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Note

Spin–Orbit Interaction in Metals, Elementary Semiconductors, and Semiconductor Compounds

The general analytic formulas for matrix elements of spin–orbit interaction in metals, elementary semiconductors, and binary semiconductor compounds which belongs to cubic crystal systems are obtained on the basis of Roothaan–Hartree–Fock atomic orbitals.

1. INTRODUCTION

It is well known that spin–orbit interaction may have important consequences on the electronic energy bands of heavy elements and heavy element compounds with a crystal structure. If we are interested in obtaining precise band structure, those interactions must be considered [1].

2. THEORY

Following Weisz's work [2], as modified by Bloom an Bergstresser [3], we can write the spin–orbit contribution to the pseudopotential Hamiltonian as

$$\langle \mathbf{k}_i, \nu \,|\, W_{so} \,|\, \mathbf{k}_j, \nu' \rangle = (\mathbf{k}_i \times \mathbf{k}_j)\, \boldsymbol{\sigma}_{\nu\nu'} \{-i\lambda^S \cos(\mathbf{k}_i - \mathbf{k}_j)\,\boldsymbol{\tau} + \lambda^A \sin(\mathbf{k}_i - \mathbf{k}_j)\,\boldsymbol{\tau}\}, \qquad (1)$$

where

$$\lambda^S = (\lambda_1 + \lambda_2)/2, \qquad \lambda^A = (\lambda_1 - \lambda_2)/2, \qquad (2)$$

are the symmetric and antisymmetric contributions to the spin–orbit Hamiltonian, $\boldsymbol{\sigma}$ is the Pauli spin operator, ν and ν' are spin indices, and $\mathbf{k}_i$, $\mathbf{k}_j$ are vectors from the reciprocal space ($\mathbf{k}_i = \mathbf{k} + \mathbf{g}_i$; $\mathbf{k}_j = \mathbf{k} + \mathbf{g}_j$).

Formula (1) is written for semiconductor compounds with zinc–blende structure. The sine and cosine terms in (1) are appropriate for the crystal structure factor of this lattice, where $\boldsymbol{\tau} = a/8\ (1, 1, 1)$ and a is the lattice constant.

The λ_1 and λ_2 are contributions of the first and second element in the mentioned binary compounds

$$\lambda_1 = \mu B_{nl}^{(1)}(k_i)\, B_{nl}^{(1)}(k_j), \qquad (3)$$

$$\lambda_2 = \alpha\mu B_{nl}^{(2)}(k_i)\, B_{nl}^{(2)}(k_j), \qquad (4)$$

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where μ is an adjustable parameter, and α is constrained such that the ratio of spin–orbit contribution for the atoms in binary compounds is the same as the spin–orbit splitting ratio for free atoms [4].

We include only contributions from the outermost p-core states. The quantum number n has the values 2, 3, 4, 5 for compounds in the Si, Ge, Sn, and Pb rows, respectively. Contribution from inner core states or d-core states can be neglected [3].

For elementary semiconductors Si, Ge, and $\alpha - \text{Sn}$ we can write,

$$\lambda^s = \lambda_1 = \lambda_2, \qquad \lambda^A = 0. \tag{5}$$

This formula is valid for metals also. In that case, the sine and cosine terms must be excluded because the geometrical structure factors of cubic metals are equal to one. Then, $B_{nl}^{(i)}(k)$ is defined by

$$B_{nl}^{(i)}(k) = C \int_0^\infty j_l(kr)\, R_{nl}^{(i)}(r)\, r^2\, dr, \tag{6}$$

where $R_{nl}^{(i)}(r)$ is the radial part of the core wave function, i denotes the element of binary compound ($i = 1, 2,$), j_l is a spherical Bessel function, while C is the normalization constant defined so that

$$\lim_{k \to 0} k^{-1} B_{nl}^{(i)}(k) = 1. \tag{7}$$

3. Analytic Formulas

Integrals defined in formulas (6) and (7) are usually solved numerically on the basis of Hartree–Fock–Slater-type orbitals tabulated in Herman–Skillman (HS) [4].

However, these integrals can be solved analytically on the basis of the radial part of the core wave function obtained by the Roothaan–Hartree–Fock (RHF) method [5. 6]

$$R_{nl}(r) = \sum_{p=1}^{N} c_{nlp} r \chi_{lp}, \tag{8}$$

where N denotes the number of basis functions (Slater-type orbitals) which have the form

$$\chi_{lp} = [(2n_{lp})!]^{-1/2} (2\zeta_{lp})^{n_{lp}+1/2}\, r^{n_{lp}-1} e^{-\zeta_{lp} r}. \tag{9}$$

The parameters c_{nlp}, n_{lp}, ζ_{lp}, and number N for each atom are given in [5, 6]. In Table I, we give these parameters for the $3p$(Zn) and $4p$ (Te) wave functions as an example.

