Scheme to calculate core hole−electron interactions in solids

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We introduce a *first-principles* scheme for calculating a core-hole potential for core-electron excitations. The scheme incorporates atomic and solid-state screening in the description of core excitations in several materials. We compare the results calculated using our scheme to experimental x-ray absorption and inelastic scattering spectra.

I. INTRODUCTION

In recent years several *first-principles* schemes including electron-hole interactions have been developed to model absorption[1−4] and inelastic scattering[5] by the valence electrons in solids. These methods have been quite accurate in describing the interactions that are present when an electron is excited from a valence band to a conduction band. The excitations from a core level have turned out to be more difficult to treat at the same level. This field has attracted much theoretical interest (for example, see Refs. 6−11). Treating core excitations is difficult in part because a combination of atomic and solid-state screening has to be considered when computing a core-hole potential. Also, the x-ray absorption near-edge structure (XANES) has proved to be extremely sensitive to the core-hole potential that the excited electron feels in its final state. We have developed a band-structure-based *first-principles* scheme that can calculate the core-hole potential accurately enough so that it can be used for calculation of XANES and similar spectroscopies.

When an electron is excited from a core state of a solid, it leaves behind a core hole. The excited electron and other electrons in the system all feel the potential produced by the core hole. How the electrons of the system respond to this potential affects XANES. Several approaches to this problem have been proposed over the years. One possibility is to use the so called $Z+1$ approximation, where the final-state density of states is calculated by doing a supercell calculation, increasing the atomic number of the site undergoing excitation by one. Also, often the excitation energies are calculated using so called Slater-transition-state approach,[12] where one half of the electron in the core orbital is removed and put in the lowest unoccupied orbital. It is also possible to calculate total-energy differences between the ground state and some specified excited state.[13] All these approximations work in some cases.

Our present method is based on parameter-free calculation of the core-hole potential and the screening potential produced by all core and valence electrons responding to the potential of the hole. The screening because of the core electrons is computed within an atomic program. The resulting, total "core" potential is, in addition, screened by the valence electrons using dielectric response calculations. These calculations are done in reciprocal space, and so we only need to do the solid-state calculations with one unit cell (and Brillouin-zone sampling). Note that, by working within an approach that employs a given approximation for the dielectric screening, we also avoid complications of needing to specify low-lying excited electron states and/or employ super-cell methods, such as might arise in Slater transition-state or total-energy-difference calculations.

In what follows, we first review how we use the core-hole potential to calculate x-ray absorption or inelastic scattering spectra. Next, we discuss how we compute the core-hole potential. Lastly, we compare our calculations with experiment and discuss the importance of the different parts of the core hole-electron interaction.

II. MODEL FOR CORE-EXCITATION SPECTROSCOPY

The basic equation of many core-excitation spectroscopies is

$$I(\eta,\omega) = \sum_F |\langle F|\hat{\mathbf{P}}_\eta|I\rangle|^2 \delta(\omega + E_I - E_F),$$

where $|F\rangle$ is the final and $|I\rangle$ initial electronic state. The energy of the final (initial) state is $E_F(E_I)$. The operator $\hat{\mathbf{P}}_\eta$ couples a solid with the probe. As an example, for low-Z x-ray absorption, the probe is effectively a dipole operator coupling core and unoccupied states. The excitation energy is ω. Assuming completeness we can rearrange this equation as

$$I(\eta,\omega) = -\frac{1}{\pi}\text{Im}\langle I|\hat{\mathbf{P}}_\eta^\dagger \frac{1}{\omega + E_I - \hat{H} + i\gamma}\hat{\mathbf{P}}_\eta|I\rangle. \quad (1)$$

Here $\hat{H}$ is the full many-body final-state Hamiltonian, and γ is a lifetime-broadening parameter. In practice we approximate $\hat{H}$ with an effective model Hamiltonian $\hat{H}_{\text{eff}}$,

$$\hat{H}_{\text{eff}} = \hat{H}_0 + \hat{V}_D + \hat{V}_X.$$

This includes a single-particle part $\hat{H}_0$, and direct $\hat{V}_D$ and exchange $\hat{V}_X$ interactions of the electron and the core hole. We expand the electron-hole wave function as

$$\Phi(\mathbf{r}_e,\mathbf{r}_h) = \sum_{n\mathbf{k}} C_{n\mathbf{k}} \phi_{n\mathbf{k}}(\mathbf{r}_e)[\chi_{\mathbf{k}-\mathbf{q}\alpha}(\mathbf{r}_h)]^*.$$

