Spin-orbit effects in the hydrogenic impurity levels of wurtzite semiconductors

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The corrections to the $E^*_n$ energy level of hydrogenic impurities in semiconductors with wurtzite crystal structure are calculated using first-order perturbation theory in the envelope-function approximation. We consider the intrinsic (Dresselhaus) spin-orbit effective Hamiltonian in the conduction band and compare its effects to the renormalized extrinsic (Rashba) spin-orbit interaction which is analogous to the spin-orbit interaction in the bare hydrogen atom. In order to evaluate the extrinsic spin-orbit interaction we obtain the renormalized coupling constant $\lambda^*$ for wurtzite semiconductors from 8-band Kane theory. We apply our theory to four representative binary semiconductors with wurtzite crystal structure, namely, GaN, ZnO, InN and AlN, and discuss the relative strength of the effects of the intrinsic and extrinsic spin-orbit contributions.

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where \( k_{\parallel}^2 = k_x^2 + k_y^2 \) and \( \alpha, b, \) and \( \gamma \) are material-dependent parameters which are obtained experimentally or via ab-initio calculations. \( \hat{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \) are the Pauli matrices. While \( \alpha \) and \( \gamma \) can vary considerably between different materials, \( b \) is roughly universal and close to 4 for all materials. Note that \( \hat{H}_{\text{int}} \) has two parts, one of them linear and the other one cubic in the wavevector \( k \). The cubic-in-\( k \) term displays an anisotropy between the \( z \)-direction and the directions in the \( xy \)-plane. This anisotropy and the presence of the linear term distinguish the intrinsic spin-orbit Hamiltonian of wurtzite semiconductors from the Dresselhaus coupling of zincblende semiconductors.

The hydrogenic Hamiltonian \( H_0 \) has the renormalized eigenvalues \( E^*_n = -E^*_n/n^2 \), where \( E^*_n = m^*e^4/2\varepsilon^2\hbar^2 \) is the effective Rydberg energy. The aim of this study is to obtain the corrections to the \( E_2 \) energy level due to the intrinsic and extrinsic spin-orbit Hamiltonians. We will work at the level of first-order perturbation theory, which is adequate due to the smallness of the spin-orbit couplings compared to the separation of the bare \( E_n \) levels. In order to diagonalize the intrinsic Hamiltonian \( \hat{H}_{\text{int}} \) in the \( E_2 \) subspace we use the basis of hydrogenic eigenstates of \( \{L^2, L_z, S^2, S_z\} \), given by

\[
\psi_{200\eta} = \left( \frac{1}{32\pi a^*} \right)^{\frac{1}{2}} \left( 2 - \frac{r}{a^*} \right) e^{-r/2a^*} |\eta\rangle,
\psi_{211\eta} = \left( \frac{1}{64\pi a^*} \right)^{\frac{1}{2}} \left( x + iy \right) a^* e^{-r/2a^*} |\eta\rangle,
\psi_{210\eta} = \left( \frac{1}{32\pi a^*} \right)^{\frac{1}{2}} z e^{-r/2a^*} |\eta\rangle,
\psi_{21-1\eta} = - \left( \frac{1}{64\pi a^*} \right)^{\frac{1}{2}} \left( x - iy \right) a^* e^{-r/2a^*} |\eta\rangle,
\]

where \( \eta = \{\uparrow, \downarrow\} \). The matrix elements of the linear-in-\( k \) terms of \( \hat{H}_{\text{int}} \) in this basis are zero; only the cubic-in-\( k \) terms contribute. Ordering the basis states as: \( \{200 \uparrow\}, \{200 \downarrow\}, \{211 \uparrow\}, \{211 \downarrow\}, \{210 \uparrow\}, \{210 \downarrow\}, \{21, -1 \uparrow\}, \) and \( \{21, -1 \downarrow\} \), the matrix of \( \hat{H}_{\text{int}} \) in the \( n = 2 \) subspace is

\[
\hat{H}_{\text{int}} = \begin{pmatrix}
0 & 0 & 0 & A & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & B & 0 & 0 & 0 \\
A & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix},
\]

where

\[
A = \frac{\gamma}{32\sqrt{2} a^3} \left( \frac{14}{15} b + \frac{133}{60} \right),
B = \frac{\gamma}{32\sqrt{2} a^3} \left( \frac{62}{15} b + \frac{433}{60} \right).
\]

