PHYSICAL REVIEW B **83**, 165210 (2011)

Double-group formulation of $\mathbf{k} \cdot \mathbf{p}$ theory for cubic crystals

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(Received 23 July 2010; revised manuscript received 3 February 2011; published 28 April 2011)

Multiband $\mathbf{k} \cdot \mathbf{p}$ theory is often implemented with the one electron Schrödinger equation without spin (single group) as the unperturbed system. The effect of spin is taken into account by considering basis functions formed by a direct product between single-group eigenstates and spinor states (which give rise to the *adapted double-group basis* after a unitary transformation), with the spin-orbit interaction also treated as a perturbation. The $\mathbf{k} \cdot \mathbf{p}$ perturbation between these states is calculated using the single-group basis functions. This approach leads to a one-to-one link between occurrence of basis states in the single group with those under the double-group classification, placing constraints on the adapted double-group basis. This paper considers energy eigenstates which form the bases of irreducible representations (IRs) of the double group and derives the direct and remote (Löwdin term) interaction matrices between the states using perturbation theory and symmetry properties of crystal lattice. The use of general double-group basis functions removes the constraints placed on the adapted double-group basis under the single-group formulation. Together with a change of paradigm in constructing atomic site wave functions using hybridized orbitals (rather than atomic orbitals), it allows direct contributions from d and higher orbitals to the valence band with additional interaction matrices permitted by symmetry. A full description of interactions between states of $\Gamma_8^{\pm}$ IRs require two linearly independent matrices and two scaling constants rather than the single matrix and scaling constant under single-group consideration. This formulation is developed from both perturbation theory and the method of invariant approach utilizing the Wigner-Eckart theorem and other group theoretical techniques for calculation of matrix elements. Crystals with diamond lattice are investigated first, with results for zincblende lattice obtained under the compatibility relation between the O_h and the T_d groups. We show that a unitary transformation of the Γ_8^- basis of the O_h group is required before they can be used in Γ_8 IR of the T_d group. Consequently, existing data and optical transition selection rules shows that the symmetry assignment of the zone-center conduction band edge state should be $\Gamma_6^-(\Gamma_7)$ in Ge (GaAs and other semiconductors with zincblende lattice) with spin-orbit split-off band as origin. In addition to the new interaction matrix between states of $\Gamma_8^{\pm}(\Gamma_8)$ IRs, the form of interband Löwdin term between $\Gamma_8^+(\Gamma_8)$ and $\Gamma_7^+(\Gamma_7)$ in the Hamiltonian used in the literature is shown to be incorrect. A linear k term between the degenerate valence band, different from those obtained previously, is shown to exist. It modifies the dispersion and density of state in the vicinity of Γ point but does not lift the Krammer's degeneracy. When quantum well, wires, and dots are considered, operator ordering in the remote interaction emerges naturally by treating wave vector as an operator acting on the envelope functions. This differs from previous schemes based on single-group formulation and a new term, arising from interfacial symmetry breaking, is identified in the valence-band Hamiltonian coupling the degenerate heavy-hole states.

DOI: 10.1103/PhysRevB.83.165210 PACS number(s): 73.21.−b, 71.15.−m, 71.20.Mq, 71.20.Nr

I. INTRODUCTION

The $\mathbf{k} \cdot \mathbf{p}$ method[1–6] has been one of the most useful tools in modeling band structure in semiconductors. The technique has been applied to the study of band structures in bulk semiconductors as well as that of heterostructures through exact envelope function theory[7] or effective mass theory.[3] The method is based on degenerate perturbation theory but has also been formulated from the theory of invariants,[6,8] which has less stringent assumptions on the self-consistent one-electron potential. One reason for the success of this method is the small number of parameters, normally determined from experiment such as cyclotron resonance, required for modeling the band structure in the vicinity of the point of expansion. Apart from original works in the scientific journals, the theory has been well described in the textbooks (see, for example, Refs. 9 and 10).

In the original work of Dresselhaus, Kip, and Kittel,[2] Luttinger and Kohn,[3] and Kane,[5] the $\mathbf{k} \cdot \mathbf{p}$ method has been developed from a single-group consideration (Schrödinger equation without spin-orbit interaction) and then adapted to include spin as a degree of freedom. Consequently, spin-orbit interaction is treated as a perturbation in parallel with the $\mathbf{k} \cdot \mathbf{p}$ perturbation. Due to its heritage, the three independent parameters (L, M, N in Refs. 2 and 5; σ, π, δ in Ref. 11) in a four-band model refer to interactions between single-group basis functions even though the basis for expansion of Hamiltonian at finite $\mathbf{k}$ includes spin. Such parameters are related to interactions between states in the *near* set under consideration mediated by the *remote* states, which is known as the Löwdin term.[12] Using double-group representations of the near states, the theory of invariants formulation[6,8,13–15] also indicates that there are three independent parameters (for the four-band partition where appropriate and in absence of external magnetic field). Explicitly or implicitly, current $\mathbf{k} \cdot \mathbf{p}$ work in the literature calculates interaction matrices utilizing single-group bases, such as $\{yz,zx,xy\}$ for valence band, which are then cast into the *adapted double-group basis* (direct product of single-group bases and spinor states followed by a unitary transformation to block diagonalize them into double-group bases). Alternatively, results from method of invariant are used. Adaptation of single-group bases into the double-group irreducible representations (IRs) of the symmetry group limits the adapted double-group bases to a subset of vector space that may be represented by a general double-group basis. Extension of earlier work by inclusion of more states in the near set was first made under single-group formulation with single-group basis by Cardona and Pollak[16] in a fifteen-band model. Generalization to the adapted double-group basis followed with eight-band,[14,15,17] fourteen-band,[18–22] twenty-band,[23] and thirty-band[24] models.

In this publication, the basic formulation of the $\mathbf{k}\cdot\mathbf{p}$ method from perturbation theory and the method of invariant is reexamined, using a general double-group classification of both the near and the remote sets of states. Under this double-group formulation, basis functions for matrix representation of the Hamiltonian are free from the constraints of the single-group formulation. The form of Hamiltonian obtained from perturbation theory is directly comparable to results obtained from the method of invariants. The removal of constraints associated with the single-group formulation allows the double-group basis to fully represent zone-center states which may contain mixed single-group characters. Such mixed characters may arise from either spin-orbit interaction or the use of hybridized orbitals (sp^3 or spd constructed from many electron configuration) as atomic site wave functions. It is argued that orbital and total angular momentum quantum numbers are not appropriate for labeling energy eigenstates due to the delocalized nature of the valence electrons. These energy eigenstates must have the correct transformation properties according to the IRs of the symmetry group of the crystal but may also contain information that adapted double-group basis functions would fail to represent. The first-order perturbation matrix and the Löwdin interaction are evaluated by considering the symmetry properties of states in both the near and remote set, using double-group representations and group theoretical techniques.[25] The perturbation matrix between eigenstates of different IRs are separated into scaling constants and linearly independent, constant matrices. The fitting parameters are naturally based on the scaling constants of the perturbation matrix between states of the relevant IRs and are related to the Luttinger parameters derived from the theory of invariants. In the case of crystals with diamond lattice, all the scaling constants of the first-order $\mathbf{k}\cdot\boldsymbol{\pi}$ perturbation matrices are real. The matrices are independent of the choice of basis and are enumerated using Wigner-Eckart theorem utilizing *multiple* sets of *standard basis functions* which are eigenstates of J^2, L^2, and S^2 and expressed in terms of linear combination of the SU(2) basis functions $|j,m_j\rangle$. The standard basis also has a designated time-reversal behavior which requires a definite phase between bases of even and odd IRs. In developing the method of invariant approach, the operators used for obtaining generator matrices and irreducible components of the perturbation are identified explicitly. Instead of using products between components of angular momentum operators to enumerate generator matrices from a single set of standard basis functions, as done in the literature, the generator matrices are obtained using a multiple set of standard basis functions from a single generating operator which transform as the irreducible perturbations. The mathematical approach is the same as in perturbation theory. An eight-band Hamiltonian is constructed using both methodologies and shown to be identical but differs in form from those in the literature. The reason for this is identified as the use of an incorrect basis for Γ_7^+ IR of the O_h group and Γ_7 and Γ_8 IRs of the T_d group.

The formulations are developed based on the diamond lattice whose point group is O_h. Compatibility relations between the T_d and O_h groups are used to obtain the Hamiltonian for crystals with a zincblende lattice from that of the diamond lattice. This also requires a unitary transformation to be performed on the Γ_8^- standard basis before they are incorporated as standard basis of the Γ_8 IR of the T_d group. Additional linear (direct interaction) and quadratic (Löwdin interaction) k terms in the Hamiltonian are identified in comparison to crystals with diamond lattice. Inter- and intraband linear k terms are shown to exist between states forbidden in crystals with diamond lattice and they depend on the ionicity of the chemical bond. The form of first-order interaction matrices are different between crystals with diamond and zincblende lattices while the Löwdin terms are similar. Time-reversal symmetry requires a phase difference between spatially even and odd parts of the energy eigenfunction in Γ_6 and Γ_7 IRs but not Γ_8 IR. Thus, the scaling constants describing first-order interactions are necessarily imaginary between the $\Gamma_8 : \Gamma_8$ IRs, complex between $\Gamma_8 : \Gamma_7$ and $\Gamma_8 : \Gamma_6$ IRs and real between $\Gamma_7 : \Gamma_6$ IRs. The form of the linear k term within the valence bands is such that they do not lift the Kramer's degeneracy.

Comparison of double-group selection rules and experimental results, indicates that the symmetry of the conduction band state at the Γ point corresponds to the Γ_6^- representation of the O_h group in Ge or the Γ_7 representation of the T_d group in GaAs. The origin of this zone center-state is established as the spin-split-off state from the antibonding orbitals. The double-group formulation is also suitable for implementing operator ordering when dealing with heterostructures. A coupling between the degenerate heavy-hole bands due to interfacial symmetry breaking is revealed.

The differences between the single-group and the double-group formulations are examined by focusing on the interaction matrices between states of the $\Gamma_8^\pm$ (Γ_8) IRs for crystals with diamond (zincblende) lattice. First-order interaction matrices referring to adapted double-group bases are only available in the literature for states derived from Γ_5 IRs of crystals with zincblende lattice (obtained from method of invariant). All necessary first-order interaction matrices between relevant single-group IRs are derived for adapted double-group bases for crystals of both type of lattices. Comparisons are then made with the general double-group formulation of the present work. This indicates that the form of first-order interaction matrices involving $\Gamma_3^\pm$ (Γ_3) derived states in the $\Gamma_8^\pm$ IR are different when compared with those involving the Γ_4^-,Γ_5^+ (Γ_5) derived $\Gamma_8^\pm$ (Γ_8) states. Thus, the single-group formulation cannot describe material systems where hybridized orbitals, with contributions from the p (containing Γ_5^+ character for VB) and d orbitals (containing Γ_3^+ character for VB), serve as atomic site wave functions. Double-group formulation, with two linearly independent matrices and two scaling constants, is able to describe these interactions involving complex hybridized orbitals. We restrict ourselves to the case of unstrained crystals, but such effects can be incorporated in the normal way if required.[8]

There has been much confusion in the literature over the labeling of IRs of the O_h and T_d groups, arising from differences in the labeling of the Γ_4 and Γ_5 IRs in the original work of Dresselhaus[4] and that used by Koster *et al.*[26] To avoid any confusion, character tables for the double groups O_h and T_d are included in Appendix A. The labeling convention used in this publication follows that of Koster *et al.*,[26] which facilitates discussions of compatibility relations between the two groups. The rest of the paper is divided into 11 sections. Sections II and III discuss general symmetry issues, relations between energy eigenstates and standard bases of IRs formed from angular momentum eigenstates, and the need for multiple standard basis/group theoretical method. Sections IV and V formulate the **k** · **p** method from a perturbation approach and Secs. VI and VII develop the method from the theory of invariant approach. The impact of this work on envelope function theory and operator ordering is discussed in Sec. VIII. Crystals with zincblende lattice are studied in Sec. IX using compatibility relations between the O_h and T_d groups. Section X addresses the issue of symmetry of zone-center conduction band states and experimental evidence for a change of symmetry assignment according to the formulation developed here. Section XI investigates the relationship between the single- and the double-group-based formulations and their applicability to physical systems and clarifies the need for a double-group formulation. Section XII summarizes the findings and discusses their implications on various multiband **k** · **p** models depending on the number of states included in the near set. Some necessary results of the single-group formulation, not available in the literature, are obtained in Appendix E and mistakes in the literature are identified.

II. SYMMETRY OF ELECTRON ENERGY EIGENFUNCTIONS IN A CRYSTAL

The time-independent one-electron Schrödinger equation may be cast in the following form after application of the Bloch's theorem:

$$\Bigg[\underbrace{\underbrace{\frac{p^2}{2m_0}+V(r)}_{H_0^s}+\underbrace{\frac{\hbar}{4m_0^2c^2}[\mathbf{p}\times\nabla V(r)]\cdot\boldsymbol{\sigma}}_{H_{so1}^s}}_{H_0}+\underbrace{\underbrace{\frac{\hbar}{m_0}\mathbf{k}\cdot\mathbf{p}}_{H_{k\cdot p}^s}+\underbrace{\frac{\hbar^2}{4m_0^2c^2}\mathbf{k}\cdot[\boldsymbol{\sigma}\times\nabla V(r)]}_{H_{so2}^s}}_{H_1}\Bigg]u_{n,\mathbf{k}}(r)=\left(E_n(\mathbf{k})-\frac{\hbar^2k^2}{2m_0}\right)u_{n,\mathbf{k}}(r). \quad (1)$$

Using the center of the Brillioun zone as the point of expansion, the term

$$H_1=\frac{\hbar}{m_0}\mathbf{k}\cdot\boldsymbol{\pi}=\frac{\hbar}{m_0}\mathbf{k}\cdot\left[\mathbf{p}+\frac{\hbar}{4m_0c^2}\boldsymbol{\sigma}\times\nabla V(r)\right]$$

is treated as a perturbation. The exact solutions of the Schrödinger equation at the point of expansion, $u_{n,k=k_0}(r)$ (with Hamiltonian given by H_0), are chosen as the basis (referred to as double-group basis) to form the matrix representation of this Hamiltonian at other **k** values away from point of expansion. These energy eigenstates $u_{n,k=k_0}(r)$ form the bases of IRs of the little group (or group of **k**) at the point of expansion under the framework of double-group classification. The symmetry of these energy eigenstates differ, in general, from those of the atomic orbitals. With the origin of reciprocal space as the point of expansion, the group of **k** is the point group of the crystal lattice. In the case of a diamond lattice, this is the O_h group. Within the framework of double group, these energy eigenstates form the bases of $\Gamma_6^\pm,\Gamma_7^\pm$, and $\Gamma_8^\pm$ IRs of the O_h group.

The double-group formulation outlined above may be compared with the single-group formulation. Solutions of the unperturbed Schrödinger equation at the point of expansion (with Hamiltonian given by H_0^s) are chosen as the single-group basis for calculation of interaction matrices between states. Then, direct products of the single-group basis with the spinor states followed by unitary transformation, are used as the basis (referred to as adapted double-group basis) to form the matrix representation of this Hamiltonian at other **k** values away from point of expansion. Under the single-group framework, the **k** · **p** perturbation $H_{k\cdot p}^s$ and spin-orbit interaction H_{so1}^s and H_{so2}^s are all treated as perturbations in parallel. Thus, the main difference between the single-group formulation in the literature and double-group formulation of this work are the basis functions of the Hamiltonian. The adapted double-group basis under the single-group formulation is constrained to those derived from single-group bases through direct product with spinor state, and so no admixture is permitted. Conversely, the presence of H_{so1}^s in the unperturbed Hamiltonian H_0 of the double-group formulation, allows some degree of mixing of the adapted double-group basis in the formation of a general double-group basis. Within the single-group formulation, interactions between states belonging to any IR can be described by a single matrix. In contrast, the use of hybrid orbitals to describe atomic site wave functions requires the removal of constraints on the double-group basis enforced by the single-group formulation. As a consequence, the interaction between states of $\Gamma_8^\pm$ IRs can only be described by two linearly independent matrices.

The action of an element in the point group transforms the eigenstates $u_{n,k=0}(r)$ within the primitive cell among the degenerate energy eigenfuctions of a particular IR. Since there may be more than one equivalent atomic site in the primitive cell, such one-electron energy eigenfunctions can be constructed from a linear combination of wave functions at the atomic sites, and their symmetry properties can be discussed in terms of equivalence representations.[27] In a diamond lattice, the two-dimensional equivalence representation is reduced to

$\Gamma_1^+ \oplus \Gamma_2^-$. Symmetry properties of the cell periodic function is given by the direct product between the equivalence representation and the IRs of the contributing state at the atomic site. The bonding $u_{n,k=0}(r)$ states need to be symmetric with respect to the inversion operation of the point group as this interchanges the two equivalent atomic sites in the primitive cell and guarantees that electron density is higher between the two equivalent sites. Conversely, the antibonding states must be antisymmetric with respect to the inversion operation.

It is customary to consider atomic orbitals,[9,28] with their associated transformation properties, as the starting wave function at the atomic site. Thus, the valence band originating from the p orbital, transforming like the basis of Γ_4^-, has $\Gamma_2^- \otimes \Gamma_4^- = \Gamma_5^+$ symmetry, while the bonding s orbital, transforming like the basis of Γ_1^+, has $\Gamma_1^+ \otimes \Gamma_1^+ = \Gamma_1^+$ symmetry. Similarly, the antibonding states formed from atomic s and p orbitals have $\Gamma_2^- \otimes \Gamma_1^+ = \Gamma_2^-$ and $\Gamma_1^+ \otimes \Gamma_4^- = \Gamma_4^-$ symmetry, respectively. With spin-orbit interaction included, the degeneracy of the bonding Γ_5^+ and antibonding Γ_4^- is lifted. Thus, the bonding s and p orbitals give rise to states with $\Gamma_1^+ \otimes \Gamma_6^+ = \Gamma_6^+$ and $\Gamma_5^+ \otimes \Gamma_6^+ = \Gamma_7^+ \oplus \Gamma_8^+$ symmetries, whereas their antibonding counterparts give rise to states with $\Gamma_2^- \otimes \Gamma_6^+ = \Gamma_7^-$ and $\Gamma_4^- \otimes \Gamma_6^+ = \Gamma_6^- \oplus \Gamma_8^-$ symmetries. The formation of direct product between single-group IRs and Γ_6^+ means the basis obtained in the double-group classification can only be in the space spanned by a direct product of the single-group bases and spinor states. Starting with these atomic orbitals leaves the energy ordering of antibonding states quite independent of atomic orbitals. The energy ordering is chosen to support what is the current understanding of the symmetry of conduction band state at Γ point, that is, Γ_7^- in Ge, Γ_6^- in Si, and Γ_6 in most of the III-V compound semiconductors with zincblende lattice. We contend that the ordering of $s^*(\Gamma_7^-)$ and $p^*(\Gamma_8^- \oplus \Gamma_6^-)$ states in Ge and $s^*(\Gamma_6)$ and $p^*(\Gamma_8 \oplus \Gamma_7)$ in GaAs and other III-V compound semiconductors are incorrect based on selection rules obtained using correct standard basis functions (Sec. X) and ample experimental evidence. The current ordering of energy states in the literature originates from unpublished work of Herman on Ge referred to in Ref. 2. Additional states above the Γ_8^- in conduction band were also given as $\Gamma_8^-(\Gamma_3^-,d^*)$, $\Gamma_6^+(\Gamma_1^+,f)$, $\Gamma_8^+ \oplus \Gamma_7^+(\Gamma_5^+,d)$, and $\Gamma_7^-(\Gamma_2^-,f^*)$ derived from d,f and d^*,f^* orbitals in the same work. More recent work reverses the order of d^* and f states.[16,24] The appearance of an antibonding state $d^*(\Gamma_3^-)$ before a bonding state $d(\Gamma_5^+)$ is puzzling.

