

UNIVERSITÉ DE BOURGOGNE

SOLID STATE PHYSICS

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# Simulation of the 3D Bloch Model

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# 1 Introduction

The foundational study of solid state physics began with the discovery of x-ray diffraction by crystals followed by subsequent publication of a series of simple calculations of the properties of crystals and electrons in crystals. The important electronic properties of solids are best expressed in crystals. [2] (page 3). The empirical pseudopotential method was developed in the 1960's as a way to solve Schrodinger's equation for bulk crystals without knowing exactly the potential experienced by an electron in the lattice. Since electrons are interacting with the crystal lattice, an electronic band structure calculation is a many body problem. Although other methods existed at the time for approximating electronic band structures, the pseudopotential method gives surprisingly accurate results considering the computing time and effort involved [3].

The basic scheme is to assume that the core electrons are tightly bound to their nuclei, and as a result valence and conduction band electrons are influenced only by the remaining potential. Since the potential can be Fourier expanded in plane waves, an eigenvalue equation for determining an E-k relationship can be established. Although the Fourier coefficients for the potentials are not known, they can be empirically determined for a given crystal by fitting calculated crystal parameters to known measurements. Cohen and Bergstresser followed these steps to determine band structures of several diamond and zincblende structures [5]. In this practical work we would like to extend the pseudopotential method to include some types of semiconductors and present band structures and pseudopotential form factors for silicon (Si), germanium (Ge), tin (Sn), gallium phosphide (GaP), gallium arsenide (GaAs), aluminum antimonide (AlSb), indium phosphide (InP), gallium antimonide (GaSb), indium arsenide (InAs), indium antimonide (InSb), zinc sulfide (ZnS), zinc selenide (ZnSe), zinc telluride (ZnTe) and cadmium telluride (CdTe).

To implement the code we used the following input data:

- Definition of the path in the BZ,
- Lattice spacing  $a$ ,
- Number of reciprocal lattice vectors (and thus number of terms kept in the description of the potential),
- Parameters of the potential [1] (page 94).

## 2 Code Description

First we start with some default commands that are essential for running a program neatly in Octave. Afterwards we have defined all the physical constants that are going to be used later on. Afterwards we continue with loading the data file that we already had before. From the data file we extract the table of  $q$  wave-vectors from the `bz.path` file. The  $q$  wave-vectors are analogical to the  $k$ -s for the one dimensional case in the textbook [1] (page 68). The Bloch model describes the spectrum of the electron energy states in

Table of wavevectors read in input file bzpath.dat

iq	is	q(1)	q(2)	q(3)	q(4)	q(5)
1	1	0.5	0.5	0.5	0.866025	0
2	1	0.48	0.48	0.48	0.831384	0.02
3	1	0.46	0.46	0.46	0.796743	0.04
4	1	0.44	0.44	0.44	0.762102	0.06
5	1	0.42	0.42	0.42	0.727461	0.08
6	1	0.4	0.4	0.4	0.69282	0.1
7	1	0.38	0.38	0.38	0.658179	0.12
8	1	0.36	0.36	0.36	0.623538	0.14
9	1	0.34	0.34	0.34	0.588897	0.16
10	1	0.32	0.32	0.32	0.554256	0.18
11	1	0.3	0.3	0.3	0.519615	0.2
12	1	0.28	0.28	0.28	0.484974	0.22
13	1	0.26	0.26	0.26	0.450333	0.24
14	1	0.24	0.24	0.24	0.415692	0.26
15	1	0.22	0.22	0.22	0.381051	0.28
16	1	0.2	0.2	0.2	0.34641	0.3
17	1	0.18	0.18	0.18	0.311769	0.32
18	1	0.16	0.16	0.16	0.277128	0.34
19	1	0.14	0.14	0.14	0.242487	0.36
20	1	0.12	0.12	0.12	0.207846	0.38
21	1	0.1	0.1	0.1	0.173205	0.4
22	1	0.08	0.08	0.08	0.138564	0.42
23	1	0.06	0.06	0.06	0.103923	0.44
24	1	0.04	0.04	0.04	0.069282	0.46
25	1	0.02	0.02	0.02	0.034641	0.48