The secular equation for \( \hat{H}_{\text{int}} \), \( \det(\hat{H}_{\text{int}} - \varepsilon \hat{I}) = 0 \), yields

\[
\varepsilon^4 - \varepsilon^2 (A^2 + B^2) + (AB)^2 = 0.
\]

The eigenvalues are then \( \varepsilon_{1,2} = \pm A \) and \( \varepsilon_{3,4} = \pm B \). The other four eigenvalues are degenerate and equal to zero. In Table I we present the non-zero energy corrections for the materials GaN, ZnO, InN and AlN, along with their \( \gamma \) and \( b \) parameters. In the last two columns we present the energy splittings \( 2A \) and \( 2B \) as percentages of the unperturbed energy \( E^*_2 \).

| Material | \( \gamma \) [meVÅ\(^2\)] | \( b \) [μeV] | \( \varepsilon_{1,2} \) [μeV] | \( \varepsilon_{3,4} \) [μeV] | \( E_2^2 \) [meV] | 2A/\( E_2^2 \) [%] | 2B/\( E_2^2 \) [%] |
|----------|----------------|--------------|----------------|----------------|----------------|----------------|----------------|
| GaN      | 400            | 3.954 ± 13.24 | 52.79 ± 11.97  | 0.22           | 0.88           |                |                |
| ZnO      | 320            | 3.855 ± 14.67 | 58.39 ± 14.65  | 0.20           | 0.80           |                |                |
| InN      | 345            | 4.885 ± 14.71 | 59.49 ± 16.20  | 0.18           | 0.73           |                |                |
| AlN      | 6.45           | 3.767 ± 3.98  | 15.81 ± 7.08   | 0.011          | 0.15           |                |                |

### III. DERIVATION OF THE EXTRINSIC SPIN-ORBIT INTERACTION

The spin-orbit Hamiltonian of an electron in vacuum in the presence of an electrostatic potential \( V_0(r) \) is given by

\[
H_{so} = \lambda \hat{\sigma} \cdot \mathbf{k} \times \nabla V_0(r).
\]

When the electron is immersed in a semiconductor in the presence of a mesoscopic potential \( V(r) \), the effective extrinsic spin-orbit Hamiltonian takes the form

\[
H_{\text{ext}} = \lambda^* \hat{\sigma} \cdot \mathbf{k} \times \nabla V(r),
\]

where \( \lambda^* \) is an effective coupling constant. This expression is valid for semiconductors with zincblende crystal structure, which presents a basic cubic symmetry. The wurtzite crystal structure has less symmetry than the zincblende, due to the special role of its \( c \)-axis. This lack of isotropy is also present in the intrinsic spin-orbit coupling given above, Eq. (3). In what follows we shall derive an expression analogous to Eq. (9) for semiconductors with wurtzite crystal structure.

We start with the \( \mathbf{k} \cdot \mathbf{p} \) crystal Hamiltonian:

\[
\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_\mathbf{k} \mathbf{p} + \mathcal{H}_{so}
\]

where

\[
\mathcal{H}_0 = \frac{p^2}{2m} + U(r),
\mathcal{H}_\mathbf{k} \mathbf{p} = \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar^2 k^2}{2m},
\mathcal{H}_{so} = \frac{\lambda}{\hbar} \hat{\sigma} \cdot \mathbf{p} \times \nabla U,
\]
and $U$ is the periodic crystal potential. We will write the

matrix of $\mathcal{H}$ in the common basis of $H_0$ and $J_z$ given by:

