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# Theory of Core Exciton Binding Energies for Excitons Near Interfaces

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## Abstract

The major chemical trends in the binding energies of core excitons near interfaces are predicted for excitons in zincblende hosts.

## 1. Introduction

In this article we report the first predictions of the major chemical trends in core exciton binding energies for intrinsic and extrinsic (impurity) excitons near interfaces, with initial emphasis directed toward the effects of the (110) GaAs/AlAs interface on the GaAs core excitons consisting of a *p* hole and an *s*-like  $A_1$ -symmetric electron. We find that a core exciton with a hole attached to a cation site has a binding energy determined primarily by the excited atom, but that an exciton with an anionic core hole, whether intrinsic or extrinsic, has a binding energy that depends primarily on the host atoms surrounding the excited atom, and to a lesser extent on the excited atom itself.

Traditionally, a core exciton has been defined as a low-lying, excited, correlated electron-hole-pair state of a nonconducting solid [1–4], whose hole is localized on a single atom. In the case of an intrinsic exciton, the hole is unable to hop to an adjacent atom during the exciton lifetime, because of the small overlap of polaronic wavefunctions centered on adjacent sites. For an impurity exciton, the hole level is normally nonresonant with the host atoms, and so the hole is trapped at the impurity.

A Wannier exciton is one in which the electron occupies a large-radius orbit about the hole and is well described by effective-mass theory for the long-range Coulomb interaction  $-e^2/\epsilon r$ . A Frenkel exciton has a small electron-hole separation, and here, as in the theory of bulk core excitons [5], we *define* a Frenkel core exciton to be one whose electron could be bound by *only* the central-cell part of the hole potential. Thus, the dominant binding agent of a Wannier exciton is the long-range electron-hole interaction, whereas the short-range interaction is sufficiently strong to bind an electron in a Frenkel exciton.

Until some recent synchrotron radiation experiments [6], it was widely believed that all excitons in zincblende hosts were Wannier excitons, with effective-mass binding energies  $Ry^* = (m^*/m \epsilon^2) Ry$  (where  $m^*/m$  is the effective mass and  $\epsilon$  is the static dielectric constant). Small departures from these already small binding energies had been noted and attributed to “central-cell” corrections.

However, synchrotron radiation measurements of core-level transitions found exciton line shapes which appeared to be markedly different from typical valence exciton line shapes [2], and so the somewhat vague term “core exciton” came to be used for what we call a core Frenkel exciton. Two outstanding scientific questions are: “Under what conditions can a host with only Wannier valence excitons support Frenkel core excitons?” and “Can one predict the Frenkel core exciton binding energies?” In this article we provide zero-order answers to these questions for excitons at interfaces using the same simple model used to predict binding energies of core excitons in bulk semiconductors [5].

## 2. Optical Alchemy Approximation

The primary difference between a core exciton and a valence exciton is that the core hole is localized and immobile in the former case, but diffuse in the latter. As a result, the interaction between the electron and the core hole is stronger than the electron–valence–hole interaction within the central cell of the hole. In fact, if the core hole is localized in a small-radius inner-shell atomic orbit, then its charge distribution is highly localized and, from the viewpoint of the electrons that participate in chemical binding, almost indistinguishable from the charge distribution of a nuclear proton. Thus, the creation of a core hole plus an electron by the absorption of a soft x ray is physically equivalent to the transmutation of the excited atom into one with an extra nuclear charge and an additional electron. For example, soft x-ray excitation “optically transmutes” Ga into Ge. This optical alchemy approximation [7] greatly simplifies the theory of core excitons, because it makes the theory equivalent to the theory of impurity levels [8]—with one pleasant difference: lattice relaxation effects important in many impurity problems can be neglected; in optical experiments, the Franck–Condon principle guarantees that the lattice does not relax during the optical transition; and the short Auger lifetime of core holes created in x-ray experiments usually guarantees that the observed recombination luminescence is emitted prior to lattice relaxation.

