Electron wave functions in diamond and zinc-blende semiconductors

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New electron wave functions at the center of the Brillouin zone are given for the valence and conduction bands of semiconductor crystals with diamond and zinc-blende lattice symmetries. They are analyzed in the absence of spin-orbit coupling and take into account the lack of inversion symmetry in zinc-blende lattices compared to diamond ones. For this reason, our wave functions differ from the traditionally used ones. In particular, for zinc-blende symmetry crystals, they provide nonvanishing intravalence band matrix elements of momentum $\hat{\mathbf{p}}$ in accordance with group theory selection rules.

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I. INTRODUCTION

This study of semiconductor crystals was initially motivated by the discrepancies which exist between theory and experiment in applied problems. The discrepancies we observed are linked to the dynamics of polarization modes in GaAs-based vertical cavity lasers.[1] They have been finally attributed[2] to incorrect evaluation of the interband transition matrix elements in dipole approximation,[3,4] when traditional wave functions[5] for conduction and valence bands have been used. The fact that wave functions, especially for valence bands, have to be modified can be seen from the following observation: lack of inversion symmetry in zinc-blende structures implies that *intraband* matrix elements of momentum operator $\hat{\mathbf{p}}$ in the valence bands are nonvanishing.

For a majority of zinc-blende semiconductors, the wave functions in the valence bands transform at the center of the Brillouin zone (BZ), as Γ_8 (heavy and light hole bands) and Γ_7 (split-off band) which are extra representations of the double group[5–9] T_d, where $\Gamma_4 \otimes D^{(1/2)} = \Gamma_8 + \Gamma_7$. The momentum $\hat{\mathbf{p}}$ transforms as the Γ_4 representation of both point and double groups T_d. Since the direct products $\Gamma_4 \otimes \Gamma_4$ (for the point group) and $\Gamma_8 \otimes \Gamma_4$ (for the double group) contain, respectively, Γ_4 and Γ_8 representations ($\Gamma_4 \otimes \Gamma_4 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$ and $\Gamma_8 \otimes \Gamma_4 = \Gamma_6 + \Gamma_7 + 2\Gamma_8$),[7] one should expect that the intravalence band matrix elements of $\hat{\mathbf{p}}$ are nonzero with and without spin-orbit interaction. However, such matrix elements are zero for traditionally employed wave functions[5–7,10,11] (e.g., without spin-orbit interaction, $\langle X|\hat{\mathbf{p}}|Y\rangle = \mathbf{0}$).

In this paper, we construct the wave functions as combinations[12,13] of cubic harmonics[14–18] (CHs). Our approach to construct the crystal wave functions is based on transformation properties of point group CHs analyzed at nonequivalent lattice sites. In our study, conduction and valence band wave functions in crystals of diamond and zinc-blende lattice symmetries are analyzed assuming that the zinc-blende lattice is a perturbation of a diamond lattice. Our wave functions take into account the lack of inversion symmetry in zinc-blende structures and lead to nonvanishing intravalence band matrix elements of the momentum operator. Since $\hat{\mathbf{p}}$ acts on coordinate functions and not on spinorial ones, we focus here on spinless wave functions. Our wave

functions for zinc-blende crystals significantly differ from the usual cubic harmonics of the point group[19] used in the fundamental work of Kane.[5] These conventional functions actually assume the spherical symmetry of the crystalline potential on each lattice site.

The paper is organized as follows. In Sec. II, we obtain the wave functions for the valence and conduction bands in diamond and zinc-blende crystal structures. In Sec. III we summarize our main results and compare our wave functions with the traditionally used ones: $|S\rangle$ for the conduction band and a set of functions $\{|X\rangle, |Y\rangle, |Z\rangle\}$ for valence bands of III–V semiconductors.

