

SOLUTION OF SECULAR DETERMINANTS FOR GROUP IV AND III-V SEMICONDUCTORS BY SYMMETRY ANALYSIS

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Abstract

A brief discussion is given of the symmetry properties of the energy band structure and the method of constructing orthogonal matrices at high symmetry points for group IV and III-V semiconductors. By means of examples it is shown how to factorize the $n \times n$ secular determinant formed by using the pseudopotential form factors of Cohen and Bergstresser (1966), thereby permitting easy numerical solution.

INTRODUCTION

During the past few years many papers have been published on the calculation of energy band structures for semiconductors. In all such calculations there are two main problems (Herring 1940), namely, determination of a suitable crystal potential and numerical solution of the crystal wave equations. In recent work the local pseudopotential model has been found to provide an adequate description of the band structure of several solids (Phillips 1958; Brust 1964; Harrison 1965; Cohen and Bergstresser 1966). The success of the pseudopotential approximation lies in the fact that very few parameters are needed to obtain a reasonable fit to experimental data. In fact Cohen and Bergstresser have shown that within the framework of the local pseudopotential model it should be possible to obtain adequate descriptions of the band structures of various semiconductors from secular determinants of order as low as 20×20 . For the sake of completeness we first present here the essential mathematical features of the pseudopotential method that are required to build up the $n \times n$ secular determinants for group IV and III-V semiconductors. We then consider the method of factorizing the secular determinants formed by using the pseudopotential form factors of Cohen and Bergstresser (1966).

PSEUDOPOTENTIAL FORMALISM OF BAND STRUCTURE

As the local pseudopotential method has been reviewed in great detail by Harrison (1965), only the essential features will be given here. The pseudopotential Schrödinger equation for an electron in a crystal can be written as

$$\{-(\hbar^2/2m)\nabla^2 + V_p\}\phi_{nk}(\mathbf{r}) = E_n(\mathbf{k})\phi_{nk}(\mathbf{r}) \quad (1)$$

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with the pseudopotential V_p given by

$$V_p = V(r) + V_R, \quad (2)$$

where $V(r)$ is the periodic crystal potential and V_R has the character of a repulsive potential which cancels in part the large attractive Coulomb potential such that in the region of the core the higher Fourier coefficients of V_p are small enough to be neglected in the first-order approximation. The functions $\phi_{nk}(r)$ are smooth pseudo-wavefunctions and are free of the convergence difficulties of the corresponding Bloch functions

$$\psi_{nk}(r) = \exp(i \mathbf{k} \cdot \mathbf{r}) U_{nk}(r), \quad (3)$$

which are obtained for the Schrödinger equation with a perfectly periodic potential $V(r)$. The matrix elements of V_p can be written as a product of a structure factor $S(\mathbf{K})$ and a pseudopotential form factor V_{K_i} , where the \mathbf{K} 's are reciprocal lattice vectors (Cohen and Bergstresser 1966). Since the potential for the zinc-blende type crystals of the III-V group is not invariant under inversion (with $\mathbf{r} \rightarrow -\mathbf{r}$), V_p is generally expressed as the sum of two potentials, one of which is symmetric and the other antisymmetric with respect to inversion. We thus have

$$V_p = \sum_{|\mathbf{K}_i|} \{S^s(\mathbf{K}_i) V_{K_i}^s + i S^a(\mathbf{K}_i) V_{K_i}^a\} \exp(i \mathbf{K}_i \cdot \mathbf{r}). \quad (4)$$