$$
\begin{align*}
&v_1 = |iS \uparrowangle \\
&v_2 = |iS \downarrow\rangle \\
&v_3 = -\frac{1}{\sqrt{2}} |(X+iY) \uparrow\rangle \\
&v_4 = -\frac{1}{\sqrt{6}} |(X+iY) \downarrow - 2|Z \uparrow\rangle \\
&v_5 = \frac{1}{\sqrt{6}} |(X-iY) \uparrow + 2|Z \downarrow\rangle \\
&v_6 = \frac{1}{\sqrt{2}} |(X-iY) \downarrow\rangle \\
&v_7 = -\frac{1}{\sqrt{3}} |(X+iY) \downarrow + |Z \uparrow\rangle \\
&v_8 = -\frac{1}{\sqrt{3}} |(X-iY) \uparrow - |Z \downarrow\rangle.
\end{align*}
$$

Here $|S\eta\rangle$ are conduction-band $s$-states, with energy $E_c$, and $|X\eta\rangle$, $|Y\eta\rangle$, and $|Z\eta\rangle$ are valence-band $p$-type states, with energy $E_v$. The energy gap is given by $E_g = E_c - E_v$. We calculate the matrix elements $\mathcal{H}_{ij} = \langle v_i | \mathcal{H} | v_j \rangle$, where $\{i,j = 1, \ldots, 8\}$, and obtain

$$
\mathcal{H} = 
\begin{pmatrix}
E_c & 0 & -\frac{1}{\sqrt{2}} P_2 k_+ & \sqrt{\frac{2}{3}} P_1 k_z & \frac{1}{\sqrt{6}} P_2 k_- & 0 & -\frac{1}{\sqrt{2}} P_1 k_z & -\frac{1}{\sqrt{3}} P_3 k_z \\
0 & E_c & 0 & \frac{1}{\sqrt{6}} P_2 k_+ & \sqrt{\frac{2}{3}} P_1 k_z & \frac{1}{\sqrt{6}} P_2 k_- & 0 & \frac{1}{\sqrt{3}} P_3 k_z \\
-\frac{1}{\sqrt{2}} P_2 k_- & 0 & E_v & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{\sqrt{2}} P_1 k_z & -\frac{1}{\sqrt{2}} P_2 k_- & 0 & E_v & 0 & 0 & 0 & 0 \\
\frac{1}{\sqrt{6}} P_2 k_+ & \sqrt{\frac{2}{3}} P_1 k_z & 0 & 0 & E_v & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt{6}} P_2 k_+ & 0 & 0 & 0 & E_v - \Delta_0 & 0 & 0 \\
-\frac{1}{\sqrt{3}} P_1 k_z & -\frac{1}{\sqrt{3}} P_2 k_- & 0 & 0 & 0 & 0 & E_v - \Delta_0 & 0 \\
\frac{1}{\sqrt{3}} P_2 k_+ & \frac{1}{\sqrt{3}} P_1 k_z & 0 & 0 & 0 & 0 & 0 & E_v - \Delta_0
\end{pmatrix}
$$

where $k_{\pm} = k_x \pm i k_y$ and $\Delta_0 = \frac{\hbar}{4 m c^2} \langle X | \frac{\partial U}{\partial x}, P_y - \frac{\partial U}{\partial y}, P_x | Y \rangle$ is the spin-orbit splitting of the valence bands. We have defined the constants $P_1$ and $P_2$ coming from the matrix elements:

$$
\frac{\hbar}{m} \langle -i S \downarrow | k \cdot p | Z \downarrow \rangle = -i \frac{\hbar}{m} k_z \langle S | p_z | Z \rangle \equiv k_z P_1,
$$

$$
\frac{\hbar}{m} \langle -i S \downarrow | k \cdot p | X \downarrow \rangle = -i \frac{\hbar}{m} k_x \langle S | p_x | X \rangle \equiv k_x P_2.
$$