II. WAVE FUNCTIONS

A. Nonprimitive translation

At the Γ point of the BZ, the wave functions are just the periodic Bloch functions $u_{n\mathbf{k}}(\mathbf{r})$. In zinc-blende symmetry crystals (such as GaAs), $u_{n\mathbf{k}}(\mathbf{r})$ are given by linear combinations of corresponding basis set of the irreducible representation (IR) of T_d group.[12,13,20–22] However, the lack of inversion symmetry has to be taken into account in zinc-blende semiconductors as opposed to the invariance of diamond semiconductors under inversion followed by nonprimitive translation on $\boldsymbol{\tau} = (\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a)$ (see the Appendix). To construct such periodic crystal wave functions, symmetrized plane wave representation[12,20,23,24] of CHs will be used. The principle issues are the number and the order of spatial harmonics involved in such orbital expansions.

In Si, Ge, and GaAs crystals, the atomic orbitals of the outermost electrons contributing to the valence bands extend to a few lattice constants from the nuclei. The related crystal wave functions are relatively flat. Therefore, in numerical simulations, the plane wave approximation method is more efficient and suitable than the method using the linear combinations of atomic orbitals.[12] Accordingly, in our simplified analytical treatment, we just use main-order spatial harmonics which form the topmost valence bands and the few first conduction bands of an empty lattice. These eight plane waves as well as their combinations, symmetrized under the T_d point group, are well-known and they are given in the Appendix [Eqs. (A1) and (A2), respectively].

The symmetrized plane waves (SPWs) of Eq. (A2) only take into account the rotations of the T_d point group. They do not take into consideration the nonprimitive translations of the lattice. Nevertheless, in Ref. 5, $|S\rangle$ and a set of $\{|X\rangle, |Y\rangle, |Z\rangle\}$ harmonics are used as conduction and valence bands wave functions with definite angular momentum quantum numbers. On the other hand, a nonprimitive translation operator $\hat{T} = \exp\{-i\boldsymbol{\tau}\hat{\mathbf{p}}/\hbar\}$, which shifts the coordinate origin from an A-type to B-type sublattice (see the Appendix), implies the following relationships between the CHs:

$$\hat{T}|S\rangle = i|-iXYZ\rangle, \quad \hat{T}|-iXYZ\rangle = i|S\rangle,$$

$$\hat{T}|-XY\rangle = i|iZ\rangle, \quad \hat{T}|iX\rangle = i|-YZ\rangle, \tag{1}$$

and those obtained by cyclic permutation (CP) of X, Y, and Z. Therefore a harmonic of $L=0$ ($L=1$) in the vicinity of an A-type ion, has $L=2$ ($L=3$) under rotations about B-type site. The wave states cannot thus be characterized by the angular momentum number L.

The matrix elements of a physical quantity must be independent of the choice of coordinate origin. For example, nonvanishing matrix elements of the momentum operator in the SPWs basis (A2) are

$$P = \langle S|\hat{p}_x|iX\rangle = \langle -iXYZ|\hat{p}_x|-YZ\rangle = \langle -XY|\hat{p}_x|iY\rangle$$

$$= \langle -XY|\hat{p}_y|iX\rangle, \tag{2}$$

where P is a real number and other relationships can be obtained by simultaneous CP of x, y, z and of X, Y, and Z. Relationships (1) and (2) are consistent with an arbitrary choice of the coordinate origin. Thus a matrix element of $\hat{\mathbf{p}}$ evaluated at the A-type sublattice site is identical to the one calculated at the B-type sublattice site, using the same states (e.g, $\langle S|\hat{p}_x|iX\rangle = \langle -iXYZ|\hat{p}_x|-YZ\rangle$). This property is inexplicitly used in Refs. 5 and 6, as $\hat{\mathbf{p}}$ is considered to be a physical quantity operator, but relationships (1) are ignored.

B. Crystal potential

In zinc-blende and diamond lattices, the effective Hartree-Fock potential $V(\mathbf{r})$ is a scalar which transforms as Γ_1 under the T_d point group rotations. The asymptotic behavior of $V(\mathbf{r})$ in the vicinity of a lattice site is given by the multipole expansion:[23,25]

$$V(\mathbf{r}) \propto V_0(r)\{\Gamma_1(s)\} + V_3(r)\left\{\frac{\Gamma_1(f)}{a^3}\right\} + V_4(r)\left\{\frac{\Gamma_1(g)}{a^4}\right\}$$

