Excitonic Effects in Core-Excitation Spectra of Semiconductors

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Core-electron excitation spectra are used widely for structural and chemical analysis of materials, but interpretation of the near-edge structure remains unsettled, especially for semiconductors. For the important Si $L_{2,3}$ edge, there are two mutually inconsistent interpretations, in terms of effective-mass excitons and in terms of Bloch conduction-band final states. We report *ab initio* calculations and show that neither interpretation is valid and that the near-edge structure is in fact dominated by short-range electron-hole interactions even though the only bound excitons are effective-mass-like.

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Excitations of electrons from core levels to available empty states are the key ingredient of several powerful spectroscopies that probe the electronic and atomic structure of bulk solids, surfaces, and interfaces. The energy thresholds for such core excitations are unambiguous signatures of the chemical identity of the elements that are present [1], while small shifts in the thresholds are indicative of different bonding coordination or charge state [2]. Because core levels are dispersionless, the spectra reflect the available excited states. Interpretation of these spectra, however, has been a very difficult task because electron-hole correlations may produce bound excitons below the band edge and also distort the continuum spectrum. The task has been complicated by several factors: broadened excitons merge with continuum excitations so that they cannot be unambiguously distinguished, band-threshold calculations are not sufficiently accurate, and the inclusion of excitonic effects in theoretical spectra was until recently [3] pursued only in limiting cases [4–7].

In the early 1970s, calculated conduction-band densities of states of ionic solids were compared with measured x-ray absorption spectra by treating the band threshold as a free parameter. It was concluded that the spectra could be interpreted in terms of band final states without excitonic effects [8]. Subsequently, it was shown that band thresholds could be established by a combination of x-ray photoemission and optical absorption data, leading to conclusions that excitonic effects in fact dominate the spectra [9]. Since then, it appears that the freedom to adjust the band threshold has been reintroduced, leading to mixed results about the role of excitonic effects in both insulators and semiconductors [6,7,10–12]. Calculations that use the $Z + 1$ approximation for excitons (modeling a core hole as an additional proton on the nucleus, i.e., increasing by one the atomic number of the atom being excited) have also produced mixed results [6,7]. More recently, Shirley [3] reported calculations of x-ray spectra of several materials by treating electron-hole interactions explicitly using the Bethe-Salpeter equation and demonstrated that large excitonic effects are present.

For semiconductors, the role of excitons in core spectra has been particularly controversial. Though calculations including the effect of core-holes demonstrated substantial excitonic effects in several systems [13], the issue is far from settled. The best illustration of the problem is provided by the Si $L_{2,3}$ edge, namely, transitions from the $2p$ core level (which is split into $2p_{1/2}$ and $2p_{3/2}$ levels) that the spectrum is a superposition of two virtually identical spectra separated by a small energy). When Brown and Rustgi [14] first reported the x-ray absorption (XAS) spectrum in 1972, they compared it with the calculated total conduction-band density of states (DOS) and noted that the latter could not account for the observations. The DOS exhibits a slow rise to a broad peak ~2 eV above threshold, whereas the observed spectrum exhibits a very steep rise and then a relative flattening. The same year, Altarelli and Dexter (AD) [4] incorporated excitonic effects in the effective-mass approximation on the basis that a core hole in Si resembles a shallow P impurity and obtained a steep initial rise in agreement with the data. In 1989, Weng *et al.* [11] revisited the issue and pointed out that one should compute a projected DOS (PDOS) because, by symmetry, $2p$ electrons sample only the s-like and d-like components of the final states. They computed the projected DOS for Si and compared it with electron-energy-loss spectra (EELS) [12]. They concluded that they could account for the observed spectra without any excitonic effects. So far no reconciliation of these contradictory points of view has been proposed. In subsequent work, Batson [15,16] claimed that a model band structure combined with AD-like excitonic effects can be used to fit the experimental data with high accuracy.