If we choose the origin of coordinates to be midway between the two atoms of the diamond or zinc-blende unit cell then

$$S^s(\mathbf{K}) = \cos(\mathbf{K} \cdot \boldsymbol{\tau}) \quad \text{and} \quad S^a(\mathbf{K}) = \sin(\mathbf{K} \cdot \boldsymbol{\tau}), \quad (5)$$

where $\boldsymbol{\tau} = a(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ is the glide translation of the crystal space group and a is the cube edge. The atomic potentials V_K^s and V_K^a are given in Table 2 of Cohen and Bergstresser (1966) for various semiconductors of group IV and III-V. The first three reciprocal lattice vectors with nonzero structure factors are $\langle 111 \rangle$, $\langle 220 \rangle$, and $\langle 311 \rangle$ with $|\mathbf{K}|^2 = 3, 8$, and 11 respectively. We can now solve the Schrödinger equation (1) by determining the roots of the secular equation (Lukes *et al.* 1971, equation (2.8))

$$\det | \{ (\mathbf{K} - \mathbf{k})^2 - E \} \delta_{\mathbf{K}\mathbf{K}'} + V_{\mathbf{K}-\mathbf{K}'} | = 0, \quad (6)$$

where the \mathbf{K} 's are measured in units of $2\pi/a$ and the \mathbf{k} 's are the reduced wave vectors lying in the first Brillouin zone. The $V_{\mathbf{K}-\mathbf{K}'}$ are nonzero only for $|\mathbf{K}-\mathbf{K}'|^2 = 3, 8$, or 11 . In the next section we show that, for wave vectors \mathbf{k} of high symmetry, equation (6) can be readily factorized, thus permitting easy numerical solution.

SYMMETRY PROPERTIES OF ENERGY BANDS OF DIAMOND AND ZINC-BLENDE LATTICES

The symmetry properties of the lattices of group IV and III-V semiconductors, which have diamond and zinc-blende structures respectively, have been discussed in great detail elsewhere (Bouckaert *et al.* 1936; Parmenter 1955; Koster 1957; Slater 1965). The diamond structure belongs to the crystallographic space group

O_h^7 and consists of two interpenetrating f.c.c. lattices displaced along the body diagonal by one-fourth of its length. The zinc-blende structure belongs to the crystallographic space group T_d^2 and the crystal lattice is similar to diamond except that two different kinds of atoms form the two f.c.c. sublattices. The zinc-blende lattice therefore does not possess a centre of inversion symmetry. The point group T_d of the zinc-blende lattice has 24 symmetry elements and is a subgroup of the diamond structure which has, in addition to the 24 symmetry elements of T_d , their product with the inversion element I which gives the full octahedral group O_h consisting of 48 elements. As the two structures have the f.c.c. translation symmetry, the Brillouin zone is the same for the two cases. This zone is shown in Figure 1, where the points and lines of symmetry are indicated as in Koster (1957).

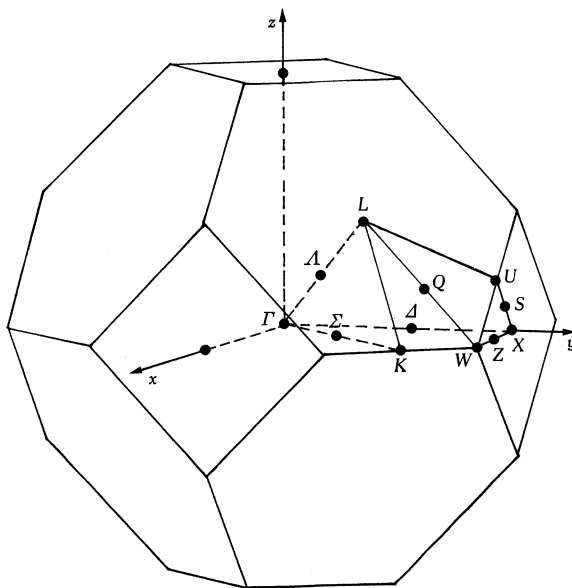


Fig. 1.—Brillouin zone for the f.c.c. lattice with the indicated points and lines of symmetry:

$$\begin{array}{lll}
 \Gamma, (2\pi/a)(0, 0, 0); & A, (2\pi/a)(\alpha, \alpha, \alpha); & L, (2\pi/a)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}); \\
 A, (2\pi/a)(0, \beta, 0); & X, (2\pi/a)(0, 1, 0); & \Sigma, (2\pi/a)(\alpha, \alpha, 0); \\
 W, (2\pi/a)(\frac{1}{2}, 1, 0); & K, (2\pi/a)(\frac{3}{4}, \frac{3}{4}, 0); & Z, (2\pi/a)(\alpha, 1, 0); \\
 S, (2\pi/a)(\alpha, 1, \alpha); & U, (2\pi/a)(\frac{1}{2}, 1, \frac{1}{2}); & Q, (2\pi/a)(\frac{1}{2}, \frac{1}{2} + \alpha, \frac{1}{2} - \alpha).
 \end{array}$$

If the symmetry group $G(\mathbf{k})$ of the wave vector \mathbf{k} is known then it is possible to predict not only the form of the various crystal wavefunctions but also the overall form of the energy bands in the reduced zone. However, the relative order of the eigenstates at a given point can only be determined by solving the crystal wave equation numerically. For high symmetry points this can be done quite easily by factorizing the secular determinant (6) by means of orthogonal matrices, as shown in the next section.

METHOD OF CONSTRUCTING ORTHOGONAL MATRICES AND FACTORIZATION OF SECULAR DETERMINANTS

In the following treatment, $\mathbf{K} \equiv (K_1 K_2 K_3)$, such as (111), (200), etc., will be used to represent the plane wave

$$\exp\{(2\pi i/a)(K_1 x + K_2 y + K_3 z)\} \quad (7)$$

with

$$|\mathbf{K}|^2 = K_1^2 + K_2^2 + K_3^2, \quad (8)$$

while $\langle K_1 K_2 K_3 \rangle$ will represent an ensemble of waves $(K_1 K_2 K_3)$, e.g. $\langle 111 \rangle$ will denote the ensemble of eight waves (111), $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}11)$, $(1\bar{1}1)$, and $(11\bar{1})$ with $|\mathbf{K}|^2 = 3$. The physical significance of $|\mathbf{K}|^2$ is that for an empty lattice it represents the energy to within a factor of $4\pi^2$; in fact

$$E = (2\pi/a)^2(K_1^2 + K_2^2 + K_3^2). \quad (9)$$

TABLE 1

IRREDUCIBLE REPRESENTATIONS FOR PLANE WAVES AT SYMMETRY POINT Γ IN DIAMOND AND ZINC-BLENDE STRUCTURES

$\langle \mathbf{K} \rangle$	$ \mathbf{K} ^2$	Number of plane waves	Diamond					Zinc-blende		
			Γ_1	Γ'_2	Γ'_{12}	Γ_{15}	Γ'_{25}	Γ_1	Γ_{12}	Γ_{15}
$\langle 000 \rangle$	0	1	1	—	—	—	—	1	—	—
$\langle 111 \rangle$	3	8	1	1	—	1	1	2	—	2
$\langle 200 \rangle$	4	6	—	1	1	—	1	1	1	1
Degeneracy of irreducible representation:			1	1	2	3	3	1	2	3

The bases states used to form the secular determinant (6) consist of plane waves with wave vectors $(\mathbf{K} + \mathbf{k})$. In the first approximation all vectors \mathbf{K} such that

$$(\mathbf{K} + \mathbf{k})^2 \leq E_1 \quad \text{with} \quad E_1 = 7$$

form the bases (Cohen and Bergstresser 1966). The second-order contribution is given by

$$E_1 < (\mathbf{K} + \mathbf{k})^2 \leq E_2 \quad \text{with} \quad E_2 = 21.$$

The method of selecting \mathbf{K} is as follows. Let plane waves be represented by

$$E = \exp\{(2\pi i/a)(\mathbf{K} \cdot \mathbf{r})\}.$$

Such a set will form a bases if it is transformed into another real wave after application of all the operators of the diamond or zinc-blende lattice, but must be rejected if an imaginary wave results since the crystal potential is only developed in terms of real waves.