$$+ V_6(r)\left\{\frac{\Gamma_1(i)}{a^6}\right\} + \cdots, \tag{3}$$

where $V_L(r)$ is the radial part of a 2^L-pole potential ($r=|\mathbf{r}|$). The angular part is given by a cubic harmonic of the form $\{\Gamma_1(L)/a^L\}$. In Eq. (3), summation is over the different orders L of Γ_1-type CHs. In particular, the angular part of a monopole (first term) is $\{\Gamma_1(s)\} \propto 1$ and the one of an octopole (second term) is $\{\Gamma_1(f)/a^3\} \propto xyz/a^3$. Note that this octopole term is absent in cubic symmetry lattices which contain the

coordinate inversion as an element of the rotational subgroup. Thus, in a lattice with full cubic symmetry (for example, in sodium), the function $\{xyz\}$ is a β-type cubic harmonic. It transforms as Γ_2^- irreducible representation of O_h point group, while the potential transforms as Γ_1^+ and contains only α-type CHs.[13,20]

1. Diamond lattice

Diamond lattice is invariant under the symmetry operator $\hat{T}\hat{I}$ (coordinate inversion followed by translation on $\boldsymbol{\tau}$). Therefore, the effective single-electron Hamiltonian, $\hat{H} = \hat{\mathbf{p}}^2/2m + V(\mathbf{r})$, and the potential (3) verify

$$\hat{H} = (\hat{T}\hat{I})\hat{H}(\hat{T}\hat{I})^{-1}, \quad \hat{V} = (\hat{T}\hat{I})\hat{V}(\hat{T}\hat{I})^{-1}. \tag{4}$$

Correspondingly, the wave functions built from SPWs basis (A2) have to be invariant or anti-invariant under operator $\hat{T}\hat{I}$. Using Eq. (1), and noting that L-order CHs (A2) are multiplied by $(-1)^L$ under the inversion $\hat{I}$, the following important wave functions are obtained at the BZ center of diamond-type semiconductors:

$$|S \pm XYZ\rangle = \frac{|S\rangle \pm i|-iXYZ\rangle}{\sqrt{2}}, \tag{5}$$

$$|-YZ \mp X\rangle = \frac{|-YZ\rangle \pm i|iX\rangle}{\sqrt{2}},$$

$$|-ZX \mp Y\rangle = \frac{|-ZX\rangle \pm i|iY\rangle}{\sqrt{2}},$$

$$|-XY \mp Z\rangle = \frac{|-XY\rangle \pm i|iZ\rangle}{\sqrt{2}}, \tag{6}$$

where functions (5) transform as Γ_1 and functions (6) as Γ_4 representations of T_d point group. Functions with the upper (lower) sign are symmetric (antisymmetric) under $\hat{T}\hat{I}$ operator (for example, $\hat{T}\hat{I}|S \pm XYZ\rangle = \pm|S \pm XYZ\rangle$). As these functions define the symmetry of $u_{n0}(\mathbf{r})$ in diamond lattice, the potential (3) is diagonal in this new basis set:

$$\hat{V}_{O_h^7}(\mathbf{r}) = V_c^s|S+XYZ\rangle\langle S+XYZ| + V_c^a|S-XYZ\rangle\langle S-XYZ|$$

$$+ \sum_{CP\{X,Y,Z\}} V_v^s|-YZ-X\rangle\langle -YZ-X|$$

$$+ \sum_{CP\{X,Y,Z\}} V_v^a|-YZ+X\rangle\langle -YZ+X|, \tag{7}$$

where summation is over cyclic permutations of X, Y, and Z. An analysis of the asymptotic behavior of potential (7) in the vicinity of a lattice site ($r \ll a$) shows that the potential contains 2^L-pole moments with L up to 6 in the expansion (3). Note that, if $V_c^s = V_c^a$ and $V_v^s = V_v^a$, the octopole terms ($\propto xyz$) cancel out and the potential (7) corresponds to a lattice with full cubic symmetry. Since we focus on diamond and zinc-blende structures, we assume that $V_c^s \neq V_c^a$ and $V_v^s \neq V_v^a$.