In this paper we present a series of calculations in terms of which we show that both of the above conflicting interpretations of the Si $L_{2,3}$ spectra fail to capture the correct physics. We then report *ab initio* calculations of the actual core-excitation spectra with and without the effect of the core hole and establish that the near-edge structure of the observed spectra is dominated by short-range electron-hole effects produced by the "central cell" part of the

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electron-hole potential. Effective-mass excitonic effects due to the long-range screened Coulombic potential play a secondary role. Thus, the dominance of short-range excitonic effects is likely to occur in other semiconductors and, even more so, in insulators where screening is far less effective.

First, we address the two conflicting interpretations of the Si $L_{2,3}$ spectrum. We note that the PDOS used by Weng *et al.* [11,12] is in fact not very different from the total DOS used by Brown and Rustgi. In Ref. [11], Weng *et al.* arrived at their conclusion by comparing the PDOS only with EELS spectra which have a much larger intrinsic broadening than XAS spectra (part of it is instrumental and part is caused by smaller electron and hole lifetimes in an EELS experiment because of the much higher particle densities). The slow rise of the PDOS definitely cannot account for the steep rise in the XAS spectrum. Furthermore, in order to match the PDOS with the EELS spectrum, one must assume a band threshold at 99.0 eV, significantly lower than the XAS threshold of 99.8 eV, which agrees with the photoemission data of Himpsel *et al.* [2]. In Ref. [12], Weng *et al.* shifted the theoretical spectrum by a smaller amount and compared with higher-resolution data, but agreement between experiment and theory is not satisfactory for either the initial rise or the position of the first peak. Overall we conclude that the PDOS cannot provide a consistent interpretation of all the relevant data. As further confirmation of this conclusion we computed the actual x-ray absorption spectrum without electron-hole interactions, which is what PDOS is supposed to approximate. The calculations were performed using an all-electron energy-band code (full-potential linearized augmented plane wave method [17]). The resulting spectrum is shown in Fig. 1 using a threshold of 99.8 eV. The absolute magnitude of the absorption coefficient has not been adjusted. It is clear that spectra calculated without electron-hole interactions are in poor agreement with the experimental spectrum.

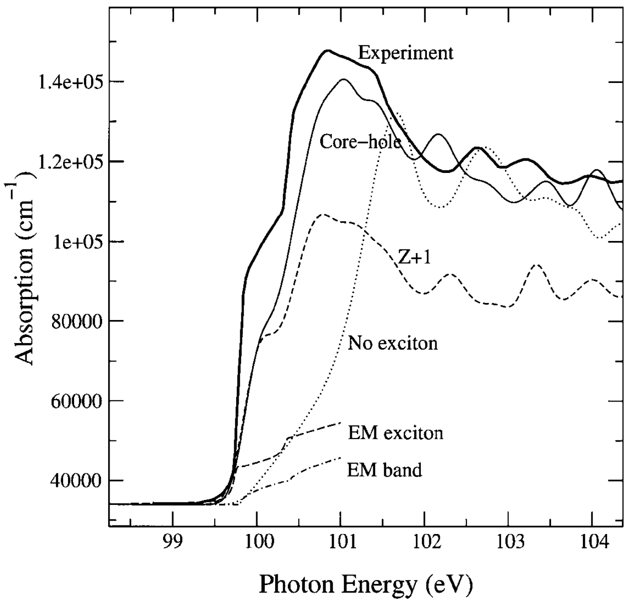

FIG. 1. Experimental and theoretical x-ray absorption spectra of the Si $L_{2,3}$ edge. Thick curve: experiment (Ref. [14]); solid curve: full calculation including electron-hole interactions with a self-consistent hole orbital; dashed curve: calculation using the $Z + 1$ model; dotted curve: calculation of excitation spectrum without electron-hole interactions; dash-dotted curve: effective-mass (parabolic band) spectrum without electron-hole interactions; long-dashed curve: effective-mass spectrum with hydrogenic excitonic effects as first done by Altarelli and Dexter (Ref. [4]).

