Full spectrum optical constant interface to the Materials Project

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ABSTRACT

Optical constants characterize the interaction of materials with light and are important properties in material design. Here we present a Python-based Corvus workflow for simulations of full spectrum optical constants from the visible and ultraviolet to hard x-ray wavelengths based on the real-space Green's function code FEFF10 and structural data from the Materials Project (MP). The Corvus workflow manager and its associated tools provide an interface to FEFF10 and the MP database. The workflow parallelizes the FEFF computations of optical constants over all absorption edges for each material in the MP database specified by a unique MP-ID. The workflow tools determine the distribution of computational resources needed for that case. Similarly, the optical constants for selected sets of materials can be computed in a single-shot. To illustrate the approach, we present results for several elemental solids in the periodic table, as well as a sample compound, and compare our predictions with experimental results. In addition, we provide a database of calculated results for all elements for which there is a stable elemental solid at standard conditions available in the Materials Project database. As in x-ray absorption spectra, these results are interpreted in terms of an atomic-like background and fine-structure contributions.

1. Introduction

Optical constants characterize the frequency dependent interaction between light and matter in the long-wavelength limit.[1] Thus they are often important characteristics in materials design.[1] These properties include the complex dielectric constant (or equivalently, relative permittivity) and index of refraction, as well as the energy-loss function, photoabsorption coefficient (or equivalently, X-ray absorption spectra (XAS) at high energy), and optical reflectivity.[2–5] Many other physical properties can be derived from the optical constants, including electron energy loss spectra (EELS), inelastic mean-free paths, the atomic scattering amplitudes, and Hamaker constants for the van der Waals interaction. For these purposes, tabulations of experimentally determined optical constants are widely used.[2–5] For practical reasons, however, such tabulations are limited to a relatively small number of well characterized materials over limited spectral ranges and limited environmental conditions. Thus here we focus on broad spectrum theoretical treatments for the systems defined in the Materials Project (MP) database.

Significant progress has been made in the fundamental theory of optical properties since the pioneering works of Nozieres and Pines,[6] Adler,[7] and Wiser.[8] In particular modern first-principles calculations based on time-dependent density functional theory (TDDFT) and the Bethe-Salpeter Equation (BSE) are now highly quantitative.[9–19] Also limited tables of theoretical optical constants of materials have been compiled over the optical range.[20,21] However, such calculations involve many-body calculations of optical response, and become computationally intractable for many materials over broad spectral ranges. In contrast, the real-space Green’s function (RSGF) approach in FEFF10 includes the key many-body effects, is highly automated and has proved to be quite accurate for general materials in the X-ray regime. Moreover the code can be semi-quantitative in the UV–VIS (ultraviolet-visible) to soft-X-ray regime.[22] Consequently, theoretical calculations based on FEFF10 provide an attractive alternative to available theoretical and experimental tabulations of optical constants for many purposes. Nevertheless, selected experimental measurements are important to validate the theory.

Recently K- and L-shell X-ray absorption near-edge structure (XANES) calculations based on the FEFF code have been added for a very large number of materials in the Materials Project database.[23–25] These data have been exploited, e.g., in machine-learning models for the interpretation of XAS data.[23,26] Our aim here is to complement these properties with a more complete set of optical constants for...
all edges from the UV–VIS to hard-X-ray energies, including both near-edge and extended XAS as well as their fine-structure. Thus, the results presented here provide a significant extension, both in the variety of optical-constant spectra, spectral range, and material properties. However, calculations that cover broad spectral ranges with multiple edges necessitate multiple FEFF runs, and hence a more elaborate algorithm for high-throughput calculations. Our approach is based on the development of the Corvus [opcons] workflow, where Corvus is the workflow engine,[27] and opcons is the target property. Note that other workflows have also been developed for ab initio calculation of optical constants,[12,18,19] although these mainly focus on the UV–VIS region, while our calculations include energies up to the hard X-ray regime. In particular, the approach imports the structural and property data from the MP, and then parallelizes and automates the calculations permitting high-throughput calculations of optical constants for materials throughout the MP database. Our procedure for theoretical calculations of optical constants over all edges essentially follows that described in detail by Prange et al.,[22] but has been updated for the FEFF10 code. In addition, refinements for including vibrational disorder via the correlated Debye model using MP data have been added and the calculations for the UV–VIS range have been simplified via a new efficient approximation for the optical dielectric properties. To illustrate the approach calculations have been carried out for all stable elemental solids at standard conditions throughout the periodic table and explicit examples are given for Cu, Ag, and Au, together with comparisons to experimental data. In addition, we show results for a sample compound Al₂O₃ to validate our approximation in the UV–VIS range. The Corvus [opcons] workflow described here is applicable to any material available in the MP database as defined by a given MP identification label (MP-ID), thus making possible routine calculations of optical constants for over 10⁵ structures. By default, the calculations are carried out with lattice vibration effects included at room temperature, while electronic temperature and thermal expansion effects are neglected. However, corrections for thermal expansion, finite temperature, and pressures other than 1 atm can be added using subsequent calculations that reuse some of the previously computed data. The workflow is naturally parallelized and, for typical settings, requires as little as minutes of wall-clock time per material on massively parallel systems.