The solution of an effective single-electron Hamiltonian with potential (7) is straightforward and yields the energy bands (E_S^s, E_S^a, E_X^s, and E_X^a) at Γ point of BZ:

$$E_S^{s,a} = \frac{3P^2}{2m} + V_c^{s,a}, \quad E_X^{s,a} = \frac{3P^2}{2m} + V_v^{s,a} \quad (8)$$

where bands E_S^s and E_S^a are nondegenerate and are associated with symmetric and antisymmetric wave functions (5), respectively. Bands E_X^s and E_X^a are associated with symmetric and antisymmetric functions (6) and each of them is triply degenerated.

Relations between matrix elements V_c^s and V_c^a as well as those between elements V_v^s and V_v^a are established by examining functions (5) and (6) along the [111] crystalline direction and noting that

$$S \propto \cos\left(\frac{3\pi}{2}\xi\right) + 3\cos\left(\frac{\pi}{2}\xi\right),$$

$$-iXYZ \propto i\sin\left(\frac{3\pi}{2}\xi\right) - 3i\sin\left(\frac{\pi}{2}\xi\right),$$

$$-XY \propto \cos\left(\frac{3\pi}{2}\xi\right) - \cos\left(\frac{\pi}{2}\xi\right),$$

$$iX \propto i\sin\left(\frac{3\pi}{2}\xi\right) + i\sin\left(\frac{\pi}{2}\xi\right), \quad (9)$$

where $\mathbf{r} = \xi\boldsymbol{\tau}$, and $\boldsymbol{\tau}$ is a vector of nonprimitive translation in a diamond lattice. Within a lattice unit cell, the symmetric states with probability densities $|S+XYZ|^2$ and $|-YZ-X|^2$ have a better overlap with the potential of both ions located at $\xi=0$ and $\xi=1$, respectively (these ions belong to different fcc sublattices). Therefore $V_c^s < V_c^a$ and $V_v^s < V_v^a$. Thus, among Γ_1-type harmonics (5), the symmetric state $|S+XYZ\rangle$ has lower energy than the antisymmetric state $|S-XYZ\rangle$, that is $E_S^s < E_S^a$. For Γ_4-type functions (6), the degenerated symmetric states $|-YZ-X\rangle$, $|-ZX-Y\rangle$, and $|-XY-Z\rangle$ have lower energy than the antisymmetric ones $|-YZ+X\rangle$, $|-ZX+Y\rangle$, and $|-XY+Z\rangle$, such that $E_X^s < E_X^a$.

In diamond and Si crystals,[11,26] the valence and conduction band wave functions transform, in the absence of spin-orbit coupling, as Γ_{25}^+ and Γ_{15}^- three-dimensional representations[29] of the point group O_h of the full cubic symmetry. It is usually assumed[11] that these are ε-type CHs in the valence bands and δ-type CHs in the conduction bands. At the same time, under T_d point group, both sets of functions transform as Γ_4 representation. Consequently, under symmetry operations of O_h^7 space group in a diamond lattice, we have to associate these states with symmetric and antisymmetric wave functions (6). Energy bands (8) are then such that $E_X^s < E_X^a < E_S^s < E_S^a$. Among these eight states, the three lowest energy states originate from the valence band states of the empty lattice.[27] Therefore, at the Γ point of BZ, the valence band energy is $E_v = E_X^s$. This band is triply degenerated and wave states u_{vYZ}, u_{vZX}, and u_{vXY} are given by symmetric functions (6) such that $u_{vYZ} = |-YZ-X\rangle$ (and CPs). The conduction band is also triply degenerated. The energy

is $E_c = E_X^a$, and wave states u_{cX}, u_{cY}, and u_{cZ} are antisymmetric functions (6) of the form $u_{cX} = |-YZ+X\rangle$ (and CPs). Contrary to traditional wave functions, we thus obtain the bonding and antibonding configurations of ε- and δ-type CHs for the valence and conduction bands.

