

A new model dielectric function for loss functions and electron damping

Eric L. Shirley

Sensor Science Division, National Institute of Standards and Technology, 100 Bureau Drive, MS 8441, Gaithersburg, MD 20899-8441, USA

ARTICLE INFO

Keywords:

Dielectric function
Lifetime damping
Loss function
Self-energy
Sum rule

ABSTRACT

Trends in the zeroth frequency moment of the imaginary part of the dielectric function are studied for a wide range of metals, semiconductors and insulators. These results are combined with estimates for the inverse-first moment (related by Kramers-Kronig relations to the static dielectric function) and knowledge of the first moment from the f-sum rule. Matching all three moments allows for construction of a model dielectric function that reasonably predicts the loss function at different values of momentum and lifetime damping effects on occupied and unoccupied electron states. This is demonstrated by comparing model results and results of detailed, first-principles calculations.

1. Introduction

Scattering rates, slowing of charged particles and lifetime damping of high-energy electron states in matter depend on a system's dynamical dielectric response. Much effort has been devoted to understanding these effects and enabling investigators to predict and quantify them for a wide range of applications. Several examples of past work are the work by Jablonski and Powell (2015), Chantler et al. (2005), the longstanding effort by Berger et al. (2010), and the recent work by Kas et al. (2007), who formulate a reasonable means of estimating the momentum-dependent loss function and apply it to damping effects for electrons, holes and electron-hole pairs (Kas et al., 2016).

Here we consider the role of valence electrons in dielectric response, whereas effects of core electrons depend much less on the system. Our approach is to use three sum rules to find the inverse-first, zeroth and first frequency moments of the imaginary part of the dielectric function calculated within the random-phase approximation (RPA). By assuming a model form for the imaginary part, the three sum rules constrain the function completely. The real parts of the dielectric and loss functions follow from time-reversal symmetry, Kramers-Kronig relations and the relationship between the two functions. Using the loss function and a free-electron Green's function helps one estimate electron damping. The model results can be compared with detailed numerical results for various quantities to test the model.

In what follows, we examine trends in the zeroth moment across several sequences of materials. Two sequences include solids consisting of first- and second-row elements with varying degrees of covalency: diamond, cubic BN, wurtzite BeO, rocksalt LiF and solid Ne; and silicon, zincblende AlP, rocksalt MgS and NaCl, and solid Ar. Another sequence considers Group IV elements, (diamond) C, Si, Ge, α -Sn and Pb. Finally,

we compare trends in the metals, Li, Na Al and Pb. The zeroth moment vanishes as wave vector $\mathbf{q}$ approaches zero, linearly in metals and quadratically in non-metals. Trends in metals can be compared to the nearly-free-electron limit (jellium), while trends in noble-gas solids can be compared to the behavior expected for independent atoms.

By using the Levine-Louie model dielectric function (Levine and Louie, 1982) for the static dielectric function, the inverse-first frequency moment of the imaginary part of the dielectric function follows from Kramers-Kronig relations. The f-sum rule gives the first frequency moment. After evaluating a model form for the imaginary part, a momentum-dependent loss function is obtained and compared to results of first-principles, numerical time-dependent density-functional theory (TD-DFT) calculations that rely on standard methodology (Onida et al., 2002). The resultant imaginary part of the “on-shell” one-electron self-energy is found for Si, MgO and LiF, and we compare results to those of detailed, numerical calculations obtained using Hedin's GW approximation (Hedin, 1965; Hedin and Lundqvist, 1969) in a manner that reflects the frequency dependence of dielectric screening, i.e., no approximation such as a plasmon-pole model was used (Soininen et al., 2003).

2. Zeroth-moment trends

In the RPA, the polarization function in a given system is given by

$$\chi_0(\mathbf{x}, \mathbf{x}'; \omega) = \frac{\delta n(\mathbf{x}, \omega)}{\delta \phi(\mathbf{x}', \omega)} = 2 \sum_{i,j} \frac{(f_i - f_j) g_i(\mathbf{x}, \mathbf{x}') g_j(\mathbf{x}', \mathbf{x})}{\varepsilon_i - \varepsilon_j - \omega \pm i\eta}. \quad (1)$$

This describes modulation of the charge density n at one point in space $\mathbf{x}$ at frequency ω because of a potential disturbance ϕ at another

E-mail address: eric.shirley@nist.gov.

