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The *OCEAN* suite: core excitations

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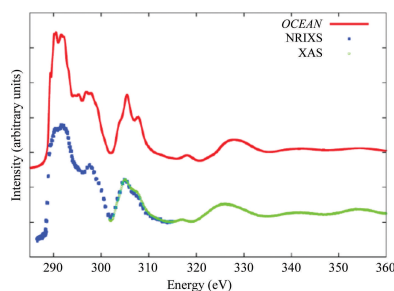
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This chapter is a high-level description of a suite of programs denoted by the acronym *OCEAN* (*Obtaining Core Excitation spectra Ab initio and with NBSE*), where NBSE denotes the underlying NIST Bethe–Salpeter equation program. The chapter discusses the main computational steps, physical approximations and scope of user input, and presents various examples of calculated results. Likely improvements and extensions, and how to access *OCEAN* and its documentation, are also discussed.

1. Introduction

OCEAN is a first-principles, pseudopotential-based tool for modelling core-level near-edge spectroscopies. Multiple scattering, another type of first-principles technique, is efficacious far above edges, spanning energy ranges that reveal structural information. Further, full-potential versions can also describe unoccupied electron states completely near X-ray edges. Pseudopotential-based tools such as *OCEAN* can also claim such completeness because all-electron counterparts to pseudized wavefunctions can be found as needed. Theoretical treatments of near-edge spectra also range from independent-electron types [for example density-functional theory (DFT)], which reflect density-of-states effects, to many-electron methods (for example configuration interaction), which include local correlation. *OCEAN* solves a form of the Bethe–Salpeter equation (BSE), *i.e.* an interacting electron-plus-hole picture of the core-excitation process, retaining some advantages of independent-electron methods and including some correlation effects. *OCEAN* generates core-excitation spectra from the outputs of plane-wave pseudopotential calculations and solves the electron–core-hole pair equation of motion (EOM). *OCEAN* can treat valence excitations (not discussed here) and core excitations. Valence excitations also matter in resonant inelastic X-ray scattering (RIXS), which has an electron–valence-hole pair final state, versus the electron–core-hole pair X-ray absorption spectroscopy (XAS) final state and RIXS intermediate state.

Section 2 discusses *OCEAN*'s methodology. A large body of work has been performed using *OCEAN* and its predecessors. Section 3 gives examples of results. These include low-*Z* near-edge spectra, multiplet spectra in *d*⁰ transition-metal (TM) compounds, spectra featuring electric dipole and quadrupole transitions in TM oxides, O 1s spectra for ice and liquid water, and results for nonresonant inelastic X-ray scattering (NRIXS), also known as X-ray Raman scattering for core excitations), a complement of electron energy-loss spectroscopy (EELS) for large momentum transfers. Section 4 discusses future devel-



opments and foreseen limitations of *OCEAN*. One growth area is including effects of nuclear motions on spectra. This can include Franck–Condon and Jahn–Teller effects, but thermal motion also matters, especially in low-*Z* compounds. Section 5 indicates how to access *OCEAN*, which continues to undergo updates, improvements and extensions, and is open-source. Others are encouraged to contact the authors regarding its use.

2. Overall flow of calculations

Calculations begin with a ground-state self-consistent-field DFT calculation (Hohenberg & Kohn, 1964; Kohn & Sham, 1965). *OCEAN* next computes random-phase approximation (RPA) or adiabatic local-density approximation (ALDA) screening of a core hole, requiring input of the macroscopic dielectric constant ϵ_∞ . Self-energy corrections may be applied to the DFT band structure. *OCEAN* assumes that excitation spectra are found using the BSE as an effective EOM for the electron–hole pair. Strongly correlated systems could be treated poorly within such a simple picture. The effective Hamiltonian includes the screened potential of the core hole, including its central and multipole parts (which account for exchange and multiplet effects), spin, core-hole orbital angular momentum and core-level spin–orbit interactions. An atomic program within *OCEAN* (Shirley, 1991) facilitates treatment of atomic effects and reconstruction of all-electron wavefunctions. Knowledge of self-energy corrections, whether full (Soininen *et al.*, 2003), model (Fister *et al.*, 2011) or on the level of the multipole self-energy methodology (Kas *et al.*, 2007), can renormalize the band structure and introduce lifetime broadening and satellite features into excitation spectra in post-processing steps applied to output. Thus, *OCEAN*’s calculations entail many effects: core-level electronic structure, a DFT description of the valence-level electronic structure, the screened core-hole potential, self-energy effects, the effective EOM of the electron–hole pair, periodicity effects (real or artificial) and final-state valence-hole effects in RIXS. Below we summarize these aspects, emphasizing the main equations describing the physics.