Figure 1: The first 25 elements of the table of  $q$  wave-vectors

the framework of the one-electron approximation using a periodic potential that is independent of time:

$$V(r) = V(r + R_n) \quad (1)$$

Here,  $n$  points to a triplet of integer numbers  $(n_1, n_2, n_3)$  identifying a vector of the direct lattice  $R_n$ , which itself is expanded on the direct lattice basis vectors  $a_1, a_2, a_3$  according to: [4]

$$R_n = n_1 a_1 + n_2 a_2 + n_3 a_3 \quad (2)$$

To continue we have defined the  $\mathbf{a}$  as orthonormal, cartesian lattice vectors. After calculating the cell volume using the formula (3). Afterwards we convert them into the reciprocal basis vectors using the formula (4).

$$V = \mathbf{a}_j \cdot (\mathbf{a}_j \times \mathbf{a}_k) \quad (3)$$

$$\mathbf{g}_i = \frac{\mathbf{a}_j \times \mathbf{a}_k}{V} \quad (4)$$

After getting the  $\mathbf{g}$  reciprocal space vectors we went on calculating the  $G$  space vectors with respect to the periodicity of the potential using the equation (4) [1] (page 9).

```

Dimensionless lattice dependent part
fcc lattice unit vectors in cartesian coordinates
a_1 a_2 a_3
0.50000 0.00000 0.50000
0.50000 0.50000 0.00000
0.00000 0.50000 0.50000
cell_volume = 0.25000

fcc reciprocal lattice unite vectors in Cartesian coordinates
g_1 g_2 g_3
1 -1 1
1 1 -1
-1 1 1
3 3 3

```

Figure 2: The values generated in the code for  $\mathbf{a}$  and  $\mathbf{g}$  vectors

$$\mathbf{G} = l_1 \mathbf{g}_1 + l_2 \mathbf{g}_2 + l_3 \mathbf{g}_3 \quad (5)$$

The pseudopotential Hamiltonian for an electron in the crystal consists of a kinetic energy term and a weak periodic potential energy term which depends only in  $r$ .

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad (6)$$

The potential  $V$  can be expanded in  $G$  reciprocal lattice vectors and can be expressed as the product of a structure factor  $S(G)$  times a pseudopotential

form factor  $V_G$ . Following this I sorted the  $G$  vectors and made a cutoff where the  $|G|^2$  is smaller than 21. Next the goal is to calculate the  $V_G$  potential. To do that it is rather logical to divide it into symmetrical and anti-symmetrical parts.

$$V(r) = \sum_{|G| \leq G_0} (S^S(G)V_G^S + iS^A(G)V_G^A)e^{-iG \cdot r} \quad (7)$$

The cubic semiconductors of the diamond or zinc-blende type have the fcc structure with two atoms, whose positions are denoted by  $r_1$  and  $r_2$ , so that  $r_1 = a(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}) = \tau$ , and  $r_2 = -\tau$ , where  $a$  is the length of unit cube, which I have already calculated above. In this case

$$S^S(G) = \cos(G \cdot r), \quad (8)$$

$$S^A(G) = \sin(G \cdot r) \quad (9)$$

In terms of atomic potentials we can write the Fourier transform of  $V_G$ .

$$V_G^S = \frac{1}{2}(V_1(G) + V_2(G)), \quad (10)$$

$$V_G^A = \frac{1}{2}(V_1(G) - V_2(G)), \quad (11)$$

$$V_1(G) = \frac{2}{V} \int V_1(r)e^{-iG \cdot r} d^3r, \quad (12)$$

and similarly for  $V_2$ , where  $V_1$  and  $V_2$  are the pseudopotentials due to single atoms in the lattice. [5]. We can write the Fourier transform of the  $V_G$  in the following form, by dividing the  $V_G$  potential into symmetric and anti-symmetric parts.

$$V_G = V_{|G|^2}^S \cos(G \cdot s) + iV_{|G|^2}^A \sin(G \cdot s) \quad (13)$$

The values of  $V_{|G|^2}^S$  and  $V_{|G|^2}^A$  are deduced from experimental data. They feature  $V_G = 0$  if  $|G|^2 > 11$  ( $4\pi/a^2$  unites). In figure (3) we can see non-zero values for a selection of semiconductors if  $|G|^2 \leq 11$ . Even if the Fourier expansion of the potential is limited to  $|G|^2 \leq 11$ , a satisfactory convergence requires that the representation of the Schrodinger equation involves all  $|G|$  vectors such that  $|G|^2 \leq 21$  [1] (page 93). To continue with the code, we used the input values from the table to generate the table of  $G$  vectors to get the values for kinetic and potential energy later on. In the code below, we have generated the values for the potential energy, which we find by checking the difference of the  $G$  depending on the distance between the elements:

	$V_3^S$	$V_8^S$	$V_{11}^S$	$V_3^A$	$V_4^A$	$V_{11}^A$
Si	-0.21	+0.04	+0.08	0	0	0
Ge	-0.23	+0.01	+0.06	0	0	0
Sn	-0.20	0.00	+0.04	0	0	0
GaP	-0.22	+0.03	+0.07	+0.12	+0.07	+0.02
GaAs	-0.23	+0.01	+0.06	+0.07	+0.05	+0.01
AlSb	-0.21	+0.02	+0.06	+0.06	+0.04	+0.02
InP	-0.23	+0.01	+0.06	+0.07	+0.05	+0.01
GaSb	-0.22	0.00	+0.05	+0.06	+0.05	+0.01
InAs	-0.22	0.00	+0.05	+0.08	+0.05	+0.03
InSb	-0.20	0.00	+0.04	+0.06	+0.05	+0.01
ZnS	-0.22	+0.03	+0.07	+0.24	+0.14	+0.04
ZnSe	-0.23	+0.01	+0.06	+0.18	+0.12	+0.03
ZnTe	-0.22	0.00	+0.05	+0.13	+0.10	+0.01
CdTe	-0.20	0.00	+0.04	+0.15	+0.09	+0.04

Figure 3: Pseudopotential form factors, in rydbergs, derived from the experimental energy band splittings

```
%Potential energy
for j = 1:kept
  for i = 1:kept
    G_diff(1:3) = G(1:3,i)-G(1:3,j);
    G_diff(5) = G_diff(1:3)'*G_diff(1:3);
    if(G_diff(5)<=Gs_max)
      for k = 1:kept
        if((G_diff(1:3)-G(1:3,k))==[0 0 0]')
          H(i,j) = cvg(k);
        endif
      endfor
    endif
  endfor
endfor
```

Afterwards, in a bigger loop we defined the kinetic energy values and the gamma eigenvalues:

Energy in eV								
TABLE OF G VECTORS (unit of $2\pi/\text{lattice spacing}$ ) AND FOURIER COEFFICIENTS OF PSEUDOPOTENTIAL (eV)								
n	G1	G2	G3	G	G ^2	Re(V_G)	Im(V_G)	
1	0	0	0	0	0	0	0	
2	-1	-1	-1	1.73205	3	1.92418	1.44313	
3	-1	-1	1	1.73205	3	-1.92418	1.44313	
4	1	-1	-1	1.73205	3	-1.92418	1.44313	
5	-1	1	-1	1.73205	3	-1.92418	1.44313	
6	1	-1	1	1.73205	3	-1.92418	-1.44313	
7	-1	1	1	1.73205	3	-1.92418	-1.44313	
8	1	1	-1	1.73205	3	-1.92418	-1.44313	
9	1	1	1	1.73205	3	1.92418	-1.44313	
10	0	-2	0	2	4	0	1.22454	
11	-2	0	0	2	4	0	1.22454	
12	0	0	-2	2	4	0	1.22454	
13	0	0	2	2	4	-0	-1.22454	
14	2	0	0	2	4	-0	-1.22454	
15	0	2	0	2	4	-0	-1.22454	
16	-2	-2	0	2.82843	8	-0	0	
17	0	-2	-2	2.82843	8	-0	0	
18	-2	0	-2	2.82843	8	-0	0	
19	0	-2	2	2.82843	8	0	0	
20	-2	0	2	2.82843	8	0	0	

Figure 4: The  $G$  pseudopotential matrix

```
%Kinetic energy
if(kept<nband)
    nband=kept;
endif

for iq = 1:nq
    printf("%4d",iq);
    for i = 1:kept
        for j = 1:3
            p(j) = q(iq, j)-G(j,i); %q index is the k vector only on diagonal
        endfor
        H(i,i) = (ekinunit*(2*pi/l)^2*(p*p'));
    endfor
    if(any(H-H'))
        printf("\nHamiltonian is not Hermitian : fatal error.\n");
        break;
    else
        [v,ev]=eig(H);
        E = real(diag(ev));
        [E perm]=sort(E);
        v = v(:,perm);
        bzs = 1000*(-1)^is(iq,1);
```