Here $\phi_{n\mathbf{k}}$ is a conduction band electron state, $\chi_{\mathbf{k-q}\alpha}$ is a Bloch sum for a core state α written in tight-binding form, and $C_{n\mathbf{k}}$ is an expansion coefficient. The parameter α represents all the indices associated with the core state: its position $\boldsymbol{\tau}$ in a unit cell and the atomic state nlm. The momentum transferred to the solid by the probe is indicated by $\mathbf{q}$. The matrix elements of $\hat{H}_{\mathrm{eff}}$ in the indicated, orthonormal, pair-state basis $\{|n\mathbf{k}\alpha\rangle\}$ are given by

$$\langle n\mathbf{k}\alpha|\hat{H}_{\mathrm{eff}}|n'\mathbf{k}'\alpha'\rangle = \delta_{\alpha\alpha'}[\delta_{nn'}\delta_{\mathbf{kk}'}(\varepsilon_{n\mathbf{k}}-E_{\alpha})$$
$$+\langle\phi_{n\mathbf{k}}|\hat{V}_D(\alpha)+\hat{V}_X(\alpha)|\phi_{n'\mathbf{k}'}\rangle]. \tag{2}$$

Here $\varepsilon_{n\mathbf{k}}$ is the single-particle energy of the conduction-band state calculated within the GW approximation,[14,15] and E_{α} is the energy of the core state. The single-particle conduction band states $\phi_{n\mathbf{k}}$ are calculated using a local-density approximation (LDA) (Ref. 16) pseudopotential[17] code and the core state using an atomic Hartree-Fock (HF) code. Vanderbilt pseudopotentials[18] were used with a plane-wave cutoff of 100, 64, and 25 Ry for LiF, diamond, and Be, respectively. The periodic part of the Bloch function was calculated using the optimized basis set of Ref. 19. A sampling of 4096 k points in the first Brillouin zone was found to give converged result in all of the cases. Physically, the excited electron feels an effective single-particle potential because of the core hole (α). The operator $\hat{\mathbf{P}}_{\eta}$ creates an electron-hole pair state $|\Phi_0\rangle = \Sigma_{n\mathbf{k}}|n\mathbf{k}\alpha\rangle\langle n\mathbf{k}\alpha|\hat{\mathbf{P}}_{\eta}|I\rangle$. We can write $I(\eta,\omega)$ as

$$I(\eta,\omega) = -\pi^{-1}\mathrm{Im}\langle\Phi_0|(\omega-\hat{H}_{\mathrm{eff}}+i\gamma)^{-1}|\Phi_0\rangle. \tag{3}$$

Using the Haydock recursion method[20] the resolvent in the Eq. (3) can be solved iteratively, within numerical accuracy, for a Hermitian matrix operator $\hat{H}_{\mathrm{eff}}$. A detailed discussion of this method in connection with optical absorption can be found in Ref. 1. A many-body transition matrix element can be identified with a single-particle matrix element by using

$$\langle n\mathbf{k}\alpha|\hat{\mathbf{P}}_{\eta}|I\rangle = \langle\phi_{n\mathbf{k}}|\hat{\mathbf{P}}_{\eta}^{(1)}|\chi_{\mathbf{k-q}\alpha}\rangle,$$

where $\hat{\mathbf{P}}_{\eta}^{(1)}$ is a one-electron operator corresponding to the coupling of one's probe to a single electron. We calculated such single-particle matrix elements using a scheme that we developed earlier[21] and later refined.[22] The current scheme[22] is similar to the projector augmented wave (PAW) method.[23] The scheme estimates the all-electron wave function in the vicinity of the excited core by applying projector functions on the pseudo wave function. This scheme applied to core spectroscopic calculations will be presented in more detail in Ref. 22. The calculated matrix elements weight different excitations that can occur with one's excitation operator $\hat{\mathbf{P}}_{\eta}^{(1)}$. The fact that we use a band-structure-based method throughout the calculation means that our calculations are parameter-free and rely on an extremely detailed treatment of the underlying one-electron wave mechanics.

