

ISSN 1574-8707 it.iucr.org

Volume I, X-ray Absorption Spectroscopy and Related Techniques ISBN: 978-1-119-43394-1

Keywords: Bethe–Salpeter equation; excited core hole; FCH; NRIXS; screening; *StoBe*; XAS; XCH; X-ray Raman scattering.



Core-hole potentials and related effects

Eric L. Shirley,^a* Lars G. M. Pettersson^b and David Prendergast^c

^aSensor Science Division, NIST, 100 Bureau Drive MS 8441, Gaithersburg, MD 20899-8441, USA, ^bDepartment of Physics, Stockholm University, S-106 91 Stockholm, Sweden, and ^cMolecular Foundry, Lawrence Berkeley National Laboratory, One Cyclotron Road, Building 67, Berkeley, CA 94720, USA. *Correspondence e-mail: eric.shirley@nist.gov

The constrained-occupancy and (linear-response) self-consistent-field methods for the screening of core-hole potentials that affect core-excitation near-edge spectra are considered. The methods are not exact, but each has distinct advantages and limitations. The excitation spectra which are referred to include X-ray absorption spectroscopy (XAS), electron energy-loss spectroscopy (EELS) and nonresonant inelastic X-ray scattering (NRIXS). The screening of interactions that arises is always accompanied by self-energy or lifetimedamping effects of electron and hole states, which are also discussed briefly.

1. Introduction

Core-excitation spectroscopies, such as electron energy-loss spectroscopy (EELS), X-ray absorption spectroscopy (XAS) and nonresonant inelastic X-ray scattering (NRIXS), probe states of a physical system that involve a core hole and a concomitant excited electron. In a one-electron picture, this is a consequence of the promotion of a core electron to an unoccupied electron level because of the experimental probe. However, electron-electron and electron-core hole interactions must also be addressed. The electron-core hole interaction can be treated by considering a two-particle equation of motion (the Bethe-Salpeter equation) for the electron-hole pair, by treating the unoccupied electronic level scheme as perturbed by the core hole, or by other techniques. In all of these approaches it is necessary to evaluate the effective screened potential of the core hole. In Section 2, we discuss the treatment of the screening of the core-hole potential.

The mutual electron-hole interaction is accompanied by interactions with the rest of a system by either particle. (Obviously, the fact that the interaction is screened already implies interactions with the rest of the system.) Individually, the electron and core hole experience self-energy effects that shift and broaden the energies of their states because of lifetime damping. We discuss these effects and their treatments in Section 3. Other effects, including vibrational effects, are beyond the present scope.

2. Core-hole potential calculation methods

The accurate inclusion of core-hole effects requires their computation in a system-specific fashion. In practice, a variety of approximations are used. One class of approximations that we consider here is the constrained-occupancy type, including the 'full core-hole' (FCH) and 'excited-electron and core-hole' (XCH) methods, which usually involve a fixed-occupancy pseudopotential or all-electron site that has a core vacancy, as well as calculations where the potential of a core hole is considered when calculating electronic spectra and/or total energy differences in a Slater transition-state or transitionpotential 'half core-hole' (HCH) framework. The other class of approximations we consider is the linear-response approach to estimate core-hole screening.

2.1. Constrained-occupancy methods

Constrained-occupancy methods operate within the framework of constrained self-consistent fields (SCFs), wherein the definition of the electron density relies on an orbital occupancy constraint that deviates from the ground-state Aufbau principle. Here, we will discuss methods where a specific occupation is assigned to the core level after excitation and where this occupation, or the associated core-hole potential, is used to define all excited states.

2.1.1. Full core-hole approach. The full core-hole (FCH) and related excited-electron and core-hole (XCH) approaches (with the latter being discussed later) attempt to model core-excited final states by focusing on the resulting core-excited electron density. In an effective single-particle approximation, this includes the effects of a core-level vacancy. Ignoring the excited electron itself, the resulting core-hole density, computed self-consistently by the use of an orbital occupancy constraint, can be associated with an effective core-hole potential which can be considered to be screened by the surrounding valence electron density and impacts valence electron states, both occupied and unoccupied.

Some of the earliest core-hole calculations were used to model the energy differences between core-excited states of the same atom in different material or chemical contexts, thereby probing chemical shifts. Pehlke & Scheffler (1993) employed the FCH approach to study chemical shifts in silicon and germanium at surfaces and in the bulk. Making use of the plane-wave pseudopotential formalism to describe such extended systems, thereby without the explicit inclusion of core orbitals within the valence-only electron density, they employed core-excited pseudopotentials to define the atomic core contribution to the screened core-hole potential for the valence electrons. The extension and development of this pseudopotential formalism for X-ray absorption spectra was made by Mauri, Cabaret and coworkers (Taillefumier et al., 2002) and was applied to several insulators and semiconductors. These authors referred to this approach as including core-hole screening to all orders, in contrast to the linear-response approaches that already existed (and are discussed later in Section 2.2). Unlike linear-response methods, in a calculation with periodic boundary conditions constrained-occupancy approaches require supercells that are constructed from multiple primitive cells, yet contain a single core-hole 'defect' in order to eliminate interaction between core holes. Hence, this is strongly analogous to the defect calculations prevalent in the study of semiconductors.

The FCH potential (the self-consistent field resulting from the core-hole orbital constraint) defines a full spectrum of effective single-particle orbitals, which can be computed explicitly up to high energies in order to determine the transition probabilities, or the associated core-excited spectral function (related to the imaginary part of the Green's function) can be used to determine the excitation spectral intensity more efficiently.

2.1.2. Excited electron and core hole. The FCH approach neglects the contribution of the excited electron within the core-excited electron density. In this way it treats all core-excited states equally, without emphasis on one final state over any other. However, it was noted that for systems with particularly localized orbitals, such as molecular solids or liquids, this had the effect of insufficiently screening the core hole, leading to overestimated absorption intensity because of the ;deeper attractive potential for the unoccupied orbitals. Explicit inclusion of the excited electron within the first available orbital was used to ameliorate this effect in water and ice (Prendergast & Galli, 2006). The effect of inclusion of the excited electron also leads to almost complete screening at relatively short distances in molecular condensed phases via Gauss's law.