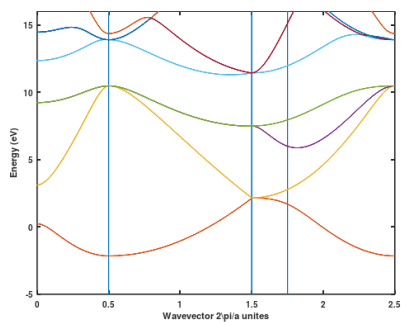
```

        fprintf(f1,"%15.6G %15.6G",q(iq,5),bzs);
    for i=1:nband
        fprintf(f1,"%15.6G",E(i));
    endfor
        fprintf(f1,"\n");

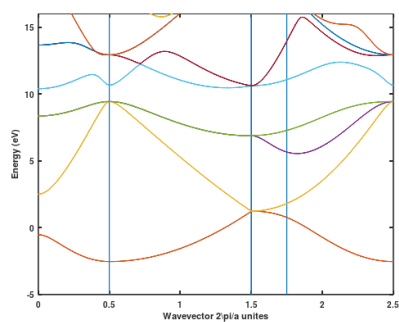
        if(q(iq,4)==0)
            #printf("\n gamma.eigenvalues")
            for i=1:nband
                gamma(i)=E(i);
                #printf("%d %15.6G \n",i, gamma(i));
            endfor
        endif
    endif
endfor
fclose(f1);
printf("\n gamma.eigenvalues \n")
for i=1:nband
    printf("%d %15.6G \n",i, gamma(i));
endfor

