Electronic bands and phonon dispersions
Problem 5:
Dielectric constants of wurtzite ZnS

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Introduction

In this exercise, our aim is to compare the band structure of wurtzite ZnS and the imaginary part of dielectric constant as a function of frequency with the ones given in *Phys. Rev.* 164, *1069 (1967)* .
ZnS is a semiconductor with the wurtzite structure. This structure has four atoms in the unit cell. The Zn atoms occupy the hcp sites while the S atoms are in one half of the tetrahedral sites. Putting the origin in the middle of the bond the Cartesian coordinates of the atoms are (where for u we take the ideal value $u = 3/8$):

$$\begin{aligned}
\mathbf{d}_{Zn_1} &= a(1/2, 1/(2\sqrt{3}), -7c/(16a)) \\
\mathbf{d}_{Zn_2} &= a(-1/2, -1/(2\sqrt{3}), c/(16a)) \\
\mathbf{d}_{S_1} &= a(1/2, 1/(2\sqrt{3}), c(u-7/16)/a) = \\
&= a(1/2, 1/(2\sqrt{3}), -c/(16a)) \\
\mathbf{d}_{S_2} &= a(-1/2, -1/(2\sqrt{3}), c(u+1/16)/a) \\
&= a(-1/2, -1/(2\sqrt{3}), 7c/(16a))
\end{aligned}$$

The size of the hexagonal Bravais lattice is $a = 3.811\text{Å}$, and for the ration c/a we can take the ideal value $c/a = \sqrt{8/3}$.
In order to introduce the notation, we have:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right]\Psi_{\mathbf{k},n}(\mathbf{r}) = \epsilon_n(\mathbf{k})\Psi_{\mathbf{k},n}(\mathbf{r}) \tag{1}$$

As shown in the lectures, using:

$$\Psi_{\mathbf{k},n}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G},n} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{2}$$

we achieve:

$$\sum_{\mathrm{G}}\left[\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2\delta_{\mathbf{G},\mathbf{G}'} + U\left(\mathbf{G}'-\mathbf{G}\right)\right]c_{\mathbf{k}+\mathbf{G},n} = \epsilon_n(\mathbf{k})c_{\mathbf{k}+\mathbf{G}',n} \tag{3}$$

where :

$$U(\mathbf{G}) = \sum_{\gamma} V^{\gamma}(|\mathbf{G}|)\sum_{s\in\gamma} e^{-i\mathbf{G}\cdot\mathbf{d}_s} \tag{4}$$

with:

$$V^{\gamma}(|\mathbf{G}|) = \int v^{\gamma}(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d^3\boldsymbol{r} \tag{5}$$

We can put $U(\mathbf{G})$ in the following form (as shown below):

$$U(\mathbf{G}) = \left[S^S(\mathbf{G})V_G^S + iS^A(\mathbf{G})V_G^A\right] \tag{6}$$

where S^S and S^A are the symmetric and antisymmetric structure factors, and V^S and V^A are the symmetric and antisymmetric form factors given by:

$$S^S(\mathbf{G}) = \frac{1}{n}\sum_j e^{-i\mathbf{G}\cdot\delta_j} \qquad S^A(\mathbf{G}) = -\frac{i}{n}\sum_j P_j e^{-i\mathbf{G}\cdot\delta j} \tag{7}$$

$$V_G^S = \frac{n}{\Omega}\int\frac{1}{2}\left[v^1(\mathbf{r}) + v^2(\mathbf{r})\right]e^{-i\mathbf{G}\cdot\mathbf{r}}d^3\boldsymbol{r} = \frac{n}{2}\left[V^1(|\mathbf{G}|) + V^2(|\mathbf{G}|)\right] \tag{8}$$

$$V_G^A = \frac{n}{\Omega}\int\frac{1}{2}\left[v^1(\mathbf{r}) - v^2(\mathbf{r})\right]e^{-i\mathbf{G}\cdot\mathbf{r}}d^3\boldsymbol{r} = \frac{n}{2}\left[V^1(|\mathbf{G}|) - V^2(|\mathbf{G}|)\right] \tag{9}$$

where n is the number of atoms per unit cell (2 for zinc blende and 4 for wurtzite), Ω is the volume of the unit cell, δ_j is the position vector of the j-th atom in the unit cell and the index j includes all the atoms of a unit cell in the summation, P_j is +1 if j denotes one type of atom and P_j is -1 if j denotes the other type of atom, and v^1(r) and v^2(r) refer to the potentials of the atoms of type 1 and type 2 , respectively.