The so-called excited-electron and core-hole (XCH) approximation had, as an obvious choice, been employed by multiple researchers before the FCH work just discussed. Mo & Ching (2000) used it to describe periodic solids within a localized atomic orbital framework both for X-ray absorption and inner-shell electron energy-loss spectra. Prior to this, it had been used in a study of the 1s core exciton in diamond by Jackson & Pederson (1991). In fact, this (only slightly) more expensive Δ SCF approach (which considers changes in the total energy of two SCF calculations with and without core excitation) is exactly what Slater was aiming to avoid through the transition-state approach.

The XCH approach, which makes use of a neutral excitedstate approximation, facilitates easier comparison of the total energies determined from core-excited electron densities, particularly for cases within different periodic lattices or inhomogeneous systems, such as surfaces, defects etc. In contrast, the longer-ranged (partially screened) Coulomb interactions of the full core-hole approach make such comparisons difficult, particularly for systems with different periodicities (and associated Madelung constants). The example of water indicated above highlighted the need for accurate relative alignment of core-excited states for atoms of the same element at different sites or in different contexts. The large configurational space of hydrogen-bonding environments found in liquid water at room temperature, sampled using molecular dynamics within a finite supercell, presented significant variations in the local on-site potential for the excited O atoms and in the polarization response of the valence electron density of the surrounding water molecules, depending on whether they are donating, accepting or lacking hydrogen bonds.

2.1.3. Slater transition state. In the Slater transition-state method (Slater & Johnson, 1972; Slater, 1972) the excitation energy is estimated as the orbital energy difference between the half-occupied initial and final levels of a variationally determined (transition) state; this corresponds to taking the

excitation halfway and using this state as a reference. Because only orbitals i and f change occupation, we can write the total energy of the system as $E(n_i, n_f)$, where the reference state is given by $n_i = n_f = 1/2$. Compared with this reference, the energy of the initial (ground) state can be written as $E(n_i + 1/2, n_f - 1/2)$ and correspondingly for the excited state $E(n_i - 1/2, n_f + 1/2)$. Expanding to second order in the occupation numbers, we use Janak's theorem (Janak, 1978) to replace the derivative of the Kohn–Sham energy with respect to the occupation number n_i by the orbital energy ε_i . We thus obtain for the ground state (with all derivatives taken at the variationally determined reference state):

$$E(n_{\rm i} + 1/2, n_{\rm f} - 1/2) = E(n_{\rm i}, n_{\rm f}) - \frac{1}{2} [\varepsilon_{\rm f}^{(1/2, -1/2)} - \varepsilon_{\rm i}^{(1/2, -1/2)}] + \frac{1}{2!} \left(\frac{1}{2}\right)^2 \left(\frac{\partial^2 E}{\partial n_{\rm i}^2} - 2\frac{\partial^2 E}{\partial n_{\rm i} \partial n_{\rm f}} + \frac{\partial^2 E}{\partial n_{\rm f}^2}\right) + \dots$$
(1)

For the desired excited state we instead obtain

$$E(n_{\rm i} - 1/2, n_{\rm f} + 1/2) = E(n_{\rm i}, n_{\rm f}) + \frac{1}{2} [\varepsilon_{\rm f}^{(1/2, -1/2)} - \varepsilon_{\rm i}^{(1/2, -1/2)}] + \frac{1}{2!} \left(\frac{1}{2}\right)^2 \left(\frac{\partial^2 E}{\partial n_{\rm i}^2} - 2\frac{\partial^2 E}{\partial n_{\rm i} \partial n_{\rm f}} + \frac{\partial^2 E}{\partial n_{\rm f}^2}\right) + \dots$$
(2)

For the transition energy $E_{\rm fi} = E_{\rm f} - E_{\rm i} = E(n_{\rm i} - 1/2, n_{\rm f} + 1/2) - E(n_{\rm i} + 1/2, n_{\rm f} - 1/2)$ we then find (to second order) $E_{\rm fi} = \varepsilon_{\rm f}(1/2, -1/2) - \varepsilon_{\rm i}(1/2, -1/2) + O[E_{\rm n}^{(3)}]$, with the last term indicating corrections third order in orbital occupancy changes.

The derivation assumes that the second-order response of the orbitals to the change in the occupation can be neglected, *i.e.* the half-occupied orbitals represent both the initial and final state characters; the first-order contribution is eliminated through self-consistency and the second-order contribution through a strict cancellation under this assumption. The same orbitals can then be used to represent both initial and final states. This simplifies the evaluation of transition moments to single-electron transitions, because it avoids contributions from the other occupied orbitals.

2.1.4. The transition-potential approximation. Each transition in the transition-state approach requires a separate calculation. Even for an isolated molecule, this makes it impractical to generate a complete X-ray absorption spectrum including valence, Rydberg and continuum states, where hundreds of states can be required for a reasonable representation. The transition-potential (TP) approach of Triguero et al. (1998) was introduced as an approximation to the Slater transition state and eliminates the state-by-state calculations by simply neglecting the half-excited electron. The variationally relaxed density of the resulting molecular ion core with the halfoccupied core hole provides a potential from which all excited states are obtained in one global diagonalization; this includes all interactions between the excited electron and the molecular ion, with the only approximation being that the electronic density of the molecular ion is kept frozen and is not allowed to relax when interacting with the excited electron.

The TP approximation to computing XAS spectra builds on the fact that the partially occupied core level is very isolated both in space and energy, and is furthermore common to all excited states; in cases where several atoms of the same element are present, the core level can still be made unique by replacing the other cores by effective core potentials or pseudopotentials or by localizing and freezing these orbitals so they cannot mix with the desired state (Leetmaa *et al.*, 2010).