<https://doi.org/10.1016/j.radphyschem.2019.02.024>

Received 15 November 2018; Accepted 8 February 2019

Available online 15 February 2019

0969-806X/ Published by Elsevier Ltd.

point. Indices i and j sum over electronic (Kohn-Sham) states, both occupied and unoccupied (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). An f or ε is a Kohn-Sham orbital occupancy or eigenvalue, respectively, and $g_i(\mathbf{x}, \mathbf{x}') = \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}')$ is a product of a Kohn-Sham orbital and its conjugate. Indices i and j sum over states of only one spin type, while the 2 multiplying the sum accounts for spin degeneracy. (We only consider paramagnetic systems.) This implies

$$\chi_0(\mathbf{x}, \mathbf{x}'; \omega) = 4 \sum_{c,v} \frac{\omega_{cv} g_c(\mathbf{x}, \mathbf{x}') g_v(\mathbf{x}', \mathbf{x})}{\omega^2 - (\omega_{cv} - i\eta)^2}. \quad (2)$$

Here v (c) sums over occupied (unoccupied) states, and $\omega_{cv} = \varepsilon_c - \varepsilon_v$. For $\omega > 0$, this gives

$$\text{Im}\chi_0(\mathbf{x}, \mathbf{x}'; \omega) = -2\pi \sum_{c,v} g_c(\mathbf{x}, \mathbf{x}') g_v(\mathbf{x}', \mathbf{x}) \delta(\omega - \omega_{cv}) \quad (3)$$

From

$$\sum_v g_v(\mathbf{x}, \mathbf{x}') + \sum_c g_c(\mathbf{x}, \mathbf{x}') = \delta^3(\mathbf{x} - \mathbf{x}'), \quad (4)$$

we also have

$$\begin{aligned} \frac{1}{\pi} \int_0^\infty d\omega \text{Im}\chi_0(\mathbf{x}, \mathbf{x}'; \omega) = \\ -n(\mathbf{x})\delta^3(\mathbf{x} - \mathbf{x}') + 2 \sum_{v,v'} g_v(\mathbf{x}, \mathbf{x}') g_{v'}(\mathbf{x}', \mathbf{x}). \end{aligned} \quad (5)$$

We define a scaled frequency moment of the dielectric function's imaginary part at wave vector $\mathbf{q}$ as

$$M_n(\mathbf{q}) = \frac{q^2}{4\pi^2} \int_0^\infty d\omega \omega^n \text{Im}\varepsilon(\mathbf{q}, \omega). \quad (6)$$

Using $\varepsilon(\mathbf{q}, \omega) = 1 - (4\pi/q^2)\chi_0(\mathbf{q}, \omega)$, we find

$$M_0(\mathbf{q}) = n_{av} - \frac{2}{V} \int d^3\mathbf{x} \int d^3\mathbf{x}' e^{-i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')} \sum_{v,v'} g_v(\mathbf{x}, \mathbf{x}') g_{v'}(\mathbf{x}', \mathbf{x}), \quad (7)$$

where n_{av} is the average valence electron density.

We studied trends in the behavior of $M_0(\mathbf{q})$ using density-functional theory (DFT) calculations (Hohenberg and Kohn, 1964) using the local-density approximation (Kohn and Sham, 1965). We worked within a plane-wave/pseudopotential framework using norm-conserving pseudopotentials with a form like that proposed by Vanderbilt (1985). A hard plane-wave cutoff was consistently used, as were experimental lattice constants. Other numerical aspects are described elsewhere (Shirley et al., 1996).