In the remainder of this work, we describe in detail the extensions and/or theoretical developments used for our high-throughput calculations of optical constants: First, the work here greatly extends the MP,[23,25] which only includes K- and L-edge XANES. In contrast, our calculated spectra cover all absorption edges in a material, as well as the UV–VIS region, and include several optical properties (Sections 2.1 and 2.2) including fine-structure. Second, we have developed and implemented a new, efficient approach for calculations of optical constants in the UV–VIS region. Third, we present a new, high-throughput workflow developed within the Corvus workflow manager that parallelizes the calculations over all edges and optical constants (Section 2.4). Fourth, the approach is now coupled to the MP database with new interface tools (Section 3), and the parallelization has been extensively improved (Section 3.4.5). This makes the workflow easily applicable to any material or subset of materials available in the MP. Unlike the references noted above, the effects of thermal vibrations are now included using an ab initio approach for Debye–Waller factors based on data extracted from the MP database (Section 2.3). Finally, while our original data base in Ref.[22] contained results for 9 elemental solids, we have presented results for 77 elements together with tools and input files that are applicable to any material in the MP database (Section 4.1).

2. Optical constants with Corvus and FEFF10

In general, the optical constants are related to the complex dielectric constant \( \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \) in the long wave-length limit, where \( \omega \) is the frequency of the electron-magnetic field. Since their real and imaginary parts are related by Kramers–Kronig (KK) transformations, they can all be calculated from the imaginary part \( \epsilon_2(\omega) \) (e.g. Fig. 1, Top). In this work, the Corvus [opcons] workflow yields the complex dielectric function \( \epsilon(\omega) \), energy loss function \( L(\omega) \), complex index of refraction \( n(\omega) \), absorption coefficient \( \mu(\omega) \), and reflectivity \( R(\omega) \) defined as follows, in terms of \( \epsilon_2(\omega) \):

\[
\epsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{dt}{t^2} \text{Im}[\epsilon(t)] = \epsilon_1(\omega) + \epsilon_2(\omega)^2
\]

\[
L(\omega) = -\text{Im}[\epsilon^{-1}(\omega)] = \epsilon_2(\omega) / \epsilon_1(\omega)^2 + \epsilon_2(\omega)^2
\]

\[
n(\omega) = n(\omega) + i\kappa(\omega) = \epsilon(\omega)^{1/2}
\]

\[
\mu(\omega) = \omega \epsilon_1(\omega) / \kappa(\omega)
\]

\[
R(\omega) = \frac{[n(\omega) - 1]^2 + \kappa(\omega)^2}{[n(\omega) + 1]^2 + \kappa(\omega)^2},
\]

where \( P \) denotes the principal part of the integral. Note that at high energies dielectric response is weak, and \( \epsilon_2(\omega) \approx L(\omega) \approx 2\omega(\mu(\omega) / c)^2 \). Sum-rules for the dielectric properties provide a qualitative check on the reliability of the results.[28] Related properties, such as the local atomic polarizability \( a(\omega) = (\epsilon(\omega) - 1)/4\pi c^2 \), the Rayleigh forward scattering amplitudes \( f(\omega) = ao(\omega) / r_0 c^2 \) (where \( r_0 = e^2 / mc^2 \) is
the classical radius of the electron, \( e \) is the speed of light and \( n = N/V \) is the atomic number density), electron energy loss spectra (EELS), inelastic mean-free paths, Hamaker constants \( e(\omega) \), etc., can also be determined, but are not yet implemented in the present Corvus \([\text{opcons}]\) workflow. For simplicity here and below we use atomic units \( e \equiv h = m = 1 \) unless otherwise needed for clarity.