2.1. Isolated-atom electronic structure

The atomic electronic structure program performs all-electron and norm-conserving pseudopotential calculations. Other options include relativistic versus nonrelativistic calculations and Hartree–Fock versus LDA calculations. In pseudopotential calculations, electron partial waves with low angular momentum *l*, up to *l* = 2 or *l* = 3, experience a different potential in the core region and are solutions of the radial Schrödinger equation with accurate scattering properties in chemically relevant energy ranges. Because *OCEAN* works within a pseudopotential context, users must provide pseudopotentials in the form $V_l(r)$ to the atomic program, which can calculate corresponding pseudized and all-electron partial waves at any energy.

All-electron (ae) wavefunctions are reconstructed from pseudized (ps) wavefunctions using ‘optimized projector

functions’ (OPFs), which are described elsewhere (Shirley, 2004) and inspired by the projector-augmented-wave method (Blöchl, 1994). The atomic program finds a few (about four) normalized OPFs that best span partial waves within a user-specified energy range and cutoff radius R_c that should enclose pseudized regions and pertinent core orbitals. Spherical harmonics times ae and ps projector functions, $\{f_{ae}(v, l, r)\}$ and $\{f_{ps}(v, l, r)\}$, form a basis for band states inside $r < R_c$. For a site at the origin, ae and ps band states and coefficients for basis functions are related by

$$\left. \begin{aligned} C_{nk}(v, l, m) &= \int_0^{R_c} dr r^2 \int d\theta \sin \theta \int d\varphi Y_{lm}^*(\theta, \varphi) f_{ps}(v, l, r) \\ &\quad \times \psi_{nk}^{ps}(r, \theta, \varphi) \\ \psi_{nk}^{ae}(r, \theta, \varphi) &= \sum_l \sum_m \sum_v C_{nk}(v, l, m) f_{ae}(v, l, r) Y_{lm}(\theta, \varphi) \end{aligned} \right\} \quad (1)$$

Reconstruction is performed when calculating transition-matrix elements, the electron–core-hole interaction and (as of version 2.0) calculating core-hole screening, the latter typically increasing screening near the nucleus, presumably because the reintroduction of radial nodes also reintroduces radial antinodes.

2.2. Density-functional theory wavefunctions

OCEAN obtains ground-state electronic structure and related quantities by using a plane-wave/pseudopotential program [for example *ABINIT* (Gonze *et al.*, 2009) or *Quantum ESPRESSO* (Giannozzi *et al.*, 2009)]. Bloch states are calculated on a regular grid throughout the full Brillouin zone. The grid can be displaced to preclude degeneracies among **k** points and accelerate convergence versus grid density.

2.3. Core-hole potential

The largest part of the electron–core-hole interaction is the spherically symmetrical central potential. It is important to screen the central potential accurately. This differs from the valence-hole case, where a model dielectric function (Levine & Louie, 1982) with local field effects (Hybertsen & Louie, 1988) suffices. Obviously, the atomic core environment is very different from a nearly free-electron gas. *OCEAN* includes screening by the excited site’s core electrons in the atomic program and by valence electrons *in situ*. If the Green’s function is

$$G(\mathbf{x}, \mathbf{x}'; E) = \sum_{n, \mathbf{k}} \frac{\psi_{n\mathbf{k}}(\mathbf{x}) \psi_{n\mathbf{k}}^*(\mathbf{x}')}{E - E_{n\mathbf{k}} \pm i\eta}, \quad (2)$$