To evaluate $M_0(\mathbf{q})$, we note that Eq. (7) involves the square of the one-electron density matrix and/or a double sum over occupied electron states. We sampled states indexed by v with crystal momentum $\mathbf{k}$ on a regular grid that samples the whole Brillouin zone. The grid was shifted to break symmetry, which accelerates convergence of results with increasing sampling density. We sampled states indicated by v' on a commensurate grid at points $\mathbf{k} + \mathbf{Q}$ for a few values of $\mathbf{Q}$, which always lay within the first Brillouin zone. For one value of $\mathbf{Q}$, this gives results for $M_0(\mathbf{q})$ for all $\mathbf{q} = \mathbf{Q} + \mathbf{G}$, where $\mathbf{G}$ can be one of many reciprocal-lattice vectors. Use of a plane-wave basis set for Bloch states and fast Fourier-transform techniques made the evaluation very efficient. Using 4–10 values of $\mathbf{Q}$ gave results for a sufficiently dense set of values of q to establish trends in the behavior of $M_0(\mathbf{q})$, which depends mostly on the magnitude of $\mathbf{q}$, i.e., q .

We used 216 values of $\mathbf{k}$ for insulating materials and 64,000 values of $\mathbf{k}$ for metallic systems. The results obtained from such sampling were sufficiently converged with respect to sampling for all practical purposes. An inconsequential exception to this rule was the small- q behavior in metals, where $M_0(\mathbf{q})$ goes to zero linearly. The results showed fluctuations in the values of $M_0(\mathbf{q})/q$ because of limited sampling of combinations of states separated by $\mathbf{q}$ inside and outside of the Fermi sea. [Recall that we are sampling combinations of occupied and unoccupied states, although only occupied states appear in Eq. (7).]

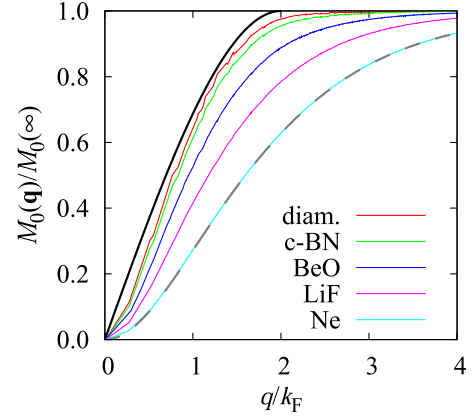


Fig. 1. The scaled zeroth moment versus scaled wave vector for five first-row compounds. The jellium and independent-atom limits are shown by a solid and dashed black curve, respectively.

In Fig. 1, we show trends in $M_0(\mathbf{q})$ for the combinations of first-row elements for the compounds indicated. Solid Ne has one atom per unit cell, wurtzite BeO has four, while diamond, cubic BN and LiF each have two. To illustrate trends most clearly, the wave vector is scaled against the canonical Fermi wave vector k_F given by $k_F^3 = 3\pi^2 n_{av}$, and the value of $M_0(\mathbf{q})$ is scaled against the value of $M_0(\mathbf{q} \rightarrow \infty)$. The moment $M_0(\mathbf{q})$ depends on the vector $\mathbf{q}$, but we plot it as, and consider it to depend, only on the magnitude q , so that the values of $M_0(\mathbf{q})$ that are found follow a smooth trend with modest scatter. Fig. 2 shows analogous trends for combinations of second-row elements for the compounds indicated in the Figure. All these compounds have eight electrons per unit, with two atoms per unit cell in every system except solid Ar. In both figures, trends are shown for the jellium limit and our DFT noble-gas atom results. The trend for jellium can be found analytically, being proportional to the volume of the Fermi sphere that is not contained within an identical sphere centered at wave vector $\mathbf{q}$. The noble-gas atom results are based on calculations of the type reported by Kotochigova et al. (Kotochigova et al., 1997a, 1997b) using the program written by the author.

In Fig. 3, we show trends for $M_0(\mathbf{q})$ for five Group-IV systems: diamond C, Si, Ge, α -Sn, and Pb, and the jellium limit. In Fig. 4, we show trends in the metals, Li, Na, Al and Pb, along with the jellium limit. Fig. 4a shows trends for $M_0(\mathbf{q})$, and Fig. 4b shows scaled trends for $M_0(\mathbf{q})/q$. The small- q limit in Fig. 4b is related to the area of the Fermi surface projected along $\mathbf{q}$. Results at small q fluctuate because of imperfect Brillouin zone sampling. We attribute the systematic departures from jellium-like behavior at small q to non-sphericity of the