We now introduce the impurity potential $V(r)$, which varies slowly in the length scale of the lattice constant. Its matrix elements in the basis $\{v_i\}$ are essentially diagonal thanks to the orthogonality of the basis set and its slow variation in atomic scale. In short, we are applying here the envelope function approximation. The matrix of $\mathcal{H} + V$ can be expressed in a compact form using the matrices $T$ familiar from group theory:

$$
T_x = \frac{1}{3\sqrt{2}} \begin{pmatrix}
-\sqrt{3} & 0 & 1 & 0 \\
0 & -1 & 0 & \sqrt{3}
\end{pmatrix},
$$

$$
T_y = -i \frac{3 \sqrt{2}}{4} \begin{pmatrix}
\sqrt{3} & 0 & 0 & 1 \\
0 & 1 & 0 & \sqrt{3}
\end{pmatrix},
$$

$$
T_z = \frac{\sqrt{2}}{3} \begin{pmatrix}
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0
\end{pmatrix}.
$$

Using these matrices, the Hamiltonian matrix becomes:

$$
\begin{pmatrix}
(E_c + V)I_{2 \times 2} & \sqrt{3} P_1 T \cdot k_x \\
\sqrt{3} P_1 T \cdot k_x & (E_v + V)I_{4 \times 4}
\end{pmatrix}
$$

$$
\begin{pmatrix}
-\frac{1}{\sqrt{3}} P_1 \hat{\sigma} \cdot k_x \\
0
\end{pmatrix}
\begin{pmatrix}
(E_v - \Delta_0 + V)I_{2 \times 2}
\end{pmatrix}.
$$
where $k_\alpha = (\alpha k_x, \alpha k_y, k_z)$ and $\alpha = P_2/P_1$.

Following the application of the Foldy-Wouthuysen transformation described by Winkler for zincblende semiconductors\textsuperscript{13} we obtain an effective equation, restricted to the conduction band, for the electronic states in the donor impurity

$$H_c = (E - V)\psi_c = (E - V)\psi_c.$$  \hspace{1cm} (19)

IV. EXTRINSIC SPIN-ORBIT CORRECTIONS TO THE 2P LEVEL OF HYDROGENIC IMPURITIES

Using Eqs. (20) and (21) we obtain the Hamiltonian of the extrinsic spin-orbit interaction due to the Coulomb potential of the hydrogenic donor impurity:

$$H_{\text{ext}} = \frac{24\lambda_w^*}{\hbar^2 \alpha^3} \xi_{2p} \mathbf{L} \cdot S,$$  \hspace{1cm} (22)

where

$$\xi_{2p} = \frac{e^2 \lambda_w^*}{24\hbar^2 \alpha^3}.$$  \hspace{1cm} (23)

As anticipated above, we simplified the Hamiltonian $H_{\text{ext}}$ by setting the ratio $\alpha = 1$ in Eq. (20). We thus revert to the standard spin-orbit coupling of the hydrogen atom, but take into account the appropriate, renormalized, coupling constant $\lambda_w^*$. The calculation of the first-order corrections to the $2p$ energy level of the impurity due to $H_{\text{ext}}$ now follows the standard treatment of spin-orbit interaction in the hydrogen atom. The common eigenvalues of $H_{\text{ext}}$ and $J_2$ are given by:

$$\epsilon_1 = \frac{1}{2} \xi_{2p} \left[ \frac{15}{4} - 2 - \frac{3 \hbar^2}{4} \right] = -\xi_{2p} \hbar^2$$  \hspace{1cm} (24)

for $j = 1/2$, and

$$\epsilon_2 = \frac{1}{2} \xi_{2p} \left[ \frac{15}{4} - 2 - \frac{3 \hbar^2}{4} \right] = \frac{1}{2} \xi_{2p} \hbar^2$$  \hspace{1cm} (25)

for $j = 3/2$. We thus obtain for the energy corrections:

$$\epsilon_1 = -\frac{e^2 \lambda^*}{12\alpha \alpha^3} \equiv -2\beta$$  \hspace{1cm} (26)

$$\epsilon_2 = \frac{e^2 \lambda^*}{24\alpha \alpha^3} \equiv \beta.$$

The numerical values of $\epsilon_1$ and $\epsilon_2$ are shown in Table III, together with the parameters needed for their evaluation. We also give the energy variation as a percentage of the unperturbed energy, $(\epsilon_2 - \epsilon_1)/\epsilon_2^*$. One can see that the splitting due to extrinsic spin-orbit interaction is four orders of magnitude smaller than the energy of the original level. This ratio is small but it is not negligible as it is, in fact, one order of magnitude larger than the one obtained for the hydrogen atom, which is equal to

$$\epsilon_1 = \frac{1}{2} \xi_{2p} \left[ \frac{15}{4} - 2 - \frac{3 \hbar^2}{4} \right] = -\xi_{2p} \hbar^2$$  \hspace{1cm} (24)

for $j = 1/2$, and

$$\epsilon_2 = \frac{1}{2} \xi_{2p} \left[ \frac{15}{4} - 2 - \frac{3 \hbar^2}{4} \right] = \frac{1}{2} \xi_{2p} \hbar^2$$  \hspace{1cm} (25)

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**TABLE II.** Coupling constant of the effective extrinsic spin-orbit interaction and auxiliary material parameters\textsuperscript{13} for wurtzite semiconductors.

| $m^*/m_0$ | $\epsilon$ | $E_g$ [eV] | $\Delta_0$ [meV] | $\lambda_w^*$ [10^{-2} \text{ Å}^2] |
|------------|------------|-------------|-----------------|-----------------|
| GaN        | 0.32       | 9.53        | 3.51            | 72.9            | 5.95            |
| ZnO        | 0.32       | 8.62        | 3.44            | 43              | 3.08            |
| InN        | 0.26       | 7.39        | 0.78            | 40              | 1.33            |
| AlN        | 0.38       | 4.27        | 5.4             | -58.5           | -1.04           |

Using the relation $(\hat{\sigma} \cdot B) = \hat{\mathbf{A}} \cdot B + i \hat{\sigma} \cdot (\mathbf{A} \times B)$, we obtain two terms from the second term in the above equation, one of which corresponds to the effective spin-orbit interaction in the conduction band:

$$H_{\text{ext}} = \lambda_w^* \hat{\sigma} \cdot (k_\alpha \times \nabla_\alpha V).$$  \hspace{1cm} (20)

where we defined $\nabla_\alpha = (\alpha \partial \overline{x}, \alpha \partial \overline{y}, \partial \overline{z})$. We have identified the coupling constant for the extrinsic spin-orbit interaction in wurtzite semiconductors:

$$\lambda_w^* = \frac{\varepsilon P_i^2}{3} \left[ \frac{2}{E_g^2} \frac{1}{(E_g + \Delta_0)^2} \right],$$  \hspace{1cm} (21)

analogous to the known coupling constant $\lambda^*$ in Eq. (9) for zincblende materials.

Note the factor $\alpha \equiv P_2/P_1$ in Eq. (20), which reflects the anisotropy of the wurtzite crystal structure. The Coulomb potential of the hydrogenic impurity, $V(r)$, that appears in Eq. (20), was introduced in Eq. (2). Actually, the spherically symmetric form given after Eq. (2) is a simplified expression which does not include the effect of the anisotropic effective mass and dielectric constant of wurtzite crystal structures\textsuperscript{13}. As a first approximation, here we will work with this spherically symmetric Coulomb potential and will also disregard the $\alpha$-dependence of $\nabla_\alpha$ and $k_\alpha$. A complete treatment of the anisotropy effects would require considering the modified eigenvalue problem of the anisotropic hydrogenic impurity, and then the effect of the factor $\alpha$ in the spin-orbit interaction. We leave this refined treatment for future work. In Table II we present the values of $\lambda_w^*$ for GaN, ZnO, InN, and AlN, along with the material parameters needed to evaluate Eq. (21).