where $E_{n\mathbf{k}}$ is a band energy and $\pm i\eta$ reflects state occupancy, then the bare and full ALDA polarization functions are

$$\left. \begin{aligned} \chi^0(\mathbf{x}, \mathbf{x}') &= 2 \int_{-\infty}^{+\infty} \frac{dt}{2\pi} [G(\mathbf{x}, \mathbf{x}'; E_F + it)]^2 \\ \chi(\mathbf{x}, \mathbf{x}') &= \chi^0(\mathbf{x}, \mathbf{x}') + \int d^3\mathbf{x}'' \int d^3\mathbf{x}''' \chi^0(\mathbf{x}, \mathbf{x}'') [v(\mathbf{x}'', \mathbf{x}''') \\ &\quad + K_{xc}(\mathbf{x}'') \delta^3(\mathbf{x}'' - \mathbf{x}''')] \chi(\mathbf{x}''', \mathbf{x}') \end{aligned} \right\} \quad (3)$$

Here $\mathbf{x}$ and $\mathbf{x}'$ are a real-space coordinate, K_{xc} is a local vertex correction and E_F is the Fermi energy. The RPA omits K_{xc} , retaining only the Coulomb interaction v . The function χ screens the core hole (already screened by core electrons) plus a sphere of charge $-e$ with radius ~ 0.2 nm. A model screens a compensating sphere of charge $+e$. Quadrature facilitates radial and angular integrations (Shirley, 2006).

Multipole interactions lead to multiplet effects and a repulsive exchange part. Slater F_k and G_k integrals are calculated in the atomic program for all-electron OPFs. A scaling-factor parameter can be affixed, for example 0.83 improves the results in first-row TM systems. It may be possible to compute solid-state (although not atomic) contributions to this factor using screening calculations within *OCEAN*.

2.4. Self-energy effects

DFT band gaps and widths differ from those revealed using photoemission and inverse photoemission, which is a quite systematic effect (Shirley, 1998a). *OCEAN* allows one to amend the band structure suitably, typically by relating quasiparticle (qp) and DFT electron-level energies according to the form

$$\left. \begin{aligned} E_{qp} &= E_{DFT} + \Delta_v + s_v(E_{DFT} - E_F) \\ E_{qp} &= E_{DFT} + \Delta_c + s_c(E_{DFT} - E_F) \end{aligned} \right\} \quad (4)$$

for occupied (v) and unoccupied (c) states, respectively, allowing rigid shifts Δ_v , Δ_c and stretches s_v , s_c of bands. The actual band shifts and stretches can be measured or calculated (Hedin, 1999). State-dependent and energy-dependent self-energy corrections can also be incorporated into an *OCEAN* calculation (Vinson & Rehr, 2012).

2.5. Electron–core-hole two-particle EOM

OCEAN considers electron–hole pair states of the form

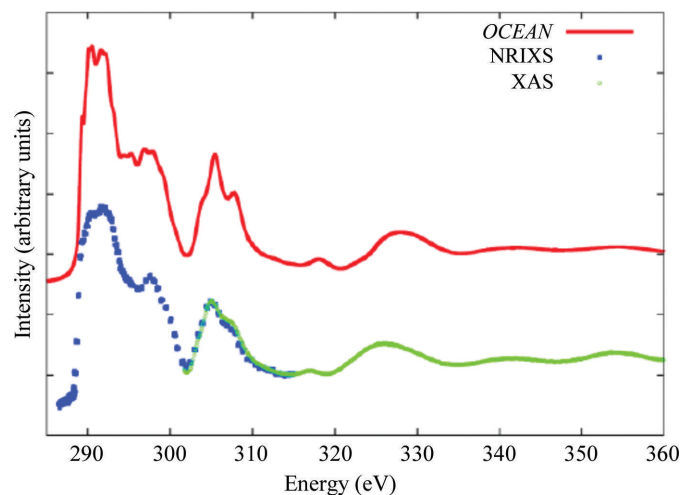


Figure 1
C 1s near-edge spectrum of diamond as calculated by *OCEAN* (top curve, blue) and as measured using NRIXS (bottom, blue points; Galambosi *et al.*, 2007) and XAS (bottom, solid green line; B. N. Ravel, private communication). As discussed in the text, NRIXS should have fewer artefact-related effects than XAS, especially in the near-edge region.