An alternative starting point for constructing the atomic site wave function is the sp^3 hybridized orbital. Hybridized orbitals, constructed from many electron configurations formed under the influence of the crystal field, have lower energy compared with sequentially filled individual atomic orbitals and is therefore a better description of the covalent bonding in the crystal. As a many-electron effect, the configuration will have four states from each atomic site as this corresponds to the number of available valance electrons per atom that are used to construct the many-electron configuration. Within this configuration of tetrahedral symmetry, two distinct energy levels are permitted upon formation of the covalent bond: the onefold degenerate state (singlet) transforming according to Γ_1^+ and the threefold degenerate states (triplet) transforming according the Γ_4^- of the O_h group.[29] While it may be tempting to ascribe the origin of these energy levels to the atomic s and p orbitals, one must remember that a many-electron configuration exists between bonding atoms. The action of the crystal field and delocalized nature of covalent bond means energy eigenstates will have contributions from symmetry complying higher spherical harmonics while maintaining the transformation properties as basis of Γ_1^+ and Γ_4^- IRs of the O_h group. In forming the covalent bond between neighboring atoms, the bonding singlet Γ_1^+ state leads to the lowest energy due to the charge distribution in the covalent bond. This lowering of energy is primarily due to screening of Coloumbic interaction between the "nucleus" (including inner shell electrons) by the bonding valence electrons.[30] The orthogonality between the bonding and antibonding states means the electron distribution of the antibonding Γ_2^- state leaves the "nucleus" most exposed, leading to the highest increase in energy. Thus, the triplet bonding states would have higher energy than the singlet bonding state but the triplet antibonding states would have lower energy than the antibonding singlet state. Going through the same symmetry arguments made in the previous paragraph, we obtain Γ_8^+,Γ_7^+, and Γ_6^+ as symmetries of the bonding states of $u_{n,k=0}(r)$ for the valence, spin-split-off, and lowest occupied band, as shown in Table I.

TABLE I. Atomic site orbitals, their representation under tetrahedral crystal field, representation of associated $u_{n,k=0}(r)$ under crystal field splitting, representation of associated $u_{n,k=0}(r)$ under spin-orbit splitting, and parity of $u_{n,k=0}(r)$. The states are ordered for Ge with increasing energy toward the last row.

Atomic Orbital	Crystal field splitting	$u_{n,k=0}$ symmetry	Spin orbit splitting	Parity
	Γ_1^+	Γ_1^+	Γ_6^+	Even
sp^3	Γ_4^-	Γ_5^+	Γ_7^+(SO) Γ_8^+(VB)	Even Even
$(sp^3)^*$	Γ_4^-	Γ_4^-	Γ_6^-(CB) Γ_8^-	Odd Odd
	Γ_1^+	Γ_2^-	Γ_7^-	Odd

As sp^3 hybridized orbitals are derived from many-electron configuration, the freedom in assigning the order of the antibonding states is lost. As shown in Table I, the lowest antibonding state $u_{n,k=0}(r)$ has the symmetry of Γ_6^-. It originates from spin splitting of the antibonding triplet states from single-group consideration outlined above and its relative position is determined using arguments based on charge distribution in the previous paragraph. It will be shown in Sec. X that such a symmetry assignment is correct and in agreement with the ample experimental evidence available. Previous symmetry assignments are flawed due to use of incorrect basis functions in the formulation of selection rules for optical transitions.

A natural extension of sp^3 hybridized orbitals as atomic site wave functions is to include the effects of d and/or f orbitals in an spd or higher hybridized orbital. As the number of available states in the one-electron picture is fixed by the number of electrons in the configuration, the bonding Γ_8^+ states may contain symmetry characters derived from bonding Γ_5^+ and Γ_3^+ IRs.

In the discussions that follow, from both perturbation theory and the method of invariant, one needs to evaluate matrix elements of various quantum mechanical operators between energy eigenstates which form the basis of any of the six available IRs of the double group. Given that the starting zone-center basis function contains multiple standard basis functions, it is desirable to acquire as much information as possible about such matrices from group theoretical methods. The results are applicable to all allowed bases of IRs of the symmetry group, including the energy eigenstates. This comes in the form of a selection rule or theory of invariant,[31] which are a special case of a general theorem derived by Koster.[25] The matrix representation of any operator, transforming as a representation Γ^γ of the symmetry group, between energy eigenstates which form the bases of IRs α^u and α^v of the symmetry group, can be described by a number of constant linearly independent matrices and their associated scaling constants. These matrices are independent of the choice of basis, whereas the scaling constants are dependent on the operator and the choice of bases or energy eigenstates. The number of linearly independent matrices is given by the number of times Γ^γ IR occurs in the decomposition of $\alpha^{u^*} \otimes \alpha^v$ into direct sums. The scaling constants are related to material parameters (invariants) in the method of invariant. If the symmetry group is the full rotation group SO(3), this theorem is reduced to the Wigner-Eckart theorem.[25,32] For intraband interactions, time-reversal symmetry must also be considered when the operator in question has well-defined behavior under time reversal.[31,33,34]

III. ENERGY EIGENSTATES AND STANDARD BASIS OF IRREDUCIBLE REPRESENTATIONS

In solving the one-electron Schrödinger equation using a perturbation approach, a specific $|j,m_j\rangle$ basis representation[2,3,28] is frequently chosen and assumed to fulfill the requirement of diagonalizing H_0, which includes the spin-orbit interaction H_{so1}^s. The last statement is subject to a number of assumptions. First, the angular momentum quantum numbers j and l are well defined "good quantum numbers." Second, the central field approximation can be made such that the spin-orbit interaction at Γ point is proportional to $\mathbf{L} \cdot \mathbf{S}$.

One can immediately see that the limited dimensions of the IRs of the O_h group cannot contain all of the $|j,m_j\rangle$ basis states for $j > 3/2$. There are two options for dealing with this problem. The total angular momentum quantum number j may be restricted to $j \leqslant 3/2$ in an *ad hoc* way, which will ensure the dimensions of representations never exceed four. However, many of the symmetry arguments concerning the matrix elements were made utilizing single-group bases $\{yz,zx,xy\}$, formed from linear combinations of $l = 2$ angular momentum states and containing components of $j = 5/2$ states. More importantly, there are no basis functions with $j \leqslant 3/2$ which transform according $\Gamma_7^\pm$ IRs of the O_h group. An alternative requirement of an energy eigenstate is that it is an eigenstate of $\mathbf{J}^2$, $\mathbf{L}^2$, and $\mathbf{S}^2$, formed from a linear combination of $|j,m_j\rangle$ with a single pair of j and l quantum numbers, and transforms according to the symmetry group representations, that is, standard basis functions. The problem with this approach is that available bases generally lead to spin-orbit split-off states with larger angular momentum quantum numbers among the two energy levels. The lowest Γ_7^+ basis derived from $l = 2$ states actually has $j = 5/2$, which yields an incorrect energy ordering of the fourfold degenerate Γ_8^+ $(j = 3/2)$ and twofold degenerate Γ_7^+ $(j = 5/2)$ states in the valence bands.

The alternative is to accept that energy eigenstates $u_{n,k=0}(r)$ are constructed from linear combinations of standard basis functions of a single angular momentum quantum number. This means that j and m_j quantum numbers are no longer well defined and cannot serve as good quantum numbers to label zone-center states. As a consequence, the central field approximation must be abandoned. In this case, states derived from Γ_1^+ of the (sp^3) or Γ_2^- of the $(sp^3)^*$ may also experience a shift in energy due to spin-orbit interaction. A more intuitive argument is that valence electrons are delocalized and do not have a well-defined angular momentum. In the case of zincblende lattice, one can also argue on parity grounds that the energy eigenstate must consist of at least two angular momentum states of opposite parity. A zincblende lattice has no center of inversion and hence the cell periodic function will not have a well-defined parity. The standard basis functions, on the other hand, have well-defined parity determined by the orbital angular momentum quantum number. Thus, the cell periodic function must be expressible as the sum of even and odd functions or a sum of at least two different angular momentum eigenstates.

In a crystal, the "good quantum numbers" that can be used to label the "one-electron" states are the wave number $\mathbf{k}$ corresponding to the translation symmetry subgroup and band index n corresponding to the point group representations. Thus, eigenstates at the Γ point can be specified by two labels $|\alpha,i\rangle$, where α distinguishes different IRs of the point group and multiple occurrence of the same IR, and i an index of eigenstate within the particular IR. In the formulation developed here, it is only assumed that such solutions of the one-electron Schrödinger equation exist, and they transform according to the IRs of the symmetry group. These energy eigenstates are expressible as a linear combination of standard basis functions of the relevant IR, which, in turn, are expressible as linear combination of $|j,m_j\rangle$ states themselves. It is therefore meaningless to discuss m_j of the energy eigenstates. Evaluation of any matrix elements then requires the group theoretical method described at the end of Sec. II.

The general formulations based on the single group in the literature and the double group here, do not require the basis for expansion of Hamiltonian to have a well-defined angular momentum quantum number, nor do they require one standard basis. In both cases, the basis function for the Hamiltonian should be expressible as linear combination of standard basis functions. In the case of single-group formulation, additional constraints are placed on the adapted double-group basis by the operation of a direct product between single-group bases and spinor states. Therefore, it assumes that the occurrence of every double-group IR has *one* corresponding single-group IR. This specifically rules out the possibility of states in the Γ_8^+ IR containing a mixture of characters from Γ_3^+, Γ_5^+, and Γ_4^- IRs of the atomic site wave function; that is, the description of the valence band by single-group consideration will not be able to incorporate the allowed d orbital.

The order of basis functions within an IR, including the zone-center energy eigenfunctions, is arbitrary. However, once the order for one set of bases is fixed by some convention, the representation matrices and hence the order of other basis functions of the same IR are completely fixed. The order of the bases given by Onodera *et al.*[35] follows the convention in the community, though the basis functions of the $\Gamma_7^{\pm}$ are not well known.

Time-reversal properties of all the double-group IRs of the O_h group are classified as type (c) by the Herring's rule[26] and time-reversal symmetry places additional relations between standard basis functions of an IR and zone-center energy eigenfunctions. If the IR has dimension $2J+1$ and the index of states in a basis set runs from $M_j = -J, -J+1, \ldots, J-1, J$ (here J and M_j only serve as a measure of dimension and index of the states and *do not* equal the angular momentum quantum number j and m_j in general), time-reversal symmetry requires the standard basis functions or energy eigenstates to satisfy the relation[26]

$$\hat{K}|J,M_j\rangle = (-1)^{(J-M_j)}|J,-M_j\rangle, \tag{2}$$

where $\hat{K}$ is the time-reversal operator and may be defined as $\hat{K} = -i\sigma_y\hat{K}_0$, where $\hat{K}_0$ is the conjugation operator.[36] The action of the time-reversal operator on a SU(2) basis function (following the Condon-Shortley phase convention) gives

$$\hat{K}|j,m_j\rangle = (-1)^l(-1)^{(j-m_j)}|j,-m_j\rangle, \tag{3}$$

where l is the orbital angular momentum quantum number. Thus, a factor of "i" is introduced in the basis functions of positive-parity IRs given in Ref. 35 in order to satisfy Eq. (2). The resulting bases, which are used in the rest of this paper, are listed in Appendix B. Two sets of bases are required for the $\Gamma_8^{\pm}$ IRs in order to provide an adequate description of interaction of states belonging to these IRs. Thus, the convention on ordering basis states is the requirement they satisfy [Eq. (2)]. The requirement that zone-center energy eigenfunctions comply with Eq. (2) means that the relative phase between even and odd bases is important, particularly when they are mapped to the basis of the T_d group through compatibility relations (see Sec. IX).

In all the matrix calculations and in construction of Cartesian tensor operators from irreducible spherical tensor operators, the Condon-Shortley phase convention is used. The Cartesian tensor operator generated from standard irreducible spherical tensor operator is always time-reversal even under the Condon-Shortley phase. For a time-reversal odd Cartesian tensor operator, the corresponding standard irreducible spherical tensor operator is scaled by a factor of $-i$.

IV. PERTURBATION-THEORY-BASED APPROACH

According to Löwdin,[12] the basis states required for the matrix description of the Hamiltonian are divided into two sets: the *near* set, which are of interest, and the *remote* set, whose effect on the near set is included as a perturbation. The effective Hamiltonian matrix element is then given by

$$H_{ij} = \langle i|H_0 + H_1|j\rangle + \sum_{\beta}\frac{\langle i|H_1|\beta\rangle\langle\beta|H_1|j\rangle}{E-E_\beta}, \tag{4}$$

where H_0 and H_1 are the unperturbed Hamiltonian and perturbation, respectively, and the summation is over the remote set of states $|\beta\rangle$. The $\mathbf{k}\cdot\boldsymbol{\pi}$ perturbation can be expressed as products of the components of $\mathbf{k}$ and the components of operator $\boldsymbol{\pi}$. Let

$$\mathbf{M}^{\mu}_{\alpha^u,\alpha^v;ij} = \frac{\hbar}{m_0}\langle\alpha^u,i|\boldsymbol{\pi}_\mu|\alpha^v,j\rangle = \frac{\hbar}{m_0}\sum_n \xi^n_{\alpha^u,\alpha^v}\mathbf{A}^{\mu,n}_{\alpha^u,\alpha^v;ij}, \tag{5}$$

where α^u and α^v are IRs with basis states $|\alpha^u,i\rangle$ and $|\alpha^v,j\rangle$, $\mathbf{A}^{\mu,n}_{\alpha^u,\alpha^v}$ are linearly independent matrices defined by Koster, and $\xi^n_{\alpha^u,\alpha^v}$ are scaling constants which are the same for all components $\boldsymbol{\pi}_\mu$. If we separate the eigenstates into IRs with corresponding transformation properties, then the Hamiltonian can be expressed in block form according to IRs of the near set as

$$\begin{aligned}\mathscr{H}_{\alpha^u,\alpha^v}(\mathbf{k}) = \mathbf{H}_0 &+ \sum_\mu k_\mu\mathbf{M}^{\mu}_{\alpha^u,\alpha^v} - \sum_\mu\sum_\nu\sum_{\alpha^\beta}k_\mu \\ &\times\frac{\mathbf{M}^{\mu}_{\alpha^u,\alpha^\beta}\mathbf{M}^{\nu}_{\alpha^\beta,\alpha^v}(2E_{\alpha^\beta}-E_{\alpha^u}-E_{\alpha^v})}{2(E_{\alpha^\beta}-E_{\alpha^u})(E_{\alpha^\beta}-E_{\alpha^v})}k_\nu,\end{aligned} \tag{6}$$

where α^u and α^v span the near set of states, α^β are all possible remote state IRs, $\mathbf{M}^{\mu}_{\alpha^u,\alpha^v}$ is a matrix as defined by Eq. (5), and the energy scaling factor $1/(E-E_\beta)$ in Eq. (4) is replaced with the average of $1/(E_{\alpha^u}-E_{\alpha^\beta})$ and $1/(E_{\alpha^v}-E_{\alpha^\beta})$ in the perturbation approximation. Hence, the explicit evaluation of the Hamiltonian using perturbation theory is reduced to finding the form of $\mathbf{M}^{\mu}_{\alpha^u,\alpha^v}$ using symmetry considerations and identifying the relevant IRs for $u_{n,k=0}(r)$.

According to group theoretical methods described at the end of Sec. II, $\mathbf{A}^{\mu,n}_{\alpha^u,\alpha^v}$ matrices are independent of the choice of basis and can be evaluated using any standard basis that transforms according to the relevant IR. As the number of such linearly independent matrices is limited, one can choose symmetry compliant standard bases,[35] which are eigenstates of $\mathbf{J^2}$, $\mathbf{L^2}$, and $\mathbf{S^2}$, to enumerate them. In such a process, the standard bases are expressible as linear combinations of eigenstates of $\mathbf{J}_z$, and the $\mathbf{A}^{\mu,n}_{\alpha^u,\alpha^v}$ matrices can be evaluated using Wigner-Eckart theorem, leading to a single matrix. When multiple linearly independent $\mathbf{A}^{\mu,n}_{\alpha^u,\alpha^v}$ matrices exist, they can be enumerated by different set of standard basis functions. Such standard basis functions belonging to representation α^u and index i may be expressed as

$$|\alpha^u,j^u,i\rangle = \sum_{m=-j^u}^{j^u} c^{u,i}_m|j^u,m\rangle,$$

where the coefficient $c^{u,i}_m$ can be found in Ref. 35. The $\mathbf{k}\cdot\boldsymbol{\pi}$ perturbation can be expressed in terms of the rank 1 irreducible spherical tensor components of $T_1^{q_\mu}$

$$\mathbf{k}\cdot\boldsymbol{\pi} = \sum_\mu k_\mu\pi_\mu = \sum_\mu k_\mu\sum_{q_\mu}d^{\mu}_{q_\mu}T_1^{q_\mu}, \tag{7}$$

where the μ is summed over $\{x,y,z\}$ and q_μ is summed over $\{-1,0,1\}$. The coefficient $d^{\mu}_{q_\mu}$ is dependent on μ and given by $(-i/\sqrt{2},0,i/\sqrt{2})$, $(1/\sqrt{2},0,1/\sqrt{2})$, and $(0,-i,0)$, respectively, for $\mu = x,y,z$. For the standard basis,

$$\begin{aligned}\mathbf{M}^{\mu}_{\alpha^u,\alpha^v;ij} &= \frac{\hbar}{m_0}\langle \alpha^u, j^u, i|\boldsymbol{\pi}_\mu|\alpha^v, j^v, j\rangle \\ &= \frac{\hbar}{m_0}\sum_{q_\mu} d_{q_\mu}\langle \alpha^u, j^u, i|T_1^{q_\mu}|\alpha^v, j^v, j\rangle \\ &= \frac{\hbar}{m_0}\sum_{q_\mu} d_{q_\mu}\sum_{m=-j^u}^{j^u}\sum_{n=-j^v}^{j^v} c_m^{u,i*}c_n^{v,j}\langle j^u, m|T_1^{q_\mu}|j^v, n\rangle \end{aligned} \tag{8a}$$

$$\begin{aligned} &= \frac{\hbar}{m_0}\langle \alpha^u, j^u||T_1||\alpha^v, j^v\rangle \sum_{q_\mu} d_{q_\mu}\sum_{m=-j^u}^{j^u}\sum_{n=-j^v}^{j^v} \\ &\quad\times \left(c_m^{u,i}\right)^* c_n^{v,j}\frac{\langle j^v 1 n q_\mu|j^v 1 j^u m\rangle}{\sqrt{2j^u+1}}, \end{aligned} \tag{8b}$$

$$\mathbf{A}^{\mu}_{\alpha^u,\alpha^v;ij} = \sum_{q_\mu} d_{q_\mu}\sum_{m=-j^u}^{j^u}\sum_{n=-j^v}^{j^v} c_m^{u,i*}c_n^{v,j}\frac{\langle j^v 1 n q_\mu|j^v 1 j^u m\rangle}{\sqrt{2j^u+1}}, \tag{8c}$$

where α^u and α^v are the IRs to which the standard bases $|\alpha^u, j^u, i\rangle$ and $|\alpha^v, j^v, j\rangle$ belong, j^u and j^v are the total angular momentum quantum numbers associated with the standard basis and IRs, $\langle \alpha^u, j^u||T_1||\alpha^v, j^v\rangle$ is the reduced tensor element of T_1 independent of $\{i,j\}$, $c_m^{u,i}, c_n^{u,j}$ are the expansion coefficients of the standard basis function indexed by $\{i,j\}$, and $\langle j^v 1 n q_\mu|j^v 1 j^u m\rangle$ is the Clebsch Gordan (Wigner) coefficient. While the reduced tensor element is an invariant in the case of a central field, it is $\mathbf{J}_z$ quantization direction dependent in a crystal.[37] Once the linearly independent matrices are found, they can be used for other bases, such as the cell periodic functions in the crystal we employ in the perturbation theory.

V. EVALUATION OF HAMILTONIAN MATRIX

Zone-center eigenstates of crystals with diamond lattice form bases of IRs, $\Gamma_6^\pm$, $\Gamma_7^\pm$, and $\Gamma_8^\pm$ of the O_h group, as discussed in Sec. II. Following the general group theoretical method described at end of Sec. II, we can determine the number of linearly independent matrices that describe the interaction between states of IRs, α^u and α^v, from the decomposition of the direct product $\alpha^{u^*} \otimes \alpha^v$ into direct sums. Table II shows the decomposition of direct product of these IRs of the O_h double group.

TABLE II. Product decomposition table of IRs of O_h group. The products of two negative-parity IRs give the same as when both IRs are positive. For each direct product, the two rows in the last 5 columns refer to product of the same and opposite parity respectively.