Using the relation $(\hat{\sigma} \cdot \mathbf{A})(\hat{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i \hat{\sigma} \cdot (\mathbf{A} \times \mathbf{B})$, we obtain two terms from the second term in the above equation, one of which corresponds to the effective spin-orbit interaction in the conduction band:

$$H_{\text{ext}} = \lambda_w^* \hat{\sigma} \cdot (k_\alpha \times \nabla_\alpha V).$$  \hspace{1cm} (20)

where we defined $\nabla_\alpha = (\alpha \partial \overline{x}, \alpha \partial \overline{y}, \partial \overline{z})$. We have identified the coupling constant for the extrinsic spin-orbit interaction in wurtzite semiconductors:

$$\lambda_w^* = \frac{\varepsilon P_i^2}{3} \left[ \frac{2}{E_g^2} \frac{1}{(E_g + \Delta_0)^2} \right],$$  \hspace{1cm} (21)

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| $m^*/m_0$ | $\epsilon$ | $E_g$ [eV] | $\Delta_0$ [meV] | $\lambda_w^*$ [10^{-2} \text{ Å}^2] |
|------------|------------|-------------|-----------------|-----------------|
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| InN        | 0.26       | 7.39        | 0.78            | 40              | 1.33            |
| AlN        | 0.38       | 4.27        | 5.4             | -58.5           | -1.04           |
It should be emphasized that this comparison between the hydrogenic impurity and the hydrogen atom was not obvious a priori, since the renormalization of the coupling constant $\lambda$ is very pronounced (6 orders of magnitude) and could have produced results radically different.

We remark that for aluminum nitride (AlN) the relation between $\varepsilon_1$ and $\varepsilon_2$ is inverted. This peculiarity originates in the particular characteristics of its electronic structure, which cause $\lambda^*$ to become negative.

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\[ H_{\text{ext}} + H_{\text{int}} = \begin{pmatrix}
-\varepsilon & 0 & 0 & A & 0 & 0 & 0 & 0 \\
0 & -\varepsilon & 0 & 0 & 0 & 0 & 0 & B \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
A & 0 & 0 & -\beta - \varepsilon + 2\sqrt{\beta} \varepsilon & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \sqrt{2}\beta & -\varepsilon & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -\varepsilon & \sqrt{2}\beta & 0 \\
0 & B & 0 & 0 & 0 & \sqrt{2}\beta & -\beta - \varepsilon & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta - \varepsilon 
\end{pmatrix}, \tag{27} \]

where $\beta$ was defined in Eq. [26] and $A$ and $B$ have been defined in Eqs. [6].

The characteristic polynomial that solves the eigenvalue problem is:

\[ \varepsilon^2 (\varepsilon - \beta)^2 (\varepsilon + 2\beta^2) (\varepsilon + 2\beta^2) = 0, \]

and the corresponding eigenvalues are:

\[ \varepsilon^2 = 0 \quad \Rightarrow \quad \varepsilon_{1,2} = 0, \]

\[ (\varepsilon - \beta)^2 = 0 \quad \Rightarrow \quad \varepsilon_{3,4} = \beta, \]

\[ \varepsilon^2 + \varepsilon \beta - (A^2 + 2\beta^2) = 0 \quad \Rightarrow \quad \varepsilon_{5,6} = -\beta \pm \sqrt{\frac{9}{4} \beta^2 + A^2}, \]

\[ \varepsilon^2 + \varepsilon \beta - (B^2 + 2\beta^2) = 0 \quad \Rightarrow \quad \varepsilon_{7,8} = -\beta \pm \sqrt{\frac{9}{4} \beta^2 + B^2}. \]

We remark that the energy corrections given in Eqs. [29]–[32] contain the previous cases (intrinsic and extrinsic spin-orbit interactions acting alone) in the appropriate limits, and they are represented schematically in Fig. [1].