To illustrate the general method of constructing orthogonal matrices let us consider specific examples for the diamond and zinc-blende structures. For the symmetry point Γ it is easily seen using the above method of selecting \mathbf{K} that only the sets $\langle 000 \rangle$, $\langle 111 \rangle$, and $\langle 200 \rangle$ are allowable bases in the first-order approximation ($E_1 \leq 7$). Now the number of plane waves corresponding to the sets $\langle 000 \rangle$, $\langle 111 \rangle$, and $\langle 200 \rangle$ are 1, 8, and 6 respectively and thus this approximation would involve a 15×15 matrix. The irreducible representations for the plane waves $\langle 000 \rangle$, $\langle 111 \rangle$, and $\langle 200 \rangle$ are given in standard group notation in Table 1 for the diamond and zinc-blende structures.

Elementary group theory shows that the ensemble of 15 waves for the diamond structure should form the bases of the reduced representation

$$\Gamma = 2\Gamma_1 + 2\Gamma'_2 + 2\Gamma'_{25} + \Gamma_{15} + \Gamma'_{12}. \quad (10)$$

The 15×15 secular determinant $D_d(\Gamma)$ will thus factorize for this structure at the symmetry point Γ as

$$D_d(\Gamma) = \begin{vmatrix} \overbrace{a_{11} \ a_{12}}^{\Gamma_1} & & & & & & & & & & \\ & \overbrace{a_{21} \ a_{22}}^{\Gamma'_2} & & & & & & & & & \\ & & \overbrace{b_{11} \ b_{12}}^{\Gamma'_{25}} & & & & & & & & \\ & & & \overbrace{b_{21} \ b_{22}}^{\Gamma'_{25}} & & & & & & & \\ & & & & \overbrace{c_{11} \ c_{12}}^{\Gamma'_{25}} & & & & & & \\ & & & & & \overbrace{c_{21} \ c_{22}}^{\Gamma_{15}} & & & & & \\ & & & & & & \overbrace{c_{11} \ c_{12}}^{\Gamma_{15}} & & & & \\ & & & & & & & \overbrace{c_{21} \ c_{22}}^{\Gamma_{15}} & & & \\ & & & & & & & & \overbrace{d_{11}}^{\Gamma'_{12}} & & \\ & & & & & & & & & \overbrace{d_{11}}^{\Gamma'_{12}} & \\ & & & & & & & & & & \overbrace{d_{11}}^{\Gamma'_{12}} \\ & & & & & & & & & & & \overbrace{e_{11}}^{\Gamma'_{12}} \\ & & & & & & & & & & & & \overbrace{e_{11}}^{\Gamma'_{12}} \end{vmatrix}, \quad (11)$$

that is, we should now break the large 15×15 determinant into:

- one second-order determinant (Γ_1 with elements a_{mn}),
- one second-order determinant (Γ'_2 with elements b_{mn}),
- three equal second-order determinants (Γ'_{25} with elements c_{mn}),
- three equal first-order determinants (Γ_{15} with elements d_{11}), and
- two equal first-order determinants (Γ'_{12} with elements e_{11}).

Similarly, for the zinc-blende structure the ensemble of 15 waves forms the bases of the reduced representation

$$\Gamma = 4\Gamma_1 + 3\Gamma_{15} + \Gamma_{12} \quad (12)$$

and as such the 15×15 determinant $D_{zb}(\Gamma)$ in this case will factorize as