$$|N, L, m_h, \sigma_h; n, \mathbf{k}, \sigma_e\rangle = a_{n\mathbf{k}, \sigma_e}^\dagger a_{NLm_h \sigma_h} |\Phi_0\rangle. \quad (5)$$

The operators act on the ground state to create the electron–hole pair. N , L , m_h and σ_h are standard quantum numbers for an atomic core level, while n , $\mathbf{k}$ and σ_e denote electron band index, crystal momentum and spin, respectively. By including core orbital angular momentum and all spin momentum degrees of freedom, multiplet and spin–orbit effects are included naturally. Thus, multiplet spectra can be computed for nominally d^0 systems such as Ti^{4+} in rutile, because there is no other electron in the $3d$ subshell. Also, DFT includes the ligand or crystal field automatically, unlike model multiplet calculations.

A spectrum can be computed using Fermi’s golden rule. A site contributes to the imaginary part of the dielectric function at X-ray wavevector $\mathbf{q}$ and energy ω according to

$$\delta\epsilon_2(\mathbf{q}, \omega) = \frac{4\pi}{\Omega} \Im \left\langle \Phi_0 \left| O^\dagger \frac{1}{\omega - H_{\text{BSE}} + i\eta} O \right| \Phi_0 \right\rangle, \quad (6)$$

where Ω is the unit-cell volume. In XAS the operator that acts on a core electron is

$$O = \mathbf{e} \cdot \mathbf{r} + \frac{i}{2} (\mathbf{e} \cdot \mathbf{r})(\mathbf{q} \cdot \mathbf{r}) + \dots \quad (7)$$

The electron coordinate $\mathbf{r}$ is relative to the nucleus, while $\mathbf{e}$ and $\mathbf{q}$ are the X-ray electric field and momentum. For NRIXS and EELS, one has $O \propto \exp(i\mathbf{Q} \cdot \mathbf{r})$ for momentum transfer $\mathbf{Q}$, and the spectrum is related to the dynamic structure factor. Spectra can be evaluated efficiently within the Haydock recursion method (Vinson *et al.*, 2011). Treating RIXS requires evaluating

$$|\Phi(\omega)\rangle = (\omega - H_{\text{BSE}} + i\eta)^{-1} O |\Phi_0\rangle, \quad (8)$$

such as by using the generalized minimal residual (GMRES) approach (Saad & Schultz, 1986). The subsequent electron–valence-hole pair can also be treated with *OCEAN* (Shirley *et al.*, 2001).

The effective Hamiltonian is $H_{\text{BSE}} = H_e + H_h + H_{\text{s.o.}} + H_C + H_M$. H_e includes the electron-band energy, H_h the average core-level binding energy, $H_{\text{s.o.}}$ core-level spin–orbit coupling, H_C the central potential of the core hole and H_M multipolar terms. The action of multipolar terms and spatially varying parts of H_C inside the OPF cutoff radius are performed within the OPF basis. The remainder of H_C is smooth, and its action is evaluated on a real-space grid using fast Fourier transform techniques. All of the above allow fast evaluation of H_{BSE} acting on an arbitrary state.

2.6. Periodicity, treatment of molecular systems and liquids

OCEAN employs periodic boundary conditions. Systems lacking translational invariance (for example molecules, liquids and surfaces) require the use of a large periodic box, possibly with multiple atomic configurations (Vinson *et al.*, 2012; Niskanen *et al.*, 2017; Petitgirard *et al.*, 2019; Spiekermann *et al.*, 2019). Additionally, nominally periodic systems lose periodicity owing to thermal or zero-point motion (Vinson *et al.*, 2014). However, judicious sampling of atomic

displacements can render an accurate averaging of spectra with only a few calculations.