## 3. Criterion for Frenkel Core Exciton Formation

The condition for a core exciton to be a localized “Frenkel” exciton or an extended “Wannier” exciton is essentially the same as the condition for the excited atom’s optical transmutant atom to produce either a localized “deep” impurity state within the band gap or a delocalized effective-mass “shallow” trap [5,8]: *an exciton state is “deep” or a Frenkel state if the portion of the “impurity” potential within the central cell, by itself, is sufficiently strong to produce a bound state.* With this in mind, we greatly reduce the complexity of the core exciton problem by neglecting the long-range part of the electron–hole interaction  $-e^2/\epsilon r$  and consider only the central-cell part. This approximation causes us to overlook energies of the order of the effective-mass binding energy  $Ry^*$ ; hence, in the present theory, all Wannier excitons are predicted to have zero binding energy. Neglecting the long-range electron–hole interaction with its small (tens of meV) binding energy is not a serious approximation, however, because Frenkel core exciton binding energies are thought to be at least an order of magnitude larger in most cases. By truncating the electron–hole interaction at the boundary of the central cell of the core hole, we obtain a simple localized defect problem, which can be formulated in terms of the known atomic structure of the optical transmutant “defect.”

#### 4. Nature of the Theory

There are no clearly superior alternatives to a partly phenomenological, semiempirical theory of core exciton binding energies [5], because no present-day *a priori* theory is capable of predicting either core exciton or deep impurity levels with the desired  $<0.1$  eV accuracy.\* The electron-hole interaction potential typically has an expectation value of several eV in the central cell. Since this strong potential is highly localized in real space, it couples to the localized atomic orbitals which generate energetically distant (ca.  $\pm 10$  eV) host Bloch states. Hence, a successful *a priori* theory of Frenkel core excitons would have to predict correctly the effective one-electron energy bands over a range of ca. 20 eV; the accuracy of these bands would have to permit impurity level predictions with a precision of  $\lesssim 0.1$  eV. Furthermore, in such a precise theory, the interaction of the defect with the host would have to be treated self-consistently with regard to both the electronic and the lattice relaxation; finally, many-electron effects would also contribute on the 0.1-eV scale of precision.

However, a central message of the present work is that it is possible to predict *changes* in core exciton binding energies with confidence, because most of the theoretical uncertainties on the 20-eV scale can be removed empirically by fixing the binding energy for one host-excited-atom combination: then the changes of atomic energies on the smaller 1-eV scale can be handled with the necessary 0.1-eV precision [8].† Thus we present a theory of the *major chemical trends* in the core exciton binding energies: we predict how these energies vary as the host changes and how, within a single host, the core exciton energies depend on the excited (impurity) atom. The present work offers a global but imprecise view for *ordering* the various exciton binding energies, and its predictions must be interpreted in that context.

#### 5. Qualitative Physics

The essential qualitative physics governing the electronic structure of a core exciton at an interface is the same as for the bulk [5] and can be illustrated with a molecular model having a single *p* hole, one valence *s* orbital per atom, and, for the bulk, only *s*-like  $A_1$  molecular electronic orbitals. Here, for clarity of presentation, we repeat the argument for core excitons in bulk GaP, and indicate how an interface alters the physics [14]. The basic picture we present here is meant to be a simple qualitative guide which captures the physical essence of the calculations reported in Sec. 6.

To be specific, consider GaP; the atomic Ga and P energy levels split into the

\* Various excellent calculations of the same defect level typically disagree by more than 0.1 eV; e.g., for the  $T_2$  vacancy level in Si, one obtains energies relative to the valence band maximum of 0.96 [9], 0.8 [10], 0.7 [11], 0.5 [12], and 0.3 eV [13].

† For example, the 0.65-eV difference between the  $A_1$  impurity levels of substitutional O in GaP and GaAs is predicted in ref. 8 to be 0.52 eV, an accuracy of  $< 0.15$  eV; whereas the predicted oxygen level itself is in error by ca. 0.4 eV (part of which may be caused by lattice relaxation). Recent experiments by S. Modesti, D. J. Wolford, B. G. Streetman, and P. Williams (unpublished) on O in  $\text{GaAs}_{1-x}\text{P}_x$  support the predictions further.

bonding and antibonding levels of the molecule GaP; in a solid of many GaP molecules, the bonding levels become the valence band and the antibonding levels become the conduction band (Fig. 1). Creation of a core exciton at the Ga site "transmutes" Ga into Ge (also termed  $\text{Ga}^*$ ); likewise a core hole attached to P converts it into  $\text{P}^* = \text{S}$ . The impurity level in or near the fundamental band gap originates from the *antibonding* level, either  $\text{Ga}^*\text{P} = \text{GeP}$  or  $\text{GaP}^* = \text{GaS}$ . These antibonding levels should be thought of as repelled upward by the bonding-antibonding splitting, and form localized Frenkel states in the gap if they are not repelled upward enough to lie within the conduction band. If, on the basis of the central-cell potential alone, the antibonding state is resonant with the conduction band, then it will form a delocalized effective-mass Wannier exciton state once the long-range Coulomb interaction is included.