Proof.

$$\left[S^S(\mathbf{G})V_G^S + iS^A(\mathbf{G})V_G^A\right] = \tag{10}$$

$$\sum_j e^{-i\mathbf{G}\cdot\delta_j}\frac{1}{2}\left[V^1(|\mathbf{G}|) + V^2(|\mathbf{G}|)\right] + \sum_j P_j e^{-i\mathbf{G}\cdot\delta j}\frac{1}{2}\left[V^1(|\mathbf{G}|) - V^2(|\mathbf{G}|)\right] = \tag{11}$$

$$= \sum_{j_1} e^{-i\mathbf{G}\cdot\delta_{j_1}}\frac{1}{2}\left[V^1(|\mathbf{G}|) + V^2(|\mathbf{G}|)\right] + \sum_{j_1} e^{-i\mathbf{G}\cdot\delta j_1}\frac{1}{2}\left[V^1(|\mathbf{G}|) - V^2(|\mathbf{G}|)\right] \tag{12}$$

$$+ \sum_{j_2} e^{-i\mathbf{G}\cdot\delta_{j_2}}\frac{1}{2}\left[V^1(|\mathbf{G}|) + V^2(|\mathbf{G}|)\right] - \sum_{j_2} e^{-i\mathbf{G}\cdot\delta j_2}\frac{1}{2}\left[V^1(|\mathbf{G}|) - V^2(|\mathbf{G}|)\right] = \tag{13}$$

$$= \sum_{j_1} e^{-i\mathbf{G}\cdot\delta_{j_1}}V^1(|\mathbf{G}|) + \sum_{j_2} e^{-i\mathbf{G}\cdot\delta_{j_2}}V^1(|\mathbf{G}|) = \sum_\gamma V^\gamma(|\mathbf{G}|)\sum_{s\in\gamma} e^{-i\mathbf{G}\cdot\mathbf{d}_s} = U(\mathbf{G}) \tag{14}$$

■

The wurtzite structure semiconductors are closely related to the zinc-blendes. The normalization of the form factors to the volume per atom allows the use of zinc-blende form factors for wurtzite without a change in normalization. The small density difference between zinc-blende and wurtzite is ignored.
If the center of the unit cell is chosen so that the position of each atom of the first type moves to the position of an atom of the second type upon spatial inversion (as in our case), then the structure factors are real (as shown below).
This can be achieved for both zinc-blende and wurtzite. When the nearest neighbor distance is the same in the wurtzite and zinc-blende structures, the lattice constants are related by $a_{ZB} = \sqrt{2}a_W$.
In zinc-blende, reciprocal lengths are measured in units of $(2\pi/a_{ZB})$ so that the reciprocal lattice vectors have the smallest possible integers as their Cartesian components. To compare these with the reciprocal lattice vectors of wurtzite, we must measure reciprocal lengths in wurtzite in units of $\left(\sqrt{2}\pi/a_W\right)$.
The form factors for the wurtzite structure, the square magnitudes for the reciprocal lattice vectors (in units of $(2\pi/a_{ZB}) = \left(\sqrt{2}\pi/a_W\right)$) and the structure factors are given in Table II of Phys. Rev. 164, 1069(1967) that we report here.

G	G^2	$\lvert S^S(\mathbf{G})\rvert$	$\lvert S^A(\mathbf{G})\rvert$	ZnS V^S	V^A
(Wurtzite)					
000	0	1	0		
001	$\frac{3}{4}$	0	0		
100	$2\frac{2}{3}$	$\frac{1}{2}$	0	−0.24	
002	3	0.71	0.71	−0.22	0.23
101	3+5/12	0.33	0.80	−0.19	0.19
102	$5\frac{2}{3}$	0.35	0.35	−0.06	0.10
003	$6\frac{3}{4}$	0	0		
210	8	1	0	+0.03	
211	$8\frac{3}{4}$	0	0		
103	9+5/12	0.80	0.33	+0.06	0.03
200	$10\frac{2}{3}$	$\frac{1}{2}$	0	+0.07	
212	11	0.71	0.71	+0.07	0.02
201	11+5/12	0.33	0.80	+0.07	0.02
004	12	0.00	1.00		0.02
202	$13\frac{2}{3}$	0.35	0.35	+0.04	0.01
104	$14\frac{2}{3}$	0.00	0.50		0.01
213	$14\frac{3}{4}$	0	0		

Figure 1: Reciprocal lattice vectors, structure factors for wurtzite and form factors, in Ry, used in this work. Column 1 contains a representative from each set of equivalent reciprocal lattice vectors. Column 2 contains the magnitudes of these vectors in units of $(2\pi/a_{ZB})$. Columns 3 and 4 contain the structure factor which are shown as two-place decimal fractions. The remaining columns contain the symmetric and antisymmetric form factors.

