Calculation of optical constants and related quantities from optical to x-ray frequencies

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Abstract. We discuss an efficient approach for calculations of optical to x-ray response based on a spectral function formalism which is implemented in an extension to the real-space Green's function code FEFF. This formalism avoids the need to compute wave-functions explicitly, and is applicable to arbitrary, aperiodic systems. Starting from the complex dielectric constant, the approach gives a number of linear optical constants, including the complex index of refraction $n = \varepsilon(\omega)^{1/2}$, the energy-loss function $\pi \text{Im} \varepsilon^{-1}(\omega)$, and the photoabsorption coefficient $\mu(\omega)$. Many other physical properties are related to these properties including inelastic mean-free paths and the photon scattering amplitude. The \textit{ab initio} calculation of these optical properties for arbitrary materials has been a long-standing problem in condensed-matter physics [2]. Thus in practice, these properties are often approximated from atomic calculations or taken from a variety of tabulated compilations [3–5]. However, such tabulations are available only for a few well-characterized materials over limited spectral ranges, while atomic calculations ignore solid-state effects. Thus our aim is to develop an efficient but general method covering a broad range of frequencies that provides a practical alternative or complement to tabulated data and atomic models.

1. Introduction

We discuss a recently developed method for theoretical calculations of \textit{optical constants}, i.e., linear optical response derived from the the long-wavelength limit $\vec{q} \to 0$ of the dielectric function $\varepsilon(\vec{q}, \omega)$ [1]. These quantities include the complex dielectric constant $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, the complex index of refraction $n = \varepsilon(\omega)^{1/2}$, the energy-loss function $-\text{Im} \varepsilon^{-1}(\omega)$, and the photoabsorption coefficient $\mu(\omega)$. Many other physical properties are related to these properties including inelastic mean-free paths and the photon scattering amplitude. The \textit{ab initio} calculation of these optical properties for arbitrary materials has been a long-standing problem in condensed-matter physics [2]. Thus in practice, these properties are often approximated from atomic calculations or taken from a variety of tabulated compilations [3–5]. However, such tabulations are available only for a few well-characterized materials over limited spectral ranges, while atomic calculations ignore solid-state effects. Thus our aim is to develop an efficient but general method covering a broad range of frequencies that provides a practical alternative or complement to tabulated data and atomic models.

The theory of dielectric response has been developed extensively over the past several decades, especially for periodic systems [2]. Recently there has been considerable progress in implementations of first principle Bethe-Salpeter Equation (BSE) approaches [6–9], as also discussed elsewhere in these proceedings. Thus, we have also investigated the GW/BSE approach using AI2NBSE [6], an efficient interface between the density functional code ABINIT [10] and the NIST BSE code [11]. An extension of AI2NBSE for core-level spectra is
now under development[12]. However computational demands currently restrict such BSE implementations to relatively small periodic systems and limited spectral ranges. As an alternative, complementary method, we discuss here an approach based on a spectral function (or density-matrix) formalism within an effective single-particle (quasi-particle) theory. This approach is a generalization of the real-space Green’s function method implemented in the FEFF codes [13; 14], which includes both core- and valence-level spectra and builds in inelastic losses and other solid state effects. Our work is intended to extend the capabilities of FEFF to enable full spectrum output for general aperiodic systems with a quality roughly comparable to current tabulations. The approach is illustrated with sample calculations of XAS and EELS and compared with experiment and with theoretical calculations based on AI2NBSE. A more complete description of our approach is given in a series of recent papers [1; 15–17], and an illustrative example that illustrates the full-spectrum capability of this approach is given in Fig. 1.

2. Spectral Function Theory of Optical Response

The starting point for our approach is the dielectric function \( \varepsilon(\omega) = 1 + 4\pi \chi(\omega) \) in terms of the electric susceptibility \( \chi(\omega) \). Formally the imaginary part of the dielectric function is related to the full susceptibility by [19]

\[
\varepsilon_2(\omega) = \frac{4\pi}{V} \text{Im} \text{Tr} \int d\bar{r} d\bar{r}' d\chi(\bar{r}, \bar{r}', \omega) d^4, \tag{1}
\]

where \( V \) is the volume of the system and \( d = \vec{\alpha} \cdot \epsilon_p e^{i \vec{k} \vec{r}} \) is the relativistic dipole transition operator between the incident photon of wave vector \( \vec{k} \) and polarization \( \epsilon_p \) and \( \vec{\alpha} \) is the Dirac-Pauli matrix. The full response \( \chi \) of the system is directly related to response \( \chi^0 \) of the non-interacting reference system by

\[
\chi = \chi^0 + \chi^0 K \chi = \chi^0 (1 - K \chi^0)^{-1}, \tag{2}
\]

where \( K \) is the particle-hole interaction kernel. Formally Eq. (2) can be expressed without reference to the occupied and unoccupied wave-functions of the system in terms of the single-particle Green’s function \( G \), from which the spectral function (or density operator) is \( \rho(E) = (-1/\pi) \text{Im} G(E) \). Thus as shown in [1] the response function can be calculated in terms of the one-particle spectral functions \( \rho(E) \) for occupied and unoccupied levels

\[
\text{Im} \chi^0 = -\frac{1}{\pi} \int_{E_F-\omega}^{E_F} \rho(\vec{r}', \vec{r}, E) \rho(\vec{r}', \vec{r}, E + \omega) dE. \tag{3}
\]
In our approach we calculate these density matrices for energies ranging from the visible to x-ray energies of order 100 KeV [1; 17]. For convenience, we separate the spectral function into two energy regions: the core region in which the atomic approximation is valid to high accuracy, and the solid-state region where solid-state effects are important

$$\rho(E) = \rho^{\text{core}}(E) \quad (E < E_{cv}), \quad \rho^{\text{val}}(E) \quad (E > E_{cv}).$$ (4)