TABLE I

Parameters for the $3p$ (Zn) and $4p$ (Te) Radial Part Core Wave Functions[a]

Zinc			Tellurium		
n_{lp}	ξ_{lp}	c_{nlp}	n_{lp}	ξ_{lp}	c_{nlp}
2	12.37110	−0.35894	2	33.61480	−0.00925
2	20.71820	−0.02867	2	22.33970	−0.22003
3	8.82555	−0.14269	3	12.13790	0.23812
3	6.89964	0.64545	3	10.60150	0.42691
3	4.13660	0.58274	4	7.18478	−0.58604
3	2.20119	0.02297	4	4.88471	−0.62258
			5	2.97927	−0.02040
			5	1.87617	0.00313
			5	1.22654	−0.00118

[a] Reference [5].

Using expansion (8) the integral in formula (6) can be represented in the form

$$\int_0^\infty j_l(kr)\,R_{nl}(r)\,r^2\,dr = \sum_{p=1}^{N} c_{nlp}[(2n_{lp})!]^{-1/2}(2\xi_{lp})^{n_{lp}+1/2} \times \int_0^\infty j_l(kr)\,r^{n_{lp}+2}e^{-\xi_{lp}r}\,dr. \tag{10}$$

By means of the well-known relations between Bessel functions

$$j_l(kr) = \sqrt{\frac{\pi}{2k}}\,r^{-1/2}J_{l+1/2}(kr), \tag{11}$$

the integral on the right side of Eq. (10) can be found in the tables [7]:

$$\begin{aligned}\int_0^\infty j_l(kr)\,r^{n_{lp}+2}e^{-\xi_{lp}r}\,dr &= \sqrt{\frac{\pi}{2k}}\int_0^\infty J_{l+1/2}(kr)\,r^{n_{lp}+3/2}e^{-\xi_{lp}r}\,dr\\ &= \sqrt{\frac{\pi}{2k}}\,\frac{(k/2)^{l+1/2}\,\Gamma(l+n_{lp}+3)}{\sqrt{(\xi_{lp}^2+k^2)^{l+n_{lp}+3}}\;\Gamma(l+\frac{3}{2})}\\ &\quad\times F\left(\frac{n_{lp}+l+3}{2},\frac{l-n_{lp}-1}{2},l+\frac{3}{2},\frac{k^2}{\xi_{lp}^2+k^2}\right),\end{aligned} \tag{12}$$

where F is the hypergeometric function and Γ is the Gamma Function.

In that way we obtained the analytic expression for integral (6)

$$B_{nl}(k) = C\frac{k^l\sqrt{\pi}}{2^{l+1}}\sum_{p=1}^{N} c_{nlp}[(2n_{lp})!]^{-1/2}(2\xi_{lp})^{n_{lp}+1/2}$$
$$\times\frac{\Gamma(l+n_{lp}+3)}{\sqrt{(\xi_{lp}^2+k^2)^{l+n_{lp}+3}}\,\Gamma(l+\frac{3}{2})}F\left(\frac{n_{lp}+l+3}{2},\frac{l-n_{lp}-1}{2},l+\frac{3}{2},\frac{k^2}{\xi_{lp}^2+k^2}\right), \tag{13}$$

where the constant C is defined from the relation

$$C^{-1} = \frac{\sqrt{\pi}}{2^{l+1}}\sum_{p=1}^{N} c_{nlp}[(2n_{lp})!]^{-1/2}(2\xi_{lp})^{n_{lp}+1/2}\frac{\Gamma(l+n_{lp}+3)}{\xi_{lp}^{l+n_{lp}+3}\Gamma(l+\frac{3}{2})}. \tag{14}$$

Hypergeometric function

$$F(a,b,c,z) = F\left(\frac{n_{lp}+l+3}{2},\frac{l-n_{lp}-1}{2},l+\frac{3}{2},\frac{k^2}{\xi_{lp}^2+k^2}\right) \tag{15}$$

is absolutely convergent in the circle

$$|z| = \frac{k^2}{\xi_{lp}^2+k^2} \leqslant 1 \tag{16}$$

because appropriate conditions are satisfied [7]:

$$a+b-c = \frac{n_{lp}+l+3}{2}+\frac{l-n_{lp}-1}{2}-\left(l+\frac{3}{2}\right) = -\frac{1}{2} < 0 \qquad c = l+\frac{3}{2}. \tag{17}$$

Integrals (13) in the $\mathbf{k} = 2\pi/a(0\,0\,0)$ point for the first few and important reciprocal lattice vectors, with $3p$ and $4p$ wave functions of Zn and Te, respectively, are calculated for cubic ZnTe and shown in Table II. Our results are compared with appropriate results obtained on the basis of numerical radial wave functions tabulated in the Herman–Skillman book [4].

Different analytic formulas for the matrix elements of the spin–orbit interaction are given by Bloom and Bergstresser [8]. They applied Slater-type approximation for the radial core wave functions of p-electron states ($l = 1$) in order to calculate integrals $B_{n1}(k)$ in formulas (3) and (4). These wave functions have the form

$$R_{n1} = c_n r^n e^{-nr/r_m}, \tag{18}$$

where r_m is the location of the main maximum of $R_{n1}(r)$ and c_n is the normalization constant. The Roothaan–Hartree–Fock approximation for the radial wave functions applied in our approach is more precise than function (18), because the orbital binding energies obtained with function (8) are lower than the respective energies obtained with (18) [4, 5].