In order to get the same square modules of G vectors in the table, we can use these primitive lattice vectors ($a \equiv a_W$):

$$\mathbf{a_1} = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right) \; ; \mathbf{a_2} = a\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right) \; ; \mathbf{a_3} = a\left(0, 0, \sqrt{\frac{8}{3}}\right) \tag{15}$$

From which, we get:

$$\mathbf{b_1} = \frac{2\pi}{a}\left(1, \frac{1}{\sqrt{3}}, 0\right) \; ; \mathbf{b_2} = \frac{2\pi}{a}\left(-1, \frac{1}{\sqrt{3}}, 0\right) \; ; \mathbf{b_3} = \frac{2\pi}{a}\left(0, 0, \sqrt{\frac{3}{8}}\right) \tag{16}$$

The form factors for the wurtzite lattice are obtained from the form factors for the zinc blende lattice by interpolation, for this reason the square modulus of G vectors, in the table, are in unit of $(2\pi/a_{ZB})$.
In order to check by hand the values in the second column got by those of the first one, we consider:

$$G^2 = \frac{8}{3}l^2 + \frac{8}{3}m^2 + \frac{3}{4}n^2 - \frac{8}{3}lm \quad \text{where} \quad \mathbf{G} = (l, m, n) \tag{17}$$

Proof.

$$G^2 = |(l,m,n)|^2 \frac{1}{\left(\frac{2\pi}{a_{ZB}}\right)^2} = (l\mathbf{b}_1 + m\mathbf{b}_2 + n\mathbf{b}_3)\cdot(l\mathbf{b}_1 + m\mathbf{b}_2 + n\mathbf{b}_3)\frac{1}{\left(\frac{2\pi}{a_{ZB}}\right)^2} = \tag{18}$$

$$= (l^2|\mathbf{b}_1|^2 + m^2|\mathbf{b}_2|^2 + n^2|\mathbf{b}_3|^2 + 2lm\mathbf{b}_1\cdot\mathbf{b}_2)\frac{1}{\left(\frac{2\pi}{a_{ZB}}\right)^2} = \tag{19}$$

$$= \left(\frac{2\pi}{a_W}\right)^2 (\frac{4}{3}l^2 + \frac{4}{3}m^2 + \frac{3}{8}n^2 - \frac{4}{3}lm) \frac{1}{\left(\frac{2\pi}{a_{ZB}}\right)^2} = \underbrace{\left(\frac{a_{ZB}}{a_W}\right)^2}_{2} (\frac{4}{3}l^2 + \frac{4}{3}m^2 + \frac{3}{8}n^2 - \frac{4}{3}lm) \tag{20}$$

$$= \frac{8}{3}l^2 + \frac{8}{3}m^2 + \frac{3}{4}n^2 - \frac{8}{3}lm \tag{21}$$

■

In order to write explicitely the structure factors, I define:

$$\mathbf{d}_1 \equiv \mathbf{d}_{Zn_1} \quad \mathbf{d}_2 \equiv -\mathbf{d}_{Zn_2} \tag{22}$$

In this way:

$$\mathbf{d}_{S_1} = \mathbf{d}_2 \quad \mathbf{d}_{S_2} = -\mathbf{d}_1 \tag{23}$$

In the code, I compute the structure factors using the following formulas:

$$S^S(\mathbf{G}) = \frac{1}{2}\left(\cos(\mathbf{G}\cdot\mathbf{d}_1) + \cos(\mathbf{G}\cdot\mathbf{d}_2)\right) \tag{24}$$

$$S^A(\mathbf{G}) = \frac{1}{2}\left(-\sin(\mathbf{G}\cdot\mathbf{d}_1) + \sin(\mathbf{G}\cdot\mathbf{d}_2)\right) \tag{25}$$