For the core-state response, an atomic approximation can be used for each level $\nu$,

$$\rho^{\text{core}}(E) = \sum_{\nu} \rho^{(\nu)}_{\text{at}}(E), \quad \rho^{(\nu)}_{\text{at}}(E) = \phi_{\nu}(\vec{r}) \phi_{\nu}(\vec{r}') \delta(E - E_{\nu}).$$ (5)

The core-valence separation energy $E_{cv}$ is chosen to be away from all occupied Kohn-Sham energy eigenvalues that separate the two regimes, and is set by default to $E_{cv} = -40$ eV; this value is about 30 eV below the Fermi level. This yields an expression equivalent to Fermi’s golden rule for the core contribution to the dielectric response

$$\epsilon_2^{\text{core}}(\omega) = \sum_{\nu} \epsilon_2^{(\nu)}(\omega) = \frac{4\pi}{\omega} \sum_{\nu} \text{Im}(\nu | d \hat{G}(\omega + \epsilon_{\nu}) d | \nu) \theta(\omega + \epsilon_{\nu} - \epsilon_F).$$ (6)

For the valence response the relativistic multiple-scattering formalism in FEFF[13] is used. There the density matrix is expressed in terms of matrix elements of the Green’s function

$$\rho^{\text{val}}(\vec{r}, \vec{r}', E) = \sum_{K,K'} R_{Kn}(\vec{r}) \rho_{Kn,K'n'} R_{K'n'}(\vec{r}', \vec{r}),$$ (7)

where $R_{Kn}$ are regular scattering states at sites $n$ and $n'$, and the matrix elements of $\rho(E)$ are

$$\rho_{Kn,K'n'} = \delta_{n,n'} \delta_{K,K'} + \text{Im} \left( i \hat{G}_{Kn,K'n'} \right)$$ (8)

This leads to the following expression for the valence contribution

$$\epsilon_2^{\text{val}}(\omega) = \frac{4\pi}{V} \int_{E_{F} - \omega}^{E_{F}} dE \sum_{n,n'} \rho_{nn'}(E) M_{nn'}(E, E + \omega) \rho_{n'n'}(E + \omega) M_{n'n'}^{T}(E + \omega, E),$$ (9)

where the dipole matrix elements at each site $n$ are given by

$$M_{n,K,K'}^{\nu}(E,E') = \int_{\vec{r}} d\vec{r} \tilde{R}_{Kn}(\vec{r}; E) d \tilde{R}_{K'n'}(\vec{r}; E')$$ (10)

and relativistic angular momentum indices $K = (\kappa, m)$ are suppressed. Finally the full spectrum is obtained by combining the valence and core contributions

$$\epsilon_2(\omega) = \sum_{\nu} \epsilon_2^{(\nu)}(\omega) + \epsilon_2^{\text{val}}(\omega).$$ (11)

This method is implemented in an extension of the FEFF[13] codes using the quasi-particle approach described in [13; 14]. A summary of the method is given in [17].
3. Theoretical Optical Constants

Our calculations start from the calculation of $\epsilon_2(\omega)$ using Eqs. (6,9,11). Next the real part $\epsilon_1(\omega)$ is obtained by a Kramers-Kronig transform. From these basic ingredients, many other optical constants can be derived, as discussed in more detail elsewhere.[1]

Index of Refraction: The index of refraction $n(\omega)$ is the square root of the dielectric function

$$n(\omega) \equiv \epsilon(\omega)^{1/2} = n(\omega) + ik(\omega). \quad (12)$$

Absorption coefficient: The photon absorption coefficient (Fig. 1) a quantity of central interest in x-ray absorption spectroscopy (XAS), is obtained from the imaginary part of $n$, i.e.,

$$\mu(\omega) = \frac{2\omega}{c}k(\omega), \quad (13)$$

Energy Loss Function: The energy loss function (Fig. 2), which is measured in electron energy loss spectra (EELS), is given by

$$-\text{Im} \epsilon^{-1}(\omega) = \frac{\epsilon_2(\omega)}{\epsilon_2^2(\omega) + \epsilon_1^2(\omega)}. \quad (14)$$

4. Discussion

These results provide a theoretical complement to standard tables and are useful in a variety of applications. For example they permit ab initio calculations self-energy shifts, inelastic losses, mean-free paths, collision stopping powers.[15; 16] For example, a many-pole self-energy model based on these results [16] makes possible improved, parameter free calculations of various photon- and electron-spectra, e.g., XAS, NRIXS, and EELS using the theoretical method described here, as discussed by Kas et al. elsewhere in these proceedings. Moreover they can be used to calculate van der Walls interactions in terms of Hamaker constants [1]. Additional optical constants and comparisons with experiment are now available on the WWW [20].

**Figure 2.** Calculated energy-loss function (dimensionless, from Eq. 14) vs energy in eV for Cu compared to experiment [4] and calculations from AI2NBSE.
Acknowledgments
We thank A. Ankudinov, C. Chantler, H. Lawler, Z. Levine, M. Newville, L. Reining, J. A. Soininen, and F. Vila for many discussions, and especially G. Hug and M. Jaouen for suggestions during the early stages of this work. This work was supported in part the US Department of Energy, Office of Basic Energy Sciences grant DE-FG02-97ER45623 and by NIH NCRR BTP Grant RR-01209 (JJK), and was facilitated by the DOE CMSN.

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