The treatment of excitations from the core- and valence-levels generally requires different considerations, so it is convenient to separate the calculations as

\[
e_2 = e_2^{\text{core}} + e_2^{\text{vd}},
\]

where \( e_2^{\text{core}} \) includes the contribution from all levels below a fixed core–valence separation energy \( E_{cv} \), which in FEFF10 is set to \(-40\) eV. Although this separation is approximate due to many-body effects, the contributions from deep core levels (and to a reasonable approximation, semi-core states) respond nearly independently from the valence.

### 2.1. Core level contributions

In this paper calculations of the optical constants are carried out using the real-space Green’s function code FEFF10 and an updated version of the approach described by Prange et al. \([22]\) FEFF uses the same real-space Green’s function formalism to calculate a variety of spectroscopies and related quantities including XAS, XES,RIXS,EELS, and Compton. Thus the calculations of the optical constants use essentially the same ingredients as those for the well-established calculations of XAS, greatly simplifying the workflow design.

Briefly, the RSGF approach in FEFF is used to calculate the contribution to \( e_2(\omega) \) from each occupied level \( i \) (i.e., absorption edge) at each unique site \( a \) in the system. For simplicity, the site index will be usually suppressed below. The core level contribution to \( e_2(\omega) \) from a given site \( a \) consists of a sum of contributions from occupied core levels \( |i| \) \([22]\) for \( \epsilon_i < E_{cv} \) given by

\[
e_2^{\text{core}} = \sum_i \frac{2}{\pi} \text{Im} \left[ \langle \omega | \hat{d}^\dagger \hat{G}(\omega + \epsilon_i) \hat{d} | i \rangle \right] \theta(\omega - \epsilon_F + \epsilon_i),
\]

where \( |i| \) is the core-orbital of interest, \( \epsilon_i \) its binding energy, \( \hat{d} \) is the transition operator, which in most cases is dipole dominated, and \( \hat{G}(\omega) \) is the one-electron Green’s function. Finally, the expression \( \theta(\omega - \epsilon_F + \epsilon_i) \) is a unit step function that turns on when the photon energy \( \omega \) is sufficient to excite the core-electron above the Fermi energy \( \epsilon_F \). If the interaction between the core- and photoelectron levels is ignored, this level of approximation is equivalent to the random phase approximation (RPA).

However, in this work we use the final-state rule approximation to the core hole interaction, in which the photoelectron Green’s function is calculated in the presence of a self-consistently screened core-hole.

One of the advantages of the RSGF approach is the separation of the propagator \( \hat{G}(\omega) \) into contributions from the central absorber at a given site and single or multiple-scattering contributions from neighboring atoms, i.e., \( \hat{G}(\omega) = \hat{G}^{\text{abs}}(\omega) + \hat{G}^{\text{sc}}(\omega) \). As a result the dielectric properties exhibit fine structure analogous to that in XAFS, i.e.,

\[
e_2 = \sum_a e_2^{\text{atomic}}[1 + \chi_a(\omega)],
\]