Removing an electron from the 1*s* level is the largest perturbation on the remaining electron density. The halfelectron in the excited levels typically interacts only weakly with the remaining molecular ion core, so that neglecting it is normally a very good approximation. When the excitation is into unoccupied, localized valence states, however, the interaction cannot be neglected. The choice of 0.5 electrons as the fractional core-occupation number of the 1*s* level minimizes the error by approximating the excitation energy as an orbitalenergy difference, but it is strictly valid only when the upper level is also half-occupied and the same orbitals can describe both the initial and the final state. The half-core-hole, TP approximation is therefore not rigid and other core occupations/core potentials may be considered (Cavalleri *et al.*, 2005; Nyberg *et al.*, 1999).

2.1.5. The core-hole potential: Newns–Anderson model. Suppose that one can regard the core-excited atom or molecule as an impurity in the band structure of the remaining system and describe the resulting spectra following the Newns–Anderson impurity model (Anderson, 1961; Newns, 1969) as illustrated in Fig. 1(a). The core-hole potential then pulls down the local atomic orbitals of the core-excited molecule, which changes the electronic interactions with the surrounding condensed phase. In this picture one can consider the core-excited atom as a local impurity with a different set of atomic orbitals interacting with the surrounding bands. If the interaction is with a broad featureless continuum of electronic states, this results in a resonance that simply corresponds to a broadening of the atomic level, with the width depending on the strength of the interaction (Fig. 1).

If there are more specific features in the density of states (DOS) the resulting resonances can be more complex, as illustrated in Fig. 1(b) for the specific case of a core-excited water molecule in hexagonal ice (Nilsson & Pettersson, 2011). The water molecular orbitals will be down-shifted because of the core-hole potential where one 1s electron has been removed. The unoccupied DOS of ice has a well defined strong resonance corresponding to the conduction band (Chen et al., 2010), but is otherwise rather featureless, decreasing in intensity towards lower energies. The strength of the core-hole potential determines the energy position of the antibonding $4a_1$ and $2b_2$ levels of the core-excited molecule and consequently how they will be broadened into resonances; the $2b_2$ level will always interact more strongly, since there is a higher DOS at similar energies in comparison to the energy region close to the lower-lying $4a_1$. The hybridization with the strong peak of the conduction band (post-edge in Fig. 1) leads to a new resonance that will mostly be of band-structure character involving the surrounding molecules. How the strength of the core-hole potential affects the hybridization is seen in Fig. 2, which shows computed XAS spectra using the transition-



Figure 1

(a) Illustration of the Newns–Anderson impurity model applied to (a) a single atomic level interacting with a featureless continuum of electronic states and (b) the XAS of ice, where the gas-phase excited states interact strongly with the continuum DOS. Reprinted with permission from Nilsson & Pettersson (2011).

potential method (Triguero *et al.*, 1998), but varying the corehole potential from half core hole to full core hole in steps of 0.1 (Leetmaa *et al.*, 2010). The spectra have been energy calibrated using the ' Δ K-S' approach of Kolczewski *et al.* (2001) and therefore have exactly the same onset in terms of DOS, but not in terms of the intensity distribution (Leetmaa *et al.*, 2010). With increasing core-hole potential both the preedge and main-edge intensities shift to lower energy, consistent with the simple picture of an increased energetic separation of



Figure 2

Computed spectra of hexagonal ice using the transition-potential approach (Triguero *et al.*, 1998) with different core-hole potentials from half core hole (0.5 CH) to full core hole (1.0 CH) in steps of 0.1; for details, see Leetmaa *et al.* (2010). The full black line gives the experimental spectrum from Nordlund *et al.* (2004) and the three main spectral regions, pre-edge, main-edge and post-edge, are indicated.

the 'impurity' states from those of the condensed phase in the Newns-Anderson model. Because of weaker hybridization with the conduction band, there will be less local 2p character and the intensity of the post-edge also diminishes. There is also a shift of the post-edge towards lower energy as the isolated core-excited orbitals are pulled down with increasing core-hole potential. Within the transition-potential approximation (Triguero et al., 1998), the best agreement with the experimental ice spectrum is with the half core-hole potential (Leetmaa et al., 2010; Iannuzzi, 2008), which also has been shown to work well for many other systems (Aziz, Freiwald et al., 2006; Cavalleri et al., 2002, 2006; Damian Risberg et al., 2007, 2009; Kolczewski & Hermann, 2003; Kolczewski et al., 2001; MacNaughton et al., 2006; Näslund et al., 2003; Nyberg et al., 2003; Ogasawara et al., 2002; Öström et al., 2004, 2006, 2007; Öström, Triguero, Nyberg et al., 2003; Öström, Triguero, Weiss et al., 2003; Pettersson et al., 1999; Schiros et al., 2006, 2007; Wilks et al., 2006; Aziz, Zimina et al., 2006; Mijovilovich et al., 2009).

2.1.6. Relaxation effects and variational core-excited states. By the use of a Δ K-S approach, an absolute energy scale can be determined by variationally computing the difference in total energy between the ground state and the first fully relaxed core-excited state for each configuration or each non-equivalent center (Kolczewski *et al.*, 2001). The lowest energy state in the TP-XAS spectrum is set equal to the Δ K-S energy, and all other states are shifted accordingly; this gives a quite reliable absolute energy scale for the onset of each spectrum (Kolczewski *et al.*, 2001; Odelius *et al.*, 2006). Considering relative energy differences within each spectrum, the accuracy relies on the fact that the relaxation effect of the state used to compute the shift (usually the lowest core-excited state) is similar in character for all shifted spectra. Because the

complete spectrum contains excitations to valence, Rydberg and continuum states, there may be different effects depending on the character of the excited state. Additional core-excited states may thus need to be determined variationally by applying the Δ K-S shifting procedure explicitly to the required number of low-lying excited states and shifting the remaining states according to the shift of the highest of the Δ K-S corrected states (Kolczewski *et al.*, 2001; Damian Risberg et al., 2007, 2009; Mijovilovich et al., 2009). In a Kohn-Sham framework, a sequence of orthogonal core-excited states can be determined variationally by requiring that the core level should be singly occupied and the system should be neutral, which defines the lowest unoccupied molecular orbital (LUMO). Removing this orbital from the basis set and repeating the calculation gives the next state and defines LUMO+1. This procedure is well defined for a few low-lying, well separated discrete transitions, but becomes impractical when the DOS becomes too high (Leetmaa et al., 2010).