$$D_{zb}(\Gamma) = \begin{vmatrix} \overbrace{f_{11} f_{12} f_{13} f_{14}}^{\Gamma_1} & & & & & \\ \overbrace{f_{21} f_{22} f_{23} f_{24}}^{\Gamma_{15}} & & & & & \\ \overbrace{f_{31} f_{32} f_{33} f_{34}}^{\Gamma_{15}} & & & & & \\ \overbrace{f_{41} f_{42} f_{43} f_{44}}^{\Gamma_{15}} & & & & & \\ & \overbrace{g_{11} g_{12} g_{13}}^{\Gamma_{12}} & & & & \\ & \overbrace{g_{21} g_{22} g_{23}}^{\Gamma_{12}} & & & & \\ & \overbrace{g_{31} g_{32} g_{33}}^{\Gamma_{12}} & & & & \\ & & \overbrace{g_{11} g_{12} g_{13}}^{\Gamma_{12}} & & & \\ & & \overbrace{g_{21} g_{22} g_{23}}^{\Gamma_{12}} & & & \\ & & \overbrace{g_{31} g_{32} g_{33}}^{\Gamma_{12}} & & & \\ & & & \overbrace{g_{11} g_{12} g_{13}}^{\Gamma_{12}} & & \\ & & & \overbrace{g_{21} g_{22} g_{23}}^{\Gamma_{12}} & & \\ & & & \overbrace{g_{31} g_{32} g_{33}}^{\Gamma_{12}} & & \\ & & & & \overbrace{h_{11}}^{\Gamma_{12}} & \\ & & & & & \overbrace{h_{11}}^{\Gamma_{12}} \end{vmatrix}, \quad (13)$$

that is, we should now break the 15×15 determinant into:

one fourth-order determinant (Γ_1 with elements f_{mn}),

three equal third-order determinants (Γ_{15} with elements g_{mn}), and

two equal first-order determinants (Γ_{12} with elements h_{11}).

The above method is in fact quite straightforward and general and exactly similar analyses can be performed at other symmetry points in Figure 1. For example, at the symmetry point X of the diamond structure the ensemble of 14 plane waves

$$\begin{aligned} (100), \quad (\bar{1}00), \quad (011), \quad (0\bar{1}\bar{1}), \quad (0\bar{1}0), \quad (01\bar{1}), \quad (120), \\ (\bar{1}\bar{2}0), \quad (\bar{1}20), \quad (\bar{1}\bar{2}0), \quad (102), \quad (10\bar{2}), \quad (\bar{1}0\bar{2}) \end{aligned}$$

should form the bases of the reduced representation

$$X^{(14)} = 3X_1^{(2)} + X_2^{(2)} + X_3^{(2)} + 2X_4^{(2)}, \quad (14)$$

where the superscripts indicate the degeneracy of a representation. Thus the secular

determinant $D_d(X)$ should factorize as

$$D_d(X) = \begin{vmatrix} \overbrace{i_{11} \ i_{12} \ i_{13}}^{X_1} & & & & & & & & \\ \overbrace{i_{21} \ i_{22} \ i_{23}}^{X_1} & & & & & & & & \\ \overbrace{i_{31} \ i_{32} \ i_{33}}^{X_1} & & & & & & & & \\ & \overbrace{i_{11} \ i_{12} \ i_{13}}^{X_1} & & & & & & & \\ & \overbrace{i_{21} \ i_{22} \ i_{23}}^{X_1} & & & & & & & \\ & \overbrace{i_{31} \ i_{32} \ i_{33}}^{X_1} & & & & & & & \\ & & \overbrace{j_{11}}^{X_2} & & & & & & \\ & & & \overbrace{j_{11}}^{X_2} & & & & & \\ & & & & \overbrace{k_{11}}^{X_3} & & & & \\ & & & & & \overbrace{k_{11}}^{X_3} & & & \\ & & & & & & \overbrace{l_{11} \ l_{12}}^{X_4} & & \\ & & & & & & \overbrace{l_{21} \ l_{22}}^{X_4} & & \\ & & & & & & & \overbrace{l_{11} \ l_{12}}^{X_4} & \\ & & & & & & & \overbrace{l_{21} \ l_{22}}^{X_4} & \end{vmatrix}, \quad (15)$$

that is, we should have

- two equal third-order determinants (X_1 with elements i_{mn}),
- two equal first-order determinants (X_2 with elements j_{11}),
- two equal first-order determinants (X_3 with elements k_{11}), and
- two equal second-order determinants (X_4 with elements l_{mn}).