Altarelli and Dexter [4] accounted for the Brown-Rustgi spectrum in terms of effective-mass excitons. The authors confined their attention to only the first 1 eV or so where the effective-mass approximation for the conduction-band density of states is valid. They adjusted the matrix element for transitions from the $2p$ core level to Bloch functions at the bottom of the conduction band and demonstrated a good fit to the near-edge experimental data. They argued that the resulting value of the matrix element is plausible. In Fig. 1 we show AD-like spectra using a matrix element extracted from the same calculation that produced the dotted curve. The dash-dotted line represents the case without effective-mass excitonic effects (i.e., the density of states multiplied by the matrix element) whereas the long-dashed line includes these effects. It is clear that, despite the initial steep rise, the AD spectrum cannot account for the observed spectrum. Note that one cannot invoke rescaling of the matrix element to bring the AD spectrum in agreement with the observed spectrum because the effective-mass excitonic correction is in principle tied to the initial rise of the calculated band spectrum (dotted curve in Fig. 1). Rescaling of this initial portion of the spectrum would require severe energy-dependent rescaling in the opposite sense at higher energies.

In principle, inclusion of electron-hole interactions in the excitation spectrum requires solution of the Bethe-Salpeter equation, as recently carried out both for valence and core-excitation spectra in a pseudopotential framework [3,18]. For core spectra, however, the hole is completely localized on a single atom so that the Bethe-Salpeter equation can be reduced to a single-particle calculation: For the Si $L_{2,3}$ edge, we impose a $1s^2 2s^2 2p^5$ configuration on one of the atoms of a large supercell and maintain that configuration throughout the self-consistency cycle of an all-electron calculation. We then calculate the corresponding one-electron excitation spectrum between the core state [19] and the available empty states that now reflect the effect of electron-hole interactions. The well-known $Z + 1$ model invokes an additional approximation in that it replaces the core hole by an extra proton on one of the nuclei in the supercell. Otherwise, the two types of calculations are identical in all respects. In both cases, there is an electron in the otherwise empty states above the valence bands that now reflect the presence of the hole or extra proton.

We have performed calculations using (a) a self-consistent hole in the core and (b) the $Z + 1$ model as described above. We employed supercells of 16, 32, and 64 atoms to test the convergence of the results. The differences between 32-atom and 64-atom results are very small. In addition to the spectrum, the calculation with the explicit core hole allows us to determine band threshold by subtracting the total energies of the initial (perfect crystal) and final (excited crystal) states. This threshold in principle would allow a positioning of the theoretical spectrum on the same energy axis as the experimental spectrum. The theoretical threshold is 100.4 eV, very close to the threshold extracted from both the XAS spectra [14] and photoemission spectra [2] experimental. Because of the theoretical error bar that may easily be of order 1 eV, we display the theoretical spectra using the experimental value for the threshold.

In Fig. 1 we show the results from a full-core-hole calculation and a $Z + 1$ calculation. We compare with the XAS spectra of Brown and Rustgi [14]. No adjustment has been made in the absolute value of the spectrum. The agreement between the full-core-hole calculation and experiment is indeed remarkable and is in sharp contrast to the other two approximations, namely, no electron-hole interactions and only effective-mass electron-hole interactions. The agreement is particularly good in the first two eV or so. The small-scale structure in the dropoff after the first peak is not reproduced in detail, which can be traced to numerical problems (convergence is very slow with number of $\mathbf{k}$ points in the Brillouin zone) and the well-known limitations of the local-density approximation in getting all the details of the conduction bands right. We further see that the $Z + 1$ approximation produces an excellent spectrum except for a scaling factor. Finally, the extended Coulomb tail, which is left out in a supercell calculation, in principle produces effective-mass excitons with very small binding energy and further steepening of the initial rise of the spectrum as it does in the AD effective-mass calculation. As Fig. 1 illustrates, any such additional effect will be only a small correction.

