

## ***Ab Initio* Inclusion of Electron-Hole Attraction: Application to X-Ray Absorption and Resonant Inelastic X-Ray Scattering**

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This work demonstrates a numerically feasible, yet realistic, calculational method for incorporating electron-core-hole interactions (core-hole effects) in the Bethe-Salpeter equation in solids, without recourse to tight-binding or analogous basis-set approximations. The method includes *ab initio* treatments of separate electron and hole dynamics and electron-hole interactions. The method is used to treat x-ray absorption (XAS), resonant inelastic x-ray scattering (RIXS), and core-hole excitons. Materials studied include LiF, NaF, KF, graphite, diamond, and *h*-BN. [S0031-9007(97)05117-X]

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Developing realistic models for optical properties of materials is a fertile field of research. Better treatments are needed to help understand and characterize known materials and revolutionize development of new materials based on improved simulations of potential properties. Empirical pseudopotential work of the 1960s and 1970s demonstrated the utility of microscopic, quantum-mechanical modeling of intrinsic semiconductor absorption spectra, even within independent-electron or mean-field pictures [1]. Nonetheless, pioneering work by Hanke and Sham [2] and others [3] suggests that improving on mean-field work, which often biases oscillator strength towards higher photon energies, implies treating electron-hole interactions in greater detail.

Ingredients of mean-field calculations—electron wave functions and band energies, including self-energy (many-body) effects—may be found *ab initio* with remarkable accuracy [4]. Realistic physical models for the screened electron-hole interaction are also available [5]. Having an *ab initio* capability is motivated by empiricism's requiring adaptations of a method for each material encountered. Yet synthesizing such detailed descriptions of electron and hole dynamics and interactions remains a daunting obstacle to be overcome before progress can be made. This Letter presents a solution of the electron-core-hole Bethe-Salpeter equation, and suitable extensions of this work could facilitate solution of the electron-valence hole analog. Objectives here include establishing feasibility of solving such equations in a model transferable to a wide range of materials and appraising the method by comparing results to experiment. The method is used to treat x-ray absorption (XAS), resonant inelastic x-ray scattering (RIXS), and core-hole exciton states. Results for graphite, *h*-BN, LiF, NaF, KF, and diamond are presented.

XAS results are dramatically affected by including the electron-hole interaction (core-hole effects): oscillator strength is transferred to lower frequencies, betraying excitons and altering continuum features. Sufficiently close to x-ray edges, band-structure effects may characterize ab-

sorption features and core-hole excitons. Present agreement with experimental XAS results improved remarkably in most cases (and somewhat in other cases) when including core-hole effects. RIXS results (modeling resonant scattering via Kramers-Heisenberg) are also influenced by core-hole effects: Expected total fluorescence yields [6] for incident  $h\nu$  rise or fall with absorption cross sections, but emission features at different  $h\nu'$  can scale similarly, so that RIXS spectra are likewise scaled [7]. This notion fails when a core electron is resonantly excited into several kinds of conduction bands (e.g.,  $\pi^*$  and  $\sigma^*$ ).

A subsidiary goal of this work is to incorporate some physical effects sufficiently well, so that discrepancies from experiment reveal signatures of omitted effects. This work includes detailed *ab initio* descriptions of one-electron states, including many-body corrections to band energies, but omits remaining renormalization of the electron propagator. Ignoring negligible core-hole hopping effects,  $\mathbf{p} \cdot \mathbf{A}$  matrix elements between *K* shell and band states as well as the separate electron and hole dynamics are well described using standard techniques. The core-hole potential is screened as is proposed in Ref. [5], which gives correct short- and long-range screening, and accurately includes differences in screening within bonds, atomic sites, etc. Because of the Pauli principle, the electron amplitude  $\Psi(\mathbf{r})$  in an electron-hole pair is constrained to be orthogonal to unperturbed orbitals of occupied bands. In a supercell calculation with a core hole placed at one site, occupied orbitals relax, changing the orthogonality constraint. However, I solve the Bethe-Salpeter equation in the Tamm-Dancoff approximation in reciprocal space, which (1) eases converging with respect to effective supercell size, because of the good scaling of this approach, (2) would be more adaptable to *L* and *M* core-hole excitations with their accompanying multiplet effects, and (3) permits conservation of total, electron-plus-hole momentum, a conservation law important to study RIXS, which is affected by interference between channels having the core hole in different, equivalent unit cells but leading to the same, valence-hole final states.