which we dub “optical fine structure” (OFS) that reflect the local geometrical structure in a material. Typically \( \chi(\omega) \) is of order a few percent within a range of order 100 eV above each edge; however, \( \chi_a(\omega) \) can be large and of order unity in the near-edge regime, within about 10 eV or so of a given edge. Thus the physical interpretation of the OFS is similar to that for EXAFS and XANES, reflecting the local geometrical structure in the vicinity of an absorbing atom. These observations also explain why a local, atomic approximation that neglects the fine structure from neighbor scattering can be a reasonable approximation, accurate to within a few percent for the core contributions to the optical constants, except close to an absorption edge. In order to show the fine structure over the entire energy range of our calculations, it is convenient to calculate the fine-structure defined as \( z_2 = (e_2 - e_2^{\text{atomic}})/e_2^{\text{atomic}} \), which is shown for Cu in Fig. 1 (bottom), together with the full and atomic approximation to \( e_2 \) (top). A corresponding approximation can also be made for any of the other optical constants. When \( e_2^{\text{core}} \approx 1 \), the fine structure in the loss function \( L(\omega) \), absorption \( \alpha \) and imaginary part of the index of refraction \( \kappa \) are similar to that in \( e_2 \). The fine structure in \( \epsilon_i \) is similar, although phase shifted by 90°.

In order to obtain optical constants over a broad energy range from the UV to hard X-rays, two FEFF calculations must be performed for each edge (i.e. each occupied atomic level \( i \)) and each unique atomic site \( a \) in the presence of the corresponding core-hole: (1) In the near edge regime within about 50 eV of a given edge full-multiple-scattering (FMS) calculations must be performed, and (2) at higher energies (the EXAFS regime), the multiple-scattering path expansion (MSP) is used. Once these calculations are performed, the results are interpolated onto a common energy grid and stitched together to yield the spectrum \( e_2(\omega) \) coming from the core-state \( |i| \). The stitching algorithm used is \([22]\)

\[
c_2(k) = \begin{cases} 
\text{FMS}(k); & k < k_0, \\
\text{MSP}(k); & k \geq k_0
\end{cases}
\]

where \( k_0 = 3 \) Å\(^{-1}\), \( k_1 = 4 \) Å\(^{-1}\), and \( k = \sqrt{2(E - E_{edge})/\mu} \) is the photoelectron wave-number. This is illustrated in Fig. 2 for the K-edge spectrum of fcc Cu.

### 2.2. Valence contributions

The contribution from the valence levels is complicated by the extended range and continuum nature of the valence wave functions and the large density of states in the valence region. In the full RSGF approach this requires sums over multiple sites as in Eq. (32) of Ref. \([22]\). Moreover, systems with strong excitonic effects often require treatments beyond the RPA such as TDDFT or the Bethe–Salpeter equation.\([10]\) Several codes are available for these advanced treatments,\([11,12,14,16]\) but they are computationally challenging for high throughput calculations. Nevertheless, neglecting these effects
Fig. 3. Comparison of the experimental [29] and calculated energy loss function for Al₂O₃ (corundum) (top) and Au (gold) (bottom) with the local approximation (see text).

Fig. 4. Comparison of the theoretical absorption μ of Ag with and without the Drude contribution, along with experimental results. [29]

Fig. 5. Comparison of the experimental [29] and theoretical ϵ₂(ω) sum rule n_eff(ω) = ∫₀^∞ dω ϵ₂(ω)/π for Cu. The horizontal dashed line indicates the ideal theoretical limit (Z = 29).

Computational Materials Science 201 (2022) 110904

J.J. Kas et al.

Consequently, in this work we use a local approximation at the absorption site to calculate the contribution from the valence electrons. In addition, we replace the valence wavefunctions with the Dirac–Fock atomic eigenfunctions, which allows us to write Eq. (32) of Ref. [22] as an integral over the local valence density of states

\[
\epsilon_{\text{val}}^2(\omega) = \sum_{\alpha} \int_{F_{\text{cv}}} \frac{d\omega}{\pi} \rho_{\alpha}(\omega') \epsilon_{\alpha}^2(\omega - \Delta - \omega'),
\]