As the formalism is exactly the same for the diamond and zinc-blende structures at all the various symmetry points, we shall consider only the Γ point in constructing the orthogonal matrices and using them to factorize the secular determinants.

The orthogonal matrices are constructed by using a bases formed from symmetrized combinations of plane waves (SCPW). These can be found in a straightforward way (Schlosser 1962; Luehrmann 1968), and as tables of SCPW for the diamond and zinc-blende lattices are readily available in the literature (see e.g. Herman 1954; Bassani and Yoshimine 1963; Bassani 1966, and references therein) we shall simply quote from these tables. Let us represent the ensemble of 15 waves at the Γ point for the two structures as

$$\begin{aligned} \alpha &= (000), & \phi_1 &= (111), & \phi_2 &= (1\bar{1}\bar{1}), & \phi_3 &= (\bar{1}1\bar{1}), & \phi_4 &= (\bar{1}\bar{1}1), \\ \phi_5 &= (\bar{1}\bar{1}\bar{1}), & \phi_6 &= (\bar{1}11), & \phi_7 &= (1\bar{1}1), & \phi_8 &= (11\bar{1}), & \psi_1 &= (200), \\ \psi_2 &= (020), & \psi_3 &= (002), & \psi_4 &= (\bar{2}00), & \psi_5 &= (0\bar{2}0), & \psi_6 &= (00\bar{2}). \end{aligned}$$

Since the SCPW for the diamond structure are

$$W_{11}(\Gamma_1) = \alpha,$$

$$W_{11}(\Gamma_1) = \sqrt{\frac{1}{8}}(\phi_1 - \phi_2 - \phi_3 - \phi_4 + \phi_5 - \phi_6 - \phi_7 - \phi_8),$$

$$W_{11}(\Gamma'_2) = \sqrt{\frac{1}{8}}(\phi_1 - \phi_2 - \phi_3 - \phi_4 - \phi_5 + \phi_6 + \phi_7 + \phi_8),$$

$$W_{11}(\Gamma'_{25}) = \sqrt{\frac{1}{8}}(\phi_1 + \phi_2 + \phi_3 - \phi_4 + \phi_5 + \phi_6 + \phi_7 - \phi_8),$$

$$W_{12}(\Gamma'_{25}) = \sqrt{\frac{1}{8}}(\phi_1 + \phi_2 - \phi_3 + \phi_4 + \phi_5 + \phi_6 - \phi_7 + \phi_8),$$

$$W_{13}(\Gamma'_{25}) = \sqrt{\frac{1}{8}}(\phi_1 - \phi_2 + \phi_3 + \phi_4 + \phi_5 - \phi_6 + \phi_7 + \phi_8),$$

$$W_{11}(\Gamma_{15}) = \sqrt{\frac{1}{8}}(\phi_1 + \phi_2 + \phi_3 - \phi_4 - \phi_5 - \phi_6 - \phi_7 + \phi_8),$$

$$W_{12}(\Gamma_{15}) = \sqrt{\frac{1}{8}}(\phi_1 + \phi_2 - \phi_3 + \phi_4 - \phi_5 - \phi_6 + \phi_7 - \phi_8),$$

$$W_{13}(\Gamma_{15}) = \sqrt{\frac{1}{8}}(\phi_1 - \phi_2 + \phi_3 + \phi_4 - \phi_5 + \phi_6 - \phi_7 - \phi_8),$$

$$W_{11}(\Gamma'_2) = 2\sqrt{\frac{1}{6}}(\psi_1 + \psi_2 + \psi_3 - \psi_4 - \psi_5 - \psi_6),$$

$$W_{11}(\Gamma'_{12}) = 2\sqrt{\frac{1}{4}}(\psi_2 - \psi_3 - \psi_5 + \psi_6),$$

$$W_{12}(\Gamma'_{12}) = 2\sqrt{\frac{1}{12}}(-2\psi_1 + \psi_2 + \psi_3 + 2\psi_4 - \psi_5 - \psi_6),$$

$$W_{11}(\Gamma'_{25}) = 2\sqrt{\frac{1}{2}}(\psi_3 + \psi_6),$$

$$W_{12}(\Gamma'_{25}) = 2\sqrt{\frac{1}{2}}(\psi_2 + \psi_5),$$

$$W_{13}(\Gamma'_{25}) = 2\sqrt{\frac{1}{2}}(\psi_1 + \psi_4),$$

it follows that the 15×15 orthogonal matrix $\mathbf{O}_d(\Gamma)$ for this symmetry point is