The Hamiltonian  $H$  was therefore  $H_0 + H_D + H_X$ ,  $H_0$  describing individual particle dynamics, and  $H_D$  and  $H_X$  the direct and exchange electron-hole interactions; cf. Fig. 1. Empirically, core-hole potentials were nearly spherically symmetric and could be fitted with analytic functions. Such symmetry is probably favored by atomic sites' high symmetries. (Calculations involving valence holes, although analogous to this work and apt to benefit equally from present algorithmic approaches, would be harder to realize because of valence holes' delocalization. In all other regards, the algorithmic developments discussed in this work should be directly transferable to the valence-hole exciton problem.) The singles-only constraint on excited many-body wave functions is well defined. While self-consistent supercell calculations account for all electronic and atomic relaxation in XAS final states, they may not use well defined  $\mathbf{p} \cdot \mathbf{A}$  matrix elements, which should be taken between initial and final many-body wave functions. Empirically, such distinctions have little effect.

Core hole-perturbed unoccupied states were constructed from unperturbed states in the lowest several conduction bands, computed on a regular Brillouin-zone grid of  $\mathbf{k}$ 's, corresponding, in terms of periodicity effects, to a supercell whose reciprocal-lattice vectors are differences between  $\mathbf{k}$ 's. Constraints on  $\Psi(\mathbf{r})$  were, therefore, these controlled approximations, only: truncating bands included and zone sampling. Unlike cluster calculations, this provided for an efficacious incorporation of long-range boundary conditions, and results presented are well converged with respect to zone sampling and bands included. Bloch functions were determined using a pseudopotential, plane-wave framework, with self-energy corrections included in band energies [8]. Analysis of full and pseudo wave functions confirmed proper treatment of electron-hole interactions, use of pseudopotentials notwithstanding. This work's restriction to  $K$ -shell x-ray absorption and emission obviated pseudopotential-inversion procedures to obtain  $\mathbf{p} \cdot \mathbf{A}$  matrix elements: *Absolute* cross sections were not sought. Computing Bloch states and the action of  $H$  thereon was accelerated by using basis functions from Ref. [9]: A band state was represented as

$$\begin{aligned}\Psi_{n\mathbf{k}}(\mathbf{r}) &= u_{n\mathbf{k}}(\mathbf{r}) \exp[i\mathbf{k} \cdot \mathbf{r}] \\ &= \sum_{\mu} C_{n\mathbf{k}}^{\mu} B_{\mu}(\mathbf{r}) \exp[i\mathbf{k} \cdot \mathbf{r}],\end{aligned}$$

and the same periodic  $B_{\mu}(\mathbf{r})$ 's were used for every  $\mathbf{k}$  and band  $n$ . With Bloch states and their energies known, computing action of  $H_0$  on  $\Psi(\mathbf{r})$  was straightforward.

Action of  $H_D$  was found using fast-Fourier-transform techniques. If we have

$$\Psi(\mathbf{r}) = \sum_{n\mathbf{k}} D_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}) \exp[i\mathbf{k} \cdot \mathbf{r}],$$

where  $\mathbf{k}$  samples the Brillouin zone, we may rewrite this as

$$\Psi(\mathbf{r}) = \sum_{\mu\mathbf{k}} E_{\mu\mathbf{k}} B_{\mu}(\mathbf{r}) \exp[i\mathbf{k} \cdot \mathbf{r}].$$

An analogous expansion for  $H_D\Psi(\mathbf{r})$  may be found in four steps: (1) Fourier transforming  $E_{\mu\mathbf{k}}$ 's with respect to  $\mathbf{k}$  onto a real-space grid, where  $H_D$ 's action is multiplication [but also dependent on  $B_{\mu}$ 's used to augment  $\Psi(\mathbf{r})$  and  $H_D\Psi(\mathbf{r})$ ]. After (2) acting with  $H_D$ ,  $H_D\Psi(\mathbf{r})$  was (3) transformed back to the  $\mathbf{k}$  domain, and (4) projected onto conduction bands included.