Direct product	Direct sum	No. of Γ_4^-	No. of Γ_1^+	No. of Γ_3^+	No. of Γ_4^+	No. of Γ_5^+
$\Gamma_8^+ \otimes \Gamma_8^\pm$	$\Gamma_1^\pm \oplus \Gamma_2^\pm \oplus \Gamma_3^\pm$	0	1	1	2	2
	$\oplus 2\Gamma_4^\pm \oplus 2\Gamma_5^\pm$	2	0	0	0	0
$\Gamma_8^+ \otimes \Gamma_7^\pm$	$\Gamma_3^\pm \oplus \Gamma_4^\pm \oplus \Gamma_5^\pm$	0	0	1	1	1
		1	0	0	0	0
$\Gamma_8^+ \otimes \Gamma_6^\pm$	$\Gamma_3^\pm \oplus \Gamma_4^\pm \oplus \Gamma_5^\pm$	0	0	1	1	1
		1	0	0	0	0
$\Gamma_7^+ \otimes \Gamma_7^\pm$	$\Gamma_1^\pm \oplus \Gamma_4^\pm$	0	1	0	1	0
		1	0	0	0	0
$\Gamma_7^+ \otimes \Gamma_6^\pm$	$\Gamma_2^\pm \oplus \Gamma_5^\pm$	0	0	0	0	1
		0	0	0	0	0
$\Gamma_6^+ \otimes \Gamma_6^\pm$	$\Gamma_1^\pm \oplus \Gamma_4^\pm$	0	1	0	1	0
		1	0	0	0	0

Given that the perturbation operator transforms according to the Γ_4^- IR of the O_h group, one can see immediately that the matrix between the Γ_7^+ and $\Gamma_6^\pm$ must be zero since Γ_4^- does not occur in the decomposed direct sum. The parity selection rule also ensures that interactions between states of representations of the same parity are forbidden, including intraband interactions. The interaction of the valence band (Γ_8^+) with the states in the Γ_6^- or Γ_7^- representation can be described by one parameter and one associated constant matrix. The interaction between states in the Γ_8^+ with states in the Γ_8^- representation requires two parameters and two linearly independent constant matrices. However, for a standard basis, direct evaluation using Wigner-Eckart theorem yields a single matrix. This implies that the two scaling constants are coupled, yielding a single-basis-dependent matrix describing the angular part of the interaction and one scaling constant. Generally, this matrix can be used as one of the linearly independent matrices while the complete set of linearly independent matrices can be generated by using different sets of standard basis. The choice of these two linearly independent matrices are, of course, arbitrary. Using the $j = 3/2$ standard basis for the Γ_8^+ and $j = 3/2$ and $j = 5/2$ for the Γ_8^- as listed in Appendix B, two sets of such linearly independent $\mathbf{A}^{\mu,n}_{\Gamma_8^+,\Gamma_8^-}$ matrices are generated. Thus, for two general $\Gamma_8^\pm$ IRs, the perturbation matrix $\mathbf{M}^{\mu}_{\Gamma_8^+,\Gamma_8^-}$ can be written as

$$\mathbf{M}^{\mu}_{\Gamma_8^+,\Gamma_8^-} = \frac{\hbar}{m_0}\left[\xi^1_{\Gamma_8^+,\Gamma_8^-}\mathbf{A}^{\mu,1}_{\Gamma_8^+,\Gamma_8^-} + \xi^2_{\Gamma_8^+,\Gamma_8^-}\mathbf{A}^{\mu,2}_{\Gamma_8^+,\Gamma_8^-}\right]. \tag{9}$$

Using the method described in Sec. IV and Eq. (8c), **A** matrices are evaluated and listed in Appendix C. The first-order interaction matrices ($K = \sum_\mu k_\mu \mathbf{M}^\mu$) are then given by

$$K_{\Gamma_6^+,\Gamma_6^-}(\xi) = K_{\Gamma_7^+,\Gamma_7^-}(\xi) = \frac{\hbar}{m_0}\xi\begin{pmatrix} k_z & k_- \\ k_+ & -k_z \end{pmatrix}, \tag{10a}$$

$$K_{\Gamma_6^-,\Gamma_8^+}(\xi) = \frac{\hbar}{m_0}\xi\begin{pmatrix} -\sqrt{3}k_+ & 2k_z & k_- & 0 \\ 0 & -k_+ & 2k_z & \sqrt{3}k_- \end{pmatrix}, \tag{10b}$$

$$K_{\Gamma_7^-,\Gamma_8^+}(\xi) = \frac{\hbar}{m_0}\xi\begin{pmatrix} k_- & 0 & \sqrt{3}k_+ & 2k_z \\ 2k_z & -\sqrt{3}k_- & 0 & -k_+ \end{pmatrix}, \tag{10c}$$

$$\begin{aligned} K_{\Gamma_8^+,\Gamma_8^-}(\xi_1,\xi_2) &= \frac{\hbar}{m_0}\xi_1\begin{pmatrix} 3k_z & \sqrt{3}k_- & 0 & 0 \\ \sqrt{3}k_+ & k_z & 2k_- & 0 \\ 0 & 2k_+ & -k_z & \sqrt{3}k_- \\ 0 & 0 & \sqrt{3}k_+ & -3k_z \end{pmatrix} \\ &\quad + \frac{\hbar}{m_0}\xi_2\begin{pmatrix} -2k_z & \sqrt{3}k_- & 0 & -5k_+ \\ \sqrt{3}k_+ & 6k_z & -3k_- & 0 \\ 0 & -3k_+ & -6k_z & \sqrt{3}k_- \\ -5k_- & 0 & \sqrt{3}k_+ & 2k_z \end{pmatrix}. \end{aligned} \tag{10d}$$

Given the phase factor placed on the basis by time-reversal symmetry as shown in Appendix B, ξ's are all real for crystals with diamond lattice. Intraband first-order interaction is forbidden by spatial symmetry, so there is no further need to consider the impact of time-reversal symmetry. The form of Eq. (10d) describing interaction between states of $\Gamma_8^{\pm}$ IRs is very different from those used in the literature,[22] which turns out to be the first term in Eq. (30a) for crystals with zincblende lattice, as shown in Sec. IX. The fact there are two linearly independent matrices in Eq. (10d) constitutes a major difference from a single-group approach that gives only one interaction matrix between states of $\Gamma_8^{\pm}$ IRs [see Eq. (32) in Sec. XI for the correct form of this matrix under single-group consideration].

Having obtained the general form of all possible first-order perturbation matrices $\mathbf{M}^{\mu}_{\alpha^u,\alpha^v}$, the Hamiltonian can be constructed according to Eq. (6). The Löwdin term can also be described by various strength parameters and $\mathbf{k}$-dependent matrices. For this purpose, we define the following strength parameters for the near set IRs α^u, α^v and remote IR α^β. If $\alpha^\beta \neq \Gamma_8^{\pm}$, or if $\alpha^\beta = \Gamma_8^{\pm}$ and $\alpha^u \neq \Gamma_8^{\pm}$ and $\alpha^v \neq \Gamma_8^{\pm}$, then

$$\zeta^{\alpha^\beta}_{\alpha^u,\alpha^v} = \frac{\xi_{\alpha^u,\alpha^\beta}\xi_{\alpha^\beta,\alpha^v}\left(2E^{\alpha^\beta} - E^{\alpha^u} - E^{\alpha^v}\right)}{m_0\left(E^{\alpha^u} - E^{\alpha^\beta}\right)\left(E^{\alpha^v} - E^{\alpha^\beta}\right)}. \tag{11}$$

If $\alpha^\beta = \Gamma_8^{-b}$ and $\alpha^u = \Gamma_8^{+a}$, but $\alpha^v \neq \Gamma_8^{\pm}$,

$$\zeta^{\Gamma_8^{-b},1}_{\Gamma_8^{+a},\alpha^v} = \frac{\xi^1_{\Gamma_8^{+a},\Gamma_8^{-b}}\xi_{\Gamma_8^{-b},\alpha^v}\left(2E^{\Gamma_8^{-b}} - E^{\Gamma_8^{+a}} - E^{\alpha^v}\right)}{m_0\left(E^{\Gamma_8^{+a}} - E^{\Gamma_8^{-b}}\right)\left(E^{\alpha^v} - E^{\Gamma_8^{-b}}\right)}, \tag{12a}$$

$$\zeta^{\Gamma_8^{-b},2}_{\Gamma_8^{+a},\alpha^v} = \frac{\xi^2_{\Gamma_8^{+a},\Gamma_8^{-b}}\xi_{\Gamma_8^{-b},\alpha^v}\left(2E^{\Gamma_8^{-b}} - E^{\Gamma_8^{+a}} - E^{\alpha^v}\right)}{m_0\left(E^{\Gamma_8^{+a}} - E^{\Gamma_8^{-b}}\right)\left(E^{\alpha^v} - E^{\Gamma_8^{-b}}\right)}. \tag{12b}$$

If $\alpha^\beta = \Gamma_8^{-b}$, $\alpha^u = \Gamma_8^{+a}$, and $\alpha^v = \Gamma_8^{+c}$ (a and c distinguish different $\Gamma_8^{\pm}$ IRs in interband Löwdin terms),

$$\zeta^{\Gamma_8^{-b},1}_{\Gamma_8^{+a},\Gamma_8^{+c}} = \frac{\xi^1_{\Gamma_8^{+a},\Gamma_8^{-b}}\xi^1_{\Gamma_8^{-b},\Gamma_8^{+c}}\left(2E^{\Gamma_8^{-b}} - E^{\Gamma_8^{+a}} - E^{\Gamma_8^{+c}}\right)}{m_0\left(E^{\Gamma_8^{+a}} - E^{\Gamma_8^{-b}}\right)\left(E^{\Gamma_8^{+c}} - E^{\Gamma_8^{-b}}\right)}, \tag{13a}$$

$$\zeta^{\Gamma_8^{-b},2}_{\Gamma_8^{+a},\Gamma_8^{+c}} = \frac{\xi^2_{\Gamma_8^{+a},\Gamma_8^{-b}}\xi^2_{\Gamma_8^{-b},\Gamma_8^{+c}}\left(2E^{\Gamma_8^{-b}} - E^{\Gamma_8^{+a}} - E^{\Gamma_8^{+c}}\right)}{m_0\left(E^{\Gamma_8^{+a}} - E^{\Gamma_8^{-b}}\right)\left(E^{\Gamma_8^{+c}} - E^{\Gamma_8^{-b}}\right)}, \tag{13b}$$

$$\zeta^{\Gamma_8^{-b},3}_{\Gamma_8^{+a},\Gamma_8^{+c}} = \frac{\xi^1_{\Gamma_8^{+a},\Gamma_8^{-b}}\xi^2_{\Gamma_8^{-b},\Gamma_8^{+c}}\left(2E^{\Gamma_8^{-b}} - E^{\Gamma_8^{+a}} - E^{\Gamma_8^{+c}}\right)}{m_0\left(E^{\Gamma_8^{+a}} - E^{\Gamma_8^{-b}}\right)\left(E^{\Gamma_8^{+c}} - E^{\Gamma_8^{-b}}\right)}, \tag{13c}$$

$$\zeta^{\Gamma_8^{-b},4}_{\Gamma_8^{+a},\Gamma_8^{+c}} = \frac{\xi^2_{\Gamma_8^{+a},\Gamma_8^{-b}}\xi^1_{\Gamma_8^{-b},\Gamma_8^{+c}}\left(2E^{\Gamma_8^{-b}} - E^{\Gamma_8^{+a}} - E^{\Gamma_8^{+c}}\right)}{m_0\left(E^{\Gamma_8^{+a}} - E^{\Gamma_8^{-b}}\right)(E^{\Gamma_8^{+c}} - E^{\Gamma_8^{-b}})}. \tag{13d}$$

Then the Löwdin terms from the situations described in Eqs. (11)–(13) are given by

$$\mathbf{L}^{\alpha^\beta}_{\alpha^u,\alpha^v} = -\frac{\hbar^2}{2m_0}\sum_{\mu,\nu} k_\mu \zeta^{\alpha^\beta}_{\alpha^u,\alpha^v}\mathbf{A}^{\mu}_{\alpha^u,\alpha_\beta}\mathbf{A}^{\nu}_{\alpha_\beta,\alpha^v}k_\nu, \tag{14}$$

$$\mathbf{L}^{\Gamma_8^{-b}}_{\Gamma_8^{+a},\alpha^v} = -\frac{\hbar^2}{2m_0}\sum_{\mu,\nu} k_\mu\left[\zeta^{\Gamma_8^{-b},1}_{\Gamma_8^{+a},\alpha^v}\mathbf{A}^{\mu,1}_{\Gamma_8^{+a},\Gamma_8^{-b}}\mathbf{A}^{\nu}_{\Gamma_8^{-b},\alpha^v} + \zeta^{\Gamma_8^{-b},2}_{\Gamma_8^{+a},\alpha^v}\mathbf{A}^{\mu,2}_{\Gamma_8^{+a},\Gamma_8^{-b}}\mathbf{A}^{\nu}_{\Gamma_8^{-b},\alpha^v}\right]k_\nu, \tag{15}$$

$$\begin{aligned}\mathbf{L}^{\Gamma_8^{-b}}_{\Gamma_8^{+a},\Gamma_8^{+c}} = -\frac{\hbar^2}{2m_0}\sum_{\mu,\nu} k_\mu\Big[&\zeta^{\Gamma_8^{-b},1}_{\Gamma_8^{+a},\Gamma_8^{+c}}\mathbf{A}^{\mu,1}_{\Gamma_8^{+a},\Gamma_8^{-b}}\mathbf{A}^{\nu,1}_{\Gamma_8^{-b},\Gamma_8^{+c}} + \zeta^{\Gamma_8^{-b},2}_{\Gamma_8^{+a},\Gamma_8^{+c}}\mathbf{A}^{\mu,2}_{\Gamma_8^{+a},\Gamma_8^{-b}}\mathbf{A}^{\nu,2}_{\Gamma_8^{-b},\Gamma_8^{+c}}\\ &+ \zeta^{\Gamma_8^{-b},3}_{\Gamma_8^{+a},\Gamma_8^{+c}}\mathbf{A}^{\mu,1}_{\Gamma_8^{+a},\Gamma_8^{-b}}\mathbf{A}^{\nu,2}_{\Gamma_8^{-b},\Gamma_8^{+c}} + \zeta^{\Gamma_8^{-b},4}_{\Gamma_8^{+a},\Gamma_8^{+c}}\mathbf{A}^{\mu,2}_{\Gamma_8^{+a},\Gamma_8^{-b}}\mathbf{A}^{\nu,1}_{\Gamma_8^{-b},\Gamma_8^{+c}}\Big]k_\nu,\end{aligned} \tag{16}$$

respectively. Considering the fourfold degenerate states (valence band Γ_8^+) resulting from the spin-orbit interaction on the Γ_4^- states of the bonding sp^3 orbital, and the remote states as identified in Table I, the contribution from terms in Eq. (15) are absent and terms from Eq. (16) are further simplified because $\zeta^{\Gamma_8^{-b},3}_{\Gamma_8^{+v},\Gamma_8^{+v}} = \zeta^{\Gamma_8^{-b},4}_{\Gamma_8^{+v},\Gamma_8^{+v}}$. Since the intraband matrix elements between the near set states are forbidden by parity, the Löwdin term between Γ_8^{+v} and Γ_8^{+v} is given by

$$\begin{aligned}H_{vv} = &-\frac{\hbar^2}{2m_0}\zeta^{\Gamma_6^-}_{\Gamma_8^{+v},\Gamma_8^{+v}}\begin{pmatrix}3k^2-3k_z^2 & -2\sqrt{3}k_-k_z & -\sqrt{3}k_-^2 & 0\\ -2\sqrt{3}k_+k_z & k^2+3k_z^2 & 0 & -\sqrt{3}k_-^2\\ -\sqrt{3}k_+^2 & 0 & k^2+3k_z^2 & 2\sqrt{3}k_-k_z\\ 0 & -\sqrt{3}k_+^2 & 2\sqrt{3}k_+k_z & 3k^2-3k_z^2)\end{pmatrix}\\ &-\frac{\hbar^2}{2m_0}\zeta^{\Gamma_7^-}_{\Gamma_8^{+v},\Gamma_8^{+v}}\begin{pmatrix}k^2+3k_z^2 & -2\sqrt{3}k_-k_z & \sqrt{3}k_+^2 & 0\\ -2\sqrt{3}k_+k_z & 3k^2-3k_z^2 & 0 & \sqrt{3}k_+^2\\ \sqrt{3}k_-^2 & 0 & 3k^2-3k_z^2 & 2\sqrt{3}k_-k_z\\ 0 & \sqrt{3}k_-^2 & 2\sqrt{3}k_+k_z & k^2+3k_z^2\end{pmatrix}\\ &-\frac{\hbar^2}{2m_0}\zeta^{\Gamma_8^-,1}_{\Gamma_8^{+v},\Gamma_8^{+v}}\begin{pmatrix}3k^2+6k_z^2 & 4\sqrt{3}k_-k_z & 2\sqrt{3}k_-^2 & 0\\ 4\sqrt{3}k_+k_z & 7k^2-6k_z^2 & 0 & 2\sqrt{3}k_-^2\\ 2\sqrt{3}k_+^2 & 0 & 7k^2-6k_z^2 & -4\sqrt{3}k_-k_z\\ 0 & 2\sqrt{3}k_+^2 & -4\sqrt{3}k_+k_z & 3k^2+6k_z^2\end{pmatrix}\end{aligned}$$

$$-\frac{\hbar^2}{2m_0}\zeta^{\Gamma_8^-,2}_{\Gamma_8^{+v},\Gamma_8^{+v}}\begin{pmatrix} 28k^2-24k_z^2 & 4\sqrt{3}k_-k_z & -\sqrt{3}(3k_-^2+5k_+^2) & 0 \\ 4\sqrt{3}k_+k_z & 12k^2+24k_z^2 & 0 & -\sqrt{3}(3k_-^2+5k_+^2) \\ -\sqrt{3}(3k_+^2+5k_-^2) & 0 & 12k^2+24k_z^2 & -4\sqrt{3}k_-k_z \\ 0 & -\sqrt{3}(3k_+^2+5k_-^2) & -4\sqrt{3}k_+k_z & 28k^2-24k_z^2 \end{pmatrix}$$
$$-\frac{\hbar^2}{2m_0}\zeta^{\Gamma_8^-,3}_{\Gamma_8^{+v},\Gamma_8^{+v}}\begin{pmatrix} 6k^2-18k_z^2 & 8\sqrt{3}k_-k_z & -\sqrt{3}(k_-^2+5k_+^2) & 0 \\ 8\sqrt{3}k_+k_z & -6k^2+18k_z^2 & 0 & -\sqrt{3}(k_-^2+5k_+^2) \\ -\sqrt{3}(k_+^2+5k_-^2) & 0 & -6k^2+18k_z^2 & -8\sqrt{3}k_-k_z \\ 0 & -\sqrt{3}(k_+^2+5k_-^2) & -8\sqrt{3}k_+k_z & 6k^2-18k_z^2 \end{pmatrix}, \tag{17}$$

where $k_\pm = k_x \pm ik_y$ and $k^2 = k_x^2 + k_y^2 + k_z^2$. Inspection of Table I shows that $\zeta^{\Gamma_6^-}_{\Gamma_8^{+v},\Gamma_8^{+v}}$ is the interaction strength parameter between the valence band states and the two-fold degenerate states (conduction band), resulting from spin-orbit perturbation on the Γ_4^- of the antibonding $(sp^3)^*$ orbital; $\zeta^{\Gamma_7^-}_{\Gamma_8^{+v},\Gamma_8^{+v}}$ is the strength parameter for interaction with the two-fold degenerate states resulting from spin-orbit perturbation on the Γ_1^+ state of the antibonding $(sp^3)^*$ orbital. The parameters $\zeta^{\Gamma_8^-,1-3}_{\Gamma_8^{+v},\Gamma_8^{+v}}$ describe the interaction between valence band states and its counterpart in the antibonding $(sp^3)^*$ orbital.