III. CORE-HOLE POTENTIAL

The interaction between the core-hole and the electron has two parts. The exchange part V_X was treated using a pseudopotential-inversion scheme.[21] It is when treating the direct part, V_D, that we have to consider screening of the core hole by the electrons in the system. We need to handle separately the screening caused by the response of the core electrons to the hole potential and the analogous screening by the valence electrons. We separate $V_D(\mathbf{r})$ into three parts,

$$V_D(\mathbf{r}) = V_{\alpha}(\mathbf{r}) + \Delta V_{\alpha}(\mathbf{r}) + \Delta V_{\mathrm{val}}(\mathbf{r}). \tag{4}$$

V_{α} is the bare potential of the core hole, ΔV_{α} is the effect of screening done by the core electrons, and ΔV_{val} is the effect of screening done by the valence electrons. In principle, because the valence electrons screen the total core potential, $V_{\alpha}+\Delta V_{\alpha}$, and the core electrons screen the potential, $V_{\alpha}+\Delta V_{\mathrm{val}}$, Eq. (4) should be solved in a self-consistent manner. In practice, we have not found it necessary to go past the first iteration. We first calculate $V_{\alpha}+\Delta V_{\alpha}$ self-consistently in the absence of valence electrons in the atomic HF program. Next we calculate the response of the valence electrons to $V_{\alpha}+\Delta V_{\alpha}$, with

$$\Delta V_{\mathrm{val}}(\mathbf{r}) = \int d^3\mathbf{r}'\{[\varepsilon^{-1}(\mathbf{r},\mathbf{r}')-\delta^3(\mathbf{r}-\mathbf{r}')]$$
$$\times[V_{\alpha}(\mathbf{r}')+\Delta V_{\alpha}(\mathbf{r}')]\},$$

using the static dielectric function ε found in the random-phase approximation (RPA).[24]

The dielectric function and (hence) core-hole potential correctly include "local-field" effects, i.e., polarization fields that are inhomogeneous on the unit-cell scale. The screening is especially sensitive to effects within the atomiclike region close to the core hole, and this is not well reproduced with model dielectric functions that only depend on the local density. The use of RPA screening for V_D also gives it the correct long-range behavior. In an earlier work by one of the authors[6] a Levine-Louie-Hybertsen (LLH) (Ref. 25) model for the core-hole screening was used. As the other aspects of the calculation have improved, it has been found that LLH underscreens the core hole and leads to exaggeration of the exciton effects. Because near-edge structure of core-excitation spectra is very sensitive to the core-hole potential, it is important that all these effects are included in one's calculation. To compare the present RPA screening model with the LLH model, we show the two valence screening potentials in Fig. 1 for a C 1s hole in diamond. Both models correctly describe the $[1-1/\epsilon]/r$ long-range behavior, whereas the LLH model gives an incorrect description of screening at short range, i.e., in the atomic region.

IV. RESULTS AND DISCUSSION

In Fig. 2, we show calculated absorption spectra with and without the electron-hole interaction, together with measured spectra,[26,27] for excitation near the Li and F K edges in LiF at small momentum transfer regardless of the excitation (electron energy-loss scattering for Li, x-ray absorption for F).
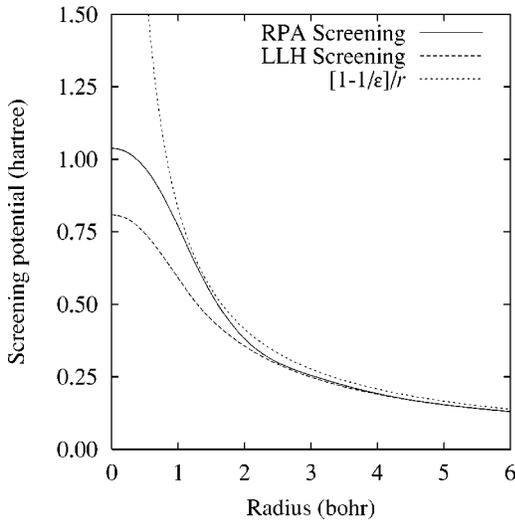
FIG. 1. Valence screening effects for a C $1s$ hole in diamond calculated by two different methods: random-phase approximation (RPA) and the Levine-Louie-Hybertsen model (LLH). The long range, $[1-1/\epsilon]/r$ behavior is also indicated.