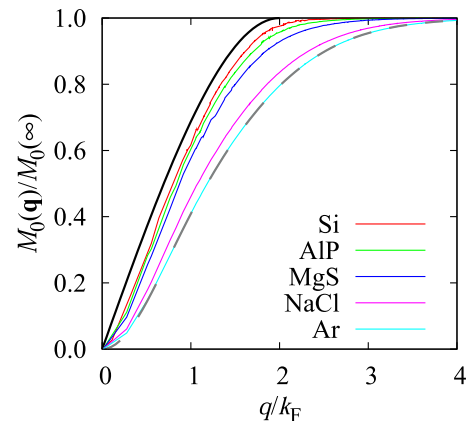


Fig. 2. The scaled zeroth moment versus scaled wave vector for five second-row compounds. The jellium and independent-atom limits are shown by a solid and dashed black curve, respectively.

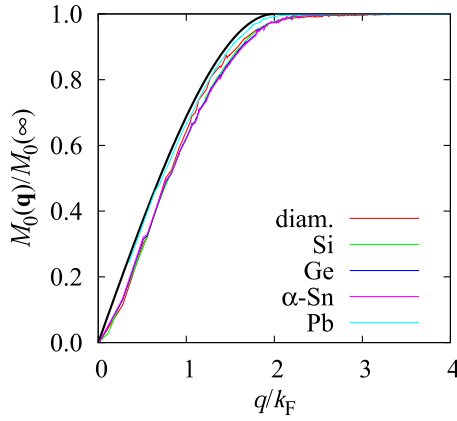


Fig. 3. The scaled zeroth moment versus scaled wave vector for Group IV elements. The jellium limit is shown by a solid black curve.

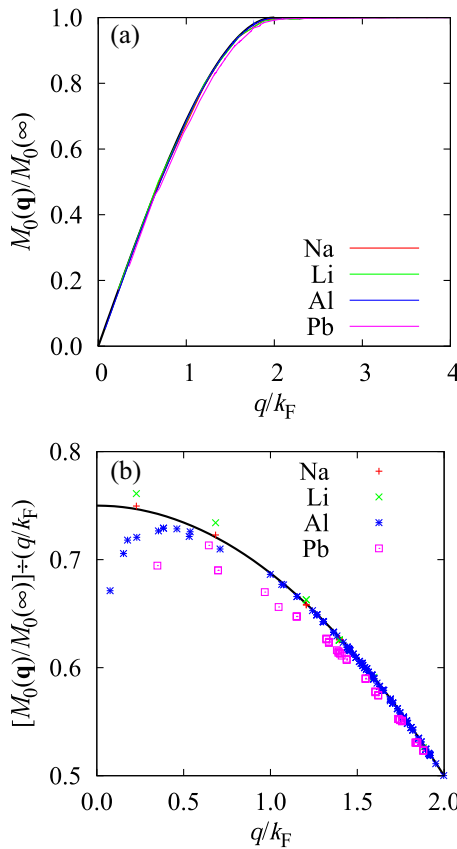


Fig. 4. (a.) The scaled zeroth moment versus scaled wave vector for four metals. The jellium limit is shown by a solid black curve. (b.) Same as for panel (a.), divided by (q/k_F) .

Fermi surface, even in an extended-zone scheme.

3. Parametrized model dielectric function

The analysis of the previous section establishes the behavior of $M_0(\mathbf{q})$. The f-sum rule implies the value of $M_1(\mathbf{q})$. We use this rule and ignore the fact that changes in the electron velocity operator because of use of non-local pseudopotentials imply that it is only approximate. Finally, $M_{-1}(\mathbf{q})$ is found from Kramers-Kronig relations by relating it to the static dielectric function of Levine and Louie. This requires use of the experimentally observed static macroscopic dielectric function, ϵ_∞ . Note then that the above three moments are found using three

unrelated approximation schemes. The Cauchy-Schwarz inequality implies that one should have $[M_0(\mathbf{q})]^2 \leq M_1(\mathbf{q})M_{-1}(\mathbf{q})$, but this inequality is occasionally violated in our method, and we discard results found for values of $\mathbf{q}$ for which the inequality is not satisfied. Alternatively, one could do well by using a single-pole approximation for such cases, because $\text{Im } \epsilon(\mathbf{q}, \omega)$ should be strongly peaked in such cases. In addition, $M_0(\mathbf{q})$ cannot exceed $M_0(\mathbf{q} \rightarrow \infty)$ for electron-counting reasons.