These results appear to suggest that one needs five ζ parameters to specify the valence band Hamiltonian in contradiction to the theory of invariants. It turns out that there are only three linearly independent matrices among the five in Eq. (17), and no new invariant is added beyond the three necessary parameters. The Luttinger parameters are related to those defined in Eqs. (11)–(13) by

$$\gamma_1 = 2\zeta^{\Gamma_6^-}_{\Gamma_8^{+v};\Gamma_8^{+v}} + 2\zeta^{\Gamma_7^-}_{\Gamma_8^{+v};\Gamma_8^{+v}} + 5\zeta^{\Gamma_8^-,1}_{\Gamma_8^{+v};\Gamma_8^{+v}} + 20\zeta^{\Gamma_8^-,2}_{\Gamma_8^{+v};\Gamma_8^{+v}}, \tag{18a}$$

$$\gamma_2 = \zeta^{\Gamma_6^-}_{\Gamma_8^{+v};\Gamma_8^{+v}} - \zeta^{\Gamma_7^-}_{\Gamma_8^{+v};\Gamma_8^{+v}} - 2\zeta^{\Gamma_8^-,1}_{\Gamma_8^{+v};\Gamma_8^{+v}} + 8\zeta^{\Gamma_8^-,2}_{\Gamma_8^{+v};\Gamma_8^{+v}} + 6\zeta^{\Gamma_8^-,3}_{\Gamma_8^{+v};\Gamma_8^{+v}}, \tag{18b}$$

$$\gamma_3 = \zeta^{\Gamma_6^-}_{\Gamma_8^{+v};\Gamma_8^{+v}} + \zeta^{\Gamma_7^-}_{\Gamma_8^{+v};\Gamma_8^{+v}} - 2\zeta^{\Gamma_8^-,1}_{\Gamma_8^{+v};\Gamma_8^{+v}} - 2\zeta^{\Gamma_8^-,2}_{\Gamma_8^{+v};\Gamma_8^{+v}} - 4\zeta^{\Gamma_8^-,3}_{\Gamma_8^{+v};\Gamma_8^{+v}}, \tag{18c}$$

$$\mu = (\gamma_3 - \gamma_2)/2 = \zeta^{\Gamma_7^-}_{\Gamma_8^{+v};\Gamma_8^{+v}} - 5\zeta^{\Gamma_8^-,2}_{\Gamma_8^{+v};\Gamma_8^{+v}} - 5\zeta^{\Gamma_8^-,3}_{\Gamma_8^{+v};\Gamma_8^{+v}}, \tag{18d}$$

$$\overline{\gamma} = (\gamma_3 + \gamma_2)/2 = \zeta^{\Gamma_6^-}_{\Gamma_8^{+v};\Gamma_8^{+v}} - 2\zeta^{\Gamma_8^-,1}_{\Gamma_8^{+v};\Gamma_8^{+v}} + 3\zeta^{\Gamma_8^-,2}_{\Gamma_8^{+v};\Gamma_8^{+v}} + \zeta^{\Gamma_8^-,3}_{\Gamma_8^{+v};\Gamma_8^{+v}}. \tag{18e}$$

Given the linear dependence between the five matrices, the relationship above cannot be inverted without additional information. One, however, can draw some conclusions from the relations in Eq. (18). The warping term in the form of $\mu = (\gamma_3 - \gamma_2)/2$ arises from the interaction of valence band with antibonding states in the Γ_8^- and Γ_7^- IRs. Therefore, it has its origin in all the antibonding $(sp^3)^*$ orbital as opposed to the s-like states[38] with Γ_7^- symmetry alone. Single-group-based perturbation theory in the literature would have just one matrix in place of the last three in Eq. (17) due to restriction on the $\Gamma_8^\pm$ basis used in the matrix calculation. However, this is equivalent to removal of independence of the three parameters $(\zeta^{\Gamma_8^-,1-3}_{\Gamma_8^{+v},\Gamma_8^{+v}})$ in front of these matrices. Such result would still be in agreement with those from the method of invariant.

Interband Löwdin terms (such as those between the valence band Γ_8^+ and the valence spin-orbit split-off band Γ_7^+) can be constructed in the same way as defined in Eq. (6). As an example, the Löwdin term between Γ_8^{+v} and Γ_7^{+v} is given below:

$$H_{vs} = -\frac{\hbar^2}{2m_0}\zeta^{\Gamma_7^-}_{\Gamma_8^+,\Gamma_7^+}\begin{pmatrix} 3k_+k_z & \left(k_x^2+k_y^2-2k_z^2\right) \\ -\sqrt{3}k_+^2 & \sqrt{3}k_+k_z \\ \sqrt{3}k_-k_z & \sqrt{3}k_-^2 \\ -\left(k_x^2+k_y^2-2k_z^2\right) & 3k_-k_z \end{pmatrix}$$
$$-\frac{\hbar^2}{2m_0}\zeta^{\Gamma_8^-,1}_{\Gamma_8^+,\Gamma_7^+}\begin{pmatrix} 3k_+k_z & -3\left(k_x^2+k_y^2-2k_z^2\right) \\ \sqrt{3}(k_+^2+2k_-^2) & \sqrt{3}k_+k_z \\ \sqrt{3}k_-k_z & -\sqrt{3}(k_-^2+2k_+^2) \\ 3\left(k_x^2+k_y^2-2k_z^2\right) & 3k_-k_z \end{pmatrix}$$
$$-\frac{\hbar^2}{2m_0}\zeta^{\Gamma_8^-,2}_{\Gamma_8^+,\Gamma_7^+}\begin{pmatrix} -12k_+k_z & 2\left(k_x^2+k_y^2-2k_z^2\right) \\ -\sqrt{3}(3k_-^2-k_+^2) & -4\sqrt{3}k_+k_z \\ -4\sqrt{3}k_-k_z & \sqrt{3}(3k_+^2-k_-^2) \\ -2\left(k_x^2+k_y^2-2k_z^2\right) & -12k_-k_z \end{pmatrix}. \tag{19}$$

This interband Löwdin term appears to be inconsistent with those given in the literature obtained from perturbation theory[3,17] or theory of invariant.[13–15] An incorrectly ordered odd basis for Γ_8 (see Sec. IX for detail) was used to derive the interband Löwdin term for crystals with zincblende lattice from perturbation theory. The generator matrices (Cartesian matrices T_i, U_i and T_{ij}, U_{ij}, where $i,j \in \{x,y,z\}$ in Ref. 15) were actually obtained from basis of the $\Gamma_8^+,(j = 3/2)$ and $\Gamma_6^+,(j = 1/2)$ instead of that of the Γ_7^+. Therefore, they are inappropriate for the generation of the Löwdin term between the Γ_8^+ and Γ_7^+ IRs. Thus, Eq. (19) should be compared with

$$H_{vs} = -\frac{\hbar^2}{2m_0}\begin{pmatrix} \sqrt{\frac{3}{2}}S^* & \sqrt{2}Q \\ \sqrt{2}R^* & \sqrt{\frac{1}{2}}S^* \\ \sqrt{\frac{1}{2}}S & -\sqrt{2}R \\ -\sqrt{2}Q & \sqrt{\frac{3}{2}}S \end{pmatrix}, \tag{20}$$

where $Q = \gamma_2'(k_\parallel^2 - 2k_z^2)$, $S = 2\sqrt{3}\gamma_3' k_- k_z$, and $R = \sqrt{3}(-\overline{\gamma'}k_-^2 + \mu' k_+^2)$. This expression is obtained from method of invariant (see Sec. VII and Appendix D) using correct basis. There are only two linearly independent matrices among the three in Eq. (19), which is in agreement with Eq. (20), leading to two invariants (γ_2' and γ_3'). The Luttinger invariants for this interband block are given in terms of ζ parameters by

$$\gamma_2' = \frac{1}{\sqrt{2}}\left[\zeta^{\Gamma_7^-}_{\Gamma_8^+,\Gamma_7^+} - 3\zeta^{\Gamma_8^-,1}_{\Gamma_8^+,\Gamma_7^+} + 2\zeta^{\Gamma_8^-,2}_{\Gamma_8^+,\Gamma_7^+}\right], \tag{21a}$$

$$\gamma_3' = \frac{1}{\sqrt{2}}\left[4\zeta^{\Gamma_8^-,2}_{\Gamma_8^+,\Gamma_7^+} - \zeta^{\Gamma_8^-,1}_{\Gamma_8^+,\Gamma_7^+} - \zeta^{\Gamma_7^-}_{\Gamma_8^+,\Gamma_7^+}\right]. \tag{21b}$$

Despite the fact that the valence band and spin-split-off band originate from the same atomic site wave function, the invariants are quite different compared with corresponding terms in Eq. (18). Apart from the obvious difference when scaling interaction parameters by terms containing eigenenergies, both the forbidden $\Gamma_7^+ : \Gamma_6^-$ direct interaction and mixture of characters derived from different single-group IRs contribute. This may be compared with the outcome of single-group work where the invariants would be the same across the valence band/spin-split-off band block.[39]

The effect of this change in the interband block Hamiltonian on the dispersion can be seen in Fig. 1, where a six-band model is applied to Ge. The Luttinger parameters are chosen to be the same in all the blocks, as in a single-group formulation[39] with $\gamma_1 = 13.35$, $\gamma_2 = 4.25$, and $\gamma_3 = 5.69$ (Ref. 40). Along the $\langle 100\rangle$ direction, it is clear that the coupling between the heavy-hole and light-hole states are enhanced, whereas the coupling between the light-hole and spin-split-off band is reduced in the double-group formulation compared with six-band model in the literature.[22] Along the $\langle 111\rangle$ direction, there is a similar reduction of coupling between the light-hole and spin-split-off states but the heavy-hole band essentially remains the same. The use of double-group formulation indicates that the Luttinger parameters are different for each block (interaction matrix) and there is a modification of dispersion away from zone center.

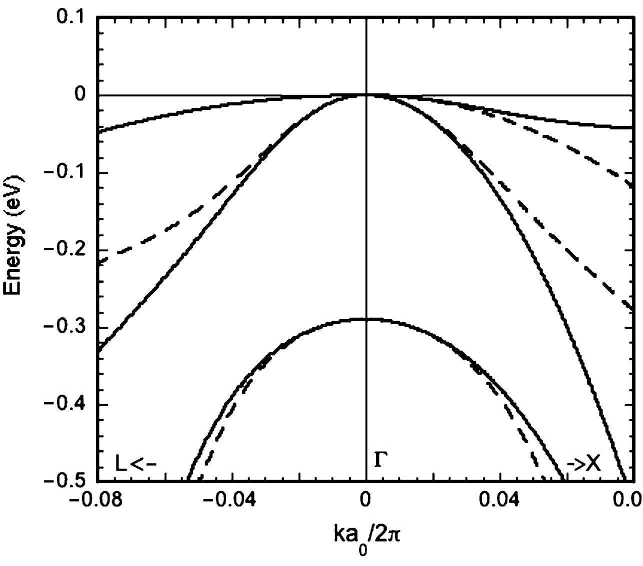

FIG. 1. Comparison of sixband models applied to Ge: present work (solid line), literature (broken line).

With the use of hybridized orbital as atomic site wave functions, the effect of higher atomic orbitals, such as the d or f orbital, are accounted for through configurations. Thus, a 16-band model is all that is permitted under this scheme. Higher unoccupied states, beyond the bonding and antibonding configuration, may lead to states belonging to multiple occurrences of $\Gamma_6^\pm$,$\Gamma_7^\pm$ and/or $\Gamma_8^\pm$ IRs. These will simply add to the ζ parameter describing the remote interactions with states of the given symmetry. Moving states in the remote set into the near set will have the reverse effect. This has been demonstrated by Pidgeon and Brown,[17] but modification of the Luttinger parameters derived from single-group considerations is rather complicated. As the linearly independent matrices $\mathbf{A}^{\mu,n}_{\alpha^u,\alpha^v}$ are basis independent, the effect on Eq. (17) is simply an addition or subtraction of ζ parameters in front of the appropriate matrices. In terms of near set interaction in multiband implementation, the matrix elements can be readily calculated using the $\mathbf{A}^{\mu,n}_{\alpha^u,\alpha^v}$ matrices and appropriate scaling constants. Any additional Löwdin term can be constructed the same way using Eq. (6). The form of Hamiltonian for an eight-band model, as well as other building blocks for multiband $\mathbf{k}\cdot\mathbf{p}$ theory, is given in Appendix D.

VI. METHOD OF INVARIANT

The $\mathbf{k}\cdot\mathbf{p}$ theory has also been formulated from method of invariant with limited assumptions on the existence of one-electron Schrödinger equation and its solutions. In this approach, the Hamiltonian described by some perturbation variable $\mathscr{K}$ should be invariant under the action of an element g of its symmetry group G; that is,

$$\mathscr{D}^{\alpha^u}(g)\mathscr{H}_{\alpha^u\alpha^v}(g^{-1}\mathscr{K})\mathscr{D}^{\alpha^v}(g^{-1}) = \mathscr{H}_{\alpha^u\alpha^v}(\mathscr{K}), \tag{22}$$

where $\mathscr{D}^{\alpha^u}(g)$ and $\mathscr{D}^{\alpha^v}(g^{-1})$ are representation matrices of the IRs whose bases are used to define the Hamiltonian. Allowing α^u and α^v to be different permits investigation of the interband terms as well as intraband terms. The theory of invariants, as described by Bir and Pikus,[8] considers the Hamiltonian as products of appropriate generator matrices $X_I^{\gamma,n}$ of dimension $l_{\alpha^u} \times l_{\alpha^v}$ and irreducible components of perturbation $\mathscr{K}_I^{m,\gamma}$, which are formed from products of Cartesian components of $\mathscr{K}_I^m$ of a particular type (e.g., quadratic in components of $\mathbf{k}$, strain, etc.) indexed by m; that is,

$$\mathscr{H}_{\alpha^u\alpha^v}(\mathscr{K}) = \sum_\gamma\sum_I\left\{\sum_n\sum_m a_\gamma^{m,n} X_I^{\gamma,n}\mathscr{K}_I^{m,\gamma}\right\}, \tag{23}$$

where $a_\gamma^{m,n}$ are the invariant parameters for generator indexed by n and irreducible perturbation indexed by m, Γ^γ is the IR to which $X_I^{\gamma,n}$ and $\mathscr{K}_I^{m,\gamma}$ forms a basis, I is the index of the basis (component) within the Γ^γ IR, and n is the index of linearly independent generators which transform according to Γ^γ. The Hamiltonian defined in Eq. (23) satisfies the invariant condition defined in Eq. (22). (In a very crude way, we are forming a "scalar" product between irreducible components of generators and a perturbation with a result that is invariant under rotation.) This expression differs from those in the literature and allows explicitly for more than one linearly

TABLE III. Generating operators and corresponding perturbation for diamond lattice.

Irreducible perturbation component ($\mathscr{K}_I$)	Spatial parity	Time reversal parity	Irrep (γ)	Invariant	Generating operators
$1,k^2$	Even	Even	Γ_1^+	γ_1	T_0^0
$\sqrt{3}(k_z^2-k^2/3)$ $k_x^2-k_y^2$	Even	Even	Γ_3^+	γ_2	T_2^0 $(T_2^2+T_2^{-2})/\sqrt{2}$
k_yk_z k_zk_x k_xk_y	Even	Even	Γ_5^+	γ_3,γ_3'	$i(T_2^1+T_2^{-1})/\sqrt{2}$ $-(T_2^1-T_2^{-1})/\sqrt{2}$ $i(T_2^{-2}-T_2^2)/\sqrt{2}$
k_x k_y k_z	Odd	Odd	Γ_4^-	ξ_1,ξ_2	$i(T_1^1-T_1^{-1})/\sqrt{2}$ $(T_1^1+T_1^{-1})/\sqrt{2}$ $-iT_1^0$

independent generator which transforms according to Γ^γ IR and multiple types of perturbation indexed by m. For the case under consideration here, the types of perturbation $\mathscr{K}^m$ are the linear and quadratic k terms. Other types of perturbation, such as strain, can be be incorporated in the same way as described by Bir and Pikus.[8]

The linear components of wave-vector transform according to Γ_4^- in the same way as an irreducible spherical tensor of rank 1 (T_1^q). Thus, the generator for this perturbation is naturally a linear combination of the index (angular)-dependent part of the matrix representation of T_1^q with respect to the energy eigenstates in representations α^u and α^v. These generators are equilvalent to $\mathbf{A}^\mu$ matrices we calculated in Sec. V and tabulated in Appendix C. The products of components of wave vector $k_\mu k_\nu,\mu,\nu \in \{x,y,z\}$ form a Cartesian tensor of rank 2. It can be expressed as a linear combination of components with different transformation properties:

$$k_\mu \cdot k_\nu = \underbrace{\frac{\mathbf{k}\cdot\mathbf{k}}{3}\delta_{\mu\nu}}_{\text{scalar}} + \underbrace{\frac{[k_\mu,k_\nu]}{2}}_{\text{axial vector}} + \underbrace{\left(\frac{\{k_\mu,k_\nu\}}{2} - \frac{\mathbf{k}\cdot\mathbf{k}}{3}\delta_{\mu\nu}\right)}_{T_2^q}, \tag{24}$$

where $[k_\mu,k_\nu]$ and $\{k_\mu,k_\nu\}$ are the commutator and anticommutator, respectively. The scalar transforms according to an irreducible spherical tensor of rank 0 (T_0^0), the axial vector transforms like angular momentum J, and the third term is a traceless symmetric Cartesian tensor which transforms like an irreducible spherical tensor of rank 2 (T_2^q) [irreducible under SO(3)]. Under the O_h point group, they transform according to Γ_1^+,Γ_4^+, and $\Gamma_3^+ \oplus \Gamma_5^+$ IRs, respectively. The decomposition of the second-rank "irreducible" spherical tensor follows the way in which the degeneracy of the $l=2$, d orbital is lifted under the action of the crystal field. To block diagonalize the rank 2 spherical tensor under the $\Gamma_3^+ \oplus \Gamma_5^+$ representations, a linear transformation of the components are made:

$$\Gamma_3^+ \begin{cases} k_2^0 & \sim \frac{1}{4}\sqrt{\frac{15}{\pi}}\sqrt{3}\left(k_z^2-k^2/3\right), \\ \left(k_2^2+k_2^{-2}\right)/\sqrt{2} & \sim \frac{1}{4}\sqrt{\frac{15}{\pi}}\left(k_x^2-k_y^2\right), \end{cases} \tag{25}$$

$$\Gamma_5^+ \begin{cases} i\left(k_2^1+k_2^{-1}\right)/\sqrt{2} \sim \frac{1}{2}\sqrt{\frac{15}{\pi}}\{k_y,k_z\}/2, \\ \left(k_2^{-1}-k_2^1\right)/\sqrt{2} \sim \frac{1}{2}\sqrt{\frac{15}{\pi}}\{k_z,k_x\}/2, \\ i\left(k_2^{-2}-k_2^2\right)/\sqrt{2} \sim \frac{1}{2}\sqrt{\frac{15}{\pi}}\{k_x,k_y\}/2. \end{cases} \tag{26}$$

The generator matrices are then naturally obtained from the index (angular)-dependent part of the matrices from the operators T_0^0 and T_2^q between states which form the bases of representations α^u and α^v. This second-rank tensor operator is reducible under the O_h group and appropriate linear combinations of the T_2^q matrices are used to ensure block diagonal form. The operators for evaluating generators and irreducible perturbation components are listed in Table III.

It is important to recognize that these generators are dependent on representation, not on specific basis. Hence, they can be obtained for a specific known basis and would be generally applicable to all bases of the relevant IR.

The effects of external magnetic field on the Hamiltonian are also frequently treated under method of invariant utilizing the antisymmetric products of wave-vector components.[15] The relation between magnetic field and antisymmetric products of wave-vector components is established through the commutator of wave-vector components as operators on the envelope function.[3] However, the vector potential necessary for the description of external magnetic field breaks the translational symmetry. The treatment of such perturbation requires the envelope function theory.[41] In any case, the time-reversal properties of quadratic k terms is different from that of the magnetic field. The treatment of the Zeeman interaction term using the antisymmetric products of wave-vector component and under the **k** · **p** framework may be inappropriate.

VII. GENERATORS IN METHOD OF INVARIANT

The number of linearly independent matrices, or generators in the present context, can be obtained using the same group theoretical techniques described at the end of Sec. II. For an irreducible perturbation component $\mathscr{K}^\gamma$ to make a contribution, some elements of the matrix representation of the generating operator must be nonzero. The contribution would be permitted by symmetry if the IR of the generating operator, which is the same as the IR of the irreducible perturbation components Γ^{γ}, occurs in the decomposition of $\alpha^{u*} \otimes \alpha^{v}$. The number of independent generators is given by the number of times Γ^{γ} occurs in the decomposition. The perturbation consists of wave-vector components that are linear, transforming according to Γ_4^-, or quadratic, transforming according to $\Gamma_4^- \otimes \Gamma_4^- = \Gamma_1^+ \oplus \Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_5^+$ of the O_h group. Table II shows the decomposition of a direct product between all possible IRs of the energy eigenstates. It is clear that linear k terms can only exist between states with IRs of opposite parity, whereas the quadratic term can only exist between states with IRs of the same parity. In addition, linear k terms are forbidden between states of $\Gamma_7^{\pm}$ and $\Gamma_6^{\mp}$ IRs. There are two linearly independent generators for linear and quadratic k terms transforming according to Γ_4^- and Γ_5^+ between bases of $\Gamma_8^{\pm}$ and $\Gamma_8^{\mp}$.