3. Sample OCEAN results

OCEAN has been used to calculate near-edge core-excitation spectra in a wide variety of systems, and RIXS spectra in a few cases. Here, we present results for several different systems and compare them with experimental results to illustrate the reasonably expected accuracy of computed spectra.

3.1. Calculations in simple systems

Diamond is a simple system offering high-quality spectra. It is easy to calculate spectra up to about 100 eV above the C 1s edge including only 60 conduction bands with good Brillouin-zone sampling. The most reliable spectroscopies at the C 1s near edge are NRIXS and EELS, followed by XAS, which might rely on electron-yield or fluorescence-yield signatures of absorption and suffer from instrument carbon build-up. Fig. 1 shows near-edge spectra obtained using OCEAN, NRIXS (Galambosi *et al.*, 2007) and, above 315 eV, XAS (B. N. Ravel, private communication). Despite the prediction of a low-lying *s*-symmetry core-hole exciton (Jackson & Pederson, 1991), EELS (Batson, 1993), NRIXS (Galambosi *et al.*, 2007) and calculations using the predecessor of OCEAN (Shirley, 1998*b*) suggested otherwise.

3.2. Multiplet calculations

Vinson *et al.* (2011) and Vinson & Rehr (2012) consider a wide range of 3*d* TM systems at the 2*p* edge of the TM species. SrTiO₃ and CaF₂ serve as standard systems and allow comparison to all-electron core BSE results (Laskowski & Blaha, 2010; Gulans *et al.*, 2014). Vinson and Rehr also

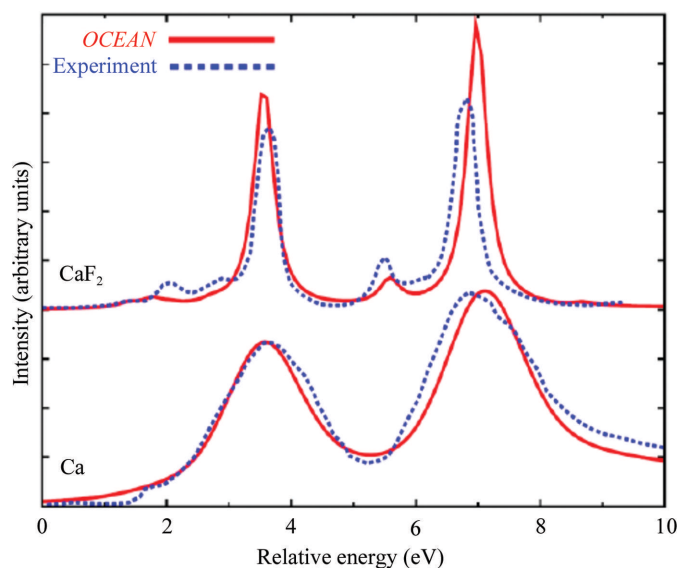


Figure 2

The near-edge structure at the Ca 2*p* edge in metallic calcium and calcium fluoride. Calculations are shown by the red solid curve, and measurements are shown by blue dashed curves for calcium fluoride (de Groot *et al.*, 1990) and metallic calcium (Fink *et al.*, 1985).

consider other systems, including metallic calcium. Results are shown in Fig. 2.

3.3. Electric dipole plus quadrupole calculations

Spectra of TM compounds can be of interest at a TM 1*s* pre-edge. OCEAN can treat such systems, which can feature dipole-allowed 1*s*→*np* and quadrupole-allowed 1*s*→*md* transitions, such as in rutile (Shirley, 2004). Perovskites such as SrTiO₃ and PbTiO₃ are of interest (Woicik *et al.*, 2007) because 3*d*–4*p* mixing causes *E_g*-symmetry Ti 3*d* states to acquire partial 4*p* character, giving rise to strong absorption cross sections that help to reveal local atomic geometries.