If the Cauchy-Schwarz inequality is obeyed, many functions can match the above three moments. The following form is convenient because the moments can be found analytically:

$$\text{Im } \epsilon(\mathbf{q}, \omega > 0) = (4\pi^2/q^2) C \Theta(\omega - E_G) \omega(\omega - E_G)^{p-1} e^{-(\omega - E_G)/\Omega}, \quad (8)$$

giving

$$\left. \begin{aligned} M_{-1} &= C \Gamma(p) \Omega^p \\ M_0 &= C [\Gamma(p+1) \Omega^{p+1} + E_G \Gamma(p) \Omega^p] \\ M_1 &= C [\Gamma(p+2) \Omega^{p+2} + 2E_G \Gamma(p+1) \Omega^{p+1} + E_G^2 \Gamma(p) \Omega^p] \end{aligned} \right\}. \quad (9)$$

Here E_G is the band gap, and we suppress the $\mathbf{q}$ -dependence of the moments, C , p and Ω . Two ratios of moments are $M_0/M_{-1} = \Omega p + E_G$ and $M_1/M_{-1} = \Omega^2 p(p+1) + 2E_G \Omega p + E_G^2$. From this, one has $\Omega p = (M_0/M_{-1} - E_G)$, $p = \Omega p / \Omega$, and $C = M_{-1} / [\Gamma(p) \Omega^p]$. However, it has been found advantageous to determine stationary points for the *logarithm* of $\text{Im } \epsilon(\mathbf{q}, \omega)$ after only Ω and p are found, normalize a *trial* $\text{Im } \epsilon(\mathbf{q}, \omega)$ so that it does not exceed unity, evaluate trial moments thereof, and normalize once more to obtain the correct moments. This avoids numerical pitfalls because of unwieldy compensating factors in Eq. (9).

Time-reversal symmetry implies $\text{Im } \epsilon(\mathbf{q}, -\omega) = -\text{Im } \epsilon(\mathbf{q}, \omega)$, and one can find $\text{Re } \epsilon(\mathbf{q}, \omega)$ efficiently through Kramers-Kronig relations using fast Fourier-transform methodology. Fig. 5 shows the loss function, $\text{Im} [-1/\epsilon(\mathbf{q}, \omega)]$, for Ar, Si and Al for several values of $\mathbf{q}$. These were obtained using the present approach and time-dependent density-function-theory (TD-DFT) calculations using the program of Lawler et al. (2008). The agreement between results supports use of the present method for many applications.

4. Electron damping calculations

Damping of electronic states because of coupling to collective excitations can be estimated using Hedin's *GW* approximation. In this approach, the electron self-energy is an effective part of an electron or hole's energy, and the self-energy's imaginary part determines the damping and lifetime broadening. The self-energy is given by

$$\Sigma(\mathbf{k}, E) = +i \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \int \frac{d\omega}{2\pi} e^{+i\eta\omega} G(\mathbf{k} + \mathbf{q}, E + \omega) W(\mathbf{q}, \omega). \quad (10)$$

Here we use the time-order free electron Green's function:

$$G(\mathbf{k} + \mathbf{q}, E + \omega) = \frac{1}{E + \omega - |\mathbf{k} + \mathbf{q}|^2/2 \pm i\eta}. \quad (11)$$

We have $W(\mathbf{q}, \omega) = \epsilon^{-1}(\mathbf{q}, \omega) V(\mathbf{q})$, where $V(\mathbf{q}) = 4\pi/q^2$ is the Fourier transform of the Coulomb interaction. We can also write $\epsilon^{-1}(\mathbf{q}, \omega) = 1 + A_R(\mathbf{q}, \omega) + A_A(\mathbf{q}, \omega)$. The first term leads to Fock exchange, which only involves the advanced part of G . The retarded term $A_R(\mathbf{q}, \omega)$ is $-i$ times the loss function for $\omega > 0$ and a real part dictated by Kramers-Kronig relations. The advanced term $A_A(\mathbf{q}, \omega)$ is $+i$ times the loss function of $|\omega|$ for $\omega < 0$ and a real part dictated by Kramers-Kronig relations. Hence, $A_R(\mathbf{q}, \omega)$ arises from poles just below the positive real axis and has a branch cut there, whereas $A_A(\mathbf{q}, \omega)$ arises from poles just above the negative real axis and has a branch cut there.