Action of  $H_X$  was assumed to matter for only  $l = 0$  and  $l = 1$  channels in the  $s$ - $p$  bonded materials considered. Ignoring minor variations in shapes of such partial waves throughout bands considered renders  $H_X$  as four projectors dependent on behavior of pseudo wave functions at atomic nuclei in free atom and solids and atomic exchange integrals,  $\langle 1sNs|V|Ns1s \rangle$  and  $\langle 1s,Np|V|Np,1s \rangle$ ,  $N$  being the valence shell.

Sampled  $\mathbf{k}$ 's formed a simple-cubic-like grid. For cubic solids, 2048  $\mathbf{k}$ 's were sampled vs 432  $\mathbf{k}$ 's in graphite and  $h$ -BN. Convergence vs sampling was accelerated by a grid shift by 0.25 times the smallest spanning vector along the (111) direction. From 8 to 12 conduction bands were used. Solution of the secular electron-core hole equation was done in several iterative methods. XAS spectra were found by a recursion method, obtaining a partial density of states for  $\mathbf{p} \cdot \mathbf{A}|\Phi_0\rangle$ , where  $|\Phi_0\rangle$  is the solid's ground state. Core-hole exciton levels were found by iterative diagonalization (preconditioned based on  $H_0$ ). For RIXS,  $|x(h\nu)\rangle \equiv (h\nu - H + i\Gamma)^{-1}\mathbf{p} \cdot \mathbf{A}|\Phi_0\rangle$  was found, for some  $h\nu$ , by iterative matrix inversion techniques, and fluorescence was found by summing over states coupled to  $|x(h\nu)\rangle$  by radiative recombination of valence electrons and core holes.

XAS results for F  $K$  edges in halides are shown in Fig. 2, including experimental results from Ref. [10]. Trends in oscillator strength, appearance of excitons, and agreement with experiment are evident when including  $H_D$  and  $H_X$ , although analogous Li  $K$ -edge results do not show the observed peak-height ratios [11]. Reproduction of other fine structures, found only when including core-hole effects, is very encouraging. XAS and RIXS results are presented in Fig. 3 for graphite, illustrating a simple scaling of emission spectra which may occur when core-hole

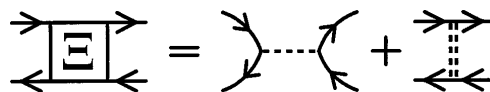


FIG. 1. Diagrammatic representation of incorporation of electron-hole scattering in Bethe-Salpeter equations. Electron-hole irreducible, four-point vertex  $\Xi$  includes direct (screened, double-dashed line) interaction between particles, and exchange (unscreened, single-dashed line) interaction. Electron and hole states are given as right- and left-going solid lines.

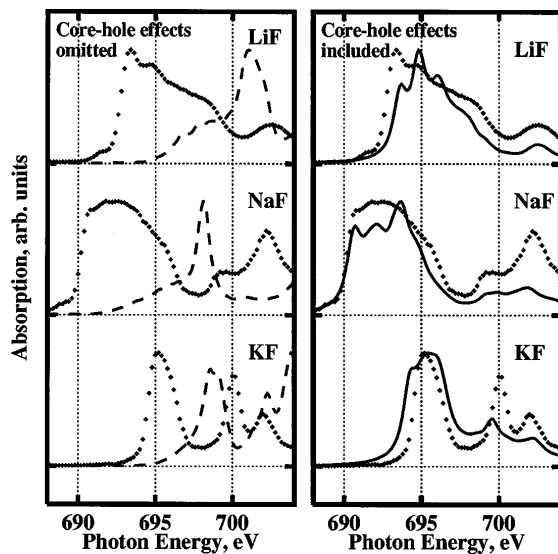


FIG. 2. XAS spectra near F  $K$  edge in LiF, NaF, and KF. Solid lines, with core-hole effects; dashed lines, without core-hole effects; points are experimental results [10].

effects are included, vs independent-quasiparticle results (cf. Ref. [12], and references therein). Double-peaked  $\sigma^*$  features (found also in  $h$ -BN) are confirmed in experiment, as in enhancement of  $\pi^*$  features [13,14].