The antibonding levels have, on the average, cation character; that is, the  $\text{Ga}^*\text{P}$  and the  $\text{GaP}^*$  levels are Ge-like and Ga-like, respectively. Because the antibonding  $\text{P}^*$  level is repelled upward from the Ga atomic level, it is not P-like and cannot ever lie in energy below the Ga dangling bond energy, no matter how negative the optical transmutant's atomic energy  $\epsilon_{\text{P}^*}$  might be. The  $\text{P}^*$  core exciton energy is "pinned" to this Ga dangling bond or P vacancy energy and the level's character is determined by its orthogonality to the "hyperdeep" bonding level. If, contrary to what is shown schematically in Figure 1, the  $\text{P}^*$  antibonding exciton level lies below the conduction band edge, it forms a localized Frenkel exciton state; the addition of the attractive long-range Coulomb potential has little effect on its localization. If, as in Figure 1, the antibonding  $\text{P}^*$  level resonates with the conduction band, the resulting exciton is a delocalized Wannier exciton.

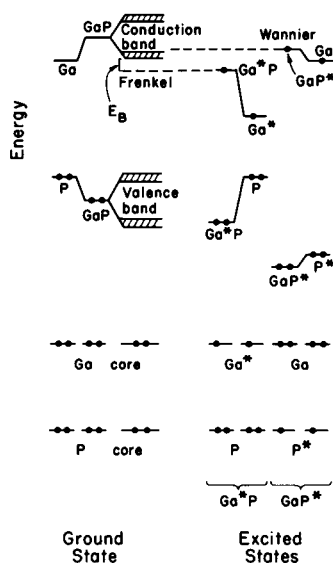


Figure 1. Schematic energy level diagram. The scale of energy is compressed and distorted (after ref. 5).

Unlike excitation of the P core, which produces pinning and a hostlike antibonding level, creation of a core hole in Ga leads to a transmutantlike ( $\text{Ga}^*$ -like or Ge-like) antibonding level. This transmutantlike level is not pinned to a nearby host level and depends primarily on the atomic structure of the transmutant. ( $\text{Ga}^*$  is influenced by pinning, but the pinning energy is more distant than for  $\text{P}^*$ .)

The effects of an interface on these exciton levels can be understood qualitatively in terms of Figure 1 also. Here we consider a cationic heterojunction, namely, an interface in which only the cations are different on opposite sides of the interface; GaP/AlP is an example of a cationic heterojunction. If the core hole is at the anion (P) site of GaP at a (110) cationic interface such as GaP/AlP, then crystal structure considerations reveal that the hole is surrounded by three Ga atoms and one Al atom. In this case the hostlike antibonding "deep" level has a strong (ca. 25%) Al character, and is affected by the differences between Ga and Al.

## 6. Theory

The theory [15] is based on the Hamiltonian  $H_{\text{total}} = H_0 + V + U = H + U$ , where  $H_0$  is the Hamiltonian for two periodic solids, GaAs and AlAs, uncoupled at the interface,  $V$  is a perturbation which creates two surfaces in each solid and then reconnects the surface atoms at opposite sides of the two interfaces, and  $U$  is the "defect" potential—the electron-hole interaction, plus the impurity-host potential difference if the core hole is attached to an impurity. All Hamiltonian matrices are based on a nearest-neighbor empirical tight-binding model in a basis with two  $s$  orbitals and three  $p$  orbitals per atom [8]. These orbitals are presumed to be symmetrically orthogonalized and therefore are Löwdin orbitals—although the nature of the theory does not require that they be displayed explicitly. The nature of the interface creation by  $V$  is depicted schematically in Figure 2 for

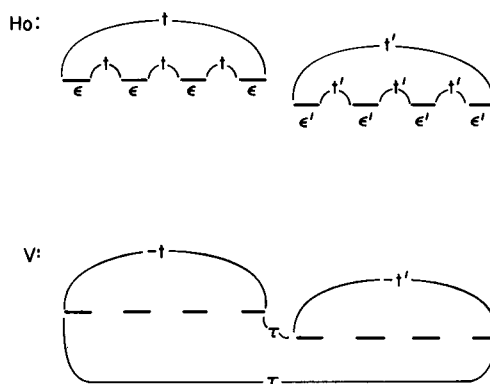


Figure 2. Schematic illustration of how an interface is constructed in the present calculation (after ref. 14).