When carrying out integration over $\mathbf{q}$, $A_R(\mathbf{q}, \omega)$ and $A_A(\mathbf{q}, \omega)$ were interpolated from their values at the closest calculated values of $\mathbf{q}$ in Eq. (10). Damping effects (synonymous with the imaginary part of the self-

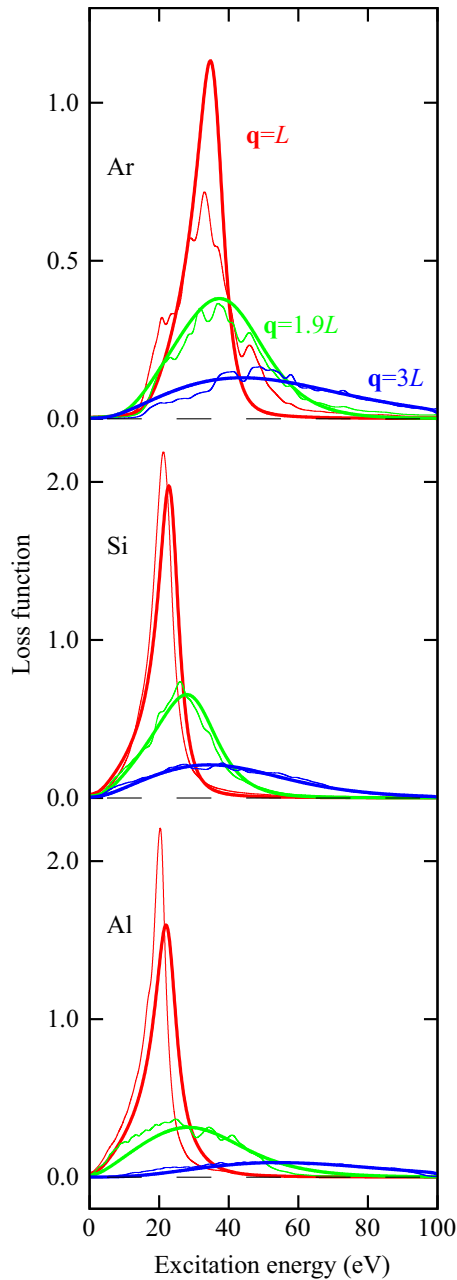


Fig. 5. Loss function in Si, Al, Ar for three wave vectors. The numerical result is indicated by the thin curve, while the model result is indicated by the bold curve.

energy) arose from the residue because of products of the advanced part of G and $A_R(\mathbf{q}, \omega)$ for $E < E_F$ and products of the retarded part of G and $A_A(\mathbf{q}, \omega)$ for $E > E_F$. Fig. 6 shows results for Si, MgO and LiF using the present model and detailed numerical calculations described elsewhere (Soininen et al., 2003). Such broadening of electron and hole features leads to concomitant broadening of spectral features in a variety of excitation spectra, including the loss functions shown in Fig. 5. However, the connection between electron or hole broadening and the latter broadening is complicated, as illustrated, for instance, by Kas et al. (2016).

5. Conclusions

Use of three sum rules has permitted construction of a parametrized

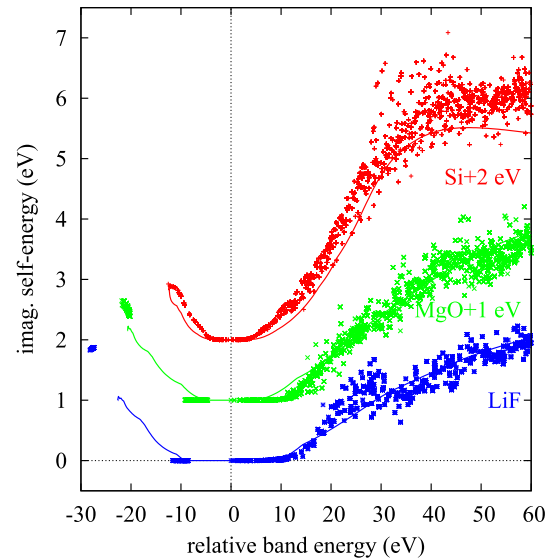


Fig. 6. Electron damping in Si, MgO and LiF, vertically offset for presentation. The points indicate results of full, numerical self-energy calculations, and the curves show the present model results.