Including  $H_D$  and  $H_X$  did not break symmetry as required to permit copious emission by radiative  $\pi \rightarrow 1s$  recombination in graphite. Thus, there may be a more subtle symmetry breaking invoked in Ref. [12] and discussed elsewhere [7,15]. Here, interference between channels with core holes on inequivalent sites was suppressed, and no quenching of symmetry breaking [16] permitting copious  $\pi$  emission was assumed. While a shortcoming in the present pseudopotential *and* past tight-binding descriptions of electron states cannot be absolutely ruled out, such "symmetry breaking" could conceivably result from doping. Finite photon momentum also achieves such symmetry breaking, but leads to much less  $\pi \rightarrow 1s$  recombination than observed and indicated by one full-potential work [17]. Cogent explanations of this and other emission [resembling ordinary x-ray emission (XES) results and experimentally observed] would be worthwhile to pursue. Others [18] have found further effects on RIXS when including core-hole effects within a tight-binding calculation, a trend not found here. In particular, the emission at 276 eV, which grows rapidly for  $h\nu$  between 1 and 1.5 eV above the  $K$  edge, is present here regardless of core-hole effects, even with zero admixture of an XES-like contribution. But this feature might be interpreted differently from that of Ref. [18], because of its vicinity to the  $\sigma$  band energy at  $M$  in this work.

XAS results for diamond are also included in Fig. 3, for comparison with graphite XAS results; modeling RIXS in diamond,  $c$ -BN and  $h$ -BN will appear elsewhere [19]. Predicted  $\pi^*$  core-hole excitons in  $h$ -BN were  $\sim 0.7$  eV

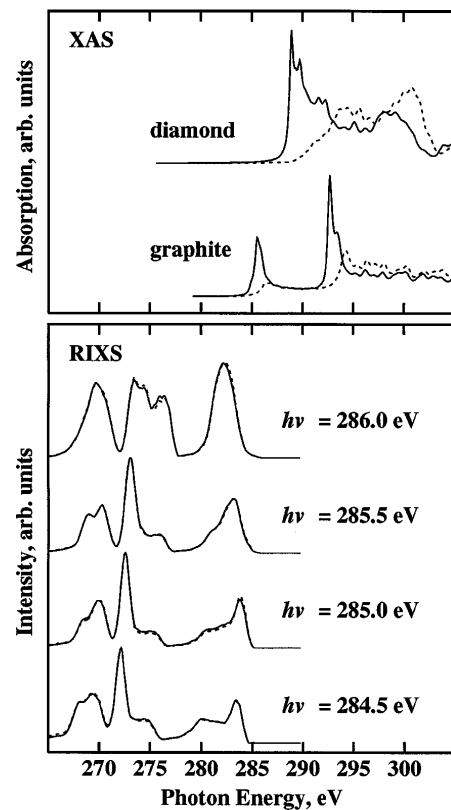


FIG. 3. XAS results for graphite and diamond and RIXS fluorescence results for graphite at indicated  $h\nu$ . The assumed C  $K$  edge was 284.5 eV; cf. Ref. [13]. Solid lines, with core-hole effects; dashed lines, without core-hole effects.

bound, those in the halides were often bound more strongly, and diamond exhibited a threefold degenerate exciton level  $\sim 0.2$  eV bound. Absent in this work is a lower, even-parity exciton, prediction of which produced considerable attention and varying results [20]. XAS supercell [13] and cluster [20] calculations for graphite and diamond, respectively, may also be compared with this work.

Roles of multiple electronic excitations and vibrational relaxation also require further attention, and this work may clarify effects of their absence. While many features of absorption and emission spectra have been simulated, further improvements in widths and heights of features, as well as describing background and analogous features, are beyond the scope of this work. Regarding multiple excitations, model calculations of two- and four-time correlation functions of  $\mathbf{p} \cdot \mathbf{A}$  operators in planar, unsaturated molecules, in which all electrons interact with a  $1s$  core hole, but not with each other, were also done. These suggested unaffected XAS results, analogs to graphite's anomalous  $\pi$  emission in RIXS, and a strong resonance fluorescence peak often suppressed by design in experiments [12,21].

In summary, this work applies a numerically feasible, yet realistic method to study x-ray absorption and

resonant, inelastic x-ray scattering in a wide variety of materials. The algorithmic technique may also benefit treatments of electron-valence hole systems.

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