

ELECTRONIC PROPERTIES ASSOCIATED WITH
DONOR IMPURITIES IN MULTIVALLEY SEMICONDUCTORS

Thesis by
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To my parents

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ABSTRACT

In this thesis we treat the theory of the electronic properties of excitons bound to a neutral donor in multivalley semiconductors. The materials considered here are Si, Ge and GaP. To deal with the effect of realistic band structures on the excitons bound to a neutral donor, we proceed in a systematic way by studying first the effects of the valley-orbit interactions on the donor states, then the energy levels of the low-lying states (including fine structures produced by the interparticle interactions) for the donor bound excitons, and finally the excitation spectroscopy for the bound multiexciton complexes (BMEC) associated with donors.

In the calculation of the valley-orbit interactions for the donor states, we have included the intervalley scattering effect for both the kinetic and potential energy terms. We find that the inclusion of intervalley kinetic energy term (which has been frequently ignored in the existing literature) is essential to stabilize the system (i.e., keep the donor states from being deep). To apply the valley-orbit interactions to more complicated systems, donor bound excitons and BMEC's, we have developed model Hamiltonians (one for each symmetry associated with the T_d point group) which yield analytic expressions for the matrix elements and produce practically the same energy eigenvalues as that of the exact donor Hamiltonian.

To understand the general electronic properties of excitons bound to neutral impurities for all electron-to-hole mass ratios, we first study this system in an idealized spherical model. Our theoretical

calculation indicates that the exciton is bound to the neutral impurity for all values of σ , the electron-to-hole mass ratio. We also find that in the spherical model, all the s-like excited states are not bound except for very small ($\sigma \lesssim .03$) or very large ($\sigma \gtrsim 10$) mass ratios. For donor bound excitons, we find that the low-lying excited states consist mainly of one-hole excitations with small admixtures of other possible excitations. The relative separations between these low-lying excited states are similar to that of a hydrogen ion, H^+ , for $\sigma \gtrsim 1$ and to that of a hydrogen molecule, H_2 , for small mass ratios ($\sigma \lesssim 0.1$).

When the effects due to realistic band structure are included, another set of low-lying excited states appears in the excitation spectrum of bound excitons. In these low-lying excited states one electron is excited into a state which can be described by a linear combination of ls-like orbitals localized in different valleys and has a crystalline symmetry that differs from the ground state. This set of excited states also plays an important role in the excitation spectrum of BMEC's associated with donors. We have calculated the excitation energies of these one-electron excited states in donor bound excitons and BMEC's. Our method is based on the Hartree-Fock approximation, which is suitable for treating the low-lying single-particle excitations. Our results for the energy separations between the ground state and the low-lying electronic excited states are in fairly good agreement with the experimental data interpreted using the shell model proposed by Kirczenow. Our calculation clarifies some

ambiguities in the interpretations of the luminescence data and provides better understanding of the BMEC's in multivalley semiconductors.

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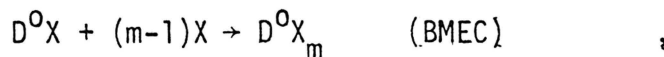
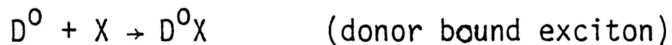
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CHAPTER 1

INTRODUCTION

The study of the electronic properties associated with impurities is essential to the understanding of semiconductor materials. Experimentally, these electronic properties can be studied by observing the optical transitions between the various electronic states. There are some fundamental excitations of the solids which are closely related to the spectroscopy and are important in determining the electronic properties. Among them are the well-known phonons and the excitons. The exciton can be viewed as an electron-hole pair bound together through their mutual coulomb interaction. Extensive studies on free excitons (FE) can be found in the literature.^(1,2)

Experimentally, it has been found that electron-hole pairs (EHP) can bind to a neutral impurity to form stable complexes^(3,4). When one EHP is bound, we denote it simply as a "bound exciton". When more than one EHP are bound to a single impurity center, we denote it as a "bound multi-exciton complex" (BMEC). If we use the symbols D^0 and X to represent a neutral donor and a free exciton, respectively, then, the formation of a donor bound exciton (one EHP bound to a neutral donor) and BMEC's can be described by the following processes:



where the symbol D^0X_m represents a system with m EHP bound to a single

neutral donor.

In Fig. I-1, a schematic diagram for the formation of bound excitons and BMEC's is shown. Physically, the bound excitons and BMEC's are very interesting finite many-body systems. Standard techniques for finite many-body systems (e.g., Hartree-Fock approximation, configuration interaction, etc.) may be applied to study the excitons bound to neutral impurities in solids. The physics of these systems is very similar to that of some well-known systems associated with electrons and positrons. In the ideal case, we may consider a donor as a hydrogen atom, an exciton as a positronium, then a bound exciton behaves like a positronium hydride ⁽⁵⁾. In some cases, a donor bound exciton may behave like a negative hydrogen ion (when the hole is much lighter than the electron) and sometimes like a H₂ molecule (when the hole is much heavier than the electron). Of course, the systems involving electrons and holes in solids are much more complicated than the associated systems involving electrons and positrons in vacuum. Some qualitative descriptions of these excited states of solids may be given as follows:

- 1) Electrons and holes in solids are described by effective masses which are determined by the curvatures of the conduction band and valence band at the extrema. These effective masses are usually an order of magnitude smaller than the free electron mass and, in many cases, anisotropic (e.g., in Si, Ge and GaP).

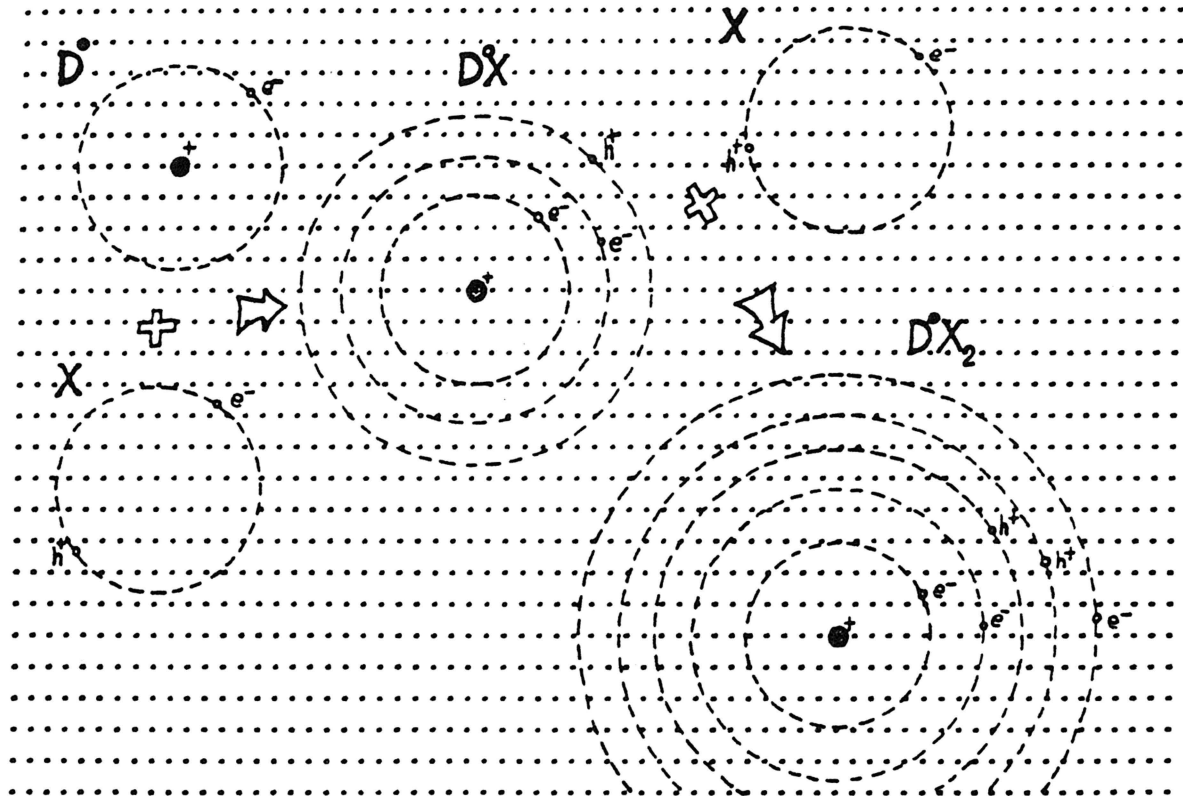


Figure I-1. Schematic diagram of the formation of bound excitons and bound multiexciton complexes in semiconductors. The periodic array of atoms in the semiconductors is indicated by dots. Impurity centers are denoted by " $\bullet$ "; electrons and holes are denoted by " e^- " and " h^+ ", respectively.

- 2) The charge distributions for these systems are spread out in space with a radius of approximately $20 \text{ \AA}$ in Si and $100 \text{ \AA}$ in Ge. The mutual interactions between these particles and the interactions between particles and the impurity center are screened by the valence electrons. This screening effect can be included by using a static dielectric function ⁽⁶⁾.
- 3) Both the smallness of the effective masses and the dielectric screening effect reduce the energy of these systems. The typical ionization energies for a free exciton and a neutral donor are $\sim 15 \text{ meV}$ and $\sim 50 \text{ meV}$ in Si. In Ge, they are about 5 times smaller. These energies are three orders of magnitude smaller than that for a hydrogen atom.

In this thesis, theoretical studies of the electronic properties of shallow donors and excitons bound to shallow donors in some semiconductors (Si, Ge and GaP) are reported. In the following subsections we discuss the neutral donor (D^0), donor bound exciton (D^0X) and BMEC (D^0X_m) separately. Since both D^0X and D^0X_m involve the same subsystem D^0 , it is easier to proceed by starting with the discussion of the neutral donor (Section A), then the donor bound exciton (Section B) and finally the BMEC's (Section C).

A. Neutral Donor (D^0)

The simplest semiconductor (e.g., GaAs) has both its valence band maximum and conduction band minimum at the center of the Brillouin

zone. The electron in this system can be described by an isotropic effective mass m^* . For a shallow donor, the wave functions associated with the bound electron states can be written as linear combinations of the Bloch functions (i.e., solutions to the electron states of the system without the impurity). The expansion coefficients (functions of $\vec{k}$) are called the "envelope functions" of the donor states. Since the binding energy of a shallow donor is only a small fraction (a few percents) of the width of the conduction band, we expect that its envelope function in $\vec{k}$ -space will be localized at the conduction band minimum (i.e., the mixing is smaller for Bloch states with higher energies and wave vectors further away from the band minimum). Within the effective mass approximation (EMA) ⁽⁷⁾, it can be shown that the Fourier transform of this envelope function in real space ($\vec{r}$ -space) satisfies the Schrödinger equation for a hydrogen atom, with the electron mass m_e replaced by the effective mass m^* , and the charge e replaced by the screened charge e/ϵ_0 , where ϵ_0 is the static macroscopic dielectric constant of the solid. However, for the materials Si, Ge and GaP, the band structures are much more complicated. In Fig. I-2, the conduction band structures for Si, Ge and GaP are plotted ⁽⁸⁾. As shown in this figure, the conduction band minima for all three materials do not occur at the center of the Brillouin zone, and cannot be described by a spherical effective mass. For Si and Ge, near each conduction band minimum the constant energy surfaces can be approximated by an ellipsoid, characterized by two effective masses, the transverse and the longitudinal. To see this in Ge,

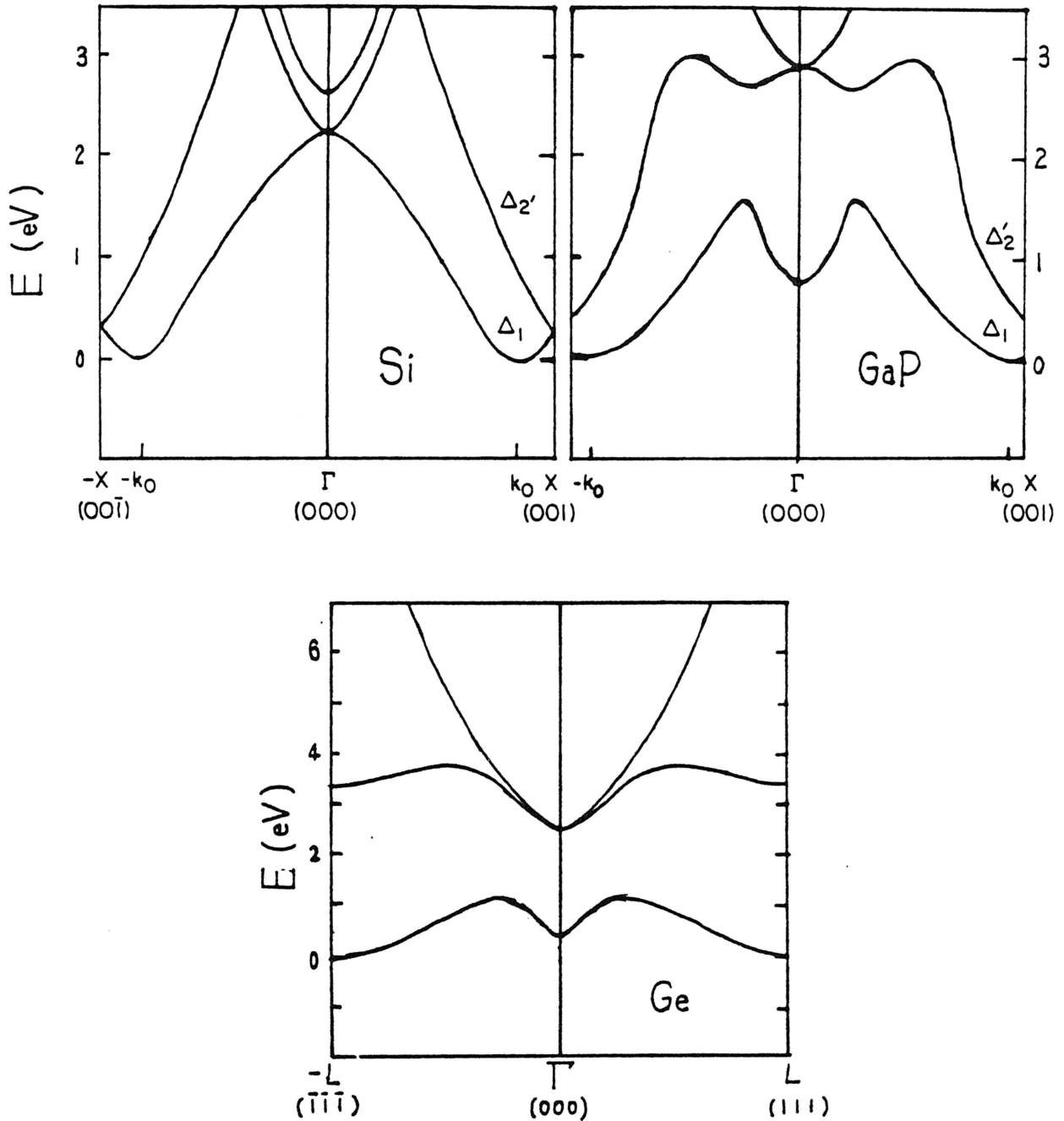


Figure I-2. Conduction band structures of Si, GaP and Ge (after Chelikowsky and Cohen ⁽⁸⁾). The positions of band minima of Si and GaP are marked " $\pm k_0$ ". The band minima of Ge occur at the L points.

we have to "cut-and-paste" the Brillouin zone, so that the two L-points are connected together. For GaP, the conduction minima occur at slightly smaller values of wave vector than the zone edge, (X point). Like in Ge, if we "cut-and-paste" the Brillouin zone such that the two X-points are connected together, we obtain a "camel's back" structure in the conduction band ⁽⁹⁾. Hence, further complications due to this camel's back structure have to be considered. We shall call the ellipsoidal (or camel's-back shaped) pocket in wave vector space ($\vec{k}$ -space) a "valley". According to symmetry, there are several equivalent valleys along different directions in these materials. The number of equivalent valleys, N is 6, 4 and 3, respectively for Si, Ge and GaP. It should be noted that in GaP each valley has two equivalent minima. These materials are usually referred to as "multivalley semiconductors". For shallow donors in multivalley semiconductors, the envelope functions of the impurity states defined in $\vec{k}$ -space are in general linear combinations of wave functions localized at the equivalent minima. Since these systems are invariant under the operations of T_d , the envelope functions must transform according to the irreducible representations of T_d . For Si and GaP, the envelope functions transform like the basis vectors associated with the representations Γ_1 (singlet), Γ_3 (doublet) and Γ_5 (triplet). The Γ_1 state is a scalar, which transforms into itself under all the representations in T_d . The two basis vectors of the Γ_3 representation transform like the functions $\sqrt{3}(x^2-y^2)$ and $(2z^2-x^2-y^2)$.

The three basis vectors of the Γ_5 representation transform like the functions x , y , and z , under the operations of the group T_d .

The schematic diagrams for these envelope functions (in $\vec{k}$ -space) associated with various symmetries for Si and Ge, respectively, are plotted in Fig. I-3. The parts of the envelope functions localized at different valleys are coupled together through the impurity potential. In the limit where this coupling vanishes, all donor states in Si (Ge) become six-fold (four-fold) degenerate (not including the spin degeneracy). This limit applies to most of the excited donor states. For the ground state this "intervalley" coupling is substantial, and the ground state will be split into several states, with each one transforming according to the Γ_1 , Γ_3 or Γ_5 representation. The energy differences between these states are called "valley-orbit splittings" (10).

In the past, a number of theoretical studies have been dedicated to the understanding of valley-orbit interaction in Si and Ge (11-14). Recently, it has been pointed out (15,16) that the above calculations have overestimated both the kinetic and potential energies by a substantial factor (≥ 2) for the process in which the electron envelope function is scattered from a given valley to other valleys. These two energy terms will be referred to as the "intervalley kinetic energy" and "intervalley potential energy", respectively. If we define the total envelope function as the sum of several envelope functions localized at the equivalent minima with no overlap between

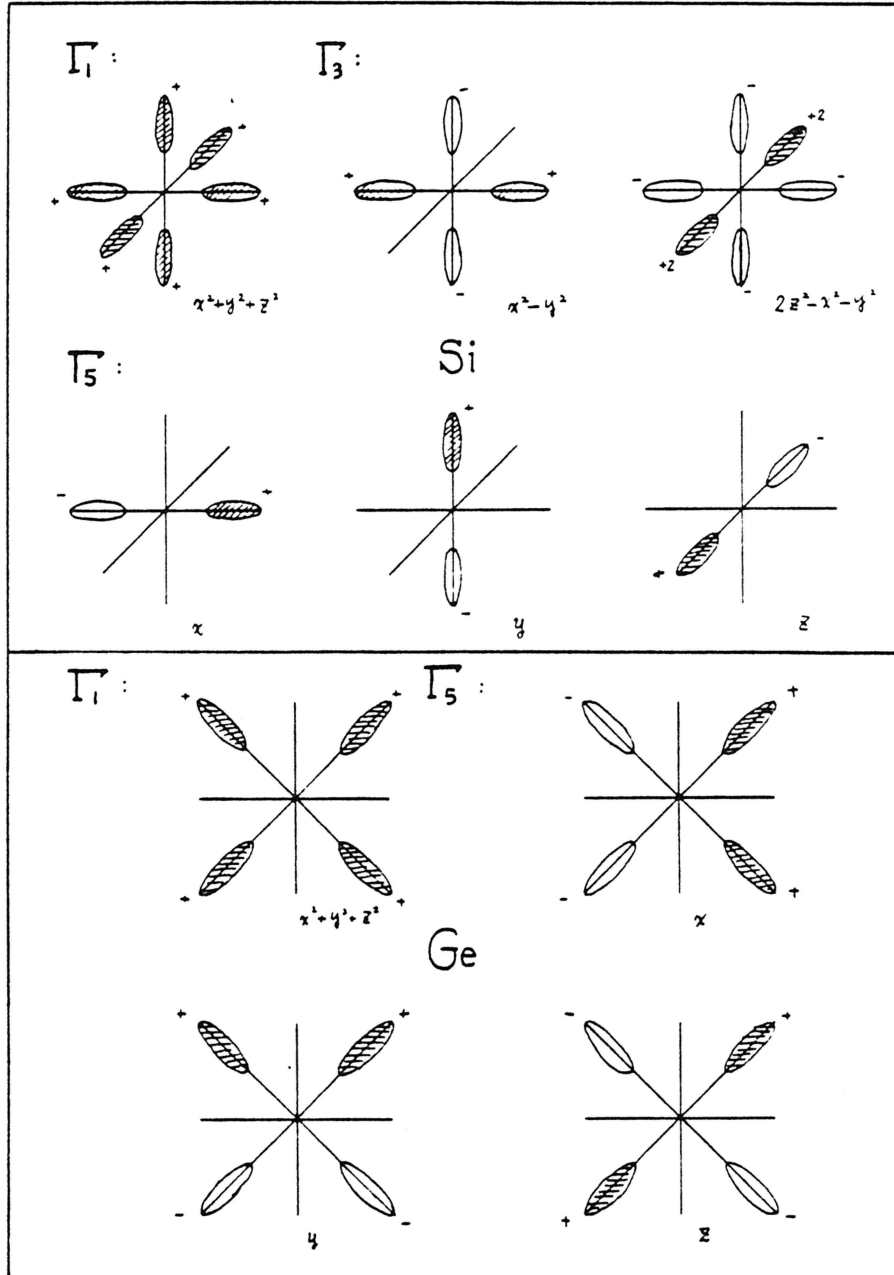


Figure I-3. Schematic diagram of the envelope functions of donor states for Si (Γ_1 , Γ_3 , and Γ_5 symmetries) and Ge (Γ_1 and Γ_5 symmetries).

these functions in $\vec{k}$ -space, then the intervalley kinetic energy is rigorously zero. Therefore, the valley-orbit splittings are completely determined by the "intervalley potential energy". In practical calculations, it is more convenient to describe the total envelope function as the sum of some standard functions (e.g., the Fourier transform in $\vec{k}$ -space of the Slater orbitals) localized at the equivalent minima. The overlap between these standard functions localized at different minima is nonzero; therefore, one has to include the intervalley kinetic energy explicitly. This intervalley kinetic energy has been shown to play an important role in determining the binding energy of the donor ground state ⁽¹⁶⁾. Unfortunately, the calculation performed in Ref. 15 has neglected this factor and is therefore unreliable. Since the conduction band is very anisotropic, many orbitals (with different angular momentum) have to be included in the expansion for the exact envelope wave functions. The number of orbitals needed can be reduced, if they are defined in an ellipsoidal coordinate system with an optimized eccentricity factor ⁽¹⁷⁾. The calculation performed in Ref. 16 only used a simple trial wave function and neglected the anisotropy of the conduction band. Therefore, no previous calculations seem to be appropriate for obtaining an accurate solution to the donor states in multivalley semiconductors.

We have made calculations for the donor states in multivalley semiconductors including the effect of realistic band structures. In Chapter 2 the donor states for various impurities in Si and Ge are studied extensively. Our calculation incorporates

the valley-orbit interaction and the ellipsoidal conduction band in a convenient way. Model Hamiltonians (one for each symmetry) are developed. These model Hamiltonians greatly reduce the computation required for applications to more complicated systems like bound excitons and BMEC's. We obtain the valley-orbit splittings for the ground state and the low-lying excited states in excellent agreement with the available experimental data.

For GaP, no calculation has been presented so far on the valley-orbit interaction in donor states, since the conduction band is not fully understood due to the complications from the camel's back structure. On the other hand, there exist a lot of interesting experimental data⁽¹⁸⁻²³⁾, which require a theory to interpret them. For example, many spectroscopic lines (obtained from either photo-absorption or luminescence) cannot be identified without understanding the effect due to the camel's back structure. Furthermore, some of these lines have anomalous oscillator strengths, which are hard to explain based on the understanding of regular donor states in Si or Ge. For example in the "two-electron transition" luminescence spectra for GaP:S, it is observed that the oscillator strength for the $2s(\Gamma_1)$ state is about ten times smaller than that for the $3s(\Gamma_1)$ state. In Chapter 3, we explore the camel's back effect on the donor states in GaP. Valley-orbit splittings on the low-lying states are calculated. We obtain the energy values for the low-lying excited states for the Γ_1 , Γ_3 , and Γ_5 symmetries, respectively.

Our results are in good agreement with the experimental data. We also find that the first Γ_1 -symmetry excited state (labelled $2s(\Gamma_1)$) is in fact a symmetric combination of p-like orbitals localized in the two equivalent minima associated with a camel's back valley. In the "two-electron transition" process one electron in the donor bound exciton recombines with the hole, leaving the other electron in an excited donor state (the final state). The oscillator strength for this process is proportional to the square of the overlap of the electron wave function in the bound exciton (which is s-like in character) with the electron wave function in the final donor excited state. This overlap is substantially smaller for a final donor state with p-like character than that with s-like character. This explains why the $2s(\Gamma_1)$ line observed in the two-electron transition luminescence ^(19,22,23) is much weaker than the $3s(\Gamma_1)$ line. We also made theoretical estimates of the oscillator strength ratios for the various luminescence lines associated with different final donor states in GaP:S. The results are in qualitatively good agreement with the experimental data ^(22,23).

B. Donor Bound Exciton (D^0X)

It was first proposed by Lampert ⁽²⁴⁾ in 1958 that the exciton can bind to a neutral donor to form a "bound exciton" (BE). In 1960, ⁽³⁾ Haynes first observed a sharp luminescence line due to the recombination

of the electron-hole pair in the BE. Since then, it has been found that the electron-hole recombination in BE's can produce lots of spectroscopic information about the material. Unfortunately, previous theoretical studies have not been very satisfactory. Several authors have treated this system in a spherical model (25-27). Their calculations are only valid for the electron-to-hole mass ratios restricted to be either very small or very large. This has led to questions concerning the binding of the exciton to a neutral impurity for a certain range of mass ratios. In the past one group has concluded that the bound exciton does not exist for the electron-to-hole mass ratios between σ_c and 10, where σ_c is somewhere between 1 and 2 (26,27). However, this is precisely the range in which the mass ratios for most practical systems (e.g., Si, Ge and GaP) lie.

In Chapter 4, we have studied the bound excitons in a spherical model for electron-to-hole mass ratios ranging from 0.01 to infinity. We first developed for each particle a model Hamiltonian which yields analytic solutions that are like the Hartree-Fock solutions. The difference between the exact Hamiltonian and the sum of single-particle model Hamiltonians can be treated as a perturbation. Then, the energies for the ground state and the s-like low-lying excited states are calculated using the second-order perturbation theory. Contrary to the predictions of some previous calculations (24,25), we obtain bound states for all mass ratios. We find that the low-lying excited states contain mainly one-hole excitations with small

admixture of other possible excitations (e.g., one-electron excitations and two-particle excitations, etc.). We shall refer to these states as the hole excited states. Our calculation predicts that the s-like hole-excited states are unbound relative to the dissociation into a free exciton plus a neutral impurity for mass ratios between 0.03 and 10. However, these states can be observed as resonances in the free exciton continuum if their lifetimes are long enough. In some materials (like GaP), the valley-orbit interaction could shift the energy of these states to greater binding so as to make some of the excited states bound.

The spherical model is not adequate for many of the well-studied semiconductors since they have a much more complicated valence and conduction band structures. Hence to make quantitative comparison with the experimental data, a theoretical study of the BE system including the effect of realistic band structures is necessary. In this thesis we present a theory for the excitons bound to shallow donors (i.e., donor bound excitons (D^0X)) in several multivalley semiconductors, Si, Ge and GaP. The results presented in Chapter 5 provide the basis for complete interpretation of the results of optical spectroscopy on these complicated systems.

The realistic band structures deviate from the spherical model substantially. In Section A, we have already discussed how to treat the multivalley conduction band properly. The valence band which determines the hole wave function is also very complicated. In Fig.

I-4 we plot the valence band structures for Si. The valence band structures for Ge and GaP are very similar to that for Si. As shown in this figure, the major complications of the valence band structures are the band degeneracies at $\vec{k}=0$ and the existence of a split-off band. With the inclusion of realistic band structures, the single particle states in the D^0X can be classified according to their transformation properties under the operations of the point group T_d . The total wave functions for the D^0X can be written as linear combinations of the products of the single-particle states which transform according to some irreducible representations of T_d . For the cases considered here, the electron-electron coupling is more important than the electron-hole coupling. Hence we can construct the two-electron product states first, then construct the three-particle product states from the two-electron product states and the single hole states. The spin states of the two electrons also have to be coupled together to produce a eigenstate of the total electron spin. According to the Pauli exclusion principle, the total wave function has to be antisymmetric with respect to the interchange of any two particles. For the present case, the electron-hole exchange interaction is negligibly small, hence, we only have to antisymmetrize the electron product states in the D^0X .

The excited states of this system can be classified into two categories: the hole-excited states similar to that defined previously in a spherical model, and the states in which one electron is excited into a state which would be degenerate with the ground state if the valley-orbit interaction were neglected. The hole-excited

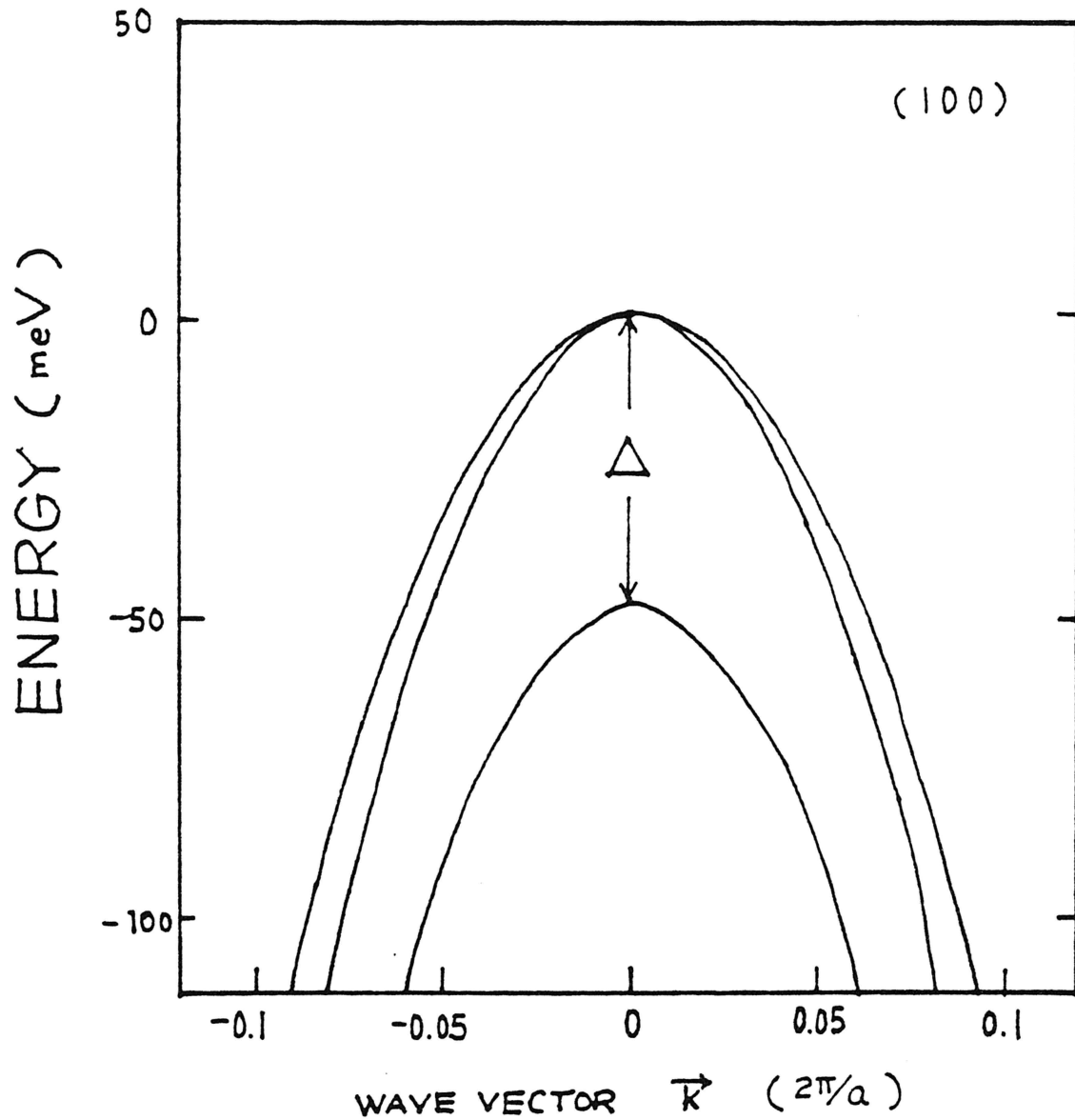


Figure I-4. Valence band structures of Si near the Γ -point along the (100) direction (see for example, E. O. Kane, J. Phys. Chem. Solids. Vol. 1, 82 (1956)). The spin-orbit splitting is denoted by Δ .

states are discussed in a spherical model (Chapter 4) and they are very similar for realistic band structures. The excited states belonging to the second category are studied extensively in Chapter 5. These states are of much interest, because they are closely related to the excitation spectra for BMEC's. Our calculation is based on the Hartree-Fock approximation, which is suitable for calculating the one-particle excitation energies for low-lying excited states. We can make detailed comparison between our theoretical results and the experimental data for the energy separations between the low-lying excited states and the ground state. Very good agreement between theory and experiment is obtained.

C. Bound Multiexciton Complexes

One of the more exciting phenomena in semiconductors is that in these systems it is possible to bind several electron-hole pairs (EHP) to a single impurity center to form a complex system called "bound multiexciton complex" (BMEC). This is an interesting finite many-body system. The mutual interactions between the particles in this system are the well-known Coulomb potential screened by a macroscopic dielectric constant. What is more striking is that when the density of EHP's in semiconductors is high enough, these EHP's can condense into an infinite many-body system around the neutral impurity. This system is known as "electron hole droplet" (EHD)⁽²⁸⁾. In 1970, Kaminskii et al⁽⁴⁾ observed a series of sharp lines (later

referred to as the KAPS lines ⁽²⁹⁾ lying at the longer wavelength side of the BE line. These lines were interpreted as originating from the recombinations of EHP's in the bound multiexciton complexes . Later this system has been studied experimentally by several authors (30-40). Theoretically, two different models have been proposed to interpret the experimental data. One is the BE-polyexciton model (by Morgan ⁽⁴¹⁾), which asserts that the excitons are loosely bound to the BE by a Van der Waals type interaction. According to this model, the recombination of an EHP near the impurity center should leave the rest of the excitons unchanged. However, the photoluminescence observed for the recombination of an EHP in the BMEC involving two EHP's (D^0X_2) in various acceptor-doped Si samples suggest that the final state for this process is a standard bound exciton ⁽³⁸⁾. This is in qualitative disagreement with the BE-polyexciton model. Furthermore, this model cannot explain the variation in the relative intensities of the Zeemann components of the KAPS lines ^(40,42).

The other model (proposed by Kirczenow ^(29,42)) is called the shell model (SM), which assumes that the wave functions of the BMEC can be classified as states belonging to various configurations in which each particle is described by a single-particle state transforming according to the irreducible representations of the point group. The coupling between states associated with different configurations is completely neglected. Although this model appears

to account for many features of the experimental data, many problems still remain. First, it is not clear why the coupling between states of different configurations can be neglected, since states of the same overall symmetry are in general coupled together by the total Hamiltonian.

Furthermore, due to inter-particle interactions, the energy levels associated with a given configuration should be split into several levels, each level corresponding to states associated with a certain overall symmetry. These levels may be closely spaced and can be referred to as fine structures. In the SM, these fine structures are completely neglected. Recently, Mayer, et al ⁽³¹⁾ and Elliott, et al ⁽⁴³⁾ have observed some fine structures in the BE in Ge and GaP, respectively. All these questions cannot be answered unless one calculates the inter-particle interactions in this system between states of all possible configurations.

We have studied the BE's in Si, Ge and GaP including the effect of realistic band structures. In Chapter 5, we calculate the fine structures in the electronic spectra of donor bound excitons and find that they are not negligible (about 0.5 meV in Si, 0.1 meV in Ge and 1.0 meV in GaP). Our calculated fine structure splittings are in reasonable agreement with the experimental data ^(31,36,37). We find that the coupling between states of different configurations is of the same order as the fine structure splittings. Hence, for states separated by energies large

compared to these fine structure splittings (e.g., the ground state and the first excited state in Si:P), the configuration coupling is negligible. But for the states which are closely spaced in energy, this coupling can be substantial.

In Chapter 6, the electronic structures of BMEC's in Si and Ge are studied. Quantitative results for the separations between the low-lying excited states and the ground state are also obtained using the Hartree-Fock approximation. The fine structures are neglected for simplicity. The excitation energies for the low-lying excited states are found to be in good agreement with the experimental data interpreted using the shell model. Our calculation clarifies some ambiguities in the interpretations of the luminescence spectra and provides a better understanding of the BMEC's in multivalley semiconductors.

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CHAPTER 2

THEORY OF DONOR STATES IN Si AND Ge

I. INTRODUCTION

The bound excited states for the donors in indirect materials, such as Si and Ge, have been successfully described by the Kohn-Luttinger effective mass approximation (EMA) ^(1,2,3). The ground states, however, because of the multivalley nature of the conduction band, are split into several states through the "valley-orbit interaction". As a result, the binding energy is increased substantially (about 35%) and a theory beyond the EMA is required. Moreover, the effect of valley-orbit splitting is extended to several s-like excited states because they have the same symmetries as the ground states, and their wave functions have to be modified to become orthogonalized to the new ground state wave functions. The splittings of the 2s-states for donors in Si were estimated to be about 1 meV by Kohn and Luttinger ⁽²⁾, using the quantum defect method. This, again, cannot be explained by the EMA.

To account for the valley-orbit splittings, Baldereschi ⁽⁴⁾ performed a quantitative calculation based on the multivalley effective mass equation (MV-EME) originally introduced by Fritzsche ⁽⁵⁾. Later, the MV-EME was also adopted by several authors ^(6,7,8,9,10) to calculate the ground state energies of donors in Si and Ge. Although the above calculations have produced results for Si in good agreement with experiment, it has been pointed out ^(11,12) that the MV-EME they used is inappropriate, because it includes spurious intervalley kinetic energy (KE) terms and neglects the overlap effects from Bloch functions in different valleys. By totally ignoring the intervalley KE terms and retaining the Bloch functions, Shindo and Nara ⁽¹¹⁾ proposed another multivalley effective mass equation. Recently, Altarelli et al ⁽¹³⁾ used this new MV-EME, intro-

ducing an Umklapp renormalization factor for the impurity potential due to the Umklapp processes, and obtained the ground state energies for Si:P and Ge:As in good agreement with experiment. However, as pointed out by Herbert and Inkson ⁽¹⁴⁾, the neglect of intervalley KE terms, could lead to unstable solution to the MV-EME, i.e., the binding energy is increased by about two orders of magnitude. Therefore, besides the Umklapp processes for the impurity potential, the correct theory for the valley-orbit interaction should also include the intervalley kinetic energies in a proper way. Most recently, Resca and Resta ^(15,16) (RR) have proposed a "spatial renormalization factor" (SRF) to replace the Umklapp renormalization factor (URF) used by Altarelli et al ⁽¹³⁾. With the use of SRF, they find that both the substitutional and interstitial donors in Si introduce a deep level ⁽¹⁶⁾. Unfortunately, the RR approach also neglected the intervalley KE term, which is of the same size as the intravalley KE term when the envelope function becomes very localized (necessary for a deep level). As will be shown in this paper, without the intervalley KE term, the use of URF also produces a deep level (unstable solution), whereas the introduction of intervalley KE stabilizes the system for substitutional donors. To account for the anisotropy of the conduction band of Si and Ge, elaborate trial wave functions (for instance, the linear combinations of ellipsoidal orbitals as used by Faulkner ⁽³⁾ for the EMA) must be used in order to produce reasonable results. The use of elaborate trial wave functions would make the evaluation of energy expectation values very complicated and further progress, such as solving the donor bound exciton problem, very difficult.

In this chapter, we report a calculation for the low-lying donor states in Si and Ge with the intervalley kinetic energies and mass anisotropy taken into account properly. We also propose a model Hamiltonian, such that when the ellipsoidal trial wave functions are used, the Hamiltonian matrix elements can be expressed analytically and give rise to the correct energy values for the ground states and all excited states. We obtained energy eigenvalues of the 6 lowest s(d)-like states for various donors in Si and Ge which are in excellent agreement with the experimental data for both the exact and the model Hamiltonians.

In Section II, the general theory for an impurity system is reviewed, and the model Hamiltonian is formulated. In Section III, the matrix elements of the exact Hamiltonian are evaluated, and the analytic expressions for the matrix elements of the model Hamiltonian are given. It is also shown that with suitable choice of some parameters, the model Hamiltonian can produce matrix elements which are almost exactly the same as those of the exact Hamiltonian. In Section IV, the numerical results for the exact Hamiltonian and model Hamiltonian are presented and shown to be almost identical. Finally, in Section V, a summary is presented.

II. THEORY

(a) Basic Problem

The single-particle Schrödinger equation of the perfect crystal perturbed by a substitutional impurity can be written as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + (V^0 + V) \right] \psi = E\psi \quad , \quad (1)$$

where V^0 is the self-consistent potential seen by each electron in the perfect crystal and V is the perturbation potential introduced by the impurity. Equation (1) can be rewritten for a pseudo wave function $\phi(\vec{r})$

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V_\phi^0 + V_\phi \right] \phi(\vec{r}) = E \phi(\vec{r}) \quad , \quad (2)$$

where V_ϕ^0 and V_ϕ are the pseudo potentials for the perfect crystal and impurity (9), respectively. Using the solutions to the problem without the impurity,

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V_\phi^0 \right] \phi_{nk}^0(\vec{r}) = E_n^0(\vec{k}) \phi_{nk}^0(\vec{r}) \quad ,$$

we can expand the solution to Eq. (2).

$$\phi(\vec{r}) = \sum_{nk} F_n(\vec{k}) \phi_{nk}^0(\vec{r}) \quad . \quad (3)$$

Substituting Eq. (3) into Eq. (2), one obtains (11)

$$H F_n(\vec{k}) = E_n^0(\vec{k}) F_n(\vec{k}) + \sum_{n'k'} \langle \phi_{nk}^0 | V_\phi | \phi_{n'k'}^0 \rangle F_{n'}(\vec{k}') = E F_n(\vec{k}) \quad . \quad (4)$$

For shallow donors, the wave functions are localized near the conduction band edges. If the other bands are separated by large energy gaps as compared to the binding energies, then one has to consider only one band. This is the case for Ge where the valleys are at the zone edge in the $[111]$ direction. In Si, however, the valleys are near the zone edge in the $[100]$ direction and the Δ_2 band and Δ_1 band are degenerate at the X-point (17). In this

case, substantial mixing of the two bands in the wavefunction $\phi(\vec{r})$ is expected. The multivalley problem for donors in Si is therefore intrinsically a two-band problem as recently pointed out by Pantelides ⁽¹⁸⁾. An equivalent formulation is to allow $\vec{k}$ to range over more than one Brillouin zone with a different zone for each band ⁽¹⁹⁾. In this formulation

$$H F(\vec{k}) \equiv E^0(\vec{k}) F(\vec{k}) + \sum_{\vec{k}'} \langle \phi_{\vec{k}}^0 | V_{\phi} | \phi_{\vec{k}'}^0 \rangle F(\vec{k}') = E F(\vec{k}) \quad . \quad (5)$$

The conduction band of Si can still be approximated very well by a parabolic function ⁽¹⁷⁾. The extension of the wave function $F(\vec{k})$ into the second Brillouin zone automatically takes into account the mixing with the Δ_2 band.

For indirect zinc blende semiconductors, the conduction band has several equivalent minima located at $\vec{k}_j$, where j ranges over the N equivalent valleys. The value of N is 6 and 4, respectively, for Si and Ge. Since the total Hamiltonian H is invariant under the point group T_d , its eigenstates should transform as the partners of certain irreducible representations, Γ , under the operations of T_d . We can write the solution to Eq. (5) with a given symmetry Γ as linear combinations of the wave functions $F_j(\vec{k}-\vec{k}_j)$ localized at N equivalent valleys ⁽²⁾, namely

$$F_{\Gamma}^{\sigma}(\vec{k}) = \sum_{j=1}^N \alpha_j^{\sigma}(\Gamma) F_j(\vec{k}-\vec{k}_j) \quad , \quad (6)$$

where the coefficients $\alpha_j^{\sigma}(\Gamma)$ are determined by group theory. σ labels the degenerate partners and the wave functions $F_j(\vec{k}-\vec{k}_j)$ are related to one another simply by the operations belonging to the group T_d . It is clear that if the

functional form of $F_j(\vec{k}-\vec{k}_j)$ is known for a given valley, then the total wave function $F_\Gamma^\sigma(\vec{k})$ is completely determined by Eq. (6). If we expand the function $F_\Gamma^\sigma(\vec{k})$ on a complete orthonormal set of functions $\{\sum_j \alpha_j^\sigma \beta_v^j(\vec{k}-\vec{k}_j)\}$, then we have, for the j^{th} valley,

$$F_j(\vec{k}-\vec{k}_j) = \sum_v C_v \beta_v^j(\vec{k}-\vec{k}_j) \quad . \quad (7)$$

Substituting Eq. (7) in Eq. (5), we obtain after the application of symmetry (8)

$$\sum_v H_{\mu v} C_v = E \sum_v N_{\mu v} C_v \quad , \quad (8)$$

where

$$H_{\mu v} = \sum_{\lambda=1}^m g_\lambda(\Gamma) H_{\mu v}^{(\lambda)} \quad (9)$$

and

$$N_{\mu v} = \sum_{\lambda=1}^m g_\lambda(\Gamma) N_{\mu v}^{(\lambda)} \quad . \quad (10)$$

$H_{\mu v}^{(\lambda)}$ and $N_{\mu v}^{(\lambda)}$ are the matrix elements for the basis wave functions associated with the intravalley ($\lambda=1$), intertransverse ($\lambda=2$), and interlongitudinal ($\lambda=3$) terms. All three terms are present in Si ($m=3$); the last term ($\lambda=3$) is absent in Ge ($m=2$). The coefficients $\{g_\lambda(\Gamma)\}$ which are obtainable from symmetry can be found in Refs. 8 and 10.

(b) Formulation of the Model Hamiltonians

In this section, we derive an expression for model Hamiltonians (one for each possible irreducible representation) which operates on the envelope function for a single valley. We obtain closed form, approximate expressions for these Hamiltonians. This is accomplished by neglecting intervalley overlap matrix elements which can be shown to yield very small corrections ($\lesssim .1\%$) to the energy eigenvalues.

Returning to Eq. (5), we can write H as the sum of the kinetic energy operator T and the potential energy operator V. We first examine the potential energy part of H. V is an integral operator whose kernel is defined by $\langle \phi_k^0 | V_\phi | \phi_{k'}^0 \rangle$. The potential V_ϕ can be written as a point charge potential $V_{PC}(\vec{r})$ plus a short-range core potential $W(\vec{r})$. Because of its short-range nature, the Fourier transform of $W(\vec{r})$ should be a smooth function over the appropriate region in k-space. Hence we can assume that the matrix element of $W(\vec{r})$ for $\vec{k}$ and $\vec{k}'$ near the band minima are given by

$$\langle \phi_{k_i}^0 | W | \phi_{k_j}^0 \rangle \equiv J_\lambda, \quad (11)$$

where J_λ takes on three values depending on whether $\vec{k}_i$ and $\vec{k}_j$ are in the same valley ($\lambda=1$), on different axes ($\lambda=2$), or on the same axis ($\lambda=3$).

The point-charge part can be written approximately as

$$\langle \phi_k^0 | V_{PC} | \phi_{k'}^0 \rangle = R_\lambda \tilde{V}_{PC}(\vec{k} - \vec{k}') \quad , \quad (12)$$

where $\tilde{V}_{PC}(\vec{q}) = \frac{-4\pi e^2}{q^2 \epsilon(\vec{q})}$ is the Fourier transform of $V_{PC}(\vec{r})$ with $\epsilon(\vec{q})$ being the wave-vector dependent dielectric function which is customarily represented by the empirical form (21,22)

$$\frac{1}{\epsilon(\vec{q})} = \frac{Aq^2}{q^2 + \alpha^2} + \frac{(1-A)q^2}{q^2 + \beta^2} + \frac{1}{\epsilon(0)} \frac{\gamma^2}{q^2 + \gamma^2} \quad (13)$$

and R_λ are the Umklapp renormalization factors as defined in Ref. 13. As before, λ implies the relationship between $\vec{k}_i$ and $\vec{k}_j$, the centers of the i^{th} and j^{th} valleys, respectively. For any two basis functions $\beta_\mu^i(\vec{k}-\vec{k}_i)$ and $\beta_\nu^j(\vec{k}-\vec{k}_j)$, the potential matrix element is given by

$$V_{\mu\nu}^{(\lambda)} = J_\lambda \beta_\mu^{i*}(0) \beta_\nu^j(0) + R_\lambda \int d^3r e^{i(\vec{k}_j - \vec{k}_i) \cdot \vec{r}} V_{PC}(\vec{r}) \beta_\mu^{i*}(\vec{r}) \beta_\nu^j(\vec{r}), \quad (14)$$

where $\beta_\nu^j(\vec{r}) e^{i\vec{k}_j \cdot \vec{r}}$ be the Fourier transform of $\beta_\nu^j(\vec{k}-\vec{k}_j)$ in real space, and similarly for $\beta_\mu^i(\vec{r}) e^{i\vec{k}_i \cdot \vec{r}}$.

We now derive a functional form for the potential term for the model Hamiltonians, which yields analytic expressions for the basis functions defined in an ellipsoidal coordinate system. All the materials treated in this paper have very anisotropic conduction bands. If we define the ratio of the longitudinal effective mass m_ℓ to the transverse effective mass m_t as the "anisotropy factor" μ , then the values of μ are about 5 for Si and 20 for Ge. To account for the anisotropic charge distribution caused by the kinetic energy term, we choose the basis functions to take the form $\beta_\mu(\vec{r}')$, with the argument $\vec{r}'$ defined as

$$\vec{r}' = (x, y, z/\zeta) \quad , \quad (15)$$

where the parameter ζ is called the "eccentricity factor". The appropriate eccentricity factor ζ can be determined by a variational calculation, where the energy expectation value of the lowest-lying state of certain symmetry is minimized. When ellipsoidal basis wave functions are used, it is convenient to write the point charge potential $V_{PC}(\vec{r})$ in an ellipsoidal coordinate system as well,

$$V_{PC}(\vec{r}) = - \frac{e^2}{\epsilon(r' \sqrt{1-g^2 \cos^2 \theta'}) r' \sqrt{1-g^2 \cos^2 \theta'}} , \quad (16)$$

with $g^2 \equiv 1 - \zeta^2$ and θ' is the polar angle in an ellipsoidal coordinate system. The matrix elements $V_{\mu\nu}^{(\lambda)}$ in Eq. (14) are rather complicated, since the term $\sqrt{1-g^2 \cos^2 \theta'}$ mixes states of angular momentum quantum number differing by an even integer. For s-like wave functions we choose the model potential to have the form (see Appendix A for derivation of this functional form)

$$V_{SM}^{(\lambda)}(\vec{r}') = \frac{J_\lambda \delta(\vec{r}')}{\zeta} - R_\lambda \frac{e^2}{\epsilon'(r') r'} \frac{f_\lambda a_o \sin(p_\lambda \Delta r')}{(p_\lambda \Delta r')} , \quad (17)$$

where

$$a_o \equiv (\sin^{-1} g)/g , \quad (18)$$

$$\Delta \equiv 2\zeta k_o ,$$

and

$$\frac{1}{\epsilon'(r')} \equiv \frac{1}{\epsilon_o} \sum_{\nu=1}^4 S_\nu e^{-h\sigma_\nu r'} \quad (19a)$$

$$\text{with } S_v = (1, A\epsilon_0, (1-A)\epsilon_0, -1) \quad (19b)$$

$$\text{and } \sigma_v = (0, \alpha, \beta, \gamma). \quad (19c)$$

f_λ , p_λ and h are adjustable parameters obtained by minimizing the differences between the matrix elements of this model potential and the exact matrix elements $V_{\mu\nu}^{(\lambda)}$. As will be shown in Sec. III, with suitable choice of the parameters f_λ , p_λ and h the matrix elements of the model potential can fit the exact matrix elements extremely well. For non-s-like states, which are only important for the expansion of excited states and have vanishing amplitude near the origin, the short-range correction and intervalley scattering terms are negligible. Thus, the effective potential is simply the hydrogenic potential screened by the dielectric constant ϵ_0 ⁽²⁾. Hence, the total model potential operator can be written approximately as

$$V_M^\Gamma(\vec{r}') \approx \sum_\lambda g_\lambda(\Gamma) V_{SM}^{(\lambda)} |0\rangle\langle 0| - \frac{e^2}{\epsilon_0 r' \sqrt{1-g^2 \cos^2 \theta'}} (1 - |0\rangle\langle 0|) \quad (20)$$

where $|0\rangle\langle 0|$ is the projection operator onto $\ell=0$ states.

The $\vec{q}$ -dependence of the dielectric function, short-range core potential, and the intervalley scattering terms have been neglected for the mixing of s-like states with non-s-like states.

The next step is to examine the kinetic energy (KE) part of the total Hamiltonian. In general, the KE matrix elements $T_{\mu\nu}^{(\lambda)}$ can be calculated exactly by carrying out the integration in k-space, i.e.,

$$T_{\mu\nu}^{(\lambda)} = \int \beta_\mu^i(\vec{k}-\vec{k}_i) E^0(\vec{k}) \beta_\nu^j(\vec{k}-\vec{k}_j) d^3k \quad (21)$$

where the full knowledge of the dispersion function for the conduction band in the extended zone scheme is required. Because of the localized nature of the envelope wave functions in k-space, it is a good approximation to write $E^0(\vec{k})$

as the sum of $E_i^0(\vec{k}-\vec{k}_i)$ defined for the i^{th} valley as

$$E_i^0(\vec{k}-\vec{k}_i) = \hbar^2(k_x^2 + k_y^2)/2m_t + \hbar^2(k_z - k_0)^2/2m_\ell, \quad (22)$$

where we have chosen $\vec{k}_i = k_0 \hat{z}$, with k_0 being the distance of the band minimum from the zone center. For Ge, the band minimum is right on the L-point. For Si, the value of k_0 used in this paper is $0.86(\frac{2\pi}{a})$ ⁽²³⁾, where a is the lattice constant. The functions $E_i(\vec{k}-\vec{k}_i)$ are truncated at the values of $\vec{k}$, where these functions centered at different valleys intersect with each other. This truncation is necessary for evaluating the intervalley KE so as to avoid the spurious overlapping of the function $\frac{\hbar^2(k_z - k_0)^2}{2m_\ell}$ with the wave functions centered at other valleys (e.g., $\vec{k}_i = -k_0 \hat{z}$) (14).

For the intravalley term, this restriction is unnecessary, and the model KE operator in real space can be written as

$$T_M^{(1)}(\vec{r}) = -\frac{\hbar^2}{2m_\ell} \left(\frac{\partial}{\partial z} \right)^2 - \frac{\hbar^2}{2m_t} \left[\left(\frac{\partial}{\partial x} \right)^2 + \left(\frac{\partial}{\partial y} \right)^2 \right], \quad (23)$$

where we have chosen the z -axis to be the longitudinal axis. For the intervalley terms, we only have to consider the matrix elements between s -like states (the others are negligibly small). As will be shown in Sec. III, we can find a simple closed-form operator to approximate the exact intervalley KE operator (defined in elliptic coordinates, $\vec{r}'$)

$$T_M^{(\lambda)}(\vec{r}') = \frac{\hbar^2}{2m_t} B \left[\overleftarrow{\left(\frac{\partial}{\partial \vec{r}'} \right)} (C e^{-\eta_\lambda \Delta r'} - (C-1)e^{-2\eta_\lambda \Delta r'}) \overrightarrow{\left(\frac{\partial}{\partial \vec{r}'} \right)} \right]; \quad \lambda = 2, 3, \quad (24)$$

with

$$B \equiv \frac{1}{3} \left(2 + \frac{1}{\mu \zeta^2} \right) , \quad (25a)$$

where $\mu \equiv m_\ell / m_t$

$$\text{and} \quad \Delta \equiv 2\zeta k_0 . \quad (25b)$$

The operators $(\frac{\partial}{\partial \mathbf{r}'})$ with arrows pointing left or right, are defined as

$$\overrightarrow{\left(\frac{\partial}{\partial \mathbf{r}'} \right)} R(\mathbf{r}') \equiv \frac{\partial R(\mathbf{r}')}{\partial \mathbf{r}'} \equiv R(\mathbf{r}') \overleftarrow{\left(\frac{\partial}{\partial \mathbf{r}'} \right)} . \quad (26)$$

C and η_λ are chosen to minimize the differences between the model matrix elements $\langle \beta_\mu | T_M^{(\lambda)} | \beta_\nu \rangle$ and the exact ones $\langle \beta_\mu | T^{(\lambda)} | \beta_\nu \rangle$. The total model KE operator is therefore written as

$$T_M^\Gamma = T_M^{(1)} + \sum_{\lambda=2}^3 g_\lambda(\Gamma) T_M^{(\lambda)} |0\rangle\langle 0| . \quad (27)$$

Combining Eq. (27) with Eq. (20), we therefore get the closed-form expression for the model Hamiltonian of symmetry Γ

$$H_M^\Gamma = T_M^\Gamma + V_M^\Gamma . \quad (28)$$

In the next section we derive the explicit expressions for the matrix elements of the exact Hamiltonian H and the model Hamiltonians, H_M^Γ , and see how closely they are related to each other.