Generators[42] applicable to all allowed double group bases of IRs, are obtained using an irreducible spherical tensor operator constructed from standard single group basis. A single irreducible spherical tensor operator is used for each IR of the perturbation, independent of the double group bases associated with the zone center energy eigenfunctions. When multiple linearly independent generators exist, as is the case when dealing with $\Gamma_8^{\pm}$, multiple sets of standard double basis functions are required. The methodology for this calculation is exactly the same as for the **A** matrices or Cartesian components derived from T_1^q. The second linearly independent generator for $\Gamma^{\gamma} = \Gamma_5^+$ between $\Gamma_8^+ : \Gamma_8^+$ IRs, is ruled out on time-reversal symmetry grounds,[6] so the associated invariant $\gamma_3' = 0$. Thus, the Hamiltonian between states of any IRs can be constructed using Eq. (23). The generators required for construction of an eight-band model are listed in Table IV. For linear k terms, the generators are the $\mathbf{A}^{\mu}$ matrices listed in Appendix C. The generators for the $\Gamma_7^+ : \Gamma_7^+$ block are identical to those of the $\Gamma_6^- : \Gamma_6^-$ block. Only those generator matrices allowed by symmetry are listed. The Hamiltonian for the eight-band case is shown in Appendix D and has exactly the same form as the Hamiltonian obtained from perturbation theory in Sec. V.

The Löwdin term between $\Gamma_8^+ : \Gamma_6^+$ IRs is also shown in Appendix D, even though it does not occur within the eight-band model. However, it has the same form as those used in the literature in place of the $\Gamma_8^+ : \Gamma_7^+$ interband block. It is easy to see that using the incorrect basis of Γ_7^+ to evaluate the generators has led to the error in the literature.[13] In addition, the odd basis used[3,15] for Γ_8 IR of the T_d group does not strictly transform according to Γ_8 (see Sec. IX). This error lead to incorrect interband Löwdin term but it does not effect the intraband Löwdin terms in the four-band model.

The approach adopted here to obtain generators differs from those in the literature where the enumeration of generators is based on a single set of standard bases and multiple forms of generating operators. These generating operators, transforming like the irreducible perturbation, were obtained from components of orbital, spin, total angular momentum, and their products.[3,8,13] They all have even spatial parity and would not be appropriate for first-order interactions where the perturbation operator $\boldsymbol{\pi}$ has odd spatial parity.

The results from the theory of invariants may be directly compared with double-group perturbation theory developed here, as there is no restriction on the basis of the $\Gamma_8^{\pm}$ IRs. Comparison with single-group formulation must be subjected to the single-group assumption which restricts the basis of $\Gamma_8^{\pm}$ IRs. In particular, there are two linearly independent matrices describing interaction between $\Gamma_8^{\pm}$ IRs [generators for the Γ_4^- irreducible perturbation, or $\mathbf{A}^{\mu}$ matrices, or Eq. (10d)], but only one in the single-group formulation [Eq. (32)]. The single-group result may, however, be obtained from the method of invariant by removing the independence of the two scaling parameters or through use of specific basis as shown in Sec. XI.

VIII. OPERATOR ORDERING IN ENVELOPE FUNCTION THEORY

Effective mass theory[3] and exact envelope function theory[7] have played a vital role in the studies of impurity states in semiconductors and semiconductor heterostructures such as quantum wells and dots. In a practical implementation of the exact envelope function theory, the nonlocal terms are generally ignored and the validity of such approximation has been discussed by Burt.[43] The boundary conditions between different semiconductors breaks translational symmetry and has been shown to cause mixing of the light-hole states in the valance band due to the "C" term and operator ordering in the "S" term.[7,11,44,45] In deriving such interfacial and ordered terms in the Hamiltonian, the wave-vector components are treated as operators on the envelope function and do not commute with material parameters in the Löwdin term[45] at the interface. Previous work has been based on single-group formulation of the $\mathbf{k}\cdot\mathbf{p}$ theory.

The double-group formulation and methodology developed here also requires similar consideration when applied to the studies of heterojunctions. The formulation can easily be extended in the same way, by considering k_{μ} and k_{ν} in Eq. (6) and Eqs. (14)–(16) as operators on envelope functions.[11,44,45] As operators, $\hat{k_{\mu}}$ and $\hat{k_{\nu}}$ in Eq. (6) do not commute with the material-dependent terms at interfaces. An ordered version of the Hamiltonian is given below for a four-band model with ζ parameters becoming spatially dependent (subscripts are dropped for brevity):

$$H = -\frac{\hbar^2}{2m_0}\begin{pmatrix} P+Q & -S & R & Z \\ -S^{\dagger} & P-Q & C & R \\ R^{\dagger} & C^{\dagger} & P^*-Q^* & (S^{\dagger})^* \\ Z^{\dagger} & R^{\dagger} & S^* & P^*+Q^* \end{pmatrix},$$

where

$$\begin{aligned} P &= \hat{k_-}[2\zeta^{\Gamma_6^-} + 3.5\zeta^{\Gamma_8^-,1} + 6\zeta^{\Gamma_8^-,2}]\hat{k_+} \\ &\quad + \hat{k_+}[2\zeta^{\Gamma_7^-} + 1.5\zeta^{\Gamma_8^-,1} + 14\zeta^{\Gamma_8^-,2}]\hat{k_-} + \hat{k_z}\gamma_1\hat{k_z}, \\ Q &= \hat{k_-}[\zeta^{\Gamma_6^-} - 0.5\zeta^{\Gamma_8^-,1} - 3\zeta^{\Gamma_8^-,2} + 6\zeta^{\Gamma_8^-,3}]\hat{k_+} \\ &\quad + \hat{k_+}[-\zeta^{\Gamma_7^-} - 1.5\zeta^{\Gamma_8^-,1} + 11\zeta^{\Gamma_8^-,2}]\hat{k_-} + \hat{k_z}(2\gamma_2)\hat{k_z}, \\ S &= \hat{k_-}\sqrt{3}(2\zeta^{\Gamma_6^-} - \zeta^{\Gamma_8^-,1} - 6\zeta^{\Gamma_8^-,2} - 7\zeta^{\Gamma_8^-,3})\hat{k_z} \\ &\quad + \hat{k_z}\sqrt{3}(2\zeta^{\Gamma_7^-} - 3\zeta^{\Gamma_8^-,1} + 2\zeta^{\Gamma_8^-,2} - \zeta^{\Gamma_8^-,3})\hat{k_-}, \\ R &= -\sqrt{3}\hat{k_-}\overline{\gamma}\hat{k_-} + \sqrt{3}\hat{k_+}\mu\hat{k_+}, \\ C &= \hat{k_-}(-2\zeta^{\Gamma_6^-} - 2\zeta^{\Gamma_8^-,1} + 18\zeta^{\Gamma_8^-,2} - 9\zeta^{\Gamma_8^-,3})\hat{k_z} \\ &\quad + \hat{k_z}(2\zeta^{\Gamma_6^-} + 2\zeta^{\Gamma_8^-,1} - 18\zeta^{\Gamma_8^-,2} + 9\zeta^{\Gamma_8^-,3})\hat{k_-}, \end{aligned}$$

TABLE IV. Generator matrices for $\Gamma_8^+ : \Gamma_8^+$, $\Gamma_8^+ : \Gamma_7^+$, and $\Gamma_6^- : \Gamma_6^-$ block. $\sigma_{x,y,z}$ are Pauli matrices.

α,β	γ	Generating operator	Generators (X_I): scaled within each occurrence of IR γ
$\Gamma_8^+ : \Gamma_8^+$	Γ_1^+	T_0^0	**1**
	Γ_3^+	$\begin{cases} T_2^0 \\ (T_2^2 + T_2^{-2})/\sqrt{2} \end{cases}$	$\sqrt{3}\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$ $\sqrt{3}\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$
	Γ_5^+	$\begin{cases} i(T_2^1 + T_2^{-1})/\sqrt{2} \\ -(T_2^1 - T_2^{-1})/\sqrt{2} \\ i(T_2^{-2} - T_2^2)/\sqrt{2} \end{cases}$	$2\sqrt{3}i\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ $2\sqrt{3}\begin{pmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ $2\sqrt{3}i\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$ $2\sqrt{3}i\begin{pmatrix} 0 & 1 & 0 & 5\sqrt{3} \\ 9 & 0 & -5\sqrt{3} & 0 \\ 0 & -5\sqrt{3} & 0 & 9 \\ 5\sqrt{3} & 0 & 1 & 0 \end{pmatrix}$ $2\sqrt{3}\begin{pmatrix} 0 & -1 & 0 & 5\sqrt{3} \\ 9 & 0 & 5\sqrt{3} & 0 \\ 0 & -5\sqrt{3} & 0 & -9 \\ -5\sqrt{3} & 0 & 1 & 0 \end{pmatrix}$ $2\sqrt{3}i\begin{pmatrix} 0 & 0 & -14 & 0 \\ 0 & 0 & 0 & 6 \\ -6 & 0 & 0 & 0 \\ 0 & 14 & 0 & 0 \end{pmatrix}$
$\Gamma_8^+ : \Gamma_7^+$	Γ_3^+	$\begin{cases} (T_2^2 + T_2^{-2})/\sqrt{2} \\ T_2^0 \end{cases}$	$\sqrt{3}\begin{pmatrix} 0 & 0 \\ -1 & 0 \\ 0 & 1 \\ 0 & 0 \end{pmatrix}$ $\sqrt{3}\begin{pmatrix} 0 & -1 \\ 0 & 0 \\ 0 & 0 \\ 1 & 0 \end{pmatrix}$
	Γ_5^+	$\begin{cases} i(T_2^1 + T_2^{-1})/\sqrt{2} \\ -(T_2^1 - T_2^{-1})/\sqrt{2} \\ i(T_2^{-2} - T_2^2)/\sqrt{2} \end{cases}$	$2\sqrt{3}i\begin{pmatrix} -\frac{\sqrt{3}}{2} & 0 \\ 0 & -\frac{1}{2} \\ \frac{1}{2} & 0 \\ 0 & \frac{\sqrt{3}}{2} \end{pmatrix}$ $2\sqrt{3}\begin{pmatrix} -\frac{\sqrt{3}}{2} & 0 \\ 0 & -\frac{1}{2} \\ -\frac{1}{2} & 0 \\ 0 & -\frac{\sqrt{3}}{2} \end{pmatrix}$ $2\sqrt{3}i\begin{pmatrix} 0 & 0 \\ 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{pmatrix}$
$\Gamma_6^- : \Gamma_6^-$	Γ_1^+	T_0^0	**1**
	Γ_4^+	J_x, J_y, J_z	$\sigma_x, \sigma_y, \sigma_z$

$$Z = \hat{k}_+(2\zeta^{\Gamma_7^-} - 10\zeta^{\Gamma_8^-,2} + 15\zeta^{\Gamma_8^-,3})\hat{k}_z$$
$$+\hat{k}_z(-2\zeta^{\Gamma_7^-} + 10\zeta^{\Gamma_8^-,2} - 15\zeta^{\Gamma_8^-,3})\hat{k}_+,$$

where the †'s indicate conjugation and reversal of the operator ordering. The interfacial coupling of the heavy-hole states via the Z term was not identified when operator ordering was first established using single-group formulation.[7,11,44] Ordering under double-group formulation differs from the literature, based on single-group formulation. Apart from the definition of material parameters, the forms of both the interband Hamiltonian between the valence band and spin-split-off band (see Sec. V) and the symmetry of the conduction band minimum state at zone center are different (see Sec. X). The latter modifies the weighting of different interactions in each part of the ordered term. A similar ordering term would exist in the conduction and spin-orbit bands if they were brought into the near set in an eight-band model. The interfacial orientation dependence of operator ordering comes from the $\mathbf{J}_z$ quantization direction dependence of the ζ parameters through that of the reduced tensor elements.[46]

IX. ZINCBLENDE LATTICE

The difference between a zincblende lattice (T_d group) and a diamond lattice (O_h group) is the lack of inversion symmetry. In a zincblende crystal, there are no equivalent atomic sites within the primitive cell and hence the equivalence representation is simply Γ_1. The starting bonding and antibonding states must again be constructed from the *spd* hybridized orbitals at the two inequivalent atomic sites within the Wigner-Seitz cell of the face centered cubic lattice. If one follows the same arguments made in Sec. II, the symmetries of the valence band and its spin-split-off band at the Γ point are Γ_8 and Γ_7, respectively, while the antibonding counterparts are Γ_8 and Γ_7. States derived from the Γ_1 of the bonding and antibonding *spd* orbitals both have Γ_6 symmetry. As argued in the case of Ge, the lowest conduction band zone center state is derived from the spin-split-off from the antibonding (*spd*) orbitals, and has Γ_7 symmetry in crystals with a zincblende lattice.

The energy eigenfunctions at the zone center form basis of the Γ_6, Γ_7, and Γ_8 IRs. The standard basis functions for these IRs of the T_d group may be derived from that of the O_h group provided appropriate compatibility relations between the T_d and O_h groups are used. The compatibility relations between the representations of the T_d and O_h groups are given by Koster *et al.*[26] and summarized in Table V.

With the exception of the Γ_8^- and Γ_3^- IRs of the O_h group, the representation matrices between compatible IRs of the O_h and T_d groups are identical for common elements of the groups. Thus, basis functions of O_h group IRs can be used directly in compatible IRs of T_d group. While compatible, the representation matrices of the Γ_8^- (O_h) and Γ_8 (T_d) group differ in sign for the improper rotational elements common to the O_h and T_d groups.[36] Thus, they must be equivalent and linked by a unitary transformation. Hence, the basis functions

TABLE V. Compatibility relations between representations of the O_h and T_d group.

O_h group	Γ_1^+, Γ_2^-	Γ_2^+, Γ_1^-	Γ_3^+, Γ_3^-	Γ_4^+, Γ_5^-	Γ_5^+, Γ_4^-	Γ_6^+, Γ_7^-	Γ_7^+, Γ_6^-	Γ_8^+, Γ_8^-
T_d group	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8

of the Γ_8^- must undergo a unitary transformation before being used as basis functions of Γ_8 for calculation of matrix elements in crystals with zincblende lattice.[47]

This transformation[48] for the basis functions is defined by the matrix

$$T_{\Gamma_8} = \begin{pmatrix} 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \\ -i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix}. \tag{27}$$

A similar transformation is required for the basis of the Γ_3^- IR, which is not relevant in the present context but given in Appendix E. While the unitary transformation is a requirement of spatial symmetry, the presence of phase factor "i" in both the even and the odd bases of Γ_8 is necessary to ensure compliance with time-reversal symmetry [Eq. (2)]. It is also noted that while the zincblende crystal lacks inversion symmetry, the standard basis functions derived from the O_h group representations all have well-defined parity. Thus, parity selection rules still exist in discussions concerning a specific set of standard basis belonging to relevant IRs in T_d group.

When we consider interaction matrices, the same symmetry arguments made in Sec. V can be applied. Components of the perturbation operator $\boldsymbol{\pi}$ transform according to the Γ_5 IR and decomposition of the direct product between Γ_6, Γ_7, and Γ_8 IRs are indicated in Table VI. One can see that the direct interactions between $\Gamma_6 : \Gamma_6$ and $\Gamma_7 : \Gamma_7$ are now forbidden by symmetry, whereas interactions between $\Gamma_7 : \Gamma_6$ are now allowed. The interband interaction between states belonging to the Γ_8 IRs requires two linearly independent matrices, as in the case of diamond lattice.

The $\mathbf{A}^\mu$ matrices describing interactions between $\Gamma_8 : \Gamma_6$ and $\Gamma_8 : \Gamma_7$ IRs are given by $\mathbf{A}^\mu_{\Gamma_8^+,\Gamma_7^-}$ and $\mathbf{A}^\mu_{\Gamma_8^+,\Gamma_6^-}$, respectively. Those $\mathbf{A}^\mu$ matrices between the $\Gamma_8^\pm$ IRs of the O_h group should be multiplied by the T_{Γ_8} matrix to give four possible matrices $\mathbf{A}^{\mu,n}_{\Gamma_8^+,\Gamma_8^-} T^T_{\Gamma_8}$ and $T^*_{\Gamma_8} \mathbf{A}^{\mu,n}_{\Gamma_8^-,\Gamma_8^+}$ for $n = 1,2$ in crystals with zincblende lattice. These four matrices are linearly dependent on each other and the following can be chosen as the two linear independent matrices:

$$\mathbf{A}^{\mu,1}_{\Gamma_8,\Gamma_8} = \mathbf{A}^{\mu,1}_{\Gamma_8^+,\Gamma_8^-} T^T_{\Gamma_8} + T^*_{\Gamma_8} \mathbf{A}^{\mu,1}_{\Gamma_8^-,\Gamma_8^+}, \tag{28}$$

$$\mathbf{A}^{\mu,2}_{\Gamma_8,\Gamma_8} = \mathbf{A}^{\mu,1}_{\Gamma_8^+,\Gamma_8^-} T^T_{\Gamma_8} - T^*_{\Gamma_8} \mathbf{A}^{\mu,1}_{\Gamma_8^-,\Gamma_8^+}. \tag{29}$$

TABLE VI. Product decomposition table of IRs of T_d group. The suffix $[\cdot]_A$ and $\{\cdot\}_S$ refer to anti-symmetrized and symmetrized products, respectively.

Direct product	Direct sum	No. of Γ_5
$\Gamma_8 \otimes \Gamma_8$	$[\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5]_A \oplus \{\Gamma_2 \oplus 2\Gamma_4 \oplus \Gamma_5\}_S$	2
$\Gamma_8 \otimes \Gamma_7$	$\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$	1
$\Gamma_8 \otimes \Gamma_6$	$\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$	1
$\Gamma_7 \otimes \Gamma_7$	$[\Gamma_1]_A \oplus \{\Gamma_4\}_S$	0
$\Gamma_7 \otimes \Gamma_6$	$\Gamma_2 \oplus \Gamma_5$	1
$\Gamma_6 \otimes \Gamma_6$	$[\Gamma_1]_A \oplus \{\Gamma_4\}_S$	0

Thus the $\mathbf{k} \cdot \boldsymbol{\pi}$ perturbation matrix between states in the Γ_8 IRs is given by

$$\begin{aligned} K_{\Gamma_8,\Gamma_8}(\xi_1,\xi_2) &= \frac{\hbar}{m_0} \sum_\mu k_\mu \left(\xi_1 \mathbf{A}^{\mu,1}_{\Gamma_8,\Gamma_8} + \xi_2 \mathbf{A}^{\mu,2}_{\Gamma_8,\Gamma_8}\right) \\ &= \frac{\hbar}{m_0} \xi_1 \begin{pmatrix} 0 & k_+ & k_z & 0 \\ -k_- & 0 & 0 & k_z \\ -k_z & 0 & 0 & -k_+ \\ 0 & -k_z & k_- & 0 \end{pmatrix} \\ &\quad + \frac{\hbar}{m_0} \xi_2 \begin{pmatrix} 0 & k_+ & -2k_z & \sqrt{3}k_- \\ k_- & 0 & -\sqrt{3}k_+ & 2k_z \\ -2k_z & -\sqrt{3}k_- & 0 & k_+ \\ \sqrt{3}k_+ & 2k_z & k_- & 0 \end{pmatrix}, \end{aligned} \tag{30a}$$

where a factor "i" from the unitary transformation matrix T_{Γ_8} is absorbed in the coefficient $\xi_{1,2}$ making them purely imaginary. It can be shown that the first matrix is associated with symmetric products of the basis states in Γ_8, whereas the second is associated with the antisymmetric products. Similarly, the interactions between states of other IRs are derived from Eqs. (10a), (10b), and (10c) and given by

$$K_{\Gamma_6:\Gamma_7} = K_{\Gamma_6^+:\Gamma_6^-}, \tag{30b}$$

$$K_{\Gamma_6:\Gamma_8} = K_{\Gamma_7^-:\Gamma_8^+}, \tag{30c}$$

$$K_{\Gamma_7:\Gamma_8} = K_{\Gamma_6^-:\Gamma_8^+}. \tag{30d}$$

Given the time-reversal requirement on the basis functions, the scaling constants ξ for the $\mathbf{k} \cdot \boldsymbol{\pi}$ interactions are purely imaginary between states of Γ_8 IRs, purely real between states of $\Gamma_6 : \Gamma_7$, and complex between states of $\Gamma_8 : \Gamma_7$ and $\Gamma_8 : \Gamma_6$. With the exceptions of $\Gamma_6 : \Gamma_6$ and $\Gamma_7 : \Gamma_7$, these direct interaction terms are permitted by symmetry between states of any IRs, including those which would be forbidden in crystals with diamond lattice (e.g., between Γ_8 and Γ_7 in valence band). However, in places where it was forbidden in crystals with diamond lattice, such interaction would be controlled by the ionicity of the bond.