Proof.

$$S^S(\mathbf{G}) = \frac{1}{n}\sum_j e^{-i\mathbf{G}\cdot\delta_j} = \frac{1}{4}(e^{-i\mathbf{G}\cdot\mathbf{d}_1} + e^{+i\mathbf{G}\cdot\mathbf{d}_2} + e^{-i\mathbf{G}\cdot\mathbf{d}_2} + e^{+i\mathbf{G}\cdot\mathbf{d}_1}) = \tag{26}$$

$$= \frac{1}{2}\left(\cos(\mathbf{G}\cdot\mathbf{d}_1) + \cos(\mathbf{G}\cdot\mathbf{d}_2)\right) \tag{27}$$

$$S^A(\mathbf{G}) = -\frac{i}{n}\sum_j P_j e^{-i\mathbf{G}\cdot\delta j} = \frac{1}{4i}(e^{-i\mathbf{G}\cdot\mathbf{d}_1} + e^{+i\mathbf{G}\cdot\mathbf{d}_2} - e^{-i\mathbf{G}\cdot\mathbf{d}_2} - e^{+i\mathbf{G}\cdot\mathbf{d}_1}) = \tag{28}$$

$$= \frac{1}{2}\left(-\sin(\mathbf{G}\cdot\mathbf{d}_1) + \sin(\mathbf{G}\cdot\mathbf{d}_2)\right) \tag{29}$$

■

If we want to verify by hand in a fast way the values of structure factors in table, it's better to rewrite the previous formulas as :

$$S^S(\mathbf{G}) = \cos\left(2\pi(\frac{l-m}{2} + \frac{l+m}{6} - \frac{4n}{16})\right)\cos\left(\pi\frac{3n}{8}\right) \tag{30}$$

$$S^A(\mathbf{G}) = \cos\left(2\pi(\frac{l-m}{2} + \frac{l+m}{6} - \frac{4n}{16})\right)\sin\left(\pi\frac{3n}{8}\right) \tag{31}$$

$$\tag{32}$$

Proof.

$$\mathbf{G}\cdot\mathbf{d}_1 = (l\mathbf{b}_1 + m\mathbf{b}_2 + n\mathbf{b}_3)\cdot a(\frac{1}{2}, \frac{1}{2\sqrt{3}}, -\frac{7c}{16a}) = \tag{33}$$

$$= 2\pi(l-m, \frac{1}{\sqrt{3}}(l+m), n\frac{a}{c})\cdot(\frac{1}{2}, \frac{1}{2\sqrt{3}}, -\frac{7c}{16a}) = \tag{34}$$

$$= 2\pi(\frac{l-m}{2} + \frac{l+m}{6} - \frac{7n}{16}) \tag{35}$$

$$\mathbf{G}\cdot\mathbf{d}_2 = (l\mathbf{b}_1 + m\mathbf{b}_2 + n\mathbf{b}_3)\cdot a(\frac{1}{2},\frac{1}{2\sqrt{3}},-\frac{c}{16a}) = \tag{36}$$

$$= 2\pi(l-m,\frac{1}{\sqrt{3}}(l+m),n\frac{a}{c})\cdot(\frac{1}{2},\frac{1}{2\sqrt{3}},-\frac{c}{16a}) = \tag{37}$$

$$= 2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{n}{16}) \tag{38}$$

Hence:

$$S^S(\mathbf{G}) = \frac{1}{2}\left[\cos\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{7n}{16})\right)+\cos\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{n}{16})\right)\right] =$$

$$= \frac{1}{2}\left[\underbrace{\cos\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{4n}{16}-\frac{3n}{16})\right)}_{\cos(a-b)}+\underbrace{\cos\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{4n}{16}+\frac{3n}{16})\right)}_{\cos(a+b)}\right] =$$

$$= \cos\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{4n}{16})\right)\cos\left(2\pi\frac{3n}{16}\right)$$

$$S^A(\mathbf{G}) = \frac{1}{2}\left[-\sin\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{7n}{16})\right)+\sin\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{n}{16})\right)\right] =$$

$$= \frac{1}{2}\left[-\underbrace{\sin\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{4n}{16}-\frac{3n}{16})\right)}_{\sin(a-b)}+\underbrace{\sin\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{4n}{16}+\frac{3n}{16})\right)}_{\sin(a+b)}\right] =$$

$$= \cos\left(2\pi(\frac{l-m}{2}+\frac{l+m}{6}-\frac{4n}{16})\right)\sin\left(2\pi\frac{3n}{16}\right)$$