III. MATRIX ELEMENTS

In this section, we evaluate the matrix elements for both the exact and model Hamiltonians and determine the parameters in model Hamiltonians which

give the best fit between the two sets of matrix elements. Slater orbitals in an ellipsoidal coordinate system are used as the basis set. The z-axis can be used as the longitudinal axis of the ellipsoidal coordinate system. Analytic expressions for the matrix elements for the model Hamiltonians are also given. For convenience we use atomic units (a.u.) with energy measured in units of $e^4 m_t / 2 \epsilon_0 \hbar^2$ (Rydberg, Ry) and distance measured in units of $\epsilon_0 \hbar^2 / m_t e^2$ (Bohr), where m_t is the transverse effective mass.

The radial part of each basis function is made up of a linear combination of ellipsoidal Slater orbitals,

$$R_{nl}(r') = \frac{r'^l e^{-b_{nl} r'}}{\sqrt{N_{nl}}} \quad , \quad (29)$$

where N_{nl} is the normalization constant,

$$N_{nl} = \frac{(2b_{nl})^{\ell+3/2}}{\sqrt{(2\ell+2)!}} \quad . \quad (30)$$

The exponents b_{nl} are chosen to cover the entire physically reasonable range.

The actual basis function $\beta_{nlm}(\vec{r}')$ is formed by taking the product of a spherical harmonic $Y_{lm}(\Omega')$ with an appropriate radial function obtained from $R_{nl}(r')$ by employing the Schmidt orthogonalization procedure (24)

$$\beta_{nlm}(\vec{r}') = R_{nl}(r') Y_{lm}(\Omega') \quad , \quad (31)$$

with

$$R_{n\ell}(r') = \sum_{n'} A_{nn'}^{\ell} \bar{R}_{n',\ell}(r') \quad (32)$$

with $A_{nn'}^{\ell}$, obtained from the Schmidt orthogonalization procedure.

(a) Exact Hamiltonian

The matrix elements of the exact Hamiltonian in this basis can be written in terms of the Slater orbitals (Eq.(29)).

$$\begin{aligned} \langle \beta_{n_1 \ell_1 m_1} | H^{(\lambda)} | \beta_{n_2 \ell_2 m_2} \rangle &= \sum_{n'_1 n'_2} A_{n_1 n'_1} A_{n_2 n'_2} \\ &\times \langle \bar{R}_{n'_1 \ell_1} Y_{\ell_1 m_1} | H^{(\lambda)} | \bar{R}_{n'_2 \ell_2} Y_{\ell_2 m_2} \rangle . \end{aligned} \quad (33)$$

We first calculate the matrix elements for the Hamiltonian $H^{(\lambda)}$ for two s-like Slater orbitals denoted as $|b_1\rangle$ and $|b_2\rangle$, (see Eq. (29)) where b is the exponent. The total matrix element may be divided into two parts, the kinetic energy $T^{(\lambda)}$ and the potential energy $V^{(\lambda)}$. For the intravalley term, we obtain

$$\langle b_1 | T^{(1)} | b_2 \rangle = 8B(b_1 b_2)^{5/2} / (b_1 + b_2)^3 , \quad (34)$$

with B given by Eq. (25a).

The intervalley kinetic energy matrix elements can be written in terms of the Fourier transforms of Slater orbitals

$$\bar{R}_b(\vec{k}) = \frac{16\pi b^{5/2}}{[b^2 + k_x^2 + k_y^2 + \zeta k_z^2]^2} \quad (35)$$

For the intervalley ($\lambda=2,3$), we have

$$\begin{aligned} \langle b_2 | T^{(\lambda)} | b_1 \rangle = & \frac{\zeta}{4\pi} \int \frac{d^3 k}{(2\pi)^3} \bar{R}_{b_2} (O^{(\lambda)}(\vec{k}-k_0 \hat{z})) E_1^0(\vec{k}-k_0 \hat{z}) \bar{R}_{b_1}(\vec{k}-k_0 \hat{z}) \\ & + \text{exchange term} \quad , \quad (36) \end{aligned}$$

where $E_1^0(\vec{k}-k_0 \hat{z})$ is defined in Eq. (22) for the valley associated with $\bar{R}_{b_1}$, $\hat{z}$ is the unit vector in the z direction and $O^{(\lambda)}$ is a rotation operator (25)

which transforms from a given valley to a transverse valley ($\lambda=2$) or a longitudinal valley ($\lambda=3$). The exchange term is produced by interchanging b_1 and b_2 .

With some approximation, Eq. (36) can be reduced to two-dimensional and one-dimensional integrals for $\lambda=2$ and 3, respectively. For the reader's interest, we put this derivation in Appendix B.

The matrix elements of the potential energy for s-like basis states are given by

$$\langle b_1 | V^{(\lambda)} | b_2 \rangle = \frac{(b_1 b_2)^{3/2}}{\pi \zeta} \left[J_{\lambda}^{+8\pi \sum_{v=1}^4 S_v} J_v^{(\lambda)}(b_1, b_2) \right] \quad (37)$$

where S_v is given by Eq. (19b). The functions $J_v^{(\lambda)}$ are given by

$$J_v^{(1)}(b_1, b_2) = \int_0^1 d\xi \frac{1}{[(b_1 + b_2)(1 + (\delta - 1)\xi^2)^{1/2} + \sigma_v]^2}, \quad (38a)$$

$$J_v^{(2)}(b_1, b_2) = \text{Re} \int_0^{2\pi} \frac{d\phi}{(2\pi)} \int_0^1 d\xi \frac{1}{[(b_1 v_1 + b_2 v_2 + \sigma_v) + ik_0(\eta_1 - \eta_2)]^2}, \quad (38b)$$

and

$$J_v^{(3)}(b_1, b_2) = \text{Re} \int_0^1 d\xi \frac{1}{\{[(b_1 + b_2)(1 + (\delta - 1)\xi^2)^{1/2} + \sigma_v] + 2ik_0\}^2}; \quad (38c)$$

where σ_v are given by Eq. (19c),

$$v_{1,2} \equiv [1 + (\delta - 1) \eta_{1,2}^2]^{1/2}, \quad (39a)$$

$$\delta \equiv \zeta^{-2},$$

and

$$\eta_{1,2} \equiv \sqrt{1 - \xi^2} \cos(\phi \pm \beta/2), \quad (39b)$$

with $\beta = 90^\circ$ for Si and 109.47° for Ge.

As discussed in Sec. IIb, the exact Hamiltonian can be approximated by the single valley effective mass Hamiltonian H_{EMA} for all the other basis states. These matrix elements for ellipsoidal Slater orbitals are given by ⁽³⁾ (for $\ell \geq \ell'$)

$$\begin{aligned} \langle b_1^{\ell m} | H_{EMA} | b_2^{\ell' m'} \rangle = & \delta_{mm'} \{ \delta_{\ell\ell'} C_{\ell}^m I_{\ell}(b_1, b_2) + D_{\ell}^m \delta_{\ell, \ell'+2j} J_{\ell\ell'}(b_1, b_2) \\ & - \delta_{\ell, \ell'+2j} \sum_{v=0}^{(\ell+\ell')/2} G_{\ell\ell'}^v(m) a_v K_{\ell\ell'}(b_1, b_2) \} \end{aligned} \quad (40)$$

where j is an integer such that $\ell'+2j$ is non-negative. The coefficients C_{ℓ}^m and D_{ℓ}^m are given by

$$C_{\ell}^m \equiv 1-(1-B) \left[1 + \frac{2\ell(\ell+1) - 6m^2}{(2\ell-1)(2\ell+3)} \right] \quad (41a)$$

and

$$D_{\ell}^m \equiv \frac{(1-B)3}{(2\ell-1)} \left[\frac{(\ell^2-m^2)}{(2\ell+1)} \frac{[(\ell-1)^2-m^2]}{(2\ell-3)} \right]^{\frac{1}{2}} \quad (41b)$$

where B is given by Eq.(25a). The coefficients a_v are given by the recursion relation

$$a_v = \frac{[(2v-1) a_{v-1} - \zeta]}{2vg^2} \quad \text{for } v \geq 1 \quad (42a)$$

with

$$a_0 = \frac{\sin^{-1} g}{g} \quad (42b)$$

The $G_{\ell\ell'}^v(m)$ are defined by

$$4\pi Y_{\ell m}^*(\Omega) Y_{\ell' m'}(\Omega) = \sum_{\nu=0}^{(\ell+\ell')/2} G_{\ell\ell'}^{\nu}(\theta) \cos^{2\nu}\theta ; \quad (43)$$

and can be obtained by carrying out this expansion (26). The coefficients I, J, and K are given by

$$I_{\ell}(b_1, b_2) = S_{12}(\ell) \left[b_1 b_2 + b^2 \frac{\ell}{(\ell+1)} \right] , \quad (44a)$$

$$J_{\ell\ell'}(b_1, b_2) = S_{12}(\ell) \left[b_2^2 + 2bb_2/(\ell+\ell' + 2) \right] , \quad (44b)$$

$$K_{\ell\ell'}(b_1, b_2) = 4S_{12}(\ell) b/(\ell+\ell' + 2) , \quad (44c)$$

where

$$S_{12}(\ell) \equiv \langle b_1 \ell | b_2 \ell \rangle = \left(\frac{\sqrt{b_1 b_2}}{b} \right)^{2\ell+3} \quad (45a)$$

and

$$b \equiv (b_1 + b_2)/2 . \quad (45b)$$

(b) Model Hamiltonian

The only part of the model Hamiltonian matrix that differs from the exact Hamiltonian matrix is that for the s-like basis states. Again we will treat the kinetic and potential energies separately.

We want to replace the intervalley contribution to the kinetic energy by that appearing to originate from a single valley.

The form of the model KE operators given in Eq. (24) is obtained by observing that the principal contribution to the integral in Eq. (36) occurs for $\bar{R}_b$ near the band minima. Hence, we can approximate the integral by replacing the tail of the basis function $\bar{R}_b$ in the other valleys by an appropriate function in the original valley.

In the first term of Eq. (36), $\bar{R}_{b_2}$ is localized in the valley outside the region where the integration is carried out. Its tail in the region of integration is a smooth function of $\vec{k}$, and can be approximated by the functional form

$$\frac{16\pi b_2^{5/2}C}{\left[(\eta_\lambda\Delta + b_2)^2 + \zeta^2(\vec{k}-\vec{k}_0\hat{z})^2\right]^2} - \frac{16\pi b_2^{5/2}(C-1)}{\left[(2\eta_\lambda\Delta + b_2)^2 + \zeta^2(\vec{k}-\vec{k}_0\hat{z})^2\right]^2}, \quad (46)$$

where η_λ and C are taken as adjustable parameters. This function has the advantage that it resembles the function $\bar{R}_{b_2}$ in the region of integration and only gives small contribution to the integral when the region of integration is extended to the whole k -space. Furthermore, when the region of integration is extended to the whole k -space, the integral can be done analytically and we obtain

$$\langle b_2 | T_M^{(\lambda)} | b_1 \rangle = 8B(b_1 b_2)^{5/2} \left[\frac{C}{(\eta_\lambda \Delta + b_1 + b_2)^3} - \frac{(C-1)}{(2\eta_\lambda \Delta + b_1 + b_2)^3} \right], \quad (47)$$

which corresponds to the matrix elements of the postulated intervalley KE operators defined in Eq. (24). It should be noted that Eq. (47) reduces to Eq. (34) when Δ is set equal to zero.

The matrix elements for the s-like part of the model potentials $V_{SM}^{(\lambda)}$ (given in Eq. (17)) can be carried out analytically. We obtain

$$\langle b_1 | V_{SM}^{(\lambda)} | b_2 \rangle = 8(b_1 b_2)^{3/2} \cdot \left[J_\lambda / (8\pi\zeta) + R_\lambda \sum_{v=1}^4 \frac{S_v a_0}{(b_1 + b_2 + h\sigma_v)^2 + p_\lambda^2 \Delta^2} \right], \quad (48)$$

where R_λ , S_v , and σ_v are defined by Eqs. (12), (19b) and (19c), respectively; p_λ and h are adjustable parameters.

(c) Fitting of the Free Parameters

There are a number of free parameters in the model Hamiltonians which are to be selected so that the matrix elements of the model Hamiltonian are as close as possible to those for the exact Hamiltonian. Fitting of the intervalley KE matrix elements results in the parameters given in Table II-1 for Si and Ge. The quality of the fit as a function of the orbital exponent for the Slater orbital is shown in Fig. II-1. The fit is superb for the range $b < 8$ a.u.; however, for larger values of b (more localized functions) deviations between the exact and model results do occur.

The fit of the intravalley PE matrix elements is accomplished by adjusting the parameter h . The values resulting in the best fit are given in Table II-1. The quality of the fit as a function of orbital exponent for the Slater orbital is shown in Fig. II-2. Again the fit is superb, and continues to be quite good

TABLE II-1. Adjustable parameters h , f_λ , P_λ , C , η_λ determined by fitting the diagonal matrix elements of various terms in the model Hamiltonian with that of the corresponding terms in the exact Hamiltonian.

material parameter	Si			Ge	
	Intra ($\lambda=1$)	Inter-trans ($\lambda=2$)	Inter-long ($\lambda=3$)	Intra ($\lambda=1$)	Inter-trans ($\lambda=2$)
f_λ	1	1	2	1	1
P_λ	1	1.005	2.265	1	1.48
η_λ		1.48	1.59		2.42
h	0.821			0.69	
C	12			25	

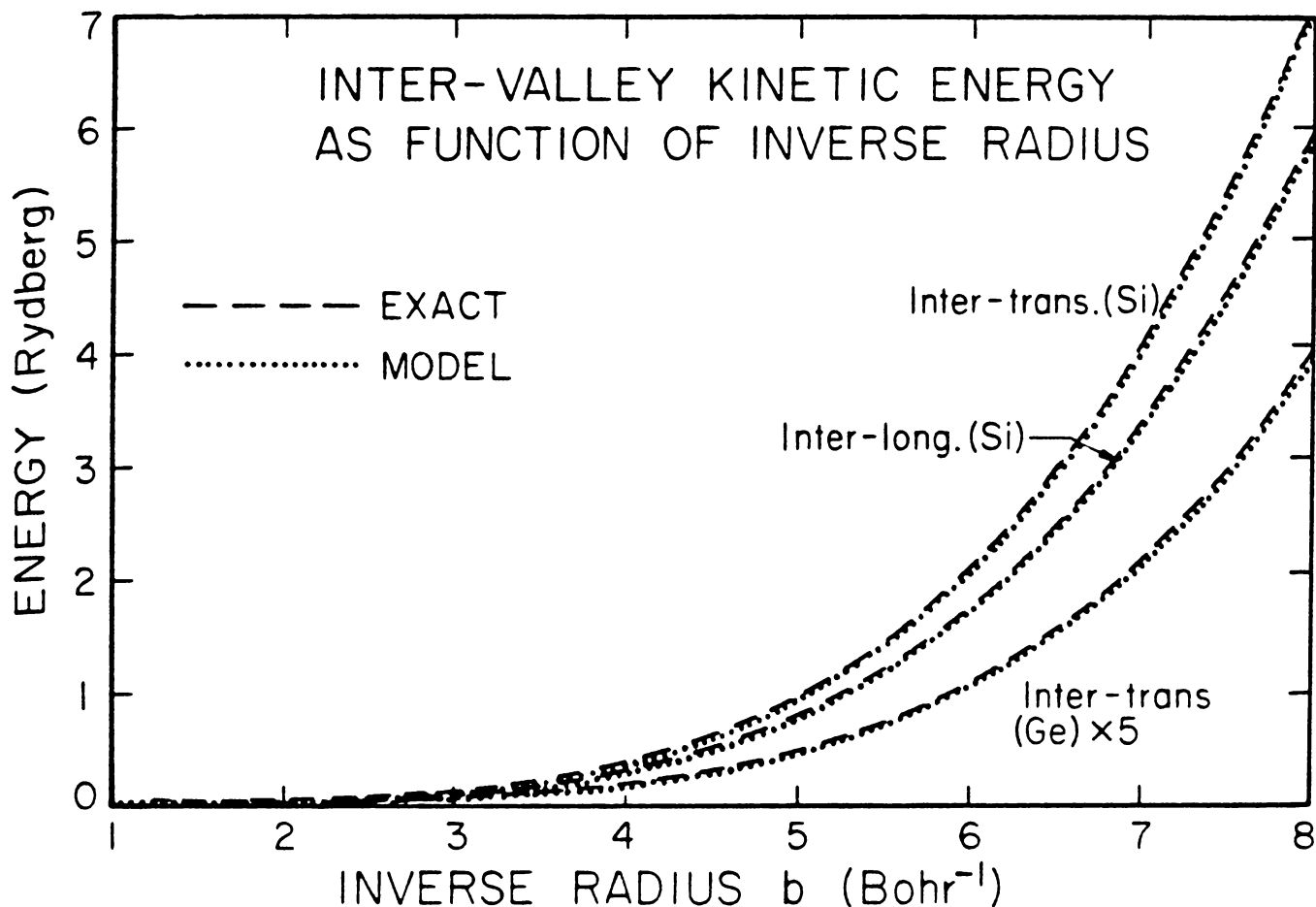


Figure II- 1. Intervalley kinetic energy plotted as a function of the inverse radius of the basis envelope wave function for the exact Hamiltonian (dashed line) and the model Hamiltonian (dotted line) for donors in Si and Ge. Atomic units are used as defined in the text.

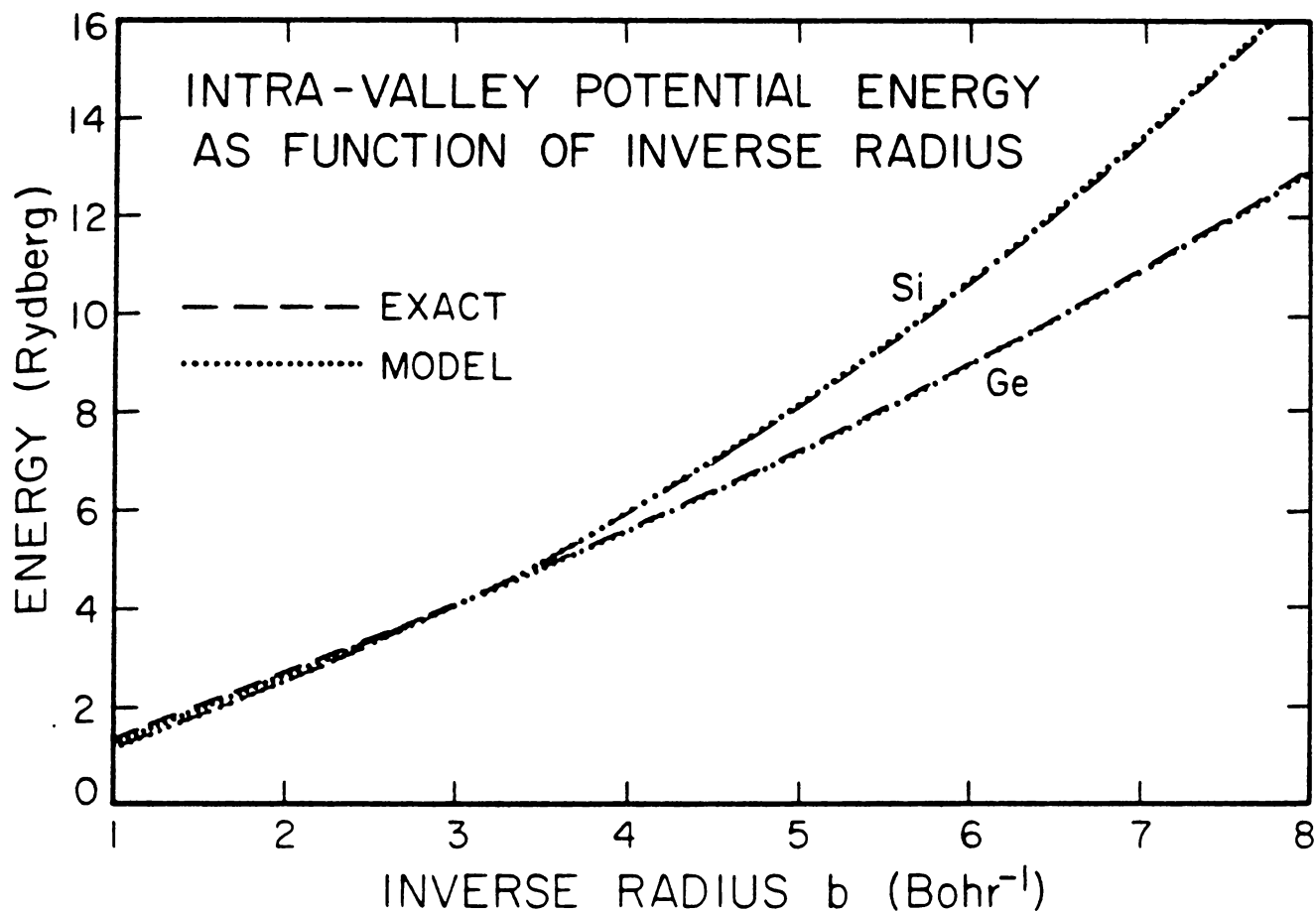


Figure II-2. Intravalley potential energy plotted as a function of the inverse radius of the basis envelope wave function for the exact Hamiltonian (dashed line) and the model Hamiltonian (dotted line) for donors in Si and Ge. Atomic units are used as defined in the text.

even for large values of b .

The fit of the intervalley PE matrix elements is carried out by adjusting the parameters p_λ and f_λ with h fixed at the value required for the intervalley PE. The parameters resulting in a very good fit are given in Table II-1. The comparison between the exact results and calculations for the model are given in Fig. II-3. The fit is quite good over the entire range of b required for our calculations.

IV. RESULTS

In this section we report the results of calculations of the various ground state and $s(d)$ -like excited states of donors in Si and Ge. Results are reported for both the model and exact Hamiltonian matrices.

The numerical work was carried out, using 10 s -like, 6 d_o -like and 4 g_o -like Slater orbitals. The parameters $b_{n\ell}$ are chosen to be $b_o/Z_{n\ell}$, with $b_o = 2$ a.u. for Si and $b_o = 4$ a.u. for Ge and

$$Z_{n\ell} = (1, 1.5, 2, 3, 4, 6, 9, 14, 0.5, 0.25) \text{ for } \ell = 0$$

$$Z_{n\ell} = (.5, .7, 1, 2, 3, 5) \text{ for } \ell = 2$$

$$Z_{n\ell} = (.5, .7, 1, 2) \text{ for } \ell = 4.$$

The eccentricity factor ζ was determined by minimizing the ground state energy. Hence, it is not clear whether our basis set is good for the excited states or not. To examine this, we calculated the eigenvalues of the EMA⁽²⁾ Hamiltonian using this basis set with $\zeta = .57$ for Si and $\zeta = .355$ for Ge, respectively. Our results for the lowest six states are listed in Table II-2 along with the results obtained by Faulkner⁽³⁾.

Our results for Si are almost identical to those of Faulkner⁽³⁾. For Ge, we obtain slightly larger ionization energies (by about .1 meV) for the

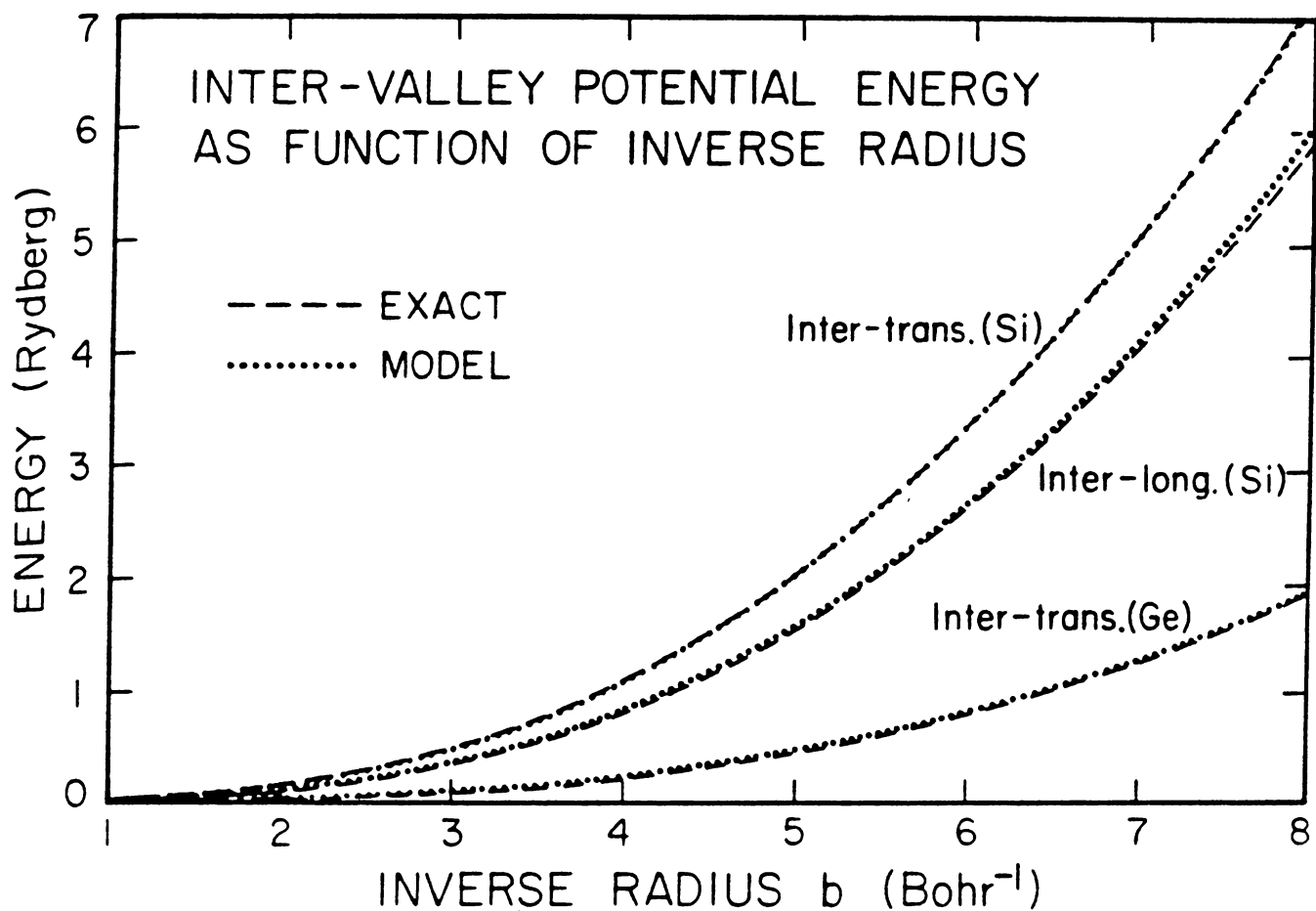


Figure II- 3. Intervalley potential energy plotted as a function of the inverse radius of the basis envelope wave function for the exact Hamiltonian (dashed line) and the model Hamiltonian (dotted line) for donors in Si and Ge. Atomic units are used as defined in the text.

TABLE II-2. Ionization energies of the 6 lowest s(d)-like states obtained in EMA for Si:P and Ge:As. The results obtained by Faulkner ⁽³⁾ are also included for comparison. All energy values are in meV.

		1s	2s	3s	3d _o	4s	4d _o
Si:P	present work	31.22	8.85	4.76	3.75	2.86	2.11
	Ref. 3	31.27	8.83	4.75	3.75	2.85	2.11
Ge:As	present work	9.81	3.59	2.14	1.43	1.19	0.94
	Ref. 3	9.81	3.52	2.01	1.34	1.17	0.87

excited states than those obtained by Faulkner. We therefore believe that our method is suitable for the ground states as well as for the excited states.

The matrix elements for the exact Hamiltonian H and the model Hamiltonian H_M were obtained as described in Sec. III, and both matrices are diagonalized numerically. The results obtained for both Hamiltonians are very close to each other (within 1%).

For the isocoric impurity P in Si, we assume the short-range core potential takes the form

$$W(\vec{r}) = P_c e^{-\sigma_c r} \frac{(27.2 \text{ eV})}{\epsilon(r)}, \quad (49)$$

with $P_c \approx 2.72$ and $\sigma_c \approx 3.33$ a.u. (27) Putting Eq. (49) into Eq. (11), we obtain 28
that $J_1 \approx -0.60$, $J_2 \approx 6.35$ and $J_3 \approx 7.11$ (in units of 10^{-3} Ry Bohr³). For As in Ge, we assume the short-range core potential has negligible effect, i.e., set $J_\lambda = 0$ in Eqs. (14), (17), and (37). The validity of this assumption may depend on the impurity pseudopotential used. It was shown by Pantelides and Sah (9) that the short-range core potential is small for an isocoric impurity, if one works within a true-potential representation. On the other hand, the Umklapp renormalization factors R_λ are obtained by using the empirical pseudopotential method (EPM). This empirical pseudopotential used for the crystal may not satisfy the criteria for internal consistency given by Pantelides (18). We therefore calculated the ground state energies for several choices of the renormalization factors R_λ . For Si, we worked out the cases with R_2 taken to be from 0.47 to 0.55 and R_3 taken to be 0.48. The results for the energies of the three split ground states calculated for both H and H_M are plotted in the upper half of Fig. II-4 against the parameter R_2 . We find that with the choice $R_2 \approx 0.53$, the theoretical results are in excellent agreement with the experimental data. For $R_2=0.38$ and $R_3=0.3$ (the values obtained from EPM) (13), we obtain for the Γ_1 ,

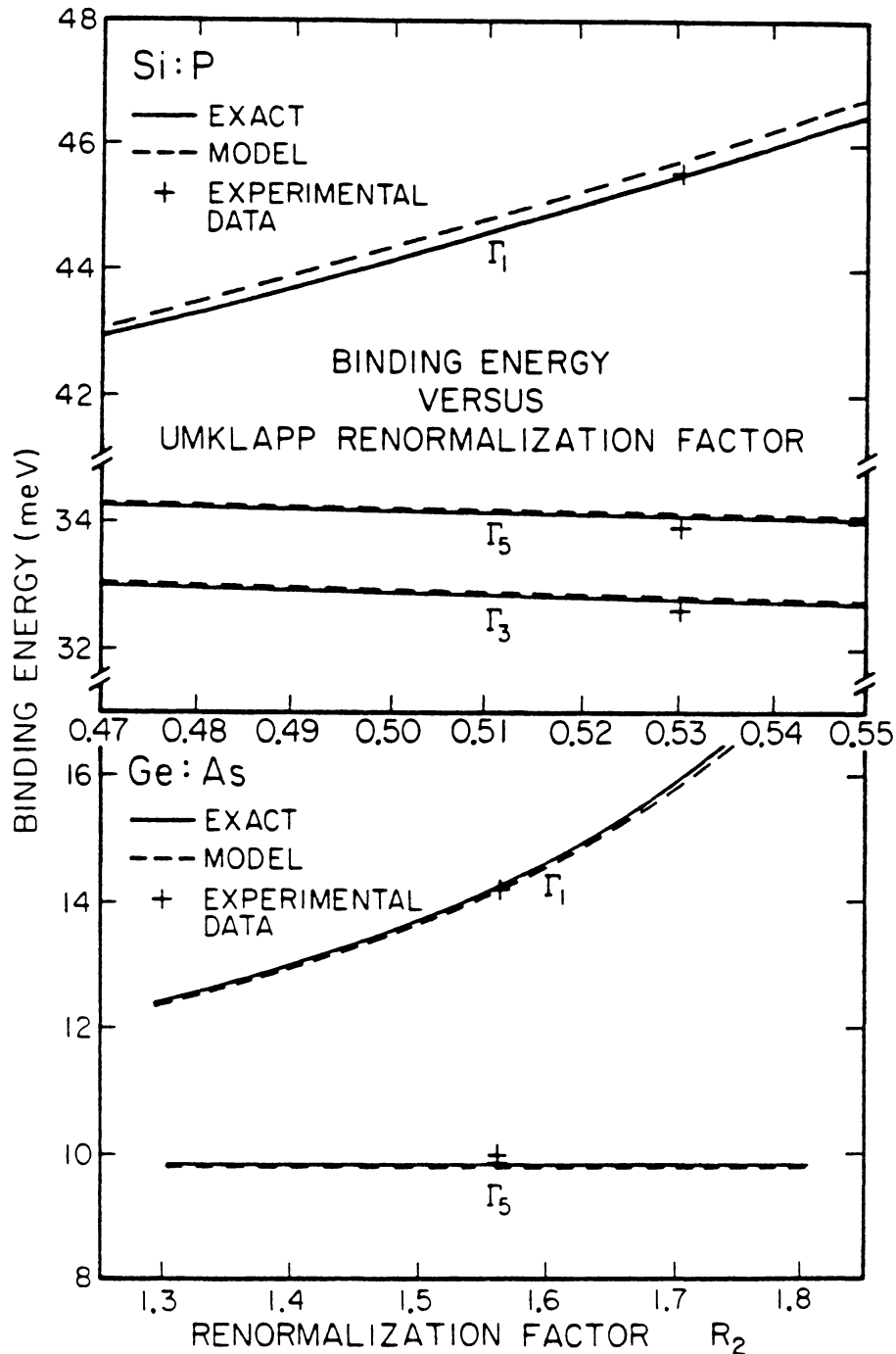


Figure II-4. Binding energies of the ground states associated with various irreducible representations plotted against the Umklapp renormalization factor R_2 for the exact Hamiltonian (solid line) and the model Hamiltonian (dashed line), for Si:P (upper half) and Ge:As (lower half), respectively. The experimental data (taken from Ref. 30 for Si:P and Ref. 34 for Ge:As) are also included (marked "+"). The energy units are meV.

Γ_5 and Γ_3 states 38.9, 35.1 and 33.5 meV, respectively, when $W(\vec{r})$ is included and 43.2, 34.3 and 33.1 meV, respectively, when $W(\vec{r})$ is neglected. For Ge:As, the energies of the split ground states are plotted in the lower half of Fig. II-4 against R_2 , with R_2 ranging from 1.3 to 1.8. For $R_2 \approx 1.56$, the results fit experimental data very well. For $R_2 = 2.33$ (the value obtained from EPM)⁽¹³⁾, we obtain very large binding energy (>20 meV), which is inconsistent with the experimental data.

To examine the stability of the Hamiltonian when the short-range core potential is neglected, we did a variational calculation using the s-like trial wave function $\bar{R}_b(\vec{r})$ as given by Eq. (29). In Fig. II-5 the energy expectation value of the Γ_1 -symmetry ground state for Si:P with a trial wave function given by Eqs. (6) and (29) is plotted against the variational parameter b . The Umklapp renormalization factors used are those from EPM⁽¹³⁾. As shown in this figure, the system is stabilized only if the intervalley KE term is included. Similar situations also hold for donors in Ge.

The charge densities of the ground states of Si:P and Ge:As are plotted in Fig. II-6 and Fig. II-7 against the radial distance r' (defined in ellipsoidal coordinates). The ground state wave function calculated within the effective mass approximation (EMA) is also included. It should be noted that the Γ_1 -symmetry ground state is much more localized in space (therefore, more spread out in k-space) than the other states. This is expected, because the tunneling of the wavefunction from a given valley to the other valleys has a large constructive effect for the Γ_1 state but small destructive effects for the Γ_3 and Γ_5 states. Therefore, the Γ_1 state should be more spread out in k-space and more strongly bound, while the Γ_3 and Γ_5 states should be a bit less spread out in k-space and less bound than the ground state of the single

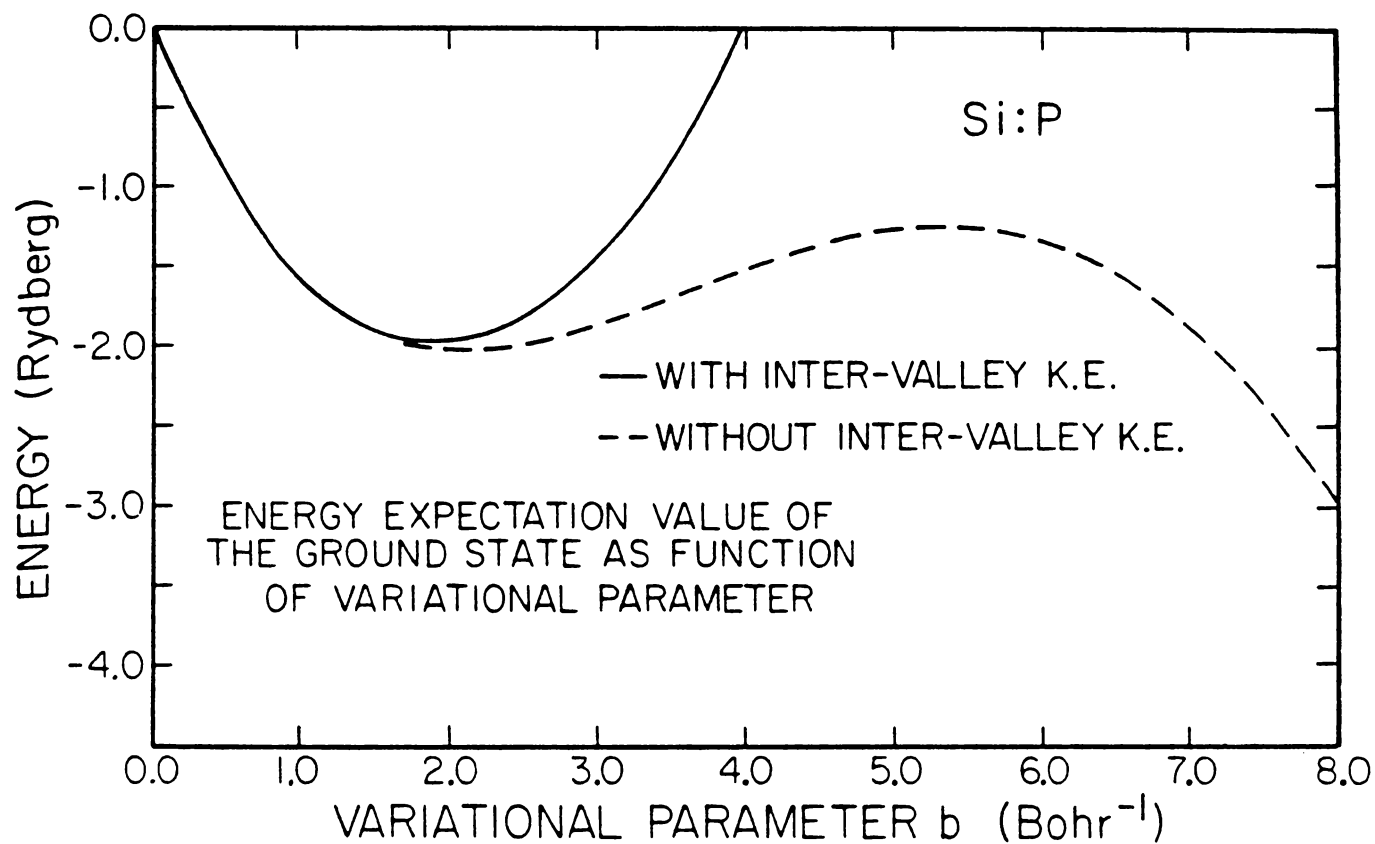


Figure II-5. Energy expectation value of the Γ_1 -symmetry ground state in Si:P is plotted as a function of variational parameter b with (solid line) and without (dashed line) the inter-valley kinetic energy.

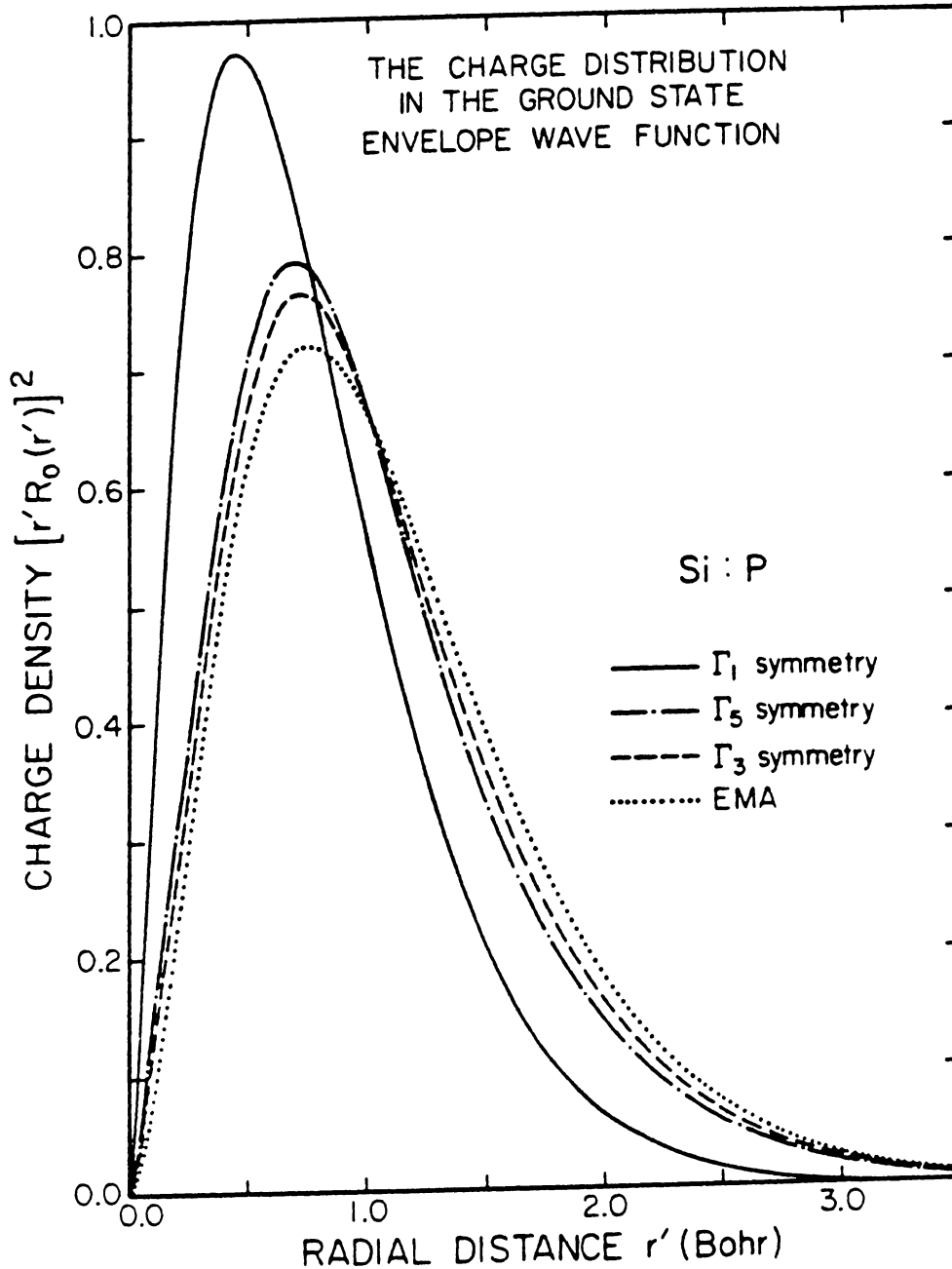


Figure II-6. Charge distribution in the ground state envelope wave function for Si:P plotted against the radial distance r' (in ellipsoidal coordinate system) for various irreducible representations. The results obtained within EMA are also included for comparison.

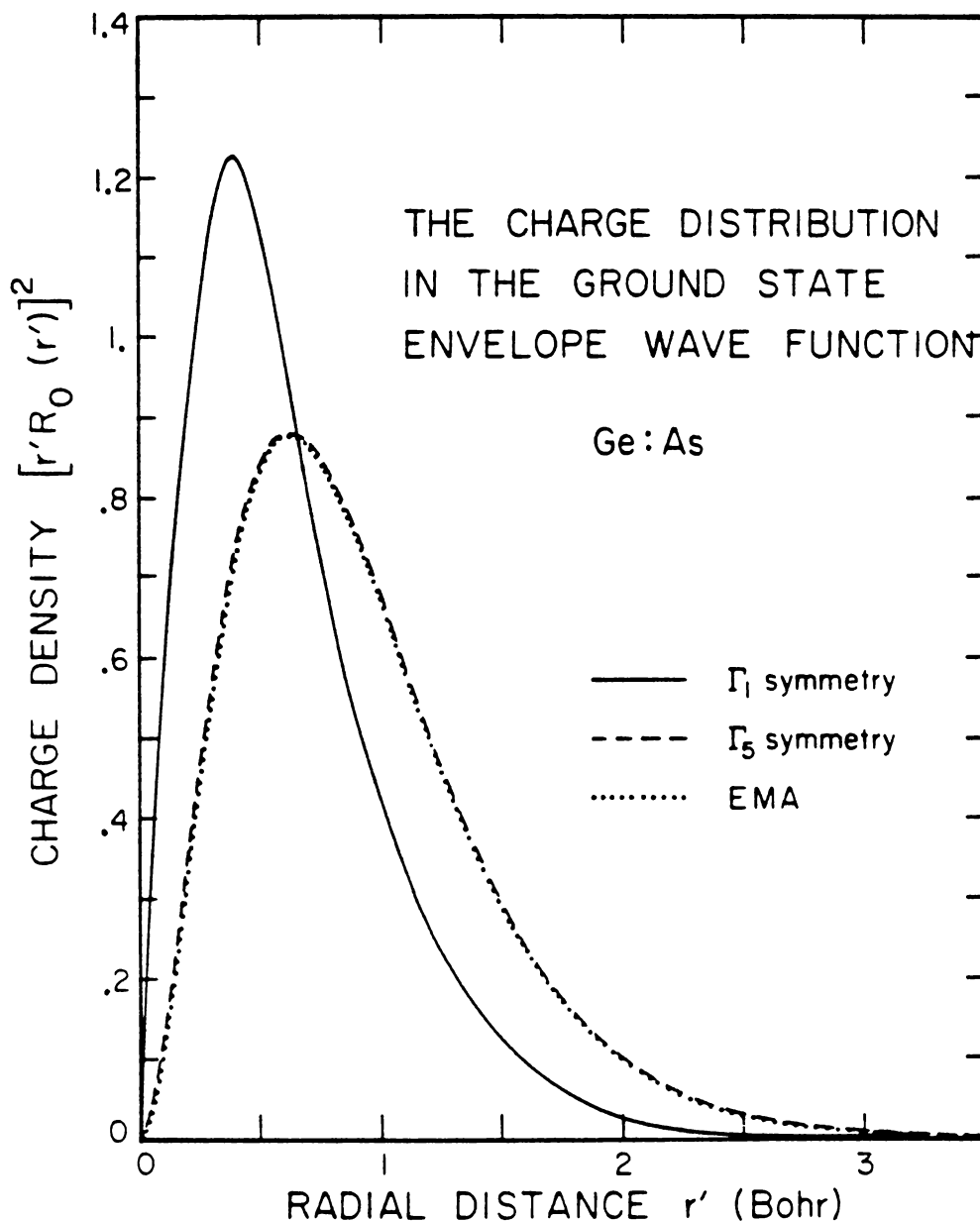


Figure II-7. Charge distribution in the ground state envelope wave function for Ge:As plotted against the radial distance r' (in an ellipsoidal coordinate system) for various irreducible representations. The results obtained within EMA are also included for comparison.

valley Hamiltonian. However, as shown in Fig. II-6, the ground state of Si calculated within EMA is more spread out than the Γ_3 and Γ_5 states. This is due to the neglect of the wave vector dependence of the dielectric function that reduces the binding. The $\ell \neq 0$ components of the ground states are found to be negligibly small. The charge densities for the s-like components and d-like components of the excited states calculated within EMA are plotted in Fig. II-8 for Si:P and Ge:As, against the radial distance r' . From the nodal structure of the excited states shown in Fig. II-8, it is noticed that the roles played by $3d_{0-}$ and $4s$ -states in Ge seem to be exchanged, as compared to that in Si. The charge densities for the s-like and d-like components of the Γ_1 -symmetry excited states are plotted against the radial distance r' in the top and bottom panels of Fig. II-9 for Si:P and Ge:As, respectively. Comparing Fig. II-9 with Fig. II-8, we find that the charge distribution of all Γ_1 -symmetry excited states except the $3d_0$ state in Si and the $4s$ state in Ge are shifted toward the center with respect to the states obtained in EMA. This is because the requirement of the orthogonality to the ground state (mainly s-like) has substantially modified all the s-like excited state wave functions. The $4s$ state in Ge, however, is intrinsically a $3d_0$ state as already mentioned and is not affected by the above requirement. On the other hand, the $3d_0$ state in Ge and $4d_0$ state in both Si and Ge, having the $4s$ and $5s$ nodal structures, are shifted toward the center to a small extent.

For non-isocoric impurities, we can adjust the core potential strength J_λ such that the calculated ground state energies fit the experimental data, with the Umklapp renormalization factors R_λ determined from the

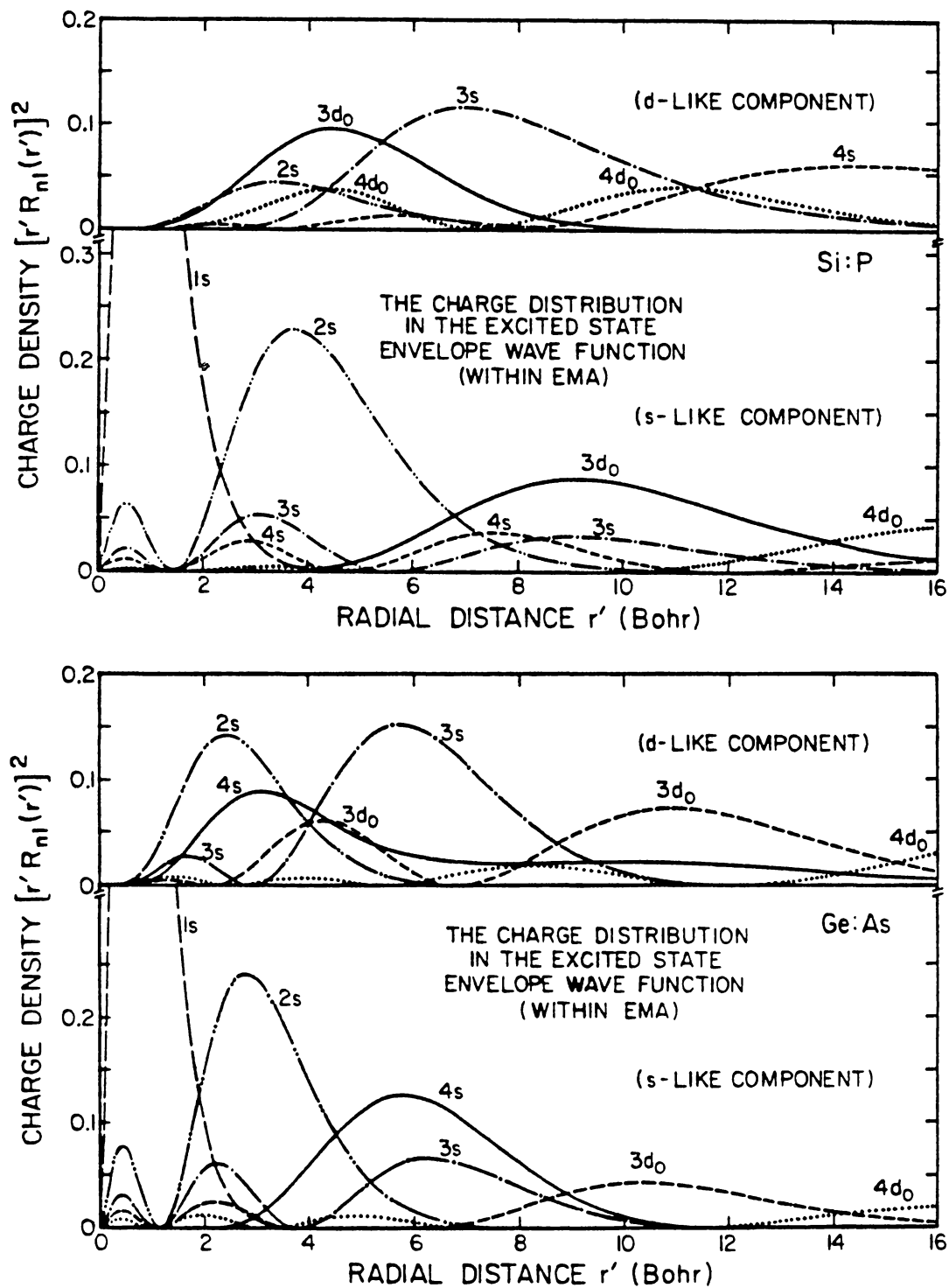


Figure II-8. Charge distribution in the excited state envelope wave function calculated within EMA for Si:P and Ge:As, plotted against the radial distance r' .

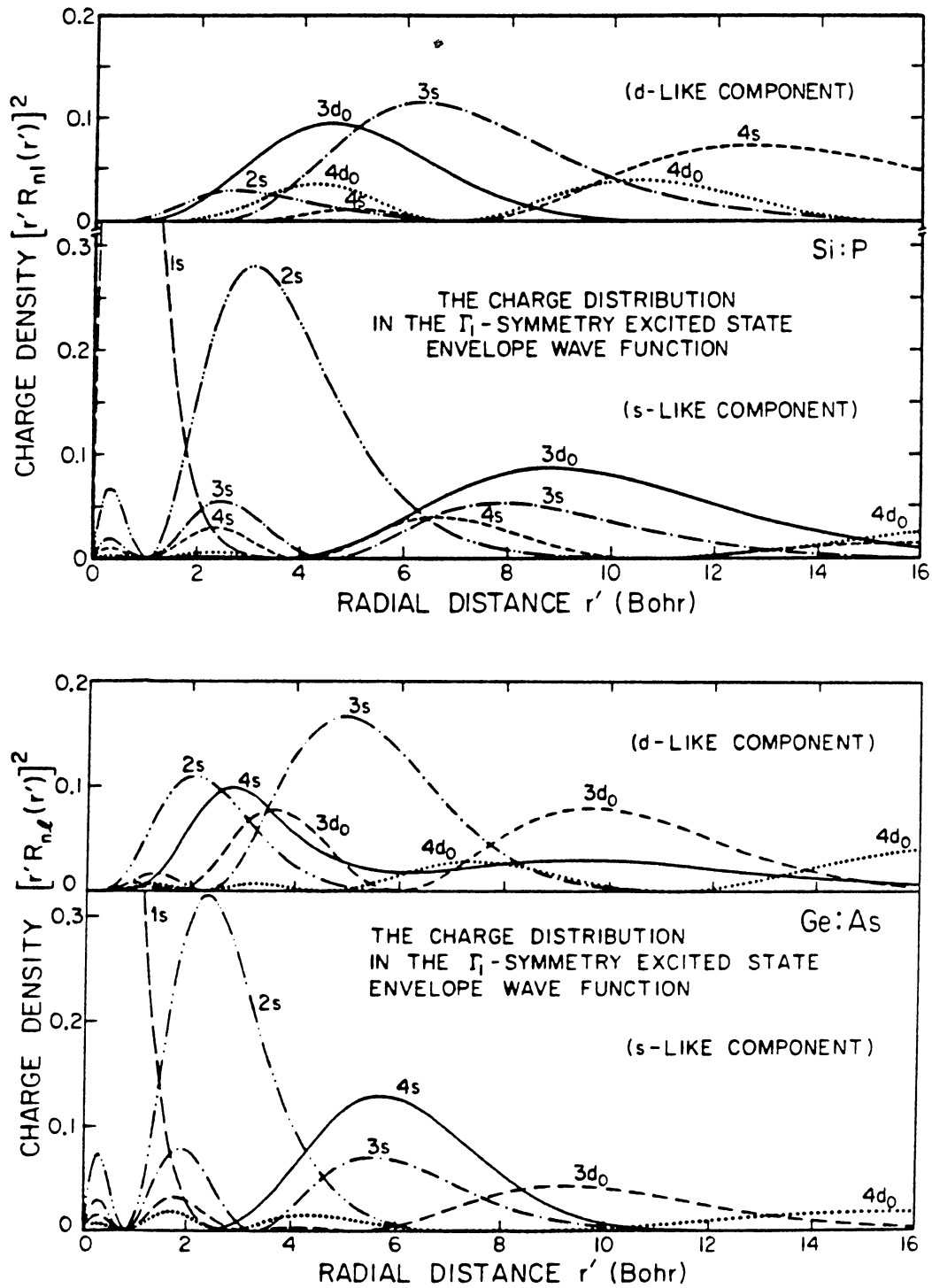


Figure II-9. Charge distribution in the Γ_1 -symmetry excited state envelope wave function for Si:P and Ge:As, plotted against the radial distance r' .

results for the isocoric impurities. In Table II-3 we listed the parameters J_λ determined for various impurities in Si and Ge. For the interstitial impurity Li in Si, we have used the Umklapp renormalization factors, $R_2 = 1.08$ and $R_3 = 1.23$ (from Ref. 13). It should be noted that for zero core potential ($J_\lambda = 0$), we obtain a large binding energy (about 600 meV) for the interstitial donors in Si. The ionization energies of the 6 lowest s(d)-like states for various impurities in Si and Ge are listed in Table II-4. The available experimental data are also included in parentheses for comparison. Excellent agreement between theory and experiment is obtained. In Table II-4 it is noticed that the ionization energies of the $3d_0$ -state in Si and the 4s state (having the $3d_0$ nodal structure) in Ge are almost independent of impurity type and the valley-orbit interaction while the ionization energies of the other states are more or less affected. This is again due to the fact that the s-like excited states have to be readjusted to become orthogonalized to the new ground state, which has been modified by the valley-orbit interaction.