Intraband first-order interactions are subject to time-reversal symmetry constraints in addition to spatial symmetry.[31,33] Since the perturbation operator $\boldsymbol{\pi}$ is time-reversal odd, such interaction is described by one linearly independent matrix as there is one Γ_5 in the decomposition of symmetrized products of $\Gamma_8 \otimes \Gamma_8$. Time-reversal symmetry requires the intraband perturbation interaction matrix ($K^{\text{intra}}_{\Gamma_8:\Gamma_8}$) to be Hermitian. In the literature, the second matrix in

Eq. (30a) is chosen from theory of invariants[8] or perturbation theory[4,28] and assumed to fulfill this requirement. However, the imaginary nature of the scaling constants make this choice incorrect. The first matrix in Eq. (30a) is, in fact, Hermitian when the imaginary scaling constant is taken into account and it is associated with symmetric products of the basis states. Therefore,

$$K^{\text{intra}}_{\Gamma_8:\Gamma_8} = \frac{\hbar}{m_0}\xi_1 \begin{pmatrix} 0 & k_+ & k_z & 0 \\ -k_- & 0 & 0 & k_z \\ -k_z & 0 & 0 & -k_+ \\ 0 & -k_z & k_- & 0 \end{pmatrix}, \tag{31}$$

where the scaling constant ξ_1 is imaginary. This correct choice is also reflected from the derivation of single-group result shown in Appendix E. This term does not lift the Kramer's degeneracy as one may expect. The dispersion from this linear term will yield an isotropic contribution to the energy of both light- and heavy-hole states which is proportional to k. This has a corresponding impact on the density of states and position of valence band maximum. Dresselhaus effect[4], previously attributed to the linear k term, must have its origin in higher-order perturbations[49] involving the third power of components of wave vector $\mathbf{k}$, where constituent interband interactions are not subject to time-reversal constraints.[50]

Generators can be obtained through the theory of invariants in the same way as for a diamond lattice, provided the correct compatibility relations are followed and an appropriate unitary transformation is made to the odd basis of Γ_8^- IR of the O_h group for use in the Γ_8 IR of the T_d group. While the IRs in the T_d group do not have defined spatial parity, the generating operator employed here and the standard basis function derived from the O_h group all have well-defined parity. Therefore, parity selection rules must be applied in matrix calculations. In addition, the admission of a linear combination of even and odd bases must be considered and the parity of the generating operator and irreducible perturbation must be the same. The selection rules derived from the direct product decomposition in Table VI shows that Löwdin terms can now exist between any IRs, while the linear k terms are now present between any IRs except $\Gamma_6 : \Gamma_6$ and $\Gamma_7 : \Gamma_7$. The generators for linear k terms are those $\mathbf{A}^{\mu}$ matrices obtained in the previous paragraphs while observing the time-reversal symmetry requirement in the intraband block. The generator for quadratic k terms are obtained from basis of the same parity as determined by the parity of generating operators. This leaves the form of the Löwdin terms exactly the same as those in the diamond lattice (i.e., ignore the parity, for example, $L_{\Gamma_8,\Gamma_7} = L_{\Gamma_8^+,\Gamma_7^+} = L_{\Gamma_8^-,\Gamma_7^-}$).

X. SYMMETRY OF CONDUCTION BAND STATE AT THE Γ POINT

In Sec. II, new zone-center symmetry assignments of Γ_6^- and Γ_7 were proposed for the conduction band states of Ge and GaAs. This stems from the use of a one-electron wave function of hybridized sp^3 or spd orbitals as atomic site wave functions rather than the use of atomic s and p orbitals. This differs from the current accepted view in the literature established in the late 1950s and early 1960s.[2,4,51–53] The currently accepted view can be traced to energy assignments made using single-group states in the unpublished work of Herman cited in Ref. 2. The determinations of conduction band state symmetry were made from ample experimental data on the polarization dependence of optical transitions between states at the zone center. The extraction of symmetry properties of states from optical data relies on selection rules formulated for the relevant states.

In deriving the selection rules, momentum matrix elements between the valence band and conduction band states are evaluated. The polarization dependence of the transitions involving the heavy holes, obtained from *Fermi's Golden Rule*, exhibits different behavior from those transitions involving the light holes. The angular dependence of these matrix elements are just the $\mathbf{A}^{\mu}_{\Gamma_8^+,\Gamma_6^-}$ and $\mathbf{A}^{\mu}_{\Gamma_8^+,\Gamma_7^-}$ matrices depending on the symmetry of the conduction band state. As the basis used in the literature to establish selection rules have $j \leqslant 3/2$, they cannot transform according to Γ_7^-, and any conclusion drawn must be flawed. Closer examination of the two matrices $\mathbf{A}^{z}_{\Gamma_8^+,\Gamma_6^-}$ and $\mathbf{A}^{z}_{\Gamma_8^+,\Gamma_7^-}$ indicates that when an electric field is polarized in the z direction, transitions from the heavy hole to Γ_7^- IR are allowed, whereas these transitions to Γ_6^- IR are forbidden. As the latter reflects experimental evidence based on absorption measurements in quantum wells[54] and electroreflectance measurement from Ge under uniaxial stress,[55] it is clear that the conduction band state at the Γ point in Ge has the Γ_6^- symmetry originating from spin-split-off band from the antibonding $(sp^3)^*$ orbital.

The symmetry of conduction band state in compound semiconductors was also identified incorrectly in the literature. Provided the odd basis of Γ_8 is obtained correctly through a unitary transformation of the basis from Γ_8^- in the O_h group, the $\mathbf{A}$ matrices are as described in Sec. IX. Again, experimental measurements[56] indicate that tansistions involving heavy holes are forbidden when the electric field is polarized in the z direction, meaning the conduction band state must have Γ_7 symmetry originating from the spin-split-off band from the antibonding $(sp^3)^*$ orbital.

The change in symmetry assignment of the lowest zone-center conduction band states should have a major impact on topics ranging from interpretation of data on the nonparabolicity of the conduction band,[18] to calculation of scattering rate or relaxation time, which are dependent on the nature of the spatial part of the wave function.[57]

XI. COMPARISON OF SINGLE- AND DOUBLE-GROUP FORMULATION

Group theoretical methods indicate that interactions between states of different IRs can always be described by linearly independent matrices and corresponding scaling constants. This is true for both single-group and double-group formulations. In single-group formulation applied to single-group basis, interactions between states of any pair of IRs can always be described by one single matrix and its corresponding scaling constant. In application of single-group formulation to the adapted double-group basis, the incorporation of spin as an extra degree of freedom does not alter the interaction between the single-group basis states. Thus, there should be only one matrix and one scaling constant describing interactions between states of the adapted double-group basis. This is achieved by restricting the adapted double-group basis to one single-group parent. In contrast, group theoretical methods show that the interaction between states of $\Gamma_8^{\pm}$ (Γ_8) IRs in crystals of diamond (zincblende) lattice, require two linearly independence matrices and two scaling constants under the more general double-group formulation of the present work. It reflects the fact that basis of $\Gamma_8^{\pm}(\Gamma_8)$ IR may be constructed from direct product of spinor states with a linear combination of single-group bases from $\Gamma_5^+,\Gamma_4^-(\Gamma_5)$; $\Gamma_4^+,\Gamma_5^-(\Gamma_4)$ or $\Gamma_3^{\pm}(\Gamma_3)$ IRs. This constitutes the main difference between the two formulations from a group theoretical perspective. Furthermore, this differentiates the two formulations in terms of their applicability to physical systems, which is discussed below after a brief outline of results of the single-group formulation not available in the literature.

It is informative to see the form of these interaction matrices obtained under single-group formulation applied to the adapted double-group basis and to make comparisons with the results of the double-group formulation shown in Eqs. (10d) and (30a) for both types of crystals. Historically, such interaction matrices have been given in terms of bases of real spherical harmonics[16] or of the direct product between these real spherical harmonics and spinor states.[10,58] The adapted double-group basis can be generated from these real spherical harmonics using method of Cracknell,[59] though care should be taken to ensure the order of the basis is in agreement with the representation matrices. In the case of T_d group for crystals with zincblende lattice, appropriate unitary transformation such as those described by Eq. (27) must be applied to the bases of Γ_8^- and Γ_3^- of the O_h group before they can be used as bases of Γ_8 and Γ_3. In the literature, the form of these matrices referring to time-reversal compliant adapted double-group basis are only available for interactions between states of Γ_8 IR originating from basis Γ_5 single-group IR.[18,20,21] We obtain all the matrices between states of $\Gamma_8^{\pm}$ (Γ_8) derived from $\Gamma_4^-,\Gamma_5^+,(\Gamma_5),\Gamma_3^-,\Gamma_3^+,(\Gamma_3)$ for crystals with diamond (zincblende) lattice in Appendix E. For crystals with diamond lattice, these are

$$K_{\Gamma_8^-(\Gamma_4^-),\Gamma_8^+(\Gamma_5^+)} = \frac{\hbar}{m_0}\xi\begin{pmatrix} k_z & 0 & 0 & k_+ \\ 0 & -k_z & k_- & 0 \\ 0 & k_+ & k_z & 0 \\ k_- & 0 & 0 & -k_z \end{pmatrix}, \tag{32}$$

$$K_{\Gamma_8^-(\Gamma_4^-),\Gamma_8^+(\Gamma_3^+)} = \frac{\hbar}{m_0}\xi\begin{pmatrix} 0 & \sqrt{3}k_- & 0 & -3k_+ \\ \sqrt{3}k_+ & 4k_z & -k_- & 0 \\ 0 & -k_+ & -4k_z & \sqrt{3}k_- \\ -3k_- & 0 & \sqrt{3}k_+ & 0 \end{pmatrix}, \tag{33}$$

where the scaling constants are all real. It is not clear that the difference between these for crystal with diamond lattice and the ones below for crystals with zincblende lattice is appreciated in previous works. For crystals with zincblende lattice, the form of interaction matrices are

$$K_{\Gamma_8(\Gamma_5),\Gamma_8(\Gamma_5)} = \frac{\hbar}{m_0}\xi\begin{pmatrix} 0 & k_+ & k_z & 0 \\ -k_- & 0 & 0 & k_z \\ -k_z & 0 & 0 & -k_+ \\ 0 & -k_z & k_- & 0 \end{pmatrix}, \tag{34}$$

$$K_{\Gamma_8(\Gamma_5),\Gamma_8(\Gamma_3)} = \frac{\hbar}{m_0}\xi\begin{pmatrix} 0 & -k_+ & -4k_z & \sqrt{3}k_- \\ 3k_- & 0 & -\sqrt{3}k_+ & 0 \\ 0 & -\sqrt{3}k_- & 0 & 3k_+ \\ \sqrt{3}k_+ & 4k_z & -k_- & 0 \end{pmatrix}, \tag{35}$$

where the scaling constants are all purely imaginary.

It is now appropriate to comment on the difference between the single-group formulation applied to adapted double-group basis and the general double formulation of the present work. The interaction matrices shown in Eqs. (32) and (33) can all be obtained by removing the independence of the two scaling constants in Eq. (10d). Conversely, the two matrices in Eqs. (32) and (33) can serve equally as the two linearly independent matrices in the general double-group formulation replacing the two in Eq. (10d). The restriction to a single interaction matrix under the single-group formulation, applied to adapted double-group basis, is brought about by restriction of the double-group basis to those that can be derived from its sole single-group parent. Thus, the single-group formulation is not capable of describing interaction between a general double-group basis, which may be derived from a mixture of Γ_5^+ and Γ_3^+ basis.

The question to be asked is whether the zone-center $\Gamma_8^{\pm}$ basis states contain a mixture of characters of Γ_5^+,Γ_3^+ and Γ_4^-,Γ_3^- parents or p and d characters. Clearly, such a situation is ruled out by default if one chooses to use atomic orbitals to represent the atomic site wave function. Therefore, the single-group formulation applied to adapted double-group basis is naturally associated with the use of atomic orbitals to describe atomic site wave functions. Under general double-group formulation, while retaining the atomic orbital description of atomic site wave functions, some degree of mixing of zone-center states by the spin-orbit interaction H_{so1}^s is present. However, the energy separation between states of the antibonding Γ_3^- and bonding Γ_5^+ is large, and any mixing would be small. Thus, the only way d character can be introduced to the energy eigenstate away from the zone center is when a d state is included in the near set and mixing is provided by the $\mathbf{k}\cdot\mathbf{p}$ perturbation. This is not an effective way of taking into account the effect of d orbitals, particularly in the valence band near the zone center.

For covalent bonding in tetrahedral geometry, it is natural to think of many electron configuration or hybridized orbitals. The *spd* hybridized orbitals are both feasible[60] and suggested by tight-binding calculations.[61] Within the $\mathbf{k}\cdot\mathbf{p}$ method, this will introduce the effect of d character directly in the one-electron zone-center states in the valence band. This mechanism of mixing of states is a many-electron effect and differs from those that may have arisen from spin-orbit interaction based on one-electron theory. Thus, the zone-center states in the $\Gamma_8^{\pm}$ IR may generally be derived from a mixture of Γ_5^+,Γ_3^+ for bonding states and Γ_4^-,Γ_3^- for antibonding states. Single-group formulation would not be able to provide adequate description of interactions between these states. The general double-group formulation of the present work becomes essential.

The perturbation-theory-based double-group formulation (see Secs. IV and V) is free from the constraint placed on its double-group basis by the single-group formulation and therefore may be compared generally with the results of method of invariant. The single-group formulation applied to adapted double-group basis may only be compared with the results of method of invariants if the restriction on the basis is taken into account.

XII. SUMMARY

This paper develops the $\mathbf{k}\cdot\mathbf{p}$ theory from the double-group perspective and considers a change of paradigm in dealing with atomic site wave functions. The atomic site wave functions are better described by the sp^3 or spd hybridized orbitals derived from many-electron configuration, compared with the atomic orbitals, s, p, and d. The double-group representation of hybridized orbitals requires the general approach of double-group formulation. In particular, the effect of d and/or f orbitals may be easily incorporated in the valence band by the double-group formulation. In contrast, single-group formulation with its zone-center energy eigenfunction in $\Gamma_8^{\pm}$ IR derived from the basis of single-group IR cannot adequately represent the zone-center energy eigenfunctions in a real crystal where contribution from d or higher orbitals in the atomic site wave function cannot be neglected. A consequence of adopting hybridized atomic orbitals is a change of symmetry and origin of the lowest conduction band zone-center states. With correct use of basis functions for the Γ_7^- IRs, the selection rules obtained are in agreement with polarization dependence of optical absorption data confirming that such states have Γ_6^- symmetry in crystals with diamond lattice originating from the spin-split-off from the anti-bonding triplet states. Previous interpretations of the same data and symmetry assignment were based on selection rules obtained from incorrect bases.

The double-group formulation developed from perturbation theory is shown to be in full agreement with method of invariants. The approach we have adopted in method of invariant differs from those in the literature in the way in which the generator matrices are obtained. Irreducible spherical tensor operators, with the correct transformation properties as the irreducible perturbations, are identified. Then linearly independent generator matrices are obtained using standard basis functions instead of using products of components of the angular momentum operator. Where more than one linearly independent generator is required, as deemed necessary by symmetry, multiple sets of standard basis functions are used to enumerate the required generator matrices. Departure from the spatially even angular momentum operator enables first-order interaction matrices to be produced directly. The results of the method of invariants can be compared with perturbation theory under the double-group consideration. Comparison with single-group formulation can be made if the restriction of basis of $\Gamma_8^{\pm}(\Gamma_8)$ is taken into account.

The development of the double-group formulation for crystals with zincblende lattice is a natural extension of the results for crystals with diamond lattice under the compatibility relation between the T_d and O_h groups. A unitary transformation of the odd basis of Γ_8^- of the O_h group is shown to be required before they can be used in the corresponding Γ_8 IR of the T_d group under the compatibility relation. This unitary transformation, together with use of correct basis functions, lead to similar change in the symmetry of the conduction band zone-center states. In this case, it has Γ_7 symmetry originating from the spin-split-off from the antibonding triplet states.

The time-reversal requirement, as detailed at end of Sec. IV, places specific phase relationships between spatially even and odd standard basis functions. This leads to fixed type (real, imaginary, or complex) of scaling constants for first-order $\mathbf{k}\cdot\mathbf{p}$ interactions depending on the type of crystal lattice and relevant IRs. Thus, the intraband first-order interaction involving the $\mathbf{k}\cdot[\boldsymbol{\sigma}\times\nabla V(r)]$ and $\mathbf{k}\cdot\mathbf{p}$ between states in the same Γ_8 IR both pickup the same first matrix in Eq. (30a), in contrast to findings in the literature. This contribution does not lift the Kramer's degeneracy.

Operator ordering in envelope function theory under the double-group formulation introduces additional coupling between the heavy-hole states due to symmetry breaking at interfaces. In addition, the change in the form of interband Hamiltonian and symmetry of conduction band zone-center states are also expected to lead to differences compared with single-group formulation in correctly operator ordered form or symmetrized form.

The formulation developed in the present work has no practical impact on the four-band model describing degenerate valence band states in crystals with diamond lattice, as shown in Sec. V. The main distinction between single- and double-group formulation, the interaction between states in the $\Gamma_8^{\pm}$ IRs, is treated under Löwdin interaction. While the double-group formulation gives a different component form of the Hamiltonian [the five matrices in Eq. (17)] compared to that seen with single-group, each individual term and the sum of all terms remain compliant with results of method of invariant. Since these invariants, as fitting parameters, are obtained from experiment, there is no practical difference between the two approaches. In crystals with zincblende lattice, additional intraband linear k terms are allowed and they have a form different from those identified by Dressulhaus[4] or Kane.[28] However, they do not lift the Kramer's degeneracy. In a six-band model including the valence band and spin-split-off bands, the formulation gives different results than those in the literature. This is primarily due to use of an incorrect basis for the Γ_7^+ IR in the calculation of the interaction matrix in the literature, which led to an incorrect form of the interband block, but the invariants γ_2' and γ_3' in this block are also different from the valence band block due to different form of material parameter and selection rules. For the same reason, the invariant parameter γ_1' (effective mass) of the spin-orbit band is also different. These differences in the form of interband block are not dependent on single- or double-group approaches. In an eight-band model with the addition of the conduction band, there is no further "practical" difference beyond what already existed in the six-band model though direct interaction between the lowest conduction band state [$\Gamma_6^-(\Gamma_7)$] and spin-split-off band in the valence band [$\Gamma_7^+(\Gamma_7)$] is now forbidden. However, the symmetry assignment of the conduction band states is now different. The form of interaction matrix between conduction band and valence band states in the literature was "accidentally" correct because the erroneous symmetry assignment of conduction band states is coupled with the use of an incorrect basis of Γ_7^- (diamond) or Γ_8 (zincblende) when calculating interaction matrix. The scaling constant for first-order interaction between valence band and conduction band is complex in the case of crystals with zincblende lattice. Again, these is not dependent on the single- or double-group approach. In fourteen-band models and beyond, where states belonging to $\Gamma_8^-(\Gamma_8)$ and $\Gamma_6^-(\Gamma_7)$ are all included in the near set, the interaction between $\Gamma_8^\pm(\Gamma_8)$ may have been treated incorrectly using adaption of single-group formulation in the literature due to the use of incorrect interaction matrices and the lack of ability to treat the effect of *d* orbitals in the valence band under single-group consideration. A fundamental change in these multiband models, as detailed earlier in this publication, is required. With very few exceptions, the form of the Hamiltonian in fourteen-band models and beyond may have been assumed to be the same for crystals with diamond and zincblende lattice. It is clear from earlier sections that this is not true for single- or double-group formulations, both in terms of the form of direct interaction matrices and the complex nature in the scaling constants in the case of crystals with zincblende lattice.