where \(\epsilon_{\alpha}^2(\omega)\) is the local atomic spectrum at a given site \(\alpha\) corresponding to atomic state \(\alpha\), and \(\rho = \rho/N\) is the normalized, angular momentum projected density of states (LDOS) with symmetry equal to that of the state \(\alpha\), and \(\Delta = E_{\text{top}} - E_{\text{edge}}\) is a shift to properly position the valence spectra, where \(E_{\text{top}}\) is the energy at the top of the gap, if one exists, and is equal to the Fermi energy otherwise. As shown for the energy loss of Al₂O₃ (top) and Au (bottom) in Fig. 3, which provide good tests for this procedure we find that the approximation is reasonably accurate when excitonic effects are small. We have found that our local approximation in Eq. (10) is significantly better than a pure atomic approximation alone. One can also define an optical fine structure \(\chi_{\text{val}}\) for the valence contributions \(\epsilon_{\text{val}}^2\), although its magnitude is typically large and of order unity (see Fig. 1), as in core-level XANES, over the optical energy range. For this reason, FMS and the local projected densities of states are needed to evaluate Eq. (10). In addition, the physical interpretation of \(\chi_{\text{val}}\) is akin to a sum of terms proportional to the joint projected density of states. [22] Even so, the valence fine structure for Cu is rather similar to the K-edge fine structure, as shown in the lower panel of Fig. 1. This makes sense, since the \(d\) - to \(p\)-state transitions dominate in the optical region, and the DOS is dominated by a single, relatively sharp occupied \(d\)-band.

Finally, the total \(\epsilon_{\alpha}(\omega)\) is obtained from a double sum over edges \(\alpha\) and unique sites in the system,

\[
\epsilon_{\alpha}(\omega) = \sum_{\alpha} n_{\alpha} \epsilon_{\alpha}^2(\omega),
\]

where \(n_{\alpha}\) denotes a unique site in the unit cell, and \(n_{\alpha} = N_{\alpha}/V\) is the corresponding number density.

2.3. Debye–Waller factors and Drude corrections

A number of other considerations are generally important in calculations of optical spectra over broad energy ranges. For example, effects of thermal vibrations are temperature dependent and strongly damp the fine-structure in the EXAFS regime. For the systems treated here we have approximated the multiple-scattering path dependent DW factors \(\exp(-2\sigma^2k^2)\) using the default correlated Debye model in FEFF10. The Debye temperature parameter can be estimated [30] from the bulk and shear elastic moduli data available in the MP database.

Drude corrections in metals can be added phenomenologically by an additional ad hoc contribution to the limiting low frequency behavior
of \( e_2(\omega) \) given by

\[
e_2(\omega) = \frac{4 n^2 \pi}{\omega} \frac{\rho^2}{\rho_0} \quad (12)
\]

where \( \sigma \) is the conductivity, \( \omega_p^2 = 4 n e^2 / m \), \( n \) is the mean conduction electron density, and \( r \) the relaxation time, which is typically of order 0.1–4.0 femtosecond at room temperature. [31] Fig. 4 shows a comparison of the absorption \( \mu \) of Ag with and without the Drude contribution, along with experiment. [29]

Thermal expansion can also be treated by calculating the expansion parameter via DFT, [32] or using parameters from the literature. Additional broadening due to electron-phonon interactions, impurities, and other mechanisms can also be important. While neglected by default, these effects can be added post facto by a Lorentzian broadening of the spectra.

Once \( e_2(\omega) \) is obtained by summing both core and valence contributions over all sites, the real part of the dielectric function is formed via a KK-transform, as in Eq. (1). A check on the completeness of the contributions over all sites, the real part of the dielectric function is formed via a KK-transform, as in Eq. (1). A check on the completeness of the calculations is provided by the optical constant sum-rules \( n_{\text{eff}}(\omega) = \int_0^\infty d\omega e_2(\omega)/\pi \), [28] as illustrated in Fig. 5.

2.4. Corvus [opcons] workflow

The Corvus [opcons] workflow is built on the concept of recursive workflow generation, wherein Corvus generates and runs a workflow with the target property [opcons], and the optical constants workflow [opcons] in turn generates and runs a [XANES] workflow for each required FEFF10 calculation. The workflow tool is described in detail together with various examples in the Corvus reference. [27] This approach determines the input files from the data in the MP database, after which all of the individual FEFF10 calculations are set up and run through the Corvus workflow manager. The Corvus [opcons] workflow then carries out the following steps: i) calculating the \( e_2(\omega) \) for a given edge; ii) applying the stitching algorithm to combine the near-edge full multiple scattering (FMS) and multiple-scattering path (MSP) calculations; iii) convolving with the density of states (Eq. (10)); iv) performing the KK-transform to obtain \( e_2 \); v) adding the Drude contribution; and vi) calculating the other optical constants following the relations in Eqs. (1). In order to facilitate automated calculations, Corvus handles the creation of FEFF10 input files from minimal user input, executes FEFF10, and translates the output. Additionally, the Corvus [opcons] workflow is designed to optimize the calculations, for example re-using output from the XANES results within the EXAFS calculations to bypass the self-consistency loop. Fig. 6 shows a schematic of the Corvus [opcons] workflow for producing the optical constants.