■

Code: Band structure

The program allow us to choose if compute the band structure or the immaginary part of dieletric constant. Here we discuss the part of the code that computes the band structure. This is based on the CB program that we have largely analized during the lectures. We discuss only the main changes:

- *set_ cb_ parameters(crystal_ name)*

  In order to set the CB parameters of ZnS wurtzite, I have defined a matrix: *cb_ parameters(12,3)* where the column 1 contains $|G|^2$ (in $(2\pi/a_W)^2$ units) of table in fig.1. In the table, $|G|^2$ are in $(2\pi/a_{ZB})^2 = (\sqrt{2}\pi/a_W)^2$ units, hence, I have divided the values of the table by 2. The column 2 and 3 contain the symmetric and antisymmetric form factors.

- *set_ lattice(at, bg, 'hex')*

  Here, I have just set the coordinates of the direct lattice primitive vectors.

- *set_ hamiltonian(xk(:,ik), ecut)*

  The main structure of the subroutine is the same. I have adapted the formulas of structure factors that we have in our case (eq.24 and eq.25). Moreover, I have coded few lines with the aim of finding which is the row of the matrix *cb_ parameters(12,3)* that contains a specific $|G|^2$ and using this information to find the associated form factors.

I would like to point out that I can make this code general with only small changes (not necessary for this excercise) for the structures as wurtzite where you need to store all the G^2 and the form factors.

Setting the plot

In order to plot the band structure of ZnS wurtzite, we must find the coordinates of the points of the path $A-L-M-\Gamma-A-H-K-\Gamma$ which are the high symmetry points shown in this figure:

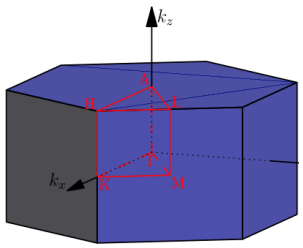

Figure 2: The Brillouin zone and a few high symmetry points.

We have (in units of $\frac{2\pi}{a}$):

$$\mathbf{A} = \left(0, 0, \frac{1}{2}\sqrt{\frac{3}{8}}\right) \qquad \mathbf{L} = \left(\frac{1}{2}, \frac{1}{2\sqrt{3}}, \frac{1}{2}\sqrt{\frac{3}{8}}\right) \qquad \mathbf{M} = \left(\frac{1}{2}, \frac{1}{2\sqrt{3}}, 0\right) \tag{39}$$

$$\mathbf{\Gamma} = (0, 0, 0) \qquad \mathbf{H} = \left(\frac{2}{3}, 0, \frac{1}{2}\sqrt{\frac{3}{8}}\right) \qquad \mathbf{K} = \left(\frac{2}{3}, 0, 0\right) \tag{40}$$

Proof. Considering the sketch in figure of the BZ on the plane z=0 (drawn with the usual procedure), we have:

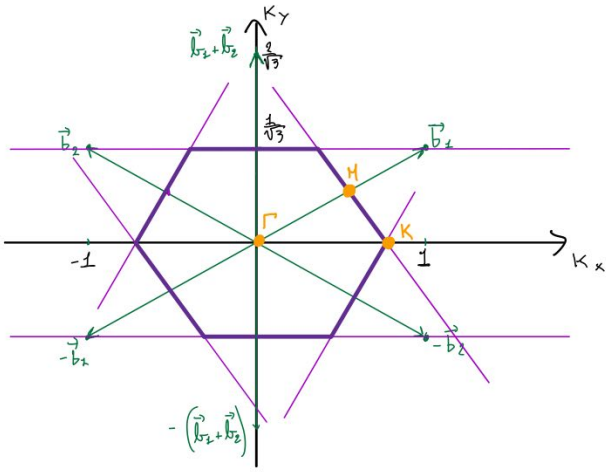

Figure 3: Sketch by hand of BZ in z=0 plane.

$$\mathbf{M} = \frac{\mathbf{b}_1}{2} = \left(\frac{1}{2}, \frac{1}{2\sqrt{3}}, 0\right) \tag{41}$$

