k$ (bohr^{-1}), $\hbar\Omega_{\rm pl}(0) = 12.3$ eV is the plasmon energy for $k = 0$ corresponding to the plasmon peak position in Fig. 2, $E_{\rm H} = 27.21$ eV is the Hartree energy, and $\alpha = 0.66$ is the plasmon dispersion coefficient. The plasmon energy $\hbar\Omega_{\rm pl}(0) = 12.3$ eV is smaller than experimental values (13.0 or 13.25 eV [9]) and the Drude plasmon energy for a free-electron gas (13.5 eV [9]). In contrast, the plasmon dispersion coefficient $\alpha = 0.66$ is almost double the experimental value (0.36 [9]) and larger than

the theoretical value in the RPA (0.44 [9]). A possible reason for these discrepancies is that the measurements [9] were based on polycrystals and hence the obtained results could be considered as average values, whereas the present calculations were performed for single-crystals.

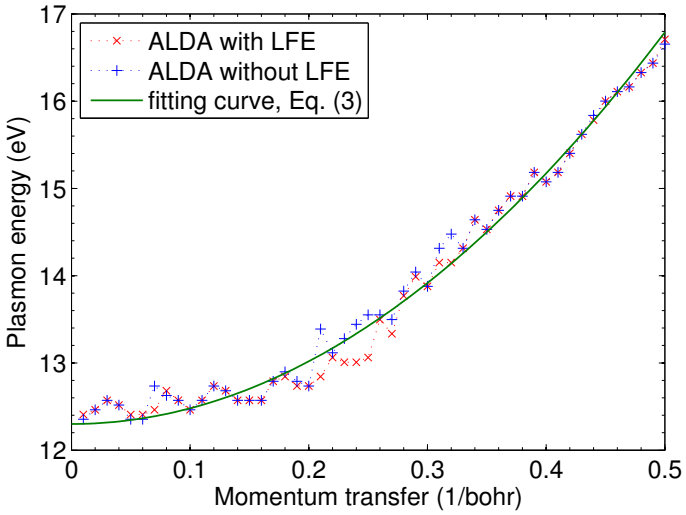

Fig. 3. Plasmon dispersion.

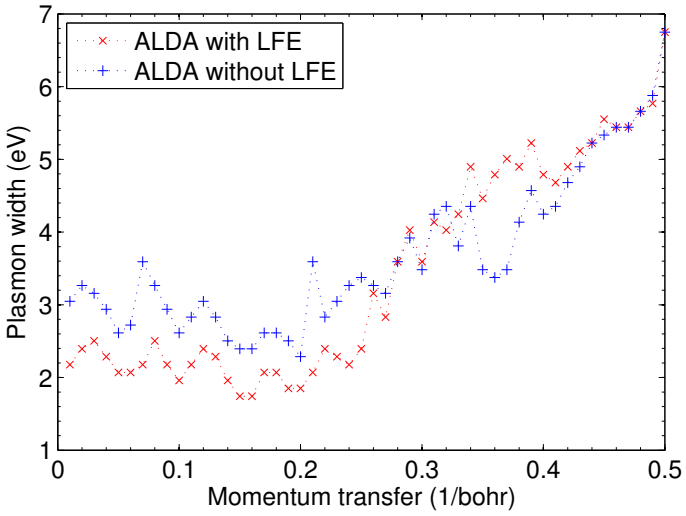

Fig. 4. Plasmon width (FWHM).

In both calculations *with* and *without* LFE, the plasmon energy (Fig. 3) increases with increasing momentum transfer. Meanwhile, the corresponding plasmon width (Fig. 4) reduces slightly before increasing strongly for momentum transfers larger than 0.2 bohr^{-1}. This linewidth broadening effect is important for inelastic scattering of low-energy electrons.

IV. CONCLUSION

We have determined the ELF for lead in the ALDA *with* and *without* LFE. The LFE can be interpreted in terms of the electronic structure. The LFE significantly influences the amplitude and FWHM of the plasmon peak, but does not play any role in the plasmon dispersion.

ACKNOWLEDGMENT

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.01-2015.02.

REFERENCES

[1] E. D. Palik, *Handbook of optical constants of solids*, vol. i, Academic, Boston, 1998.
[2] R. H. Ritchie and A. Howie, *Philos. Mag.* **36** (1977) 463.
[3] D. R. Penn, *Phys. Rev. B* **35** (1987) 482.
[4] I. Abril, R. Garcia-Molina, C. Denton, F. Pérez-Pérez and N. Arista, *Phys. Rev. A* **58** (1998) 357.
[5] J. D. Bourke and C. T. Chantler, *J. Phys. Chem. Lett.* **6** (2015) 314.
[6] H. T. Nguyen-Truong, *J. Phys. Chem. C* **119** (2015) 7883.
[7] J. Lindhard, *Mat. Fys. Medd. Dan. Vid. Selsk.* **28** (1954) 8.
[8] N. D. Mermin, *Phys. Rev. B* **1** (1970) 2362.
[9] M. Knupfer, K. Widder, M. Sing, O. Knauff and J. Fink, *Eur. Phys. J. B* **6** (1998) 323.
[10] W. S. M. Werner, K. Glantschnig and C. Ambrosch-Draxl, *J. Phys. Chem. Ref. Data* **38** (2009) 1013.
[11] A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner and C. Draxl, *J. Phys. Condens. Matter* **26** (2014) 363202.
[12] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. a. Vydrov, G. E. Scuseria, L. a. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.* **100** (2008) 136406.
[13] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz, *Wien2k: An augmented plane wave plus local orbitals program for calculating crystal properties*, Vienna University of Technology: Vienna, Austria, 2001.
[14] H. T. Nguyen-Truong, *Appl. Phys. Lett.* **108** (2016) 172901.