TABLE III. Extrinsic spin-orbit corrections to the $2p$ energy level of hydrogenic donor impurities for four important wurtzite semiconductors, along with relevant material parameters.

| Material | $a^*$ [Å] | $\lambda_w^*$ [10$^{-2}$ Å$^2$] | $R_y^*$ [meV] | $\varepsilon_1$ [µeV] | $\varepsilon_2$ [µeV] | $(\varepsilon_2 - \varepsilon_1)/E^2$ [%] |
|----------|----------|-----------------|----------|-----------------|-----------------|-----------------|
| GaN | 15.8 | 5.95 | 11.97 | -1.94 | 0.968 | 0.024 |
| ZnO | 14.1 | 3.08 | 14.65 | -1.56 | 0.779 | 0.016 |
| InN | 15.2 | 1.33 | 16.20 | -0.625 | 0.313 | 0.0058 |
| AlN | 5.9 | -1.04 | 70.85 | 14.50 | -7.25 | -0.031 |
FIG. 1. Schematic representation of the corrections to the energy level $E_2^*$ of hydrogenic donor impurities to first order in the intrinsic and extrinsic spin-orbit interactions combined.

nally, we calculate the eigenvalues $\varepsilon_i$ ($i = 3, \ldots, 8$) using the values of $A$, $B$ and $\beta$ corresponding to GaN, ZnO, InN and AlN; the results are given in Table IV.

|       | $\varepsilon_{3,4}$ | $\varepsilon_5$ | $\varepsilon_6$ | $\varepsilon_7$ | $\varepsilon_8$ |
|-------|---------------------|-----------------|-----------------|-----------------|-----------------|
| GaN   | 0.23                | -13.36          | 13.13           | -54.71          | 54.48           |
| ZnO   | 4.90                | -49.39          | 44.94           | -60.78          | 56.33           |
| InN   | 0.76                | -15.42          | 14.66           | -61.31          | 60.63           |
| AlN   | -20.15              | -20.44          | 40.58           | -17.56          | 37.70           |

TABLE IV. Energy corrections due to the combined intrinsic and extrinsic spin-orbit interactions to the energy level $E_2^*$ of hydrogenic donor impurities for four important binary semiconductors with wurtzite crystal structure.

VI. CONCLUSION

We have studied theoretically the effects of the spin-orbit interaction on the $E_2^*$ energy level of hydrogenic donor impurities embedded in semiconductors with wurtzite crystal structure. Both the intrinsic (Dresselhaus) and extrinsic (Rashba) spin-orbit interactions have been considered, first acting separately and then together. The study was carried out at the level of first-order perturbation theory, which turns out to be appropriate given the relative magnitude of the corrections to the unperturbed energy spacings. Furthermore, in order to evaluate the extrinsic spin-orbit interaction it was necessary to calculate the renormalized coupling constant $\lambda^*$ for wurtzite semiconductors from 8-band Kane theory.

We applied our calculations to four currently important semiconductors, i.e. GaN, ZnO, InN, and AlN. A general conclusion of these calculations is that both spin-orbit couplings produce relative energy corrections that are bigger than the standard spin-orbit corrections to the $E_2$ energy level of the hydrogen atom. While for GaN, ZnO, InN we conclude that the intrinsic spin-orbit interaction produces larger energy corrections than the extrinsic one, that is not the case for AlN, where both interactions have comparable effects. Another anomaly shown by AlN is the fact that its effective coupling constant $\lambda^*$ is negative. This causes the eigenvalues $\varepsilon_{3,4}$, which are positive for GaN, ZnO and InN, to become negative for AlN. These anomalies of AlN are due to the specific features of its electronic structure which determine the relevant parameters $\Delta_0$, $\gamma_w$, and $a^*$. Finally, we have found that the combined action of both types of spin-orbit coupling leads to an almost complete breaking of the degeneracy of the unperturbed energy level.

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