3.4. Complex systems

Vinson *et al.* (2012) modelled the O 1*s* spectra of liquid water and two ice phases as presented in Fig. 3. Calculations for the liquid sample multiple molecular configurations. Care is required to estimate core-level shifts for inequivalent sites, such as oxygen sites in water, as discussed elsewhere (Pasquarello *et al.*, 1996).

3.5. Resonant inelastic X-ray scattering

Direct RIXS calculations are more involved because they entail core-excited and valence-excited state calculations. Diamond was an early subject of RIXS measurements (Ma *et al.*, 1992; Carlisle *et al.*, 1999) and calculations (Shirley, 2000). OCEAN is able to capture several of the changes in X-ray emission for incident energy from 5 to 25 eV above the C 1*s* edge.

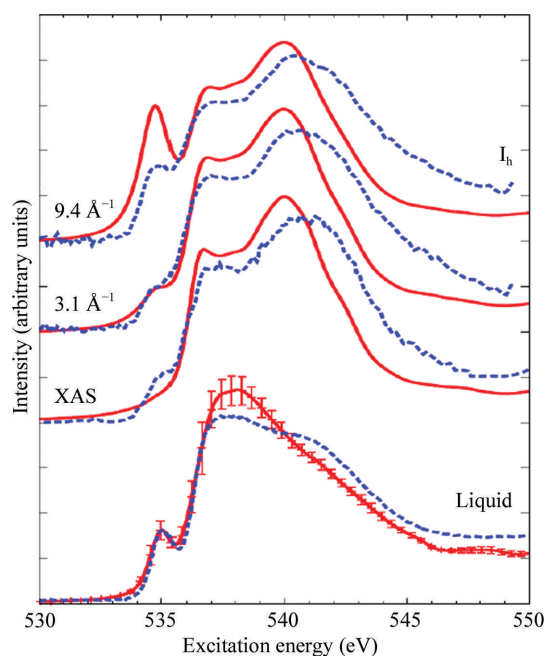


Figure 3

O 1*s* near-edge spectra in the I_h phase of ice and liquid water. Calculated results are shown by red solid lines. Measured results (blue dashed lines) were obtained using NRIXS (Pylkkänen *et al.*, 2010) and XAS (Tse *et al.*, 2008) in ice and scanning transmission X-ray microscopy in liquid water (Nilsson *et al.*, 2010).

3.6. Momentum-dependent results

LiF demonstrates the ability of NRIXS to probe excitations of different symmetries. A small peak below the dipole-allowed F 1s edge was attributed to a vibrationally allowed, *s*-symmetry core-hole exciton. *OCEAN* and NRIXS (Hämäläinen *et al.*, 2002; Vinson *et al.*, 2011) at various momentum transfers confirmed this, as shown in Fig. 4. Finite-temperature molecular-dynamics simulations provide snapshots of atomic positions that make the pre-edge feature optically allowed (Pascal *et al.*, 2014). Others (Tse *et al.*, 2014) have also compared measured and calculated NRIXS of pressurized silicon to study the pressure-induced insulator-to-metal transition in this material.

4. Future directions

Working only within a single electron–hole pair picture undermines *OCEAN*'s treatment of strongly correlated systems, although its output might guide the development of model Hamiltonians for such systems. Larger supercells can lessen the effects of artificially imposed periodicity. Many effects of atomic displacements and multi-electron excitations are becoming treatable in a statistically averaged sense by combining the results of different atomic configurations and/or post-processing results.