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ 0 & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{2}} & 0 & 0 & \sqrt{\frac{1}{2}} \\ 0 & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{2}} & 0 & 0 & \sqrt{\frac{1}{2}} & 0 \\ 0 & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{2}} & 0 & 0 & \sqrt{\frac{1}{2}} & 0 & 0 \\ 0 & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & \sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & -\sqrt{\frac{1}{8}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sqrt{\frac{1}{3}} & \frac{1}{2}\sqrt{\frac{1}{3}} & \frac{1}{2}\sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & -\frac{1}{2}\sqrt{\frac{1}{3}} & -\frac{1}{2}\sqrt{\frac{1}{3}} \end{bmatrix}.$$

Similarly for the Γ point of the zinc-blende structure the SCPW are

$$W_{11}(\Gamma_1) = \alpha,$$

$$W_{11}(\Gamma_1) = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 - \phi_4),$$

$$W_{21}(\Gamma_1) = \frac{1}{2}(\phi_5 - \phi_6 - \phi_7 - \phi_8),$$

$$W_{11}(\Gamma_{15}) = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 - \phi_4),$$

$$W_{12}(\Gamma_{15}) = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 + \phi_4),$$

$$W_{13}(\Gamma_{15}) = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 + \phi_4),$$

$$W_{21}(\Gamma_{15}) = \frac{1}{2}(-\phi_5 - \phi_6 - \phi_7 + \phi_8),$$

$$W_{22}(\Gamma_{15}) = \frac{1}{2}(-\phi_5 - \phi_6 + \phi_7 - \phi_8),$$

$$W_{23}(\Gamma_{15}) = \frac{1}{2}(-\phi_5 + \phi_6 - \phi_7 - \phi_8),$$

$$W_{11}(\Gamma_1) = 2\sqrt{\frac{1}{6}}(\psi_1 + \psi_2 + \psi_3 - \psi_4 - \psi_5 - \psi_6),$$

$$W_{11}(\Gamma_{15}) = 2\sqrt{\frac{1}{2}}(\psi_3 + \psi_6),$$

$$W_{12}(\Gamma_{15}) = 2\sqrt{\frac{1}{2}}(\psi_2 + \psi_5),$$

$$W_{13}(\Gamma_{15}) = 2\sqrt{\frac{1}{2}}(\psi_1 + \psi_4),$$

$$W_{11}(\Gamma_{12}) = 2\sqrt{\frac{1}{4}}(\psi_2 - \psi_3 - \psi_5 + \psi_6),$$

$$W_{12}(\Gamma_{12}) = 2\sqrt{\frac{1}{12}}(-2\psi_1 + \psi_2 + \psi_3 + 2\psi_4 - \psi_5 - \psi_6),$$

and the corresponding matrix $\mathbf{O}_{zb}(\Gamma)$ is

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & \sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{2}} & 0 & 0 & \sqrt{\frac{1}{2}} \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{2}} & 0 & 0 & \sqrt{\frac{1}{2}} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{1}{2}} & 0 & 0 & \sqrt{\frac{1}{2}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sqrt{\frac{1}{3}} & \frac{1}{2}\sqrt{\frac{1}{3}} & \frac{1}{2}\sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & -\frac{1}{2}\sqrt{\frac{1}{3}} & -\frac{1}{2}\sqrt{\frac{1}{3}} \end{bmatrix}.$$

When the orthogonal matrix \mathbf{O} so formed is applied to the original matrix \mathbf{D} such that

$$\bar{\mathbf{D}} = \mathbf{O} \mathbf{D} \mathbf{O}^{-1},$$

the determinant of $\bar{\mathbf{D}}$ will be automatically factorized in the form (11) or (13). Thus for example the 15×15 secular determinants $D(\Gamma)$ formed by using the pseudopotentials V_3 , V_4^a , V_8 , and V_{11} of Cohen and Bergstresser (1966) factorize as follows for the diamond and zinc-blende structures at the symmetry point Γ .