The ΔK -S energy correction also corrects for the neglect of relaxation because of the interaction of the excited electron with the full core-hole state. However, the exchange-correlation functionals used in density-functional theory (DFT) are only approximate, and the absolute energy scale thus also depends on which functional is used (Takahashi & Pettersson, 2004). The main contribution to the functional dependency is because of the core level, which is where the electron density is the highest, while the relative energies of core-excited states are much less affected (Takahashi & Pettersson, 2004). This opens the possibility of calibrating the calculations further if a suitable reference can be found where the error in the functional can be evaluated against some other higher level calculation or experiment. In such cases the ΔK -S shifted spectrum may be corrected to within a few tenths of an electronvolt of experiment through a computationally derived empirical shift for functional-dependent and relativistic effects (Leetmaa et al., 2006, 2008, 2010).

This empirical correction depends on the chemical environment in a molecule, such that it is in general not possible to define a unique and generally applicable correction for each element and functional (Takahashi & Pettersson, 2004); a sufficiently similar system must be found for the calibration in each case. Still, even in the absence of a reliable empirical correction to the absolute energy scale, chemical shifts between, for example, different O atoms at an oxide surface (Kolczewski & Hermann, 2003, 2004; Kolczewski *et al.*, 2007; Cavalleri *et al.*, 2007, 2009), different waters or OH groups on a metal (Schiros *et al.*, 2006, 2007) or inequivalent atoms in a molecule can be very reliably obtained through just the Δ K-S correction, because the functional dependency largely cancels out when taking differences (Takahashi & Pettersson, 2004).

2.2. Linear-response self-consistent-field screening

Linear-response self-consistent-field (SCF) screening derives its name from the fact that the total (tot) screened potential includes the external (ext) potential because of the core hole and the induced (ind) potential because of the change in the electronic charge density. The latter charge density is itself affected by the total potential. Proper treatment of the screening must be self-consistent and can be achieved, for instance, in the random-phase approximation (RPA) or in the adiabatic local-density approximation (ALDA) that incorporates an exchange-correlation kernel into the RPA equations of motion. An ALDA treatment tends to screen a core-hole potential more effectively than an RPA treatment, and the difference between the two results depends on the system studied. Near-edge spectra are sufficiently sensitive to screening effects so that no single approximation has been found to be sufficiently well controlled to always render the most accurate spectra.

The starting point of an SCF screening calculation is obtained from the solution of the ground-state Schrödingerlike Kohn–Sham equations:

$$\left(-\frac{1}{2}\nabla^2 + V_{\rm at} + V_{\rm H} + V_{\rm xc} + \delta\varphi\right)\psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}).$$
 (3)

Here, $\psi_{n\mathbf{k}}$ and $\varepsilon_{n\mathbf{k}}$ are a Kohn–Sham orbital and energy, respectively, while V_{at} , V_{H} and V_{xc} are the atomic, Hartree and exchange-correlation potentials, respectively. Formally, some of these operators may be nonlocal. The potential perturbation $\delta\varphi$ is only included when the core hole is present, and effects of the core hole are only included in first-order perturbation theory. The total perturbing potential is the combination of the external potential and the induced potential:

$$\delta\varphi_{\rm tot}(\mathbf{r}) = \delta\varphi_{\rm ext}(\mathbf{r}) + \delta\varphi_{\rm ind}(\mathbf{r}). \tag{4}$$

To find the response of the system to a disturbance, the oneelectron Green's function is useful. Written in real space and in the energy domain, with imaginary infinitesimals for occupied and unoccupied Kohn–Sham levels, and not yet accounting for spin, it is

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_{n\mathbf{k}} \frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}^*(\mathbf{r}')}{E - \varepsilon_{n\mathbf{k}} \pm i\eta}.$$
 (5)

In terms of the Green's function, the induced density because of a static total potential disturbance can be found using the formula for the functional derivative,

$$\frac{\delta n(\mathbf{r})}{\delta \varphi_{\text{tot}}(\mathbf{r}')} = \chi^0(\mathbf{r}, \mathbf{r}'; \omega = 0)$$
$$= 2i \int_{-\infty}^{+\infty} \frac{dt}{2\pi} [G(\mathbf{r}, \mathbf{r}'; E + it)]^2.$$
(6)

Here, the factor of two accounts for spin. What is actually of interest, however, is the induced density because of an external potential disturbance:

$$\frac{\delta n(\mathbf{r})}{\delta \varphi_{\text{ext}}(\mathbf{r}')} = \chi(\mathbf{r}, \mathbf{r}'; \omega = 0).$$
(7)

The two response functions are related by the Dyson-like RPA or ALDA equation of motion,

$$\chi(\mathbf{r}, \mathbf{r}'; \omega = 0) = \chi^0(\mathbf{r}, \mathbf{r}'; \omega = 0) + \int d^3 \mathbf{s} \int d^3 \mathbf{s}' \chi^0(\mathbf{r}, \mathbf{s}; \omega = 0) \nu(\mathbf{s}, \mathbf{s}') \chi(\mathbf{s}', \mathbf{r}'; \omega = 0).$$
(8)

Here, the electron–electron interaction that folds the induced potential into what the electrons sense includes the Coulomb potential v_c and an exchange-correlation kernel K_{xc} ,

$$v(\mathbf{s}, \mathbf{s}') = v_{\mathbf{c}}(\mathbf{s}, \mathbf{s}') + K_{\mathbf{x}\mathbf{c}}(\mathbf{s})\delta^3(\mathbf{s} - \mathbf{s}').$$
(9)

Given χ^0 , finding χ amounts to a matrix-inversion problem. In practice, the real-space points can sample a grid that includes radial quadrature grids (uniform or extended Legendre) and an angular quadrature grid (Sloan & Womersley, 2004). Finally, the induced potential results from solution of the Poisson equation. It has been helpful to screen the potential of a core hole plus that of a -e charge sphere at radius of about 2 Å, and screen the potential of a compensating +e charge sphere using a model dielectric function, which is a sufficiently accurate treatment. Soininen & Shirley (2001) demonstrated a scheme performed entirely within reciprocal space, while Shirley (2006) demonstrated the above real-space methodology. In either case, screening by core electrons can be carried out within an atomic program.