Including electron-hole interactions greatly improves agreement between measured and calculated spectra. The significant feature in the Li K edge spectrum is the core exciton about 3 eV below the particle-hole continuum. Its energy and weight appear to be reasonably well calculated. The experimental near x-ray edge structure for the F K edge is also well predicted by the calculation. While the fluorine sites in LiF already have nominally filled valence shells, we note that core-hole effects are nonetheless strong on the F site.

The calculated absorption spectrum near the C K edge in diamond is shown in Fig. 3, together with a measured excitation spectrum.[28] Two calculations are shown. One calculation includes only the direct part, V_D, of the core-hole potential and the other includes both V_D and V_X. Including the exchange part V_X significantly affects the spectrum only close to the edge, and improves agreement with the measured spectrum. We note that core-hole effects appear exaggerated in the diamond calculation, a trend that also occurs in multiple-scattering calculations. It is unclear at this time why this difficulty arises.

Calculated and experimental[29] spectra for x-ray Raman scattering from Be K electrons in Be are shown in Fig. 4. Experimental and calculated spectra exhibit similar behavior. The most important features in the experimental spectra are the peaks close to the edge (112 eV) and approximately 15 eV above the edge. The calculated spectra also have these peaks, but the spectral weight above the edge is underestimated. Spectral damping because of the lifetime of the final-state electron is taken into account only within an "on-shell" GW scheme,[14] and this contributes in part to this discrepancy. However, the calculated spectra have the correct qualitative dependence on the direction of the momentum transfer.

V. SUMMARY

We would like to take this opportunity to discuss the relationship of the band structure (BS) based approach used
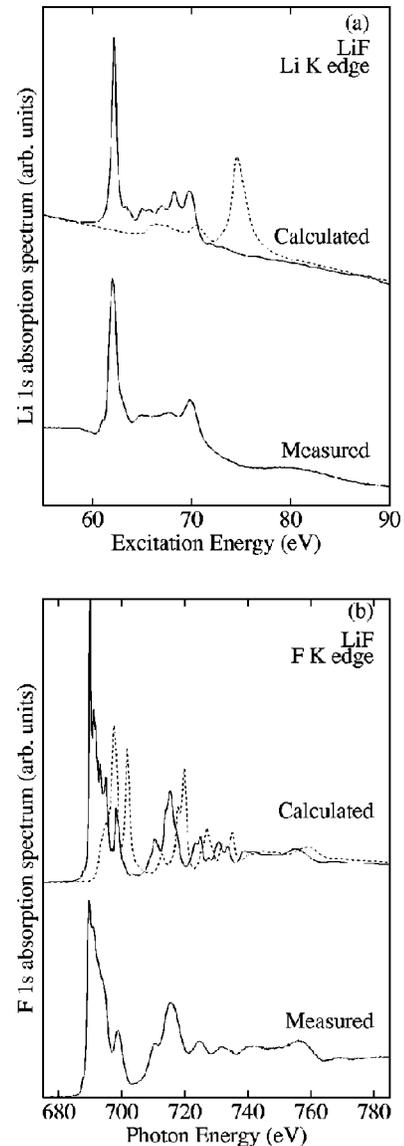

FIG. 2. Calculated x-ray absorption spectra near the Li (a) and F (b) K edges in LiF, with and without the core hole-electron interaction (solid and dashed, respectively), compared to measured spectra (Refs. 26,27). A linear baseline was added to the calculated Li spectrum.