(1) *Diamond Structure*

$$\begin{aligned} \Gamma_1 &= \begin{vmatrix} 0 & -2V_3^s \\ -2V_3^s & 3(2\pi/a)^2 + 3V_8^s \end{vmatrix}, \\ \Gamma'_2 &= \begin{vmatrix} 3(2\pi/a)^2 + 3V_8^s & \sqrt{6}(V_3^s + V_{11}^s) \\ \sqrt{6}(V_3^s + V_{11}^s) & 4(2\pi/a)^2 + 4V_8^s \end{vmatrix}, \\ \Gamma'_{25} &= \begin{vmatrix} 3(2\pi/a)^2 - V_8^s & \sqrt{2}(V_3^s - V_{11}^s) \\ \sqrt{2}(V_3^s - V_{11}^s) & 4(2\pi/a)^2 \end{vmatrix}, \\ \Gamma_{15} &= | 3(2\pi/a)^2 - V_8^s |, \\ \Gamma'_{12} &= | 4(2\pi/a)^2 - 2V_8^s |. \end{aligned}$$

(2) *Zinc-blende Structure*

$$\begin{aligned} \Gamma_1 &= \begin{vmatrix} 0 & \sqrt{2}(V_3^s + iV_3^a) & \sqrt{2}(V_3^s - iV_3^a) & -i\sqrt{6}V_4^a \\ \sqrt{2}(V_3^s - iV_3^a) & 3(2\pi/a)^2 + 3V_8^s & -3iV_4^a & -\sqrt{3}(V_8^s + iV_8^a) \\ \sqrt{2}(V_3^s + iV_3^a) & 3iV_4^a & 3(2\pi/a)^2 + 3V_8^s & \sqrt{3}(V_8^s - iV_8^a) \\ i\sqrt{6}V_4^a & -\sqrt{3}(V_8^s - iV_8^a) & \sqrt{3}(V_8^s + iV_8^a) & 4(2\pi/a)^2 + 4V_8^s \end{vmatrix}, \\ \Gamma_{15} &= \begin{vmatrix} 3(2\pi/a)^2 - V_8^s & -iV_4^a & -V_D^s - iV_D^a \\ iV_4^a & 3(2\pi/a)^2 - V_8^s & V_D^s - iV_D^a \\ -V_D^s + iV_D^a & V_D^s + iV_D^a & 4(2\pi/a)^2 \end{vmatrix}, \\ \Gamma_{12} &= | 4(2\pi/a)^2 - 2V_8^s |, \end{aligned}$$

where

$$\begin{aligned} V_s^s &= V_3^s + V_{11}^s, & V_s^a &= V_3^a + V_{11}^a, \\ V_D^s &= V_3^s - V_{11}^s, & V_D^a &= V_3^a - V_{11}^a. \end{aligned}$$

In a similar way the secular determinants formed from the Cohen and Bergstresser (1966) pseudopotentials for other symmetry points in Figure 1 can be easily factorized using the readily available SCPW tables.

CONCLUSIONS

The aim of this work has been to emphasize the usefulness of symmetry analysis in energy band calculations. Since symmetry arguments not only greatly simplify the calculations but also often give much insight into the physical situation, it is always advisable to carry out a symmetry analysis before undertaking any quantum mechanical calculations of problems in crystal physics. The present symmetry analyses have shown how to eliminate a number of structure factors and enable the easy factorization of higher order determinants at high symmetry points.

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