2.3. Exchange and multipolar terms

The treatment of core-excited states in a Bethe–Salpeter approach implies solving an effective electron–hole pair Hamiltonian of the form described in Shirley *et al.* (2020). In its simplest form, the Hamiltonian can be expressed using

$$H = H_{\rm e} + H_{\rm h} + H_{\rm eh}.$$
 (10)

Here, $H_{\rm e}$ includes effects related to the electron (affecting its band energy, including many-body corrections thereto), $H_{\rm h}$ includes effects related to the core hole (its binding energy and spin-orbit terms) and H_{eh} includes interaction effects including the central potential, as well as exchange interaction and multipolar terms describable in a fashion akin to Slater F_k and G_k integrals, as described in Shirley et al. (2020) and references therein. Treatments such as constrained-occupancy approaches are encapsulated within SCF treatments of corehole screening and the concomitant effective electron-core hole interaction, and so are less amenable to the inclusion of exchange and multipolar terms. This is because calculations in periodic boundary conditions usually do not consider corehole spin and orbital angular momentum degrees of freedom. Conversely, nonspherical parts of the screened core-hole potential because of the reduced symmetry of the environment of a core-excited site are at present readily included only in the constrained-occupancy approaches.

2.4. On the assessment of core-level shifts

Total binding energies are difficult to determine theoretically, but the relative change in the binding energy, *i.e.* the shift in X-ray photoelectron spectroscopy (XPS) peaks between similar species in different situations, is smaller and easier to estimate. These can be viewed simply as the difference in chemical binding energy of the final-state core-ionized atom in the different situations that are compared. This is the so-called Z + 1 approximation, where it is realized that removing a screening core electron from the viewpoint of the valence electrons is equivalent to increasing the nuclear charge by one unit (Mårtensson & Nilsson, 1995; Xia *et al.*, 2018).

In the FCH and XCH frameworks, within the same periodic supercell or cluster model, chemical shifts in the X-ray absorption of atoms in different chemical environments could be calculated through total energy differences. For example, comparing atoms a and b of the same element X, we realize that they share the same ground-state energy $(E_a^0 = E_b^0 = E^0)$, but very possibly different core-excited total energies $(E_a^* \neq E_b^*)$. Hence, the associated chemical shift in their first excited state might be more accurately approximated using the total energy difference $E_b^* - E_a^*$. This was found to be a superior approximation to merely using the orbital energy differences from the different core-excited self-consistent fields. Furthermore, when comparing excitations from different systems (subject to the same boundary conditions), which may have different ground-state energies, a more inclusive expression should be adopted. For configurations *i* and j, and atom indices a and b for the same element X, we can determine the difference in excitation energies as $[E_b^*(j) - E_b^0(j)] - [E_a^*(i) - E_a^0(i)]$. Such comparisons still require an overall alignment with an experimental reference because of the inaccuracies of most density-functional approximations for describing core-excited state energies.

In the same framework but with different periodic boundary conditions, such as comparing O atoms in different oxides, an additional theoretical reference is required for useful relative alignment of the calculated spectra. We make convenient use of an isolated atom placed within the supercells employed for each specific case and draw a connection to formation (or atomization) energy differences between the ground and excited states. This was independently developed within the XCH approach for molecules and solids (England et al., 2011; Jiang et al., 2013), but was previously employed by Hamann and Muller for electron energy-loss (Hamann & Muller, 2002) and by Pickard and coworkers for X-ray absorption (Rez et al., 1999). Specifically, the formation energy difference of the excited and ground states reveals differences in the total energies of the excited and ground state of the relevant system and the core-excited atom,

$$\begin{bmatrix} E_a^*(i) - \sum_n e_n^*(i) \end{bmatrix} - \begin{bmatrix} E_a^0(i) - \sum_n e_n^0(i) \end{bmatrix}$$

= $[E_a^*(i) - e_a^*(i)] - [E_a^0(i) - e_a^0(i)]$
= $[E_a^*(i) - E_a^0(i)] - [e_a^*(i) - e_a^0(i)],$ (11)

where the final expression groups together the total energies of system *i* in its excited and ground states, and the excited and ground-state energies of the isolated atom X_a under the same boundary conditions as system *i*.

In the other constrained-occupancy methods, core-level shifts are computed through a ΔK -S calculation between the ground state and the fully core-ionized state. Absolute values of the core binding energy (CBE) depend strongly on the

functional used, while shifts relative to a reference do so to a lesser extent (Takahashi & Pettersson, 2004). A particularly challenging case is provided by the so-called ESCA molecule, ethyl trifluoroacetate, with four inequivalent C atoms for which the chemical shifts span 7.5 eV. Here the self-interaction error on the CBEs is found to be significant, and hybrid functionals are necessary to get the shifts even qualitatively correct (Van den Bossche *et al.*, 2014).