TABLE II

$\mathbf{k} = 2\pi/a(0\,0\,0) +$ reciprocal lattice vectors		Zinc (B_{31})		Tellurium (B_{41})	
Units	Atomic units	Our results	HS[a]	Our results	HS[a]
(0 0 0)	0	0	0	0	0
(1 1 1)	0.948	0.64263	0.76102	0.59026	0.37170
(2 0 0)	1.095	0.66482	0.81897	0.62239	0.40167
(2 2 0)	1.549	0.64071	0.88603	0.61678	0.43885
(3 1 1)	1.816	0.58477	0.86118	0.56440	0.42696

Note. Integrals B_{3p} and B_{4p} for Zn and Te in the cubic ZnTe compound for the point $\mathbf{k} = 2\pi/a(0\,0\,0)$ are calculated by means of formula (13) and compared with the results obtained on the basis of the radial part for the core wave functions (HS).

[a] Reference [4].

In Bloom–Bergstresser's analytic expressions the dependence of the $B_{n1}(k)$ integrals of the respective components in the crystal compound is neglected. They used the approximation

$$B^1_{n1}(k) \sim B^2_{n1}(k) = B_{n1}(k) \tag{19}$$

in (3) and (4). The values of $B_{n1}(k)$ for the group IV atoms are used for compounds in the same row, or the average of the group IV values for skew compounds.

4. EXAMPLE: BAND STRUCTURE OF ZNTE IN THE SYMMETRY POINTS

For illustration we give results for energy bands of ZnTe in the points $\Gamma(0\,0\,0)$, $X(1\,0\,0)$, and $L(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ (in $2\pi/a$ units) from the first Brillouin zone obtained by means of WCPB pseudopotential [9]. Our approach is based on the double expansion technique for the exact inclusion of the spin–orbit interaction influence on the band structure of ZnTe. In order to apply the double expansion technique it is necessary to solve an eigenvalue problem of the one electron pseudo-Hamiltonian without spin–orbit interaction. For this, we use the Brust–Löwdin perturbation technique [10]. With this technique the secular equation for the eigenvalues of order L can be reduced to solving a truncated secular equation of order N ($N \leqslant L$). In our example $L = 89$ and $N = 51$ provide necessary convergence of the solutions of the truncated secular equation. The eigenfunctions obtained in this way have been used for the formation of new trial functions. After that, new trial functions have been applied for solving the eigenvalue problem of the Hamiltonian with spin–orbit term included.

Electron energy levels for the valence and conduction bands in the points Γ, X, and

TABLE III

ZnTe Band Structure in the Points $\Gamma(0\,0\,0)$, $X(1\,0\,0)$, and $L(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ (in $2\pi/a$ Units) Obtained in Our Approach

Energy levels (eV)	Γ	X	L
1	0	1.065113	0.782226
2	10.953309	7.369872	7.455286
3	11.121069	9.908073	10.590770
4	11.126609	9.959153	10.693075
5	13.419953	14.598116	14.177149
6	16.898658	14.971985	17.566808
7	17.020027	22.399764	17.624563
8	17.025535	22.472072	20.119371

L are given in Table III. These results are in accordance with the experimental arrangement of levels.

In Table IV our results for the spin–orbit splitting (eV) in the single group notation are compared with respective results from [9]. These values were obtained with the spin–orbit parameter from [9], $\mu = 0.0010$.

The big difference in the values of the spin–orbit splitting for the levels Γ_{15v} and L_{3v} is because of the different accuracy of the methods compared. In [9] simple perturbation technique and very crude approximation for the radial wave fuctions was applied.

In Table V the orbital binding enrgies for $3p$ and $4p$ states of Zn and Te, respectively (obtained by different methods) are compared.

The Roothaan–Hartree–Fock method [5, 6] aplied in this work, gives more accurate results for the binding energies than Herman–Skillman method [4] (lower binding energies in Table V for the RHF method).

TABLE IV

Spin–Orbit Splitting (eV) in the Single Group Notation for Cubic ZnTe

	Our results	WCPB[a]
Γ_{15v}	0.17	0.92
L_{3v}	0.10	0.58
X_{5v}	0.37	0.46
Γ_{15c}	0.13	0.16
L_{3c}	0.06	0.07

[a] Reference [9].

TABLE V

Binding Energy for $3p$ and $4p$ States of Zn and Te (in Atomic Units)

	HS[a]	RHF[b]	RDF[c]
Zn	−3.3305	−3.83931	−3.837162[d] −3.957845*
Te	−4.4605	−4.95263	−4.836864[d] −5.308623*

[a] Reference [4].
[b] Reference [5].
[c] Relativistic Dirac–Fock method [11].
[d] No * means $j = \frac{3}{2}$; * means $j = \frac{1}{2}$.

5. CONCLUDING REMARKS

The formulas obtained in this paper considerably simplify the band structure calculations with the spin–orbit interaction included. In this manner the numerical integration using the large number of data for radial wave functions from the Herman–Skillman tables [4] is avoided. Our results for $B_{nl}(k)$ integrals are also more accurate because we use better approximation for the radial part of core wave functions.

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