4.1. Vibrational effects

Debye–Waller (DW) effects are ubiquitous in core spectra, affecting electron-scattering processes because of displacements of atoms from equilibrium positions, as has been reviewed elsewhere (Rehr & Albers, 2000). Others (Story *et al.*, 2014) show how spectra can include some vibrational effects to all orders using a cumulant approach and system-specific knowledge of vibrational properties that is obtained

elsewhere. Near-edge features are also affected for reasons outside the above DW treatment. One can also vary atomic coordinates by sampling phonon modes or using molecular-dynamics amenable to disordered systems (Vinson *et al.*, 2014; Brouder *et al.*, 2010; Nemausat *et al.*, 2015; Pascal *et al.*, 2014; Prendergast & Galli, 2006; Niskanen *et al.*, 2017). Others (de Groot *et al.*, 1990) cite vibrational effects in d^0 transition-metal compounds for broadening in cases of strong ligand–TM hybridization, for example *E–e* Jahn–Teller effects couple E_g electron states and e_g modes. *OCEAN* can help to determine the coupling strength to use in effective Jahn–Teller Hamiltonians (Tinte & Shirley, 2008; Gilmore & Shirley, 2010) to amend computed spectra. Still others (Zacharias & Giustino, 2016) have analysed valence edges, and core edges should also be treatable.

4.2. Satellite effects

Multi-electron excitations broaden spectral features whenever an electron and/or hole state is far from the Fermi level. The ‘electron–hole continuum’ part of the loss function smoothens the onset of broadening (Soininen *et al.*, 2003; Kas *et al.*, 2007; Fister *et al.*, 2011). Multi-electron excitation also transfers spectral weight to satellites, as largely captured by a cumulant approach related to Hedin’s GW self-energy (Hedin, 1999). This improves calculated photoemission (Guzzo *et al.*, 2011; Gumhalter *et al.*, 2016; Lischner *et al.*, 2015) and near-edge (Kas *et al.*, 2015) spectra. Others (Kas *et al.*, 2016) have presented a method that allows the inclusion of all losses, including interference between intrinsic and extrinsic losses because of the coupling of all particles to the valence electron density. Including such effects should become a standard aspect of calculations performed using tools such as *OCEAN*.

The systems that *OCEAN* can treat are limited by our use of the BSE. Many-electron effects are included only with a more complete description of departures from the ground-state wavefunction. However, even Coster–Kronig decay (Coster & Kronig, 1935) and charge-transfer effects can be studied in limited cases if response-theory analysis of the environment facilitates an enhanced description of on-site excitations, with adequate separability of excitations near a site versus at longer range.

5. Access to OCEAN

Interested parties should access <http://ocean-code.com>, which offers the source code and documentation. As of version 2, *OCEAN* also incorporates valence BSE capabilities. Its flexible input format allows future use with many DFT programs. *ABINIT* and *Quantum ESPRESSO*, both of which are open source, are already accommodated. Scaling of computation time, memory and storage requirements, and a parallelized version of *OCEAN* that should be particularly helpful for large unit cells or large-scale structures have been discussed elsewhere (Gilmore *et al.*, 2015).

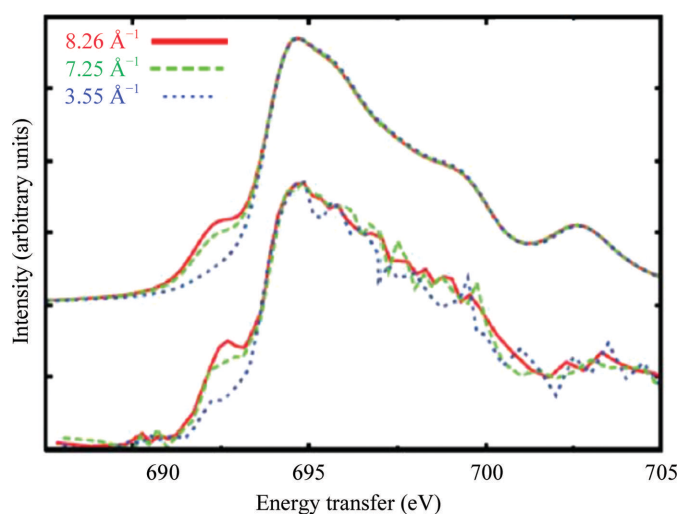


Figure 4
F 1s near-edge spectra obtained by NRIXS for several momentum transfers in LiF, as calculated (top) and measured (bottom; Hämäläinen *et al.*, 2002).

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