3. Materials Project interface tools

3.1. Global structure of Corvus [opcons] simulations

MP optical constants simulations are set up in two steps: (1) The crv_mp_mk_set command reads the command line inputs, creates a request to the MP, downloads all the structures available matching the query, generates a set of materials to run and calculates the total number of edges in the set. (2) The crv_mp_run_set command runs all the calculations required for the set, distributed in serial or parallel mode according to the resources provided. In the following section we describe their usage in detail.

3.2. Usage: crv_mp_mk_set

The basic input of a typical Corvus [opcons] calculation is set up using the crv_mp_mk_set command:

```
crv_mp_mk_set [OPTIONS] Set_Name
```

where “Set_Name” is a text label that will be used throughout to refer to the set of materials. This label is used to name the directory where the calculations will be done and the results stored. crv_mp_mk_set can be used to query the MP database in three different ways (see options below): (1) Query an arbitrary class of materials selected by the formula, (2) automatically query some or all of the elemental solids, for which the tools have an internal database of MP-IDs, and finally, (3) an individual material with a given MP-ID. The full set of options can be obtained with “crv_mp_mk_set --h”. Here we focus on some of the most computationally relevant ones.
3.2.1. Required options

\texttt{--k APIKEY} API key used to interact with the MP REST interface

This option is required for the command to be able to interact with the MP database. See Section 3.4.4 for details.

3.2.2. System selection options

\texttt{--f FORMULA} Use chemical formula \texttt{FORMULA} to define a set of materials.

\texttt{--pt} Create a set for all the solid elements in the periodic table using the structure available in the Materials Project which is the most stable phase in standard conditions (25°C and 1 atm).

\texttt{--ptel PT_ELEMS} Same as \texttt{--pt}, but only for a list of specific elements

\texttt{--mpid MP-ID} Select the individual system with Materials Project identification label MP-ID (Default: “mp-30”)

These options are mutually exclusive. If none of them are present the command generates input for a test run on Cu, a traditional choice since FEFF was first deployed.

3.2.3. Selection fine-tuning options

\texttt{--mxpt MXNAPT} Maximum atomic number to use while creating the periodic table with \texttt{--pt} (Default: 99)

\texttt{--enpct EN_PCT} Keep only \texttt{EN_PCT}% of lowest energy systems (Default: 100%)

\texttt{--nedg MXNEDGES} Keep only systems with fewer than \texttt{MXNEDGES} edges (Default: 250)

These options help trim the raw selection generated by the system selection options.

3.2.4. Auxiliary options

\texttt{--nSCF NSCF} Number of neighbor shells to use in SCF (Default: 1)

\texttt{--nFMS NFMS} Number of neighbor shells to use in FMS (Default: 2)

\texttt{--symprec SYM_PREC} Symmetry precision (in Å) used by symmetrizer (Default: 0.01 Å)

These options control the setup of the optical constants calculations by defining how many shells to use in the SCF and FMS steps, as well as the precision of the symmetrization procedure used to reduce the number of unique sites. The shell selection is performed using the Jenks natural breaks classification method as implemented in the jenks.py Python module. Additionally, vibrational broadening can also be controlled by requesting that a correlated Debye model be used.