V. SUMMARY

We have constructed the model Hamiltonian for the donors in Si and Ge. The matrix elements of this model Hamiltonian can be expressed analytically, if Slater-type basis wave functions are used. This Hamiltonian yields almost identical results as the exact Hamiltonian, and because of its simplicity, can be applied to more complicated systems such as donor bound excitons and bound multiexciton complexes (BMEC). We have also calculated the six lowest energy eigenvalues for the s(d)-like states of each symmetry for various impurities in Si and Ge. Our results are in excellent agreement with the available experimental data.

TABLE II-3. Short-range core potential strength parameters J_λ determined from fitting the calculated ground state energies with the experimental data for non-isocoric impurities in Si and Ge. The units of J_λ are 10^{-3} Rydberg Bohr³.

material parameter	Si:As	Si:Sb	Si:Li	Ge:Sp	Ge:Sb
J_1	18.62	36.83	57.36	0.975	8.05
J_2	-4.88	-3.92	90.88	0.975	8.05
J_3	2.62	26.33	84.43	-----	-----

TABLE II-4. Ionization energies of the 6 lowest s(d)-like states for various impurities in Si and Ge. The available experimental values are included in parentheses. All energy values are in meV.

			1s	2s	3s	3d ₀	4s	4d ₀
Si	Γ_1	P	45.5 (45.5) ^a	10.3 (10.6) ^b	5.22 (5.3) ^b	3.75 (3.75) ^c	3.11 (3.1) ^b	2.16 (2.2) ^b
		As	53.7 (53.7) ^b	10.9 (11.2) ^b	5.39 (5.3) ^b	3.75	3.20 (3.2) ^b	2.19 (2.2) ^b
		Sb	42.7 (42.7) ^a	10.0	5.15	3.75	3.07	2.14
		Li	31.2 (31.2) ^f	8.85	4.76	3.74	2.86	2.10
	Γ_5	P	34.2 (33.9) ^a	9.19 (9.05) ^c	4.88	3.75	2.92	2.11
		As	32.6 (32.6) ^a	9.01	4.82	3.75	2.89	2.10
		Sb	32.9 (32.9) ^a	9.04	4.83	3.75	2.89	2.10
		Li	33.0 (33.0) ^b	9.06 (9.0) ^b	4.84 (4.8) ^b	3.75	2.90	2.10
	Γ_3	P	32.7 (32.6) ^a	9.03 (9.05) ^c	4.82	3.75	2.89	2.10
		As	31.2 (31.2) ^a	8.85	4.76	3.75	2.86	2.10
		Sb	30.5 (30.5) ^a	8.76	4.73	3.74	2.84	2.10
		Li	33.0 (33.0) ^b	9.06 (9.0) ^b	4.84 (4.8) ^b	3.75	2.90	2.10
Ge	Γ_1	P	12.9 (12.9) ^e	3.90	2.27	1.51	1.20	0.96
		As	14.2 (14.2) ^e	4.01 (4.1) ^d	2.32 (2.4) ^d	1.53 (1.5) ^d	1.20	0.97
		Sb	10.3 (10.3) ^e	3.65	2.16	1.45	1.19	0.94
	Γ_5	P,As,Sb	9.81	3.59	2.14	1.43	1.19	0.94
		P As Sb	(10.1) ^e (10.0) ^e (10.0) ^e					

- a. Aggarwal and Ramdas (30)
b. Sauer (31)
c. Thewalt (32)
d. Gross et al (33)
e. Reuszer and Fisher (34)
f. Aggarwal et al (35)

APPENDIX A

FUNCTIONAL FORM FOR THE MODEL POTENTIALS

In the spherical model, the intervalley potentials are equal to their spherical average, i.e.,

$$\begin{aligned} V^{(\lambda)}(\vec{r}) &= J_{\lambda} \delta(\vec{r}) - R_{\lambda} e^2 \int e^{i(\vec{k}_j - \vec{k}_i) \cdot \vec{r}} \frac{1}{\epsilon(\vec{r})r} \frac{d\Omega}{4\pi} \\ &= J_{\lambda} \delta(\vec{r}) - R_{\lambda} \frac{e^2}{\epsilon(\vec{r})r} \frac{\sin(\Delta_{\lambda} r)}{(\Delta_{\lambda} r)}, \end{aligned} \quad (A1)$$

where $\Delta_{\lambda} \equiv |\vec{k}_i - \vec{k}_j|$ for $\lambda = 1, 2, 3$ as before. In an ellipsoidal coordinate system (with $\vec{r}' \equiv (x, y, z/\zeta)$), the spherical average for $V^{(\lambda)}(\vec{r})$ is

$$V_S^{(\lambda)}(\vec{r}') = J_{\lambda} \int \delta(\vec{r}) \frac{d\Omega'}{4\pi} - R_{\lambda} e^2 \int e^{i(\vec{k}_j - \vec{k}_i) \cdot \vec{r}} \frac{1}{\epsilon(\vec{r})r} \frac{d\Omega'}{4\pi} \quad (A2)$$

Comparing Eq. (A2) with Eq. (A1), we can approximate $V_S^{(\lambda)}(\vec{r})$ by the expression

$$V_{SM}^{(\lambda)}(\vec{r}') = J_{\lambda} \delta(\vec{r}')/\zeta - R_{\lambda} \frac{e^2}{\epsilon'(r')r'} \frac{f_{\lambda} a_o \sin(p_{\lambda} \Delta r')}{(p_{\lambda} \Delta r')} \quad (A3)$$

where $\frac{1}{\epsilon'(r')} \equiv \frac{1}{\epsilon_o} \sum_{v=1}^4 S_v e^{-h\sigma_v r'}$, $\Delta \equiv 2\zeta k_o$,

$$a_o \equiv \int_0^1 \frac{d(\cos\theta')}{\sqrt{1 - g^2 \cos^2\theta'}} = \sin^{-1} g/g, \text{ with } g^2 \equiv 1 - \zeta^2$$

and

f_{λ} , p_{λ} and h are adjustable parameters.

APPENDIX B

MATRIX ELEMENTS FOR INTERVALLEY KINETIC ENERGY

In this appendix we derive a simplified expression for Eq. (36) for the intervalley KE matrix elements. Substituting Eq. (22) and Eq. (35) into Eq. (36), we obtain

$$\begin{aligned} & \langle b_2 | T^{(2)} | b_1 \rangle \\ &= \frac{\zeta(b_1 b_2)^{5/2}}{4\pi} \int_0^\infty k_\zeta dk_\zeta \int_{-\beta/2}^{\pi-\beta/2} d\phi \int_{-\infty}^\infty dk_x \frac{[\frac{1}{\mu}(k_z - k_0)^2 + k_x^2 + k_y^2]}{[b_2^2 + k_x^2 + \zeta^2(k_t - k_0)^2 + k_s^2][b_1^2 + k_x^2 + k_y^2 + \zeta^2(k_z - k_0)^2]^2} \\ &+ \text{exch.} \quad , \end{aligned}$$

$$\text{with } k_t \equiv k_\zeta \cos(\phi + \beta) \quad \text{and} \quad k_s \equiv k_\zeta \sin(\phi + \beta) \quad (B1)$$

and

$$\begin{aligned} & \langle b_2 | T^{(3)} | b_1 \rangle \\ &= (b_1 b_2)^{5/2} \int_0^\infty dk_z \int_{-\infty}^\infty dk_x \int_{-\infty}^\infty dk_y \frac{[\frac{1}{\mu}(k_z - k_0)^2 + k_x^2 + k_y^2]}{[b_2^2 + k_x^2 + k_y^2 + \zeta^2(k_z + k_0)^2]^2 [b_1^2 + k_x^2 + k_y^2 + \zeta^2(k_z - k_0)^2]^2} \\ &+ \text{exch.} \quad , \end{aligned} \quad (B2)$$

where we have used $k_\zeta \cos \phi = k_z$ and $k_\zeta \sin \phi = k_y$ and extended the region of integration to infinity along the direction where the function in the integral quickly decreases to zero as k increases. For $\lambda = 2$, only the integration over k_x can be carried out analytically (we have chosen the x-axis normal to the plane spanned by the two valleys).

$$\begin{aligned} \langle b_2 | T^{(2)} | b_1 \rangle &= \frac{\zeta(b_1 b_2)^{5/2}}{2} \int_0^\infty dk_\zeta k_\zeta \int_{-\beta/2}^{\pi-\beta/2} d\phi \frac{[I(k_\zeta, \phi) (\frac{1}{\mu}(k_z - k_0)^2 + k_y^2) + 1]}{pq(p+q)^3} \\ &+ \text{exch.} \quad , \end{aligned} \quad (B3)$$

where

$$I(k_\zeta, \phi) = \left(\frac{1}{p^2} + \frac{1}{p^2} + \frac{3}{pq} \right) ,$$

$$p^2 \equiv b_1^2 + \zeta^2 (k_\zeta \cos \phi - k_0)^2 + k_\zeta^2 \sin^2 \phi ,$$

$$q^2 \equiv b_2^2 + \zeta^2 (k_\zeta \cos(\phi + \beta) - k_0)^2 + k_\zeta^2 \sin^2(\phi + \beta) ,$$

where

$$\beta = 90^\circ \text{ for Si and } 109.47^\circ \text{ for Ge.}$$

For $\lambda=3$, only the integration over k_x and k_y can be carried out analytically.

$$\langle b_1 | T^{(3)} | b_2 \rangle = \frac{2\zeta(b_1 b_2)^{5/2}}{\pi^2} \int_0^\infty dk_z \left[\frac{1}{\mu} (k_z - k_0)^2 I(k_z) + J(k_z) \right] + \text{exch.} , \quad (B4)$$

where

$$I(k_z) = \frac{1}{(p_+ - p_-)^2} \left[\frac{1}{p_+} + \frac{1}{p_-} \right] - \frac{2}{(p_+ - p_-)^3} \ln(p_+/p_-)$$

and

$$J(k_z) = \frac{(p_+ + p_-)}{(p_+ - p_-)^3} \ln(p_+/p_-) - \frac{2}{(p_+ - p_-)^2}$$

with

$$p_\pm \equiv b_1^2 + (k_z \pm k_0)^2 \zeta^2$$

$$p_- \equiv b_2^2 + (k_z - k_0)^2 \zeta^2 .$$

The remaining integrals must be carried out numerically.

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CHAPTER 3

THEORY OF DONOR STATES IN GaP

I. INTRODUCTION

In the last chapter, we have studied extensively, the donor states in the multivalley semiconductors Si and Ge. In this chapter we study the donor states in another multivalley semiconductor, GaP.

The donor states in GaP are of particular interest, because they exhibit several unique features. First, the valley-orbit splitting for the ground state in GaP is conspicuously large ⁽¹⁾ (~ 50 meV) in contrast to that in other indirect materials (10 - 20 meV for Si and 0 - 4 meV for Ge) ⁽²⁾. Second, the energy levels for the excited states deviate substantially from the predictions based on the Kohn-Luttinger effective mass theory (KL-EMT) with ellipsoidal band parameters ^(3,4).

Recently it has been proposed that in GaP the minimum of the conduction band does not occur at the zone edge (X point), but at slightly smaller values of wave vector ⁽⁵⁾. This position of the minimum leads to a "camel's back" structure produced by the two closely spaced minima. This camel's back structure causes the donor spectrum in GaP to be qualitatively different from that in Si and Ge. For example, the luminescence spectra for the even-parity excited states obtained from the "two-electron" transition experiment ^(3,6,7) show some irregular behavior in the oscillator strength. In particular, the transition to the $2s(\Gamma_1)$ final state in GaP:S_p (GaP doped by S in the P-site) yields an oscillator strength that is about ten times smaller than that for the transition to the $3s(\Gamma_1)$ state.

This observation suggests that the $2s(\Gamma_1)$ state in GaP:S_p must have a very different nodal structure from the regular 2s-like state of a hydrogen-like system.

Previously, several authors have studied the camel's back structure in the conduction band of GaP. Altarelli et al ⁽⁸⁾ have explored theoretically the implications of the camel's back structure for the free exciton spectrum. By fitting the experimental effective masses for GaP ⁽⁹⁾ and the exciton density of states ⁽¹⁰⁾, they find a value for the height of the maximum separating the two minima (ΔE) of approximately 4 meV and a value for the displacement (k_0) in wave vector space of the conduction band minimum from the zone edge of approximately $0.06 (\frac{2\pi}{a_0})$ where a_0 is the cubic lattice constant. These calculations have been confirmed qualitatively by measurements of the derivative of the exciton density of states by Humphreys et al ⁽¹¹⁾. Recently, Glinskii et al ⁽¹²⁾ have calculated the dispersion in the free exciton spectrum for GaP and compared their results with data from Dean and Thomas ⁽¹³⁾ to obtain $\Delta E = 3.5 \pm 0.3$ meV and $k_0 = 0.084 \pm 0.002 (\frac{2\pi}{a_0})$.

The influence of the camel's back on the excitation spectrum of the donors has been studied less extensively. Kopylov et al ⁽¹⁴⁾ have measured the energy separation between the $2p_0$ and $2p_{\pm}$ states of the neutral donor in sulfur-, tellurium-, and oxygen-doped GaP. They fit their values to a simple variational calculation to obtain $\Delta E = 3$ meV and $k_0 = 0.08 (\frac{2\pi}{a_0})$.

In this chapter we present an extensive theoretical study of

the energies of low-lying discrete states for donors in GaP using the Rayleigh-Ritz variational method. We first study the donor spectrum when the valley-orbit interaction is neglected. By comparing the energy separations between the odd parity donor states (which are not affected by the valley-orbit interaction by symmetry) with the experimental values, we obtain the camel's back parameters similar to that obtained by Glinskii et al ⁽¹²⁾. Given these parameters, we study the effect of the valley-orbit interaction on the even-parity donor states. We obtain a theoretical spectrum in reasonably good agreement with the experimental data. Our results provide a clear identification of the origins for the optical transitions observed in GaP.

We find that the envelope function of the $2s(\Gamma_1)$ state is a symmetric combination of 6 p-like orbitals localized at the 6 equivalent band minima. It behaves like a 2s state if we view the two closely spaced minima near the X-point as belonging to a single valley with a camel's back structure, but like a 2p state if we view the 6 minima as belonging to 6 separated valleys. The p-like character of each component in the $2s(\Gamma_1)$ state accounts for the irregular oscillator strength for the two-electron transition spectra observed in GaP:S_p. We estimate the relative oscillator strengths for this process with the final donor states being $1s(\Gamma_1)$, $2s(\Gamma_1)$ and $3s(\Gamma_1)$, etc. Qualitatively good agreement is obtained between theory and experiment. The results of this chapter will be applied in Chapter 5 to the calculation for the exciton spectra of donor bound excitons in GaP.

In Section II, we discuss the theory for donor states in GaP, both with and without the valley-orbit interaction. In Section III, we discuss how we obtain the camel's back parameters and how the camel's back structure affects the donor spectrum. We also compare our theoretical results with the available experimental data. In Section IV, we summarize our results.

II. THEORY

In this section, we discuss the theory for treating the donor in GaP with and without the valley-orbit interaction.

A. Effective Mass Hamiltonian

Using $\vec{k} \cdot \vec{p}$ perturbation theory, Lawaetz ⁽⁵⁾ proposed an energy expression for each valley of the conduction band of GaP:

$$E_s(\vec{k}) = k_x^2 + k_y^2 + \frac{k_z^2}{\mu} - \sqrt{\frac{Qk_z^2}{\mu} + \frac{\Delta^2}{4}} + \left(\frac{\Delta}{2} + \Delta E\right) \quad (1)$$

where we have introduced normalized units in which distance and energy are measured in units of $\frac{\epsilon_0 \hbar^2}{m_t e^2}$, the Bohr and $\frac{e^4 m_t}{2\epsilon_0 \hbar^2}$, the transverse mass Rydberg (Ry), respectively. The parameter ϵ_0 is the static dielectric constant and m_t is the transverse conduction band effective mass. The parameter μ is the anisotropy factor, i.e., the ratio of the longitudinal-to-transverse effective masses. The parameter Q is related to the $\vec{k} \cdot \vec{p}$ parameter P defined by Lawaetz ⁽⁵⁾ by the expression

$$Q = \mu p^2$$

The parameter Δ is the energy spacing between the X_{1C} and X_{3C} conduction band states. The camel's back height is represented by the parameter ΔE . The offset ΔE is used in Eq. (1) such that the absolute energy is zero at the conduction band minima, i.e., $k_z = k_0$. If we examine Eq. (1) for a minimum, we find that when $Q > \Delta$ a minimum occurs at a value of k_z :

$$k_0 = \sqrt{\frac{\mu(Q^2 - \Delta^2)}{4Q}} \quad (2)$$

and the height of the camel's back E is given by

$$\Delta E = \frac{(Q - \Delta)^2}{4Q} \quad (3)$$

The values of some of these parameters have been measured accurately. Onton ⁽¹⁵⁾ has determined that the value of Δ is 355 ± 3 meV. The value of m_t is determined by cyclotron resonance to be $0.254 m_e$ ⁽⁹⁾. The value of ϵ_0 has been found to be 11.02 ⁽¹⁶⁾. The value of m_ℓ is uncertain due to the camel's back structure; hence, we consider values of the anisotropy parameter μ between 3 and 5 as suggested by pseudopotential calculations ⁽¹⁷⁾. The value of Q is treated as a parameter to be determined.

Within the single-valley effective mass approximation, the envelope functions of the donor states satisfy the Schrödinger equation with the effective mass Hamiltonian ⁽¹⁸⁾

$$H_s = E_s(-i\nabla) - \frac{2}{r}, \quad (4)$$

where $E_s(-i\nabla)$ is an operator defined by the equation

$$\int \psi^*(\vec{r}) E_s(-i\nabla) \phi(\vec{r}) d^3r \equiv \int \psi^*(\vec{k}) E_s(\vec{k}) \phi(\vec{k}) \frac{d^3k}{(2\pi)^3} \quad (5)$$

for any arbitrary functions ψ and ϕ . $\psi(\vec{k})$ and $\phi(\vec{k})$ are the Fourier transform of $\psi(\vec{r})$ and $\phi(\vec{r})$, respectively; and $E_s(\vec{k})$ is given by Eq. (1).

In practice, the conduction band of GaP consists of three equivalent valleys along the $[100]$, $[010]$ and $[001]$ directions. Therefore, the envelope functions for the donor states should satisfy the multivalley effective mass equation (see Chapter 2)

$$H F(\vec{r}) = E F(\vec{r}) \quad (6a)$$

with

$$H = E(-i\nabla) + V(\vec{r}) \quad (6b)$$

where $E(-i\nabla)$ is related to $E(\vec{k})$ in the same way as $E_s(-i\nabla)$ is related to $E_s(\vec{k})$; $E(\vec{k})$ being the energy expression for the multivalley conduction band. $V(\vec{r})$ is the impurity pseudo potential ⁽¹⁹⁾. For convenience, we will approximate $E(\vec{k})$ by the sum of three truncated valley functions,

$$E(\vec{k}) \approx \sum_{j=1}^3 E_j(\vec{k}-\vec{k}_j) \quad , \quad (7a)$$

where, for $j = 1$:

$$E_1(\vec{k}-\vec{k}_1) \begin{cases} E_s(\vec{k}-\vec{k}_1) & \text{if } k_z \geq |k_x| \text{ and } k_z \geq |k_y| \\ 0 & \text{otherwise} \end{cases} \quad (7b)$$

The center of the first valley is taken to be $\vec{k}_1 \equiv k_m \hat{z}$. $E_2(\vec{k}-\vec{k}_2)$ (or $E_3(\vec{k}-\vec{k}_3)$) can be obtained by applying an operation O_2 (or O_3) of T_d , i.e., a rotation of $\pi/2$ about the y (or x) axis, on $E_1(\vec{k}-\vec{k}_1)$. For the isocoric impurity S in GaP, we assume that the central-cell core potential is negligibly small ⁽¹³⁾. Therefore, the impurity potential $V(\vec{r})$ will be approximated by

$$V(\vec{r}) \approx \begin{cases} -\frac{2}{r} & \text{for intravalley term} \\ -R_2 \frac{2 \epsilon_0}{\epsilon(\sqrt{2}k_m)r} & \text{for intervalley term} \end{cases} \quad (8)$$

R_2 is the Umklapp renormalization factor required to account for the Umklapp process in the intervalley scattering term ⁽²⁰⁾. $\epsilon(\sqrt{2}k_m)$ is the wavevector ($\vec{q}$) dependent dielectric function evaluated at $q = \sqrt{2} k_m$, the magnitude of the momentum transfer for the intervalley scattering. The value for $\epsilon_0/\epsilon(\sqrt{2} k_m)$ used in the present calculation is 4.8 ⁽²¹⁾.

B. Solution to the Effective Mass Equation

(i) Without the valley-orbit interaction

The single-valley effective Hamiltonian (Eq. 4) can be rewritten as

$$H_S = H_{EMA} - f(k_z) + (\Delta/2 + \Delta E) \quad (9a)$$

where

$$f(k_z) = \sqrt{Qk_z^2/\mu + \Delta^2/4} \quad , \quad (9b)$$

and H_{EMA} is the sum of the remaining terms, which corresponds to the Kohn-Luttinger effective mass Hamiltonian (18).

The Hamiltonian H_S is invariant under the operations of parity and rotation about the z axis. Therefore, the states of different parity or different projection of angular momentum are decoupled. In the present calculation, only three series of states are considered, i.e., the s-series, p_0 -series and $p_{\pm}$ -series. The s-series includes even parity states with quantum numbers $m = 0$ and $\ell = 0, 2, 4, \dots$; the p_0 - and $p_{\pm}$ -series include odd parity states with $m = 0$ and ± 1 , respectively, and $\ell = 1, 3, 5, \dots$.

To calculate the energies of the low-lying discrete states, we expand their envelope functions $F(\vec{r})$ on a set of "basis" functions $\{\beta_{n\ell m}(\vec{r})\}$. Namely,

$$F(\vec{r}) = \sum_{n\ell m} C_{n\ell m} \beta_{n\ell m}(\vec{r}) \quad (10)$$

$$\sum_{n'\ell'm'} \langle n\ell m | H_S | n'\ell'm' \rangle C_{n'\ell'm'} = E \sum_{n'\ell'm'} \langle n\ell m | n'\ell'm' \rangle C_{n'\ell'm'} \quad (11)$$

where we have used the simplified notation $|n\ell m\rangle$ for $|\beta_{n\ell m}\rangle$.

The basis functions are chosen to be products of spherical harmonics and Slater orbitals defined in an ellipsoidal coordinate system with eccentricity factor ζ , viz.,

$$\bar{\beta}_{n\ell m}(\vec{r}') = (r')^\ell e^{-b_{n\ell} r'} Y_{\ell m}(\Omega'), \quad (12)$$

where

$$\vec{r}' \equiv (x, y, z/\zeta).$$

All the matrix elements of H_{EMA} can be expressed analytically⁽²²⁾.

The matrix elements of $f(k_z)$ can be expressed as one-dimensional integrals in $\vec{k}$ -space. We find

$$\begin{aligned} \langle n'\ell'm' | f(k_z) | \bar{n}\ell m \rangle &= \delta_{m'm} \left(\frac{2}{\pi}\right) (-i)^{\ell'} (i)^\ell \int dk k^2 R_{n'\ell'}(k) R_{n\ell}(k) \\ &\times \sum_{\nu=0}^{(\ell+\ell')/2} G_{\ell'\ell}^\nu(m) U_\nu(k), \end{aligned} \quad (13)$$

where ℓ and ℓ' differ only by an even integer, and

$$R_{n\ell}(k) \equiv \int r^\ell j_\ell(kr) e^{-b_{n\ell} r} r^2 dr$$

$$= \frac{[2(\ell+1)]!! b_{n\ell} k^\ell}{(b_{n\ell}^2 + k^2)^{\ell+2}} \quad (14)$$

is the radial part of the Fourier transform of the Slater orbitals as defined in Eq. (12). The coefficients $G_{\ell', \ell}^\nu(m)$ are determined by the relation

$$4\pi Y_{\ell', m}^*(\theta, \phi) Y_{\ell m}(\theta, \phi) = \sum_{\nu=0}^{(\ell+\ell')/2} G_{\ell', \ell}^\nu(m) \cos^{2\nu} \theta \quad ; \quad (15)$$

and

$$U_\nu(k) \equiv \int_0^1 x^{2\nu} \sqrt{Qk^2 x^2 / \mu \zeta + \Delta^2 / 4} dx \quad (16)$$

which can be evaluated analytically with the result

$$U_0 = \frac{R}{2} + \frac{a}{2\sqrt{c}} \ln \left(\frac{R+\sqrt{c}}{\sqrt{a}} \right) ,$$

and

$$U_\nu = (R^3 - (2\nu-1)a U_{\nu-1}) / 2(\nu+1)c, \quad \text{for } \nu \geq 1 ,$$

where

$$R \equiv \sqrt{c+a} ,$$

$$c \equiv Qk^2 / \mu \zeta^2 ,$$

and

$$a \equiv \Delta^2/4 \quad .$$

The matrix equation, Eq. (11), can be solved numerically to obtain the eigenvalues E and eigenvectors.

(ii) With the valley-orbit interaction

One can describe the envelope functions for the donor states as linear combinations of functions in $\vec{k}$ -space localized at the center of each valley (the X-point), which transform according to the irreducible representation $\Gamma_1(A_1)$ or $\Gamma_3(E)$ of the T_d point group. Alternatively, one can describe the envelope functions as linear combinations of functions centered at each of the six equivalent minima. Within each valley, they are either symmetric or antisymmetric combinations of functions located at the two closely-spaced minima. We shall call them the symmetric and antisymmetric "dumbbell" functions (DF), respectively. Linear combinations of symmetric DF's localized in different valleys can transform according to the irreducible representation $\Gamma_1(A_1)$ or $\Gamma_3(E)$, whereas the antisymmetric DF's will transform as the three basis vectors of the $\Gamma_5(T_2)$ representation. If we expand the angular part of each envelope function in terms of spherical harmonics, we find that both even and odd harmonics have to be included, since the dumbbell functions of the same parity made from them will be coupled together.

To calculate the energies of the donor states, we expand their envelope functions localized within each valley in terms of the dumbbell-like Slater-type orbitals (DSTO's). In $\vec{k}$ -space, the DSTO's are defined as

$$\beta_{n\ell m}^{\pm}(\vec{k}) = \frac{\zeta}{\sqrt{2}} \left[\bar{\beta}_{n\ell m}(k_x, k_y, \zeta(k_z + k_0)) \pm \bar{\beta}_{n\ell m}(-k_x, -k_y, \zeta(-k_z + k_0)) \right], \quad (17a)$$

where

$$\bar{\beta}_{n\ell m}(k_x, k_y, k_z) \equiv \frac{4\pi b_{n\ell} k^{\ell} [2(\ell+1)]!!}{(b^2 + k^2)^{\ell+2}} Y_{\ell m}(\Omega_k) \quad (17b)$$

is the Fourier transform in $\vec{k}$ -space of $\bar{\beta}_{n\ell m}(\vec{r}')$ as given by Eq. (12). In Eq. (17a), " $\pm$ " labels the symmetric or antisymmetric DSTO's, ζ is the eccentricity factor, and k_0 is given by Eq. (2). Linear combinations of the symmetric DSTO's localized at different valleys can produce basis states, which transform as basis vectors of the irreducible representations Γ_1 and Γ_3 , i.e.,

$$\beta_{n\ell m}^{\Gamma}(\vec{k}) = \sum_{j=1}^3 \alpha_j(\Gamma) \beta_{n\ell m}^+ (O_j^{-1}(\vec{k} - \vec{k}_j)); \quad \Gamma = \Gamma_1 \text{ or } \Gamma_3, \quad (18)$$

where

$$\alpha_j(\Gamma_1) = (1, 1, 1)/\sqrt{3},$$

and

$$\alpha_j(\Gamma_3) = (1, -1, 0)/\sqrt{2} \quad \text{or} \quad (1, 1, -2)/\sqrt{6} \quad .$$

$\vec{k}_j$ indicates the positions of the three equivalent X-points, and O_j represents an operation of T_d , which transforms a valley on the z-axis into the j^{th} valley. The antisymmetric DSTO's themselves transform as three basis vectors (labelled by j) of the Γ_5 -representation, i.e.,

$$\beta_{n\ell m}^{\Gamma_5 j}(\vec{k}) = \beta_{n\ell m}^{-1}(\vec{O}_j^{-1}(\vec{k} - \vec{k}_j)); \quad j = 1, 2, 3 \quad . \quad (19)$$

The mixing of antisymmetric envelope functions associated with different valleys is rigorously zero, according to symmetry; hence, the Γ_5 states are not affected by the valley-orbit interaction.

Expanding the total envelope wave function of symmetry Γ as

$$F^{\Gamma}(\vec{k}) = \sum_{n\ell m} C_{n\ell m} \beta_{n\ell m}^{\Gamma}(\vec{k}) \quad , \quad (20)$$

We readily obtain the matrix equation in $\vec{k}$ -space

$$\sum_{n'\ell'm'} \langle \beta_{n\ell m}^{\Gamma} | H | \beta_{n'\ell'm'}^{\Gamma} \rangle C_{n'\ell'm'}^{\Gamma} = E_{n'\ell'm'}^{\Gamma} \sum_{n\ell m} \langle \beta_{n\ell m}^{\Gamma} | \beta_{n'\ell'm'}^{\Gamma} \rangle C_{n\ell m}^{\Gamma} \quad , \quad (21)$$

where H is the multi-valley effective mass Hamiltonian defined by

Eq. (6b). The matrix elements in Eq. (21) include intravalley and intervalley terms. In Appendix A, we derive the general expression for all the intravalley terms and the intervalley terms associated with s-like orbitals of both the Hamiltonian and overlap matrix elements. The intervalley terms associated with other orbitals are neglected, since only the ground state envelope function (which includes mostly s-like components) has appreciable spreading in $\vec{k}$ -space. Eq. (21) can be solved numerically to obtain the eigenvalues E and eigenvectors.

III. RESULTS AND DISCUSSION

A. Determination of the Camel's Back Parameters

To determine the camel's back parameters Q and μ , we solve the single-valley effective mass equation (Eq. (11)) for several values of Q and μ . The numerical work was carried out using 10 Slater orbitals (given by Eq. (12)) for $\ell = 0$ or 1, 6 orbitals for $\ell = 2$ or 3, and 4 orbitals for $\ell = 4$ or 5. The parameters $b_{n\ell}$ were chosen to be $b_0/(\ell+1) Z_{n\ell}$, with $b_0 = 5 \text{ Bohr}^{-1}$ and

$$\begin{aligned} Z_n &= (1, 1.5, 2, 3, 4, 6, 9, 14, 21, 32) , & \text{for } \ell = 0 \text{ or } 1, \\ &= (.5, .7, 1, 2, 3, 5) , & \text{for } \ell = 2 \text{ or } 3, \\ &= (.5, .7, 1, 2) , & \text{for } \ell = 4 \text{ or } 5. \end{aligned}$$

The eccentricity factor ζ is chosen to minimize the energy expectation value of the Hamiltonian for the lowest energy basis wave function for each symmetry.

To compare our method with the accurate results obtained by Faulkner ⁽²²⁾ at the KL-EMT limit ($Q = 0$), we also did a calculation at this limit for $\mu^{-1/3} = 0.6$. Our calculated eigenvalues agree with Faulkner's within 0.001 Ry for all the states of interest.

To see how the energy values of the low-lying states vary as the parameter Q changes, we plot the calculated energy values for the 6 lowest states for the s -series (even parity) and the 4 lowest states for each of the p_0 and $p_{\pm}$ series (odd parity) as functions of Q/Δ in Fig. III-1 and Fig. III-2, respectively, for the case $\mu = 4$. As shown in these figures, for $Q/\Delta < 1$, the whole spectrum decreases monotonically as Q/Δ increases, and behaves qualitatively the same as that calculated by the KL-EMT ⁽¹⁸⁾. This is due to the fact that, for $Q/\Delta < 1$, the conduction band is approximately parabolic with an effective mass given by

$$m_{\ell}^* = \mu m_t / 2(1 - Q/\Delta) \quad . \quad (22)$$

When $Q/\Delta > 1$, then the camel's back appears at the conduction band edge, and the spectrum behaves very differently from that obtained by the KL-EMT.

We determine the best parameter Q by fitting the calculated energy spacing between the $2p_0$ and $2p_{\pm}$ states to that of the experi-

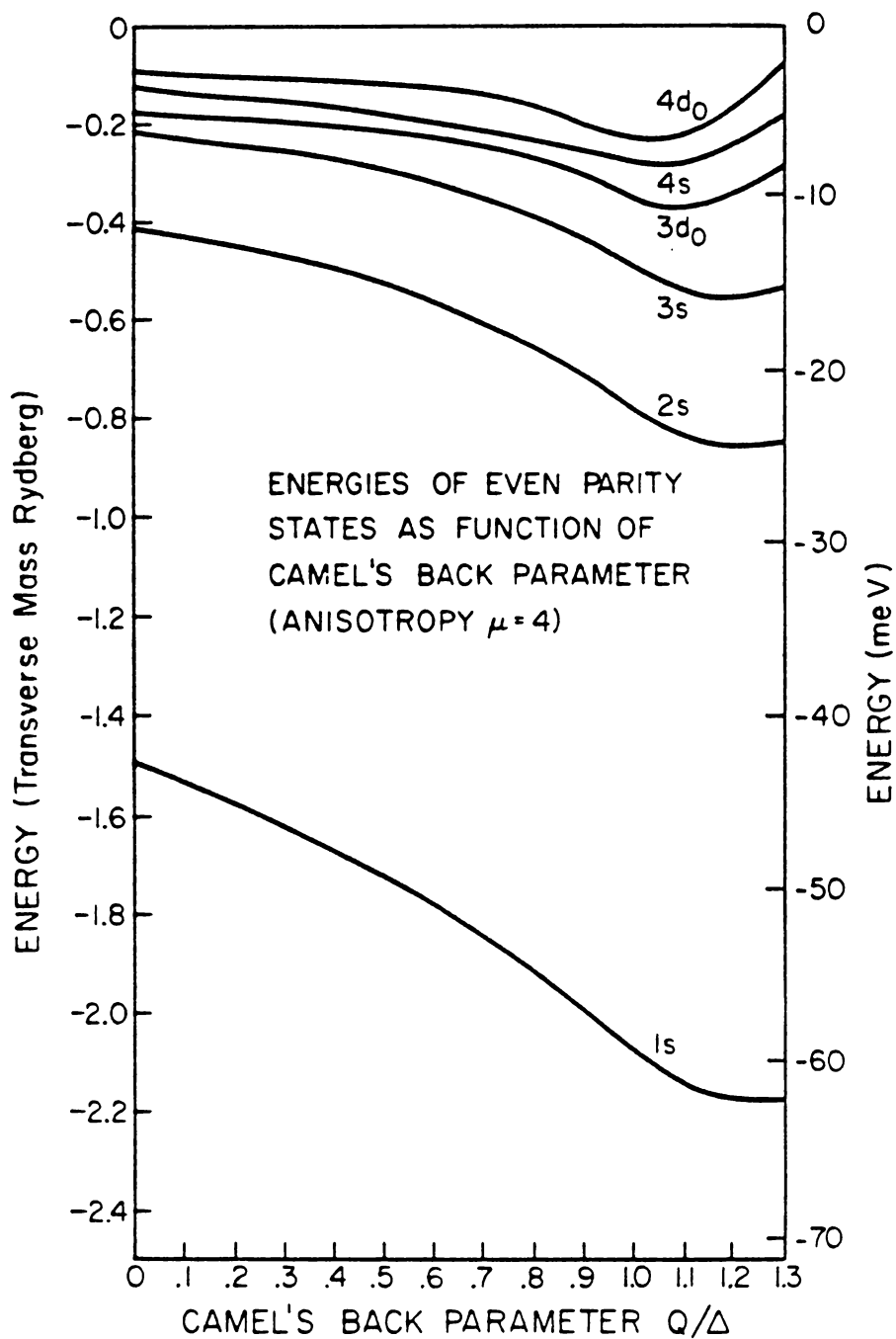


Figure III-1 Energies of the 6 lowest states for the s-series plotted as a function of camel's back parameter Q/Δ .

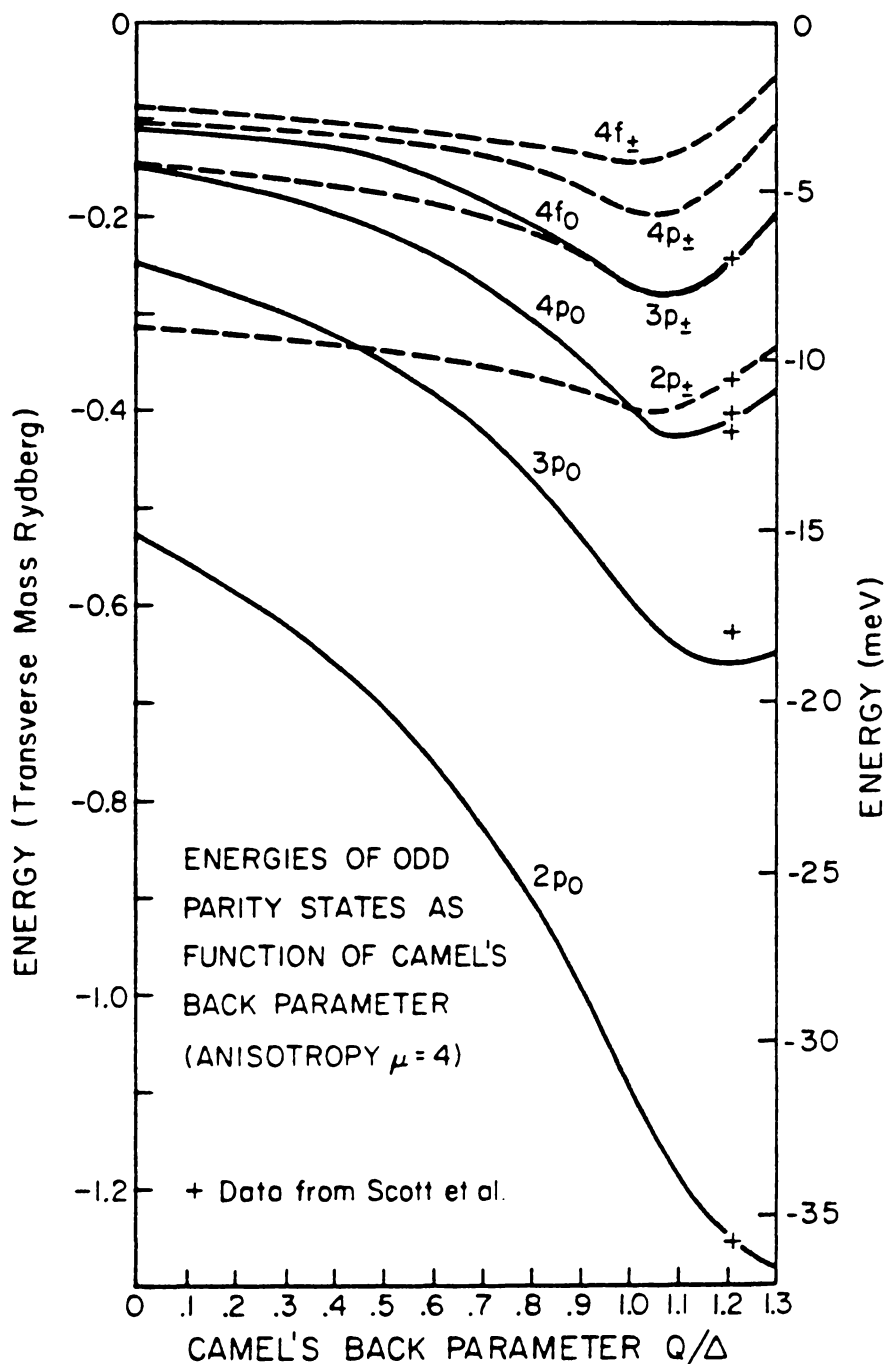


Figure III-2. Energies of the 4 lowest states for each of the p_0 $p_{\pm}$ series, plotted as a function of camel's back parameter Q/Δ . Also included are the experimental data (marked "+") observed in GaP:S_p by Scott et al (23).

mental value observed by Scott et al ⁽²³⁾. The best fit is obtained at $Q/\Delta = 1.39, 1.29, 1.21, 1.17$ and 1.13 for $\mu = 3, 3.5, 4, 4.5$ and 5 , respectively. Substituting these values of Q/Δ into Eq. (3), we obtain that $\Delta E = 9.7, 5.8, 3.2, 2.2$ and 1.3 meV. Substituting the pairs of values for Q/Δ and μ into Eq. (2) we obtain $k_0 = 0.095, 0.090, 0.083, 0.080$ and 0.074 ($\frac{2\pi}{a_0}$).

Comparing our results for ΔE and k_0 with the experimental values obtained by Humphreys et al ⁽¹¹⁾, we conclude that μ should be about 4 and Q/Δ about 1.21, which are in good agreement with the results obtained by Glinskii et al ⁽¹²⁾.

B. Donor States without Valley-Orbit Interaction

Knowing the suitable parameters for the camel's back structure, we then repeat the above calculation, including four more orbitals (with the parameter $Z_{n\ell} = 8, 12$ for $\ell = 2$ or 3 and $Z_{n\ell} = 3, 5$ for $\ell = 4$ or 5) and with the eccentricity factor ζ varied independently to find the lowest upper bound for each eigenvalue of the Hamiltonian. The ionization energies, eccentricity factors and percentages in various orbitals of the lowest 6 states for each series are listed in Table III-1, along with the available experimental data. The notation used to label the states is the same as that used by Faulkner ⁽²²⁾. As noted from Table III-1, all the states except the lowest of each series have large amounts of admixture of the higher orbitals. The ionization energies for the $1s, 2p_0$ and $2p_{\pm}$ states obtained in the

present paper are about 5% larger than that obtained by a simple variational calculation (14).

To compare our theoretical results with the experimental data (3,6,7,23), we assume that the theoretical energies for the $2p_{\pm}$ level relative to the conduction band edge is the same as the experimental energies (24). This assumption allows us to predict the values of the ionization energies for various impurities by adding the theoretical ionization energy for $2p_{\pm}$ to the experimentally observed spacing between the ground state and $2p_{\pm}$ level. The procedure yields the values 85.3 meV, 107.3 meV, and 93.1 meV for the binding energies of the donors Si_{Ga} , S_{P} , and Te_{P} , respectively, in GaP. The experimental ionization energies of the other states listed in Table III-1 are also obtained by matching the $2p_{\pm}$ level with our theoretical results. To illustrate this point further, we plot in Fig. III-3 our theoretical spectrum for the odd parity states along with the experimental spectra observed in $\text{GaP}:\text{Si}_{\text{Ga}}$, $\text{GaP}:\text{S}_{\text{P}}$, and $\text{GaP}:\text{Te}_{\text{P}}$, respectively. As shown in Fig. III-3, the agreement between theory and experiment is fairly good for the low-lying states (with ionization energy greater than 0.21 Ry, or 6 meV). For the highly excited states, the appropriate assignment for the experimentally observed lines is difficult.

We did not include the effects of the valley-orbit interaction which results from the fact that the conduction band in GaP has three equivalent valleys along the $[100]$, $[010]$, and $[001]$ directions. If one includes the valley-orbit interaction, all the even parity states

TABLE III-1. Ionization energies, eccentricity factors, and percentages in various orbitals of the lowest 6 states for each of the s , p_0 and $p_{\pm}$ series for the donors in GaP. The experimental data for ionization energies observed in GaP:S_p, GaP:Si_{Ga} and GaP:Te_p are also listed for comparison.

State	Eccentricity ζ	Percentages in Various Orbitals			Ionization Energy (meV)	
		$s, p_0, p_{\pm}$	$d_0, f_0, f_{\pm}$	$g_0, h_0, h_{\pm}$	Theory	Experiment
1s	.45	94.7	5.2	0.1	61.95	107.3 ^a , 93.1 ^e , 85.34 ^c
2s	.41	56.1	40.9	3.0	24.37	26.0 ^a
3s	.39	27.5	66.7	5.8	15.77	17.1 ^a
3d ₀	.35	32.9	39.7	27.3	10.33	12.4 ^a
4s	.31	34.3	53.2	12.5	7.23	
4d ₀	.35	18.8	46.5	34.7	5.71	
2p ₀	.42	94.7	5.2	0.1	35.64	35.84 ^b , 36.8 ^e
3p ₀	.36	76.5	22.5	1.0	18.93	17.9 ^b , 18.56 ^d , 18.47 ^c
4p ₀	.32	53.2	43.9	2.9	12.37	12.0 ^b
4f ₀	.28	36.2	42.1	21.7	7.78	7.77 ^c
5p ₀	.30	31.6	55.2	13.2	6.14	
5f ₀	.26	24.8	37.6	37.6	4.40	
2p _±	.24	79.8	19.5	0.7	10.54	10.54 ⁺
3p _±	.26	41.8	51.1	7.1	7.39	6.94 ^b
4p _±	.24	12.1	66.9	21.0	5.01	
4f _±	.18	26.0	20.9	53.1	3.41	
5p _±	.24	28.7	52.9	18.4	2.17	
5f _±	.16	23.6	37.0	39.4	1.13	

a. Observed in GaP:S_p by Dean et al⁷ (All the states are of Γ_1 symmetry)

b. Observed in GaP:S_p by Scott et al²³

c. Observed in GaP:Si_{Ga} by Carter et al³

d. Observed in GaP:Te_p by Onton et al⁶

e. Observed in GaP:Te_p by Kopylov et al¹⁴

+ The experimental values are obtained by matching the $2p_{\pm}$ state with theory.

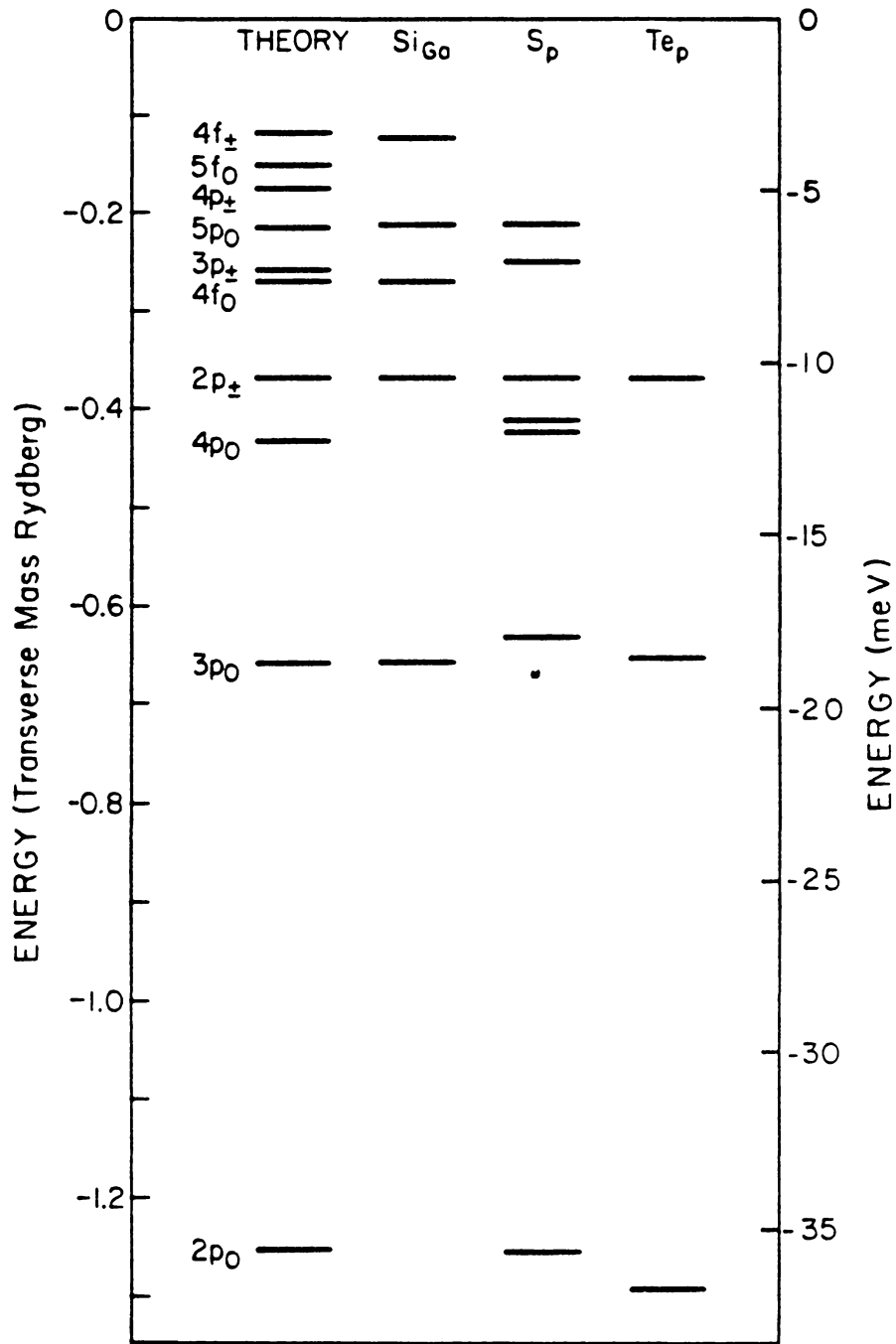


Figure III-3. Theoretical spectrum of the odd parity donor states in GaP. The experimental spectra observed in GaP:Si_{Ga} (3), GaP:S_p (23), and GaP:Te_p (6,7) are juxtaposed for comparison.

will be split into a singlet state (of Γ_1 symmetry) and a doublet state (of Γ_3 symmetry). The odd parity states are unaffected by the intervalley scattering, and thus are not split. For the even parity states, our theoretical energy values should be close to that of the experimental Γ_3 states since the intervalley scattering effect on the Γ_3 states is much smaller than on the Γ_1 states. The experimental data are only available for the Γ_1 states. The differences between theoretical and experimental energy values for these states are estimated to be about 2 meV for the excited states.

C. Donor States with Valley-Orbit Interaction

To include the effects of the valley-orbit interaction, we must solve the multivalley effective mass equation (Eqs. (6) and (21)). We use the basis functions defined in Eqs. (18) and (19) with exponents $b_{n\ell}$ given by

$$b_{n\ell} = b_0 / z_{n\ell}; \quad b_0 = 2 \text{ Bohr}^{-1} \text{ and}$$

$$z_{n\ell} = \begin{cases} (1, 2, 4, 8, 16, 32, 64, 1/2, 1/4, 1/8) & \text{for } \ell = 0 \\ (1, 2, 4, 8, 16, 1/2) & \text{for } \ell = 1 \\ (1, 2, 4, 8) & \text{for } \ell = 2 \end{cases}$$

Orbitals with $\ell \geq 3$ are neglected.

The eccentricity factor ζ is determined by minimizing the energy

expectation value of the single valley Hamiltonian on the trial wave function β_{000}^+ given by Eq. (17). We obtain a value of 0.48 for ζ .

We have computed the valley-orbit interactions for several values of the Umklapp renormalization factor R_2 . The results for the energies of the lowest Γ_1 -symmetry, Γ_3 -symmetry and Γ_5 -symmetry states are plotted in Fig. III-4 as functions of R_2 . The energies of the Γ_5 -symmetry states are independent of R_2 as expected. Fitting this curve for the ground state to the experimental data ^(1,7,23) (marked "+"), we obtain a value for $R_2 \approx 0.91$. In Table III-2, we have listed the ionization energies and percentages in various orbitals of the 6 lowest states for each of the Γ_1 , Γ_3 and Γ_5 symmetries. The experimental data observed in GaP:S are also included in parentheses for comparison ^(1,7,23). The agreement between theory and experiment is fairly good, even though we neglected the electron-phonon interaction, and made some rather crude approximations for the Hamiltonian. An interesting feature of the energy spectrum is that the ordering of Γ_3 and Γ_5 -symmetry states is reversed with respect to that of Si. This is due to the fact that the distance $\vec{k}$ between the two conduction band minima on the same axis (displaced by one reciprocal lattice vector) in GaP is two times shorter than that in Si. This yields a strong overlap between the envelope functions located at the two minima in the camel's back valley and hence reduces the binding energy for the Γ_5 -symmetry (odd parity) state substantially.

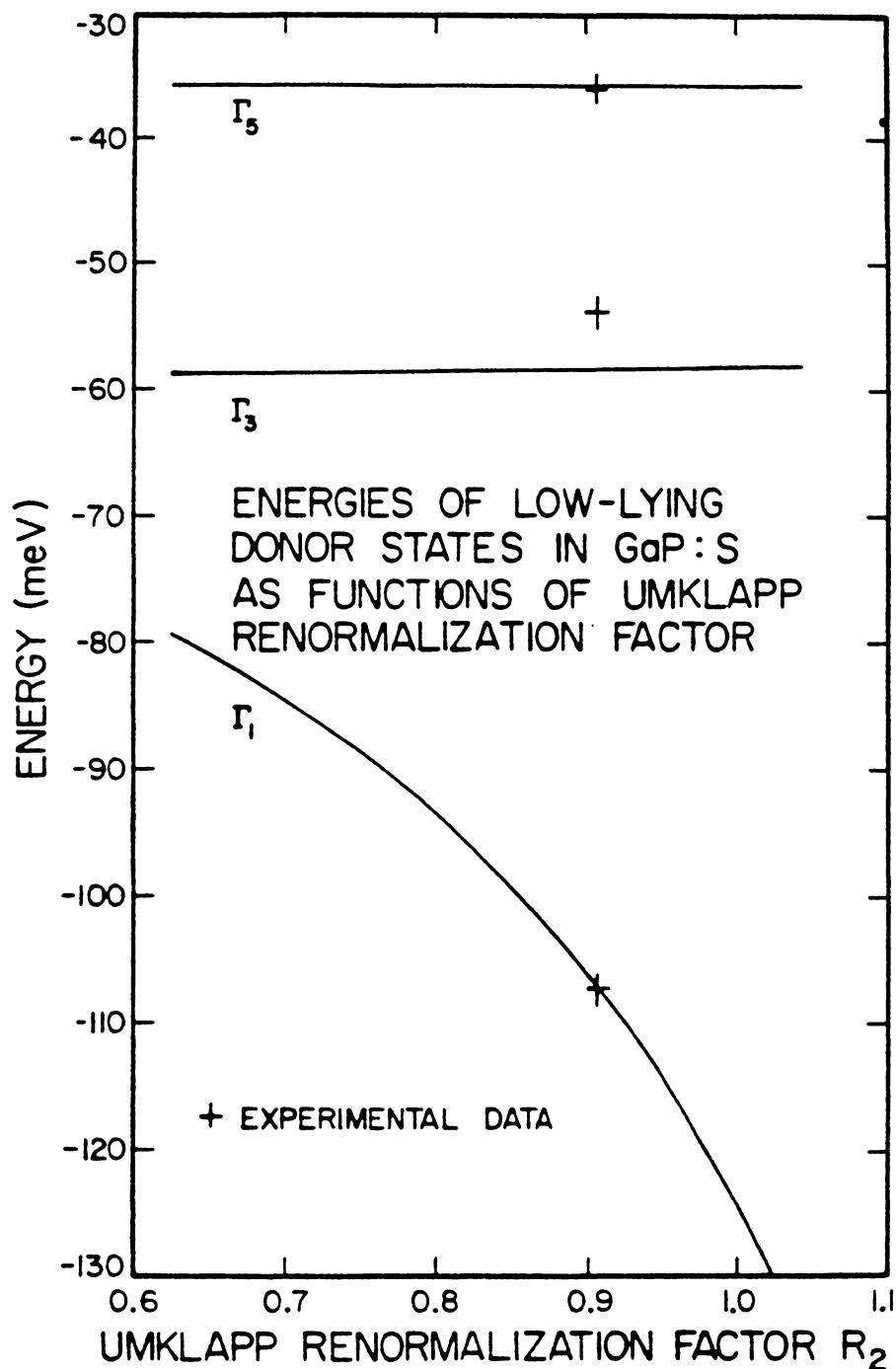


Figure III-4. Energies of the lowest-lying states for Γ_1 , Γ_3 and Γ_5 symmetries are plotted as functions of the Umklapp renormalization factor R_2 . The experimental data (marked by "+") are taken from Dean et al (Ref. 7), Manchon et al (Ref. 1) and Scott et al (Ref. 23) for the Γ_1 , Γ_3 and Γ_5 states, respectively.