In Ge crystal,[11,26] in the absence of the spin-orbit coupling, the valence band wave functions transform as Γ_{25}^+ while the conduction band state belongs to the Γ_2^- representation of O_h point group. These functions belong to, respectively, Γ_4 and Γ_1 representations of the T_d point group. Under symmetry operations of O_h^7 space group, we have to associate these states with symmetric wave functions in Eqs. (6) and (5) assuming that the order of the energy bands (8) is $E_X^s < E_S^s < E_X^a < E_S^a$. The valence band is triply degenerated. The energy is $E_v = E_X^s$ and wave functions have the symmetric form $u_{vYZ} = |-YZ-X\rangle$ (and CPs). The wave state of nondegenerated conduction band $E_c = E_S^s$ is $u_{cXYZ} = |S+XYZ\rangle$. As in the valence bands of Si crystal, we obtain the bonding configurations of ε- and δ-type CHs contrary to traditional ε-type CHs. In the conduction band, we obtain the bonding configuration of α- and β-type CHs instead of the usual β-type harmonic.

In diamond lattice-symmetry crystals, all intraband matrix elements of momentum $\hat{\mathbf{p}}$ vanish. For example,

$$\langle -YZ \mp X|\hat{p}_z|-ZX \mp Y\rangle = \frac{\pm i}{2}\langle -YZ|\hat{p}_z|iY\rangle - \frac{\pm i}{2}\langle iX|\hat{p}_z|-ZX\rangle$$

$$= 0. \quad (10)$$

2. Zinc-blende lattice

In a III–V semiconductor crystal with zinc-blende symmetry lattice, the $\hat{T}\hat{I}$ operation is absent. The potential can be considered as a perturbed potential of a crystal with diamond lattice (7):

$$\hat{V}_{T_d^2}(\mathbf{r}) = \hat{V}_{O_h^7}(\mathbf{r}) + \Delta\hat{V}(\mathbf{r}). \quad (11)$$

The perturbation $\Delta\hat{V}$ accounts for the reduced symmetry of the T_d^2 space group lattice and results in off-diagonal terms in the Hamiltonian expressed in the basis of functions (5) and (6). The general form of $\Delta\hat{V}(\mathbf{r})$ is

$$\Delta\hat{V}(\mathbf{r}) = V_c^{AB}|S-XYZ\rangle\langle S+XYZ| + V_c^{AB^*}|S+XYZ\rangle\langle S-XYZ|$$

$$+ \sum_{CP\{X,Y,Z\}} V_v^{AB}|-YZ+X\rangle\langle -YZ-X|$$

$$+ \sum_{CP\{X,Y,Z\}} V_v^{AB^*}|-YZ-X\rangle\langle -YZ+X|. \quad (12)$$

Other off-diagonal terms do not appear because the Hamiltonian with potential (11) has to be of the block-diagonal form with respect to Γ_1 and Γ_4 representations of T_d group. The energy bands of such Hamiltonian at the BZ center are given by

$$E_c^\pm = \frac{3P^2}{2m} + \frac{V_c^a + V_c^s}{2} \pm \frac{1}{2}\sqrt{(V_c^a - V_c^s)^2 + 4|V_c^{AB}|^2}, \quad (13)$$

$$E_v^\pm = \frac{3P^2}{2m} + \frac{V_v^a + V_v^s}{2} \pm \frac{1}{2}\sqrt{(V_v^a - V_v^s)^2 + 4|V_v^{AB}|^2}, \quad (14)$$

where $E_c^- < E_c^+$ and $E_v^- < E_v^+$. The bands E_c^+ and E_c^- are non-degenerated, while both E_v^+ and E_v^- bands are triply degenerated. The wave functions of corresponding states are

$$u_c^+ = C_c|S - XYZ\rangle + \frac{\delta_c^*}{C_c}|S + XYZ\rangle, \quad (15)$$

$$u_c^- = C_c|S + XYZ\rangle - \frac{\delta_c}{C_c}|S - XYZ\rangle, \quad (16)$$

$$u_{vX}^+ = C_v|-YZ + X\rangle + \frac{\delta_v^*}{C_v}|-YZ - X\rangle, \quad u_{vY}^+, \quad u_{vZ}^+, \quad (17)$$

$$u_{vX}^- = C_v|-YZ - X\rangle - \frac{\delta_v}{C_v}|-YZ + X\rangle, \quad u_{vY}^-, \quad u_{vZ}^-, \quad (18)$$

with

$$C_{c,v} = \frac{1}{\sqrt{2}}\sqrt{1 + \delta_{c,v}\frac{V_{c,v}^a - V_{c,v}^s}{V_{c,v}^{AB}}},$$

$$\delta_{c,v} = \frac{V_{c,v}^{AB}}{\sqrt{(V_{c,v}^a - V_{c,v}^s)^2 + 4|V_{c,v}^{AB}|^2}}. \quad (19)$$