In order to find the point K, we consider:

$$\mathbf{b}_1 \cdot (\mathbf{x} - \frac{\mathbf{b}_1}{2}) = 0 \;\rightarrow\; (x - \frac{1}{2}) + \frac{1}{\sqrt{3}}(y - \frac{1}{2\sqrt{3}}) = 0 \tag{42}$$

Setting y=0, we get:

$$x = \frac{2}{3} \;\rightarrow\; \mathbf{K} = \left(\frac{2}{3}, 0, 0\right) \tag{43}$$

We can get the other points just adding $\frac{\mathbf{b}_3}{2} = (0, 0, \frac{1}{2}\sqrt{\frac{3}{8}})$ to the previous ones . ■

These coordinates are to be inserted into the input file for the program. In order to set the labels of x-axis of the band structure plot, we need to know the distance between the path points which can be easily found (e.g.$|\mathbf{A} - \mathbf{L}| = \frac{1}{\sqrt{3}}$; $|\mathbf{M} - \mathbf{K}| = \frac{1}{3}$).

Comparing the band structures

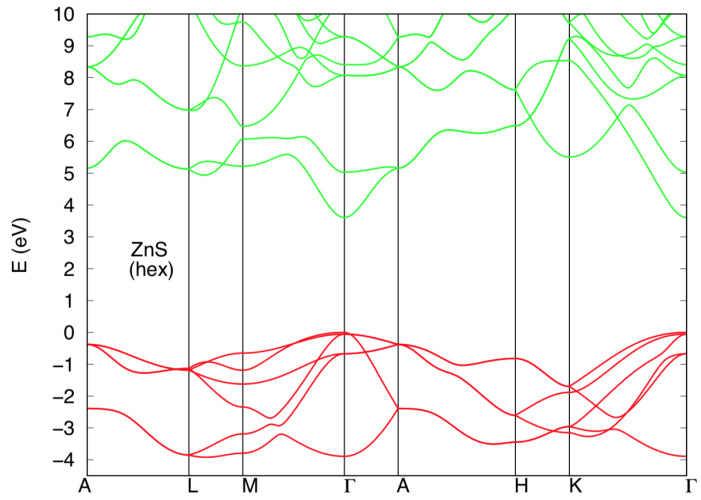

Figure 4: Band structure that I plotted using CB program (setting $nbands = 25$, $E_{CUT} = 27.0$ in units of $\mathrm{Ry}(2\pi/a)^2$).

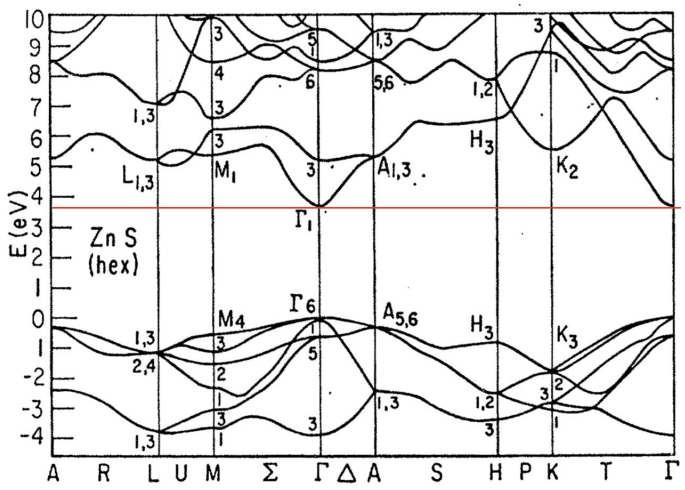

Figure 5: Band structure of ZnS wurtzite in Phys. Rev. 164, 1069. I put a red horizontal line that intersects the lowest point of the conduction bands.

The two plots are quite similar to the eye.
We observe that we have a direct gap in the point Γ. We can measure the distance between the highest point of the valence bands (in red) and the lowest point of the conduction bands (in green):

$$d_{gap} \simeq 3.6 \tag{44}$$

(where I used the energy values of these points in the output file of the program.)
This value is in agreement with what we can see by figure 5. Moreover, the other gaps seems also to be in agreement.