TABLE III-2. Ionization energies and percentages in various orbitals of the 6 low-lying states for each of the Γ_1 , Γ_3 and Γ_5 symmetries. The experimental data for GaP:S_p are also included for comparison.

SYMMETRY	STATE	PERCENTAGES IN VARIOUS ORBITALS			IONIZATION ENERGY (meV)	
		s	p _o	d _o	Theory	Experiment
Γ_1	1s	99.38	0.60	0.02	107.3	107.3 ^a
	2s	7.74	90.76	1.50	25.36	26.0 ^a
	3s	82.59	1.92	15.49	17.70	17.1 ^a
	3d _o	10.12	73.05	16.83	11.08	12.4 ^a
	4s	23.11	18.93	57.96	9.56	9.7 ^a
	4d _o	54.98	14.04	30.98	6.90	
Γ_3	1s	99.04	0.22	0.74	58.25	53.8 ^b
	2s	7.07	90.75	2.18	24.25	----
	3s	64.55	9.42	26.03	15.97	----
	3d _o	5.81	89.89	4.30	10.12	----
	4s	27.65	4.99	67.36	8.77	----
	4d _o	59.54	7.23	33.23	6.80	----
Γ_5	1s	98.5	0.90	0.06	35.71	35.84 ^f
	2s	20.67	79.28	0.05	19.16	17.9 ^c
	3s	49.41	17.53	33.06	13.52	12.0 ^c
	3d _o	14.57	62.33	23.10	8.83	----
	4s	21.51	32.38	46.11	7.39	----
	4d _o	66.5	6.60	26.90	6.33	----

a. Dean et al ⁷

b. Manchon et al ¹

c. Scott et al ²³

The ionization energy for the lowest Γ_3 -symmetry obtained here is approximately 10% larger than the experimental value. This discrepancy may be caused by the neglect of the short-range core potential (25). It should be noticed that the Γ_5 -symmetry states presented here correspond to the states belonging to the $2p_0$ -series obtained in Part B, in which these functions are described by a set of basis functions localized at the center of the "camel's back" valley (the X-point). The ionization energies for these states obtained here are slightly larger than those obtained previously. This indicates that the expansion of the envelope wave functions on the DSTO's is superior to the expansion on the previously used basis functions.

Another interesting feature of our result is that the $2s(\Gamma_1)$ state is mainly made up of the p_0 -like orbitals (91%), whereas the $3s(\Gamma_1)$ state is mainly made up of the s-like orbitals (see Table III-1). This predominantly p-like character of the $2s(\Gamma_1)$ state accounts for the irregular oscillator strength for the two-electron transition observed in the luminescence spectrum from GaP:S (3,6,7) and GaP:Te (6,7). To illustrate this point further, we calculated the ratios of oscillator strengths for the $1s(\Gamma_1)$, $3s(\Gamma_1)$, $3d_0(\Gamma_1)$ and $4s(\Gamma_1)$ states to the $2s(\Gamma_1)$ state. In the two-electron transition process, the photoluminescence results from the recombination of an electron-hole pair in the donor bound exciton, leaving one electron in an excited donor state (the final state). To calculate the oscillator strength of the luminescence line, we have to know the electron wave function in the bound exciton. We approximate the 3-particle bound exciton wave

function by the following form

$$\psi_{b_1 b_2 b_3}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \propto \left[\beta_{b_1}(\vec{r}_1) \beta_{b_2}(\vec{r}_2) + \beta_{b_2}(\vec{r}_1) \beta_{b_1}(\vec{r}_2) \right] e^{-b_3 r_3} \chi(1,2) \chi(3) \quad (23)$$

where $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_3$ are the coordinates for the two electrons and the hole respectively; $\chi(1,2)$ and $\chi(3)$ are the two electron product spinor (a singlet) and the hole spinor (a quartet), respectively, and

$$\beta_b(\vec{r}) \equiv \sqrt{2} e^{-b \sqrt{x^2+y^2+z^2}/\zeta^2} \cos(k_0 z) \quad (24)$$

The exponents b_1 , b_2 and b_3 are variational parameters determined by minimizing the energy expectation value of the total Hamiltonian in the trial wave function $\psi_{b_1 b_2 b_3}$. The eccentricity factor ζ is the same as for the donor states. To obtain reasonable results, the donor Hamiltonian is modified by increasing the factor R_2 slightly such that a variational calculation using the trial wave function $\beta_b(\vec{r})$ will reproduce the binding energy for the ground donor state. A value of 1.125 for R_2 is found to be appropriate for this purpose. The optimized values for the parameters b_1 , b_2 and b_3 are found to be 3.5, 1.0 and .56 Bohr⁻¹, respectively. This set of parameters yields a total energy -134.4 meV for the bound exciton in GaP:S, which is not too far from the experimental value -149 meV (26). The oscillator strength for the two-electron transition process with a final donor state $|n\rangle$ is given by

$$f_n \propto |\langle n | \beta_{b_1} \rangle \langle \beta_{b_2} | M | \beta_{b_3} \rangle + \langle n | \beta_{b_2} \rangle \langle \beta_{b_1} | M | \beta_{b_3} \rangle|^2 \quad (25)$$

where $\langle \beta_b | M | \beta_{b_3} \rangle$ represents the optical matrix element for an electron in state $|\beta_b\rangle$ to recombine with a hole in state $|\beta_{b_3}\rangle$.⁽²⁸⁾ Since the state $|\beta_{b_1}\rangle$ is much more spread out in $\vec{k}$ -space than the state $|\beta_{b_2}\rangle$ ($b_1 \approx 3.5 b_2$), we expect that $|\langle \beta_{b_1} | M | \beta_{b_3} \rangle| \gg |\langle \beta_{b_2} | M | \beta_{b_3} \rangle|$.⁽²⁹⁾

Therefore, Eq. (26) can be approximated by

$$f_n \propto |\langle n | \beta_{b_2} \rangle|^2 \cdot |\langle \beta_{b_1} | M | \beta_{b_3} \rangle|^2 \quad (26)$$

Then the ratio of f_n to f_{2s} (the oscillator strength for the 2s final donor state) is simply

$$f_n/f_{2s} = |\langle n | \beta_{b_2} \rangle|^2 / |\langle 2s | \beta_{b_2} \rangle|^2 \quad (27)$$

According to Eq. (27), we obtained that

$$f_{1s} : f_{2s} = f_{3s} : f_{3d_0} : f_{4s} \approx 30 : 1 : 13 : 2 : 1$$

For comparison, we plot in Fig. III-5, the two-electron transition spectrum observed in GaP:S by Dean et al⁽⁷⁾. The line positions for the lowest excited states predicted by the present calculation are marked by arrows. As shown in this figure, the theoretical predictions for both line position and oscillator strength are in

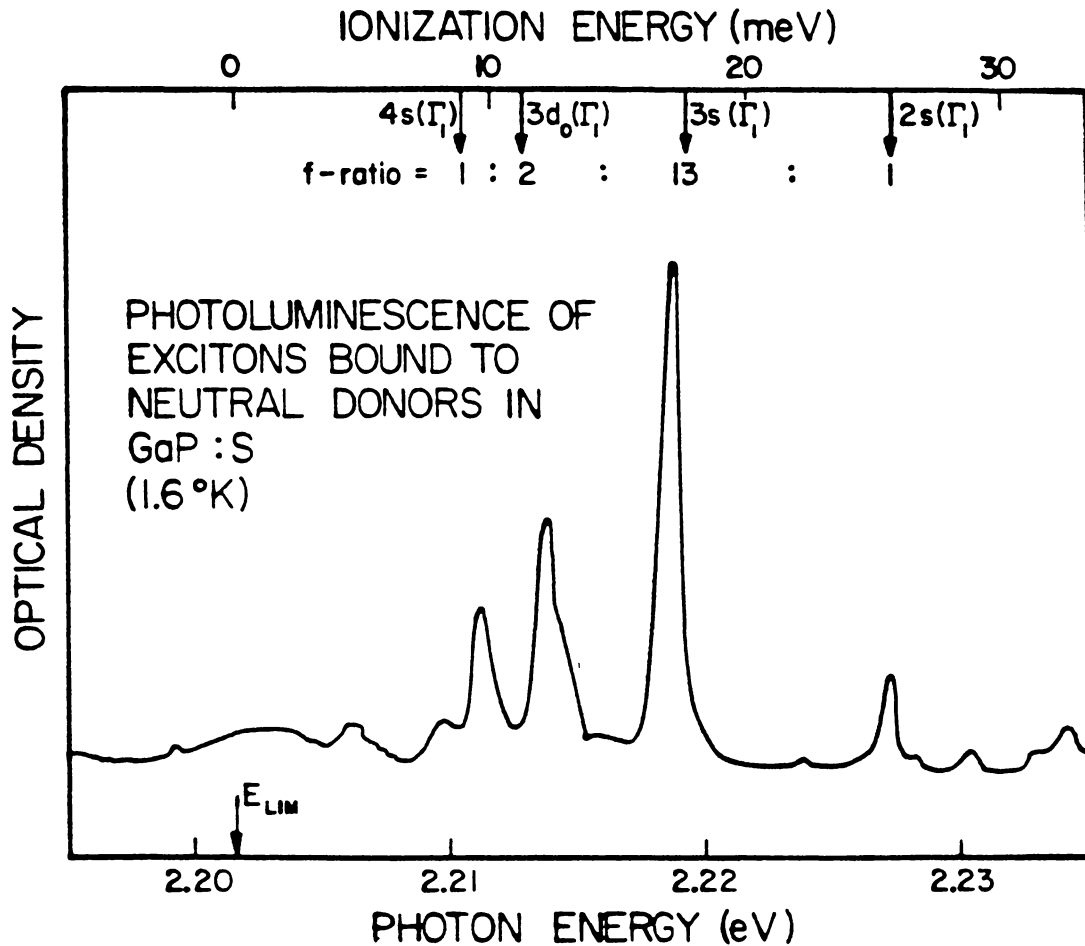


Figure III-5. Two-electron transition spectrum for GaP:S. The data are taken from Dean et al (Ref. 7). The arrows indicate the theoretical predictions for the line positions. The relative ratios for oscillator strength (f-ratios) of these lines predicted using Eq. (27) are shown under the arrows. E_{LIM} is the position of the series limit for the donor states, predicted by subtracting the binding energy (107.3 meV) of the donor ground state from the line position of the bound exciton luminescence.

reasonable agreement with the experimental data.

IV. SUMMARY

In this chapter, we have studied extensively the effect of the camel's back structure on the donor spectra. We have calculated the energies of the 6 lowest states for each of the s , p_0 , and $p_{\pm}$ series of donors in GaP with and without valley-orbit interaction. We determine the camel's back parameters by fitting our theoretical spectrum with the experimental data. These parameters are consistent with those obtained by Glinskii ⁽¹²⁾. The energy values of the low-lying odd parity state are in good agreement with the experimental values.

We have calculated the valley-orbit interaction for the even parity donor states in GaP:S. We find a valley-orbit splitting of 71.6 meV between the Γ_1 and Γ_5 states and 49.0 meV between the Γ_1 and Γ_3 states. These values are in reasonable agreement with the experimental data. We have estimated the ratios of oscillator strength for the low-lying Γ_1 -symmetry (even parity) states. Both the energy values and oscillator strength are in close agreement with the experimental data. Our study provides an understanding of the effects on the donor states of GaP due to the camel's back structure and the valley-orbit interaction. Our calculation explains the large valley-orbit splitting for the donor ground state in GaP and the irregular oscillator strength ratio for two-electron transitions observed in GaP:S and GaP:Te ^(3,6,7).

APPENDIX A: DERIVATION OF THE MATRIX ELEMENTS

In this appendix, we derive both the Hamiltonian and overlap matrix elements for the basis functions defined in Eq. (3) and Eq. (4). It is readily shown that

$$\begin{aligned} \langle \beta_{n\ell m}^{\Gamma} | H | \beta_{n'\ell'm'}^{\Gamma} \rangle &= \langle \beta_{n\ell m}^{\pm}(\vec{k}-\vec{k}_m, \hat{z}) | H | \beta_{n'\ell'm'}^{\pm}(\vec{k}-\vec{k}_m, \hat{z}) \rangle \delta_{nnm}, \\ &+ g(\Gamma) \langle \beta_{n\ell m}^{\pm}(\vec{k}-\vec{k}_m, \hat{z}) | H | \beta_{n'\ell'm'}^{\pm}, O_j^{-1}(\vec{k}-\vec{k}_j) \rangle \delta_{nnm}, \end{aligned} \quad (A1)$$

and similarly,

$$\begin{aligned} \langle \beta_{n\ell m}^{\Gamma} | \beta_{n'\ell'm'}^{\Gamma} \rangle &= \langle \beta_{n\ell m}^{\pm}(\vec{k}-\vec{k}_m, \hat{z}) | \beta_{n'\ell'm'}^{\pm}(\vec{k}-\vec{k}_m, \hat{z}) \rangle \delta_{nnm} + g(\Gamma) \langle \beta_{n\ell m}^{\pm}(\vec{k}-\vec{k}_m, \hat{z}) | \beta_{n'\ell'm'}^{\pm} \\ &\times (O_j^{-1}(\vec{k}-\vec{k}_j)) \rangle \delta_{nnm}, \end{aligned} \quad (A2)$$

where $g(\Gamma) = 2, -1$ and 0 for $\Gamma = \Gamma_1, \Gamma_3$ and Γ_5 , respectively. O_j represents an operation in T_d , which transforms a valley on the z -axis into the j^{th} valley. It is convenient to evaluate the kinetic energy term in $\vec{k}$ -space and the potential energy term in real space. For convenience, we define the functions $G_{\ell m}^{\vee}(k_z)$ by the relation

$$k^\ell Y_{\ell m}(\Omega_k) \equiv \sqrt{\frac{1}{4\pi}} \sum_{v=0}^{\ell-m} G_{\ell m}^v(k_z) (k_x^2 + k_y^2)^{v+m/2} e^{im\phi_k}, \quad (A3)$$

where Ω_k is the solid angle and ϕ_k the azimuthal angle for $\vec{k}$ with respect to the z-axis.

Substituting Eqs. (3), (4), (7) and (8)'s into Eqs. (A1) and (A2), we obtain for the intravalley term that the kinetic energy matrix elements are

$$\langle \beta_{n\ell m}^\pm | E(\vec{k}) | \beta_{n'\ell'm}^\pm \rangle = \left[T_{m\ell\ell'}^{nn'}(0) \pm T_{m\ell\ell'}^{nn'}(k_0) \right], \quad (A4a)$$

with

$$T_{m\ell\ell'}(k_0) \equiv \frac{b_{n\ell} b_{n'\ell'} [2(\ell+1)]!! [2(\ell'+1)]!! \zeta^2}{2\pi} \sum_{v=0}^{\ell-m} \sum_{v'=0}^{\ell'-m} \sum_{i=1}^2 \sum_{j=1}^2 \quad (A4b)$$

$$\times \int_{-\infty}^{\infty} G_{\ell m}^v(z_i) G_{\ell' m'}^{v'}(z_j) [I_{\ell\ell'}^{v+v'+m+1}(k_z) + I_{\ell\ell'}^{v+v'+m}(k_z) E_\ell(k_z)] dk_z,$$

where

$$I_{\ell\ell'}^v(k_z) \equiv \int_0^\infty \frac{x^v dx}{(b_{n\ell}^2 + z_i^2 + x)^{\ell+2} (b_{n'\ell'}^2 + z_j^2 + x)^{\ell'+2}} \quad (A5a)$$

with

$$z_i \equiv [(-1)^i k_z - k_0] \zeta$$

and

$$E_{\ell}(k_z) = \frac{k_z^2}{\mu} - \sqrt{Qk_z^2/\mu + \Delta^2/4} + \Delta/2 + \Delta E. \quad (A5b)$$

The potential energy matrix elements are

$$\langle \beta_{n\ell m}^{\pm} | V | \beta_{n'\ell'm'}^{\pm} \rangle = 2 [V_{m\ell\ell'}^{nn'}(0) \pm V_{m\ell\ell'}^{nn'}(k_0)] \quad , \quad (A6a)$$

with

$$V_{m\ell\ell'}^{nn'}(k_0) = \text{Re} \left\{ (-i)^{\ell+\ell'} \int_0^1 \frac{d\xi Q_{\ell m}(\xi) Q_{\ell' m}(\xi) (\ell+\ell'+1)!}{\sqrt{1-g_1\xi^2} (b_{n\ell} + b_{n'\ell'} - 2ik_0\xi\zeta)^{\ell+\ell'+2}} \right\} \quad , \quad (A6b)$$

$$g_1 \equiv 1 - \zeta^2 \quad , \quad \xi \equiv \cos\theta \quad , \quad (A6c)$$

where

$$Q_{\ell m}(\xi) = \left[\frac{(2\ell+1)(\ell-m)!}{(\ell+m)!} \right]^{\frac{1}{2}} P_{\ell}^m(\xi) \quad (A6d)$$

and P_{ℓ}^m is the associated Legendre function. The overlap matrix elements are

$$\langle \beta_{n\ell m}^{\pm} | \beta_{n'\ell'm'}^{\pm} \rangle = \frac{M(n\ell m, n'\ell'm') \zeta \sqrt{(2\ell+2)! (2\ell'+2)!}}{(2b_{n\ell})^{\ell+3/2} (2b_{n'\ell'})^{\ell'+3/2}} \quad , \quad (A7a)$$

and

$$M(nlm, n'l'm) = \delta_{ll'} (-1)^{l+l'} \sum_{v=0}^{l+l'} F_{ll'}^m(v) \sum_{k=0}^v \frac{(l+l'+1-k)! f(v,k)}{(l+l'+2)! \rho^{k+1}} \\ \times \operatorname{Re} \left[\frac{(i)^{l+l'-k-1}}{(1-i\rho)^{l+l'+2-k}} \right], \quad (A7b)$$

where we have defined

$$\rho \equiv 2\zeta k_0 (b_{nl} + b_{n'l'}) \quad , \quad (A7c)$$

$$f(v,k) \begin{cases} (-1)^k v(v-1)\dots(v-k+1) & \text{if } k > 0 \\ 1 & \text{if } k = 0 \end{cases} \quad . \quad (A7d)$$

The coefficients $F_{ll'}^m(v)$ are related to $Q_{lm}(\xi) Q_{l'm}(\xi)$ by

$$Q_{lm}(\xi) Q_{l'm}(\xi) = \sum_{v=0}^{l+l'} F_{ll'}^m(v) \xi^v \quad (A7e)$$

For intervalley terms, only symmetric s-like dumbbell functions are considered. We therefore drop out the indices (lm) of the basis functions, β 's. The intervalley kinetic energy matrix elements are given by

$$\begin{aligned}
 & \langle \beta_n^+ (\vec{k} - k_m \hat{z}) | E(\vec{k}) | \beta_n^+, (O_2^+ (\vec{k} - \vec{k}_2)) \rangle \\
 &= \left[T'_{nm} + T'_{n'n} \right] \quad (A8a)
 \end{aligned}$$

with

$$\begin{aligned}
 T'_{nm} &\equiv \langle \beta_n^+ (\vec{k} - k_m \hat{z}) | E_1(\vec{k}) | \beta_n^+, (O_2^+ (\vec{k} - \vec{k}_2)) \rangle \\
 &= \frac{(8\pi)^2 b_n b_{n'} \zeta^2}{2\pi} \int_0^{k_m} dk_z \int_{-k_z}^z \frac{dk_x dk_y}{(2\pi)^3} \left\{ \frac{1}{[b_n^2 + k_x^2 + k_y^2 + (k_z - k_o - k_m)^2 \zeta^2]^2} \right. \\
 &\quad + \frac{1}{[b_n^2 + k_x^2 + k_y^2 + (k_z + k_o - k_m)^2 \zeta^2]^2} \left. \right\} \\
 &\quad + \frac{1}{[b_{n'}^2 + k_y^2 + k_z^2 + (k_x + k_o - k_m)^2 \zeta^2]^2} \left\{ [k_y^2 + k_x^2 + E_\ell(k_z - k_m)] \right. \\
 &\quad \left. \left. + \frac{1}{[b_{n'}^2 + k_y^2 + k_z^2 + (k_x + k_o - k_m)^2 \zeta^2]^2} \right\} \right. \\
 &= \frac{2b_n b_{n'} \zeta^2}{\pi} \int_0^{k_m} d\rho \rho \int_{-\pi/4}^{\pi/4} d\phi [I(\rho, \phi) (E_\ell(\rho \cos \phi - k_m) + \rho^2 \sin^2 \phi) + J(\rho, \phi)] \quad (A8b)
 \end{aligned}$$

with

$$J(\rho, \phi) \equiv \sum_{i=1}^4 \frac{1}{p_i q_i (p_i + q_i)^3} \quad (A8c)$$

and

$$I(\rho, \phi) \equiv \sum_{i=1}^4 \frac{1}{p_i q_i (p_i + q_i)^3} \left[\frac{1}{p_i^2} + \frac{1}{q_i^2} + \frac{3}{p_i q_i} \right] , \quad (A8d)$$

where

$$p_i = b_n^2 + (\rho \cos \phi - k_m + \sigma_i k_o)^2 \zeta^2 + \rho^2 \sin^2 \phi ,$$

$$q_i = b_{n'}^2 + (\rho \sin \phi - k_m + \delta_i k_o)^2 \zeta^2 + \rho^2 \cos^2 \phi$$

and

$$\sigma_i = (1, 1, -1, -1)$$

$$\delta_i = (1, -1, 1, -1) \quad \text{for } i = 1, 2, 3, 4$$

Similarly, we obtain for the overlap matrix elements

$$\langle \beta_n^+ (\vec{k} - k_o \hat{z}) | \beta_n^+ (O_2^T (\vec{k} - \vec{k}_2)) \rangle = [N'_{nn'} + N'_{n'n}]$$

with

$$N'_{nn'} = \frac{2b_n b_{n'} \zeta^2}{\pi} \int_0^{k_m} d\rho \rho \int_{-\pi/4}^{3\pi/4} d\phi I(\rho, \phi) \quad (A9)$$

where $I(\rho, \phi)$ is given by Eq. (A8d). In deriving Eqs. (A8) and (A9), we have redefined the basis functions as

$$\beta^+(\vec{k} - \vec{G} - \vec{k}_m \hat{z}) = \beta^+(\vec{k} - \vec{k}_m \hat{z})$$

and the band energy expression

$$E_j(\vec{k} - \vec{G} - \vec{k}_m \hat{z}) = E_j(\vec{k} - \vec{k}_m \hat{z}) ,$$

with $G = (0,0,2) k_m$, when $k_m < k_z < 2k_m$. It should be noted that only with this redefinition, can the $\beta_{n\ell m}^\Gamma(\vec{k})$ defined in Eqs. (3) and (4) transform rigorously according to the representation Γ of T_d .

The intervalley potential energy matrix elements are given by

$$\begin{aligned} & \langle \beta_n^+(\vec{k} - k_o \hat{z}) | V | \beta_n^+(\vec{O}_2^-(\vec{k} - \vec{k}_2)) \rangle \\ &= \frac{R_2 \epsilon_o}{\epsilon(\sqrt{2}k_m)} \operatorname{Re} \left(\int_0^{2\pi} \frac{d\phi}{(2\pi)} \int_0^1 d\xi \frac{1}{[b_n v_1 + b_n v_2 + i k_o (\eta_1 - \eta_2)]^2} \right) \quad (A10) \end{aligned}$$

with

$$v_{1,2} \equiv [1 + (\xi^2 - 1) \eta_{1,2}^2]^{\frac{1}{2}}$$

and

$$\eta_{1,2} \equiv \sqrt{1 - \xi^2} \cos(\phi \pm \pi/4)$$

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24. The $2p_{\pm}$ level was selected because it is relatively unaffected by the short range part of the impurity potential.
25. The inclusion of the short-range core potential will reduce the ground state energy to some extent and we will have to choose a slightly larger value for the parameter R_2 to fit the experimental binding energy. However, once we fix the binding energy, all the Γ_1 -symmetry excited states are practically unaffected by the short-range core potential.

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29. The hole and electron envelope wavefunctions are centered at the Γ -point and at the X-point of the Brillouin zone, respectively. Therefore, the optical matrix element $\langle \beta_b | M | \beta_{b_3} \rangle$ is proportional to the overlap of the tail of the electron envelope wavefunction with the hole envelope wavefunction at the Γ -point. If we use a normalized s-like DSTO of exponent b to describe the electron, then the optical matrix element square is proportional to b^5 .

CHAPTER 4

BOUND EXCITONS IN A SPHERICAL MODEL

I. INTRODUCTION

In order to understand the general properties of bound excitons, we first have to study this system in a simple spherical model, in which electrons and holes are described by spherical effective masses, m_e^* and m_h^* , respectively. The effect due to the realistic band structures (valley-orbit interaction and mass anisotropy) and short-range core potential will be discussed in the next chapter. In the spherical model this system behaves like a H_2 -molecule or a H^- (negative hydrogen ion) at very small ($\sigma < 0.1$) and very large ($\sigma > 10$) mass ratios (core particle to outer particle), respectively. In this chapter we will study how the energy spectrum of this system changes from the H_2 -molecule limit to the H^- limit.

Since the original estimates given by Hopfield ⁽¹⁾, there have been a number of calculations dedicated to the binding energy of the excitons to neutral impurities, for various values of the electron to hole mass ratio, σ . With the exception of the calculation based on the local density approximation by Wünsche et al ⁽²⁾, the calculations divide into two groups, one valid for $0 \leq \sigma < 1$ and the other valid for $1 < \sigma \leq \infty$. Further, the calculation by Wünsche et al ⁽²⁾ is not valid for $\sigma > 10$ or $\sigma < 0.1$. Hence, none of the techniques are accurate throughout the entire range of σ . This fact has led to some discussion of the binding energy in the crucial range where $\sigma \sim 1$. Munschy and coworkers ^(3,4) have reported that the exciton is not bound to a neutral impurity for $\sigma_c < \sigma < 2.5$, where σ_c is some

constant with $1 < \sigma_c < 2$. While the recent work of Wünsche et al ⁽²⁾ shows binding in this range of σ , the deviation of the results from the accurate values as $\sigma \rightarrow \infty$ has led to continuing questions concerning the existence of an instability.

Furthermore, all the previous calculations are designed for the evaluation of binding energies, and hence cannot predict the energy levels for the excited states. The excited state spectra of the bound exciton (BE) have been of great interest because of its bearing on the structure of bound multiexciton complex (BMEC). Further, the absorption data reported by P. Dean ⁽⁸⁾ for GaP indicate the existence of many excited states.

In this chapter, we report on a theory of the bound excitons, which is valid for all mass ratios of interest ($\sigma \geq 0.01$) and is able to predict the ground state energies as well as the excitation energies for the low-lying excited states. Our approach is to develop single-particle model Hamiltonians which yield analytic solutions that are like the Hartree-Fock solutions. The difference between the total Hamiltonian and the sum of the model Hamiltonians are treated as a perturbation. The energies of the ground state and the low-lying excited states are then calculated using second order perturbation theory. Our results for the ground state energies agree with the previous calculations in the various regions where they are valid and indicate that the exciton is bound for all values of σ . It is found that the excited states are not bound with respect to the dissociation

into a free exciton plus a neutral impurity, for core particle to outer particle mass ratio (σ) in the range between 0.03 and 10. These excited states may appear as resonances if the lifetime for decaying into continuum states with one free exciton is long enough. However, in some cases (e.g., exciton bound to a donor in GaP) the valley-orbit splitting is so large that the total energy of the core particles could be pulled down by a large enough amount to make some of these states bound. The results for the energies of the low-lying excited states can be compared with the available experimental data. Good agreement between theory and experiment is obtained.

II. THEORY

In the single-particle picture, we consider the bound exciton system as consisting of an impurity center, two core particles (electrons or holes), and one outer particle (hole or electron). The excited states can be described by one-particle, two-particle and three-particle excitations. In the present calculation, we are only concerned with the ground state and the s-like one-particle excitations for the outer particle, since these are the low-lying states of interest.

For definiteness, we solve the problem for donor bound excitons.

For acceptor bound excitons, one only has to exchange the roles played by electrons and holes. Within the spherical band effective mass approximation, the total Hamiltonian to be solved can be written as

$$H = -\nabla_1^2 - \nabla_2^2 - \sigma \nabla_3^2 - 2 \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right) + 2 \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right), \quad (1)$$

with subscripts 1 and 2 representing the two core electrons and 3 representing the outer hole. We have introduced standard atomic units with distance measured in units of $\epsilon_0 \hbar^2 / m_e^* e^2$, the Bohr, and energy measured in units of $\frac{e^4 m_e^*}{2 \epsilon_0^2 \hbar^2}$, the donor Rydberg (Ry). The parameter

is $\sigma = m_e^* / m_h^*$ with m_e^* and m_h^* the electron and hole effective masses, respectively. This Hamiltonian can be rewritten in the form

$$H = T + V_{\text{eff}} + (v - V_{\text{eff}}), \quad (2)$$

where T is the sum of the single-particle kinetic energies in Eq. (1) and v includes all the potential terms. The V_{eff} is a sum of single-particle model potentials $\bar{V}^{(i)}$,

$$V_{\text{eff}} = \sum_{i=1}^3 \bar{V}^{(i)}, \quad (3)$$

which are selected so as to minimize the effects of the term $v - V_{\text{eff}}$. If we define

$$H_0 = T + V_{\text{eff}}, \quad (4)$$

then H_0 can be written as the sum of single particle Hamiltonians

$$H_0 = \sum_{i=1}^3 H_0^{(i)}, \quad (5)$$

where $H_0^{(i)}$ for the electrons are

$$H_0^{(i)} = -\nabla_i^2 + \bar{V}^{(i)} \quad \text{for } i=1,2 \quad (6)$$

and $H_0^{(i)}$ for the hole is

$$H_0^{(3)} = -\nabla_3^2 + \bar{V}^{(3)} \quad (7)$$

We want to select the soluble model potentials so that they are as close as possible to the self-consistent potential seen by each particle due to the others and due to the impurity, $V_{sc}^{(i)}$. Hence, we first examine the approximate form of the self-consistent potential for the hole. If we take a trial wavefunction for the electrons of the form e^{-br} with b as a variational parameter, then we find that $V_{sc}^{(3)}$ is given by

$$V_{sc}^{(3)}(r_3) = 2b \left(\frac{2e^{-2\chi}}{\chi} (1+\chi) - \frac{1}{\chi} \right) \quad (8)$$

where χ is br_3 . Examining the expression in Eq. (8), we find the potential can be accurately represented by the soluble potential

$$\bar{V}^{(3)}(r_3) = \frac{A}{r_3^2} - \frac{B}{r_3} \quad (9)$$

where A and B are suitably chosen parameters. The lowest energy solution ⁽⁹⁾ to Eq. (7) is

$$\phi_0^{(3)}(\vec{r}_3) = \left[\frac{1}{\Gamma(\tau_0+1)} \left(\frac{2b}{Z_0} \right)^{\tau_0+1} \right]^{\frac{1}{2}} r_3^{\tau_0/2-1} e^{-br_3/Z_0} Y_{00}(\Omega_3) \quad (10)$$

where the parameters τ_0 and Z_0 are related to A and B by

$$\tau_0 = 1 + \sqrt{1 + 4A/\sigma} \quad \text{and} \quad Z_0/b = \sigma\tau_0/B \quad ,$$

As noted above we expect the electron wavefunction to be approximately hydrogenic, that is

$$\phi(r) = e^{-br} \quad , \quad (11)$$

This wavefunction is the solution to a Hamiltonian consisting of the kinetic energy and a potential given by

$$V(r) = \frac{-2b}{r} \quad , \quad (12)$$

Hence, we take the model potential for electrons to be

$$V^{(i)}(r_i) = \frac{-2b}{r_i} \quad (13)$$

for $i=1,2$.

The three-body trial wavefunction used for a variational calculation of the energy for the total Hamiltonian given in Eq. (1) is taken to be a product of two electron wavefunctions given by Eq. (11) and one hole wavefunction given by Eq. (10). The values of the parameters b , τ_0 and Z_0 appearing in these wavefunctions are determined by minimizing the total energy E_V . The results of this calculation for the range of mass ratio between 0.001 and ∞ are given in Table IV-1. Examination of this table shows that τ_0 increases rapidly with decreasing values of σ for $\sigma < .01$. Large values of τ_0 make numerical calculations difficult since the power of the radius in Eq. (10)

is very large.

With the adjustable parameters determined in the above procedure, the self-consistent potential seen by each electron, $V_{sc}^{(i)}$ can be also calculated analytically based on the trial wavefunctions $\phi_0^{(i)}$.

We obtain, say for $i = 1$

$$V_{sc}^{(1)}(r_1) = -\frac{2b}{\chi} \{ e^{-2\chi/Z_0} [1 + \frac{\tau_0^{-1}}{\sigma} \sum_{k=1}^{\infty} \frac{1}{k!} (1-k/\tau_0) (2\chi/Z_0)^k] - [1 - e^{-2\chi(1+\chi)}] \} \quad (14)$$

where $\chi \equiv br_1$.

To compare the model potentials with the self-consistent ones, we have plotted them as a function of the normalized radial coordinate (br) on Fig. IV-1 for the core particle (top) and the outer particle (bottom), for two typical mass ratios ($\sigma = 0.2$ and 5). As shown in these figures, the deviations of the model potentials from the self-consistent ones are small except for short distances.

The radial probability of the s-like zeroth order wavefunctions for the outer particle is plotted in Fig. IV-2 against the radial coordinate normalized to the core radius, (l/b), for two different mass ratios. It is found that the hole wavefunctions behave like vibrational states as the mass ratio σ decreases, and approach the hydrogen-like states as σ increases.

We can consider the difference between the exact Hamiltonian and the sum of the model Hamiltonians as a perturbation. For the two core electrons, we will denote the one-particle excited states of their model Hamiltonian as $|a_\ell\rangle$ and $|b_\ell\rangle$, and the associated excita-

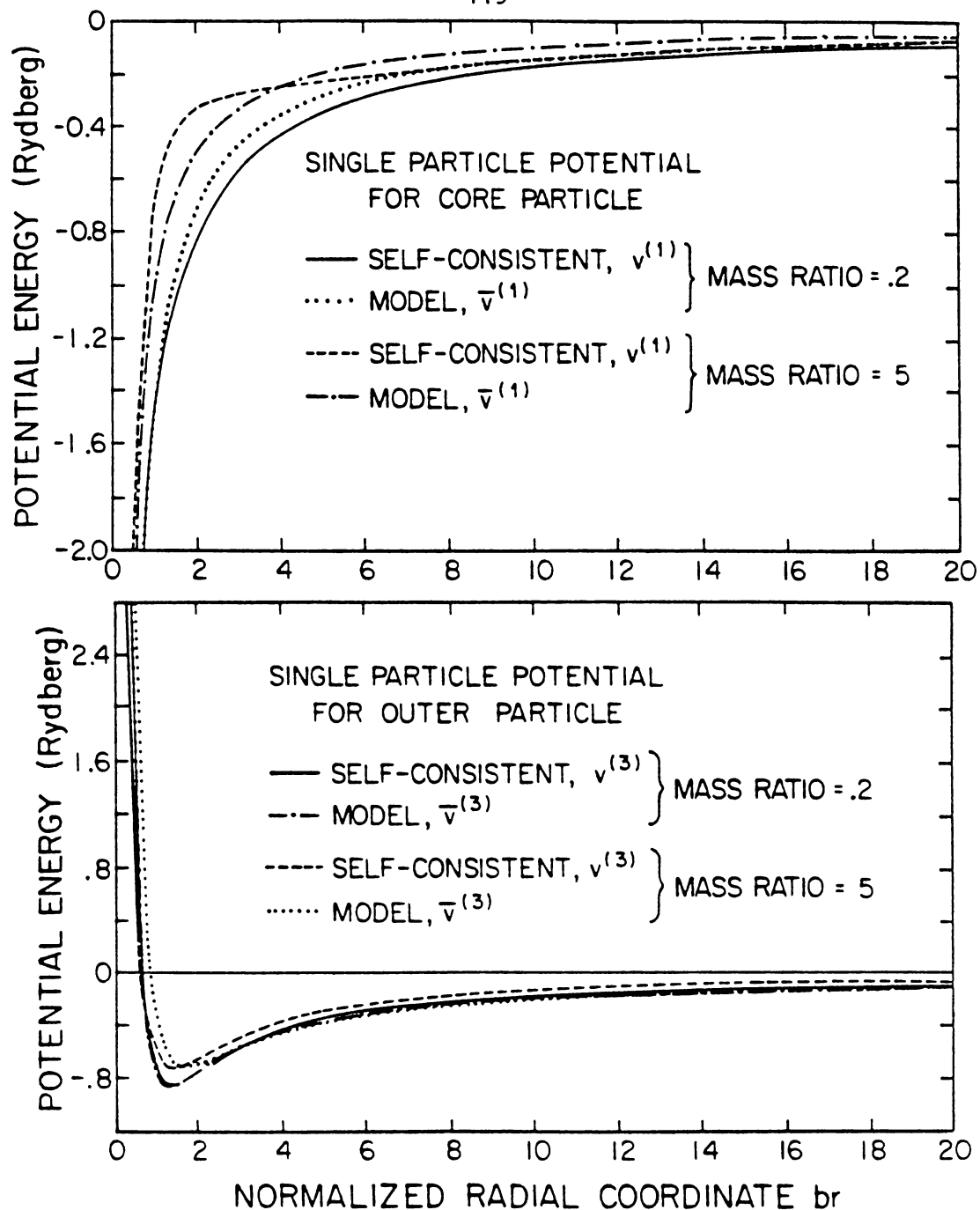


Figure IV-1 Model potential ($\bar{V}^{(1)}$ and $\bar{V}^{(3)}$) and self-consistent potential ($\bar{V}_{sc}^{(1)}$ and $\bar{V}_{sc}^{(3)}$) plotted as a function of the normalized radial coordinate (br), for core particle (upper half) and outer particle (lower half), for two mass ratios ($\sigma=0.2$ and 5).

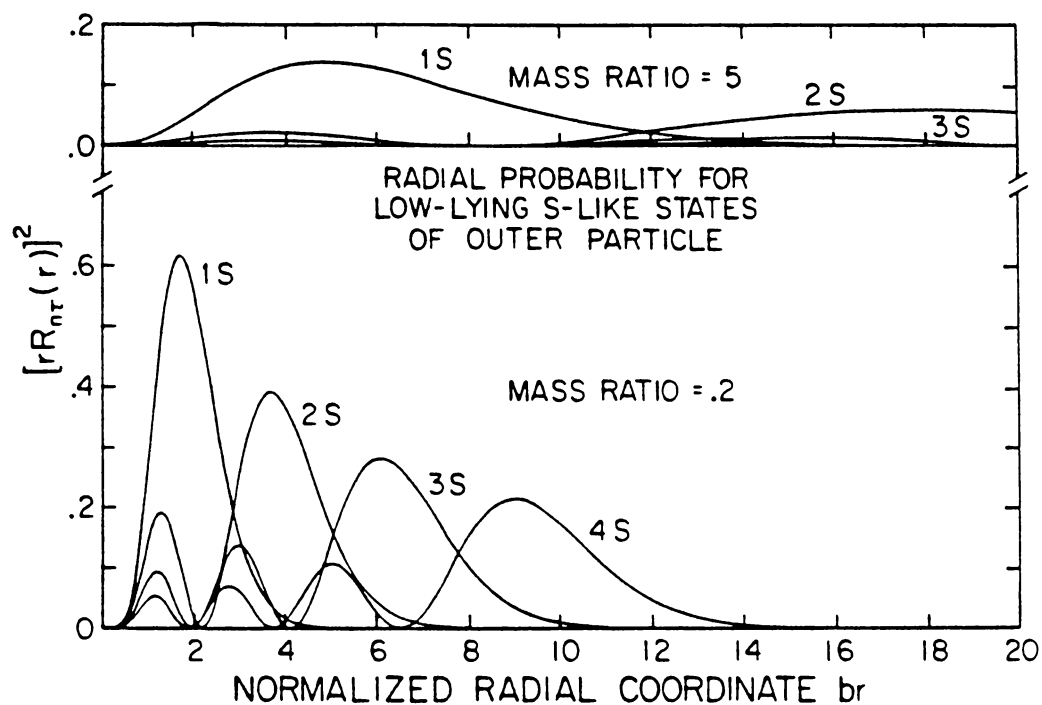


Figure IV-2 Radial probability of the S-like one-particle basis wave functions for the outer particle plotted against the radial coordinate normalized to the radius ($1/b$) of the core particles, for two mass ratios: $\sigma = .2$ and $\sigma = 5$.

tion energies as ϵ_{a_ℓ} and ϵ_{b_ℓ} . Similarly, for the outer hole, we will denote the one-particle excited states of its model Hamiltonian as $|c_\ell\rangle$ and the associated excitation energy as ϵ_{c_ℓ} . The subscript ℓ for these states represents the angular momentum quantum number. We then denote the ground state of the zeroth order Hamiltonian, H_0 as $|o\rangle$, and the two particle excited states as $|a_\ell b_\ell\rangle$ for two electrons, or $|a_\ell c_\ell\rangle$, for one electron and one hole.

Using second-order perturbation theory, the total energy of the ground state is given by

$$E_0 = \langle o|H|o\rangle - 2 \sum_{a_0} \frac{|\langle o|\Delta V^{(1)}|a_0\rangle|^2}{\epsilon_{a_0}} - \sum_{c_0} \frac{|\langle o|\Delta V^{(3)}|c_0\rangle|^2}{\epsilon_{c_0}} \\ - 2 \sum_{\ell} (2\ell+1) \sum_{a_\ell c_\ell} \frac{|\langle oo|\frac{2}{r_{13}}|a_\ell c_\ell\rangle|^2}{\epsilon_{a_\ell} + \epsilon_{c_\ell}} - \sum_{\ell} (2\ell+1) \sum_{a_\ell b_\ell} \frac{|\langle oo|\frac{2}{r_{12}}|a_\ell b_\ell\rangle|^2}{\epsilon_{a_\ell} + \epsilon_{b_\ell}} \quad (15)$$

In this expression $\Delta V^{(1)}$ and $\Delta V^{(3)}$ are the difference between the self-consistent and model potentials defined as $(V_{sc}^{(1)} - \bar{V}^{(1)})$ and $(V_{sc}^{(3)} - \bar{V}^{(3)})$ for electrons and holes, respectively, where $V_{sc}^{(3)}$, $\bar{V}^{(3)}$, $\bar{V}^{(1)}$ and $V_{sc}^{(1)}$ are as given in Eqs. (8), (9), (13) and (14), respectively. The total energy when the outer hole is excited in an s-like orbital $|c_0\rangle$ is given by

$$\begin{aligned}
 E_{c_0} = & \langle c_0 | H | c_0 \rangle + \frac{|\langle c_0 | \Delta V^{(3)} | o \rangle|^2}{\epsilon_{c_0}} - \sum_{c'_0} \frac{|\langle c_0 | \Delta V^{(3)} | c'_0 \rangle|^2}{\epsilon_{c'_0} - \epsilon_{c_0}} \\
 & - 2 \sum_{a_0} \frac{|\langle o c_0 | \frac{2}{r_{13}} | a_0 o \rangle|^2}{\epsilon_{a_0} - \epsilon_{c_0}} \\
 & - 2 \sum_{a'_0} \frac{|(\langle o o | \frac{2}{r_{13}} | a'_0 o \rangle + \langle o | \Delta V^{(1)} | a'_0 \rangle) - \langle o c_0 | \frac{2}{r_{13}} | a'_0 c_0 \rangle|^2}{\epsilon_{a'_0}} \\
 & - 2 \sum_{\ell} (2\ell+1) \sum_{a'_\ell c'_\ell} \frac{|\langle o c_0 | \frac{2}{r_{13}} | a'_\ell c'_\ell \rangle|^2}{\epsilon_{a'_\ell} + \epsilon_{c'_\ell} - \epsilon_{c_0}} \\
 & - \sum_{\ell} (2\ell+1) \sum_{a_\ell b_\ell} \frac{|\langle o o | \frac{2}{r_{12}} | a_\ell b_\ell \rangle|^2}{\epsilon_{a_\ell} + \epsilon_{b_\ell}} \quad (16)
 \end{aligned}$$

The sum in the third term is over all states like $|c'_0\rangle$ except the state $|c_0\rangle$. The last term in Eq.(16) represents the electron correlation energy of the frozen core, which cancels the corresponding term in Eq.(15) exactly. The excitation energies for the S-like hole excited states can be obtained by taking the differences between Eq. (16) and Eq. (15)

To obtain better convergence for the ground state energy, we have adopted the second-order Brillouin-Wigner ⁽¹¹⁻¹²⁾ perturbation theory, in which the ground state energy is given by the expression

$$E_{BW} = E_V + \Delta E_2(E_{BW}). \quad (17)$$

where ΔE_2 is the second order correction. If we let

$$\Delta E \equiv E_{BW} - E_0 \quad (18)$$

where E_0 is defined to be the sum of the lowest eigenvalues of single-particle model Hamiltonians, then

$$\begin{aligned} \Delta E_2 = & -2 \sum_{a_0} \frac{|\langle 0 | \Delta V^{(1)} | a_0 \rangle|^2}{\epsilon_{a_0} - \Delta E} - \sum_{c_0} \frac{|\langle 0 | \Delta V^{(3)} | c_0 \rangle|^2}{\epsilon_{c_0} - \Delta E} \\ & - \sum_{\ell} (2\ell+1) \sum_{a_{\ell} b_{\ell}} |\langle 00 | \frac{2}{r_{12}} | a_{\ell} b_{\ell} \rangle|^2 / (\epsilon_{a_{\ell}} + \epsilon_{b_{\ell}} - \Delta E) - 2 \sum_{\ell} (2\ell+1) \\ & \sum_{a_{\ell} c_{\ell}} |\langle 00 | \frac{2}{r_{13}} | a_{\ell} c_{\ell} \rangle|^2 / (\epsilon_{a_{\ell}} + \epsilon_{c_{\ell}} - \Delta E) \end{aligned} \quad (19)$$

In Eq. (19), the first two terms only involve one particle excitations and in large part correct the energy for the difference between the self-consistent Hartree-Fock ground state and our model ground state. The third and fourth terms in Eq. (19) give the contribution due to electron-electron and electron-hole correlation, respectively.

III. RESULTS AND DISCUSSION

The numerical calculations were carried out by including 6 discrete

states and 18 continuum states with wave numbers k ranging from 0 to 4 (a.u.) for each angular momentum ℓ . The other discrete states contribute only about 3% to the sum, because the matrix elements converge like $(1/n)^{2\ell+3}$, where n is the principal quantum number. The contributions from high energy continuum states are also negligible, since the energy denominator is proportional to k^2 , and the matrix elements of those high energy states are small due to their fast oscillatory behavior.

We will discuss the results for the ground state and excited states separately.

A. Ground State

To obtain the ground state energies, the implicit equation Eq. (19), was solved by iteration. The results as a function of mass ratio σ are given in Table IV-1 along with dissociation energy

$$W_{BW}(\sigma) = E_{FE+NI}(\sigma) - E_{BW}(\sigma) \quad . \quad (20)$$

To analyze the results of this calculation, we have plotted in Fig. IV-3 the energies as a function of σ including various terms in Eq. (19). For comparison, we have also included the ground state energy, E_V , obtained in the previous variational calculation and the energy of a free exciton (FE) plus neutral impurity (NI) given by the expression

$$E_{FE+NI} = - \frac{2+\sigma}{1+\sigma} \quad . \quad (21)$$

Since E_{FE+NI} is lower than E_V , the variational calculation does not yield a bound state for the exciton to a neutral donor.

TABLE IV-1. Values of the variational parameters, τ_0 , Z_0 and b ; ground state energy from the variational calculation, E_V ; ground state energy from the Brillouin-Wigner perturbation scheme, E_{BW} ; and dissociation energy W_{BW} as a function of the electron to hole effective mass ratio σ . All the units in the table are atomic units based on electron effective mass as discussed in the text.

σ	τ_0	Z_0	b (bohr ⁻¹)	E_V (Ry)	E_{BW} (Ry)	W_{BW} (Ry)
.0011	82	.033	.932	-1.749		
.01	26	.108	.916	-1.706	-2.250	.260
.03	17	.172	.898	-1.662	-2.224	.253
.05	13	.230	.886	-1.634	-2.141	.189
.125	8	.399	.861	-1.566	-1.980	.099
.2	7	.481	.843	-1.522	-1.921	.088
.4	5	.744	.814	-1.445	-1.762	.048
.6	4	1.004	.796	-1.392	-1.662	.037
.8	4	1.080	.779	-1.354	-1.603	.048
1.0	4	1.155	.767	-1.322	-1.555	.055
1.25	3	1.64	.760	-1.289	-1.488	.044
1.667	3	1.814	.745	-1.249	-1.428	.053
2.5	3	2.16	.725	-1.192	-1.348	.062
5.0	3	3.21	.700	-1.100	-1.233	.066
8.0	2	6.696	.695	-1.054	-1.171	.060
∞		-----	.6875	-0.945	-1.057	.057

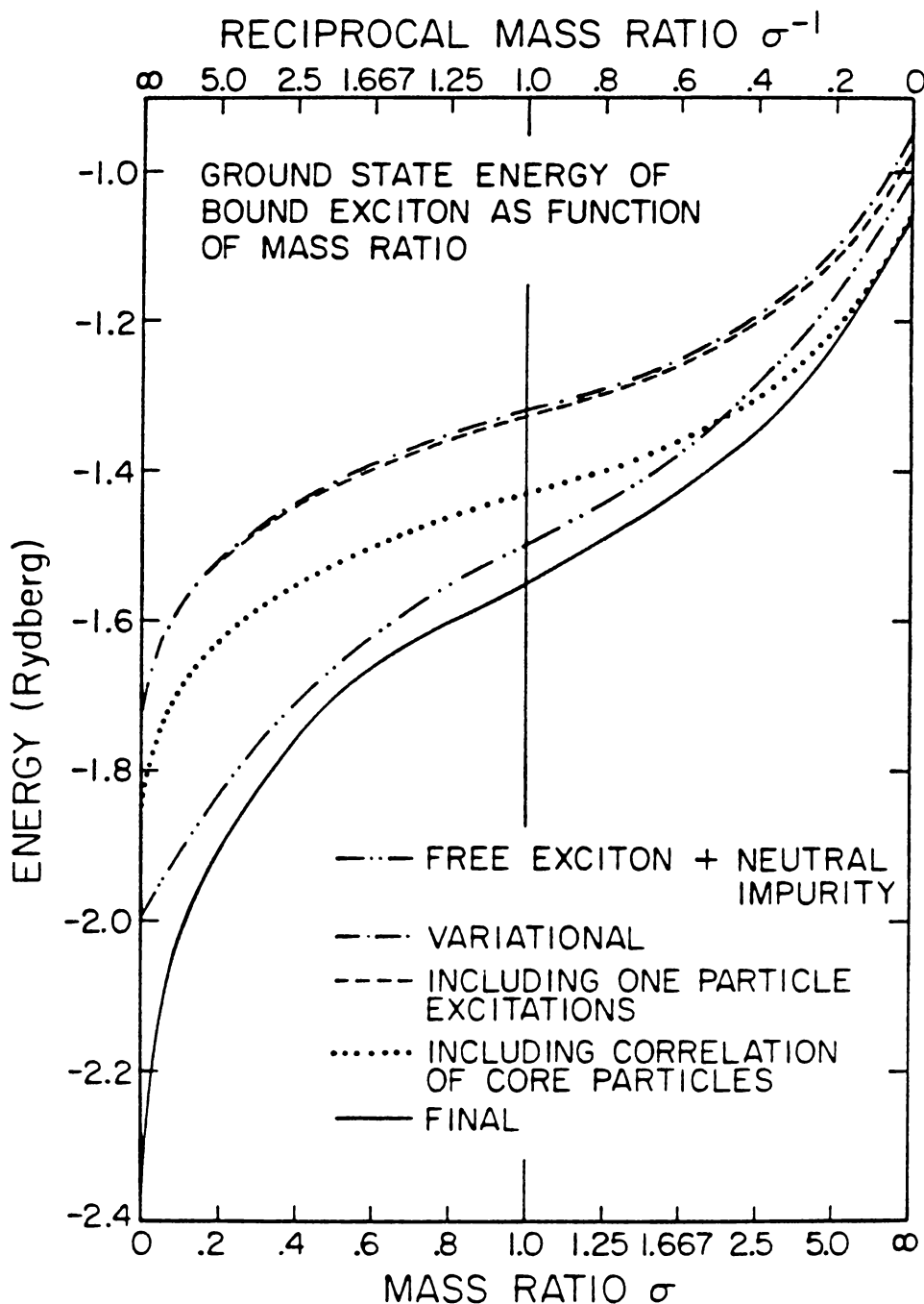


Figure IV-3. Ground state energies as a function of mass ratio σ of the BE system. The energy is defined to be zero when all particles are ionized. The dash-dot-dash line is E_V calculated by the variational method. The dashed line is E_V plus the first two terms in Eq. (19). The dotted line is E_V plus the first two terms in Eq. (19). The solid line is E_{BW} . The total energy of FE + NI system is also plotted for comparison (dash-dot-dot).

The results plotted here show that the correction due to the single particle excitations is quite small in keeping with the fact that our model Hamiltonian produces nearly self-consistent wavefunctions. The inclusion of electron-electron correlation (or correlation due to core particles) produces a bound state only over a limited range of σ . When all the terms in Eq. (19) are included binding occurs over the entire range of σ .

To compare our results with those of other authors, we have plotted our values of the dissociation energy along with theirs as a function of σ in Fig. IV-4. Our results agree to within 3% with those obtained for H^- which are appropriate for $\sigma = \infty$. At $\sigma = 1$, we find a value which is within 6% of that obtained by Navin et al ⁽⁵⁾ for a large scale variational calculation for positronium hydride. Our results show that $W_{BW}(\sigma)$ is relatively independent of σ for $1 < \sigma < \infty$ and takes on a value of about 0.05 Ry. This value is approximately half the value observed experimentally in excitons bound to acceptors. This discrepancy may be due to deviations from spherical symmetry in real semiconductors.

In contrast to the results of Stebe and Munschy ⁽⁴⁾, we find that the exciton is bound for all mass ratios. This difference is due to the importance of electron-hole correlations in our calculation, for if we neglect electron-hole correlation we obtain results very similar to those of Stebe and Munschy (see Fig. IV-3). Our results are close to those of Wünche et al ⁽²⁾ for $0.8 < \sigma < 2$ but deviate substantially for $\sigma > 2$. Our results agree with Munschy et al ⁽³⁾ near $0.2 < \sigma < 0.5$

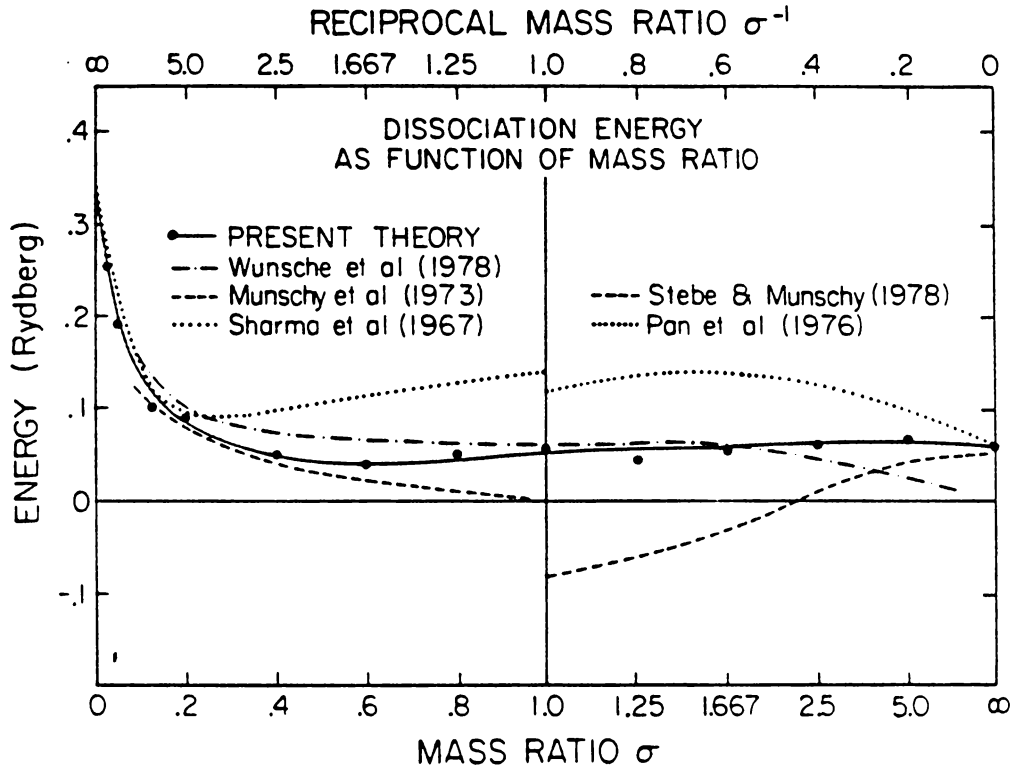


Figure IV-4 Dissociation energy $W(\sigma)$, calculated by Wunsche, et al (2) (- · - · -); Munschy, et al (3) (- - -) for $\sigma < 1$; Pan, et al (7) (· · · · ·) for $\sigma > 1$, and present theory (—). For our results the dots shown indicate the values at the points where numerical calculations were performed.

and with Sharma, et al ⁽⁶⁾ for $\sigma < 0.2$,

B. S-like Low-lying Excited States

The numerical results for the first three S-like excited states, and the ionization energy E_i of the outer particle obtained from the expression

$$E_i = E(H^-) - E_{BW} \quad (22)$$

with $E(H^-)$ being the ground state energy of the H^- (negative hydrogen ion), are listed in Table IV-2, and plotted in Fig. IV-5. For mass ratio σ greater than 20, the outer particle sits so far away from the core that the excitation of this particle has very little effect on the core. Therefore, the ionization energies for the ground state and the excited states of the outer particle can be calculated in good approximation by simply evaluating the energy expectation values of the sub-Hamiltonian

$$H^{(3)} = -\sigma \nabla_3^2 + V_{sc}^{(3)}(r_3) \quad , \quad (23)$$

where $V_{sc}^{(3)}$ is defined in Eq. (8). The excitation energies are then obtained by taking the differences between the ionization energies of the excited states and that of the ground state.