Expressions for $u_{vY}^\pm$ and $u_{vZ}^\pm$ follow from $u_{vX}^\pm$ by cyclic permutation of X, Y, and Z. Functions $u_c^\pm$ transform as Γ_1 and functions $u_{vX,Y,Z}^\pm$ as Γ_4 representations of T_d point group.

In GaAs crystal, at the BZ center, the valence band wave functions[9] (heavy hole, light hole, and split-off bands) form the bases of $\Gamma_4 \otimes D^{(1/2)} = \Gamma_8 + \Gamma_7$ representations of T_d point group. Conduction band states belong to $\Gamma_1 \otimes D^{(1/2)} = \Gamma_6$ representation. In the absence of spin-orbit interaction, valence and conduction band wave functions transform as Γ_4 and Γ_1 representations. It follows that if we take into account the T_d^2 space group of the crystal lattice, these states have to be associated with wave functions (18) and (16), such that the bands (13) and (14) are ordered according to the energy scale: $E_v^- < E_c^- < E_v^+ < E_c^+$. The valence band is triply degenerated. The energy is $E_v = E_v^-$, and the wave states are given by the functions $u_{vX,Y,Z}^-$ in Eq. (18). In the conduction band of energy $E_c = E_c^-$, the wave function is u_c^- in Eq. (16).

In crystals with zinc-blende lattice, the momentum operator $\hat{p}$ has nonzero intraband matrix elements in the Γ_4 bands formed by wave functions (17) or (18). For example, in the valence band of GaAs, the intraband matrix elements are of the form:

$$\langle u_{vX}^-|\hat{p}_z|u_{vY}^-\rangle = i(\delta_v - \delta_v^*)\langle -YZ|\hat{p}_z|iY\rangle \simeq -2P\frac{\text{Im}(V_v^{AB})}{V_v^a - V_v^s}, \quad (20)$$

where it is assumed [see Eq. (21)] that $|\delta_v| \ll 1$. Other nonvanishing matrix elements can be obtained from Eq. (20) by cyclic permutation of $x(X)$, $y(Y)$, and $z(Z)$.

One of the most important consequences of these results is that the $\mathbf{k} \cdot \hat{\mathbf{p}}$ Hamiltonian restricted on valence bands has

linear terms in $\mathbf{k}$. This indicates that there exists an energy band which is linear in $\mathbf{k}$ in the vicinity of the BZ center. On the contrary to what has previously been assumed for GaAs,[11,30] energy terms, which are linear in $\mathbf{k}$, exist even in the absence of spin-orbit coupling. These linear terms are small,[30] which implies $|\delta_v| \ll 1$ in Eq. (19), and

$$C_{c,v} \simeq 1, \quad \delta_{c,v} \simeq \frac{V_{c,v}^{AB}}{V_{c,v}^a - V_{c,v}^s}. \quad (21)$$

Note that in the conduction band of GaAs (15), like in the other band of Γ_1 symmetry (16), the intraband matrix element is null.

III. DISCUSSIONS AND CONCLUSION

The core of our analysis is the polynomial representation of wave functions. The wave functions and the crystal potential are represented in the form of CHs polynomials. Our analytical expressions for the electron wave states account for nonprimitive translations of the diamond lattice and the lack of inversion symmetry in the zinc-blende structures. These expressions significantly differ from the traditionally used ones.