3.2.5. Calculation control options

\texttt{--dr} Dry run, collect and display information without actually creating a set

\texttt{--v} Make the command output more verbose

3.2.6. Examples

A typical invocation of \texttt{crv_mp_mk_set} is as follows

\texttt{crv_mp_mk_set --k [APIKEY] --f "FeO" --enpct 20 --nedg 250 --nSCF 2 --nFMS 4 --v --dw --temp 298.0 IronOxides}
creates a set of 3 systems (Fig. 7) after screening for energy, symmetry and total number of edges. The command also requests that the Debye temperature be estimated, and that the calculation be done at room temperature. Inside the set directory, the structures are organized by reduced formula and MP-ID. A typical Corvus [opcons] directory created with crv_mp_mk_set contains, for each material, a template Corvus [opcons] input (Fig. 8) and a few auxiliary files with structural information. A set for the Li, Be and B elemental solids can be generated using:

```
crv_mp_mk_set --k [APIKEY] --v --ptel 'Li,Be,B'
```

while a single compound (one of the forms of Mg$_3$N, in this case) can be set up with:

```
crv_mp_mk_set --k [APIKEY] --v --mpid mp-1185783
```

More examples can be found in Ref. [37].

### 3.3. Usage: crv_mp_run_set

After a set is created, the actual optical constants can be computed with the crv_mp_run_set command:

```
crv_mp_run_set [OPTIONS] Set_Name
```

where “Set_Name” is again the label for the set to run. As for “crv_mp_mk_set”, the full set of options can be obtained with “crv_mp_run_set --h”, but here we focus on some of the most computationally relevant ones.

#### 3.3.1. Options to control the number of processors

```
--np NP_TOT Total number of processors to be used in the run (Default: 1)
--ppn PPN Number of processors per node (Default: 1)
--nn NNODES Number of nodes with PPN processors per node to be used in the run (Default: 1)
```

If more than one of these options are specified, the command will choose max(NP_TOT, PPN*NNODES) as the total number of processors to use.

#### 3.3.2. Options to estimate computational cost

```
--t Estimate total runtime up to NP_TOT processors
--sf SER_FRAC Fraction of serial code to estimate parallel runtimes (Default: 0.5)
```

If the “--t” runtime option is present, instead of running the set, crv_mp_run_set prints out estimates of the cost of the calculation from 1 to NP_TOT processors relative to the cost of a single edge calculations performed in serial mode.

#### 3.3.3. Auxiliary options

```
--v Generate verbose output (timings, etc.)
--dr Dry run: Do everything but actually run
```

#### 3.3.4. Examples

A typical instance of crv_mp_run_set to run the set IronOxides created in the previous example (Fig. 7) is as follows:

```
crv_mp_run_set --ppn 64 --nn 45 --v IronOxides
```

or

```
crv_mp_run_set --np 2880 --v IronOxides
```

Given that the set contains 45 edges, for maximum efficiency we assign one node with 64 processors to each edge, or a total of 2880 processors, thus effectively running all materials simultaneously. FEFF10 then computes each individual edge parallelizing over the energy grid with 64 processors.
3.4. Requirements

3.4.1. Code distribution

Both Corvus [38] and FEFF10[39] are open source and are available on GitHub. Detailed installation instructions can be found in Ref. [37].

3.4.2. Corvus requirements

The Corvus workflow manager is implemented in Python 3. In addition, it requires the Numpy [40] and Scipy [41] packages, as well as a few other packages depending on the required functionality. The Corvus workflows that are possible will be determined by the specific external software packages installed on the system. In this case, the optical constants workflow only requires the appropriate version of FEFF10.

3.4.3. FEFF10 requirements

To run efficiently, a parallel execution is important. Thus, the FEFF code requires a Fortran90 compiler with some flavor of MPI-2 for compilation. FEFF has been tested with a wide variety of compilers and MPI-2 implementations.

3.4.4. Corvus [opcons] specific requirements

The crv_mp_mk_set and crv_mp_run_set tools are also implemented in Python 3 and, in addition to the Corvus requirements, they need the pymatgen package.[42] In order to use the MPRes method in pymatgen to access the Materials Project database directly, users need to have an MP account and a valid API key. For the work presented in this paper, we used pymatgen v2022.0.9, and MP v2019.05.

3.4.5. Performance analysis

The CPU time for a given material scales linearly with the number of edges and unique atom positions in a unit cell and, depending on the SCF and FMS settings, typically takes between a few minutes and 1/2 hr. Thus, when the available number of processors is equal or greater than the total number of edges, linear parallelization is simply achieved by assigning a processor or more to each edge, up to about 32–64 processors. More processors per edge becomes less efficient at the level of FEFF calculations. In other cases, and for high-throughput runs for many different materials, the wall-clock time depends on how the set is structured (e.g., how many edges per material in the set) and how the calculations are distributed in the workflow. In that case, there are no simple rules to determine the optimal parallel distribution. To help with this issue, the crv_mp_run_set tool includes an option (“-t”) to estimate how well a given system of interest will parallelize for a certain range of number of processors (“-np”) relative to the fully serial calculation.