The spectrum of excited states exhibits a number of physically interesting features. First, for mass ratios greater than one, the spectrum is more hydrogenic. To illustrate this point, we have plotted the energy in the unit of acceptor Rydberg $\left(\frac{m_h^* e^4}{2\epsilon_0 \hbar^2} \right)$, the

TABLE IV-2. Energies of the S-like low-lying excited states and the ionization of the outer particle (measured from the ground state). The energy units in this table are donor Rydberg as defined in the text.

σ	2S	3S	4S	E_i
.01	.174	.310	.373	1.194
.03	.256	.427	.550	1.168
.05	.296	.482	.609	1.085
.125	.371	.552	.664	.924
.2	.381	.546	.633	.865
.4	.378	.510	.570	.706
.6	.361	.468	.516	.606
.8	.335	.414	.464	.547
1.0	.304	.386	.421	.499
1.25	.288	.357	.385	.432
1.667	.252	.307	.332	.372
2.5	.199	.240	.261	.292
5.0	.125	.148	.158	.177
8.0	.085	.101	.107	.116
20.0	.0362	.0430	.0454	.0485
50.0	.0149	.0177	.0186	.0199
100.0	.00748	.00887	.00936	.00998

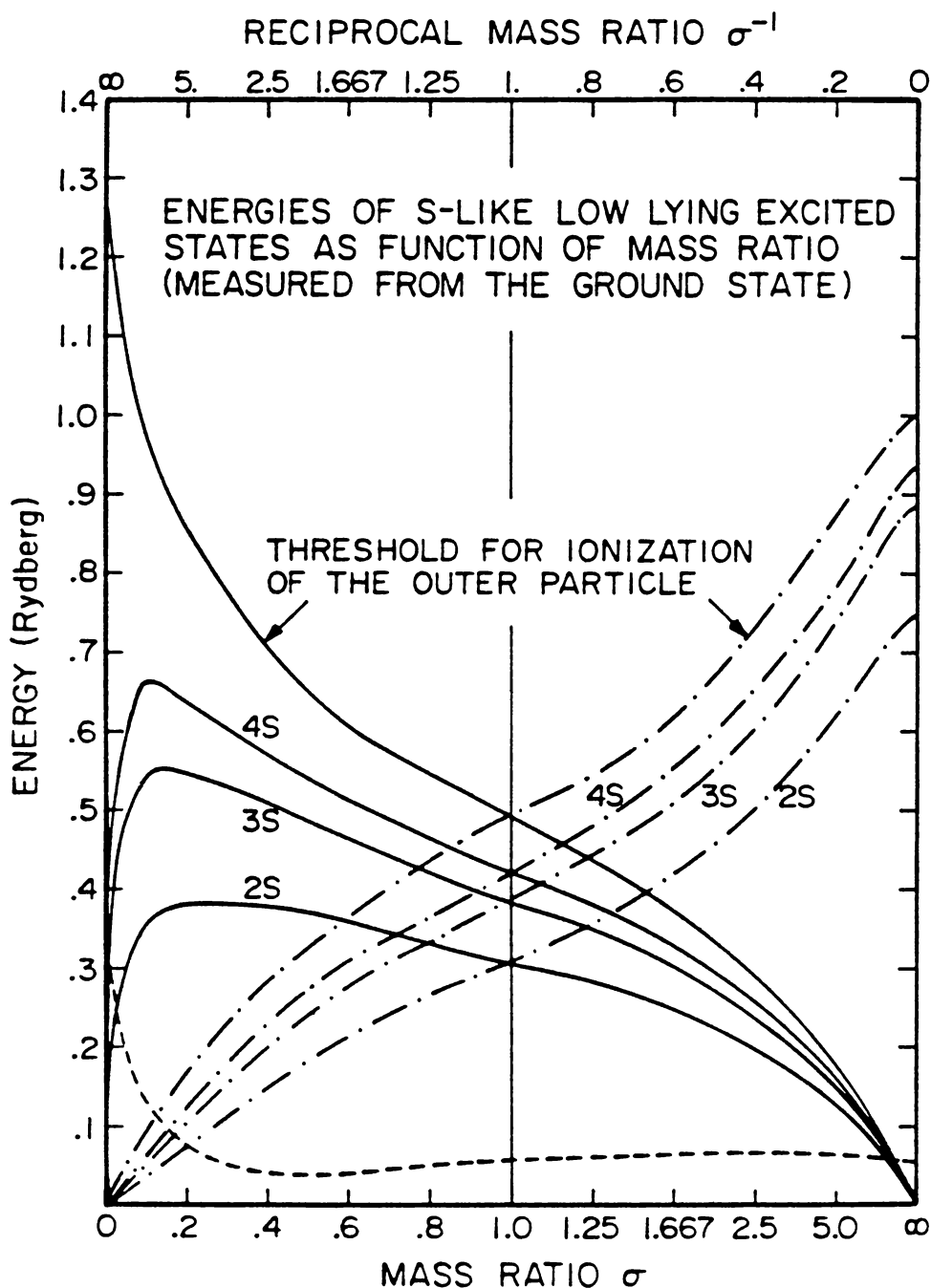


Figure IV-5 Energies of S-like low-lying excited states (measured from the ground state) plotted against mass ratio σ in donor Rydberg (solid line) and in acceptor Rydberg (dot-dash-dot line). The dissociation energy of the bound exciton (into a free exciton plus neutral donor) is also plotted in donor Rydberg (dashed line) for comparison.

dash-dot-dashed curves in Fig. IV-5. Since the excited states in these cases are those for holes outside a rigid, nearly coulombic core, we would expect the difference between the excited state energy on this scale to be approximately independent of σ and as in the hydrogen atom. On the other hand the spacing between the excited states and ground state decreases rapidly with decreasing σ since the electron-hole correlation effect is more important for the ground state than the excited states.

Second, the excited state spectrum in units of the donor Rydberg shows a maximum as a function of σ . The maxima all occur in the range $\sigma = 0.1 \sim 0.3$. The physical reason for this transition is the changeover from the hydrogenic spectrum at large σ to that analogous to the vibrational spectrum of H_2 which is appropriate in the limit of small σ .

Third, we can examine the question of whether or not the states are bound. In Fig. IV-5 we have plotted the dissociation energy for bound excitons into a neutral donor and free exciton in donor Rydbergs ⁽²⁾ (see dashed line). As can be seen from this figure, all these excited states are unbound for $0.03 < \sigma < 10$. For very small and very large values of σ , there are still some bound states.

A somewhat more realistic treatment of the problem would include valley-orbit splitting and other short-range corrections for the core particles. However, we do not expect these effects to make substantial corrections to the excitation energies when the outer particle is excited. On the other hand if one goes beyond the spherical model to

include anisotropic effective masses and inter-valley scattering, the ground state will be split, resulting in many other excited states.

We can make comparisons of our results with experimental results for donors in GaP obtained by Dean ⁽⁸⁾ and Elliott et al ⁽¹³⁾. To make this comparison we must assign a value to the ratio of the effective mass for electrons and holes. This ratio is given by the ratio of the binding energy of an electron to a donor to that for a hole to an acceptor. The experimental value for the binding energy of an electron in Γ_3 state for the sulfur donor in GaP ^(14,15) is 54 meV. The theoretical value in the hydrogenic model for the binding energy of holes is 56.3 meV. ⁽¹⁶⁾ The ratio of these two quantities gives a value of σ of approximately one. We therefore choose a mass ratio $\sigma \sim 1$ and a Rydberg ~ 54 meV for GaP. With this choice, we obtain the energy values 16.4 meV, 20.9 meV, 22.7 meV, and 27.0 meV for the 2S, 3S, 4S states, and the ionization threshold, respectively. The experimental values observed by Dean ⁽⁸⁾ are 16 meV for 0' state and 22.5 meV for 0" state. More recently, Elliott et al ⁽¹³⁾ have observed some excited states for exciton bound to GaP:S at 16.6 meV and 22.4 meV, which are close to our predicted values. This agreement is particularly interesting since we have not included the anisotropy of the valence bands and the spin-orbit interaction which have been found to be important for the acceptor ⁽¹⁶⁻¹⁸⁾. While all these states are unbound in our calculation, the 2S excited state is found to be bound in GaP. This binding is due to a large valley-orbit splitting which leads to extra binding for the core states.

IV. SUMMARY

We have devised a method for calculating the ground state energy and the excitation energies for the low-lying excited states. This method is valid for all mass ratios greater than 0.01. This calculation indicates that excitons are bound for all mass ratios. It is found that for mass ratios σ between 0.03 and 10 the excited states are not bound with respect to the dissociation into a free exciton, but some of them will become bound if the valley-orbit interaction is taken into account (as in GaP). Some of these states may appear as resonances if the lifetime of decaying into the free exciton continuum is long enough. These results have been compared with some experimental data, and qualitatively good agreement is obtained.

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12. We also applied the Rayleigh-Schrodinger (RS) perturbation theory to this problem. We find that for $\sigma \geq .4$, the Brillouin-Wigner (BW) and RS values give the same total energy within 1% (or 20% for the dissociation energy). For $\sigma \leq 0.2$ the RS method gives binding energies approximately 40% lower than those obtained by the BW method.
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CHAPTER 5

EXCITATION SPECTRA OF DONOR BOUND EXCITONS IN MULTIVALLEY SEMICONDUCTORS

I. INTRODUCTION

In the last chapter, we treated the bound exciton system in a spherical model. In this chapter we discuss the effect due to the anisotropy of the realistic band structures on the electronic excitation spectra of donor bound excitons in Si, Ge and GaP.

The luminescence due to the radiative recombination of excitons bound to neutral impurities in Si was first observed by Haynes ⁽¹⁾ (1960) and later studied more extensively by Dean et al ⁽²⁾ (1967). Kaminskii et al ⁽³⁾ (1970) observed a series of sharp lines (known as the KAPS lines) in the luminescence spectra of lightly doped Si, which they attributed to the electron-hole recombination in the BMEC. The explanation of the origin of the KAPS lines was further strengthened later by Sauer ⁽⁴⁾ (1973), Kosai and Gershenson ⁽⁵⁾ (1974), and Dean et al ⁽⁶⁾ (1976). Kirczenow ⁽⁷⁾ (1977) proposed a shell model (SM) for the BE and the BMEC, which appears to account for the major features of the experimental data. This model has recently been reviewed in detail by Thewalt ⁽⁸⁾ (1978). In the SM, many states of the same configuration ⁽⁹⁾ are assumed to be degenerate; for example, the $\{2\Gamma_3; \Gamma_8\}$ ⁽¹⁰⁾ state is 16-fold degenerate. In practice the linear combinations of those states, which transform according to different representations of the tetrahedral group of the total Hamiltonian, are in general associated with different energy eigenvalues. For instance, the product states of Γ_3 electrons can be decomposed into states transforming according to the Γ_1 , Γ_2 and Γ_3 representations. The products of these states with the Γ_8 hole state can be further decomposed into states transforming according to the

representations Γ_8 , Γ_8 , and $\Gamma_6 + \Gamma_7 + \Gamma_8$, respectively. Without including the interparticle interaction, it is not possible to predict these fine structure splittings. Some of these fine structure splittings have recently been observed for the BE in Ge:P by Mayer and Lightowlers ⁽¹¹⁾ (1979) and in GaP:S by Elliott et al ⁽¹²⁾ (1980). These lines cannot be explicitly identified without going beyond the shell model (SM).

In this chapter, we present a theoretical calculation of the excitation spectrum for the donor bound exciton system in which the effects of realistic band structures and the interparticle interactions are properly taken into account. The fine structure splittings for the states of various configurations are obtained for several donors in Si and Ge and one donor (sulphur) in GaP, respectively. We find that the charge density of the electrons is ellipsoidally distributed. When the major axes of the ellipsoids associated with the two electrons are not oriented parallel to each other (e.g. two electrons localized in valleys on different axes), the mutual interaction between them (the nonparallel mutual interaction) is a few percent less than in the case where the two major axes are parallel to each other (the parallel mutual interaction). This difference in parallel and nonparallel mutual interactions is the major source for the coupling between states of different configurations but same overall symmetry to which the two-electron product states belong; for example, the coupling between the $(\Gamma_1\Gamma_1)\Gamma_1$, $(\Gamma_3\Gamma_3)\Gamma_1$ and $(\Gamma_5\Gamma_5)\Gamma_1$ states (where the notation $(\Gamma_3\Gamma_3)\Gamma_1$ means that the two electrons of Γ_3 symmetry couple together to form a pro-

duct state of Γ_1 symmetry). The strength of this coupling depends sensitively on the ratio of the relative magnitude of the difference in parallel and nonparallel mutual interaction to the energy spacing between the states of various configurations. For example, in Si:P the coupling between the ground state of configuration $(\Gamma_1\Gamma_1)\Gamma_1$ and the states of other configurations but same overall symmetry is negligibly small (less than 1%), because this level is well separated in energy from the states it couples to. For some of the excited states, this coupling is substantial (e.g., the mixing between $(\Gamma_3\Gamma_3)\Gamma_1$ and $(\Gamma_5\Gamma_5)\Gamma_1$ in Si:P is about 10%).

The hole wavefunction, in general, can be described by a spherical (s-like) wavefunction plus some admixture of the quadrupole (d-like) wavefunction. The electron-hole interaction which mixes the s-like and the d-like parts of the hole state produces the coupling between states of different electron and hole configurations but of the same overall symmetry to which the total wavefunction belongs; for example, the coupling between the $[(\Gamma_1\Gamma_5)\Gamma_5 \Gamma_8] \Gamma_8$ and $[(\Gamma_1\Gamma_1)\Gamma_1 \Gamma_8] \Gamma_8$ states (where the notation $[(\Gamma_1\Gamma_5)\Gamma_5 \Gamma_8] \Gamma_8$ means that the Γ_1 and Γ_5 electrons first couples together to form a product state of Γ_5 symmetry, which then couples to the Γ_8 hole states to form a new product state of Γ_8 symmetry). We find that the fine structure splitting due to the electron-hole interaction is about 5 times smaller than the corresponding splitting in the free exciton system. Our results for the energy spacings between various states are in good agreement with the experimental data available.

This chapter is organized in the following way: in Sec. II, the general theory for solving the donor bound exciton is presented. The theory for a donor system incorporating the intervalley scattering with the anisotropic conduction band is also reviewed. In Sec. III, the calculation method is discussed. In Sec. IV, the results are discussed and the comparison with the experimental data is made. Finally, in Sec. V we present our conclusions.

II. GENERAL THEORY

In this section, we present the theory for the donor bound exciton (D^0X) in multivalley semiconductors. In the last chapter, we studied this system in a spherical model. We found that for electron-to-hole mass ratios greater than 1, the D^0X system is best described by a D^- (negatively ionized donor) core plus an outer hole. For the materials considered here (Si, Ge and GaP), the electron-to-hole mass ratios are about 1. Hence, we expect that the electron-electron interaction plays a more important role than the electron-hole interaction for the D^0X in Si, Ge and GaP. To include the effects of realistic band structures, the interaction of each electron with the donor has to be considered explicitly. We first discuss the interaction of an electron with the donor, then treat the D^- core including the electron-electron interaction and finally we study the donor bound exciton (D^0X). Group theory is used to classify the eigenstates of the total Hamiltonian. For the materials considered here, all these

systems are invariant under the tetrahedral group T_d ; therefore, their eigenstates can be classified by the representations of T_d . The neutral donor system has been studied extensively (13-15). In Chapters 2 and 3 we presented a calculation for the donors in Si, Ge and GaP, respectively. The intervalley scattering, short-range correction and effects due to anisotropic conduction band were properly included. These results will be applied here to the interaction between the electrons with the donor in D^0X .

A. Interaction of an Electron with the Donor

The single-particle Hamiltonian for the electron in D^0X interacting with the donor is the same as that for a neutral donor system. The solutions to the neutral donor Hamiltonian have been studied in Chapter 2 for Si and Ge and in Chapter 3 for GaP, and are briefly reviewed here. In the indirect materials, the conduction band has several equivalent minima. The number of equivalent minima, N , is 4 in Ge and 6 in Si and GaP. The bound eigenstates of the donor Hamiltonian are constructed from linear combinations of wavefunctions localized at the N equivalent minima, the expansion coefficients being determined by group theory. The bound states for donors in Ge are then classified as the Γ_1 (singlet) states and the Γ_5 (triplet) states, and those in Si are classified as the Γ_1 (singlet), Γ_3 (doublet) and Γ_5 (triplet) states.

The general solution associated with the Hamiltonian of the donor system can be expanded in terms of pseudo-Bloch functions $\phi_{\vec{k}}^{\zeta}(\vec{r})$ for the conduction bands of the unperturbed crystal as

$$\psi^{\Gamma\mu}(\vec{r}) = \sum_{\vec{k}} F^{\Gamma\mu}(\vec{k}) \phi_{\vec{k}}^{\zeta}(\vec{r}) \quad , \quad (1)$$

where Γ labels the representation of T_d and μ labels the partners of the representation Γ ; the summation $\sum_{\vec{k}}$ stands for $\int \frac{d^3k}{(2\pi)^3}$ in the extended zone scheme. The envelope function $F^{\Gamma\mu}(\vec{k})$ satisfies the Schrödinger equation

$$H F^{\Gamma\mu}(\vec{k}) = E F^{\Gamma\mu}(\vec{k}) \quad , \quad (2)$$

where H is an integral operator in $\vec{k}$ -space defined as

$$H F(\vec{k}) \equiv E_c(\vec{k}) F(\vec{k}) + \sum_{\vec{k}'} \langle \vec{k} | V_{\phi} | \vec{k}' \rangle F(\vec{k}') \quad , \quad (3)$$

where $E_c(\vec{k})$ is the dispersion relation for conduction bands in the extended zone scheme; V_{ϕ} is the impurity pseudo-potential and $|\vec{k}'\rangle$ represents the pseudo-Bloch function $\phi_{\vec{k}'}^{\zeta}(\vec{r})$ associated with the conduction band. To solve Eq. (2) it is convenient to expand $F^{\Gamma\mu}(\vec{k})$ on a complete set of basis wavefunctions of symmetry Γ , $\{\beta_m^{\Gamma\mu}(\vec{k})\}$ as

$$F^{\Gamma\mu}(\vec{k}) = \sum_m C_{\Gamma}(m) \beta_m^{\Gamma\mu}(\vec{k}) \quad . \quad (4)$$

Each basis wavefunction can be written in turn as linear combinations of wavefunctions localized at the N equivalent minima denoted by $\vec{k}_i$, $i = 1, \dots, N$,

$$\beta_m^{\Gamma\mu}(\vec{k}) = \sum_{i=1}^N \alpha_i^{\Gamma}(\mu) \beta_m^i(\vec{k} - \vec{k}_i) \quad , \quad (5)$$

where the wavefunctions $\beta_m^i(\vec{k} - \vec{k}_i)$, $i = 1, \dots, N$, are transformed into each other under certain operations of T_d , and the coefficients $\alpha_i^{\Gamma}(\mu)$ are determined entirely by group theory.

Substituting Eq. (4) into Eq. (2) and projecting out the basic wavefunction, we obtain a matrix equation for the coefficients $C_{\Gamma}(m)$,

$$\sum_{m', \Gamma} \langle m | H | m' \rangle_{\Gamma} C_{\Gamma}(m') = E_{\Gamma} C_{\Gamma}(m) \quad , \quad (6)$$

where $\langle \vec{k} | m \rangle_{\Gamma}$ denote the basis state $\beta_m^{\Gamma}(\vec{k})$ and H is defined in Eq. (3). Each Hamiltonian matrix element, $\langle m | H | m' \rangle_{\Gamma}$ in Eq. (6) can be written as the sum of the kinetic energy (KE) and potential energy (PE) matrix elements. Both matrix elements contain the intravalley term as well as intervalley scattering terms. The KE matrix elements may be evaluated by carrying out the integral in $\vec{k}$ -space. The conduction band energy expression $E_c(\vec{k})$ may be approximated by the sum of several truncated valleys, each valley being described by a ellipsoidal expression (for Si and Ge) or a camel's back expression (for GaP). The PE matrix elements may be evaluated in real space, where the

kernel associated with the PE operator is written approximately as

$$\langle \vec{k} | V_{\phi} | \vec{k}' \rangle \sim J_{\lambda} + V_{pc}(\vec{k}-\vec{k}') R_{\lambda}, \quad (7)$$

with $\vec{k}$ and $\vec{k}'$ restricted in the neighborhood of the center of the i^{th} and j^{th} valleys, respectively. The J_{λ} 's represent the short-range interaction strength factors as defined in Chapter 2. For non-isocoric impurities, they are taken as empirical parameters fitted to the binding energies of the donor ground states. The R_{λ} 's are Umklapp renormalization factors as defined in Ref. 15; the index $\lambda = 1, 2, 3$ corresponds to the intravalley, intertransverse and inter-longitudinal valley terms, respectively. The function $V_{pc}(\vec{q})$ represents the Fourier transform of the screened point charge potential ⁽¹²⁾.

All parameters J_{λ} and R_{λ} have been determined in the previous chapters. However, in the calculation of bound exciton states, we adjust the J_{λ} parameters slightly so that the use of a smaller set of basis functions (necessary for the bound exciton) will reproduce the ionization energies for the donor ground states (one for each symmetry associated with T_d).

B. D⁻ Core

The D⁻ core is made up of two electrons and a positively charged impurity center. The total Hamiltonian of this two-electron system can be written as

$$H_{D^-} = H^{(1)} + H^{(2)} + v_{ee}^{(1,2)} \quad , \quad (8)$$

where $H^{(1)}$ and $H^{(2)}$ are the single-particle Hamiltonians as defined in Equation (3). $v_{ee}^{(1,2)}$ represents the electron-electron mutual interaction whose Fourier transform is

$$\tilde{v}(\vec{q}) = \frac{4\pi e^2}{\epsilon(\vec{q})q^2} \quad , \quad (9)$$

where $\epsilon(\vec{q})$ is the wavevector-dependent dielectric function, the same as used in Chapters 2 and 3. The exact eigenstate of H_{D^-} can be expanded in terms of products of two pseudo-Bloch functions as

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{\vec{k}_1, \vec{k}_2} D(\vec{k}_1, \vec{k}_2) \phi_{\vec{k}_1}^c(\vec{r}_1) \phi_{\vec{k}_2}^c(\vec{r}_2) \quad . \quad (10)$$

The coefficients $D(\vec{k}_1, \vec{k}_2)$ satisfy the Schrödinger equation

$$H_{D^-} D(\vec{k}_1, \vec{k}_2) = E D(\vec{k}_1, \vec{k}_2) \quad , \quad (11)$$

where H_{D^-} is the integral operator defined as

$$\begin{aligned} H_{D^-} D(\vec{k}_1, \vec{k}_2) \equiv & [E_c(\vec{k}_1) + E_c(\vec{k}_2)] D(\vec{k}_1, \vec{k}_2) + \sum_{\vec{k}_1'} \langle \vec{k}_1 | v_\phi | \vec{k}_1' \rangle D(\vec{k}_1', \vec{k}_2) \\ & + \sum_{\vec{k}_2'} \langle \vec{k}_2 | v_\phi | \vec{k}_2' \rangle D(\vec{k}_1, \vec{k}_2') + \sum_{\vec{k}_1', \vec{k}_2'} \langle \vec{k}_1, \vec{k}_2 | v_{ee} | \vec{k}_1', \vec{k}_2' \rangle D(\vec{k}_1', \vec{k}_2') \quad . \end{aligned} \quad (12)$$

The single-particle potential energy terms can be approximated by the expression given in Eq. (6).

Since H_D is invariant under T_d , it is convenient to expand its exact eigenstates in terms of linear combinations of products of single-particle wavefunctions, which transform according to the irreducible representations of T_d . To avoid confusion, we use τ to label the irreducible representation associated with single-particle states and Γ_e to label the irreducible representation associated with the two-electron product states. If we denote the single-particle states as $|\tau_1\mu_1;m\rangle$ and $|\tau_2\mu_2;n\rangle$ for particles 1 and 2, respectively, (where μ_1 and μ_2 label the partners of the representations τ_1 and τ_2 ; and m and n label the remaining quantum numbers for the two particles), then we can write the product basis states (transforming as a basis vector μ_e of the representation Γ_e) as

$$|m\ n; (\tau_1\tau_2)\Gamma_e\mu_e\rangle = \sum_{\mu_1\mu_2} C_{\tau_1\tau_2}(\mu_1\mu_2;\Gamma_e\mu_e) |\tau_1\mu_1;m\rangle \cdot |\tau_2\mu_2;n\rangle \quad (13)$$

where $C_{\tau_1\tau_2}(\mu_1\mu_2;\Gamma_e\mu_e)$ are the coupling coefficients for group T_d , and can be found in Ref. 17. For Si or GaP, τ_1 and τ_2 can be any of the representations $\Gamma_1, \Gamma_3, \Gamma_5$ and Γ_e can be any of the representations $\Gamma_1, \Gamma_3, \Gamma_4$ or Γ_5 . For Ge, Γ_1 and Γ_2 can be either Γ_1 or Γ_5 , and Γ_e can be $\Gamma_1, \Gamma_3, \Gamma_4$ or Γ_5 . Since the total Hamiltonian is spin-independent, we may choose the basis states to be eigenstates of the total spin operator. This can be accomplished by using symmetric (labelled by

"+" or antisymmetric (labelled by "-") (if the two electrons are in different orbitals) combinations of the states defined in Eq. (13).

Namely,

$$|mn, (\tau_1 \tau_2) \Gamma_{e\mu_e}^{\pm}\rangle = \frac{f_{mn}^{\tau_1 \tau_2}}{\sqrt{2}} [|mn; (\tau_1 \tau_2) \Gamma_{e\mu_e}^{\pm}\rangle \pm |nm; (\tau_2 \tau_1) \Gamma_{e\mu_e}^{\pm}\rangle] \quad (14)$$

with

$$f_{mn}^{\tau_1 \tau_2} \equiv \begin{cases} 1/\sqrt{2} & \text{if } m=n \text{ and } \tau_1 = \tau_2 \\ 1 & \text{otherwise} \end{cases}, \quad (15)$$

where we have assumed implicitly that a singlet (triplet) two-electron spinor is multiplied by the symmetric (antisymmetric) space state to make the total wavefunction antisymmetric under the exchange of the two electrons.

The exact envelope wavefunction $D(\vec{k}_1, \vec{k}_2)$ can be expanded in terms of the above basis states. Then, the expansion coefficients, denoted by $C(mn, (\tau_1 \tau_2) \Gamma_{e\mu_e}^{\pm})$, will be determined by the standard configuration-interaction matrix equation

$$\begin{aligned} \sum_{mn} \langle m'n'; (\tau_1' \tau_2') \Gamma_{e\mu_e}^{\pm} | H_D | mn; (\tau_1 \tau_2) \Gamma_{e\mu_e}^{\pm} \rangle C(mn, (\tau_1 \tau_2) \Gamma_{e\mu_e}^{\pm}) \\ = E C(m'n', (\tau_1' \tau_2') \Gamma_{e\mu_e}^{\pm}) \end{aligned} \quad (16)$$

where the states of different symmetries have been decoupled. The Hamiltonian matrix in Eq. (16) involves the sum of two donor Hamiltonian matrices $\tau_1 \langle n' | H^{(1)} | n \rangle_{\tau_1}$ and $\tau_2 \langle n' | H^{(2)} | n \rangle_{\tau_2}$ and the mutual interaction matrix. In Appendix A, we derive the expression for the electron-electron interaction matrix elements. We obtain

$$\begin{aligned} & \langle m'n'; (\tau_1' \tau_2') \Gamma_{e\mu_e}^\pm | v_{ee}(12) | mn; (\tau_1 \tau_2) \Gamma_{e\mu_e}^\pm \rangle \\ & \approx [U_0(m'n', mn) \delta_{\tau_1 \tau_1'} \delta_{\tau_2 \tau_2'} + \sum_{\lambda=1}^4 U_\lambda(m'n', mn) G_\lambda^e(\tau_1' \tau_2', \tau_1 \tau_2)] \\ & \times f_{mn}^{\tau_1 \tau_2} f_{m'n'}^{\tau_1' \tau_2'} \pm \text{exchange term} \quad , \quad (17) \end{aligned}$$

where U_0 represents the intravalley mutual interaction between two electrons with charge distributions along the same axis and $(U_0 - U_1)$ represents the intravalley mutual interaction between two electrons with charge distributions along different axes; U_2 and U_3 represent the contributions from the momentum-conserving intervalley scattering schemes (longitudinal and transverse) and U_4 the contribution from momentum-non-conserving intervalley scattering schemes. For Ge and GaP, there is no U_2 term. The exchange term is obtained from the direct term by exchanging the roles of the two electrons in the final state. The G-matrices describing the electron-electron couplings are given in Table A-1 for Si and GaP and A-2 for Ge. As will be shown in Sec. III, the net contribution of U_1 , U_2 , U_3 and U_4 terms is less than 5% of the total energy. In the zeroth order approximation, the terms involving U_1 , U_2 , U_3 and U_4 are neglected. The energy levels

can therefore be labelled by the symmetry representation of single-particle states. For Si:P, the ordering of the energy levels for the lowest states of various configurations is (starting from the lowest): $(\Gamma_1\Gamma_1)$, $(\Gamma_1\Gamma_5)$, $(\Gamma_5\Gamma_5)$, $(\Gamma_3\Gamma_5)$, and $(\Gamma_3\Gamma_3)$. For Ge:As, it is $(\Gamma_1\Gamma_1)$, $(\Gamma_1\Gamma_5)$, and $(\Gamma_5\Gamma_5)$. This ordering is mainly determined by the sum of energies in single particle states as predicted by the "shell model". But the spacing between energies of various configurations is much smaller than that between the sum of one-particle energies in donor states belonging to various representations.

It is noted from Eq. (17) that in the absence of the coupling terms U_1 , U_2 , U_3 , and U_4 , the spin singlet and triplet states for the mixed configurations (i.e., $(\Gamma_1\Gamma_3)$, $(\Gamma_1\Gamma_5)$ and $(\Gamma_5\Gamma_3)$) are degenerate (since the exchange term vanishes). For the symmetric configurations (i.e., $(\Gamma_1\Gamma_1)$, $(\Gamma_5\Gamma_5)$, and $(\Gamma_3\Gamma_3)$), the spin triplet states lie at much higher energies than the spin singlet states in analogy to the $2S_{3/2}$ and $1S_{1/2}$ states in the He system ⁽¹⁶⁾. When all the coupling terms are included, the states originally labelled by the symmetry representation of single particle states are now split into several states labelled by the symmetry representation of the total Hamiltonian. For the mixed configurations, these states are also split into spin singlet and triplet states.

The above symmetry arguments can also be applied to the donor bound exciton (D^0X) system, which is further complicated by the presence of a Γ_8 -symmetry hole.

c. Donor Bound Exciton (D^0X)

The D^0X is formed by attracting one hole to a D^- core.

Therefore the total Hamiltonian is equal to the sum of the Hamiltonian for a D^- core, H_D^- , the single particle Hamiltonian, $H^{(3)}$ for a hole interacting with the donor and the electron-hole interaction terms.

Namely,

$$H_{D^0X} = H_D^-(1,2) + H^{(3)} - v_{eh}(13) - v_{eh}(23) \quad (18)$$

where we have labelled the coordinates of the two core electrons by 1,2 and that of the hole by 3; the electron-hole interaction v_{eh} has the same Fourier transform $\tilde{v}(\vec{q})$ as Eq. (9). If we expand the exact eigenstate of H_{D^0X} in terms of the products of two pseudo-Bloch functions associated with the conduction band, $\phi_{\vec{k}_1}^C$ and $\phi_{\vec{k}_2}^C$, and one pseudo-Bloch function associated with the valence band, $\phi_{\vec{k}_3}^V$, as

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \sum_{\vec{k}_1, \vec{k}_2, \vec{k}_3} B(\vec{k}_1, \vec{k}_2, \vec{k}_3) \phi_{\vec{k}_1}^C(\vec{r}_1) \phi_{\vec{k}_2}^C(\vec{r}_2) \phi_{\vec{k}_3}^V(\vec{r}_3) \quad , \quad (19)$$

then the coefficients $B(k_1, k_2, k_3)$ must satisfy the Schrödinger equation

$$H_{D^0X} B(\vec{k}_1, \vec{k}_2, \vec{k}_3) = E B(\vec{k}_1, \vec{k}_2, \vec{k}_3) \quad , \quad (20)$$

where H_{D^0X} is an integral operator defined by

$$\begin{aligned}
 H_{D^0X} B(\vec{k}_1, \vec{k}_2, \vec{k}_3) &\equiv H_D - (1, 2) B(\vec{k}_1, \vec{k}_2, \vec{k}_3) + E_V(\vec{k}_3) B(\vec{k}_1, \vec{k}_2, \vec{k}_3) \\
 &+ \sum_{\vec{k}_3'} \langle \vec{k}_3 | V_\phi | \vec{k}_3' \rangle B(\vec{k}_1, \vec{k}_2, \vec{k}_3') - \sum_{\substack{\vec{k}_1' \vec{k}_3' \\ 1 \ 3}} \langle \vec{k}_1' \vec{k}_3' | v_{eh} | \vec{k}_1 \vec{k}_3 \rangle B(\vec{k}_1', \vec{k}_2, \vec{k}_3') \\
 &- \sum_{\vec{k}_2' \vec{k}_3'} \langle \vec{k}_2 \vec{k}_3 | v_{eh} | \vec{k}_2' \vec{k}_3' \rangle B(\vec{k}_1, \vec{k}_2', \vec{k}_3')
 \end{aligned} \tag{21}$$

where $\hat{H}_D - (1, 2)$ is defined by Eq. (12), $E_V(\vec{k}_3)$ is the dispersion relation for the valence band measured from the top of the valence band, and V_ϕ is the impurity pseudo-potential. Since the hole wavefunction is localized near the zone center, it is a good approximation to replace $\langle \vec{k}_3 | V_\phi | \vec{k}_3' \rangle$ by the point charge potential $\tilde{V}_{pc}(\vec{k}_3 - \vec{k}_3')$ as defined in Ref. 13. Expanding the products of the periodic parts of the pseudo-Bloch functions $u_{\vec{k}_1}(\vec{r}_1) u_{\vec{k}_1'}^*(\vec{r}_1)$ and $u_{\vec{k}_3}(\vec{r}_3) u_{\vec{k}_3'}^*(\vec{r}_3)$ in Fourier series with coefficients $c(\vec{k}_1, \vec{k}_1'; \vec{G}_1)$ and $c(\vec{k}_3, \vec{k}_3'; \vec{G}_3)$, respectively, we can write the electron-hole interaction as

$$\begin{aligned}
 \langle \vec{k}_1 \vec{k}_3 | v_{eh} | \vec{k}_1' \vec{k}_3' \rangle &= \sum_{\vec{G}_1 \vec{G}_3} \tilde{v}(\vec{G}_1 + \vec{k}_1 - \vec{k}_1' - \vec{k}_3') c(\vec{k}_1, \vec{k}_1'; \vec{G}_1) c^*(\vec{k}_3', \vec{k}_3; \vec{G}_3) \\
 &\cdot \delta(\vec{G}_1 + \vec{k}_1 - \vec{k}_1', \vec{G}_3 + \vec{k}_3' - \vec{k}_3) \quad ,
 \end{aligned} \tag{22}$$

where $\vec{G}_1, \vec{G}_3$ are reciprocal lattice vectors and $\delta(\vec{k}, \vec{k}') \equiv \delta(\vec{k} - \vec{k}')$, the

Dirac delta function. The term has appreciable contribution only when $\vec{k}_3$ and $\vec{k}'_3$ are near the zone center; therefore, the momentum conservation can be satisfied only when $\vec{G}_1 = 0$ and $\vec{G}_3 = 0$. Hence, we can write approximately

$$\langle \vec{k}_1 \vec{k}_3 | v_{eh} | \vec{k}'_1 \vec{k}'_3 \rangle = \tilde{v}(\vec{k}_1 - \vec{k}'_1) \delta(\vec{k}_1 - \vec{k}'_1, \vec{k}_3 - \vec{k}'_3) \quad . \quad (23)$$

Similarly, for the mutual interaction between the second electron and the hole,

$$\langle \vec{k}_2 \vec{k}_3 | v_{eh} | \vec{k}'_2 \vec{k}'_3 \rangle = \tilde{v}(\vec{k}_2 - \vec{k}'_2) \delta(\vec{k}_2 - \vec{k}'_2, \vec{k}_3 - \vec{k}'_3) \quad . \quad (24)$$

These interactions correspond to the operators

$$\frac{4\pi e^2}{\epsilon(r_{13}) r_{13}} \quad \text{and} \quad \frac{4\pi e^2}{\epsilon(r_{23}) r_{23}} \quad ,$$

where $\frac{1}{\epsilon(r)r}$ is the Fourier transform of $\frac{1}{\epsilon(q)q^2}$ in real space. The valence band dispersion function $E_v(\vec{k}_3)$ is very anisotropic. If we transform Eq. (21) in real space, the kinetic energy operator for the hole can be written in the following form as introduced by Baldereschi and Lipari (17,18) (B-L) in the limit of strong spin-orbit interaction

$$E_v(-i \frac{\partial}{\partial \vec{r}_3}) = \sigma \left[-\nabla_3^2 - \frac{1}{9} \mu (P^{(2)} J^{(2)}) + \frac{1}{9} \delta \{ [P^{(2)} \times J^{(2)}] \begin{smallmatrix} (4) \\ 4 \end{smallmatrix} \right. \right. \\ \left. \left. + \frac{1}{5} \sqrt{70} [P^{(2)} \times J^{(2)}] \begin{smallmatrix} (4) \\ 0 \end{smallmatrix} + [P^{(2)} \times J^{(2)}] \begin{smallmatrix} (4) \\ -4 \end{smallmatrix} \} \right] \quad (25)$$

where σ is the ratio of electron transverse effective mass to hole effective mass defined as $\sigma \equiv \gamma_1 m_t^* / m_0$ (m_0 being the free electron mass), $\mu = (6\gamma_3 + 4\gamma_2)/5\gamma_1$ and $\delta = (\gamma_3 - \gamma_2)/\gamma_1$, with γ_1 , γ_2 and γ_3 being the parameters proposed by Luttinger ⁽¹⁹⁾ for the description of the valence band dispersion relation near the center of the Brillouin zone; $P^{(2)}$ and $J^{(2)}$ are the second rank symmetric tensors for the linear and angular momentum, respectively, as introduced by B-L.

In the limit of strong spin-orbit interaction, the hole wavefunctions transform as partners of the double group representations of T_d . We shall label the representations associated with the hole states by Γ_h and that with the two-electron product states by Γ_e . The basis wavefunctions which have overall symmetry $\Gamma_\mu^\pm$ can be constructed from the linear combinations of products of two-electron states (of symmetry $(\tau_1 \tau_2) \Gamma_e^\pm$) and hole states (of symmetry Γ_h). We shall denote our basis functions $|mnp; [(\tau_1 \tau_2) \Gamma_e^\pm \Gamma_h] \Gamma_\mu^\pm \rangle$, where the symbol $[(\tau_1 \tau_2) \Gamma_e^\pm \Gamma_h] \Gamma_\mu^\pm$ indicates how the total wavefunction of overall symmetry $\Gamma_\mu^\pm$ is made by the two-electron product states (of symmetry $(\tau_1 \tau_2) \Gamma_e^\pm$) and the hole state (of symmetry Γ_h). The indices mn and p represent

the remaining quantum numbers for the two electrons and hole, respectively. The exact envelope wavefunction $B(\vec{k}_1, \vec{k}_2, \vec{k}_3)$ can be expanded in terms of these basis states. The coefficients for expansion, $C(mnp, [(\tau_1 \tau_2) \Gamma_e^\pm, \Gamma_h^\pm] \Gamma_\mu^\pm)$ can be determined by the standard configuration-interaction matrix equation,

$$\sum_{m'n'p'} \sum_{\tau_1 \tau_2, \Gamma_e \Gamma_h} \langle m'n'p'; [(\tau_1' \tau_2') \Gamma_e'^\pm, \Gamma_h'^\pm] \Gamma_\mu'^\pm | H_{D^0X} | mnp; [(\tau_1 \tau_2) \Gamma_e^\pm, \Gamma_h^\pm] \Gamma_\mu^\pm \rangle \times C(mnp, [(\tau_1 \tau_2) \Gamma_e \Gamma_h] \Gamma_\mu^\pm) = E^{\Gamma^\pm} C(m'n'p', [(\tau_1' \tau_2') \Gamma_e'^\pm, \Gamma_h'^\pm] \Gamma_\mu'^\pm). \quad (26)$$

The only difference between the Hamiltonian matrix elements for the D^0X and D^- systems is the additional term involving matrix elements for the single hole Hamiltonian $H^{(3)}$ and that for the electron-hole mutual interactions. The matrix elements for $H^{(3)}$ are the same as that for an acceptor system except for a reversed sign in the potential energy part. Hence, we can treat them in the same way as Refs. 17,18. The electron-hole interaction terms lead to further complication and will be treated in greater detail here. In Appendix B, we derive the matrix elements for the electron-hole interaction with the electron states restricted to s-like (ellipsoidal) orbitals and the hole states restricted to s-like and d_0 -like (spherical) orbitals. We obtain a general expression for the electron-hole interaction term

$$\begin{aligned}
 & \langle m'n'p' | [(\tau_1' \tau_2') \Gamma_e^\pm \Gamma_h^\pm] \Gamma^\pm | v(13) | mnp; [(\tau_1 \tau_2) \Gamma_e^\pm \Gamma_h^\pm] \Gamma^\pm \rangle \\
 & = J^\Gamma ([(\tau_1' \tau_2') \Gamma_e^\pm \Gamma_h^\pm], [(\tau_1 \tau_2) \Gamma_e^\pm \Gamma_h^\pm]) V_{13}(m'p', mp) \delta_{\tau_2 \tau_2'} \delta_{nn'} \\
 & \times f_{mn}^{\tau_1 \tau_2} f_{m'n'}^{\tau_1' \tau_2'} \quad \pm \text{exchange term} \quad , \quad (27)
 \end{aligned}$$

where $V_{13}(m'p', mp)$ is the matrix element for the Coulomb mutual interaction, i.e.,

$$V_{13}(m'p', mp) = \langle m'p' | \frac{2}{r_{13}} | mp \rangle \quad . \quad (28)$$

J^Γ represents the electron-hole coupling matrix between states of different configurations but same overall symmetry, Γ . The exchange term is obtained from the first term by exchanging the roles of the two electrons. The J-matrices depend on the orbital symmetry of the single-hole states p and p' . For hole states p, p' of the same orbital symmetry (i.e., both s-like or both d-like), all the J-matrices are equal to the identity matrix. For hole states p, p' of different orbital symmetries (e.g. one s-like and one d-like) the J matrices are nontrivial and are listed in Table B-2 for Si and GaP and Table B-3 for Ge. It is noted that all the matrices given in Table B-2 and Table B-3 can be diagonalized with the resulting eigenvalues equal to either 1 or -1. This is the same as one would have obtained if the electron in each of the equivalent valleys had been considered to interact with the hole independently.

To illustrate the use of Tables B-2 and B-3, we take the states associated with the configuration $[(15)\Gamma_5\Gamma_8]\Gamma^\pm$ in Si as an example. Here we use (i,j) to denote the labelling $(\Gamma_i\Gamma_j)$. The electron-hole interaction coupling a s-like and a d-like hole states can be written as

$$\begin{aligned} & \langle [(15)\Gamma_5\Gamma_8]\Gamma^\pm | v(13) + v(23) | [(15)\Gamma_5\Gamma_8]\Gamma^\pm \rangle \\ &= \{ \langle [(15)\Gamma_5\Gamma_8]\Gamma | v(13) + v(23) | [(15)\Gamma_5\Gamma_8]\Gamma \rangle \\ & \pm \langle [(51)\Gamma_5\Gamma_8]\Gamma | v(13) + v(23) | [(51)\Gamma_5\Gamma_8]\Gamma \rangle \} , \end{aligned} \quad (29)$$

where we used the relation $[(15)\Gamma_5\Gamma_8]\Gamma^\pm = \frac{1}{2} \{ [(15)\Gamma_5\Gamma_8]\Gamma \pm [(51)\Gamma_5\Gamma_8]\Gamma \}$ and the fact that all cross terms vanish as indicated in Table B-2. Writing the above matrix elements in terms of the J-matrices and the electron-hole coupling strength $\bar{V}_{eh}$, with $\bar{V}_{eh} \equiv 2a_s a_d V_{sd}$, (where a_s and a_d are the coefficients associated with the s-like and d-like components respectively, in the hole ground state, and V_{sd} is the electron-hole interaction coupling the s-like and d-like components of the hole states),

We obtain

$$\begin{aligned} & \langle [(15)\Gamma_5\Gamma_8]\Gamma^\pm | v(13) + v(23) | [(15)\Gamma_5\Gamma_8]\Gamma^\pm \rangle \\ &= [J^\Gamma((15)\Gamma_5\Gamma_8, (15)\Gamma_5\Gamma_8) + J^\Gamma((51)\Gamma_5\Gamma_8, (51)\Gamma_5\Gamma_8)] \bar{V}_{eh} , \end{aligned} \quad (30)$$

which equals $\bar{V}_{eh}$, $-\bar{V}_{eh}$, $4/5 \bar{V}_{eh}$, and $-4/5 \bar{V}_{eh}$ for $\Gamma = \Gamma_6, \Gamma_7, \Gamma_8$ and Γ_8' , respectively. There is also an off-diagonal term $-3/5 \bar{V}_{eh}$ for the coupling between states with $\Gamma = \Gamma_8$ and $\Gamma = \Gamma_8'$. Since the two states are degenerate in the absence of electron-hole interaction, we can simply diagonalize the J-matrix coupling the states $[(51)\Gamma_5\Gamma_8]\Gamma_8$ and $[(51)\Gamma_5\Gamma_8]\Gamma_8'$ and obtain the eigenvalues -1 and 1 . We therefore obtain the values $\bar{V}_{eh}$ and $-\bar{V}_{eh}$ for the two mixed states associated with $\Gamma = \Gamma_8$ and Γ_8' , which diagonalize the J-matrix. In other words, the initially four-fold degenerate hole states are now split into two levels (one classified as $\Gamma_6 + \Gamma_8$, another classified as $\Gamma_7 + \Gamma_8'$) due to the presence of a Γ_5 electron. This is expected, since the Γ_5 electron in Si occupies valleys on the same axis thus producing an electron-hole splitting in the same manner as in a free exciton system. If we apply this argument to the states associated with the same configuration in Ge, we obtain the values $\bar{V}_{eh}$, $\bar{V}_{eh}$, $-4/5 \bar{V}_{eh}$, and $1/5 \bar{V}_{eh}$ for the diagonal terms with $\Gamma = \Gamma_6, \Gamma_7, \Gamma_8$ and Γ_8' , respectively, and a value $-2/5 \bar{V}_{eh}$ for the off-diagonal term of the J-matrix coupling the $\Gamma = \Gamma_8$ and $\Gamma = \Gamma_8'$ states. This J-matrix also couples the above two states with the $[(11)\Gamma_1\Gamma_8]\Gamma_8$ state as shown in Table B-3. If we neglect the coupling between the $[(11)\Gamma_1\Gamma_8]\Gamma_8$ state and the $[(51)\Gamma_5\Gamma_8]\Gamma_8, \Gamma_8'$ states (this is approximately valid due to the fact that the energy of the $[(11)\Gamma_1\Gamma_8]\Gamma_8$ state is lower than the $[(51)\Gamma_5\Gamma_8]\Gamma_8$ state by a large value compared to $\bar{V}_{eh}$), we can diagonalize the sub-matrix which couples the two states of the same electronic symmetry

(51) Γ_5 , and obtain the eigenvalues 0 and -1. We therefore conclude that the Γ_5 electron will split the hole state into three levels with approximately equal spacing with the highest level classified as $\Gamma_6 + \Gamma_7$ and the lower two levels classified as Γ_8 symmetry. This is particularly interesting, because it reflects the fact that the Γ_5 electrons in Si and in Ge are intrinsically different in that the former occupies valleys along the same axis and the latter has the same probability in all four valleys.

III. CALCULATION METHOD

Our calculation is based on the Hartree-Fock approximation. It is assumed that the fine structure in the excitation spectrum is approximately unaffected by the correlation effect, although this effect plays an important role in the binding of the system. Our calculation procedure is divided into three steps. In the first step (zeroth-order approximation), both the electron-electron coupling terms (U_1, U_2, U_3 and U_4) and the electron-hole coupling term ($\bar{V}_{eh}$) are neglected. In the second step, the electron-electron coupling terms are included. In the final step, all coupling terms are included. In the first step, the states of different electronic configurations, denoted as $(\Gamma_1 \Gamma_2)$, are completely decoupled. We can therefore carry out the calculation for each configuration separately. The Hartree-Fock solutions are expanded in terms of a set of basis functions. For each of the two electrons with symmetry μ , we use seven basis functions defined by

linear combinations of Slater-type orbitals (STO), namely,

$$\beta_{b_n}^{\mu}(\vec{r}) \equiv \sum_{j=1}^N \alpha_j(\mu) e^{i\vec{k}_j \cdot \vec{r}} e^{-b_n \sqrt{x^2+y^2+z^2}/\zeta^2}, \quad (31)$$

where $\alpha_j(\mu)$ are the expansion coefficients, which make the basis functions $\beta_{b_n}^{\mu}(\vec{r})$ transform as a basis vector (labelled by μ) associated with an irreducible representation of T_d , and

$$b_n = b_0/z_n; \quad n = 1, \dots, 7$$

with

$$b_0 = 2 \text{ bohr}^{-1} \text{ for Si (or GaP) and } 4 \text{ bohr}^{-1} \text{ for Ge}$$

and

$$z_n = \begin{cases} (1, 2, 4, 8, 16, 1/2, 1/4) & \text{for Si and Ge} \\ (1, 2, 4, 8, 1/2, 1/4, 1/8) & \text{for GaP} \end{cases}$$

The eccentricity factor ζ is determined by minimizing the energy expectation value of the effective mass Hamiltonian in the state $\beta_{b_n}^{\mu}$. The best value of ζ was found to be 0.57 for Si, 0.48 for GaP and 0.355 for Ge. It should be noted that for GaP, the STO's localized at two minima along the same axis are combined into dumbbell-like Slater-type orbitals, (DSTO) (see Chapter 3). The fact that the ground state in the neutral donor system has very little admixture of higher angular momentum states (defined in the ellipsoidal coordinates) makes it a good approximation to expand the electron wavefunction in each valley in terms of s-like STO's or DSTO's (see Chapters 2 and 3).

For the hole, however, the mixing of s-like and d-like orbitals is appreciable. Hence we use 7 s-like and 7 d-like basis functions with their radial parts given by

$$f_{c_n}(r_3) = \begin{cases} \sqrt{4c_n^3} e^{-c_n r_3} & \text{for } \ell=0 \\ \sqrt{\frac{4c_n^5}{3}} r_3 e^{-c_n r_3} & \text{for } \ell=2 \end{cases}, \quad (32)$$

where $c_n = c_0/z_n$, $n=1, \dots, 7$ with $c_0 = 0.5 \text{ Bohr}^{-1}$. The z_n 's are the same as used for the electrons. The angular parts of the s-like and d-like basis functions are $|\ell=0, J=3/2; F=3/2, F_z\rangle$ and $|\ell=2, J=3/2; F=3/2, F_z\rangle$, respectively, when J is the spin associated with the valence band, and F is the total angular momentum associated with ℓ and J .

In the first step, the expansion coefficients in Eq. (26) are decomposed in the product of three terms, viz.

$$C(mnp, [(\tau_1 \tau_2) \Gamma_e \Gamma_h] \Gamma^\pm_\mu) = C_{\tau_1}(m) C_{\tau_2}(n) C_{\Gamma_h}(p) \quad (33)$$

Then, Eq. (26) can be simplified to

$$\begin{aligned} \sum_{mnp} \langle m'n'p' | H_{D^0X} | mnp \rangle_{\tau_1 \tau_2} C_{\tau_1}(m) C_{\tau_2}(n) C_{\Gamma_h}(p) &= E_0(\tau_1, \tau_2) C_{\tau_1}(m') \\ &\times C_{\tau_2}(n') C_{\Gamma_h}(p') \end{aligned}, \quad (34)$$

where

$$\begin{aligned}
 \langle m'n'p' | H_{D^0X} | mnp \rangle_{\tau_1 \tau_2} &\equiv \tau_1 \langle m' | H^{(1)} | m \rangle_{\tau_1} \delta_{nn'} \delta_{pp'} + \tau_2 \langle n' | H^{(2)} | n \rangle_{\tau_2} \\
 &\times \delta_{pp'} \delta_{mm'} + \Gamma_h \langle p' | H^{(3)} | p \rangle_{\Gamma_h} \delta_{mm'} \delta_{nn'} - \langle m'p' | v_{eh} | mp \rangle \delta_{nn'} \delta_{\ell_3' \ell_3} \\
 &- \langle n'p' | v_{eh} | np \rangle \delta_{mm'} \delta_{\ell_3' \ell_3} + \langle m'n' | v_{ee} | mn \rangle \delta_{pp'} \quad (35)
 \end{aligned}$$

with ℓ_3, ℓ_3' indicating the angular momentum quantum number of the hole states. Eq. (34) can be solved for the coefficients $C_{\tau_1}(m)$, $C_{\tau_2}(n)$ and $C_{\Gamma_h}(p)$ self-consistently by iteration.

In the second step, the correction due to the electron-electron coupling is included. We evaluate the contributions due to the terms $U_\lambda (\lambda=1,2,3,4)$ in the zeroth order ground state wavefunctions obtained in the first step. It is found that for Ge, the intervalley scattering terms U_3 and U_4 are two orders of magnitude smaller than the U_1 term and can be neglected. The zeroth-order ground states of various configurations are now coupled together through the off-diagonal matrix elements of G_λ^Γ . The sub-Hamiltonians defined for each symmetry $\Gamma_e^\pm$ by

$$H_{\Gamma_e^\pm}(\tau_1 \tau_2, \tau_1' \tau_2') = E_0(\tau_1, \tau_2) \delta_{\tau_1 \tau_1'} \delta_{\tau_2 \tau_2'} + \sum_{\lambda=1}^4 U_\lambda G_\lambda^{\Gamma_e^\pm}(\tau_1 \tau_2, \tau_1' \tau_2') \quad (36)$$

(with $E_0(\tau_1\tau_2)$ being the eigenvalues obtained in the zeroth order approximation) are then diagonalized separately. The energy levels except the lowest one are now split into several states, each one associated with an irreducible representation of the group T_d . The coupling coefficient between states of different electronic configurations are also obtained. We shall denote the energy eigenvalues of $H_e^{\Gamma_e^{\pm}}(\tau_1\tau_2, \tau_1'\tau_2')$ as $E_1[(\tau_1\tau_2)\Gamma_e^{\pm}]$. In the final step, the electron-hole coupling term V_{eh} is included. As shown in Table B-2 and B-2, this term only couples the states which are separated by an energy large compared to V_{eh} or the states associated with the same electronic configuration. In the former case, the coupling can be neglected. In the latter case, the zeroth order energies are degenerate. If we diagonalize the sub-matrices which couple the states associated with the same electronic configurations, we obtain the eigenvalues -1 and 1 for most of them; the others are between -1 and 1. We therefore repeat the Hartree-Fock calculations for each electronic configuration $(\tau_1\tau_2)$ with the J-matrices set equal to 1 and -1. The contributions of V_{eh} to the Hamiltonian matrix for J-coefficients between -1 and 1 can be obtained simply by interpolation.