In the traditional wave function basis, in particular in the one employed by Kane,[5] the expansion of the potential operator is $\hat{V}(\mathbf{r}) = V_c|S\rangle\langle S| + V_v|X\rangle\langle X| + V_v|Y\rangle\langle Y| + V_v|Z\rangle\langle Z|$. In the vicinity of a lattice site, this potential is of spherical symmetry because $(x^2 + y^2 + z^2)/a^2$ transforms under rotations as an s-type spherical harmonic. In the framework of the crystal field theory, as initiated by Bethe, this is a crude approximation. The crystal field theory assumes that if an atom is a part of a crystal structure, the electrostatic potential which is experienced by an electron in that atom is no longer spherically symmetrical but has the symmetry of the corresponding crystallographic group.[23] From expression (3) for the multipole expansion of potential, we find out that only a monopole term of this expansion is taken into account when traditional wave functions are used. It must be noticed that our expressions for potentials in diamond (7) and zinc-blende [(11) and (12)] structures take into account 2^L-pole moments of potential with L up to 6. These are the main-order terms associated with different energy bands. They do not result from a perturbation analysis.

Consider two well-known commutators of an arbitrary potential $V(\mathbf{r})$ and angular momentum $\hat{\mathbf{L}}$:

$$[\hat{\mathbf{L}}, V(\mathbf{r})] = -i[\mathbf{r} \times \nabla V],$$

$$[\hat{\mathbf{L}}^2, V(\mathbf{r})] = 2(\mathbf{r} \cdot \nabla V) + \mathbf{r}(\mathbf{r} \cdot \nabla)\nabla V - \mathbf{r}^2\nabla^2 V - 2i[\mathbf{r} \times \nabla V]\hat{\mathbf{L}}. \quad (22)$$

These operators are only null for a central symmetry field [i.e., $V(\mathbf{r}) = V(|\mathbf{r}|)$ and $\nabla V = \mathbf{r}/r\, \partial V/\partial r$]. Therefore the spherical symmetry of the traditional crystalline potential allows the quantum number L to be assigned to an electron wave state in the crystal,[23,31] which is actually a well-known fact. Thus, without spin-orbit coupling,[5] the conduction band was

previously associated to the unique s-state $|S\rangle$ of $L=0$ and the valence band to p-states $\{|X\rangle, |Y\rangle, |Z\rangle\}$ of $L=1$. Apart from the fact that the conventional functions do not distinguish the diamond and zinc-blende lattices, the restriction of wave function to a unique order L of symmetry orbitals corresponds to a crystal-field approximation, in which an electron transfer is not allowed.[23] The wave functions have to include symmetry orbitals of different orders L in order to take the possibility of an electron transfer in the crystal into account.

Our wave functions are the eigensolutions of the Hamiltonian taking multipole potential contributions into account. Since the potentials used for diamond [Eq. (7)] and zinc-blende [Eqs. (11) and (12)] structures are different, the corresponding wave functions explicitly account for the lack of inversion symmetry in zinc-blende with respect to diamond. They provide nonzero intraband matrix elements of $\hat{\mathbf{p}}$ in the Γ_4-symmetry bands of zinc-blende lattice crystals, in accordance with the group theory selection rules. In particular, the valence band wave functions for GaAs [Eq. (18)] result in matrix elements of $\hat{\mathbf{p}}$ given by Eq. (20). In accordance with the same selection rules, we have vanishing matrix elements of $\hat{\mathbf{p}}$ in the conduction band of GaAs [wave function Eq. (16)]. In diamond symmetry crystals, the matrix elements of $\hat{\mathbf{p}}$ are null for intraband transitions in both conduction and valence bands [wave functions (5) and (6), and matrix elements (10)].

If we now compare our wave functions for zinc-blende [Eqs. (15)–(18)] with expansion on symmetry orbitals given by Dresselhaus [see Eqs. (14) and (17) of Ref. 7], the higher order CHs are taken into account by a small perturbation of the two lowest order CHs associated with wave functions of the unperturbed diamond structure.[13] On the contrary, in our expressions, even for the unperturbed diamond structure, the higher-order CHs (with $L=2$ or 3) and the harmonics of the two lowest orders (of $L=0$ or 1) contribute equally in the wave functions [Eqs. (5) and (6)]. The same holds for our wave functions in zinc-blende semiconductors. As required in crystal-field symmetry, these wave states are no longer the proper states of the angular momentum operator $\hat{\mathbf{L}}$. High-order cubic harmonics do not simply improve the accuracy of wave functions, but drastically tailor the transformation properties.