In the linear-response approach, a core-level shift can be estimated as follows. Let $E_{\rm B}^{\rm ref}$ be a large, system-independent constant that is the main part of the core-binding energy, and $V_{\rm KS}(\tau)$ be the ground-state Kohn–Sham potential at the core-excited nucleus located at τ . The core-level binding energy can then be estimated to be

$$E_{\rm B} = E_{\rm B}^{\rm ref} - V_{\rm KS}(\boldsymbol{\tau}) - \frac{1}{2}\delta\varphi_{\rm ind}(\boldsymbol{\tau}). \tag{12}$$

The factor of one-half arises from adiabatically turning on the core-hole potential. This method has been used to good effect in the extreme case of ammonium nitrate (NH₄NO₃), which features nitrogen sites with nominal oxidation numbers of -3 (NH₄⁺) and +5 (NO₃⁻) (Vinson *et al.*, 2014). Such an *ad hoc* approach still constitutes an uncontrolled approximation, because it attributes physicality to the Kohn–Sham potential and assumes the validity of the linear-response theory for the valence screening of the core hole.

3. Self-energy effects

3.1. Core-hole lifetime effects

Once created, core holes can decay in a variety of fashions. Krause & Oliver (1979) tabulate lifetime broadening effects because of Auger processes and radiative recombination. Atomic programs such as the Cowan code (Cowan, 1981) can be used to consider lifetimes as well, although most of this work is performed in isolated atoms. Kas *et al.* (2016) have begun treating core-hole lifetime damping and satellite effects within the context of realistic solid-state calculations. In principle, effects such as Coster–Kronig transitions should be treatable using a GW-type self-energy, if the dynamical screening effects of the valence electrons can be treated in an RPA fashion, especially because so few core levels contribute to the electron Green's function that appears explicitly in the self-energy.

3.2. Electron self-energy lifetime damping

Electron self-energy damping effects have been treated by several workers, including the large body of work by Powell, Tanuma and coworkers (see, for example, Kas *et al.*, 2016), Fleszar (Fleszar & Hanke, 1997) and Soininen and coworkers (Soininen *et al.*, 2003). Most treatments consider the fact that a fast photoelectron can scatter through other electronic excitations describable in the form of the momentum-dependent loss function. Experimentally, knowledge of the loss function is mostly obtainable from electron energy-loss scattering (EELS), nonresonant inelastic X-ray scattering (NRIXS) or measurement of optical constants. Typically, this is restricted to small values of momentum transfer from the electron to the system. Of course, it has recently become possible to carry out calculations that sample momentum space explicitly, as described in the work by Fleszar and Soininen and coworkers. Alternatively, it is often sufficient to include the salient effects of momentum dependence of the loss function only, without a severe cost in accuracy. Kas et al. (2007) have introduced a socalled 'multipole self-energy' that mimics the continuous loss function with a set of discrete poles, each of which disperses with momentum according to a prescription. In a method first described by Fister et al. (2011), a model self-energy is introduced with certain properties. These include a jellium-like model for a bulk solid, with the loss function being known from a modified, momentum-dependent Lindhard function with static properties found according to a model dielectric function by Levine & Louie (1982), adherence to the f-sum rule and a zeroth frequency momentum of the imaginary part being related to properties of the density matrix that can be extracted from the output of a band-structure calculation,

$$\frac{1}{\pi} \int_{0}^{\infty} d\omega \ \omega^{0} \chi_{0,L}''(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{2} |\rho_{1}(\mathbf{x}, \mathbf{x}')|^{2} - \langle n(\mathbf{x}) \rangle \delta^{3}(\mathbf{x} - \mathbf{x}').$$
(13)

Here, ρ_1 denotes the one-particle density matrix for one spin, *n* denotes the electron density and $\chi_{0,L}''$ denotes the imaginary part of the Lindhard dielectric function. (Its momentum dependence is inferred following transformation to Fourier space and ignoring effects because of the direction of momentum.) Once a model loss function is in hand, its convolution with a model Green's function (for example that in a free-electron gas) leads to a reasonable self-energy (Shirley, 2020).

4. Summary

In short, there are a variety of methods that can be used to determine the effective, screened potential because of a core hole that electrons in a physical system experience. We note that all methods have their strengths, but also weaknesses. The HCH transition potential, with its unscreened half-core hole, can run into difficulties describing the transition between a fully interacting, fully screened chemisorbed molecule and the gas phase as the molecule desorbs, followed in XAS using modern free-electron X-ray lasers (Wang et al., 2020). XCH is excellent for conducting systems where the states are delocalized and the screening electron does not affect the remaining states to a great extent. It also works well for semiconductors with a small band gap, but for insulators with a more dielectric response populating a specific localized screening state may artificially modify the higher localized excited states. One should thus be aware of the different approximations involved in each approach. A comparison of the C 1s near-edge spectrum in C_{60} is shown in Fig. 3.

Beyond the main effects, one can also consider exchange and multipolar electron-core hole interactions, lifetime



Figure 3

C 1s near-edge spectrum of C₆₀ using linear-response core-hole screening and the BSE (*OCEAN*), the XCH approach and the *StoBe* program. The varying degrees of chemical realism of the unoccupied states are reflected in the accuracy of the associated spectral features and are inversely correlated with computational efficiency (Fossard *et al.*, 2017).

damping and other effects beyond the scope of this description. In addition, all of the work discussed here assumes the overall validity of a self-consistent-field or independentelectron picture for the system of valence electrons, so that studying intrinsically multi-reference and strongly correlated systems might require one to exercise greater caution.

Acknowledgements

ELS acknowledges multiple helpful discussions with J. J. Rehr, J. J. Kas and J. T. Vinson. Much of the GW work and core-hole screening work was performed in collaboration with J. A. Soininen. LGMP acknowledges long-term collaboration with A. Nilsson and H. Ågren as well as the favor of working with L. Triguero, M. Leetmaa, M. P. Ljungberg, K. T. Wikfeldt and H. Öberg during their PhD studies.

References

- Anderson, P. W. (1961). Phys. Rev. 124, 41-53.
- Aziz, E. F., Freiwald, M., Eisebitt, S. & Eberhardt, W. (2006). *Phys. Rev. B*, **73**, 075120.