We have expanded the hole wavefunction in terms of s-like and d-like orbitals (with total angular momentum $F \equiv L + J = 3/2$). Therefore, the contributions due to the other orbitals (e.g., with $L = 2$ and $F = 7/2, 5/2, 1/2$, and $L = 4, 6, \dots$ etc.) ⁽²¹⁾ are not included. For simplicity, we include the correction due to these orbitals by

multiplying the values of $\bar{V}_{eh}$ obtained above by a correction factor f_c , where f_c is the ratio of the electron-hole splitting for the free exciton system obtained with and without the orbitals associated with $L = 2$ and $F = 7/2, 5/2, 1/2$; and $L = 4, 6, \dots$ etc. For this purpose, we have calculated the ground state splitting of the free exciton for Si, GaP and Ge, using the basis set given by Eq. (32) and the band parameters used by Lipari and Altarelli (20,21). We obtain a value for this splitting of 0.92, 1.95 and 0.58 meV for Si, GaP and Ge, respectively. Comparing our results with the accurate results obtained by Lipari and Altarelli (20,21), we obtain that $f_c = 0.5, 1$ and 2 for Si, GaP and Ge, respectively.

The remaining task is to diagonalize the sub-Hamiltonians defined by

$$H^{\Gamma^{\pm}}((\tau_1\tau_2)\Gamma_e\Gamma_8, (\tau_1\tau_2)\Gamma_e'\Gamma_8) = E_1[(\tau_1\tau_2)\Gamma_e^{\pm}] \delta_{\Gamma_e\Gamma_e'} + \bar{V}_{eh} \{ J^{\Gamma^{\pm}}[(\tau_1\tau_2)\Gamma_e, (\tau_1\tau_2)\Gamma_e'] + J^{\Gamma^{\pm}}[(\tau_2\tau_1)\Gamma_e, (\tau_2\tau_1)\Gamma_e'] \} , \quad (37)$$

where $E_1[(\tau_1\tau_2)\Gamma_e^{\pm}]$ is the eigenvalue of $H^{\Gamma_e^{\pm}}(\tau_1\tau_2, \tau_1'\tau_2')$ obtained in the previous step. The final results for the energy eigenvalues will be denoted as $E[(\tau_1\tau_2)\Gamma_e^{\pm}\Gamma_8]_{\Gamma^{\pm}}$.

IV. RESULTS AND DISCUSSION

We will discuss our results for Si, Ge and GaP separately.

A. Si

Tables V-1 to V-4 show the ground state energies for various configurations of the D^0X obtained in three calculation steps (denoted by E_0 , E_1 and E for the zeroth order approximation (ZOA), ZOA plus electron-electron coupling, and ZOA plus all couplings, respectively,) for Si doped by the impurities P, As, Sb, and Li, respectively. For illustration, the theoretical spectrum for Si:P is plotted in Fig. V-1, showing the systematic change of the energy levels in various approximations. The smallness of the fine structure splitting, as compared to the total binding energies, justifies the validity of the first order approximation used to evaluate the various fine structure terms. For example, for the $\{\Gamma_1\Gamma_5; \Gamma_8\}$ states in Si:P, we have $\bar{V}_{eh} \approx U_2 \approx U_3 = \frac{1}{5} U_1 \approx \frac{1}{500} E_0(\Gamma_1\Gamma_5)$. As shown in Fig. V-1, when the electron-electron and electron-hole coupling terms are neglected, we obtain one energy level for each configuration and the ordering is the same as predicted by the shell model. When the electron-electron (dominated by U_1) coupling is included, all levels except the $(\Gamma_1\Gamma_1)$ state are split into several states. We find that the mixing of configurations is appreciable only for the states of the same overall symmetry and close in energy. The admixture of configurations $(\Gamma_3\Gamma_3)\Gamma_1^+$ and $(\Gamma_5\Gamma_5)\Gamma_1^+$ in the ground state $(\Gamma_1\Gamma_1)\Gamma_1^+$ is less than 0.1%, whereas the mixing between $(\Gamma_3\Gamma_3)\Gamma_1^+$ and $(\Gamma_5\Gamma_5)\Gamma_1^+$ is substantial (about 9%). The $(\Gamma_3\Gamma_3)\Gamma_3^+$ state also couples strongly with the $(\Gamma_5\Gamma_5)\Gamma_3^+$ state (about 8% mixing). The remaining states only couple with each other

TABLE V-1

Total energies of the lowest-lying states of various configurations of the D^0X calculated in three steps (E_0 , E_1 and E) for Si:P. All energies are in meV. The notation $\Gamma_e^\pm$ in the fourth column stands for the irreducible representation to which the two-electron product wave function belongs; "+" indicates a spin singlet or triplet.

Material	First Step		Second Step		Final, E			
	Configu- ration	E_0	$\Gamma_e^\pm$	E_1	Γ_6	Γ_7	Γ_8	Γ_8'
Si:P	$\{\Gamma_3\Gamma_3;\Gamma_8\}$	-42.59	Γ_1^+	-42.58	-	-	-42.57	-
			Γ_3^+	-42.89	-42.89	-42.89	-42.90	-
			Γ_2^-	-43.25	-	-	-	-43.25
	$\{\Gamma_3\Gamma_5;\Gamma_8\}$	-43.39	Γ_5^+	-43.16	-43.21	-43.12	-43.21	-43.12
			Γ_4^-	-43.96	-43.94	-43.97	-43.97	-43.95
			Γ_4^+	-44.04	-44.03	-44.06	-44.06	-44.03
			Γ_5^-	-44.06	-44.11	-44.02	-44.11	-44.02
	$\{\Gamma_5\Gamma_5;\Gamma_8\}$	-44.09	Γ_1^+	-44.08	-	-	-44.04	-
			Γ_3^+	-44.16	-44.10	-44.23	-44.20	-
			Γ_5^+	-44.67	-44.64	-44.71	-44.71	-44.64
			Γ_4^-	-44.76	-44.80	-44.73	-44.80	-44.73
	$\{\Gamma_1\Gamma_3;\Gamma_8\}$	-53.00	Γ_3^+	-53.13	-53.09	-53.17	-53.13	-
			Γ_3^-	-53.35	-53.31	-53.39	-53.35	-
	$\{\Gamma_1\Gamma_5;\Gamma_8\}$	-53.22	Γ_5^+	-53.34	-53.38	-53.30	-53.38	-53.30
			Γ_5^-	-53.64	-53.68	-53.60	-53.68	-53.60
	$\{\Gamma_1\Gamma_1;\Gamma_8\}$	-57.36	Γ_1^+	-57.67	-	-	-57.67	-

TABLE V-2

Total energies of the lowest-lying states of various configurations of the D^0X , calculated in three steps (E_0 , E_1 and E) for Si:As.

Material	First Step		Second Step		Final, E			
	Configuration	E_0	Γ_e^+	E_1	Γ_6	Γ_7	Γ_8	Γ_8'
Si:As	$\{\Gamma_3\Gamma_3;\Gamma_8\}$	-41.09	Γ_1^+	-41.09	-	-	-41.08	-
			Γ_3^+	-41.39	-41.39	-41.39	-41.40	-
			Γ_2^-	-41.72	-	-	-	-41.72
	$\{\Gamma_3\Gamma_5;\Gamma_8\}$	-41.92	Γ_5^+	-41.71	-41.76	-41.76	-41.75	-41.68
			Γ_4^-	-42.48	-42.47	-42.49	-42.49	-42.47
			Γ_4^+	-42.55	-42.54	-42.57	-42.56	-42.54
			Γ_5^-	-42.57	-42.62	-42.54	-42.61	-42.54
	$\{\Gamma_5\Gamma_5;\Gamma_8\}$	-42.65	Γ_1^+	-42.65	-	-	-42.61	-
			Γ_3^+	-42.73	-42.67	-42.80	-42.77	-
			Γ_5^+	-43.22	-43.19	-43.25	-43.25	-43.19
			Γ_4^-	-43.30	-43.33	-43.27	-43.33	-43.27
	$\{\Gamma_1\Gamma_3;\Gamma_8\}$	-60.69	Γ_3^+	-60.76	-60.72	-60.80	-60.76	-
			Γ_3^-	-60.91	-60.87	-60.95	-60.91	-
	$\{\Gamma_1\Gamma_5;\Gamma_8\}$	-60.82	Γ_5^+	-60.88	-60.92	-60.84	-60.92	-60.84
			Γ_5^-	-61.07	-61.11	-61.03	-61.11	-61.03
	$\{\Gamma_1\Gamma_1;\Gamma_8\}$	-66.65	Γ_1^+	-66.87	-	-	-66.87	-

TABLE V-3

Total energies of the lowest-lying states of various configurations of the D^0X , calculated in three steps (E_0 , E_1 and E) for Si:Sb.

Material	First Step		Second Step		Final, E			
	Configu- ration	E_0	$\Gamma_e^{\pm}$	E_1	Γ_6	Γ_7	Γ_8	Γ_8'
Si:Sb	$\{\Gamma_3\Gamma_3;\Gamma_8\}$	-40.28	Γ_1^+	-40.33	-	-	-40.32	-
			Γ_3^+	-40.61	-40.61	-40.61	-40.62	-
			Γ_2^-	-40.89	-	-	-	-40.89
	$\{\Gamma_3\Gamma_5;\Gamma_8\}$	-41.79	Γ_5^+	-41.57	-41.61	-41.53	-41.61	-41.53
			Γ_4^-	-42.32	-42.31	-42.33	-42.33	-42.31
			Γ_4^+	-42.39	-42.38	-42.40	-42.40	-42.38
			Γ_5^-	-42.40	-42.44	-42.37	-42.44	-42.37
	$\{\Gamma_5\Gamma_5;\Gamma_8\}$	-42.96	Γ_1^+	-42.91	-	-	-42.88	-
			Γ_3^+	-42.99	-42.93	-43.05	-43.02	-
			Γ_5^+	-43.53	-43.50	-43.56	-43.56	-43.50
			Γ_4^-	-43.62	-43.65	-43.59	-43.65	-43.59
	$\{\Gamma_1\Gamma_3;\Gamma_8\}$	-50.11	Γ_3^+	-50.25	-50.21	-50.29	-50.25	-
			Γ_3^-	-50.46	-50.42	-50.50	-50.46	-
	$\{\Gamma_1\Gamma_5;\Gamma_8\}$	-50.54	Γ_5^+	-50.67	-50.71	-50.63	-50.71	-50.63
			Γ_5^-	-50.99	-51.03	-50.96	-51.03	-50.96
	$\{\Gamma_1\Gamma_1;\Gamma_8\}$	-54.25	Γ_1^+	-54.48	-	-	-54.58	-

TABLE V-4

Total energies of the lowest-lying states of various configurations of the D^0X , calculated in three steps (E_0 , E_1 and E) for Si:Li.

Material	First Step		Second Step		Final, E			
	Configuration	E_0	$\Gamma_e^{\pm}$	E_1	Γ_6	Γ_7	Γ_8	Γ_8'
Si:Li	$\{\Gamma_3\Gamma_3;\Gamma_8\}$	-43.01	Γ_1^+	-43.47	-	-	-43.46	-
			Γ_3^+	-43.68	-43.68	-43.68	-43.69	-
			Γ_2^-	-43.67	-	-	-	-43.67
	$\{\Gamma_3\Gamma_5;\Gamma_8\}$	-43.06	Γ_5^+	-43.22	-43.27	-43.17	-43.27	-43.17
			Γ_4^-	-43.63	-43.61	-43.64	-43.64	-43.61
			Γ_4^+	-43.72	-43.70	-43.74	-43.74	-43.70
			Γ_5^-	-43.73	-43.78	-43.69	-43.78	-43.69
	$\{\Gamma_5\Gamma_5;\Gamma_8\}$	-43.10	Γ_1^+	-42.79	-	-	-42.78	-
			Γ_3^+	-43.13	-43.07	-43.20	-43.14	-
			Γ_5^+	-43.68	-43.65	-43.71	-43.71	-43.65
			Γ_4^-	-43.76	-43.79	-43.73	-43.79	-43.73
	$\{\Gamma_1\Gamma_3;\Gamma_8\}$	-42.23	Γ_3^+	-42.13	-42.10	-42.16	-42.13	-
			Γ_3^-	-42.85	-42.82	-42.88	-42.85	-
	$\{\Gamma_1\Gamma_5;\Gamma_8\}$	-42.27	Γ_5^+	-42.06	-42.09	-42.03	-42.09	-42.03
			Γ_5^-	-42.90	-42.93	-42.87	-42.93	-42.87
	$\{\Gamma_1\Gamma_1;\Gamma_8\}$	-41.25	Γ_1^+	-41.44	-	-	-41.44	-

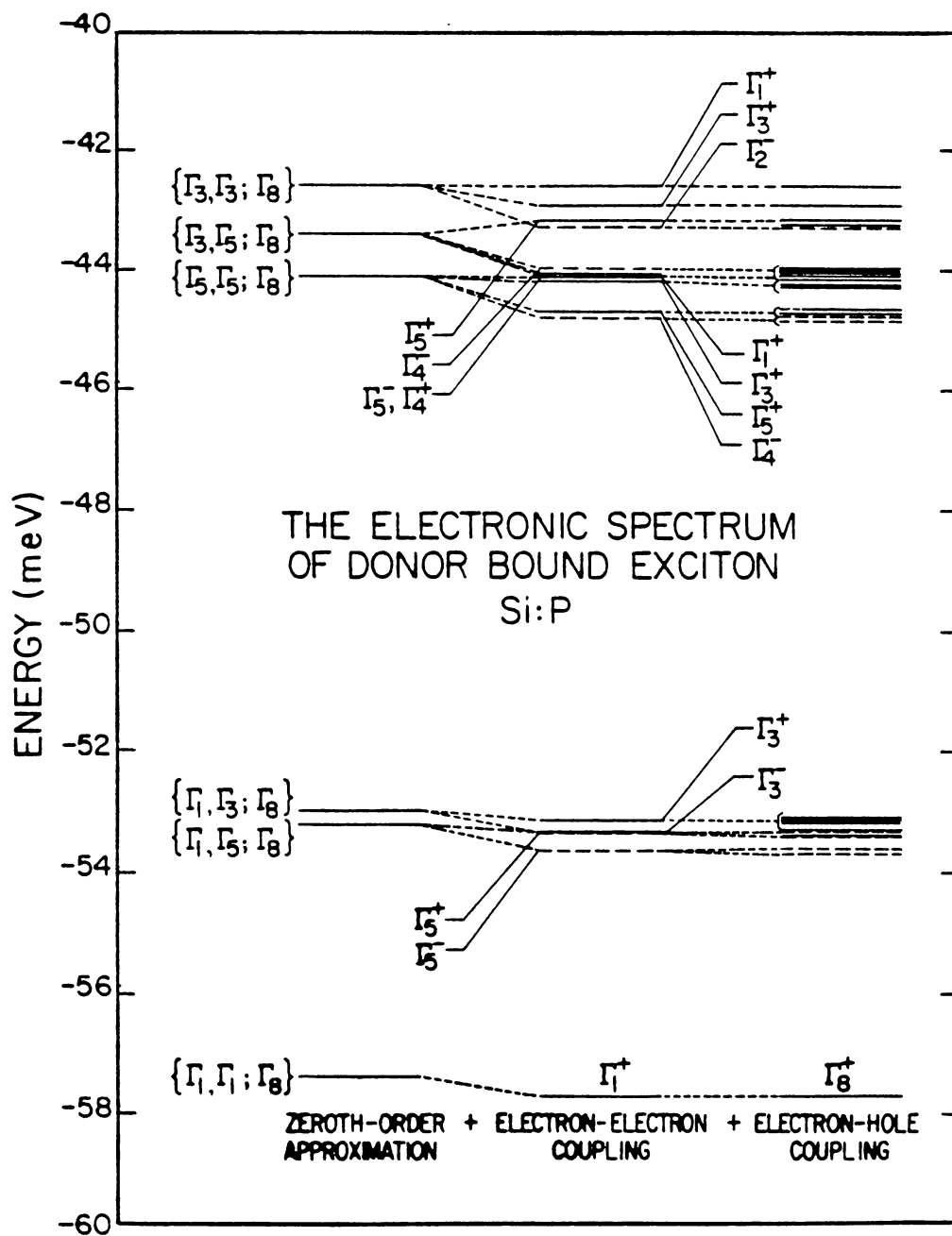


Figure V-1. Theoretical electronic spectrum for D^0X in Si:P plotted in three consecutive steps: zeroth order approximation (ZOA), ZOA plus electron-electron coupling and ZOA plus all coupling terms. The notations for the symmetry labels are defined in the text.

weakly (less than 1%). When the electron-hole coupling is included, the states are split further and mixing is only important between states associated with the same electronic configuration. The splitting due to the electron-hole coupling is an order of magnitude smaller than the splitting due to the electron-electron coupling and therefore difficult to observe experimentally.

We can compare our theoretical results with the experimental data. The energy level schemes for D^0X and D^0 in Si:P are plotted in Fig. V-2, also included are the experimental data obtained by Lightowlers et al ⁽²²⁾. All possible optical transitions are indicated by arrows. The whole excitation spectrum has been shifted by a uniform correlation energy (of approximately 7.0 meV). As shown in this figure, the agreement between theory and experiment is very good. All the peaks except the α_1 line observed in the luminescence data are a superposition of several lines. Our theoretical spectrum predicts a line due to the optical transition from the $(\Gamma_1\Gamma_5)\Gamma_5^-$ state of D^0X to the Γ_5 state of D^0 near the same energy position of the δ' line. This line was first observed by Thewalt ⁽²³⁾ and cannot be explained by the shell model. For As and Sb similar theoretical spectra can be obtained using Tables V-2 and V-3, respectively. For Si:As, the energy spacings between the group of states associated with the $\{\Gamma_1\Gamma_3;\Gamma_8\}$ and $\{\Gamma_1\Gamma_5;\Gamma_8\}$ configurations and the ground state obtained in present calculations are about 1.5 meV larger than the experimental value for the spacing between the δ -line and α_1 line ⁽²²⁾. On the other hand, by looking at the optical transitions from the $\{\Gamma_1\Gamma_3;\Gamma_8\}$ and $\{\Gamma_1\Gamma_5;\Gamma_8\}$ D^0X

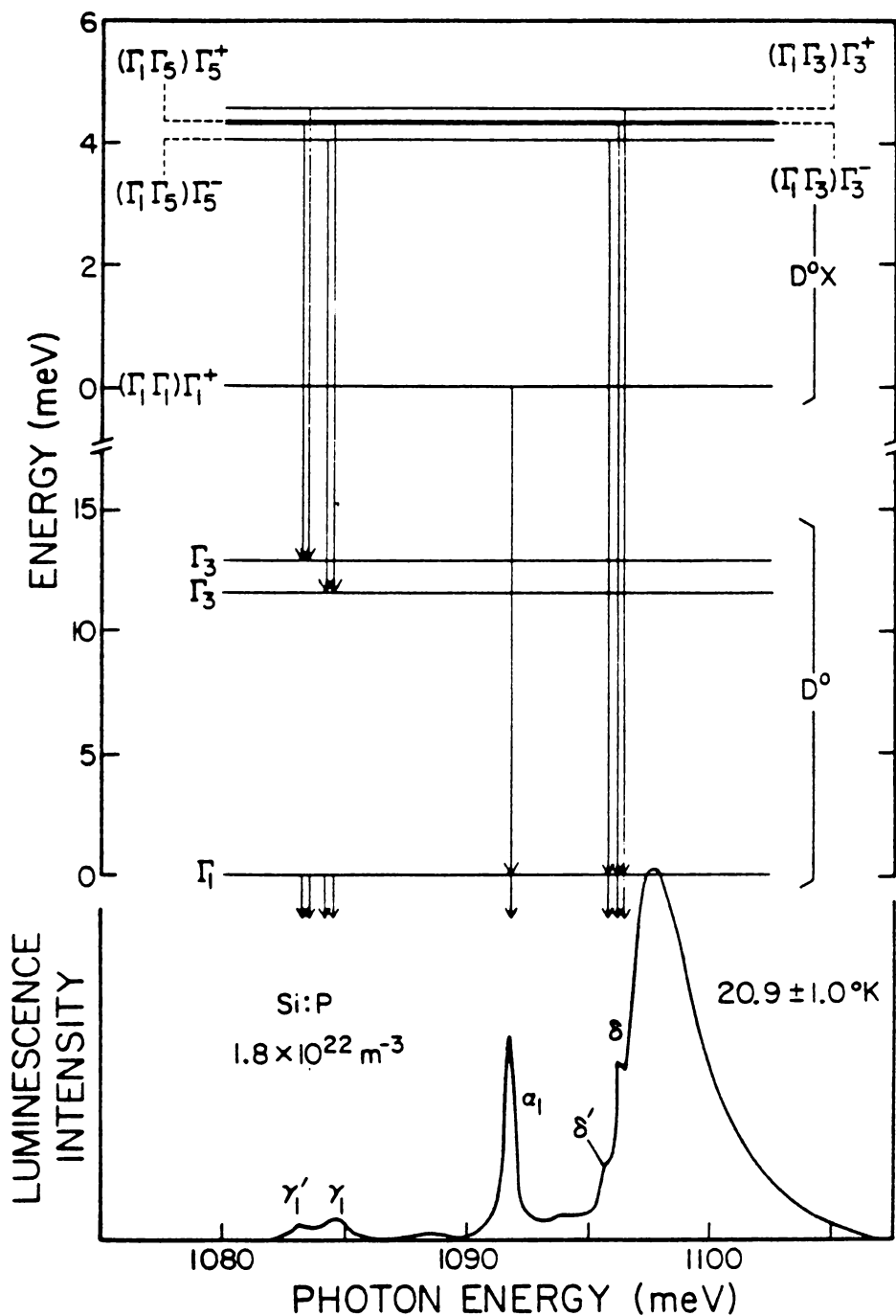


Figure V-2. Theoretically predicted transition lines (indicated by arrows) plotted accompanied with the experimental data for D^0X in Si:P. The data are taken from Lightowlers et al. (22).

excited states to the Γ_3 and Γ_5 donor excited states (γ lines), Elliott et al ⁽²⁴⁾ have obtained a value ≈ 5.8 meV for the energy separation between the $\{\Gamma_1 \Gamma_3; \Gamma_8\}$ and $\{\Gamma_1 \Gamma_5; \Gamma_8\}$ excited states and the ground state in Si:As. This value is in good agreement with the present calculation. We therefore attribute the δ -line ⁽²²⁾ observed in Si:As to the optical transition involving a p-like hole excited state.

For Li, an interstitial donor in Si, the energy spectrum is qualitatively different than that for the other donors (substitutional). The major difference is that in Si:Li, the ordering for the donor states are inverted (the Γ_3 and Γ_5 states have lower energies than the Γ_1 state ⁽²⁵⁾). In the top panel of Fig. V-3, we plot our theoretical spectrum for D^0X in Si:Li, showing the systematic change of the energy levels obtained in the zeroth order approximation (ZOA) and ZOA plus electron-electron coupling. As shown in this figure, in the zeroth order approximation, the states $\{2\Gamma_5; \Gamma_8\}$ and $\{2\Gamma_3; \Gamma_8\}$ are nearly degenerate, so are the states $\{\Gamma_1 \Gamma_5; \Gamma_8\}$ and $\{\Gamma_1 \Gamma_3; \Gamma_8\}$. This is expected, since the Γ_3 and Γ_5 donor states in Si:Li are degenerate. When the electron-electron coupling term is included, these levels split into a group of states approximately 1 meV wide in energy. To compare our results with the experimental data ⁽²⁶⁻²⁸⁾, we plot the energy level scheme for D^0 in the middle panel of Fig. V-3 and the experimental spectrum obtained by Thewalt ⁽²⁷⁾ in the bottom panel. The observed optical transitions are indicated by arrows. Again, the

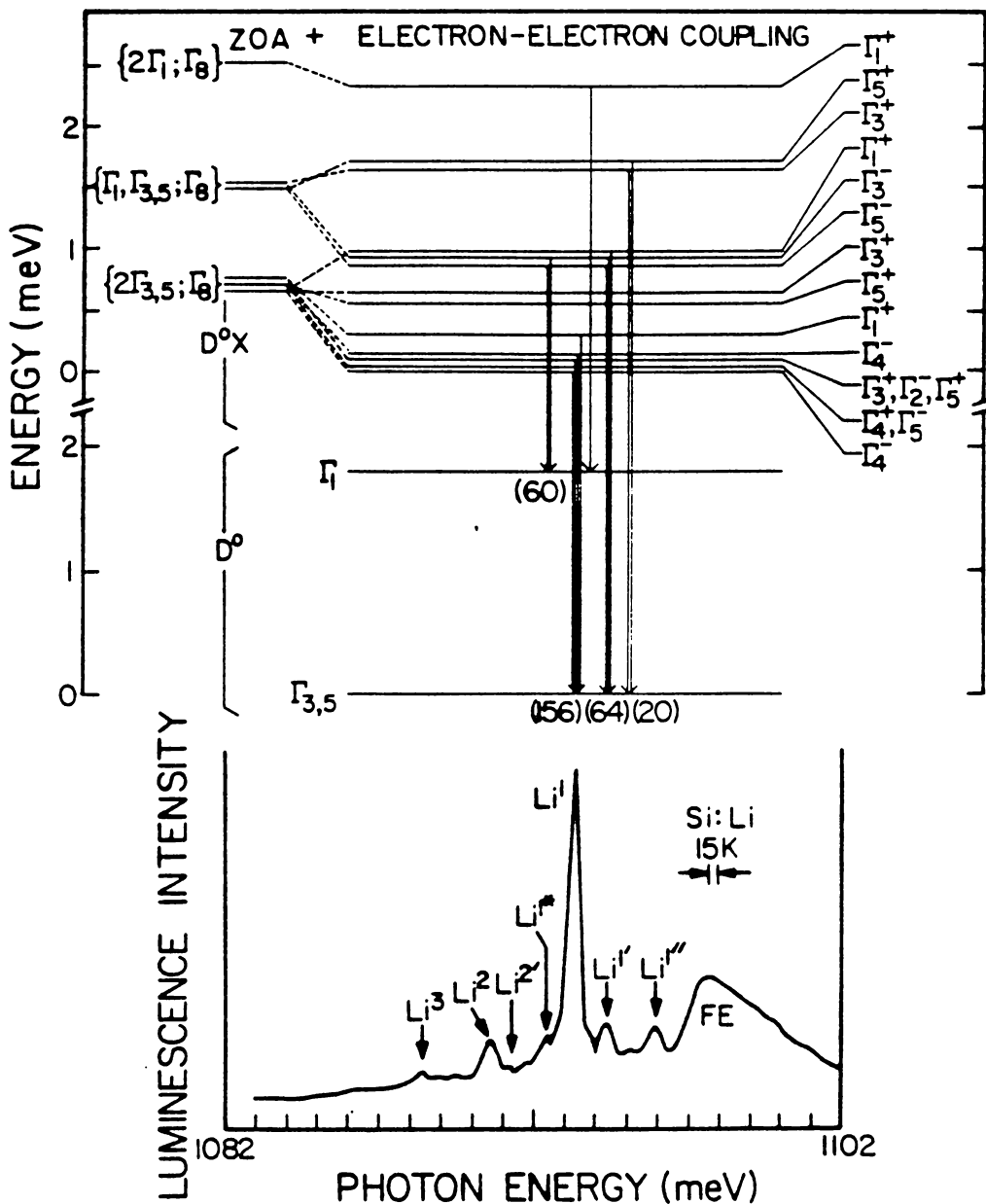


Figure V-3. Theoretical electronic spectrum in Si:Li plotted in two steps: zeroth order approximation (ZOA), ZOA plus electron-electron coupling. The energy level scheme for the neutral donor is plotted in the middle panel (after Ref. 25). Theoretically predicted transition lines are indicated by arrows. The experimental data taken from Thewalt (Ref. 27) are plotted in the bottom panel for comparison.

whole theoretical spectrum is shifted by the correlation energy of 7.3 meV. The number of nearly degenerate states associated with a line is indicated in parentheses. It is found that the main bound exciton line (marked "Li¹") and the line marked "Li^{1'}" correspond to the transitions from a group of 156 states associated with the configuration $\{2\Gamma_{3,5};\Gamma_8\}$, and a group of 60 states associated with the configuration $\{\Gamma_1 \Gamma_{3,5};\Gamma_8\}$ (plus 4 states associated with the configuration $\{2\Gamma_{3,5};\Gamma_8\}$), respectively, to the $\Gamma_{3,5}$ donor ground state. The line marked "Li^{1*}" corresponds to the transition from a group of 60 states associated with the configuration $\{\Gamma_1 \Gamma_{3,5};\Gamma_8\}$ to the Γ_1 excited donor state. There is a small hump between the lines marked Li^{1'} and Li¹", which may correspond to the transition from a group of 20 states associated with the $\{\Gamma_1 \Gamma_{3,5};\Gamma_8\}$ configuration (which are separated from the ground states by approximately 1 meV) to the donor ground state. This point has to be examined by further experiment. The line marked "Li¹" cannot be identified with any transitions from an electronic excited state obtained in the present calculation and therefore may be attributed to the transition from a hole excited state as proposed by several authors (28-30).

We can estimate the correlation energy for the ground state by taking the difference between the experimental and the theoretical value for the dissociation energy. The theoretical dissociation energy is obtained by subtracting the binding energy for the neutral donor and for the free exciton from the total binding energy for the donor bound exciton. The binding energies for the neutral donors are 45.5, 53.7,

42.7 and 33.0 meV for Si:P ⁽²⁹⁾, Si:As ⁽²⁹⁾, Si:Sb ⁽²⁹⁾, and Si:Li⁽³⁰⁾, respectively. The binding energy for the free exciton is about 14.7 meV ⁽³¹⁾. Combining these results with the Hartree-Fock calculation for the total energy, we obtain the dissociation energies -2.5, -1.5, -2.8 and -3.9 meV for Si:P, Si:As, Si:Sb and Si:Li, respectively.

The negative values of the dissociation energy indicate that the system is not bound in the Hartree-Fock approximation. The experimental value for the dissociation energy is about 4.5, 5.5, 4.2 and 3.4 meV for Si:P ⁽²³⁾, Si:As ⁽²²⁾, Si:Sb ⁽²²⁾, and Si:Li ⁽²⁶⁾, respectively.

Taking the difference between the experimental and theoretical values for the dissociation energy, we obtain approximately the same correlation energy, 7 meV for Si doped with P, As, and Sb and 7.3 meV for Li. In a previous calculation for the ground state energy of bound excitons in a spherical model (Chapter 4) we obtained a correlation energy about .20 Rydberg for an electron-to-hole mass ratio of 1.

Taking a Rydberg to be the binding energy of the donor in Si (31.3 meV) calculated in the Kohn-Luttinger effective mass approximation (EMA) ⁽³²⁾, we obtain a correlation energy 6.3 meV, which is in reasonably good agreement with the value estimated from comparing our Hartree-Fock calculation with the experimental data for practical systems.

B. Ge

In Table V-5, the ground state energies for various configurations obtained in three steps (denoted by E_0 , E_1 and E for the zeroth order approximation (ZOA), ZOA plus electron-electron coupling, and ZOA plus all coupling terms, respectively) are listed for Ge:P, Ge:As and Ge:Sb. The theoretical spectrum for Ge:P showing the systematic change of the energy levels in various steps is plotted in Fig. V-4. Again, it is found that the electron-electron and electron-hole coupling terms are small compared to the total binding energy. For example, for the $\{\Gamma_1\Gamma_5; \Gamma_8\}$ states in Ge:P, we have $\bar{V}_{eh} \approx 20$ $U_3 \approx 20$ $U_4 \approx \frac{1}{3} U_1 \approx \frac{1}{100} E_0(\Gamma_1\Gamma_5)$. The terms U_3 and U_4 are negligibly small, and were completely ignored in our calculation. The spectrum of Ge is simpler than Si. The electron-electron coupling is small compared to the energy separation between states of the same symmetry. The mixing between the $(\Gamma_1\Gamma_1)\Gamma_1^+$ state and the $(\Gamma_5\Gamma_5)\Gamma_1^+$ state is about 0.34%, and that between the $(\Gamma_1\Gamma_5)\Gamma_5^+$ and $(\Gamma_5\Gamma_5)\Gamma_5^+$ states is about 0.34%, and that between the $(\Gamma_1\Gamma_5)\Gamma_5^+$ and $(\Gamma_5\Gamma_5)\Gamma_5^+$ states is about 0.38%. There is no mixing between the other states shown in this figure. The further splitting due to the electron-hole coupling is explicitly shown in this figure. Again, only mixing between states associated with the same electronic configuration is included. The splitting due to the electron-hole coupling is found to be comparable to the splitting due to the electron-electron coupling, and can be observed experimentally. To compare our results with the experimental values, we plot the energy level scheme and the theoretical spectra in Fig. V-5 for Ge:P and Fig. V-6 for Ge:As,

TABLE V-5

Total energies of the lowest-lying states of various configurations, calculated in three steps (E_0 , E_1 and E) for Ge:P, Ge:As and Ge:Sb. All energies are in meV.

Material	First Step		Second Step		Final, E			
	Configuration	E_0	Γ_e^+	E_1	Γ_6	Γ_7	Γ_8	Γ_8'
Ge:P	$\{\Gamma_5\Gamma_5;\Gamma_8\}$	-13.07	Γ_1^+	-13.18	-	-	-13.07	-
			Γ_5^+	-13.28	-13.35	-13.35	-13.18	-13.39
			Γ_3^+	-13.53	-13.56	-13.56	-13.55	-
			Γ_4^-	-13.53	-13.44	-13.44	-13.63	-13.53
	$\{\Gamma_1\Gamma_5;\Gamma_8\}$	-15.19	Γ_5^+	-15.37	-15.49	-15.49	-15.26	-15.37
			Γ_5^-	-15.52	-15.64	-15.64	-15.41	-15.52
	$\{\Gamma_1\Gamma_1;\Gamma_8\}$	-16.20	Γ_1^+	-16.62	-	-	-16.62	-
Ge:As	$\{\Gamma_5\Gamma_5;\Gamma_8\}$	-12.94	Γ_1^+	-13.04	-	-	-12.94	-
			Γ_5^+	-13.16	-13.22	-13.22	-13.06	-13.26
			Γ_3^+	-13.40	-13.43	-13.43	-13.42	-
			Γ_4^-	-13.40	-13.31	-13.31	-13.50	-13.40
	$\{\Gamma_1\Gamma_5;\Gamma_8\}$	-16.34	Γ_5^+	-16.48	-16.60	-16.60	-16.36	-16.48
			Γ_5^-	-16.60	-16.72	-16.72	-16.49	-16.60
	$\{\Gamma_1\Gamma_1;\Gamma_8\}$	-17.61	Γ_1^+	-18.05	-	-	-18.05	-
Ge:Sb	$\{\Gamma_5\Gamma_5;\Gamma_8\}$	-12.94	Γ_1^+	-12.99	-	-	-12.85	-
			Γ_5^+	-13.01	-13.09	-13.09	-12.91	-13.15
			Γ_3^+	-13.40	-13.42	-13.42	-13.41	-
			Γ_5^-	-13.40	-13.31	-13.31	-13.50	-13.40
	$\{\Gamma_1\Gamma_5;\Gamma_8\}$	-13.10	Γ_5^+	-13.50	-13.60	-13.60	-13.41	-13.50
			Γ_5^-	-13.57	-13.67	-13.67	-13.48	-13.57
	$\{\Gamma_1\Gamma_1;\Gamma_8\}$	-13.25	Γ_1^+	-13.67	-	-	-13.67	-

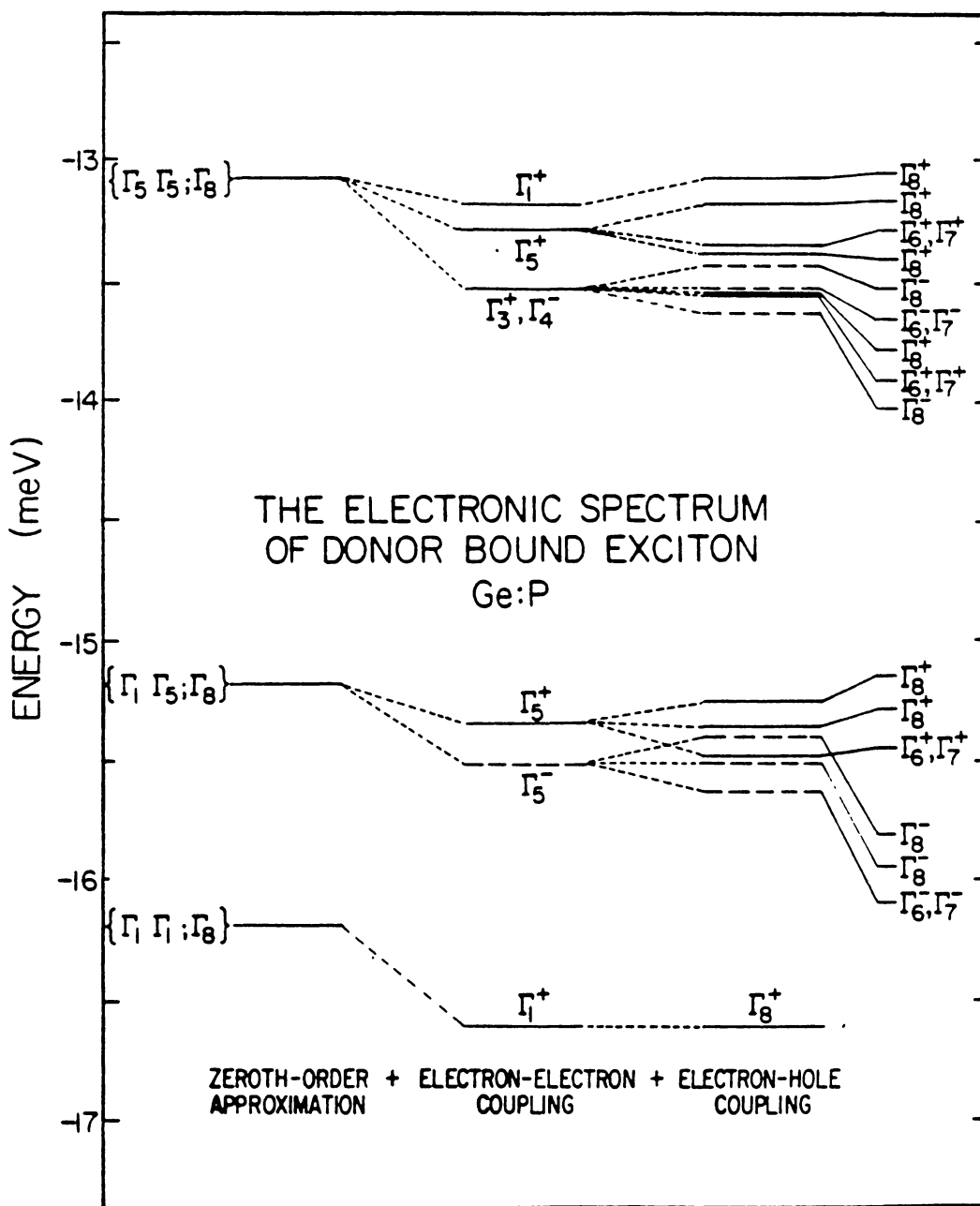


Figure V-4. Theoretical electronic spectrum of donor bound excitons in Ge:P plotted in three steps: zeroth order approximation (ZOA), ZOA plus electron-electron coupling and ZOA plus are coupling terms. The notations for symmetry labels are defined in the text.

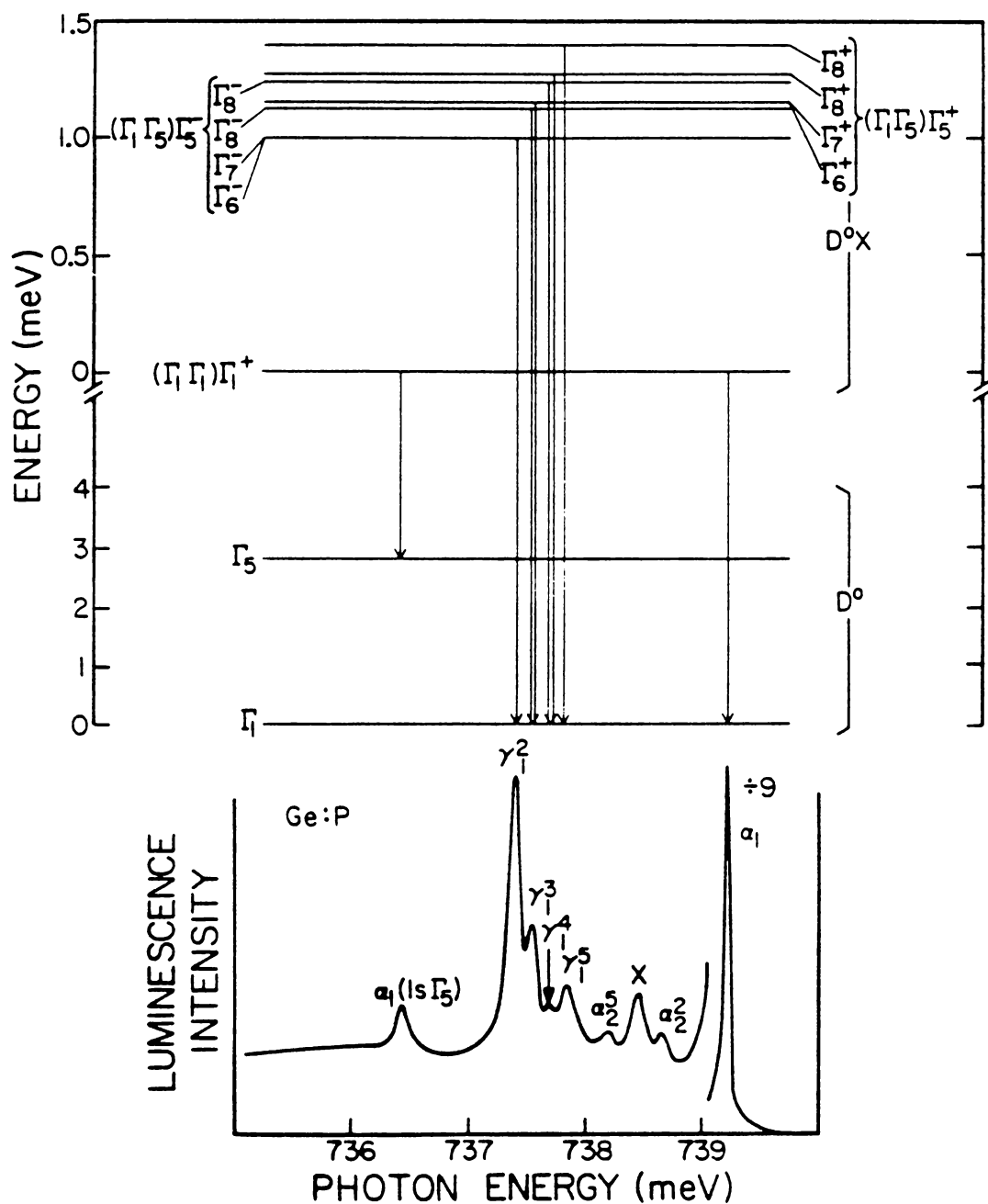


Figure V-5. Theoretical spectrum of the optical transition from donor bound exciton to neutral donor in Ge:P plotted accompanied with the experimental luminescence spectrum. The theoretical predicted transitions are indicated by arrows. The data are taken from Mayer et al (Ref. 11).

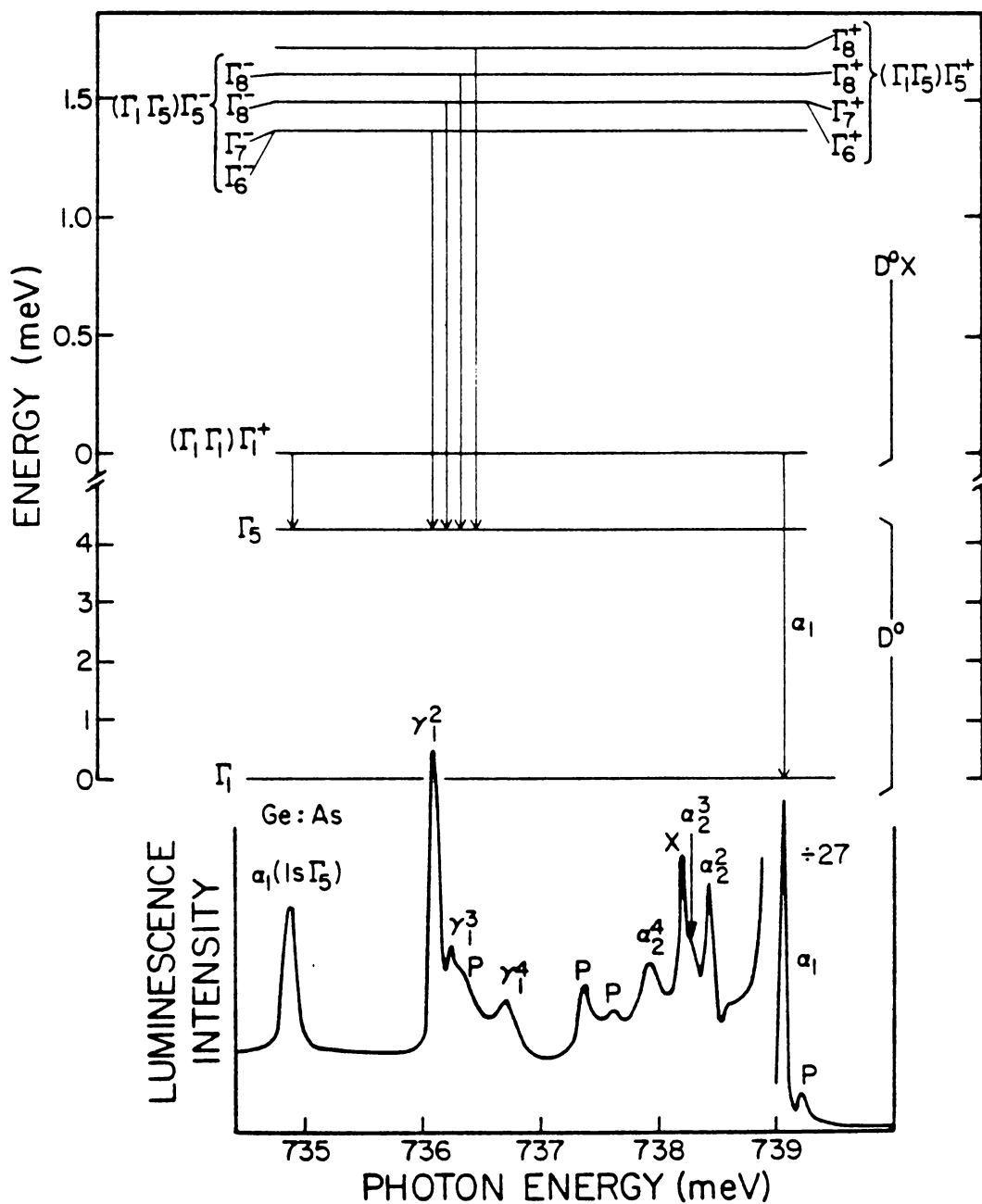


Figure V-6. Theoretical spectrum of optical transitions from D^0X for Ge:As, plotted accompanied with the experimental luminescence spectrum. The theoretically predicted transitions are indicated by arrows. The data are taken from Mayer et al (Ref. 11).

accompanied with the experimental spectra obtained by Mayer and Lightowlers⁽¹¹⁾. The whole theoretical spectrum is shifted by a correlation energy (of about 1.7 meV) so that the line associated with the ground-state to ground-state transition matches the experimental data (α_1 line). With this assignment, the theoretical spectrum fits the experimental data quite well. The spacing between the first-excited-state to ground-state transition and the α_1 line agree with the experimental value (for the separation between α_1 and γ_1^2 lines) to within 0.05 meV. In the phonon-assisted absorption spectrum obtained by Henry and Lightowlers,⁽²⁸⁾ a line labelled δ^1 (LA) is observed, which is due to the transition from the ground state of the neutral donor to the first excited state of the bound exciton. The position of this excited state is about 0.2 meV in Ge:P and 0.45 meV in Ge:As below the lowest electronic excited state obtained in our calculation. Since the no-phonon transitions from this state to the donor Γ_5 state are not observed, we attribute this state to the first hole excited state (denoted as $2P_{3/2}$) in the donor bound exciton system. The no-phonon transition between the ground state and this $2P_{3/2}$ hole excited state is forbidden, because the overlap of the electron and hole envelope function vanishes according to symmetry.

We can also estimate the correlation energy in the same way as we did for Si. The binding energies for the neutral donors are 12.9, 14.2 and 10.3 meV for Ge:P, Ge:As and Ge:Sb, respectively⁽³³⁾. The binding energy for the free exciton is about 4.15 meV⁽³⁴⁾. Accordingly,

we obtain the dissociation energy -0.43, -0.30 and -0.78 meV for Ge:P, Ge:As and Ge:Sb, respectively. The experimental values for the dissociation energy for Ge:P and Ge:As are 1.3 meV and 1.45 meV, respectively ⁽¹¹⁾. Thus we obtain correlation energies of about 1.7 meV for both Ge:P and Ge:As. Using the result from our previous calculation in a spherical model and taking a Rydberg to be 9.8 meV (the binding energy calculated in EMA ⁽³²⁾), we obtain a correlation energy 1.96 meV for the bound exciton with electron to hole mass ratio equal to 1. This is again in reasonable agreement with the value estimated above for a practical system.

C. GaP

The ground state energies for various configurations, obtained in three steps, zeroth order approximation, ZOA, (denoted E_0), ZOA plus electron-electron coupling (denoted E_1) and ZOA plus all coupling terms (denoted E) for GaP:S are listed in Table V-6. These energy spectra are plotted in Figure V-7, showing the systematic change. As shown in this figure, the electron-electron coupling and electron-hole coupling terms are small compared to the total binding energy. For example, for the $\{\Gamma_1 \Gamma_3; \Gamma_8\}$ states, we have

$$\bar{V}_{eh} \approx 13 U_3 \approx \frac{1}{4} U_1 \approx \frac{1}{500} E_0(\Gamma_1 \Gamma_3) .$$

All electron-electron couplings are negligibly small $\leq 1\%$. The largest

TABLE V-6

Total energies of the low-lying states of various configurations of the D^0X calculated in three steps (E_0 , E_1 , and E) for GaP:S. All energies are in meV.

Material	First Step		Second Step		Final, E			
	Configuration	E_0	Γ_e^+	E_1	Γ_6	Γ_7	Γ_8	Γ_8'
GaP:S	{ $\Gamma_5\Gamma_5;\Gamma_8$ }	-47.2	Γ_1^+	-47.2	-	-	-47.0	-
			Γ_3^+	-47.2	-47.0	-47.4	-47.4	-
			Γ_5^+	-47.5	-47.4	-47.6	-47.6	-47.4
			Γ_4^-	-47.5	-47.6	-47.4	-47.6	-47.4
	{ $\Gamma_5\Gamma_5;\Gamma_8$ }	-66.5	Γ_5^+	-66.4	-66.6	-66.1	-66.6	-66.1
			Γ_4^-	-66.7	-66.6	-66.5	-66.6	-66.5
			Γ_4^+	-66.7	-66.7	-66.8	-66.8	-66.7
			Γ_5^-	-66.8	-67.0	-66.8	-67.0	-66.8
	{ $\Gamma_3\Gamma_3;\Gamma_8$ }	-71.7	Γ_1^+	-72.2	-	-	72.1	-
			Γ_3^+	-73.7	-73.7	-73.7	-73.7	-
			Γ_2^-	-75.1	-	-	-	75.1
	{ $\Gamma_1\Gamma_5;\Gamma_8$ }	-113.9	Γ_5^+	-113.8	-114.0	-113.6	-114.0	-113.6
			Γ_5^-	-113.9	-114.1	-113.7	-114.1	-113.7
	{ $\Gamma_1\Gamma_3;\Gamma_8$ }	-114.2	Γ_3^+	-114.8	-114.6	-115.0	-114.8	-
			Γ_3^-	-115.6	-115.4	-115.8	-115.6	-
	{ $\Gamma_1\Gamma_1;\Gamma_8$ }	-133.4	Γ_1^+	-133.7	-	-	-133.7	-

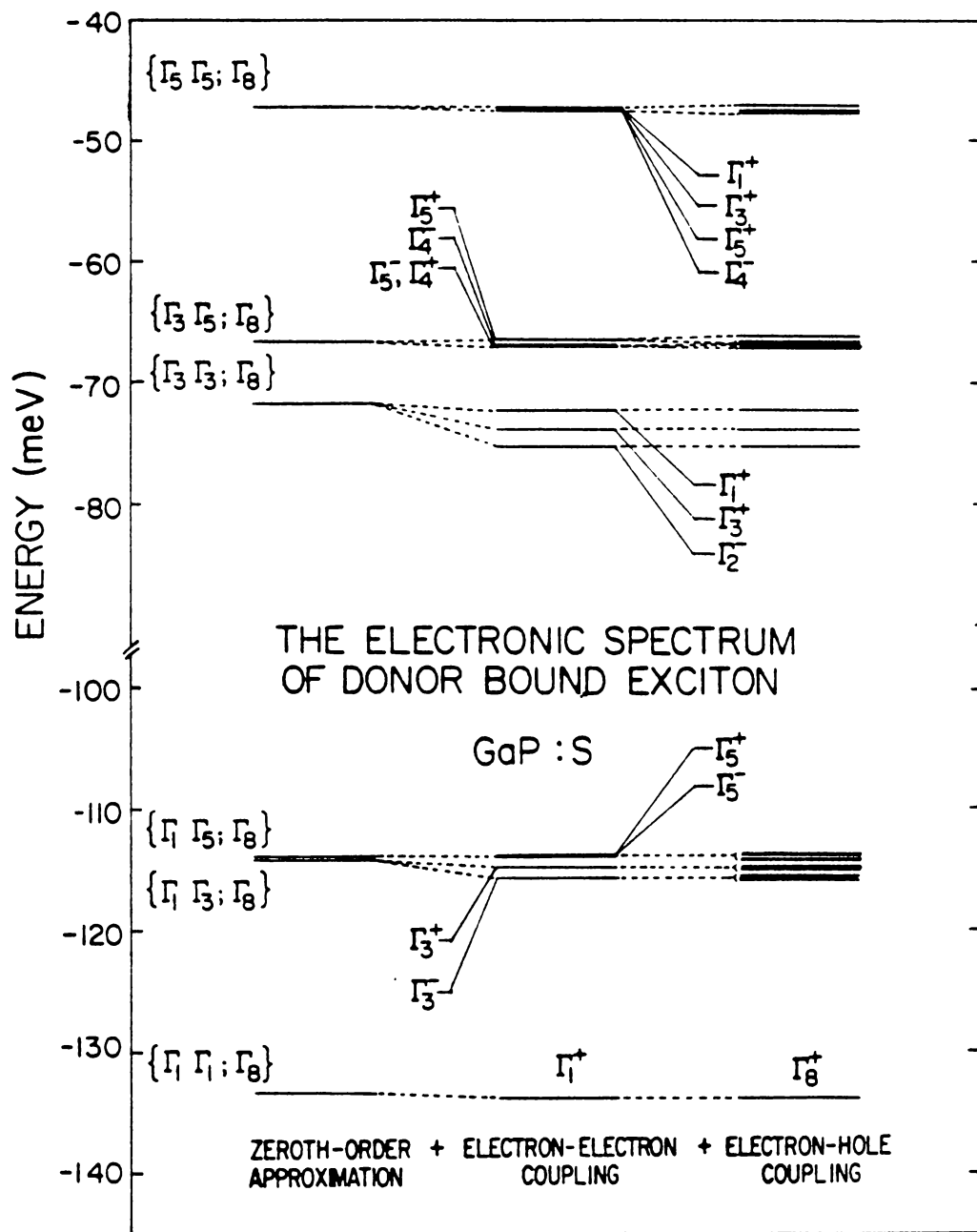


Figure V-7. Theoretical electronic spectrum of donor bound excitons in GaP:S plotted in three steps: zeroth order approximation (ZOA), ZOA plus electron-electron coupling and ZOA plus all coupling terms. The notations for symmetry labels are defined in the text.

mixing due to electron-electron coupling is about 0.1% (between the $(\Gamma_3\Gamma_3)\Gamma_3^+$ and $(\Gamma_5\Gamma_5)\Gamma_3^+$ states). It is noted that the $(\Gamma_1\Gamma_3)$ and $(\Gamma_1\Gamma_5)$ states are very close in energy (separated by about 1 meV). This result is of particular interest since in the neutral donor, the Γ_3 and Γ_5 states are separated by about 20 meV. This energy separation between Γ_3 and Γ_5 states is reduced by a factor of 20 in the bound exciton. This drastic change in energy separation is a combined effect resulting from the screening of the impurity potential due to the Γ_1 electron and the camel's back structure in the conduction band. We find that for the $(\Gamma_1\Gamma_3)$ and $(\Gamma_1\Gamma_5)$ states in D^0X , the Γ_1 electron tends to retain its wavefunction as in the D^0 system. Therefore, the potential seen by the Γ_3 (or Γ_5) electron in D^0X is largely screened. This causes the wavefunction of the Γ_3 (or Γ_5) electron to be much more localized in $\vec{k}$ -space than in the case for a D^0 . The overlap between the wavefunctions localized near the two minima associated with a camel's back valley is greatly reduced; hence, the binding energies for the Γ_3 and Γ_5 electrons become similar.