While the change of atomic orbitals to hybridized orbitals as atomic site wave function is the most significant difference in underlying physics, the impact of the present work is largely restricted to multiband models where states from more than one $\Gamma_8^\pm(\Gamma_8)$ IRs are included in the near set. The correction to current formulation in the literature due to use of incorrect basis will have the most practical implication on most implementations currently used. The change in the symmetry in conduction band edge state means any calculation which makes use of the $\Gamma_7^-(\Gamma_6)$ symmetry of the spatial part of the wave function in diamond (zincblende) crystal will need re-evaluation. These are numerous and include scattering rate/relaxation time calculations for both bulk materials and heterostructures and dispersion of valence band away from zone center.

ACKNOWLEDGMENTS

The authors would like to thank P. Stavrinou for getting us interested in the **k** · **p** problem, P. Stavrinou and D. Vvedensky for reading the manuscript and D. Panov for his help on compatibility relations. The authors also benefited from discussions with M. Foulkes at Imperial and B. F. Zhu, D. Ruan, and E. Y. Shang of Tsinghua University. W.E. and R.W. acknowledge the Engineering and Physical Science Research Council (UK) for the provision of studentships.

APPENDIX A: CHARACTER TABLE OF THE DOUBLE GROUPS O_h AND T_d

APPENDIX B: SOME STANDARD BASIS FUNCTIONS FOR IRS OF THE O_h GROUP

TABLE VII. Character table of the double O_h group arranged as $T_d \otimes i$. The number of elements in each class is listed in the second row. Classes labeled with * contain the glide operation. The rows of the table have been arranged to reflect the compatibility relations between the O_h and the T_d groups. The character table of the T_d group is just the top left quadrant of the table if one ignores the parity labels of the representations.

			$\{E\}$	$\{\frac{C_2}{C_2}\}$	$\{S_4\}$	$\{\frac{\sigma_d}{\sigma_d}\}$	$\{C_3\}$	$\{\overline{E}\}$	$\{\overline{S_4}\}$	$\{\overline{C_3}\}$	$\{i^*\}$	$\{\frac{\sigma_h^*}{\sigma_h^*}\}$	$\{C_4^*\}$	$\{\frac{C_2'^*}{C_2'^*}\}$	$\{S_6^*\}$	$\{\overline{i^*}\}$	$\{\overline{C_4^*}\}$	$\{\overline{S_6^*}\}$
Koster	BSW	Mulliken	1	3/3	6	6/6	8	1	6	8	1	3/3	6	6/6	8	1	6	8
Γ_1^+	Γ_1	A_1^g	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2^+	Γ_2	A_2^g	1	1	−1	−1	1	1	−1	1	1	1	−1	−1	1	1	−1	1
Γ_3^+	Γ_{12}	E^g	2	2	0	0	−1	2	0	−1	2	2	0	0	−1	2	0	−1
Γ_4^+	$\Gamma_{15'}$	T_1^g	3	−1	1	−1	0	3	1	0	3	−1	1	−1	0	3	1	0
Γ_5^+	$\Gamma_{25'}$	T_2^g	3	−1	−1	1	0	3	−1	0	3	−1	−1	1	0	3	−1	0
Γ_6^+	Γ_6	E'^g	2	0	$\sqrt{2}$	0	1	−2	$-\sqrt{2}$	−1	2	0	$\sqrt{2}$	0	1	−2	$-\sqrt{2}$	−1
Γ_7^+	Γ_7	E''^g	2	0	$-\sqrt{2}$	0	1	−2	$\sqrt{2}$	−1	2	0	$-\sqrt{2}$	0	1	−2	$\sqrt{2}$	−1
Γ_8^+	Γ_8	G^g	4	0	0	0	−1	−4	0	1	4	0	0	0	−1	−4	0	1
Γ_2^-	$\Gamma_{2'}$	A_2^u	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1
Γ_1^-	$\Gamma_{1'}$	A_1^u	1	1	−1	−1	1	1	−1	1	−1	−1	1	1	−1	−1	1	−1
Γ_3^-	$\Gamma_{12'}$	E^u	2	2	0	0	−1	2	0	−1	−2	−2	0	0	1	−2	0	1
Γ_5^-	Γ_{25}	T_2^u	3	−1	1	−1	0	3	1	0	−3	1	−1	1	0	−3	−1	0
Γ_4^-	Γ_{15}	T_1^u	3	−1	−1	1	0	3	−1	0	−3	1	1	−1	0	−3	1	0
Γ_7^-	$\Gamma_{7'}$	E''^u	2	0	$\sqrt{2}$	0	1	−2	$-\sqrt{2}$	−1	−2	0	$-\sqrt{2}$	0	−1	2	$\sqrt{2}$	1
Γ_6^-	$\Gamma_{6'}$	E'^g	2	0	$-\sqrt{2}$	0	1	−2	$\sqrt{2}$	−1	−2	0	$\sqrt{2}$	0	−1	2	$-\sqrt{2}$	1
Γ_8^-	$\Gamma_{8'}$	G^u	4	0	0	0	−1	−4	0	1	−4	0	0	0	1	4	0	−1

TABLE VIII. First standard bases for $\Gamma_6^{\pm}$, $\Gamma_7^{\pm}$ and $\Gamma_8^{\pm}$ IRs of the O_h group.

IRs	$\lvert J,M_j\rangle$	$\lvert j,m_j\rangle$	$\lvert l,m_l\rangle\{\alpha,\beta\}$	$\{x,y,z\}\{\alpha,\beta\}$
Γ_6^+	$\begin{cases} \lvert\frac{1}{2},\overline{\frac{1}{2}}\rangle \\ \lvert\frac{1}{2},\frac{1}{2}\rangle \end{cases}$	$\begin{cases} i\lvert\frac{1}{2},\frac{1}{2}\rangle \\ i\lvert\frac{1}{2},\overline{\frac{1}{2}}\rangle \end{cases}$	$\begin{cases} i\alpha \\ i\beta \end{cases}$	$\begin{cases} i\alpha \\ i\beta \end{cases}$
Γ_6^-	$\begin{cases} \lvert\frac{1}{2},\overline{\frac{1}{2}}\rangle \\ \lvert\frac{1}{2},\frac{1}{2}\rangle \end{cases}$	$\begin{cases} \lvert\frac{1}{2},\frac{1}{2}\rangle \\ \lvert\frac{1}{2},\overline{\frac{1}{2}}\rangle \end{cases}$	$\begin{cases} -\sqrt{\frac{1}{3}}\lvert 1,0\rangle\alpha+\sqrt{\frac{2}{3}}\lvert 1,1\rangle\beta \\ \sqrt{\frac{1}{3}}\lvert 1,0\rangle\beta-\sqrt{\frac{2}{3}}\lvert 1,\overline{1}\rangle\alpha \end{cases}$	$\begin{cases} -z\alpha-(x+iy)\beta \\ z\beta-(x-iy)\alpha \end{cases}$
Γ_7^+	$\begin{cases} \lvert\frac{1}{2},\overline{\frac{1}{2}}\rangle \\ \lvert\frac{1}{2},\frac{1}{2}\rangle \end{cases}$	$\begin{cases} i[\sqrt{\frac{5}{6}}\lvert\frac{5}{2},\overline{\frac{3}{2}}\rangle-\sqrt{\frac{1}{6}}\lvert\frac{5}{2},\frac{5}{2}\rangle] \\ i[\sqrt{\frac{5}{6}}\lvert\frac{5}{2},\frac{3}{2}\rangle-\sqrt{\frac{1}{6}}\lvert\frac{5}{2},\overline{\frac{5}{2}}\rangle] \end{cases}$	$\begin{cases} i[\sqrt{\frac{1}{6}}\lvert 2,\overline{2}\rangle\alpha+\sqrt{\frac{4}{6}}\lvert 2,\overline{1}\rangle\beta-\sqrt{\frac{1}{6}}\lvert 2,2\rangle\alpha] \\ i[\sqrt{\frac{1}{6}}\lvert 2,2\rangle\beta+\sqrt{\frac{4}{6}}\lvert 2,1\rangle\alpha-\sqrt{\frac{1}{6}}\lvert 2,\overline{2}\rangle\beta] \end{cases}$	$\begin{cases} iz(x-iy)\beta+xy\alpha \\ -iz(x+iy)\alpha-xy\beta \end{cases}$
Γ_7^-	$\begin{cases} \lvert\frac{1}{2},\overline{\frac{1}{2}}\rangle \\ \lvert\frac{1}{2},\frac{1}{2}\rangle \end{cases}$	$\begin{cases} \sqrt{\frac{5}{6}}\lvert\frac{5}{2},\overline{\frac{3}{2}}\rangle-\sqrt{\frac{1}{6}}\lvert\frac{5}{2},\frac{5}{2}\rangle \\ \sqrt{\frac{5}{6}}\lvert\frac{5}{2},\frac{3}{2}\rangle-\sqrt{\frac{1}{6}}\lvert\frac{5}{2},\overline{\frac{5}{2}}\rangle \end{cases}$	$\begin{cases} -\sqrt{\frac{25}{42}}\lvert 3,\overline{2}\rangle\alpha+\sqrt{\frac{10}{42}}\lvert 3,\overline{1}\rangle\beta+\sqrt{\frac{1}{42}}\lvert 3,2\rangle\alpha-\sqrt{\frac{6}{42}}\lvert 3,3\rangle\beta \\ \sqrt{\frac{25}{42}}\lvert 3,2\rangle\beta-\sqrt{\frac{10}{42}}\lvert 3,1\rangle\alpha-\sqrt{\frac{1}{42}}\lvert 3,\overline{2}\rangle\beta+\sqrt{\frac{6}{42}}\lvert 3,\overline{3}\rangle\alpha \end{cases}$	$\begin{cases} 3ixyz\alpha-(x^2-y^2)z\alpha+z^2(x-iy)\beta+ixy(x+iy)\beta \\ 3ixyz\beta+(x^2-y^2)z\beta+z^2(x+iy)\alpha-ixy(x-iy)\alpha \end{cases}$
Γ_8^+	$\begin{cases} \lvert\frac{3}{2},\overline{\frac{3}{2}}\rangle \\ \lvert\frac{3}{2},\overline{\frac{1}{2}}\rangle \\ \lvert\frac{3}{2},\frac{1}{2}\rangle \\ \lvert\frac{3}{2},\frac{3}{2}\rangle \end{cases}$	$\begin{cases} i\lvert\frac{3}{2},\frac{3}{2}\rangle \\ i\lvert\frac{3}{2},\frac{1}{2}\rangle \\ i\lvert\frac{3}{2},\overline{\frac{1}{2}}\rangle \\ i\lvert\frac{3}{2},\overline{\frac{3}{2}}\rangle \end{cases}$	$\begin{cases} i[-\sqrt{\frac{1}{5}}\lvert 2,1\rangle\alpha+\sqrt{\frac{4}{5}}\lvert 2,2\rangle\beta] \\ i[-\sqrt{\frac{2}{5}}\lvert 2,0\rangle\alpha+\sqrt{\frac{3}{5}}\lvert 2,1\rangle\beta] \\ i[-\sqrt{\frac{3}{5}}\lvert 2,\overline{1}\rangle\alpha+\sqrt{\frac{2}{5}}\lvert 2,0\rangle\beta] \\ i[-\sqrt{\frac{4}{5}}\lvert 2,\overline{2}\rangle\alpha+\sqrt{\frac{1}{5}}\lvert 2,\overline{1}\rangle\beta] \end{cases}$	$\begin{cases} iz(x+iy)\alpha-2xy\beta+i(x^2-y^2)\beta \\ -\sqrt{3}iz(x+iy)\beta+\frac{i}{\sqrt{3}}(x^2+y^2-2z^2)\alpha \\ -\sqrt{3}iz(x-iy)\alpha-\frac{i}{\sqrt{3}}(x^2+y^2-2z^2)\beta \\ iz(x-iy)\beta-2xy\alpha-i(x^2-y^2)\alpha \end{cases}$
		$\begin{cases} i[-\sqrt{\frac{1}{6}}\lvert\frac{5}{2},\frac{3}{2}\rangle-\sqrt{\frac{5}{6}}\lvert\frac{5}{2},\overline{\frac{5}{2}}\rangle] \\ i\lvert\frac{5}{2},\frac{1}{2}\rangle \\ -i\lvert\frac{5}{2},\overline{\frac{1}{2}}\rangle \\ i[\sqrt{\frac{1}{6}}\lvert\frac{5}{2},\overline{\frac{3}{2}}\rangle+\sqrt{\frac{5}{6}}\lvert\frac{5}{2},\frac{5}{2}\rangle] \end{cases}$	$\begin{cases} i[-\sqrt{\frac{4}{30}}\lvert 2,1\rangle\alpha-\sqrt{\frac{1}{30}}\lvert 2,2\rangle\beta-\sqrt{\frac{25}{30}}\lvert 2,\overline{2}\rangle\beta] \\ i[\sqrt{\frac{3}{5}}\lvert 2,0\rangle\alpha+\sqrt{\frac{2}{5}}\lvert 2,1\rangle\beta] \\ i[-\sqrt{\frac{3}{5}}\lvert 2,0\rangle\beta-\sqrt{\frac{2}{5}}\lvert 2,\overline{1}\rangle\alpha] \\ i[\sqrt{\frac{4}{30}}\lvert 2,\overline{1}\rangle\beta+\sqrt{\frac{1}{30}}\lvert 2,\overline{2}\rangle\alpha+\sqrt{\frac{25}{30}}\lvert 2,2\rangle\alpha] \end{cases}$	$\begin{cases} 2i[z(x+iy)\alpha+2ixy\beta]-3i(x^2-y^2)\beta \\ -2\sqrt{3}iz(x+iy)\beta-\sqrt{3}i(x^2+y^2-2z^2)\alpha \\ -2\sqrt{3}iz(x-iy)\alpha+\sqrt{3}i(x^2+y^2-2z^2)\beta \\ 2i[z(x-iy)\beta+2ixy\alpha]+3i(x^2-y^2)\alpha \end{cases}$
Γ_8^-	$\begin{cases} \lvert\frac{3}{2},\overline{\frac{3}{2}}\rangle \\ \lvert\frac{3}{2},\overline{\frac{1}{2}}\rangle \\ \lvert\frac{3}{2},\frac{1}{2}\rangle \\ \lvert\frac{3}{2},\frac{3}{2}\rangle \end{cases}$	$\begin{cases} \lvert\frac{3}{2},\frac{3}{2}\rangle \\ \lvert\frac{3}{2},\frac{1}{2}\rangle \\ \lvert\frac{3}{2},\overline{\frac{1}{2}}\rangle \\ \lvert\frac{3}{2},\overline{\frac{3}{2}}\rangle \end{cases}$	$\begin{cases} \lvert 1,1\rangle\alpha \\ \sqrt{\frac{2}{3}}\lvert 1,0\rangle\alpha+\sqrt{\frac{1}{3}}\lvert 1,1\rangle\beta \\ \sqrt{\frac{2}{3}}\lvert 1,0\rangle\beta+\sqrt{\frac{1}{3}}\lvert 1,\overline{1}\rangle\alpha \\ \lvert 1,\overline{1}\rangle\beta \end{cases}$	$\begin{cases} -(x+iy)\alpha \\ \sqrt{\frac{1}{3}}[2z\alpha-(x+iy)\beta] \\ \sqrt{\frac{1}{3}}[2z\beta+(x-iy)\alpha] \\ (x-iy)\beta \end{cases}$
		$\begin{cases} -\sqrt{\frac{1}{6}}\lvert\frac{5}{2},\frac{3}{2}\rangle-\sqrt{\frac{5}{6}}\lvert\frac{5}{2},\overline{\frac{5}{2}}\rangle \\ \lvert\frac{5}{2},\frac{1}{2}\rangle \\ -\lvert\frac{5}{2},\overline{\frac{1}{2}}\rangle \\ \sqrt{\frac{1}{6}}\lvert\frac{5}{2},\overline{\frac{3}{2}}\rangle+\sqrt{\frac{5}{6}}\lvert\frac{5}{2},\frac{5}{2}\rangle \end{cases}$	$\begin{cases} \sqrt{\frac{2}{42}}\lvert 3,1\rangle\alpha-\sqrt{\frac{5}{42}}\lvert 3,2\rangle\beta+\sqrt{\frac{30}{42}}\lvert 3,\overline{3}\rangle\alpha-\sqrt{\frac{5}{42}}\lvert 3,\overline{2}\rangle\beta \\ -\sqrt{\frac{3}{7}}\lvert 3,0\rangle\alpha+\sqrt{\frac{4}{7}}\lvert 3,1\rangle\beta \\ -\sqrt{\frac{3}{7}}\lvert 3,0\rangle\beta+\sqrt{\frac{4}{7}}\lvert 3,\overline{1}\rangle\alpha \\ \sqrt{\frac{2}{42}}\lvert 3,\overline{1}\rangle\beta-\sqrt{\frac{5}{42}}\lvert 3,\overline{2}\rangle\alpha+\sqrt{\frac{30}{42}}\lvert 3,3\rangle\beta-\sqrt{\frac{5}{42}}\lvert 3,2\rangle\alpha \end{cases}$	$\begin{cases} -2r^2(x+iy)\alpha+5(x^2-y^2)[-z\beta+(x-iy)\alpha] \\ \frac{2r^2}{\sqrt{3}}[2z\alpha-(x+iy)\beta]+\frac{5}{\sqrt{3}}(r^2-3z^2)[z\alpha+(x+iy)\beta] \\ \frac{2r^2}{\sqrt{3}}[2z\beta+(x-iy)\alpha]-\frac{5}{\sqrt{3}}(r^2-3z^2)[-z\beta+(x-iy)\alpha] \\ 2r^2(x-iy)\beta-5(x^2-y^2)[z\alpha+(x+iy)\beta] \end{cases}$

APPENDIX C: $\mathbf{A}^{\mu}_{\alpha^u,\alpha^v}$ MATRICES FOR REPRESENTATIONS IN THE DOUBLE GROUP O_h

The angular parts of the components of the **p** matrix between states of each of the IRs are basis independent and are calculated using the method described in Sec. II and Eq. (8c). They are listed below:

$$\mathbf{A}^{x}_{\Gamma_6^+,\Gamma_6^-} = \mathbf{A}^{x}_{\Gamma_7^+,\Gamma_7^-} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{A}^{y}_{\Gamma_6^+,\Gamma_6^-} = \mathbf{A}^{y}_{\Gamma_7^+,\Gamma_7^-} = i\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{A}^{z}_{\Gamma_6^+,\Gamma_6^-} = \mathbf{A}^{z}_{\Gamma_7^+,\Gamma_7^-} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$\mathbf{A}^{x}_{\Gamma_8^+,\Gamma_6^-} = \begin{pmatrix} -\sqrt{3} & 0 \\ 0 & -1 \\ 1 & 0 \\ 0 & \sqrt{3} \end{pmatrix}, \quad \mathbf{A}^{y}_{\Gamma_8^+,\Gamma_6^-} = i\begin{pmatrix} \sqrt{3} & 0 \\ 0 & 1 \\ 1 & 0 \\ 0 & \sqrt{3} \end{pmatrix}, \quad \mathbf{A}^{z}_{\Gamma_8^+,\Gamma_6^-} = \begin{pmatrix} 0 & 0 \\ 2 & 0 \\ 0 & 2 \\ 0 & 0 \end{pmatrix},$$

$$\mathbf{A}^{x}_{\Gamma_8^+,\Gamma_7^-} = \begin{pmatrix} 1 & 0 \\ 0 & -\sqrt{3} \\ \sqrt{3} & 0 \\ 0 & -1 \end{pmatrix}, \quad \mathbf{A}^{y}_{\Gamma_8^+,\Gamma_7^-} = i\begin{pmatrix} 1 & 0 \\ 0 & -\sqrt{3} \\ -\sqrt{3} & 0 \\ 0 & 1 \end{pmatrix}, \quad \mathbf{A}^{z}_{\Gamma_8^+,\Gamma_7^-} = \begin{pmatrix} 0 & 2 \\ 0 & 0 \\ 0 & 0 \\ 2 & 0 \end{pmatrix},$$

$$\mathbf{A}^{x,1}_{\Gamma_8^+,\Gamma_8^-} = \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}, \quad \mathbf{A}^{y,1}_{\Gamma_8^+,\Gamma_8^-} = i\begin{pmatrix} 0 & -\sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & -2 & 0 \\ 0 & 2 & 0 & -\sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}, \quad \mathbf{A}^{z,1}_{\Gamma_8^+,\Gamma_8^-} = \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix},$$

$$\mathbf{A}^{x,2}_{\Gamma_8^+,\Gamma_8^-} = \begin{pmatrix} 0 & \sqrt{3} & 0 & -5 \\ \sqrt{3} & 0 & -3 & 0 \\ 0 & -3 & 0 & \sqrt{3} \\ -5 & 0 & \sqrt{3} & 0 \end{pmatrix}, \quad \mathbf{A}^{y,2}_{\Gamma_8^+,\Gamma_8^-} = i\begin{pmatrix} 0 & -\sqrt{3} & 0 & -5 \\ \sqrt{3} & 0 & 3 & 0 \\ 0 & -3 & 0 & -\sqrt{3} \\ 5 & 0 & \sqrt{3} & 0 \end{pmatrix}, \quad \mathbf{A}^{z,2}_{\Gamma_8^+,\Gamma_8^-} = \begin{pmatrix} -2 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 \\ 0 & 0 & -6 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}.$$

APPENDIX D: EIGHT-BAND HAMILTONIAN

The eight-band Hamiltonian is given below in Table IX. The Löwdin terms (L) are given in terms of Luttinger parameters and linear k terms (K) are given explicitly. The Luttinger parameters for each block are different in general. The same results are obtained from both perturbation theory and method of invariant. While the Löwdin term between Γ_6^+ and Γ_8^+ does not occur in the eight-band model, it is given for comparison, as it is the one used incorrectly in place of $L_{\Gamma_7^+,\Gamma_8^+}$ in the literature. Entries in the Hamiltonian for the zincblende crystal are given inside a bracket. When there is no corresponding entry in the diamond lattice (L or K), the term for the zincblende lattice is weak and dependent on the ionicity of the chemical bond.