- Aziz, E. F., Zimina, A., Freiwald, M., Eisebitt, S. & Eberhardt, W. (2006). J. Chem. Phys. 124, 114502.
- Cavalleri, M., Hermann, K., Guimond, S., Romanyshyn, Y., Kuhlenbeck, H. & Freund, H.-J. (2007). *Catal. Today*, **124**, 21–27.
- Cavalleri, M., Hermann, K., Knop-Gericke, A., Hävecker, M., Herbert, R., Hess, C., Oestereich, A., Döbler, J. & Schlögl, R. (2009). J. Catal. **262**, 215–223.
- Cavalleri, M., Näslund, L.-Å., Edwards, D. C., Wernet, P., Ogasawara, H., Myneni, S., Ojamäe, L., Odelius, M., Nilsson, A. & Pettersson, L. G. M. (2006). J. Chem. Phys. 124, 194508.
- Cavalleri, M., Odelius, M., Nordlund, D., Nilsson, A. & Pettersson, L. G. M. (2005). *Phys. Chem. Chem. Phys.* **7**, 2854–2858.
- Cavalleri, M., Ogasawara, H., Pettersson, L. G. M. & Nilsson, A. (2002). Chem. Phys. Lett. 364, 363–370.
- Chen, W., Wu, X. & Car, R. (2010). Phys. Rev. Lett. 105, 017802.
- Cowan, R. D. (1981). *The Theory of Atomic Structure and Spectra*. Berkeley: University of California Press.
- Damian Risberg, E., Eriksson, L., Mink, J., Pettersson, L. G. M., Skripkin, M. Y. & Sandström, M. (2007). *Inorg. Chem.* 46, 8332–8348.
- Damian Risberg, E., Jalilehvand, F., Leung, B., Pettersson, L. G. M. & Sandström, M. (2009). *Dalton Trans.*, pp. 3542–3558.
- England, A. H., Duffin, A. M., Schwartz, C. P., Uejio, J. S., Prendergast, D. & Saykally, R. J. (2011). *Chem. Phys. Lett.* **514**, 187–195.
- Fister, T. T., Schmidt, M., Fenter, P., Johnson, C. S., Slater, M. D., Chan, M. K. & Shirley, E. L. (2011). J. Chem. Phys. 135, 224513.
- Fleszar, A. & Hanke, W. (1997). Phys. Rev. B, 56, 10228-10232.
- Fossard, F., Hug, G., Gilmore, K., Kas, J. J., Rehr, J. J., Vila, F. D. & Shirley, E. L. (2017). *Phys. Rev. B*, 95, 115112.
- Hamann, D. R. & Muller, D. A. (2002). Phys. Rev. Lett. 89, 126404.
- Iannuzzi, M. (2008). J. Chem. Phys. 128, 204506.
- Jackson, K. A. & Pederson, M. R. (1991). *Phys. Rev. Lett.* **67**, 2521–2524. Janak, J. F. (1978). *Phys. Rev. B*, **18**, 7165–7168.
- Jiang, P., Prendergast, D., Borondics, F., Porsgaard, S., Giovanetti, L., Pach, E., Newberg, J., Bluhm, H., Besenbacher, F. & Salmeron, M. (2013). J. Chem. Phys. 138, 024704.
- Kas, J. J., Rehr, J. J. & Curtis, J. B. (2016). Phys. Rev. B, 94, 035156.
- Kas, J. J., Sorini, A. P., Prange, M. P., Cambell, L. W., Soininen, J. A. & Rehr, J. J. (2007). *Phys. Rev. B*, **76**, 195116.
- Kolczewski, C. & Hermann, K. (2003). J. Chem. Phys. 118, 7599-7609.
- Kolczewski, C. & Hermann, K. (2004). Surf. Sci. 552, 98-110.
- Kolczewski, C., Hermann, K., Guimond, S., Kuhlenbeck, H. & Freund, H.-J. (2007). *Surf. Sci.* **601**, 5394–5402.
- Kolczewski, C., Püttner, R., Plashkevych, O., Ågren, H., Staemmler, V., Martins, M., Snell, G., Schlachter, A. S., Sant'Anna, M., Kaindl, G. & Pettersson, L. G. M. (2001). J. Chem. Phys. 115, 6426–6437.
- Krause, M. O. & Oliver, J. H. (1979). J. Phys. Chem. Ref. Data, 8, 329– 338.
- Leetmaa, M., Ljungberg, M., Ogasawara, H., Odelius, M., Näslund, L. Å., Nilsson, A. & Pettersson, L. G. M. (2006). J. Chem. Phys. 125, 244510.
- Leetmaa, M., Ljungberg, M. P., Lyubartsev, A. P., Nilsson, A. & Pettersson, L. G. M. (2010). J. Electron Spectrosc. Relat. Phenom. 177, 135–157.
- Leetmaa, M., Wikfeldt, K. T., Ljungberg, M. P., Odelius, M., Swenson, J., Nilsson, A. & Pettersson, L. G. M. (2008). J. Chem. Phys. 129, 084502.
- Levine, Z. H. & Louie, S. G. (1982). Phys. Rev. B, 25, 6310-6316.
- MacNaughton, J. B., Wilks, R. G., Lee, J. S. & Moewes, A. (2006). J. Phys. Chem. B, 110, 18180–18190.
- Mårtensson, N. & Nilsson, A. (1995). J. Electron Spectrosc. Relat. Phenom. 75, 209–223.
- Mijovilovich, A., Pettersson, L. G. M., Mangold, S., Janousch, M., Susini, J., Salome, M., de Groot, F. M. F. & Weckhuysen, B. M. (2009). J. Phys. Chem. A, **113**, 2750–2756.
- Mo, S.-D. & Ching, W. Y. (2000). Phys. Rev. B, 62, 7901-7907.
- Näslund, L. Å., Cavalleri, M., Ogasawara, H., Nilsson, A., Pettersson,
 L. G. M., Wernet, P., Edwards, D. C., Sandström, M. & Myneni, S.
 (2003). J. Phys. Chem. A, 107, 6869–6876.