The magnitude of the electron-hole coupling is about 0.2 meV, which is never important for the states of different configurations, since the smallest energy separation between states of different configurations and with non zero electron-hole coupling is about 70 meV (between $\{\Gamma_1\Gamma_3;\Gamma_8\}$ and $\{2\Gamma_3;\Gamma_8\}$). To compare our results with the available experimental data, we plot the energy level schemes for the D^0X and the D^0 for GaP:S in Fig. V-8 accompanied with the experimental

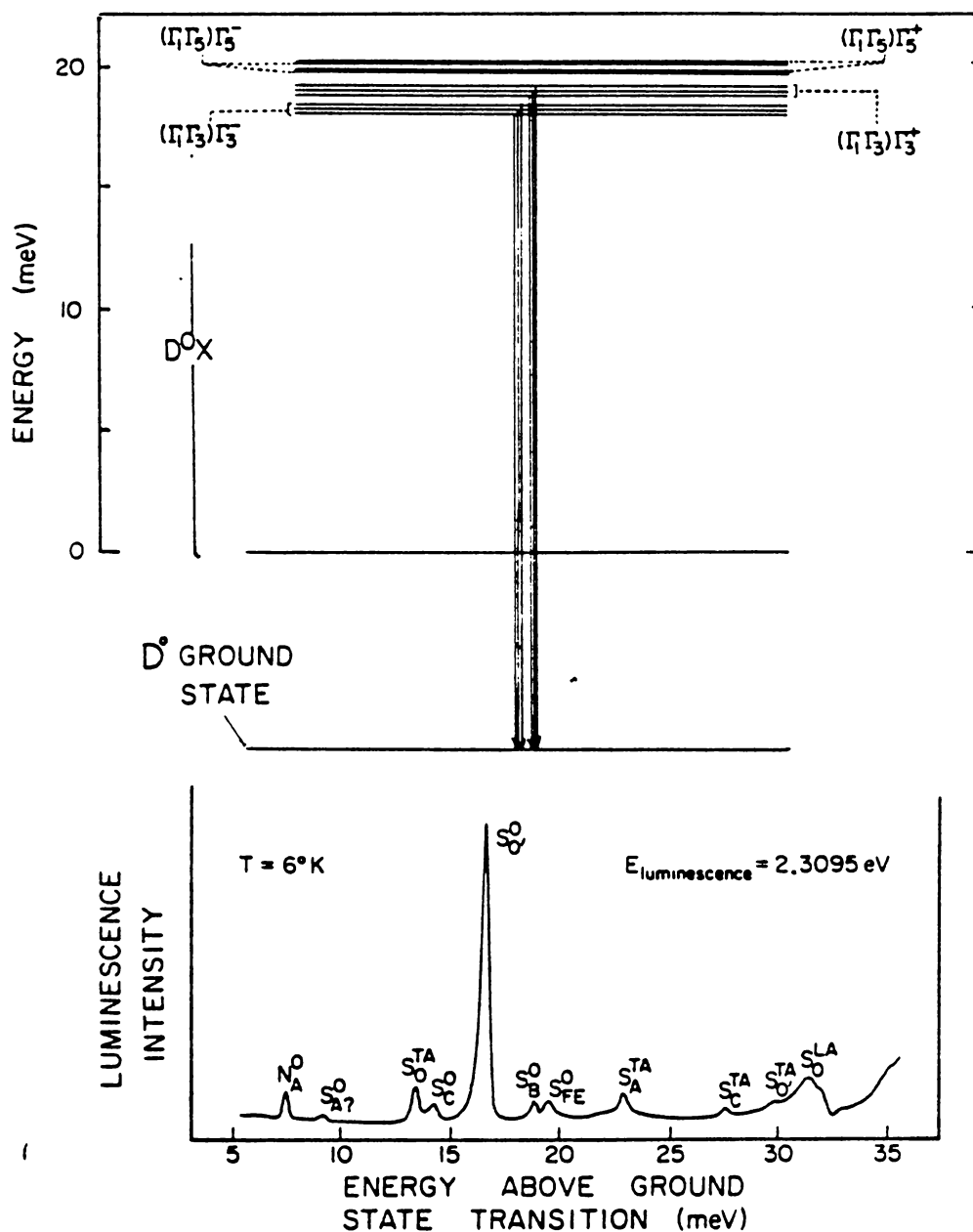


Figure V-8. Theoretical spectrum of optical transitions from the recombination of an electron-hole pair in D^0X for GaP:S, plotted accompanied with the experimental luminescence spectrum. The theoretically predicted transitions are indicated by arrows. The data are taken from Elliott et al (Ref. 12).

spectra obtained by Elliott et al.⁽¹²⁾. We can predict the optical transitions due to the recombination of an electron-hole pair in the D^0X . The theoretically predicted transitions are indicated by the arrows in Fig. V-8, where we have shifted the whole bound exciton spectrum by a correlation energy of about 15 meV, so that the line associated with the ground-to-ground state transition matches the experimental data (the zero of the energy axis). The detailed comparison between theory and experiment is difficult, because the luminescence associated with this set of excited states is rather weak. As shown in the figure, the line marked S_B^0 may correspond to the transition from the $\{\Gamma_1\Gamma_3;\Gamma_8\}$ states of the D^0X to the donor ground state. The line marked S_O^0 , corresponds to the 2s hole excited state as discussed in Chapter 2. The lines marked S_A^0 and S_C^0 cannot be understood from the present calculation.

V. CONCLUSION

We have developed the theory for the fine structure in the excitation spectrum of donor bound excitons for Si, Ge and GaP doped by various impurities. This fine structure is produced mainly by the valley-orbit interaction for the two electrons and the valley-anisotropy splitting due to the electron-hole interaction. This theory allows us to go beyond the shell model and interpret the detailed structure of the spectrum for donor bound excitons observed in Si and Ge doped with various impurities as well as GaP:S. Using the energy eigenvalues calculated in the Hartree-Fock approximation, we obtain the theoretical

excitation spectrum in good agreement with the available experimental data. Therefore, we conclude that the correlation energy has little effect on the energy differences between the low-lying electronic excited states discussed here and the ground state, although it is important in determining the binding energy. The present work has provided a better understanding of the electronic properties and excitons bound to neutral donors in multivalley semiconductors.

APPENDIX A. MUTUAL INTERACTION BETWEEN TWO ELECTRONS IN D^-

In this appendix, we derive the expression for the matrix elements of the mutual interaction between two-electron product states denoted by

$$|m'n'; (\tau_1' \tau_2') \Gamma_e^{\pm} \mu_e\rangle \text{ and } |mn; (\tau_1 \tau_2) \Gamma_e^{\pm} \mu_e\rangle.$$

According to the definition of these states (see Eqs. (13) and (14)) we can write the matrix elements of the mutual interaction as

$$\begin{aligned} & \langle m'n'; (\tau_1' \tau_2') \Gamma_e^{\pm} \mu_e | v(12) | mn; (\tau_1 \tau_2) \Gamma_e^{\pm} \mu_e \rangle \\ & \equiv \sum_{\substack{\mu_1 \mu_2 \\ \mu_1' \mu_2'}} c_{\tau_1' \tau_2'}^{(\mu_1' \mu_2', \Gamma_e)} c_{\tau_1 \tau_2}^{(\mu_1 \mu_2, \Gamma_e)} [\langle m'n', \mu_1' \mu_2' | W | mn, \mu_1 \mu_2 \rangle \\ & \pm \langle m'n', \mu_1' \mu_2' | W | nm, \mu_2 \mu_1 \rangle] f_{mn}^{\tau_1 \tau_2} f_{m'n'}^{\tau_1' \tau_2'} \end{aligned} \quad (A1)$$

with

$$\langle \mu_1' \mu_2' | W | \mu_1 \mu_2 \rangle \equiv \sum_{\substack{\vec{k}_1 \vec{k}_1' \\ \vec{k}_2 \vec{k}_2'}} \beta^{\mu_1'}(\vec{k}_1') \beta^{\mu_2'}(\vec{k}_2') \langle \vec{k}_1' \vec{k}_2' | v | \vec{k}_1 \vec{k}_2 \rangle \beta^{\mu_1}(\vec{k}_1) \beta^{\mu_2}(\vec{k}_2). \quad (A2)$$

In Eq. (A2) the indices mn and $m'n'$ have been dropped for simplicity. Using the Fourier expansion in the reciprocal lattice vector

space for the product of the periodic parts of the Bloch functions

$|\vec{k}_1'\rangle$ and $|\vec{k}_1\rangle$ (or $|\vec{k}_2'\rangle$ and $|\vec{k}_2\rangle$), with coefficients $c(\vec{k}_1, \vec{k}_1'; \vec{G}_1)$ (or $c(\vec{k}_2, \vec{k}_2'; \vec{G}_2)$), we can write the kernel for mutual interaction as

$$\begin{aligned} \langle \vec{k}_1' \vec{k}_2' | v | \vec{k}_1 \vec{k}_2 \rangle &= \sum_{G_1 G_2} \tilde{v}(\vec{G}_1 + \vec{k}_1 \vec{k}_1') c(\vec{k}_1, \vec{k}_1'; \vec{G}_1) c^*(\vec{k}_2', \vec{k}_2; \vec{G}_2) \\ &\cdot \delta(\vec{G} + \vec{k}_1 - \vec{k}_1', \vec{G}_2 \vec{k}_2' - \vec{k}_2) \end{aligned} \quad (A3)$$

Substituting Eq. (5) and Eq. (A3) into Eq. (A2), we obtain

$$\langle \mu_1' \mu_2' | W | \mu_1 \mu_2 \rangle = \sum_{ii'jj'} \alpha_i'(\mu_1') \alpha_j'(\mu_2') \alpha_i(\mu_1) \alpha_j(\mu_2) W(i, i', j, j') \quad (A4)$$

where

$$\begin{aligned} W(i, i', j, j') &\equiv \sum_{G_1 G_2} \sum_{\substack{k_1 k_1' \\ k_2 k_2'}} \beta_i'^*(\vec{k}_1' - \vec{k}_i) \beta_j'^*(\vec{k}_2' - \vec{k}_j) \tilde{v}(\vec{G}_1 + \vec{k}_1 - \vec{k}_1') \\ &\cdot c(\vec{k}_1, \vec{k}_1'; \vec{G}_1) c^*(\vec{k}_2', \vec{k}_2; \vec{G}_2) \delta(\vec{G}_1 + \vec{k}_1 - \vec{k}_1', \vec{G}_2 + \vec{k}_2' - \vec{k}_2) \beta_i(\vec{k}_1 - \vec{k}_i) \beta_j(\vec{k}_2 - \vec{k}_j) \end{aligned} \quad (A5)$$

The R.H.S. of Eq. (A5) can be sorted into three classes:

$$(1) \Delta\vec{k}_1 = \Delta\vec{k}_2 = 0 \quad (2) \Delta\vec{k}_1 = \Delta\vec{k}_2 \neq 0 \quad (3) \Delta\vec{k}_1 \neq \Delta\vec{k}_2$$

$$\text{where} \quad \Delta\vec{k}_1 \equiv \vec{k}_i' - \vec{k}_i \quad \text{and} \quad \Delta\vec{k}_2 \equiv \vec{k}_j' - \vec{k}_j,$$

We will discuss the three classes separately:

$$(1) \quad \Delta \vec{k}_1 = \Delta \vec{k}_2 = 0 \text{ (intra-intra)}$$

Only the terms with $\vec{G}_1 = 0$ and $\vec{G}_2 = 0$ have appreciable contribution. Transforming Eq. (A5) into real space, we readily obtain

$$W(i,i,j,j) = \int d^3r_1 d^3r_2 \beta_i^*(\vec{r}_1) \beta_j^*(\vec{r}_2) v(r_{12}) \beta_i(\vec{r}_1) \beta_j(\vec{r}_2) \quad , \quad (A6)$$

which takes two different values depending on whether the major axes of the ellipsoid charge distributions of two particles are parallel to each other.

We define

$$W(i,i,j,j) = \begin{cases} U_0 & \text{if } \vec{k}_i \parallel \vec{k}_j \\ U_0 - U_1 & \text{if } \vec{k}_i \text{ not parallel to } \vec{k}_j \end{cases} \quad (A7)$$

This case contributes a term to $\langle \mu'_1 \mu'_2 | W | \mu_1 \mu_2 \rangle$ as

$$W_1(\mu'_1 \mu'_2, \mu_1 \mu_2) = U_0 \delta_{\mu_1 \mu'_1} \delta_{\mu_2 \mu'_2} + U_1 G_1(\mu'_1 \mu'_2, \mu_1 \mu_2) \quad (A8)$$

where

$$G_1(\mu'_1 \mu'_2, \mu_1 \mu_2) \equiv -\delta_{\mu_1 \mu'_1} \delta_{\mu_2 \mu'_2} + \sum_{i||j} \alpha_i(\mu'_1) \alpha_j(\mu'_2) \alpha_i(\mu_1) \alpha_j(\mu_2). \quad (A9)$$

The summation is over terms with $\vec{k}_i \parallel \vec{k}_j$ only.

$$2) \quad \Delta \vec{k}_1 = \Delta \vec{k}_2 \neq 0 \quad (\text{inter-inter})$$

We must have either $(\vec{k}_i = \vec{k}_j, \text{ and } \vec{k}_i = \vec{k}_j)$ or $(\vec{k}_i = -\vec{k}_j \text{ and } \vec{k}_i = -\vec{k}_j)$. Only the terms with $\vec{G}_1 = \vec{G}_2$ have appreciable contribution, due to the restriction of the delta function in Eq. (A3). Analogous to the Umklapp renormalization factors introduced for the single-particle potential energy term ⁽¹⁵⁾, we define

$$R(i, i', j, j') \equiv \sum_{\vec{G}} c(\vec{k}_i, \vec{k}_{i'}; \vec{G}) c(\vec{k}_j, \vec{k}_j; \vec{G}) \tilde{v}(\vec{G} + \vec{k}_i - \vec{k}_{i'}) / \tilde{v}(\vec{k}_i - \vec{k}_{i'}) \quad (\text{A10})$$

as the renormalization factors for the mutual interaction term. With the restriction $\Delta \vec{k}_1 = \Delta \vec{k}_2$, it is easy to prove that $c(\vec{k}_j, \vec{k}_j; \vec{G}) = c(\vec{k}_i, \vec{k}_{i'}; \vec{G})$, and Eq. (A10) is simplified to

$$R(i, i') = \sum_{\vec{G}} |c(\vec{k}_i, \vec{k}_{i'}; \vec{G})|^2 \tilde{v}(\vec{G} - \Delta \vec{k}_1) / \tilde{v}(\Delta \vec{k}_1) \quad , \quad (\text{A11})$$

where we have dropped the dependence on j and j' . With the use of the renormalization factors $R(i, i')$ and transforming Eq. (A5) into real space, we readily obtain

$$W(i, i', j, j') = R(i, i') \int d^3r_1 d^3r_2 \beta_{i'}'^* (\vec{r}_1) \beta_i (\vec{r}_1) e^{i\Delta \vec{k}_1 \cdot \vec{r}_1} v(r_{12}) \\ \beta_j'^* (\vec{r}_2) \beta_j (\vec{r}_2) e^{-i\Delta \vec{k}_2 \cdot \vec{r}_2} \quad (\text{A12})$$

Introducing the Fourier transforms for the function $\beta_i'^* (\vec{r}_i) \beta_i (\vec{r}_1)$
 $e^{i\Delta\vec{k}_1 \cdot \vec{r}_1}$ as $I_{i,i}(\vec{q}-\Delta\vec{k}_1)$ and similarly for $\beta_j'^* (\vec{r}_2) \beta_j (\vec{r}_2) e^{-i\Delta\vec{k}_2 \cdot \vec{r}_2}$,
 we can rewrite Eq. (A12) as

$$W(i,i',j,j') = R(i,i') \int \frac{d^3q}{(2\pi)^3} \tilde{v}(\vec{q}) I_{i,i}(\vec{q}-\Delta\vec{k}_1) I_{j,j}^*(\vec{q}-\Delta\vec{k}_1) \quad (A13)$$

The function $I_{i,i}(\vec{q}-\Delta\vec{k}_1) \cdot I_{j,j}^*(\vec{q}-\Delta\vec{k}_1)$ is sharply peaked at $\vec{q} = \Delta\vec{k}_1$,
 and $\tilde{v}(\vec{q})$ is a smooth function there. Therefore, we can write approxi-
 mately

$$W(i,i',j,j') \simeq R(i,i',j,j') \cdot \tilde{v}(\Delta\vec{k}_1) \int \frac{d^3q}{(2\pi)^3} I_{i,i}(\vec{q}) I_{j,j}^*(\vec{q}) \quad (A14)$$

We define

$$W(i,i',j,j') = \begin{cases} U_2 & \text{for longitudinal scattering scheme} \\ U_3 & \text{for transverse scattering scheme} \end{cases}$$

For longitudinal scattering, we must have $\vec{k}_{i'} = -\vec{k}_i$ and $\vec{k}_{j'} = -\vec{k}_j$,
 and the restriction $\Delta\vec{k}_1 = \Delta\vec{k}_2$ requires $\vec{k}_{i'} = -\vec{k}_j$. This case contributes
 a term $U_2 G_2(\mu_1' \mu_2', \mu_1 \mu_2)$ to $W(\mu_1' \mu_2', \mu_1 \mu_2)$,

$$G(\mu_1' \mu_2', \mu_1 \mu_2) \equiv \sum_i \alpha_{-i}(\mu_1') \alpha_i(\mu_2') \alpha_i(\mu_1) \alpha_{-i}(\mu_2) \quad (A15)$$

where $\alpha_{-i}(\mu_1')$ is the component associated with $\vec{k}_i' = -\vec{k}_i$, similarly for $\alpha_{-i}(\mu_2)$. For the transverse scattering, we obtain a contribution $U_3 G_3(\mu_1' \mu_2', \mu_1 \mu_2)$ to $W(\mu_1' \mu_2', \mu_1 \mu_2)$ with

$$G_3(\mu_1' \mu_2', \mu_1 \mu_2) \equiv \sum_{\substack{\text{over all} \\ \text{transverse scattering terms satisfying} \\ \text{the restriction } \Delta \vec{k}_1 = \Delta \vec{k}_2}} \alpha_i(\mu_1') \alpha_j'(\mu_2') \alpha_i(\mu_1) \alpha_j(\mu_2) \quad (A16)$$

$$3) \quad \Delta \vec{k}_1 \neq \Delta \vec{k}_2$$

With the change of variables $\vec{k}_1 \rightarrow \vec{k}_1 - \vec{G}_1$ and $\vec{k}_2 \rightarrow \vec{k}_2 + \vec{G}_2$, Eq. (A5) can be rewritten as

$$W(i, i', j, j') = \sum_{\vec{G}_1 \vec{G}_2} \sum_{\substack{\vec{k}_1 \vec{k}_1' \\ \vec{k}_2 \vec{k}_2'}} \beta_i^{*'}(\vec{k}_1' - \vec{k}_i') \beta_j^{*'}(\vec{k}_2' - \vec{k}_j') \tilde{v}(\vec{k}_1 - \vec{k}_1') \quad (A17)$$

$$\cdot c(\vec{k}_1 - \vec{G}_1, \vec{k}_1'; \vec{G}_1) c^*(\vec{k}_2', \vec{k}_2 + \vec{G}_2; \vec{G}_2) \delta(\vec{k}_1 - \vec{k}_1', \vec{k}_2' - \vec{k}_2) \beta_i(\vec{k}_1 - \vec{G}_1 - \vec{k}_i) \beta_j(\vec{k}_2 - \vec{k}_j + \vec{G}_2)$$

Replacing $c(\vec{k}_1 - \vec{G}_1, \vec{k}_1'; \vec{G}_1)$ and $c^*(\vec{k}_2', \vec{k}_2 + \vec{G}_2; \vec{G}_2)$ by their values at $\vec{k}_1 - \vec{G}_1 = \vec{k}_i, \vec{k}_1' = \vec{k}_i', \vec{k}_2 + \vec{G}_2 = \vec{k}_j$ and $\vec{k}_2' = \vec{k}_j'$, respectively, and transforming Eq. (A17) into real space, we obtain

$$\begin{aligned}
 W(i,i',j,j') &= \sum_{\vec{G}, \vec{G}_2} c(\vec{k}_i, \vec{k}_j, ; \vec{G}_1) c^*(\vec{k}_{j'}, \vec{k}_j; \vec{G}_2) \\
 &\cdot \int d^3r_1 d^3r_2 \beta_{i'}^*(\vec{r}) \beta_i(\vec{r}_1) e^{i(\Delta\vec{k}_1 - \vec{G}_1) \cdot \vec{r}_1} v(r_{12}) \beta_{j'}^*(\vec{r}_2) \beta_j(\vec{r}_2) e^{-i(\Delta\vec{k}_2 - \vec{G}_2) \cdot \vec{r}_2} \\
 &= \sum_{\vec{G}_1 \vec{G}_2} C(\vec{k}_i, \vec{k}_{i'}; \vec{G}) C^*(\vec{k}_{j'}, \vec{k}_j; \vec{G}_2) \int \frac{d^3q}{(2\pi)^3} I_{i',i}(\vec{q} - \Delta\vec{k}_1 - \vec{G}_1) I_{j,j'}^*(\vec{q} - \Delta\vec{k}_2 + \vec{G}_2) \tilde{v}(\vec{q})
 \end{aligned} \tag{A18}$$

where $I_{i',i}(\vec{q})$ and $I_{j,j'}(\vec{q})$ are the Fourier transforms of $\beta_{i'}^*(\vec{r}_1) \times \beta_i(\vec{r}_1)$ and $\beta_{j'}^*(\vec{r}_2) \times \beta_j(\vec{r}_2)$, respectively. Since $I_{i',i}(\vec{q} - \Delta\vec{k}_1 + \vec{G}_1)$ and $I_{j,j'}^*(\vec{q} - \vec{k}_2 + \vec{G}_2)$ are sharply peaked at $\vec{q} = \vec{G}_1 - \Delta\vec{k}_1$ and $\vec{q} = \vec{G}_2 - \Delta\vec{k}_2$, respectively. The integral appearing in the R.H.S. of Eq.(A18) is negligibly small unless the momentum is approximately conserved, i.e.,

$$\vec{G}_1 - \Delta\vec{k}_1 = \vec{G}_2 - \Delta\vec{k}_2 \tag{A19}$$

In Si, Eq. (A19) can be satisfied only for some very special cases. For example, if $\Delta\vec{k}_1 = 0$ and $\Delta\vec{k}_2 = (0,0,2) k_0$, then the term with $\vec{G}_1=0$ and $\vec{G}_2=(0,0,2) \frac{2\pi}{a}$ leads to appreciable contribution to the integral in Eq. (A18). However the coefficient $c^*(\vec{k}_{j'}, \vec{k}_j; \vec{G}_2)$ in these cases happens to be nearly zero (less than 10^{-4}), which renders the net contribution to $W(i,i',j,j')$ negligible.

In Ge, the restriction $\Delta \vec{k}_1 = \Delta \vec{k}_2$ and Eq. (A19) can be satisfied simultaneously only if $\vec{k}_i, \vec{k}_i, \vec{k}_j$, and k_j , are at four different minima. Combining Eq. (A18) and Eq. (A19), and replacing $\tilde{v}(\vec{q})$ by its value at $\vec{q} = \vec{G}_1 - \Delta \vec{k}_1$, we obtain

$$W(i, i', j, j') = \sum_{\vec{G}_1} c(\vec{k}_i, \vec{k}_i, ; \vec{G}_1) c^*(\vec{k}_j, \vec{k}_j, ; \vec{G}_1 - \vec{k}_1 + \vec{k}_2) \tilde{v}(\vec{G}_1 - \vec{k}_1)$$

$$, \int \frac{d^3 q}{(2\pi)^3} I_{ii'}(\vec{q}) I_{jj'}(\vec{q})$$

$$\equiv U_4$$

This class contributes a term $U_4 G_4(\mu_1' \mu_2', \mu_1 \mu_2)$ to $\langle \mu_1' \mu_2' | W | \mu_1 \mu_2 \rangle$ with

$$G_4(\mu_1' \mu_2', \mu_1 \mu_2) \equiv \sum_{i \neq i', j \neq j'} \alpha_i(\mu_1') \alpha_{j'}(\mu_2') \alpha_i(\mu_1) \alpha_j(\mu_2) \quad (A20)$$

Collecting all the contributions to $\langle \mu_1' \mu_2' | W | \mu_1 \mu_2 \rangle$ from various terms, we obtain

$$\langle \mu_1' \mu_2' | W | \mu_1 \mu_2 \rangle = U_0 \delta_{\mu_1 \mu_1'} \delta_{\mu_2 \mu_2'} + \sum_{\lambda=1}^4 U_\lambda G_\lambda(\mu_1' \mu_2', \mu_1 \mu_2) \quad (A21)$$

Substituting this equation into (A1), we obtain the final expression with the indices mn and $m'n'$ written explicitly

$$\begin{aligned}
 & \langle m'n'; (\tau_1' \tau_2') \Gamma_e^{\pm} \mu_e | v(12) | (\tau_1 \tau_2) \Gamma_e^{\pm} \mu_e; mn \rangle \\
 &= f_{mn}^{\tau_1 \tau_2} f_{m'n'}^{\tau_1' \tau_2'} \left[U_0(m'n', mn) \delta_{\tau_1 \tau_1'} \delta_{\tau_2 \tau_2'} + \sum_{\lambda=1}^4 U_{\lambda}(m'n', mn) \right. \\
 & \times G_{\lambda}^{\Gamma_e}(\tau_1' \tau_2', \tau_1 \tau_2) \left. \right] \\
 &+ \text{exchange term} \tag{A22}
 \end{aligned}$$

where

$$\begin{aligned}
 G_{\lambda}^{\Gamma}(\tau_1' \tau_2', \tau_1 \tau_2) \equiv \sum_{\substack{\mu_1 \mu_2 \\ \mu_1' \mu_2'}} C_{\tau_1 \tau_2}^{(\mu_1' \mu_2', \Gamma \mu)} C_{\tau_1' \tau_2'}^{(\mu_1 \mu_2, \Gamma \mu)} \\
 \cdot G_{\lambda}(\mu_1' \mu_2', \mu_1 \mu_2) \quad ; \quad \lambda = 1, 2, 3, 4. \tag{A23}
 \end{aligned}$$

The exchange term is obtained from the direct term by exchanging the roles of the two electrons. The non-vanishing submatrices for the matrices G_{λ}^{Γ} are listed in Table A-1 for Si and Table A-2 for Ge.

TABLE A-1: The electron-electron-coupling matrices for Si; (ij) is the simplified notation for $(\Gamma_i \Gamma_j)$, the state in which the two electrons are transformed according to the representations Γ_i and Γ_j , respectively.

Γ_1^1				Γ_2^1				Γ_3^1							
G_1^1	(11)	(33)	(55)	G_2^1	(11)	(33)	(55)	G_3^1	(11)	(33)	(55)				
(11)	-2/3	$\sqrt{2}/3$	$1/\sqrt{3}$	(11)	1/6	$\sqrt{2}/6$	$-\sqrt{3}/6$	(11)	4/3	$\sqrt{2}/3$	$-2/\sqrt{3}$				
(33)		-1/3	$\sqrt{2}/3$	(33)		1/3	$-1/\sqrt{6}$	(33)		5/3	$-2\sqrt{6}/3$				
(55)			0	(55)			1/2	(55)			2				
Γ_2^2				Γ_3^2				Γ_4^2							
G_1^2	(33)			G_2^2	(33)			G_3^2	(33)						
(33)	-1			(33)	0			(33)	-1						
Γ_3^3				Γ_4^3				Γ_5^3							
G_1^3	(13)	(31)	(33)	(55)	G_2^3	(13)	(31)	(33)	(55)	G_3^3	(13)	(31)	(33)	(55)	
(13)	-2/3	1/3	0	$1/\sqrt{3}$	(13)	1/6	0	0	$-\sqrt{3}/6$	(13)	-2/3	1/3	0	$1/\sqrt{3}$	
(31)		-2/3	0	$1/\sqrt{3}$	(31)		1/6	0	$\sqrt{3}/6$	(31)		-2/3	0	$1/\sqrt{3}$	
(33)			-2/3	$-1/\sqrt{3}$	(33)			1/6	$\sqrt{3}/6$	(33)			1/3	$1/\sqrt{3}$	
(55)				0	(55)				1/2	(55)				-1	
Γ_4^4				Γ_5^4				Γ_6^4							
G_1^4	(35)	(53)	(55)	G_2^4	(35)	(53)	(55)	G_3^4	(35)	(53)	(55)				
(15)	-1	0	0	(35)	0	0	0	(35)	0	1	0				
(53)		-1	0	(53)		0	0	(53)		0	0				
(55)			-1	(55)			0	(55)			-1				
Γ_5^5				Γ_6^5				Γ_7^5							
G_1^5	(15)	(51)	(35)	(53)	(55)	G_2^5	(15)	(51)	(35)	(53)	(55)				
(15)	-2/3	1/3	$\sqrt{2}/3$	$\sqrt{2}/3$	0	(15)	-1/6	1/6	$-\sqrt{2}/6$	$\sqrt{2}/6$	0	(15)	0	$-\sqrt{2}/3$	0
(51)		-2/3	$\sqrt{2}/3$	$\sqrt{2}/3$	0	(51)		-1/6	$\sqrt{2}/6$	$\sqrt{2}/6$	0	(51)	0	$-\sqrt{2}/3$	0
(35)			-1/3	2/3	0	(35)			-1/3	1/3	0	(35)	0	1/3	0
(53)				-1/3	0	(53)				-1/3	0	(53)	0	0	0
(55)					-1	(55)					0	(55)			1

TABLE A-2: The electron-electron coupling matrices for Ge; the notation is the same as used in Table II.

$\begin{array}{c cc} \Gamma_1 \\ G_1 & (11) & (55) \\ \hline (11) & -3/4 & \sqrt{3}/4 \\ (55) & & -1/4 \end{array}$	$\begin{array}{c cc} \Gamma_1 \\ G_3 & (11) & (55) \\ \hline (11) & 7/4 & -5\sqrt{3}/4 \\ (55) & & 13/4 \end{array}$	$\begin{array}{c cc} \Gamma_1 \\ G_4 & (11) & (55) \\ \hline (11) & 3/2 & -\sqrt{3}/2 \\ & & 0 \end{array}$
$\begin{array}{c c} \Gamma_3 \\ G_1 & (55) \\ \hline (55) & -1 \end{array}$	$\begin{array}{c c} \Gamma_3 \\ G_3 & (55) \\ \hline (55) & 1 \end{array}$	$\begin{array}{c c} \Gamma_3 \\ G_4 & (55) \\ \hline (55) & 9/4 \end{array}$
$\begin{array}{c c} \Gamma_4 \\ G_1 & (55) \\ \hline (55) & -1 \end{array}$	$\begin{array}{c c} \Gamma_4 \\ G_3 & (55) \\ \hline (55) & -1 \end{array}$	$\begin{array}{c c} \Gamma_4 \\ G_4 & (55) \\ \hline (55) & 0 \end{array}$
$\begin{array}{c ccc} \Gamma_5 \\ G_1 & (15) & (51) & (55) \\ \hline (15) & -3/4 & 1/4 & \sqrt{2}/4 \\ (51) & & -3/4 & \sqrt{2}/4 \\ (55) & & & -1/2 \end{array}$	$\begin{array}{c ccc} \Gamma_5 \\ G_3 & (15) & (51) & (55) \\ \hline (15) & -1/4 & 3/4 & -\sqrt{2}/4 \\ (51) & & -1/4 & -\sqrt{2}/4 \\ (55) & & & 1/2 \end{array}$	$\begin{array}{c ccc} \Gamma_5 \\ G_4 & (15) & (51) & (55) \\ \hline (15) & -1/2 & -1/2 & 1/\sqrt{2} \\ (51) & & -1/2 & 1/\sqrt{2} \\ (55) & & & -3/2 \end{array}$

APPENDIX B. MATRIX ELEMENTS FOR ELECTRON-HOLE INTERACTION

In this appendix we derive an expression for the matrix elements for the electron-hole interaction in D^0X . The electron states are restricted to s-like (defined in an ellipsoidal coordinate system) orbitals and the hole states restricted to s-like and d-like (in a spherical coordinate system) orbitals. The single-particle basis wave functions for the hole are chosen as eigenstates of the total angular momentum defined as

$$\vec{F} = \vec{J} + \vec{L} \quad ,$$

where $\vec{J}$ is the spin and $\vec{L}$ is the orbital angular momentum of the hole. For the ground state (of Γ_8 symmetry), the s-like and d-like orbitals are the most important ones for expansion. These basis functions are denoted by

$$\phi_p^{\mu_h}(\vec{r}_3) \equiv f_p(r_3) |0, 3/2; 3/2, \mu_h\rangle \quad \text{or} \quad f_p(r_3) |2, 3/2; 3/2, \mu_h\rangle \quad , \quad (B1)$$

where

$$|0, 3/2; 3/2, \mu_h\rangle = Y_{00}(\Omega_3) \chi_{\mu_h} \quad ; \quad \mu_h = \pm 3/2, \pm 1/2 \quad ,$$

$$|2, 3/2; 3/2, \pm 3/2\rangle = \frac{1}{\sqrt{5}} Y_{20}(\Omega_3) \chi_{\pm 3/2} - \sqrt{\frac{2}{5}} (Y_{2\pm 1}(\Omega_3) \chi_{\pm 1/2} - Y_{2\pm 2}(\Omega_3) \chi_{\mp 1/2})$$

and

$$|2, 3/2; 3/2, \pm 1/2\rangle = \frac{-1}{\sqrt{5}} Y_{20}(\Omega_3) \chi_{\pm 1/2} + \sqrt{\frac{2}{5}} (Y_{2\pm 2}(\Omega_3) \chi_{\mp 3/2} + Y_{2\mp 1}(\Omega_3) \chi_{\pm 3/2}) \quad ,$$

with χ_{μ_h} being the spin-3/2 spinor,

Let's now consider the electron-hole interaction with the electron being in a valley labelled by i , with the envelope wave function denoted by $\beta_m^i(\vec{r}_1)$, where the major axis of the ellipsoidal charge distribution is taken to be $\hat{z}_i$. If we choose the quantization axis of the hole $\hat{z}_3$ to be parallel to $\hat{z}_i$, then the potential seen by the hole, defined by

$$V_h^{m'm}(\vec{r}_3) \equiv \int \beta_m^{i*}(\vec{r}_1) \beta_m^i(\vec{r}_1) v(13) d^3r_1 \quad (B2)$$

will not mix its four partners of the Γ_8 representation. Namely, we can write

$$\langle \beta_{m',\phi}^{i,\mu_h'} | v(13) | \beta_{m,\phi}^{i,\mu_h} \rangle = V_{13}(m'p',mp) \delta_{\mu_h,\mu_h'} (-1)^{|\mu_h|+1/2} \quad (B3)$$

$$V_{13}(m'p',mp) = \begin{cases} \int f_{p'}^*(r_3) V_h^{m'm}(\vec{r}_3) f_p(r_3) \frac{d^3r_3}{(4\pi)} , & \text{when } \ell' = \ell \\ \int f_{p'}^*(r_3) V_h^{m'm}(\vec{r}_3) f_p(r_3) Y_{00}^*(\Omega_3) Y_{20}(\Omega_3) d^3r_3/\sqrt{5}, & \text{when } \ell' \neq \ell \end{cases} \quad (B4)$$

with ℓ' and ℓ (restricted to 0 or 2) being the angular momenta associated with p' and p , respectively. Since the electron basis functions $\beta_m^{\mu_1}(\vec{r}_1)$ (defined in Eq. (5)) are linear combinations of the envelope functions $\beta_m^i(\vec{r}_1)$ localized at different valleys and oriented

along different axes $\hat{z}_i$, the electron-hole interaction can be written in general as

$$\langle \beta_{m', \phi_{p'}}^{\mu_1', \mu_h'} | v(13) | \beta_{m, \phi_p}^{\mu_1, \mu_h} \rangle = j(\mu_1, \mu_1'; \mu_h, \mu_h') V_{13}(m'p', mp), \quad (B5)$$

where the coupling coefficients of $j(\mu_1, \mu_1'; \mu_h, \mu_h')$ can be determined by symmetry. To obtain these j -coefficients, we need to know the transformation properties of the matrix elements under the operations in T_d . For simplicity, we drop out the indices $(m'p', mp)$ in Eq. (B5) and denote $V_{13}(m'p', mp)$ as V_{ss}, V_{dd} and V_{sd} , respectively, for the cases $(\ell' = \ell = 0)$, $(\ell' = \ell = 2)$ and $(\ell' \neq \ell)$. If we transform the coordinate frame of the hole by a rotation about the y axis of an angle γ , and then followed by a rotation about the new z -axis of an angle β , the potential $V_h(\vec{r}_3)$ will mix the four partners of the hole state in the following way:

$$\begin{aligned} \langle \phi_{\sigma}^{\mu_h'} | V_h(\vec{r}_3) | \phi_{\sigma}^{\mu_h} \rangle &= V_{\sigma\sigma} \delta_{\mu_h \mu_h'} \quad \text{for } \sigma = s, d, \\ \langle \phi_s^{\pm 1/2} | V_h(\vec{r}_3) | \phi_d^{\pm 3/2} \rangle &= -\sqrt{2} d_{0\pm 1}^{(2)}(\beta) V_{sd} e^{\pm i\gamma}, \\ \langle \phi_s^{\pm 3/2} | V_h(\vec{r}_3) | \phi_d^{\pm 1/2} \rangle &= \sqrt{2} d_{0\mp 1}^{(2)}(\beta) V_{sd} e^{\mp i\gamma}, \\ \langle \phi_s^{\pm 1/2} | V_h(\vec{r}_3) | \phi_d^{\mp 3/2} \rangle &= \sqrt{2} d_{0\mp 2}^{(2)}(\beta) V_{sd} e^{\mp 2i\gamma}, \\ \langle \phi_s^{\mp 3/2} | V_h(\vec{r}_3) | \phi_d^{\pm 1/2} \rangle &= \sqrt{2} d_{0\pm 2}^{(2)}(\beta) V_{sd} e^{\pm 2i\gamma}, \end{aligned} \quad (B6)$$

where the d-matrices are defined in Ref, 33. Substituting Eq. (5), (B2) and (B6) into Eq. (B5), we readily obtain the j-coefficients. For the s-s and d-d terms, we obtain no couplings, i.e.,

$$j(\mu_1, \mu_1'; \mu_h, \mu_h') = \delta_{\mu_1 \mu_1'} \delta_{\mu_h \mu_h'}$$

The coupling occurs for the s-d term, and we list these coupling coefficients $j(\mu_1, \mu_1'; \mu_h, \mu_h')$ in Table B-1.

The basis states for the D^0X are linear combinations of the products of two-electron states and hole states, which transform according to irreducible representations of T_d , i.e.,

$$|mnp; [(\tau_1 \tau_2) \Gamma_e^\pm \Gamma_h] \Gamma^\pm \mu\rangle = \sum_{\mu_e \mu_h} C_{\Gamma_e \Gamma_h}(\mu_e \mu_h, \Gamma \mu) |mn; (\tau_1 \tau_2) \Gamma_e^\pm \mu_e\rangle |\Gamma_h \mu_h; p\rangle \quad (B7)$$

where $|(\tau_1 \tau_2) \Gamma_e^\pm \mu_e; mn\rangle$ is the two-electron product states defined by Eq. (13) and (14), and $|\Gamma_h \mu_h; p\rangle$ is the hole state given by (B1). Therefore the matrix elements for electron-hole interaction are

$$\begin{aligned} & \langle m'n'p'; [(\tau_1' \tau_2') \Gamma_e^\pm \Gamma_h'] \Gamma'^\pm \mu' | V_{13} | mn; [(\tau_1 \tau_2) \Gamma_e^\pm \Gamma_h] \Gamma^\pm \mu \rangle \\ &= \sum_{\mu_e \mu_h} C_{\Gamma_e \Gamma_h}(\mu_e \mu_h, \Gamma \mu) \sum_{\mu_1 \mu_2} C_{\tau_1 \tau_2}(\mu_1 \mu_2, \Gamma_e \mu_e) \sum_{\mu_e' \mu_h'} C_{\Gamma_e' \Gamma_h'}(\mu_e' \mu_h', \Gamma' \mu') \\ & \quad \sum_{\mu_1' \mu_2'} C_{\tau_1' \tau_2'}(\mu_1' \mu_2', \Gamma_e' \mu_e') \cdot \delta_{\tau_2 \tau_2'} \delta_{\mu_2 \mu_2'} \delta_{n'n} j(\mu_1, \mu_1'; \mu_h, \mu_h') V_{13}(m'p', mp) \\ & \quad f_{mn}^{\tau_1 \tau_2} f_{m'n'}^{\tau_1' \tau_2'} + \text{exchange term} \quad , \end{aligned} \quad (B8)$$

TABLE B-1. j-coefficients defined in Eq. (B5) for the coupling between s-like and d-like states of the hole, due to the electron-hole interaction listed for Si and Ge, respectively. The four basis vectors of the Γ_8 -representation for the hole are labelled by $\mu_h = 1/2, 3/2$. For the electron we denote the single basis vector of the Γ_1 -representation by ω , the two basis vectors of the Γ_3 representation by u_1 and u_2 , and the three basis vectors of the Γ_5 -representation by v_1, v_2 and v_3 , respectively, (only non-vanishing coefficients are listed).

Si: (μ_1, μ_1)	(μ_h, μ_h)		Ge: (μ_1, μ_1) / (μ_h, μ_h)					
	$(\pm 3/2, \pm 3/2)$	$(\pm 1/2, \pm 1/2)$	$(\pm 3/2, \pm 1/2)$ $(\pm 1/2, \pm 3/2)$	(ω, μ_1)	$(\pm 1/2, \pm 3/2)$	$(\pm 3/2, \pm 1/2)$	$(\pm 1/2, \pm 3/2)$	$(\pm 3/2, \pm 1/2)$
(ω, u_1)	$1/\sqrt{2}$	$-1/\sqrt{2}$	0	(ω, v_1)	$-i/\sqrt{3}$	$i/\sqrt{3}$	0	0
(ω, u_2)	0	0	$1/\sqrt{2}$	(ω, v_2)	$1/\sqrt{3}$	$1/\sqrt{3}$	0	0
(ω, v_1)	$-1/2\sqrt{3}$	$1/2\sqrt{3}$	$1/2$	(ω, v_3)	0	0	$\pm i/\sqrt{3}$	$\pm i/\sqrt{3}$
(ω, v_2)	$-1/2\sqrt{3}$	$1/2\sqrt{3}$	$-1/2$	(v_1, v_2)	0	0	$\pm i/\sqrt{3}$	$\pm i/\sqrt{3}$
(ω, v_3)	$1/\sqrt{3}$	$-1/\sqrt{3}$	0	(v_3, v_1)	$\pm 1/\sqrt{3}$	$\pm 1/\sqrt{3}$	0	0
(u_1, u_1)	$1/2$	$-1/2$	0	(v_3, v_2)	$-i/\sqrt{3}$	$i/\sqrt{3}$	0	0
(u_2, u_2)	$-1/2$	$1/2$	0					
(u_1, u_2)	0	0	$-1/2$					
(v_1, v_1)	$-1/2$	$1/2$	$\sqrt{3}/2$					
(v_2, v_2)	$-1/2$	$1/2$	$-\sqrt{3}/2$					
(v_3, v_3)	1	1	0					
(u_1, v_1)	$1/2\sqrt{6}$	$-1/2\sqrt{6}$	$-1/2\sqrt{2}$					
(u_1, v_2)	$1/2\sqrt{6}$	$-1/2\sqrt{6}$	$1/2\sqrt{2}$					
(u_1, v_3)	$2/\sqrt{3}$	$-2/\sqrt{3}$	0					
(u_2, v_1)	$-1/2\sqrt{2}$	$1/2\sqrt{2}$	$\sqrt{3}/8$					
(u_2, v_2)	$-1/2\sqrt{2}$	$1/2\sqrt{2}$	$-\sqrt{3}/8$					

where $f_{mn}^{\tau_1\tau_2}$ is given by Eq. (15), and all the C-coefficients can be found in Ref. 10. The exchange term is obtained from the first term by exchanging the roles of the two electrons. If we define an electron-hole coupling matrix for each over-all symmetry Γ , by

$$J^\Gamma([(\tau_1'\tau_2')\Gamma_e'\Gamma_h'],[(\tau_1\tau_2)\Gamma_e\Gamma_h]) \equiv \sum_{\mu_e\mu_h} C_{\Gamma_e\Gamma_h}(\mu_e\mu_h,\Gamma\mu) \sum_{\mu_1\mu_2} C_{\tau_1\tau_2}(\mu_1\mu_2,\Gamma_e\Gamma_e) \cdot \sum_{\mu_e'\mu_h'} C_{\Gamma_e'\Gamma_h'}(\mu_e'\mu_h',\Gamma\mu) \sum_{\mu_1'} C_{\tau_1'\tau_2'}(\mu_1'\mu_2',\Gamma_e'\Gamma_e') j(\mu_1,\mu_1';\mu_h,\mu_h') \quad , \quad (B9)$$

then Eq. (B8) reduces to

$$\begin{aligned} & \langle m'n'p'; [(\tau_1'\tau_2')\Gamma_e'\Gamma_h']\Gamma^\pm\mu | v(13) | mmp; [(\tau_1\tau_2)\Gamma_e\Gamma_h]\Gamma^\pm\mu \rangle \\ &= J^\Gamma([(\tau_1'\tau_2')\Gamma_e'\Gamma_h'],[(\tau_1\tau_2)\Gamma_e\Gamma_h]) V_{13}(m'p',mp) \delta_{\tau_2\tau_2'} \delta_{nn'} f_{mm'}^{\tau_1\tau_1'} f_{nn'}^{\tau_2\tau_2'} \\ & \pm \text{exchange term} \end{aligned} \quad (B10)$$

The electron-hole coupling matrices (J-matrices) are listed in Table B-2 for Si (or GaP) and B-3 for Ge, respectively.

TABLE B-2. Coupling matrices $J[(\tau_1 \tau_2) \Gamma_e \Gamma_8, (\tau_1 \tau_2) \Gamma_e \Gamma_8]$ of the electron-hole interaction $v_{eh}(1,3)$ calculated for Si; the states in various configurations $[(\Gamma_i \Gamma_j) \Gamma_e, \Gamma_8]$ are denoted by the simplified notation $(ij) \Gamma_e^*$.

$J^{\Gamma_6} \begin{array}{c c} & (31) \Gamma_3 \\ \hline (31) \Gamma_3 & -1 \end{array}$	$J^{\Gamma_6} \begin{array}{c c} & (51) \Gamma_5 \\ \hline (51) \Gamma_5 & 1 \end{array}$	$J^{\Gamma_6} \begin{array}{c c} & (53) \Gamma_4 \\ \hline (53) \Gamma_4 & -1 \end{array}$	$J^{\Gamma_6} \begin{array}{c c} & (53) \Gamma_5 \\ \hline (53) \Gamma_5 & 1 \end{array}$	$J^{\Gamma_6} \begin{array}{c c} & (55) \Gamma_3 \\ \hline (55) \Gamma_3 & -1 \end{array}$
$J^{\Gamma_6} \begin{array}{c cc} & (13) \Gamma_3 & (33) \Gamma_3 \\ \hline (13) \Gamma_3 & 0 & 1 \\ (33) \Gamma_3 & 1 & 0 \end{array}$	$J^{\Gamma_6} \begin{array}{c cc} & (55) \Gamma_4 & (55) \Gamma_5 \\ \hline (55) \Gamma_4 & 1/2 & -\sqrt{3}/2 \\ (55) \Gamma_5 & & -1/2 \end{array}$	$J^{\Gamma_6} \begin{array}{c ccc} & (15) \Gamma_5 & (35) \Gamma_5 & (35) \Gamma_4 \\ \hline (15) \Gamma_5 & 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ (35) \Gamma_5 & & 1/2 & -1/2 \\ (35) \Gamma_4 & & & 1/2 \end{array}$		
$J^{\Gamma_7} \begin{array}{c c} & (31) \Gamma_3 \\ \hline (31) \Gamma_3 & 1 \end{array}$	$J^{\Gamma_7} \begin{array}{c c} & (51) \Gamma_5 \\ \hline (51) \Gamma_5 & -1 \end{array}$	$J^{\Gamma_7} \begin{array}{c c} & (53) \Gamma_4 \\ \hline (53) \Gamma_4 & 1 \end{array}$	$J^{\Gamma_7} \begin{array}{c c} & (53) \Gamma_5 \\ \hline (53) \Gamma_5 & -1 \end{array}$	$J^{\Gamma_7} \begin{array}{c c} & (55) \Gamma_3 \\ \hline (55) \Gamma_3 & 1 \end{array}$
$J^{\Gamma_7} \begin{array}{c cc} & (13) \Gamma_3 & (33) \Gamma_3 \\ \hline (13) \Gamma_3 & 0 & -1 \\ (33) \Gamma_3 & & 0 \end{array}$	$J^{\Gamma_7} \begin{array}{c cc} & (55) \Gamma_4 & (55) \Gamma_5 \\ \hline (55) \Gamma_4 & -1/2 & -\sqrt{3}/2 \\ (55) \Gamma_5 & & 1/2 \end{array}$	$J^{\Gamma_7} \begin{array}{c ccc} & (15) \Gamma_5 & (35) \Gamma_5 & (35) \Gamma_4 \\ \hline (15) \Gamma_5 & 0 & -1/\sqrt{2} & 1/\sqrt{2} \\ (35) \Gamma_5 & & -1/2 & -1/2 \\ (35) \Gamma_4 & & & -1/2 \end{array}$		

TABLE B-2 (Continued)

Γ_8	$(11)\Gamma_1$	$(31)\Gamma_3$	Γ_8 J^8	$(55)\Gamma_1$	$(55)\Gamma_3$	Γ_8 J^8	$(51)\Gamma_5$	$[(51)\Gamma_5]'$
$(11)\Gamma_1$	0	1	$(55)\Gamma_1$	0	1	$(51)\Gamma_5$	4/5	-3/5
$(31)\Gamma_3$		0	$(55)\Gamma_3$		0	$[(51)\Gamma_5]'$		-4/5

Γ_8	$(53)\Gamma_5$	$[(53)\Gamma_5]'$	Γ_8 J^8	$(53)\Gamma_4$	$[(53)\Gamma_4]'$	Γ_8 J^8	$(13)\Gamma_3$	$(33)\Gamma_1$	$(33)\Gamma_3$
$(53)\Gamma_5$	4/5	-3/5	$(53)\Gamma_4$	4/5	-3/5	$(13)\Gamma_3$	0	$1/\sqrt{2}$	0
$[(53)\Gamma_5]'$		-4/5	$[(53)\Gamma_4]'$		-4/5	$(33)\Gamma_1$		0	-1/2
						$(33)\Gamma_3$			0

Γ_8	$(15)\Gamma_5$	$[(15)\Gamma_5]'$	$(35)\Gamma_5$	$[(35)\Gamma_5]'$	$(35)\Gamma_4$	$[(35)\Gamma_4]'$	Γ_8 J^8	$(55)\Gamma_5$	$[(55)\Gamma_5]'$	$(55)\Gamma_4$	$[(55)\Gamma_4]'$
$(15)\Gamma_5$	0	0	$4/5\sqrt{2}$	$-3/5\sqrt{2}$	0	$1/\sqrt{2}$	$(55)\Gamma_5$	-2/5	$3/10$	$\sqrt{3}/2$	0
$[(15)\Gamma_5]'$		0	$-3/5\sqrt{2}$	$-4/5\sqrt{2}$	$-1/\sqrt{2}$	0	$[(55)\Gamma_5]'$		2/5	0	$-\sqrt{3}/2$
$(35)\Gamma_5$			2/5	-3/10	0	-1/2	$(55)\Gamma_4$			2/5	3/10
$[(35)\Gamma_5]'$				-2/5	1/2	0	$[(55)\Gamma_4]'$				-2/5
$(35)\Gamma_4$					-2/5	3/10					
$[(35)\Gamma_4]'$						2/5					

* For $\Gamma_e = \Gamma_4$ or Γ_5 , the product $\Gamma_e \times \Gamma_8$ includes two Γ_8 representations; the two corresponding product states for arbitrary electron configurations $[(ij)\Gamma_e \Gamma_8]$ Γ_8 and $[(ij)\Gamma_e \Gamma_8]'$ are denoted by $(ij)\Gamma_e$ and $[(ij)\Gamma_e]'$, respectively.

TABLE B-3. Coupling matrices of the electron-hole interaction $v_{eh}(1,3)$ calculated for Ge; all notations are the same as in Table B-2. The J^{Γ_7} matrices are omitted, because they are the same as the J^{Γ_6} matrices.

J^{Γ_6}	$(51)\Gamma_5$
$(51)\Gamma_5$	1

J^{Γ_6}	$(15)\Gamma_5$	$(55)\Gamma_5$	$(55)\Gamma_3$	$(55)\Gamma_4$
$(15)\Gamma_5$	0	$1/\sqrt{2}$	$1/\sqrt{3}$	$1/\sqrt{6}$
$(55)\Gamma_5$		$1/2$	$-1/\sqrt{6}$	$-1/2\sqrt{3}$
$(55)\Gamma_3$			0	$1/\sqrt{2}$
$(55)\Gamma_4$				$-1/2$

J^{Γ_8}	$(11)\Gamma_1$	$(51)\Gamma_5$	$[(51)\Gamma_5]'$
$(11)\Gamma_1$	0	$-1/\sqrt{5}$	$2/\sqrt{5}$
$(51)\Gamma_5$		$-4/5$	$-2/5$
$[(51)\Gamma_5]'$			$-1/5$

J^{Γ_8}	$(55)\Gamma_1$	$(55)\Gamma_3$	$(55)\Gamma_4$	$[(55)\Gamma_4]'$	$(55)\Gamma_5$	$[(55)\Gamma_5]'$	$(15)\Gamma_5$	$[(15)\Gamma_5]'$
$(55)\Gamma_1$	0	0	0	0	$-\sqrt{2}/15$	$2\sqrt{2}/\sqrt{15}$	$-1/\sqrt{15}$	$2/\sqrt{15}$
$(55)\Gamma_3$		0	$\sqrt{2}/\sqrt{5}$	$1/\sqrt{10}$	$-\sqrt{2}/\sqrt{15}$	$-1/\sqrt{30}$	$2/\sqrt{15}$	$1/\sqrt{15}$
$(55)\Gamma_4$			$2/5$	$1/5$	$\sqrt{3}/5$	$-1/5\sqrt{3}$	$-\sqrt{6}/5$	$\sqrt{2}/5\sqrt{3}$
$[(55)\Gamma_4]'$				$1/10$	$-1/5\sqrt{3}$	$3\sqrt{3}/10$	$\sqrt{2}/5\sqrt{3}$	$-3\sqrt{6}/10$
$(55)\Gamma_5$					$-2/5$	$-1/5$	$-2\sqrt{2}/5$	$-\sqrt{2}/5$
$[(55)\Gamma_5]'$						$-1/10$	$-\sqrt{2}/5$	$-\sqrt{2}/10$
$(15)\Gamma_5$							0	0
$[(15)\Gamma_5]'$								0

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9. Here a "configuration" is labelled by $\{\Gamma_i \Gamma_j; \Gamma_8\}$, where Γ_i and Γ_j are the irreducible representations of T_d point group associated with the single-particle states of the two electrons and Γ_8 that associated with the hole.
10. Throughout this chapter we will label the irreducible representations using the notation given in G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-two Point Groups (MIT Press, Cambridge, Mass. 1963) p. 88 ff.

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CHAPTER 6
THEORY OF BOUND MULTIEXCITON COMPLEXES
IN MULTIVALLEY SEMICONDUCTORS

I. INTRODUCTION

In the last chapter, we have studied the excitation spectra of donor bound excitons in multivalley semiconductors. In this chapter, we extend our theory to bound multiexciton complexes (BMEC) for donors in multivalley semiconductors. In these systems, a number of electron-hole pairs (EHP) are bound to a neutral impurity. Photoluminescence resulting from the recombination of an EHP in BMEC's typically yields a series of sharp lines lying at the long wavelength side of the associated BE luminescence line.⁽¹⁾ These spectra were first reported by Kaminski et al⁽²⁾ and later by several authors⁽³⁾. Some theoretical speculations have been put forward to explain these experimental spectra^(4,5). Kirczenow⁽⁵⁾ has speculated that the characteristics of these states for donors can be understood by assigning electrons to single-particle electron states for neutral donors, the so-called shell model. This model accounts for all the available spectral information⁽³⁾. Local density functional formalism calculation⁽⁶⁾ for a model semiconductor have indicated the existence of a shell structure. However, this model is idealized to the extent that detailed comparison between theory and experiment cannot be carried out to check the validity of this conclusion.