here to other approaches to core spectroscopy.[7–11] The effective Hamiltonian presented here and the associated core hole-electron interaction potential include the same physical processes as the one applied to optical absorption[1,2] and to NRIXS.[5] A detailed discussion on the physical effects included in $\hat{H}_{\mathrm{eff}}$ in the case of core spectroscopy can also be found in Ref. 21, where a simpler model was used for the screening of the core hole. One of the main advantages of BS approaches is that the main convergence-controlling parameter is the number of k points in the first Brillouin zone. For example, in LiF it is much easier to do a calculation using 4096 k points than the, in priciple equivalent, 8192 atom supercell calculation. The RPA model screening of the core hole used here can be considered nearly equivalent to doing a self-consistent LDA supercell calculation with a core hole
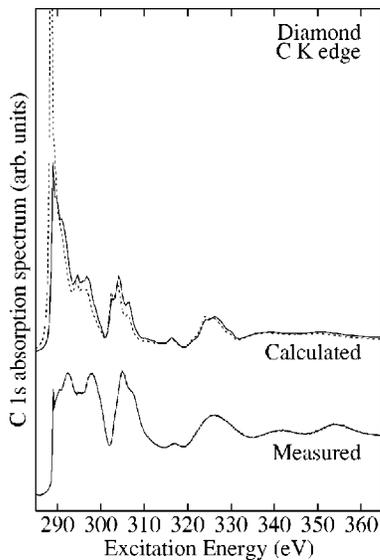
FIG. 3. Calculated x-ray absorption spectra near the C K edge in diamond, compared to a measured excitation spectrum (Ref. 28). Calculated results including the full core hole-electron interaction are indicated by a solid line, whereas the dashed line indicates results that omit V_X.

FIG. 4. Calculated and measured (Ref. 29) spectra of Be K edge in Be. The momentum transfer is 2.4 Å^{-1}. Experimental results for momentum transfer along the c axis are given by the circles, experimental results for momentum transfer along a [100] direction are given by the squares, and experimental results for momentum transfer along a [110] direction are given by the triangles. The respective calculated spectra are given by the solid line, the dashed line and the dotted line. The offset of the calculated spectra is indicated by the horizontal line.

present. However, the current scheme would be rather straightforward to implement using a better model for the core hole screening, if one becomes available. The matrix elements are calculated using single-particle wave functions and the relaxation of the single-particle states is not accounted for in this work. The supercell approaches account for relaxation effects at some level but they also normally use single-particle matrix elements. Modeling of the electron-hole pair in a single-particle basis also permits explicit momentum conservation, which is important when using the model to study finite-momentum-transfer experimental methods such as NRIXS (as was done in the case of Be), electron-energy-loss spectroscopy or resonant inelastic x-ray scattering.

VI. CONCLUSION

We have presented a general *first-principles* scheme for calculating the core-hole potential that can be used to ana-
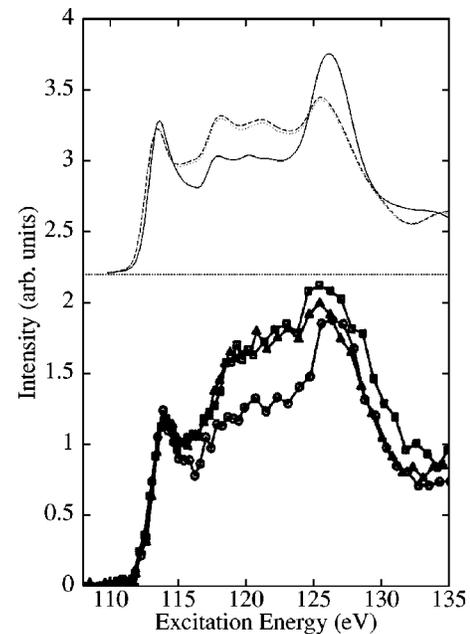
lyze different core spectroscopies. The scheme was used to calculate x-ray absorption spectra at the Li and F K edges in LiF and C K edge in diamond. Additionally, the scheme was applied to x-ray Raman scattering from Be K electrons in Be. The results show that the scheme is quite robust and can be applied to wide range of materials.

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