Newns, D. M. (1969). Phys. Rev. 178, 1123-1135.

- Nilsson, A. & Pettersson, L. G. M. (2011). Chem. Phys. 389, 1-34.
- Nordlund, D., Ogasawara, H., Wernet, P., Nyberg, M., Odelius, M., Pettersson, L. G. M. & Nilsson, A. (2004). *Chem. Phys. Lett.* 395, 161–165.
- Nyberg, M., Luo, Y., Triguero, L., Pettersson, L. G. M. & Ågren, H. (1999). *Phys. Rev. B*, **60**, 7956–7960.
- Nyberg, M., Odelius, M., Nilsson, A. & Pettersson, L. G. M. (2003). J. Chem. Phys. 119, 12577–12585.
- Odelius, M., Cavalleri, M., Nilsson, A. & Pettersson, L. G. M. (2006). *Phys. Rev. B*, **73**, 024205.
- Ogasawara, H., Brena, B., Nordlund, D., Nyberg, M., Pelmenschikov, A., Pettersson, L. G. M. & Nilsson, A. (2002). *Phys. Rev. Lett.* **89**, 276102.
- Öström, H., Föhlisch, A., Nyberg, M., Weinelt, M., Heske, C., Pettersson, L. G. M. & Nilsson, A. (2004). *Surf. Sci.* **559**, 85–99.
- Öström, H., Ogasawara, H., Näslund, L.-Å., Andersson, K., Pettersson, L. G. M. & Nilsson, A. (2007). J. Chem. Phys. 127, 144702.
- Öström, H., Ogasawara, H., Näslund, L.-Å., Pettersson, L. G. M. & Nilsson, A. (2006). *Phys. Rev. Lett.* **96**, 146104.
- Öström, H., Triguero, L., Nyberg, M., Ogasawara, H., Pettersson, L. G. M. & Nilsson, A. (2003). *Phys. Rev. Lett.* **91**, 046102.
- Öström, H., Triguero, L., Weiss, K., Ogasawara, H., Garnier, M. G., Nordlund, D., Nyberg, M., Pettersson, L. G. M. & Nilsson, A. (2003). J. Chem. Phys. **118**, 3782–3789.
- Pehlke, E. & Scheffler, M. (1993). Phys. Rev. Lett. 71, 2338-2341.
- Pettersson, L. G. M., Hatsui, T. & Kosugi, N. (1999). *Chem. Phys. Lett.* **311**, 299–305.
- Prendergast, D. & Galli, G. (2006). Phys. Rev. Lett. 96, 215502.
- Rez, P., Alvarez, J. R. & Pickard, C. (1999). Ultramicroscopy, 78, 175– 183.
- Schiros, T., Haq, S., Ogasawara, H., Takahashi, O., Öström, H., Andersson, K., Pettersson, L. G. M., Hodgson, A. & Nilsson, A. (2006). *Chem. Phys. Lett.* **429**, 415–419.

- Schiros, T., Näslund, L.-Å., Andersson, K., Gyllenpalm, J., Karlberg, G. S., Odelius, M., Ogasawara, H., Pettersson, L. G. M. & Nilsson, A. (2007). J. Phys. Chem. C, 111, 15003–15012.
- Shirley, E. L. (2006). Ultramicroscopy, 106, 986-993.
- Shirley, E. L. (2020). Radiat. Phys. Chem. 167, 108165.
- Shirley, E. L., Vinson, J. & Gilmore, K. (2020). *Int. Tables Crystallogr. I*, https://doi.org/10.1107/S1574870720003407.
- Slater, J. C. (1972). Adv. Quantum Chem. 6, 1-92.
- Slater, J. C. & Johnson, K. H. (1972). Phys. Rev. B, 5, 844-853.
- Sloan, I. H. & Womersley, R. S. (2004). Adv. Comput. Math. 21, 107-125.
- Soininen, J. A., Rehr, J. J. & Shirley, E. L. (2003). J. Phys. Condens. Matter, 15, 2573–2586.
- Soininen, J. A. & Shirley, E. L. (2001). Phys. Rev. B, 64, 165112.
- Taillefumier, M., Cabaret, D., Flank, A. & Mauri, F. (2002). *Phys. Rev. B*, **66**, 195107.
- Takahashi, O. & Pettersson, L. G. M. (2004). J. Chem. Phys. 121, 10339–10345.
- Triguero, L., Pettersson, L. G. M. & Ågren, H. (1998). Phys. Rev. B, 58, 8097–8110.
- Van den Bossche, M., Martin, N. M., Gustafson, J., Hakanoglu, C., Weaver, J. F., Lundgren, E. & Grönbeck, H. (2014). J. Chem. Phys. 141, 034706.
- Vinson, J., Jach, T., Elam, W. T. & Denlinger, J. D. (2014). *Phys. Rev. B*, **90**, 205207.
- Wang, H.-Y., Schreck, S., Weston, M., Liu, C., Ogasawara, H., LaRue, J., Perakis, F., Dell'Angela, M., Capotondi, F., Giannessi, L., Pedersoli, E., Naumenko, D., Nikolov, I., Raimondi, L., Spezzani, C., Beye, M., Cavalca, F., Liu, B., Gladh, J., Koroidov, S., Miedema, P. S., Costantini, R., Pettersson, L. G. M. & Nilsson, A. (2020). *Phys. Chem. Chem. Phys.* 22, 2677–2684.
- Wilks, R. G., MacNaughton, J. B., Kraatz, H.-B., Regier, T. & Moewes, A. (2006). J. Phys. Chem. B, 110, 5955–5965.
- Xia, Y., Koenis, M. A. J., Collados, J. F., Ortiz, P., Harutyunyan, S. R., Visscher, L., Buma, W. J. & Nicu, V. P. (2018). *ChemPhysChem*, **19**, 561–565.