The net conclusion is unambiguous that the central-cell potential produced by the core hole has a substantial effect on the continuum final states, even though the long-range Coulombic tail produces only very shallow hydrogenic bound excitons. The origin of this effect can be traced to the fact that a short-range potential perturbs the conduction-band continuum by introducing broad resonances [20] (a similar effect is predicted for small quantum dots embedded in a bulk semiconductor [21]). Because the central-cell potential is relatively weak, these resonances do not descend into the band gap to produce deep states (a sulfur impurity, for which the central-cell potential is roughly double that of phosphorus, in fact causes an s-like deep state [20]). Thus, if it were not for the screened Coulombic tail of the potential, the extra electron of a P impurity would simply occupy the lowest conduction-band Bloch state that is largely unaffected by the central-cell potential. The screened Coulombic tail, however, binds it into hydrogenic effective-mass shallow levels. These results also suggest that core spectra from P impurities would result in strongly bound excitons below the continuum spectrum [22].

The all-electron calculations of core-excitation spectra are demanding even with high-performance parallel computers. Similar calculations would be even more demanding for SiO_2 and much worse for more complex systems such as the Si-SiO_2 and SiC-SiO_2 interfaces [23]. The preferred experimental method is EELS because of its spatial resolution [24]. Theoretical EELS spectra need not be as accurate as XAS spectra because of the increased broadening. For these reasons, we investigated the suitability of simply using projected densities of states of the relevant $Z + 1$ system instead of doing the full x-ray absorption calculation. One advantage of such an approach is the ability to use pseudopotential codes that are generally more efficient. The one ambiguity in such a calculation is the relative contributions of the s-projected and d-projected densities of states. Our full calculations for the Si $L_{2,3}$ spectrum in crystalline Si yield a s/d ratio of 1.1. We used this ratio with projected densities of states computed with a first-principles ultrasoft pseudopotential code [25]. The resulting spectrum, suitably broadened for an EELS spectrum is shown in Fig. 2. Agreement between experiment and theory is satisfactory.

In summary, we have demonstrated that short-range electron-hole interactions dominate the core-excitation spectrum of the $L_{2,3}$ edge in Si. These results have

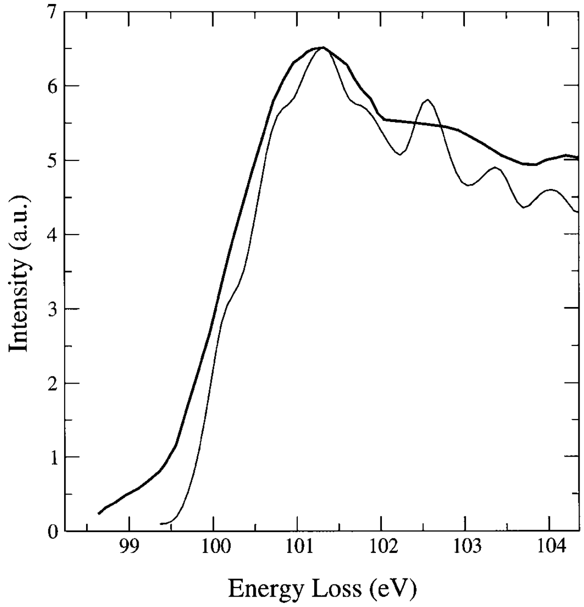

FIG. 2. Experimental and theoretical EELS spectra. Thick curve: experimental curve obtained with a VG Microscope HB501 UX using 100 kV acceleration voltage and collection semiangle of 13 mrad; solid curve: theoretical spectrum using the PDOS as described in the text.

profound implications for other semiconductors and especially for insulators for which dielectric screening is weaker, resulting in even stronger core-hole potentials. It is, therefore, imperative to avoid a free adjustment of theoretical band spectra on the energy axis, claiming agreement with data and hence no excitonic effects. Clear conclusions about the role of electron-hole interactions require at least $Z + 1$ calculations and/or determination of the band threshold using photoemission data.

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