In III–V semiconductors with important spin-orbit interaction (e.g., in GaAs), the wave functions with definite full angular momentum J and its projection M_J are usually employed.[5,7,9] However, as we discussed above, nonspherically symmetrical potential does not allow one to use such spherical harmonics as wave functions.

In this work, the spin-orbit coupling has not yet been taken into account. Nevertheless it is possible to appreciate its impact on allowed radiative transitions in zinc-blende semiconductors. In GaAs, at the center of the BZ, a set of interband optical transitions, such as $|\frac{1}{2}; \pm\frac{1}{2}\rangle \rightarrow |\frac{3}{2}; \mp\frac{3}{2}\rangle$ (in the usual $|J; M_J\rangle$ notation), is forbidden in the dipole approximation by M_J selection rule. At the same time, at a general point of BZ ($\mathbf{k} \neq 0$), these transitions are allowed due to band mixing effect. We expect that in the case of functions (16) and (18) used as an angular part of the basis set, such transitions will be allowed even at the center of the Brillouin zone.

APPENDIX: SYMMETRIZED PLANE WAVES OF T_d GROUP

The lattice of a zinc-blende symmetry crystal is composed of two interpenetrating face-centered-cubic (fcc) sublattices of different ions (of type A and B, respectively). It has a symmorphic space group T_d^2, associated with fcc subgroup of translations and T_d subgroup of rotations.[9]

In diamond symmetry crystals, two fcc sublattices are identical. The diamond lattice has O_h^7 space group[27] and its invariant subgroup of rotations and nonprimitive translations contains 48 elements: 24 elements of T_d and 24 additional elements composed from (i) rotations of T_d followed by (ii) inversion about the same lattice site and then by (iii) nonprimitive translations on $\boldsymbol{\tau} = (\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a)$ along the main cube diagonal (a is the period of fcc sublattice).

At the center of the BZ of zinc-blende and diamond-type semiconductors, there are eight plane waves originating from nearest equivalent Γ-points of reciprocal lattice at $(\pm 2\pi/a, \pm 2\pi/a, \pm 2\pi/a)$ that form the topmost valence bands of empty lattice:[27]

$$F_s = \frac{e^{i(2\pi/a)(x+y+z)}}{(2\pi)^{3/2}},$$

$$F_x = \frac{e^{i(2\pi/a)(x-y-z)}}{(2\pi)^{3/2}},$$

$$F_y = \frac{e^{i(2\pi/a)(-x+y-z)}}{(2\pi)^{3/2}},$$

$$F_z = \frac{e^{i(2\pi/a)(-x-y+z)}}{(2\pi)^{3/2}} \tag{A1}$$

and their complex conjugated $F_s^*, F_x^*, F_y^*, F_z^*$. These periodic functions are normalized on a lattice unit cell[6] and provide a representation that is reducible under the symmetry operations of the tetrahedron point group:[28]

$$S = \frac{1}{\sqrt{8}}\{F_s + F_x + F_y + F_z + \text{c.c.}\};$$

$$-iXYZ = \frac{1}{\sqrt{8}}\{F_s + F_x + F_y + F_z - \text{c.c.}\};$$

$$-YZ = \frac{1}{\sqrt{8}}\{F_s + F_x - F_y - F_z + \text{c.c.}\}, \quad -ZX, \quad -XY;$$

$$iX = \frac{1}{\sqrt{8}}\{F_s + F_x - F_y - F_z - \text{c.c.}\}, iY, iZ,$$

where the symmetrized combinations of plane waves[28] (SPWs) of types $-ZX$ and $-XY$ (or iY and iZ) follow from $-YZ$ (or iX, respectively) by simultaneous cyclic permutations of x, y, z and of X, Y, and Z. In these expressions, c.c. stands for complex conjugated; capital letters indicate the main term of Taylor expansion on parameter $|\mathbf{r}|/a$ and correspondence to the CHs. The phases of $\Gamma_4(p)$ and $\Gamma_4(d)$ harmonics [and of $\Gamma_1(s)$ and $\Gamma_1(f)$ harmonics, respectively] are such that both SPWs sets give identical representations of the T_d group.

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