the case of a one-dimensional monatomic one-orbital-per-atom tight-binding model. The matrix elements of  $H_0$  are determined by fitting known band structures [16–18], for a variety of zincblende hosts, the on-site matrix elements are found to be approximately proportional [12,16] to atomic energies, and the anion–cation transfer matrix elements scale as the inverse square of the bond length. Thus, since we neglect lattice relaxation,  $U$  is diagonal in a Löwdin basis [19]. (Lattice relaxation is presumed to be an almost monotonic function of trap depth, which does not alter the relative ordering of deep levels.) The central-cell interaction  $U$  is proportional to a difference in atomic energies, e.g., for a core hole bound to N at a As site in GaAs, it is proportional to the difference between O and P energies, O being the transmutant of N. Thus, we are led to the Koster–Slater eigenvalue equation for a localized central-cell perturbation [20],

$$\det [1 - G(E)U] = 0 \quad (1)$$

where we have  $G = (E - H)^{-1}$  and  $G = G^0 + G^0 V G$ , with  $G^0$  being  $(E - H_0)^{-1}$ . Equation (1) was solved using Bloch functions, labeled by two-dimensional wavevectors and layer index, defined for each layer of atoms and constructed from Löwdin orbitals indexed by atomic site and orbital symmetry  $l$ . To simplify the presentation of the results, we use the empirical rule [14]  $U_{l=0} \approx 2U_{l=1}$  for the “defect” potential felt by the electron in the central cell.

The resulting predicted deep  $s$ -like electron energy levels for an As-substitutional defect with a core hole in the bulk of GaAs and at the 110 interface with AlAs are given in Figure 3.

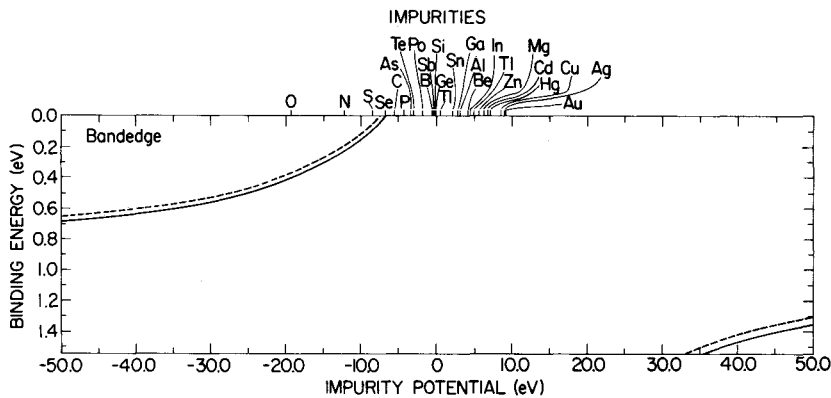


Figure 3. Predicted core exciton binding energies of bulk (solid) Frenkel excitons with  $A_1$  electrons and a core hole bound to an impurity at the As site of GaAs, as a function of the matrix element  $U$ . Relevant impurities are listed above the figure at their respective energies. The effect of the atom being at a (110) GaAs/AlAs interface is denoted by a dashed line. Wannier core excitons on this figure are depicted as being unbound, because we neglect the long-range electron–hole interaction.



## 7. Discussion

We have predicted and exhibited the chemical trends in binding energies of  $A_1$  symmetric electron states associated with anion-site core excitons both in the bulk and perturbed by a (110) GaAs/AlAs interface. These binding energies exhibit a small change in energy  $\Delta E \cong +0.02$  eV, when the core exciton is moved from the bulk to the interface. This weak dependence on the interface for GaAs/AlAs can be expected because the GaAs/AlAs interface is weak [21] in the sense that the cations involved, Ga and Al, have similar atomic orbital energies, and furthermore all the anions are identical As atoms. Calculations for the stronger interfaces [22]\* yield larger interface-induced core exciton energy shifts for the excitons with  $A_1$  electrons.<sup>†</sup> In some cases, the interface converts a Wannier core exciton into a Frenkel state.

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\* The interfaces studied include GaAs/ZnSe, GaAs/Ge, ZnSe/Ge, GaAs/GaP, Si/GaP,  $\text{In}_{0.47}\text{Ga}_{0.53}\text{As}/\text{InP}$ ,  $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{P}_y/\text{InP}$ , and others.

<sup>†</sup> The exciton consisting of a core hole and a  $T_2$  ( $p$ -like) electron polarized across the interface is normally most strongly perturbed.

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