dielectric function. This reproduces salient features of the loss function at different values of momentum reasonably well. The resulting loss function was also used to estimate electron damping in various systems. From comparison of model and detailed, numerical results, we conclude that this work presents a practical and accurate method for estimating valence electrons' contributions to quantities such as stopping powers and electron damping and associated mean free paths.

References

- Berger, M.J., Hubbell, J.H., Seltzer, S.M., Chang, J., Coursey, J.S., Sukumar, R., Zucker, D.S., Olsen, K., 2010. XCOM: Photon Cross Sections Database. <https://dx.doi.org/10.18434/T48G6X>.
- Chantler, C.T., Olsen, K., Dragoset, R.A., Chang, J., Kishore, A.R., Kotochigova, S.A., Zucker, D.S., 2005. X-ray form factor, attenuation, and scattering tables. <https://dx.doi.org/10.18434/T4HS32>.
- Hedin, L., 1965. New method for calculating 1-particle Green's function with application to electron gas problems. *Phys. Rev.* 139, A796.
- Hedin, L., Lundqvist, S., 1969. Effects on electron-electron and electron phonon interactions on the one-electron states of solids. *Solid State Phys.* 23, 1.
- Hohenberg, P.C., Kohn, W., 1964. Inhomogeneous electron gas. *Phys. Rev.* 136, B864.
- Jablonski, A., Powell, C.J., 2015. Effective attenuation lengths for photoelectrons emitted by high-energy laboratory X-ray sources. *J. Electron. Spect. Relat. Phenom.* 199, 27.
- Kas, J.J., Sorini, A.P., Prange, M.P., Campbell, L.W., Soininen, J.A., Rehr, J.J., 2007. Many-pole model of inelastic losses in x-ray absorption spectra. *Phys. Rev. B* 76, 195116.
- Kas, J.J., Rehr, J.J., Curtis, J.B., 2016. Particle-hole cumulant approach for inelastic losses in x-ray spectra. *Phys. Rev. B* 94, 035156.
- Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140, A1133.
- Kotochigova, S., Levine, Z.H., Shirley, E.L., Stiles, M.D., Clark, C.W., 1997a. Local-density-functional calculations of the energy of atoms. *Phys. Rev. A* 55, 191.
- Kotochigova, S., Levine, Z.H., Shirley, E.L., Stiles, M.D., Clark, C.W., 1997b. Local-density-functional calculations of the energy of atoms (vol 55, pg 191, 1997). *Phys. Rev. A* 56, 5191.
- Lawler, H.M., Rehr, J.J., Vila, F., Dalosto, S.D., Shirley, E.L., Levine, Z.H., 2008. Optical to UV spectra and birefringence of SiO₂ and TiO₂: first-principles calculations with excitonic effects. *Phys. Rev. B* 78, 205108.
- Levine, Z.H., Louie, S.G., 1982. New model dielectric function and exchange-correlation potential for semiconductors and insulators. *Phys. Rev. B* 25, 6310.
- Onida, G., Reining, L., Rubio, A., 2002. Electronic excitations: density-functional versus many-body Green's function approaches. *Rev. Mod. Phys.* 74, 601.
- Shirley, E.L., Terminello, L.J., Klepeis, J.E., Himpel, F.J., 1996. Detailed theoretical photoelectron angular distributions for LiF(100). *Phys. Rev. B* 53, 10296.
- Soininen, J.A., Rehr, J.J., Shirley, E.L., 2003. Electron self-energy calculation using a general many-pole approximation. *J. Phys. Cond. Matter* 15, 2573.
- Vanderbilt, D., 1985. Optimally smooth norm-conserving pseudopotentials. *Phys. Rev. B* 32, 8412.