```

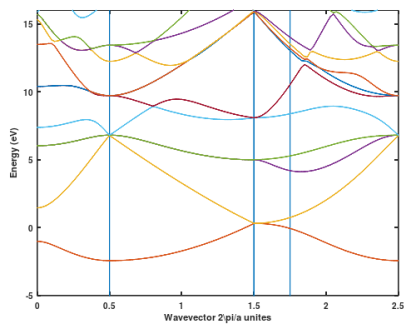
### 3 Graphs



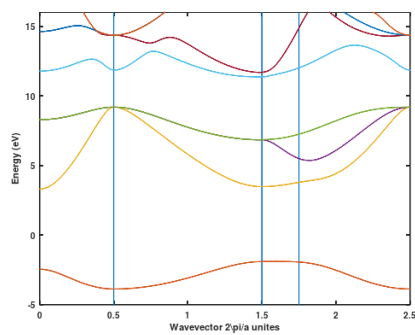
(a) Si



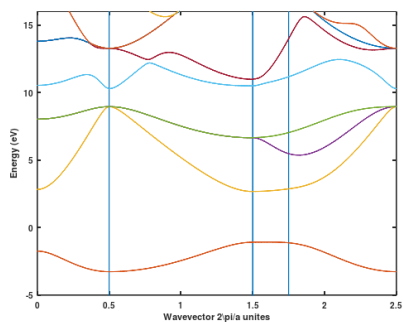
(b) Ge



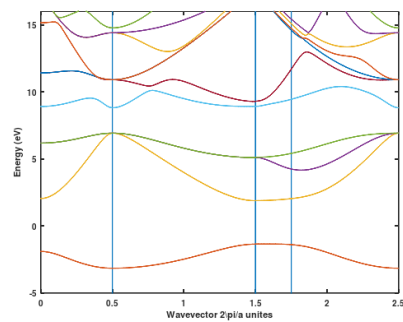
(a) Sn



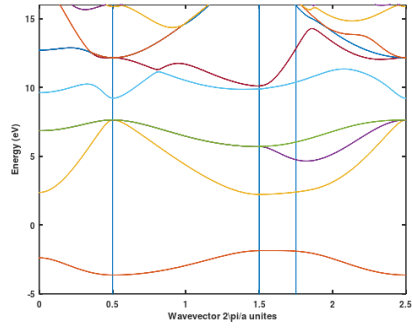
(b) GaP



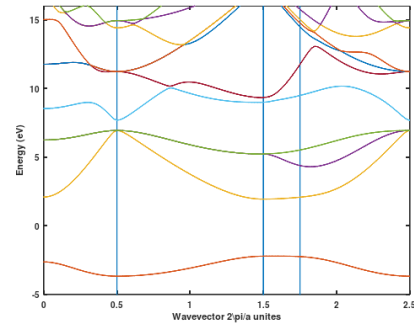
(a) GaAs



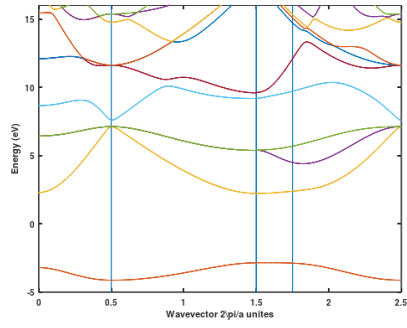
(b) AlSb



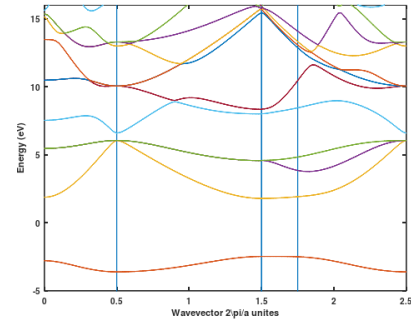
(a) InP



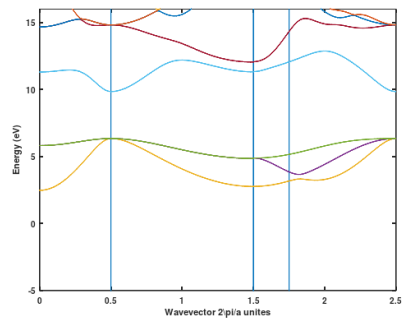
(b) GaSb



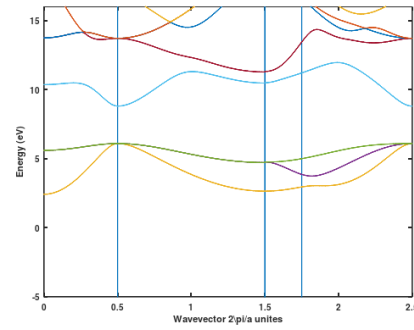
(a) InAs



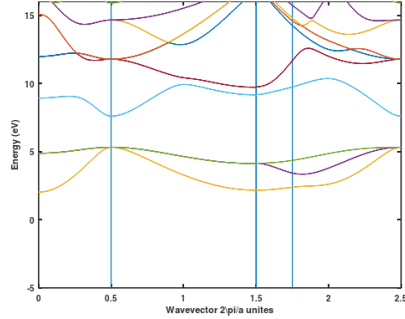
(b) InSb



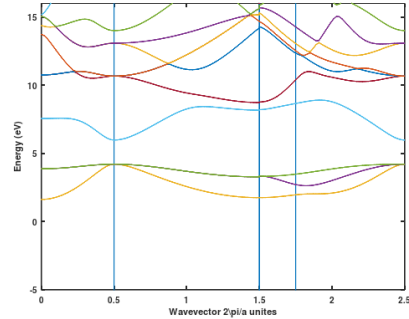
(a) ZnS



(b) ZnSe



(a) ZnTe



(b) CdTe

## 4 Conclusion

We graphed the pseudopotential form factors obtained for these 14 cubic semiconductors. One might expect a slight change in the symmetric potential upon going from example from Ge to GaAs. However, other symmetric potentials were tried for all heteropolar compounds, and no significant improvement of the fit to experiment was found. For all of these  $V_3^S$  is large and negative. The form factor passes through zero in the region of  $G^2 = 8$ , and is positive but small for  $G^2 = 11$ . The overall sign of the antisymmetric form factors has no effect and is taken to be positive. The antisymmetric potential is stronger for the more ionic crystals: it is zero for the homopolar substances, while in the II-IV compounds it is about as strong as symmetric potentials [5]. After simulating the fcc band structure and comparing with the results of the [5], we had very similar results, and the differences are substantiated by the difference in unit systems and the uncertainties of computer. As a result this code helped us visualize the structure of crystals to better understand the 3D BZ structure.

## References

- [1] Alain Dereux, "Selected Chapters of Solid State Physics" (28 November 2017)
- [2] Charles Kittel, "Introduction to Solid State Physics" (Eight edition)
- [3] Aaron J. Danner, "An introduction to the empirical pseudopotential method"
- [4] Bloch, F. (1928) Zeitschrift fur Physik, 52, 555-600.
- [5] M. L. Cohen and T. K. Bergstresser, "Band Structures and Pseudopotential Form Factors for Fourteen Semiconductors of the Diamond and Zinc-blende Structures", Phys. Rev. 141, (14 January 1966)
- [6] The GitHub code for the experiments  
<https://github.com/UndineStein/Solid-State-Physics-Project>