4. Example applications

4.1. Optical constants of the elements

As an illustration, we have carried out calculations for the most stable structure (at room temperature and nominally 1 atm) of each of the elemental solids listed in the MP with data imported for a given MP-ID. Some of the most important factors limiting the quality of the results are the SCF and FMS radii used in the simulations. The results can be obtained online at http://feff.phys.washington.edu/optical-constants/ [36]. Fig. 9 (top) shows a comparison of the results using an increasing number of near-neighbor shells for $\epsilon_2$ of copper. We find that 3 and 6 shells in the SCF and FMS modules, respectively, produce converged results above 10–20 eV.

Overall, the results are in reasonable agreement with experimental tabulations,[29] and illustrate that, except close to an edge or in the optical region, $\epsilon_2$ can be approximated reasonably by the atomic approximation, ignoring the fine structure. For example, Fig. 9 shows a comparison to experiment [29] of Cu $\epsilon_2$ (top) and real index of refraction Au (bottom) computed with converged SCF and FMS radii and including the density of states convolution in Eq. (10). These results show that Eq. (10) is only semi-quantitative in the visible range. Fig. 10 shows a periodic table of the elements and associated MP-IDs that are currently available and can be freely viewed and downloaded at http://feff.phys.washington.edu/optical-constants/ [36].

4.2. Optical constants of the Al$_2$O$_3$ materials in the MP

In addition to the elemental solids, we have also computed several aluminum oxides. For example, Fig. 3 shows a comparison to experiment [29] of the energy loss for the full energy range for the corundum form of Al$_2$O$_3$. In order to demonstrate the set capabilities of the Corvus [opcons] workflow, we calculated results for a sub-set of those listed in the MP with formula Al$_2$O$_3$. The results for the loss function up to the Al L-edges are shown in the main panel of Fig. 11, while the inset highlights the O K-edge region. The differences in the near edge structure, as well as those in the optical reflect the different symmetries present in the system. For example, there is a mixture of Al sites in octahedral and tetrahedral symmetry in the first two materials, which are both monoclinic, while the last material is trigonal, and contains only Al in octahedral symmetry. Similarly, the oxygen sites in the first two systems are a mixture of sites in tetrahedral and trigonal symmetry. These changes in symmetry lead to differences in electronic structure, which are directly related to the features seen in the near edge spectra.

5. Conclusions

We have presented an optical constants (“opcons”) workflow built with the Python-based Corvus workflow manager for high-throughput simulations of full spectrum optical constants from the UV–VIS to hard X-ray wavelengths for materials defined in the MP database. The calculations are based on the efficient RSGF code FEFF10 and an approximate treatment of the valence contributions using structural data from the MP database specified by a unique MP materials ID. As for the XAS, the results can be represented in terms of an atomic-like background and an optical fine-structure (OFS) analogous to EXAFS. Except close to an edge where the fine-structure is substantial, the background dominates and can be calculated efficiently over the full spectrum. The fine-structure is edge-specific and as in EXAFS, reflects the structure of the environment of a given absorber in the material. The calculations are set up automatically using Corvus auxiliary tools.
and the workflow parallelizes the FEFF computations over edges and sites with an optimal distribution of computational resources. Representative results show that the workflow produces accurate optical properties over a broad range of energies. Although this algorithm includes mean-free paths and Debye–Waller factors, multiplet splitting, excitonic effects, and long-range contributions to the valence spectra are currently neglected. Consequently, the present results may only be semi-quantitative in the UV–VIS regime.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

We have computed the optical properties for all elemental solids (stable at standard conditions) in the periodic table for which structures are available in the Materials Project database, using the approach in this work. The data is available through an online periodic table tree/convert-to-3. The data is also available at http://feff.phys.washington.edu/optical-constants/installation.html.

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