Example of odd basis ($j = 3/2, l = 1$) and even basis ($j = 3/2, l = 2$) of the Γ_8 IR in the T_d group (after unitary transformation from basis of O_h group) given in the $|j,m_j\rangle$ basis. The superscript O and E indicate that the $|j,m_j\rangle$ are derived from odd and even orbital angular momentum state. They, or a linear combination of them, satisfy the time-reversal requirement of Eq. (2):

$$\text{odd}\begin{cases} i\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle^{O}, \\ -i\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle^{O}, \\ -i\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle^{O}, \\ i\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle^{O}, \end{cases} \qquad \text{even}\begin{cases} i\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle^{E}, \\ i\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle^{E}, \\ i\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle^{E}, \\ i\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle^{E}. \end{cases} \tag{D1}$$

TABLE IX. Eight band Hamiltonian in block form indexed by IRs of the relevant states. Entries for crystals with zincblende lattice are given in parenthesis.

	CB Γ_6^- (Γ_7)	VB Γ_8^+ (Γ_8)	SO Γ_7^+ (Γ_7)
CB Γ_6^- (Γ_7)	$-L_{\Gamma_6^-,\Gamma_6^-} + E_g \cdot \mathbf{1}$ $(-L_{\Gamma_7,\Gamma_7} + E_g \cdot \mathbf{1})$	$K_{\Gamma_6^-,\Gamma_8^+}$ $(L_{\Gamma_7,\Gamma_8} + K_{\Gamma_7,\Gamma_8})$	$\mathbf{0}$ (L_{Γ_7,Γ_7})
VB Γ_8^+ (Γ_8)	$K_{\Gamma_8^+,\Gamma_6^-}$ $(L_{\Gamma_8,\Gamma_7} + K_{\Gamma_8,\Gamma_7})$	$L_{\Gamma_8^+,\Gamma_8^+}$ $(L_{\Gamma_8,\Gamma_8} + K_{\Gamma_8,\Gamma_8})$	$L_{\Gamma_8^+,\Gamma_7^+}$ $(L_{\Gamma_8,\Gamma_7} + K_{\Gamma_8,\Gamma_7})$
SO Γ_7^+ (Γ_7)	$\mathbf{0}$ (L_{Γ_7,Γ_7})	$L_{\Gamma_7^+,\Gamma_8^+}$ $(L_{\Gamma_7,\Gamma_8} + K_{\Gamma_7,\Gamma_8})$	$L_{\Gamma_7^+,\Gamma_7^+} + \Delta \cdot \mathbf{1}$ $(L_{\Gamma_7,\Gamma_7} + \Delta \cdot \mathbf{1})$

Direct interactions (K terms) can be found in Eqs. (10a), (10b), (10c), and (10d) for crystals with diamond lattice and Eqs. (30b), (30c), (30d), and (30a) for crystals with zincblende lattice. Löwdin interactions are given below:

$$L_{\Gamma_6^-,\Gamma_6^-}(\gamma_1) = L_{\Gamma_7^+,\Gamma_7^+}(\gamma_1) = L_{\Gamma_7,\Gamma_7}(\gamma_1) = -\frac{\hbar^2}{2m_0}\begin{pmatrix} P & 0 \\ 0 & P \end{pmatrix}, \tag{D2}$$

$$L_{\Gamma_6^+,\Gamma_7^+}(\gamma_3) = L_{\Gamma_6^-,\Gamma_7^-}(\gamma_3) = L_{\Gamma_6,\Gamma_7}(\gamma_3) = -\frac{\hbar^2}{2m_0}\begin{pmatrix} -2\sqrt{3}i\gamma_3 k_x k_y & -S^* \\ -S & 2\sqrt{3}i\gamma_3 k_x k_y \end{pmatrix}, \tag{D3}$$

$$L_{\Gamma_7^+,\Gamma_8^+}(\gamma_2,\gamma_3) = L_{\Gamma_7,\Gamma_8}(\gamma_2,\gamma_3) = -\frac{\hbar^2}{2m_0}\begin{pmatrix} \sqrt{\frac{3}{2}}S & \sqrt{2}R & \frac{1}{\sqrt{2}}S^* & -\sqrt{2}Q \\ \sqrt{2}Q & \frac{1}{\sqrt{2}}S & -\sqrt{2}R^* & \sqrt{\frac{3}{2}}S^* \end{pmatrix}, \tag{D4}$$

$$L_{\Gamma_6^+,\Gamma_8^+}(\gamma_2,\gamma_3) = L_{\Gamma_6,\Gamma_8}(\gamma_2,\gamma_3) = -\frac{\hbar^2}{2m_0}\begin{pmatrix} -\frac{1}{\sqrt{2}}S^* & -\sqrt{2}Q & \sqrt{\frac{3}{2}}S & -\sqrt{2}R \\ \sqrt{2}R^* & \sqrt{\frac{3}{2}}S^* & \sqrt{2}Q & -\frac{1}{\sqrt{2}}S \end{pmatrix}, \tag{D5}$$

$$L^{\mathrm{Intra}}_{\Gamma_8^+,\Gamma_8^+}(\gamma_1,\gamma_2,\gamma_3) = L^{\mathrm{Intra}}_{\Gamma_8,\Gamma_8}(\gamma_1,\gamma_2,\gamma_3) = -\frac{\hbar^2}{2m_0}\begin{pmatrix} P+Q & -S & R & 0 \\ -S^* & P-Q & 0 & R \\ R^* & 0 & P-Q & S \\ 0 & R^* & S^* & P+Q \end{pmatrix}, \tag{D6}$$

$$L^{\mathrm{Inter}}_{\Gamma_8,\Gamma_8}(\gamma_1,\gamma_2,\gamma_3,\gamma_3') = L^{\mathrm{Intra}}_{\Gamma_8,\Gamma_8}(\gamma_1,\gamma_2,\gamma_3) - \frac{\hbar^2}{2m_0}\gamma_3'\begin{pmatrix} 0 & 0 & -3ik_x k_y & 6k_+k_z \\ 4\sqrt{3}k_+k_z & 0 & 6k_-k_z & ik_x k_y \\ -ik_x k_y & -6k_+k_z & 0 & -4\sqrt{3}k_-k_z \\ -6k_-k_z & 3ik_x k_y & 0 & 0 \end{pmatrix}, \tag{D7}$$

where $k_\pm = k_x \pm ik_y$, $k_\parallel^2 = k_x^2 + k_y^2$, $k^2 = k_x^2 + k_y^2 + k_z^2$, $P = \gamma_1 k^2$, $Q = \gamma_2(k_\parallel^2 - 2k_z^2)$, $S = 2\sqrt{3}\gamma_3 k_- k_z$, and $R = -\sqrt{3}\bar{\gamma}k_-^2 + \sqrt{3}\mu k_+^2$. A linear combination of Γ_5^+ generators in Table IV was used to obtain the last matrix of Eq. (D7).

APPENDIX E: FIRST-ORDER k · p INTERACTIONS IN SINGLE-GROUP FORMULATION FOR SINGLE-GROUP REAL HARMONIC BASIS AND ADAPTED DOUBLE-GROUP BASIS

Group theoretical methods show that the first-order **k** · **p** interaction between basis states of any IRs under single-group formulation, can be described by one matrix and one scaling constant. Therefore, the matrix can be obtained from a given set of bases belonging to the relevant IRs. First, we consider the real spherical harmonic basis of the O_h group, which is generally available in the literature.[62–64,65] Referring to the real spherical harmonic basis of $\{1\}(\Gamma_1^+)$, $\{xyz\}(\Gamma_2^-)$, $\{x,y,z\}(\Gamma_4^-)$, $\{yz,zx,xy\}(\Gamma_5^+)$, $\{yz(6x^2-y^2-z^2),\ zx(6y^2-z^2-x^2),\ xy(6z^2-x^2-y^2)\}(\Gamma_5^+)$, $\{(2z^2-x^2-y^2)/\sqrt{3},\ x^2-y^2\}(\Gamma_3^+)$, and $\{xyz(x^2-y^2),\ xyz(x^2+y^2-2z^2)/\sqrt{3}\}(\Gamma_3^-)$, the first-order **k** · **p** interaction matrix can be evaluated using the Wigner-Eckart theorem and most have been given in the literature:[9,10,58]

$$K^R_{\Gamma_5^+:\Gamma_2^-} = K^R_{\Gamma_4^-:\Gamma_1^+} = \frac{\hbar}{m_0}\xi\begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix}, \tag{E1a}$$

$$K^R_{\Gamma_4^-:\Gamma_5^+} = K^R_{\Gamma_5^+:\Gamma_4^-} = \frac{\hbar}{m_0}\xi\begin{pmatrix} 0 & k_z & k_y \\ k_z & 0 & k_x \\ k_y & k_x & 0 \end{pmatrix}, \tag{E1b}$$

$$K^R_{\Gamma_4^-:\Gamma_3^+} = \frac{\hbar}{m_0}\xi\begin{pmatrix} -k_x & \sqrt{3}k_x \\ -k_y & -\sqrt{3}k_y \\ 2k_z & 0 \end{pmatrix}, \tag{E1c}$$

$$K^R_{\Gamma_5^+:\Gamma_3^-} = \frac{\hbar}{m_0}\xi\begin{pmatrix} \sqrt{3}k_x & k_x \\ -\sqrt{3}k_y & k_y \\ 0 & -2k_z \end{pmatrix}, \tag{E1d}$$

where the superscript R indicates the use of real spherical harmonic basis. In crystals with zincblende lattice, one has to consider the possibility of zone-center basis functions containing both even and odd parts. All of the single-group bases of the O_h group can be mapped across to the compatible IRs of the T_d group (see Table V), with the exception of the basis of Γ_3^- IR. A unitary transformation is required (see Sec. IX for details) on the basis of Γ_3^- to ensure the representation matrices are the same for all elements common to the O_h and T_d groups.[66] Therefore, even and odd bases of Γ_5 and an even basis of Γ_3 are obtained from Γ_5^+, Γ_4^- and Γ_3^+, respectively, whereas the odd basis of Γ_3 is given by the basis of Γ_3^- transformed by

$$T_{\Gamma_3} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}. \tag{E2}$$

The interaction matrix between $\Gamma_5 : \Gamma_5$ and $\Gamma_5 : \Gamma_3$ IRs is given by

$$K^R_{\Gamma_5,\Gamma_5}(\xi) = K_{\Gamma_4^-,\Gamma_5^+}(\xi_1) + K_{\Gamma_5^+,\Gamma_4^-}(\xi_2), \tag{E3a}$$

$$K^R_{\Gamma_5,\Gamma_3}(\xi) = K_{\Gamma_4^-,\Gamma_3^+}(\xi_1) + K_{\Gamma_5^+,\Gamma_3^-}(\xi_2) \cdot T^T_{\Gamma_3}. \tag{E3b}$$

Since the matrices $K^R_{\Gamma_4^-,\Gamma_5^+}$ and $K^R_{\Gamma_5^+,\Gamma_4^-}$, and $K^R_{\Gamma_4^-,\Gamma_3^+}$ and $K^R_{\Gamma_5^+,\Gamma_3^-} \cdot T^T_{\Gamma_3}$ have the same form, both sets can be combined to give single matrix and scaling constants as required by group theory:

$$K^R_{\Gamma_5,\Gamma_5}(\xi) = K^R_{\Gamma_4^-,\Gamma_5^+}(\xi), \quad \xi = \xi_1 + \xi_2, \tag{E4a}$$

$$K^R_{\Gamma_5,\Gamma_3}(\xi) = K^R_{\Gamma_4^-,\Gamma_3^+}(\xi), \quad \xi = \xi_1 + \xi_2. \tag{E4b}$$

All of the scaling constants in Eqs. (E1), (E3), and (E4) remain purely imaginary. Performing a direct product between single-group and spinor states, the interaction matrices are in block diagonal form with the single-group result occurring twice along the main diagonal.

Several comments can now be made on differences between interaction matrices derived in single-group formulation using the single-group basis here and those derived in the literature. The difference between $K^R_{\Gamma_5^+:\Gamma_3^-}$ and $K^R_{\Gamma_4^-:\Gamma_3^+}$ is not due to convention but governed by the relevant representation matrices. It is also necessary to ensure the interaction between the Γ_5 and the Γ_3 under the T_d group is described by a single matrix as required by group theory under compatibility relations. This may not have been realized in previous work,[10,16,58] where $K^R_{\Gamma_4^-:\Gamma_3^+}$ is used in place of $K^R_{\Gamma_5^+:\Gamma_3^-}$ (use of basis for Γ_3^+ in place of Γ_3^-). With regard to selection rules of the first-order interaction matrices, the presence of k_z indicates a nonzero z component momentum matrix (p_z) element between the relevant states. Therefore, p_z can only couple basis states between $xy[\Gamma_5^+(\Gamma_5)]$ and $xyz[\Gamma_2^-(\Gamma_1)]$ or $z[\Gamma_4^-(\Gamma_5)]$ and $1[\Gamma_1^+(\Gamma_1)]$ for interactions between $\Gamma_5^+ : \Gamma_2^-(\Gamma_5 : \Gamma_1)$ or $\Gamma_4^- : \Gamma_1^+(\Gamma_5 : \Gamma_1)$. As the xy (z and xy) basis only occurs in the heavy-hole states of the adapted double-group basis of crystals with diamond (zincblende) lattice, light polarized in the z direction can only couple heavy hole to the Γ_2^- (Γ_1) conduction band state, contrary to experimental evidence for transition to the lowest conduction band state at zone center. Therefore, the symmetry of the lowest conduction band state is the Γ_4^- (Γ_5) in crystals with diamond (zincblende) lattice. The same conclusion was obtained using selection rules based on general double-group formulation in Sec. X. The adapted double-group basis can be obtained from the real spherical harmonic basis of the single group by following the method of Cracknell,[59] or more simply through inspection of the last column of the standard group basis of $\Gamma_8^\pm$ listed in Appendix B. After appropriate normalization, we have

$$\phi^i_{\Gamma_8^-}(x,y,z : \Gamma_4^-) = \phi^i_{\Gamma_8^-}(j = 3/2), \tag{E5}$$

$$\phi^i_{\Gamma_8^+}(yz,zx,xy : \Gamma_5^+) = \sqrt{\frac{3}{5}}\phi^i_{\Gamma_8^+}(j = 3/2) + \sqrt{\frac{2}{5}}\phi^i_{\Gamma_8^+}(j = 5/2), \tag{E6}$$

$$\phi^i_{\Gamma_8^+}(\{x^2 - y^2, (2z^2 - x^2 - y^2)/\sqrt{3}\} : \Gamma_3^+) = \sqrt{\frac{2}{5}}\phi^i_{\Gamma_8^+}(j = 3/2) - \sqrt{\frac{3}{5}}\phi^i_{\Gamma_8^+}(j = 5/2). \tag{E7}$$

Once the adapted double-group basis functions are known in terms of real spherical harmonics, or standard basis functions as above, the interaction matrices can either be obtained by a transformation from known single-group results or calculated using the Winger-Eckart theorem described in Sec. V. An additional factor of 3 weighting for interaction between $j = 3/2 : j = 5/2$ compared to $j = 3/2 : j = 3/2$ interaction is required to account for the difference in reduced tensor elements $\langle 3/2 \| p \| 3/2 \rangle$ and $\langle 3/2 \| p \| 5/2 \rangle$. The $\mathbf{k} \cdot \mathbf{p}$ interaction matrix between states of $\Gamma_8^\pm$ IRs derived from single-group bases (single-group IRs are indicated within brackets) are given by

$$K_{\Gamma_8^-(\Gamma_4^-),\Gamma_8^+(\Gamma_5^+)} = \frac{\hbar}{m_0}\xi_1 \begin{pmatrix} k_z & 0 & 0 & k_+ \\ 0 & -k_z & k_- & 0 \\ 0 & k_+ & k_z & 0 \\ k_- & 0 & 0 & -k_z \end{pmatrix}, \tag{E8}$$

$$K_{\Gamma_8^-(\Gamma_4^-),\Gamma_8^+(\Gamma_3^+)} = \frac{\hbar}{m_0}\xi_1 \begin{pmatrix} 0 & \sqrt{3}k_- & 0 & -3k_+ \\ \sqrt{3}k_+ & 4k_z & -k_- & 0 \\ 0 & -k_+ & -4k_z & \sqrt{3}k_- \\ -3k_- & 0 & \sqrt{3}k_+ & 0 \end{pmatrix}. \tag{E9}$$

In the case of zincblende crystals, one has to consider that zone-center states may contain both even and odd parts of the basis. The even part of the Γ_8 basis is just given by the basis of Γ_8^+, whereas the odd part of the basis is given by the basis of Γ_8^- transformed by the matrix T^{Γ_8} given by Eq. (27). The interaction matrix is generally given by

$$\begin{aligned} K_{\Gamma_8(\Gamma_5),\Gamma_8(\Gamma_5)}(\xi) &= T^*_{\Gamma_8} \cdot K_{\Gamma_8^-(\Gamma_4^-),\Gamma_8^+(\Gamma_5^+)}(\xi_1) \\ &\quad + K_{\Gamma_8^+(\Gamma_5^+),\Gamma_8^-(\Gamma_4^-)}(\xi_2) \cdot T^T_{\Gamma_8} \\ &= \frac{\hbar}{m_0}\xi \begin{pmatrix} 0 & k_+ & k_z & 0 \\ -k_- & 0 & 0 & k_z \\ -k_z & 0 & 0 & -k_+ \\ 0 & -k_z & k_- & 0 \end{pmatrix}, \end{aligned} \tag{E10}$$

$$\begin{aligned} K_{\Gamma_8(\Gamma_5),\Gamma_8(\Gamma_3)}(\xi) &= T^*_{\Gamma_8} K_{\Gamma_8^-(\Gamma_4^-),\Gamma_8^+(\Gamma_3^+)}(\xi_1') \\ &\quad + K_{\Gamma_8^+(\Gamma_5^+),\Gamma_8^-(\Gamma_3^-)}(\xi_2') T^T_{\Gamma_8} \\ &= \frac{\hbar}{m_0}\xi \begin{pmatrix} 0 & -k_+ & -4k_z & \sqrt{3}k_- \\ 3k_- & 0 & -\sqrt{3}k_+ & 0 \\ 0 & -\sqrt{3}k_- & 0 & 3k_+ \\ \sqrt{3}k_+ & 4k_z & -k_- & 0 \end{pmatrix}. \end{aligned} \tag{E11}$$

When using these interaction matrices derived from a single-group formulation of multiband $\mathbf{k} \cdot \mathbf{p}$ theory, one must pay particular attention to the order of the adapted double-group basis, the single-group parent IR from which the relevant states originate, the type of crystal, and the possibility of complex scaling constants when dealing with crystals with a zincblende lattice.

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