The calculation performed in the last chapter yields results for the energy separations between the low-lying one-electron excited states and the ground state of the D^0X in Si and Ge in good agreement with the experimental data. This lends support to the interpretation of the gross features of the spectra in terms of the shell model⁽⁵⁾.

In this chapter, we present a theoretical calculation for the excitation spectra of BMEC's associated with donors in Si and Ge including the multivalley character of the conduction band. Our theoretical calculation provides a better understanding of these interesting many-body systems in semiconductors. We find that the excitation energy for one Γ_1 symmetry electron being excited into a state of either Γ_3 or Γ_5 symmetry in BMEC's is approximately independent of the number of EHP. This condition holds for most donors in Si and Ge. Our results for the excitation energies of BMEC's associated with donors in Si are in good agreement with the experimental data. For donors in Ge, only the optical transitions from the ground state of the $m = 2$ BMEC to the excited states of the bound exciton are available. Hence, our theoretical calculation for the excited states of BMEC's associated with donors in Ge cannot be compared with the experimental data but may serve as a guidance for later experimental work.

This chapter is organized in the following way. In Section II, we present a general theory for BMEC's in semiconductors. In Section III, we discuss our calculational method for the BMEC's associated with donors in Si and Ge. In Section IV, we discuss our theoretical results and compare them with the available experimental data. Finally, a conclusion is presented in Section V.

II. GENERAL THEORY

In this section, we discuss the general theory for BMECs in semiconductors. For definiteness, we will treat BMECs associated with donors. This discussion may be applied to BMECs associated with acceptors as well. For BMECs associated with donors, denoted by D^0X_m (where m is the number of EHP's), the effective mass Hamiltonian⁽⁷⁾ can be written as

$$H_{D^0X_m} = \sum_{i=1}^{m+1} h_e(\vec{r}_i) + \sum_{j=1}^m h_h(\vec{s}_j) + \sum_{i<i'}^{m+1} v_{ee}(i, i') + \sum_{j<j'}^m v_{hh}(j, j') - \sum_{i=1}^{m+1} \sum_{j=1}^m v_{eh}(i, j) \quad (1)$$

where h_e and h_h represent the single-particle Hamiltonian for an electron and a hole, respectively, interacting with the donor; v_{ee} , v_{hh} and v_{eh} represent the electron-electron, hole-hole and electron-hole interactions, respectively. We have used the indices i (or i') to label the $(m+1)$ electrons and j (or j') to label the m holes. We use $\vec{r}$ to represent the spatial coordinate of an electron and $\vec{s}$ to represent both the spatial coordinate and spin of a hole. This Hamiltonian is invariant under the point group T_d . Therefore, the exact eigenfunctions of $H_{D^0X_m}$ should transform according to the irreducible representations (labelled Γ) of T_d , i.e.,

$$H_{D^0\chi_m} \psi^{\Gamma\mu}(\{\vec{r}_i\}\chi_j, \{\vec{s}_j\}) = E^{\Gamma} \psi^{\Gamma\mu}(\{\vec{r}_i\}\chi_i, \{\vec{s}_j\}) \quad , \quad (2)$$

where $\psi^{\Gamma\mu}$ is an eigenfunction of $H_{D^0\chi_m}$ which transforms like a basis vector (labelled μ) of the representation Γ . E^{Γ} is the associated eigenvalue. χ_i is the spinor associated with the i^{th} electron. To solve Eq. (2), one can expand $\psi^{\Gamma\mu}$ on a complete set of basis wave functions with symmetry $\Gamma\mu$.

$$\psi^{\Gamma\mu}(\{\vec{r}_i\}\chi_i, \{\vec{s}_j\}) = \sum_{\alpha n} D_{\alpha n}^{\Gamma\mu} \beta_{\alpha n}^{\Gamma\mu}(\{\vec{r}_i\}\chi_i, \{\vec{s}_j\}) \quad . \quad (3)$$

It is customary to choose $\beta_{\alpha n}^{\Gamma\mu}$ as a linear combination of the Hartree-Fock (HF) solutions associated with the configuration αn , where α labels the "crystalline configuration", $\{\Gamma_i, i=1, \dots, m+1; \Gamma_j, j=1, \dots, m\}$ ⁽⁸⁾ and n labels the "atomic configuration", $\{n_i, i=1, \dots, m+1; n_j=1, \dots, m\}$. In analogy to atomic physics, n_i (or n_j) denotes the orbital symmetry (s, p, d, ...) and the principal quantum number (1, 2, 3, ...); Γ_i (or Γ_j) denotes the crystalline symmetry $\Gamma_1, \Gamma_3, \Gamma_5 \dots$ (or $\Gamma_8, \Gamma_6, \Gamma_7, \dots$). Then

$$\begin{aligned} \beta_{\alpha n}^{\Gamma\mu}(\{\vec{r}_i\}\chi_i, \{\vec{s}_j\}) = & \sum_{\substack{\{\mu_i\chi_i, i=1, \dots, m+1\} \\ \{\mu_j, j=1, \dots, m\}}} C(\Gamma\mu | \{\Gamma_i\mu_i\chi_i, \Gamma_j\mu_j\}) A\left(\prod_{i=1}^{m+1} \phi_{n_i}^{\Gamma_i\mu_i}(\vec{r}_i)\chi_i\right) \\ & \times A\left(\prod_{j=1}^m \phi_{n_j}^{\Gamma_j\mu_j}(\vec{s}_j)\right), \end{aligned} \quad (4)$$

where $\phi_{n_i}^{\Gamma_i\mu_i}(\vec{r}_i)$ and $\phi_{n_j}^{\Gamma_j\mu_j}(\vec{s}_j)$ are the Hartree-Fock single-particle solutions with symmetry $(\Gamma_i\mu_i)$ and $(\Gamma_j\mu_j)$ for the electron and hole, respectively. $C(\Gamma\mu | \{\Gamma_i\mu_i\chi_i, \Gamma_j\mu_j\})$ are the coupling coefficients (including spinors) which can be determined by group theory. The symbol A stands for the operation "taking a Slater determinant". The hole spinors χ_j have been absorbed into the double group representations Γ_j . We treat the electrons and holes as nonidentical particles, since the electron-hole exchange is usually negligible. Substituting Eq. (3) into Eq. (2), we readily obtain

$${}_{\alpha' n'}^{\Sigma,} \langle \beta_{\alpha n}^{\Gamma\mu} | H_{D^0\chi_m} | \beta_{\alpha' n'}^{\Gamma\mu} \rangle \cdot D_{\alpha' n'}^{\Gamma\mu} = E^{\Gamma} D_{\alpha n}^{\Gamma\mu}. \quad (5)$$

In Eq. (5), the matrix $\langle \beta_{\alpha n}^{\Gamma\mu} | H_{D^0\chi_m} | \beta_{\alpha' n'}^{\Gamma\mu} \rangle$ is usually referred to as the "configuration interaction" (C-I) matrix. The standard procedure

of solving Eq. (2) is to solve the Hartree-Fock equations for $\phi_{n_i}^{\Gamma_i \mu_i}$ and $\phi_{n_j}^{\Gamma_j \mu_j}$, and then diagonalize the C-I matrix to find $D_{\alpha n}^{\Gamma \mu}$ and the eigenvalues E^Γ . In practice, the C-I calculation is unmanageable when the number of particles becomes large. Eq. (5) will be greatly simplified, if the coupling of states belonging to different crystalline configurations (labelled by α) can be neglected, i.e.,

$$\langle \beta_{\alpha}^{\Gamma \mu} | H_{D^0 X_m} | \beta_{\alpha', n'}^{\Gamma \mu} \rangle = \delta_{\alpha \alpha'} \langle \beta_{\alpha n}^{\Gamma \mu} | H_{D^0 X_m} | \beta_{\alpha', n'}^{\Gamma \mu} \rangle \quad (6)$$

Eq. (6) is valid, provided

$$|\langle \beta_{\alpha n}^{\Gamma \mu} | H_{D^0 X_m} | \beta_{\alpha', n'}^{\Gamma \mu} \rangle| \ll |E_{\alpha}^{\Gamma} - E_{\alpha'}^{\Gamma}| \quad , \quad (7)$$

for $\alpha \neq \alpha'$, where E_{α}^{Γ} and $E_{\alpha'}^{\Gamma}$ are the energy expectation values of

$H_{D^0 X_m}$ in the states of interest. In this chapter, we are interested

in the states containing mainly the lowest-lying HF solutions ($\beta_{\alpha 0}^{\Gamma \mu}$)

for low-lying crystalline configurations (α), where we labelled the lowest-lying atomic configuration by $n=0$.

It is conceivable that

$$|\langle \beta_{\alpha n}^{\Gamma \mu} | H_{D^0 X_m} | \beta_{\alpha', n'}^{\Gamma \mu} \rangle| \ll |\langle \beta_{\alpha 0}^{\Gamma \mu} | H_{D^0 X_m} | \beta_{\alpha', 0}^{\Gamma \mu} \rangle| \quad (8)$$

for either $n > 0$ or $n' > 0$,

since these couplings are determined by the inter-particle interactions, which are larger for states more localized in space and the states associated with the lowest-lying atomic configuration (labelled by $n=0$) are much more localized in space than the high-lying states ($n>0$). The criterion (Eq. (7)) for Eq. (6) to be valid then reduces to

$$|\langle \beta_{\alpha 0}^{\Gamma \mu} | H_{D^0 X_m} | \beta_{\alpha' 0}^{\Gamma \mu} \rangle| \ll |E_{\alpha}^{\Gamma} - E_{\alpha'}^{\Gamma}| \quad (9)$$

for $\alpha \neq \alpha'$.

The matrix element $\langle \beta_{\alpha 0}^{\Gamma \mu} | H_{D^0 X_m} | \beta_{\alpha' 0}^{\Gamma \mu} \rangle$ ($\alpha \neq \alpha'$) can be written as the sum of the matrix elements for the electron-electron interactions, electron-hole interactions and hole-hole interactions. As discussed in the previous chapter, both the electron-electron and electron-hole couplings between the lowest-lying states associated with different crystalline configurations are of the same order of magnitude as the fine structure splittings ($\lesssim 0.5$ meV for Si and $\lesssim 0.1$ meV for Ge). It will be shown in Section III that this argument also holds for the hole-hole coupling. The fine structure splittings due to the hole-hole interaction is similar to the splittings of the low-lying states of the acceptor bound exciton through the "j-j coupling" scheme. In the $D^0 X_m$ system, however, all the holes are loosely bound, and these fine structure splittings will be much smaller than for the acceptor bound exciton.

When these coupling terms are neglected, Eq. (5) can be re-written for each crystalline configuration α and overall symmetry Γ_μ as

$$\sum_{n'} \langle \beta_{\alpha n}^{\Gamma_\mu} | H_{D^0 X_m} | \beta_{\alpha n'}^{\Gamma_\mu} \rangle \cdot D_{\alpha n'}^{\Gamma_\mu} = E_\alpha^\Gamma D_{\alpha n}^{\Gamma_\mu} \quad (10)$$

From Eq. (10), it is observed that the energy spectra of the BMEC's (labelled by E_α^Γ) can be described approximately by assigning electrons and holes to various configurations (labelled by α). This approximation has been used in the shell model to interpret the experimental data for the BMEC's observed in Si and Ge. In the shell model, it is further assumed that the ordering of the energy levels associated with various crystalline configurations is determined by the single-particle states contained within the crystalline configurations. It is not clear whether or not this assumption holds unless Eq. (10) is solved for various crystalline configurations. It is conceivable that the correlation energy obtained by solving Eq. (10) will be approximately independent of the labelling α for the states close to each other in energy. Therefore the ordering of the states containing mainly lowest-lying HF solutions (labelled by $n=0$) is approximately determined by the energy expectation values for the associated Hartree-Fock solutions, i.e., $\langle \beta_{\alpha 0}^{\Gamma_\mu} | H_{D^0 X_m} | \beta_{\alpha 0}^{\Gamma_\mu} \rangle$. For our purpose here (finding the energy differences between these states and the ground state), we only solve the Hartree-Fock equations for the energies

$\langle \beta_{\alpha 0}^{\Gamma \mu} | H_{D^0 \chi_m} | \beta_{\alpha 0}^{\Gamma \mu} \rangle$. For BMEC's with the number of EHP's (m) less than five, all the electrons and holes can be assigned to states of different spin or crystalline symmetries. For the states of interest, all the four holes should occupy the Γ_8 representation. In this case, if we neglect the exchange interaction between electrons of the same spin but different crystalline symmetries and that between holes (which again yields the fine structure splittings of the same size as that produced by the other coupling schemes), then the problem of solving the Hartree-Fock equations reduces to that of solving the Hartree self-consistent equations. In the next section, we describe the calculation method used to solve the self-consistent Hartree equations for BMEC's associated with donors in Si and Ge.

III. CALCULATION METHOD

To obtain the self-consistent Hartree solutions, we expand each of the single-particle wavefunctions ($\phi^{\Gamma_i \mu_i}(\vec{r}_i)$ or $\phi^{\Gamma_i \mu_j}(\vec{s}_j)$) on a set of basis functions, denoted by $\beta_{b_i}^{\mu_i}(\vec{r}_i)$ and $\beta_{b_j}^{\mu_j}(\vec{s}_j)$ for the electron and hole, respectively ,

$$\phi_o^{\Gamma_i \mu_i}(\vec{r}_i) = \sum_{b_i} C_{\Gamma_i}(b_i) \beta_{b_i}^{\mu_i}(\vec{r}_i) ,$$

and

(11)

$$\phi_o^{\Gamma_8 \mu_j}(\vec{s}_j) = \sum_{b_j} C_{\Gamma_8}(b_j) \beta_{b_j}^{\mu_j}(\vec{s}_j) .$$

For electrons, the basis functions are selected to be linear combinations of seven ellipsoidal Slater-type orbitals (ESTO) of the form

$$\beta_{b_n}^{\mu}(\vec{r}) = \sum_j^N \alpha_j(\mu) e^{i\vec{k}_j \cdot \vec{r}} e^{-b_n \sqrt{x^2+y^2+z^2}/\zeta^2} \quad (12)$$

where $\alpha_j(\mu)$ are proper coefficients chosen to make this basis function transform as a basis vector (labelled by μ) associated with an irreducible representation of the group T_d ⁽³⁾. The $\vec{k}_j$ are the positions of the N equivalent conduction band minima. ζ is the eccentricity factor determined by minimizing the energy expectation value of the donor Hamiltonian in the state $\beta_{b_n}^{\mu}(\vec{r})$, in which the exponent b is also allowed to vary. We find that the value of ζ are 0.57 and 0.355 for Si and Ge, respectively, and they are approximately the same for the Γ_1 , Γ_3 and Γ_5 states. The exponents are chosen to be

$$b_n = b_0/z_n; n = 1, \dots, 7$$

with

$$b_0 = 2 \text{ bohr}^{-1} \text{ for Si and } 4 \text{ bohr}^{-1} \text{ for Ge;}$$

$$z_n = (1, 2, 4, 8, 16, 1/2, 1/4) \text{ for Si and Ge} \quad , \quad (13)$$

For the holes, seven s-like and seven d-like Slater-type orbitals (STO) are used to account for the warping of the valence band. Linear combinations of the products of these STO's and the $j=3/2$ spinors, which

transform as basis vectors associated with the Γ_8 -representation of T_d are constructed to form the basis wavefunctions for the hole ⁽⁹⁾, viz.

$$\beta_{b_n}^\mu = \begin{cases} e^{-b_n r} |\ell=0, j=3/2; F=3/2, F_z=\mu\rangle & \text{for } \ell=0 \\ re^{-b_n r} |\ell=2, j=3/2; F=3/2, F_z=\mu\rangle & \text{for } \ell=2 \end{cases}, \quad (14)$$

where $\vec{F} \equiv \vec{\ell} + \vec{j}$; $b_n = C_0/Z_n$, $n=1, \dots, 7$ with $C_0 = 0.5 \text{ bohr}^{-1}$ and Z_n 's given by Eq. (13). States with $F \neq 3/2$ are not included, because they are not directly coupled to the s-like orbitals. The single-particle Hamiltonian seen by a given electron (say, $i=1$) due to the average charge distribution of other particles is

$$H_e(\vec{r}_1) \equiv h_e(\vec{r}_1) + \sum_{i=2}^{m+1} \int |\phi_o^{\Gamma_i \mu_i}(\vec{r}_i)|^2 v_{ee}(1,i) d^3 r_i \\ - \sum_{j=1}^m \int |\phi_o^{\Gamma_j \mu_j}(\vec{s}_j)|^2 v_{eh}(1,j) d^3 s_j, \quad (15)$$

where h_e is the donor Hamiltonian and v is the mutual Coulomb interaction. Similarly, the Hamiltonian seen by a given hole (say, $j=1$) is

$$H_h(\vec{s}_1) \equiv h_h(\vec{s}_1) - \sum_{i=1}^{m+1} \int |\phi_o^{\Gamma_i \mu_i}(\vec{r}_i)|^2 v_{eh}(1,i) d^3 r_i \\ + \sum_{j=2}^m \int |\phi_o^{\Gamma_j \mu_j}(\vec{s}_j)|^2 v_{hh}(1,j) d^3 s_j. \quad (16)$$

To obtain the Hartree-Fock solution for each configuration, we first set up the Hamiltonian matrix for one particle H_e or H_h with the remaining single-particle wavefunctions fixed by an initial guess. This matrix is then diagonalized to obtain an improved solution for the coefficients $C_{\Gamma_i}(b_i)$ and $C_{\Gamma_8}(b_j)$. This process is repeated for each particle and the whole procedure is then iterated until a self-consistent solution is obtained. The matrix elements for H_e are the sum of the matrix elements for a donor Hamiltonian, h_e , electron-electron interaction and electron-hole interaction. The matrix elements for H_h are the sum of the matrix elements for a hole Hamiltonian, h_h , electron-hole interaction and hole-hole interaction. All these matrix elements except the hole-hole interaction term have been discussed in the previous chapters, and are briefly reviewed here.

For the donor Hamiltonian, h_e , we include the intra- and inter-valley terms for both the kinetic and potential energies as well as the effect of the short-range core potential. The short-range core potential is approximated by a contact potential (i.e., $J_\lambda \delta(\vec{r})$) with strength parameters J_λ (where $\lambda = 1, 2, 3$ for intravalley, inter-transverse and interlongitudinal scattering terms, respectively) determined semi-empirically. Since we only include the s-like ESTO's, the energy eigenvalues obtained by diagonalizing h_e on this basis set are slightly higher (about 1%) than the exact eigenvalues of h_e . For our purpose here, we readjust the parameters J_λ slightly to fit the energies of the lowest-lying states of h_e associated with various

symmetries (Γ_1, Γ_3 and Γ_5) (in the present basis set) to the experimental results. For the hole Hamiltonian h_h , we neglect the mixing with the split-off band. This is a valid approximation, since the orbit energy of the hole (the lowest eigenvalue of H_h) is small compared to the separation between the top of the valence band and the split-off band. For the electron-electron interaction, the matrix elements can be written as

$$\langle \mu_1 \mu_2 | v_{ee}(1,2) | \mu'_1 \mu'_2 \rangle = U_0 \delta_{\mu_1 \mu'_1} \delta_{\mu_2 \mu'_2} + \sum_{\lambda=1}^4 U_{\lambda} G_{\lambda}(\mu_1 \mu_2, \mu'_1 \mu'_2)$$

where $\mu_1(\mu'_1)$ and $\mu_2(\mu'_2)$ denote the single-particle symmetries of the two electrons (labelled by 1 and 2), respectively. U_0 represents the intravalley mutual interaction between two electrons with major axes of their ellipsoidal charge distributions along the same axis. U_{λ} ($\lambda = 1, 2, 3, 4$) are terms which lead to splittings within a given crystalline configuration and couple states of different crystalline configurations but same overall symmetry. G_{λ} ($\lambda = 1, \dots, 4$) are the electron-electron coupling matrices defined in Chapter 5. In the present calculation, the terms involving U_{λ} ($\lambda = 1, 2, 3, 4$) are neglected. For the electron-hole interaction, the matrix elements can be written as

$$\begin{aligned} \langle \mu_e \mu_h | v_{eh} | \mu'_e \mu'_h \rangle &= (V_{ss} + V_{dd}) \delta_{\mu_e \mu'_e} \delta_{\mu_h \mu'_h} \\ &+ V_{sd} j(\mu_e \mu'_e, \mu_h \mu'_h) \end{aligned} \quad (17)$$

where μ_e (μ_e') and μ_h (μ_h') denote the single-particle symmetries of the electron and hole, respectively. V_{ss} , V_{dd} and V_{sd} represent the mutual interactions between the ellipsoidal charge distribution of the electron and the charge distribution of the hole. V_{ss} and V_{dd} represent the coupling between two s-like and two d-like hole states, respectively; V_{sd} represents the coupling between one s-like and one d-like hole state. j is the electron-hole coupling matrix defined in Chapter 5. In the present calculation, the electron-hole coupling term (involving V_{sd}) is neglected.

The hole-hole interaction has not been treated previously and is discussed here in more detail. In Appendix A, we derive the hole-hole interaction matrix elements between the two-hole states denoted by $|\mu_1\mu_2\rangle$ and $|\mu_1'\mu_2'\rangle$, with μ_1 (μ_1') and μ_2 (μ_2') labelling the basis vectors of the Γ_8 representation for the two holes. It is shown in this appendix that the off-diagonal terms (with $\mu_1' \neq \mu_1$ or $\mu_2' \neq \mu_2$) are two orders of magnitude smaller than the diagonal term (with $\mu_1' = \mu_1$ and $\mu_2' = \mu_2$). Therefore, the mixing of hole states through the off-diagonal term (hole-hole coupling) can be neglected. Neglecting these off-diagonal terms, we can write the matrix elements for the hole-hole interaction as (see Appendix A for derivation)

$$\langle \mu_1 \mu_2 | v_{hh} | \mu_1 \mu_2 \rangle = \begin{cases} 2 \int f_{b_1}(r_1) f_{b_1'}(r_1) \frac{1}{r_>} f_{b_2}(r_2) f_{b_2'}(r_2) r_1^2 r_2^2 dr_1 dr_2, & \text{for } \ell_1 = \ell_1' \text{ and } \ell_2 = \ell_2' \\ \\ \frac{2}{25} \int f_{b_1}(r_1) f_{b_1'}(r_1) \frac{r_<^2}{r_>} f_{b_2}(r_2) f_{b_2'}(r_2) r_1^2 r_2^2 dr_1 dr_2, & \text{for } \ell_1 \neq \ell_1' \text{ and } \ell_2 \neq \ell_2' \\ \\ 0 & \text{otherwise} \end{cases} \quad (18)$$

where $f_{b_1}(f_{b_1'})$ and $f_{b_2}(f_{b_2'})$ are the radial parts of the basis functions ($\beta_{b_i}^{\mu_i}$'s) given by Eq. (14); $\ell_1(\ell_1')$ and $\ell_2(\ell_2')$ denote the angular momenta associated with the states $\beta_{b_1}^{\mu_1}(\beta_{b_1'}^{\mu_1'})$ and $\beta_{b_2}^{\mu_2}(\beta_{b_2'}^{\mu_2'})$, respectively.

In the next section, we discuss our theoretical results for the energies of the lowest-lying HF states associated with various configurations for several donors in Si and Ge.

IV RESULTS AND DISCUSSION

We discuss our results for Si and Ge separately.

A. Si

The total energies of the low-lying states for D^0X_m in Si:P, Si:As and Si:Sb are listed in Table VI-1. For complexes with $m \geq 2$, some states with configurations of the type $\{\Gamma_1, \Gamma_3, \Gamma_5; 2\Gamma_8\}$, in which

TABLE VI-1 Total energies of the low-lying states for D^0X_m in Si:P, Si:As and Si:Sb obtained in Hartree-Fock approximation. All energies are in meV.

Complex	Configuration	Si:P	Si:As	Si:Sb
D^0X	$\{2\Gamma_1; \Gamma_8\}$	-57.36	-66.65	-54.25
	$\{\Gamma_1, \Gamma_5; \Gamma_8\}$	-53.22	-60.82	-50.54
	$\{\Gamma_1, \Gamma_3; \Gamma_8\}$	-53.00	-60.69	-50.11
D^0X_2	$\{2\Gamma_1, \Gamma_5; 2\Gamma_8\}$	-64.29	-73.70	-61.11
	$\{2\Gamma_1, \Gamma_3; 2\Gamma_8\}$	-64.25	-73.69	-61.02
	$\{\Gamma_1, 2\Gamma_5; 2\Gamma_8\}$	-60.04	-67.44	-57.36
	$\{\Gamma_1, 2\Gamma_3; 2\Gamma_8\}$	-59.73	-67.23	-56.76
D^0X_3	$\{2\Gamma_1, 2\Gamma_5; 3\Gamma_8\}$	-70.75	-80.10	-67.55
	$\{2\Gamma_1, 2\Gamma_3; 3\Gamma_8\}$	-70.65	-80.04	-67.35
	$\{\Gamma_1, 3\Gamma_5; 3\Gamma_8\}$	-66.59	-73.80	-63.88
	$\{\Gamma_1, 3\Gamma_3; 3\Gamma_8\}$	-66.21	-73.52	-63.14
D^0X_4	$\{2\Gamma_1, 3\Gamma_5; 4\Gamma_8\}$	-76.96	-86.26	-73.70
	$\{2\Gamma_1, 3\Gamma_3; 4\Gamma_8\}$	-76.84	-86.16	-73.44
	$\{\Gamma_1, 4\Gamma_5; 4\Gamma_8\}$	-72.76	-79.79	-70.01
	$\{\Gamma_1, 4\Gamma_3; 4\Gamma_8\}$	-72.32	-79.43	-69.17

three electrons are assigned to different symmetry states, are not listed. These states can be inserted between states with configurations of the types

$$\{\Gamma_1, 2\Gamma_3; 2\Gamma_8\} \text{ and } \{\Gamma_1, 2\Gamma_5; 2\Gamma_8\} \quad .$$

It should be noted that the separations between these states are of the same order of magnitude as the fine structure splittings; therefore, all these states are strongly mixed together and the assignment of electrons and holes into single-particle states is no longer a good description for these states in BMEC. However, a shell model ⁽⁵⁾ in which states associated with the Γ_3 and Γ_5 single-particle symmetries are considered as belonging to a single crystalline configuration is still a good description of the BMEC.

In the photoluminescence spectrum from the BMEC two series of lines (α_m and β_m) are observed ⁽¹⁰⁾. In the shell model ⁽⁵⁾, the α -series and β -series luminescence are interpreted as the ground-to-excited state and ground-to-ground state transitions respectively ^(5,10), i.e.,

$$\alpha_m \text{ transition: } \{2\Gamma_1, (m-1)\Gamma_{3,5}; m\Gamma_8\} \rightarrow \{\Gamma_1, (m-1)\Gamma_{3,5}; (m-1)\Gamma_8\}$$

$$\beta_{m-1} \text{ transition: } \{2\Gamma_1, (m-1)\Gamma_{3,5}; m\Gamma_8\} \rightarrow \{2\Gamma_1, (m-2)\Gamma_{3,5}; (m-1)\Gamma_8\} \quad .$$

The excitation energies of these excited states can therefore be

deduced from the separations between the positions of the α_m and β_{m-1} lines. A systematic study of these energy separations for various donors in Si has been given by Elliott et al ⁽¹¹⁾. In Fig.VI-1 we plot our theoretical predictions of these separations obtained in the present approximation and the experimental data ⁽¹⁰⁻¹²⁾. For Si:As, we have reassigned the β_2 , β_3 and β_4 lines. We have relabelled the β_2 and β_3 lines in Ref. 11 as β_3 and β_4 and assumed that the β_2 line is hidden under the TO phonon-assisted α_1 line. Hence, we cannot precisely locate the β_2 line as indicated by a range in the figure. This relabelling of lines in Si:As results in the $\alpha_{m+1} - \beta_m$ separations being almost independent of the index m as in Si:P and Si:Sb. Good agreement between theory and experiment is found for all complexes.

We can make systematic studies of the correlation energies of D^0X_m in Si. We define the dissociation energies δE_m by

$$\delta E_m \equiv [E_{m-1} + E_x] - E_m$$

where E_m and E_x are the ground state energies for D^0X_m and a free exciton, respectively. Expanding the free exciton wavefunction on our basis set, we obtain a value -14.2 meV for E_x , which is slightly higher than the experimental value -14.7 meV ⁽¹³⁾ and the theoretical value obtained with a larger basis set ⁽¹⁴⁾. Taking the difference between the experimental values for the dissociation energies, δE_m (SM) ⁽¹⁰⁻¹²⁾ (from the luminescence data interpreted using the shell model ⁽⁵⁾) and the HF

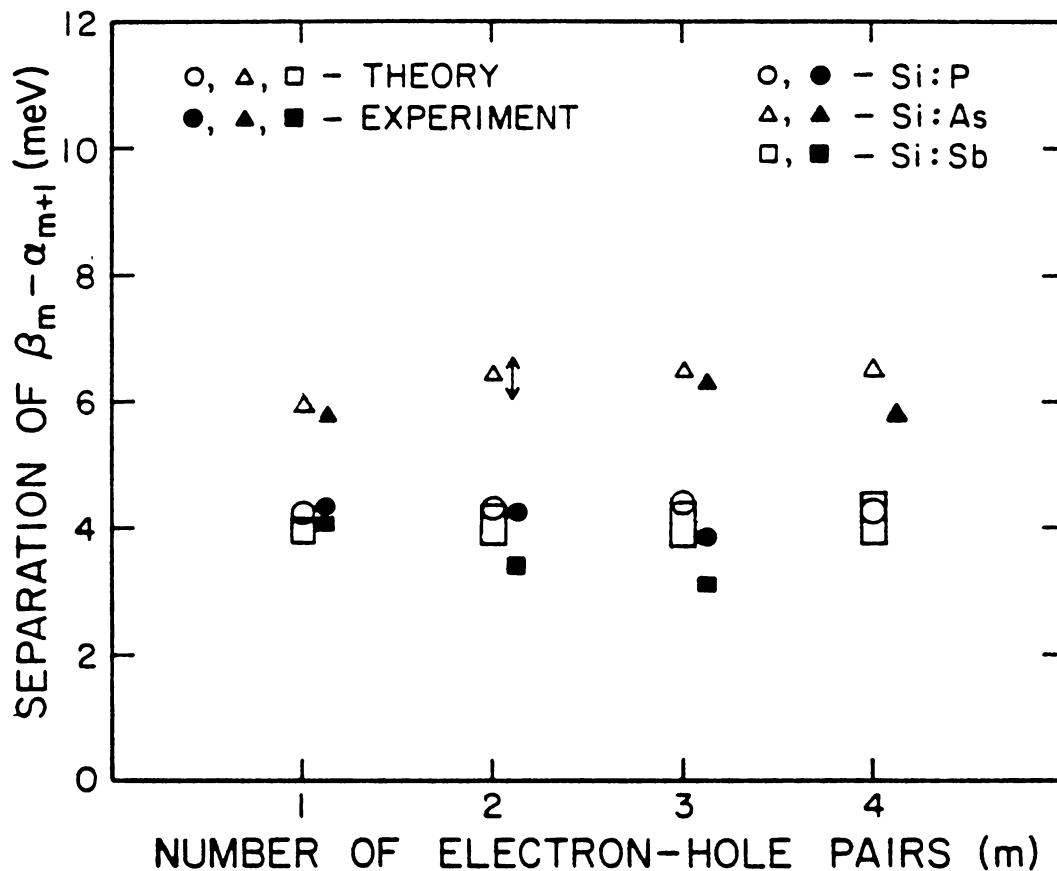


Figure VI-1. Theoretical and experimental energy separations between the α_{m+1} and β_m lines and plotted against the number of electron-hole pairs bound to a donor. The experimental data are taken from Ref. 10 for Si:P and Ref. 11 for Si:Sb and Si:As (see text for reinterpretation).

values $\delta E_m(\text{HFA})$, we can obtain the correlation energies δE_m^{corr} for binding one EHP in the $(m-1)$ complex. In Table VI-2, we list the values of $\delta E_m(\text{HFA})$, $\delta E_m(\text{SM})$ and δE_m^{corr} for D^0X_m in Si:P, Si:As and Si:Sb. In Fig. VI-2 the correlation energies per EHP so obtained (δE_m^{corr}) are plotted against the number of EHP in D^0X_m , for various donors in Si. As shown in this figure, δE_m^{corr} increases monotonically, reaching a limiting value $\delta E_{\text{EHD}}^{\text{corr}}$, the correlation energy per EHP in the electron-hole droplet (EHD). The value 17 meV for $\delta E_{\text{EHD}}^{\text{corr}}$ is obtained by taking the difference between the experimental binding energy ⁽¹⁵⁾ and the binding energy calculated in HFA ⁽¹⁶⁾. For Si:As, we have relabelled the β_2 , β_3 and β_4 lines as before. The value of δE_2^{corr} is indicated by a range in the figure, because we cannot precisely locate the β_2 line.

B. Ge

In Table VI-3, we list the total energies of the ground states ($\{2\Gamma_1, (m-1)\Gamma_5; m\Gamma_8\}$) and the one-electron excited states ($\{\Gamma_1, m\Gamma_5; m\Gamma_8\}$) for complexes D^0X_m obtained in the present approximation for Ge:P, Ge:As and Ge:Sb. For illustration purposes, we plot in Fig. VI-3, the energy separations between these one-electron excited states and the ground states ($\beta_m - \alpha_{m+1}$ separations) for complexes associated with various donors. As shown in this figure, the energy separations for all donors are approximately independent of the index m (the number of EHP in D^0X_m). The energy separations for the first one-electron excited states for bound excitons (D^0X) in Ge:P and Ge:As are in

TABLE VI-2. Systematics for the dissociation energies (δE_m (HFA) and δE_m (SM)) and correlation energies (δE_m^{corr}) per EHP of D^0X_m for donors in Si. All energies are in meV.

Material	No. of EHP (m)	δE_m (HFA)	δE_m (SM)	δE_m^{corr}
Si:P	1	-2.3	4.5 ^a	6.8
	2	-7.4	3.8 ^a	11.2
	3	-7.7	6.7 ^a	14.4
	4	-8.0	9.0 ^a	17.0
Si:As	1	-1.2	5.5 ^b	6.7
	2	-7.3	3.2 ^b	10.5
	3	-7.8	5.4 - 5.9 ^b	13.2 - 13.7
	4	-8.0	8.3 ^b	16.3
Si:Sb	1	-2.6	4.2 ^c	6.8
	2	-7.5	4.1 ^b	11.6
	3	-7.7	7.2 ^b	14.9
	4	-8.1	9.5 ^b	17.6

a. Thewalt (Ref. 10)

b. Elliott et al (Ref. 11)

c. Mayer et al (Ref. 17)

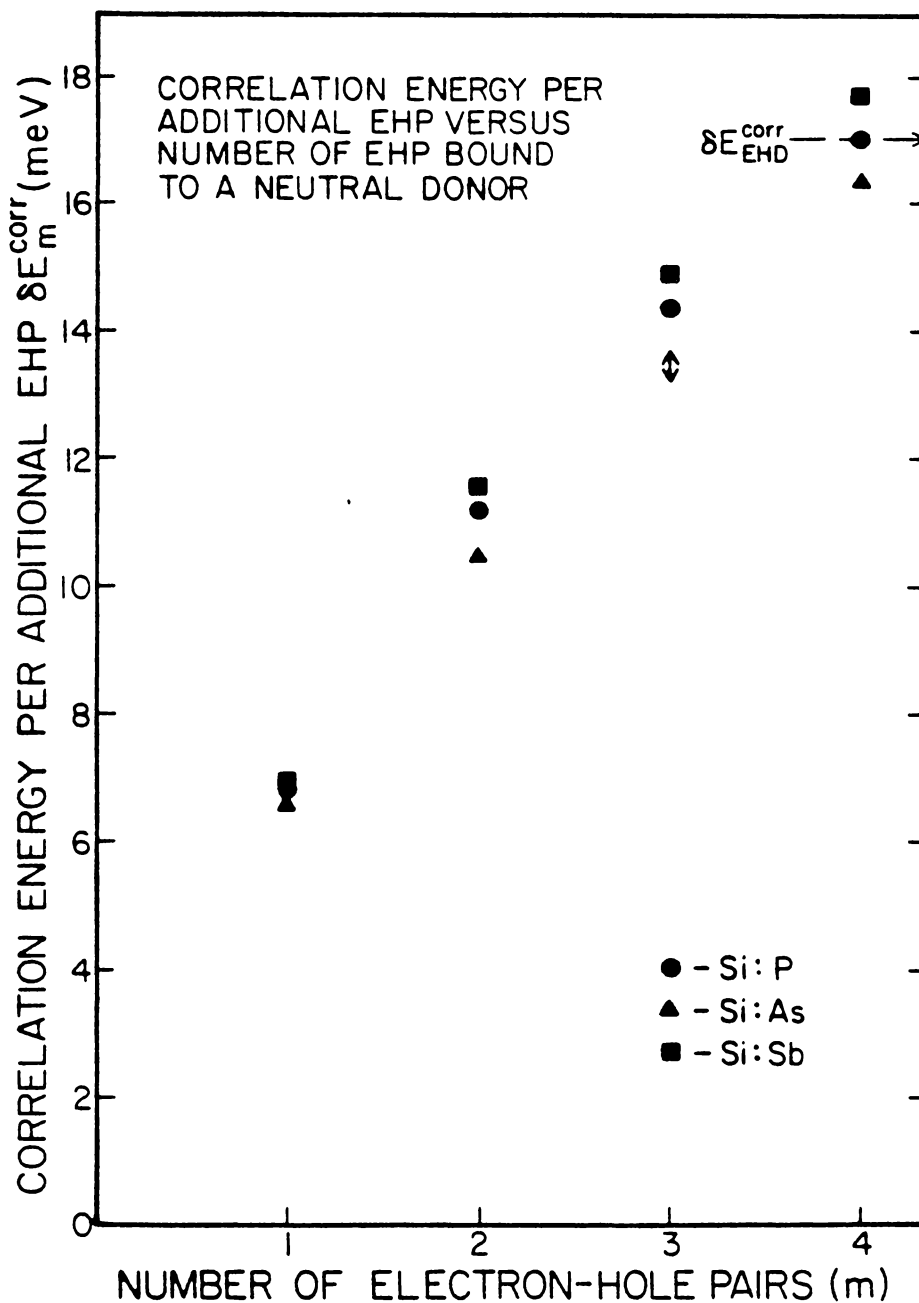


Figure VI-2. Correlation energies per electron-hole pair (EHP) plotted against the number of EHP bound to a neutral donor for Si:P, Si:As and Si:Sb. The experimental data used for obtaining these correlation energies are taken from Ref. 10 for Si:P and Ref. 11 for Si:Sb and Si:As.

TABLE VI-3. Total energies of the low-lying states for D^0X_m in Ge:P, Ge:As and Ge:Sb, obtained in Hartree-Fock approximation, All energies are in meV.

Complex	Configuration	Ge:P	Ge:As	Ge:Sb
D^0X	$\{2\Gamma_1; \Gamma_8\}$	-16.12	-17.73	-13.35
	$\{\Gamma_1, \Gamma_5; \Gamma_8\}$	-15.10	-16.43	-13.20
D^0X_2	$\{2\Gamma_1, \Gamma_5; 2\Gamma_8\}$	-18.11	-19.56	-15.09
	$\{\Gamma_1, 2\Gamma_5; 2\Gamma_8\}$	-17.02	-18.15	-14.98
D^0X_3	$\{2\Gamma_1, 2\Gamma_5; 3\Gamma_8\}$	-19.81	-21.26	-16.82
	$\{\Gamma_1, 3\Gamma_5; 3\Gamma_8\}$	-18.71	-19.81	-16.69
D^0X_4	$\{2\Gamma_1, 3\Gamma_5; 4\Gamma_8\}$	-21.36	-22.81	-18.49
	$\{\Gamma_1, 4\Gamma_5; 4\Gamma_8\}$	-20.25	-21.34	-18.27

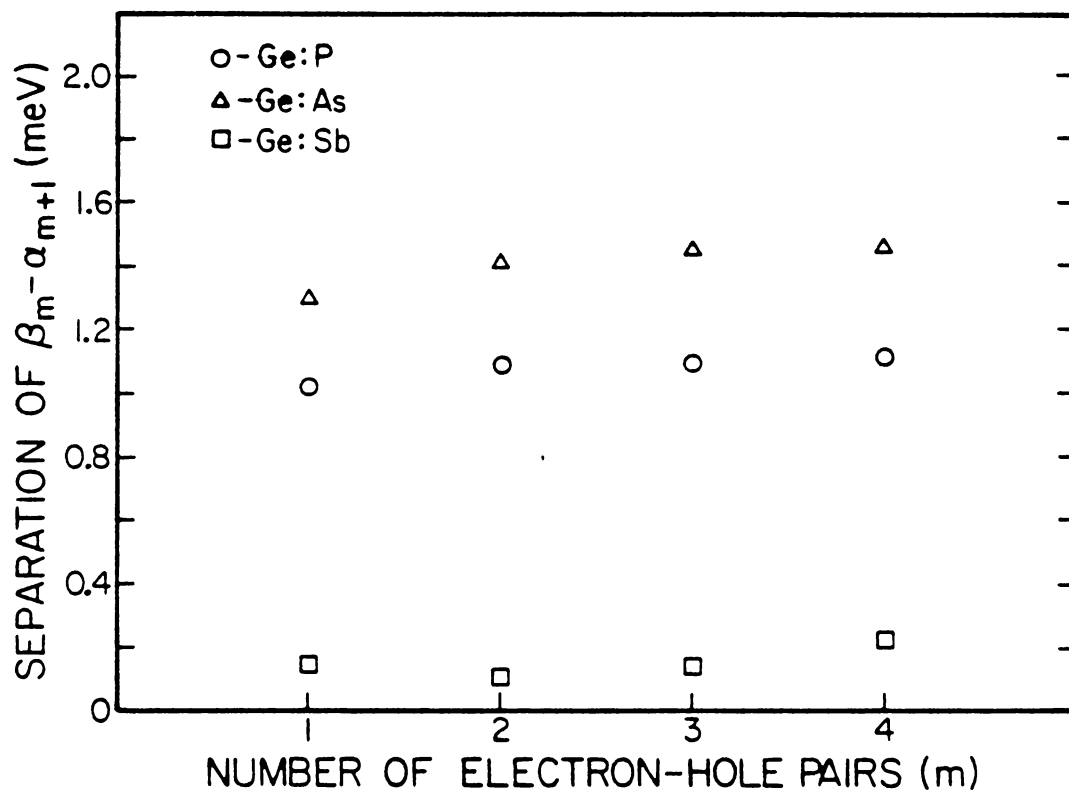


Figure VI-3. Energy separations between the one-electron excited states and the ground state for D^0X_m in Ge:P, Ge:As and Ge:Sb, plotted against the number of EHP.

good agreement (to within 0.1 meV) with the experimental data (the separations between the $\alpha_1(1s\Gamma_5)$ and γ_1^2 lines) observed by Mayer et al (17). The experimental data for the other $\beta_m - \alpha_{m+1}$ separations are not available for a comparison with our theoretical results. The observation of the luminescence from higher complexes in Ge is difficult because these lines are mixed with the luminescence associated with electron-hole-droplets and are difficult to resolve (18). Nonetheless, our theoretical calculation provides some understanding of the BMEC's associated with donors in Ge.

V. CONCLUSION

We have calculated the electronic excitation spectra of the BE and BMEC's for donors in Si and Ge. Good agreement between our calculation and the experimental data interpreted using the shell model strongly suggests that the BE and BMEC's can be understood in terms of a shell-like model. Throughout this calculation we have neglected correlation effects which are essential in obtaining the correct binding energies. These correlation energies are estimated to be approximately 10 meV for each EHP in the D^0X_m in Si. The correlation effect could be included by expanding the total wavefunction in terms of the HF solutions. However, we expect the splittings evaluated on the "correlated" states to be still of the same order of magnitude as before. Hence, we conclude that the correlation effect, although substantial in magnitude, does not affect the splittings substantially. Our cal-

culatation clarifies some ambiguities in the interpretations of the luminescence spectra and provides a better understanding of the BMEC's in multivalley semiconductors.

APPENDIX A MATRIX ELEMENTS OF THE HOLE-HOLE INTERACTION

In this appendix, we derive the expression for the hole-hole interaction matrix elements of the type

$$\langle \mu_1 \mu_2 | v_{hh} | \mu'_1 \mu'_2 \rangle \equiv \langle \beta_{b_1}^{\mu_1} \beta_{b_2}^{\mu_2} | v_{hh}(1,2) | \beta_{b'_1}^{\mu'_1} \beta_{b'_2}^{\mu'_2} \rangle, \quad (A1)$$

where β_b^μ 's are given by Eq. (14) with b and μ denoting the exponent and symmetry (index for the Γ_8 representation), respectively. More specifically, we can write

$$\beta_b^\mu(\vec{r}) = f_b(r) \sum_m C_{\ell}(\mu, m) Y_{\ell m}(\Omega) \chi_{\mu-m}, \quad (A2)$$

$$\text{where } f_b(r) = \begin{cases} e^{-br} & \text{for } \ell=0 \\ re^{-br} & \text{for } \ell=2 \end{cases} \quad (A3)$$

The coefficients $C_{\ell=0}(\mu, m=0) = 1$ for all μ and $\sqrt{5}C_{\ell=2}(\mu, m)$ are listed in Table A-1. Substituting Eq.(A2) into Eq.(A1) and using the relation

$$v_{hh}(1,2) = \frac{2}{|\vec{r}_1 - \vec{r}_2|} = \sum_{LM} \frac{8\pi}{(2L+1)} \frac{r_{<}^L}{r_{>}^{L+1}} Y_{LM}^*(\Omega_1) Y_{LM}(\Omega_2), \quad (A4)$$

we obtain

$$\begin{aligned}
 \langle \mu_1 \mu_2 | v_{hh} | \mu'_1 \mu'_2 \rangle = & 4\pi \sum_{m_1 m_2} C_{\ell_1}(\mu_1, m_1) C_{\ell'_1}(\mu'_1, \mu'_1 - \mu_1 + m_1) C_{\ell_2}(\mu_2, m_2) \\
 & \times C_{\ell'_2}(\mu'_2, \mu'_2 - \mu_2 + m_2) \sum_{LM} J_L(b_1, b_2, b'_1, b'_2) \cdot \int Y_{\ell_1 m_1}^*(\Omega_1) \\
 & \times Y_{\ell'_1, \mu'_1 - \mu_1 + m_1}(\Omega_1) Y_{LM}^*(\Omega_1) d\Omega_1 \cdot \int Y_{\ell_2 m_2}^*(\Omega_2) Y_{\ell'_2, \mu'_2 - \mu_2 + m_2}(\Omega_2) \\
 & \times Y_{LM}^*(\Omega_2) d\Omega_2 \quad , \tag{A5}
 \end{aligned}$$

where

$$\begin{aligned}
 J_L(b_1, b_2, b'_1, b'_2) \equiv & \frac{2}{(2L+1)} \int f_{b_1}(r_1) f_{b'_1}(r_1) \frac{r_1^L}{r_1^{L+1}} f_{b_2}(r_2) \\
 & \times f_{b'_2}(r_2) r_1^2 r_2^2 dr_1 dr_2 \quad . \tag{A6}
 \end{aligned}$$

In Eq.(A5), the integrals over $d\Omega_1$ and $d\Omega_2$ yield coefficients proportional to $\delta_{\mu'_1 - \mu_1, M}$ and $\delta_{\mu'_2 - \mu_2, M}$, respectively. Therefore $\langle \mu_1 \mu_2 | v_{hh} | \mu'_1 \mu'_2 \rangle$ vanishes unless

$$\mu'_1 - \mu_1 = \mu'_2 - \mu_2 \quad . \tag{A7}$$

We discuss the diagonal terms ($\mu_1 = \mu'_1$ and $\mu_2 = \mu'_2$) and off-diagonal terms ($\mu_1 \neq \mu'_1$ and $\mu_2 \neq \mu'_2$) separately.

1. Diagonal term ($\mu_1 = \mu'_1$ and $\mu_2 = \mu'_2$) :

(a) $\ell_1 = \ell'_1$ and $\ell_2 = \ell'_2$

$$\begin{aligned}
 \langle \mu_1 \mu_2 | v_{hh} | \mu_1 \mu_2 \rangle &= 4\pi \sum_L J_L(b_1, b_2, b'_1, b'_2) \int \sum_{m_1} |C_{\ell_1}(\mu_1, m_1) Y_{\ell_1 m_1}(\Omega_1)|^2 \\
 &\times Y_{L0}^*(\Omega_1) d\Omega_1 \cdot \int \sum_{m_2} |C_{\ell_2}(\mu_2, m_2) Y_{\ell_2 m_2}(\Omega_2)|^2 Y_{L0}(\Omega_2) d\Omega_2 \\
 &= J_0(b_1, b_2, b'_1, b'_2)
 \end{aligned} \tag{A8}$$

where we have used the relation (see Table A-1)

$$\sum_m |C_{\ell}(\mu, m) Y_{\ell m}(\Omega)|^2 = \frac{1}{(2\ell+1)} \sum_m |Y_{\ell m}(\Omega)|^2 = \frac{1}{4\pi} \tag{A9}$$

(b) $\ell_1 \neq \ell'_1$ and $\ell_2 \neq \ell'_2$

$$\begin{aligned}
 \langle \mu_1 \mu_2 | v_{hh} | \mu_1 \mu_2 \rangle &= \frac{1}{5} \sum_L J_L(b_1, b_2, b'_1, b'_2) \cdot \int Y_{20}(\Omega_1) Y_{L0}(\Omega_1) d\Omega_1 \\
 &\cdot \int Y_{20}(\Omega_2) Y_{L0}(\Omega_2) d\Omega_2 \\
 &= \frac{1}{5} J_2(b_1, b_2, b'_1, b'_2)
 \end{aligned} \tag{A10}$$

(c) For the other cases ($\ell_1 = \ell'_1$ and $\ell_2 \neq \ell'_2$) and ($\ell_1 \neq \ell'_1$ and $\ell_2 = \ell'_2$),

$$\langle \mu_1 \mu_2 | v_{hh} | \mu_1 \mu_2 \rangle = 0$$

Substituting Eq. (A3) into Eqs. (A8) and (A10), we obtain

$$\begin{aligned} & \langle \beta_{b_1}^{\mu_1} \beta_{b_2}^{\mu_2} | v_{hh} | \beta_{b'_1}^{\mu_1} \beta_{b'_2}^{\mu_2} \rangle \\ &= 64 (b_1 b'_1 b_2 b'_2)^{3/2} \left[\frac{1}{\alpha_1^2 \alpha_2^2 (\alpha_1 + \alpha_2)} + \frac{1}{\alpha_1 \alpha_2 (\alpha_1 + \alpha_2)^3} \right], \text{ for } \ell_1 = \ell'_1 = \ell_2 = \ell'_2 = 0 \end{aligned} \quad (A11a)$$

$$= \frac{256 (b_1 b'_1 b_2 b'_2)^{5/2}}{\alpha_1^4 \alpha_2^4 x^7} [2(\alpha_1^4 + \alpha_2^4)x^2 + 10\alpha_1 \alpha_2 x^4 - 25\alpha_1^3 \alpha_2^3], \text{ for } \ell_1 = \ell'_1 = \ell_2 = \ell'_2 = 2 \quad (A11b)$$

$$= \frac{128 (b_1 b'_1)^{3/2} (b_2 b'_2)^{5/2}}{\alpha_2^4 \alpha_1^2 x^5} [x^{4+\alpha_2} x^3 + \alpha_1 \alpha_2^2 x + 2\alpha_1 \alpha_2^3], \text{ for } \ell_1 = \ell'_1 = 0 \quad (A11c)$$

and $\ell_2 = \ell'_2 = 2$

$$= \frac{256 (b_1 b_2)^{3/2} (b'_1 b'_2)^{5/2}}{\alpha_1 \alpha_2 x^5}, \text{ for } \ell_1 = \ell_2 = 0 \text{ and } \ell'_1 = \ell'_2 = 2 \quad (A11d)$$

where

$$\alpha_1 \equiv b_1 + b'_1, \quad \alpha_2 \equiv b_2 + b'_2 \text{ and } x \equiv \alpha_1 + \alpha_2$$

The other cases can be obtained from Eq. (A11) by symmetry.

2. Off-diagonal terms ($\mu_1 \neq \mu'_1$ and $\mu_2 \neq \mu'_2$) :

Let $M \equiv \mu'_1 - \mu_1 \neq 0$, then $\mu'_2 - \mu_2 = M$ (from Eq. (A7)).

Eq.(A5) can be written as

$$\langle \mu_1 \mu_2 | \psi_{hh} | \mu'_1 \mu'_2 \rangle = [(2\ell_1+1)(2\ell'_1+1)(2\ell_2+1)(2\ell'_2+1)]^{\frac{1}{2}}$$

$$\sum_{m_1 m_2} C_{\ell_1}(\mu_1, m_1) C_{\ell'_1}(\mu'_1, M+m_1) C_{\ell_2}(\mu_2, m_2) C_{\ell'_2}(\mu'_2, m_2-M)$$

$$(-1)^{m_1} (-1)^{m_2} (-1)^M \cdot \sum_{L \geq |M|} (2L+1) J_L(b_1, b_2, b'_1, b'_2)$$

$$\begin{pmatrix} \ell_1 & \ell'_1 & L \\ -m_1 & m_1=M & -M \end{pmatrix} \begin{pmatrix} \ell_1 & \ell'_1 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2 & \ell_2 & L \\ -m_2 & m_2-M & M \end{pmatrix} \begin{pmatrix} \ell_2 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix}, \quad (A12)$$

where we have used the relation

$$\int Y_{\ell m} Y_{\ell' m'} Y_{LM} d\Omega = \left[\frac{(2\ell+1)(2\ell'+1)(2L+1)}{4\pi} \right]^{\frac{1}{2}}$$

$$\begin{pmatrix} \ell & \ell' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \ell' & L \\ m & m' & M \end{pmatrix} \quad (A13)$$

The R.H.S. of Eq. (A12) vanishes for $\ell_1 = \ell'_1 = 0$ or

$\ell_2 = \ell'_2 = 0$, since the coefficient

$$\begin{pmatrix} 0 & 0 & L \\ m & m' & M \end{pmatrix} = 0 \quad \text{unless } L = M = 0$$

Therefore, the most important contribution to $\langle \mu_1 \mu_2 | v_{hh} | \mu_1' \mu_2' \rangle$ (Eq. (A12)) comes from $\ell_1 = \ell_2 = 0$ and $\ell_1' = \ell_2' = 2$ (or equivalent cases, e.g., $\ell_1 = \ell_2' = 0$ and $\ell_1' = \ell_2 = 2$, etc.). For this case, we obtain

$$\begin{aligned} \langle \mu_1 \mu_2 | v_{hh} | \mu_1' \mu_2' \rangle &= C_2(\mu_1', M) C_2(\mu_2', -M) J_2(b_1, b_2, b_1', b_2') \\ &\leq \frac{2}{5} J_2(b_1, b_2, b_1', b_2') \end{aligned} \quad (\text{A14})$$

We can compare the size of the contribution for Eq. (A14) to that from Eq. (A11). If we assume that in the ground state, the hole wavefunction ϕ_h is described by

$$\phi_h = a_s \phi_s + a_d \phi_d, \quad (\text{A15})$$

with ϕ_s and ϕ_d being the s-like and d-like components of ϕ_h , respectively, then Eq. (A14) will yield a contribution to the total energy of magnitude

$$\frac{4}{5} a_s a_d J_2(b_s, b_s, b_d, b_d), \quad (\text{A16})$$

with b_s and b_d being the exponent associated with the wavefunctions ϕ_s and ϕ_d , respectively. Taking $b_s = b_d$ and $\frac{4}{5} a_s a_d \approx 0.3$, we obtain a contribution from (A16) about 2% of that from the hole-hole interaction given by Eq. (A11a).

TABLE A-1. Expansion coefficients $\sqrt{5} C_{\ell}(\mu, m)$ for the $\ell=2$ hole basis functions on the products of spherical harmonics and $j = 3/2$ spinors

$\sqrt{5}C_2(\mu, m)$		μ			
		-3/2	-1/2	1/2	3/2
m	-2	$\sqrt{2}$	$\sqrt{2}$	0	0
	-1	$-\sqrt{2}$	0	$\sqrt{2}$	0
	0	1	-1	-1	1
	1	0	$\sqrt{2}$	0	$-\sqrt{2}$
	2	0	0	$\sqrt{2}$	$\sqrt{2}$

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