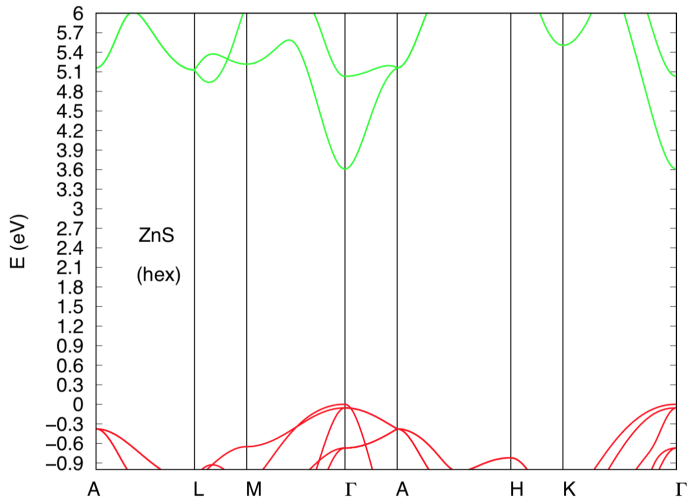

Figure 6: Zoom of the direct gap.

Immaginary part of dieletric constant

The imaginary part of the dielectric constant, in c.g.s. units, can be written as:

$$\epsilon_{2,i}(\omega) = \frac{e^2}{\pi m^2 \omega^2} \sum_{v,c} \int_{BZ} \delta\left(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega\right) |p_{vc}|^2 \, d^3k \tag{45}$$

where p_{vc} is the matrix element of the p_z (p_x) operator between valence and conduction Bloch functions when the field is parallel (perpendicular) to the c axis:

$$p_{vc} = \langle \Psi_{\mathbf{k},v} | \, \hat{p}_i \, | \Psi_{\mathbf{k},c} \rangle \quad \text{with } i = x, z \tag{46}$$

We show now the following result:

$$p_{vc} = \hbar V \sum_{\mathbf{G}} c^*_{\mathbf{k}+\mathbf{G},v} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i \tag{47}$$

Proof.
We have:

$$\Psi_{\mathbf{k},c}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G},c} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{48}$$

Then,

$$\hat{p}_i \, |\Psi_{\mathbf{k},c}\rangle = -i\hbar \frac{d}{dx_i} |\Psi_{\mathbf{k},c}\rangle = \hbar \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \tag{49}$$

$$p_{vc} = \langle \Psi_{\mathbf{k},v} | \, \hat{p}_i \, | \Psi_{\mathbf{k},c} \rangle = \hbar \int d\mathbf{r} \sum_{\mathbf{G}'} c^*_{\mathbf{k}+\mathbf{G}',v} e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = \tag{50}$$

$$= \hbar \sum_{\mathbf{G},\mathbf{G}'} c^*_{\mathbf{k}+\mathbf{G}',v} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i \underbrace{\int d\mathbf{r} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}}_{V\delta_{G,G'}} = \hbar V \sum_{\mathbf{G}} c^*_{\mathbf{k}+\mathbf{G},v} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i \tag{51}$$

■

Therefore:

$$\epsilon_{2,i}(\omega) = \frac{e^2}{\pi m^2 \omega^2} \sum_{v,c} \int_{BZ} \delta\left(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega\right) |p_{vc}|^2 \, d^3k = \tag{52}$$

$$= \frac{V^2 \hbar^2 e^2}{\pi m^2 \omega^2} \sum_{v,c} \int_{BZ} \delta\left(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega\right) \left| \sum_{\mathbf{G}} c^*_{\mathbf{k}+\mathbf{G},v} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i \right|^2 d^3k \tag{53}$$

$$\tag{54}$$

We use the fact that :

$$\int_{BZ} d^3k \to \frac{(2\pi)^3}{V} \sum_{\mathbf{k}} \quad \text{with } V = \mathrm{N}\Omega = \mathrm{N_1 N_2 N_3}\Omega \tag{55}$$

where N= $\mathrm{N_1 N_2 N_3}$ is the number of k points in the sum and Ω is the volume of the unit cell. Hence:

$$\epsilon_{2,i}(\omega) = (2\pi)^3 \frac{V \hbar^2 e^2}{\pi m^2 \omega^2} \sum_{\mathbf{k}} \sum_{v,c} \delta\left(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega\right) \left| \sum_{\mathbf{G}} c^*_{\mathbf{k}+\mathbf{G},v} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i \right|^2 \tag{56}$$

We use one of the equivalent definitions of Dirac Delta:

$$\delta(t) = \lim_{\sigma \to 0} \frac{1}{\sqrt{2\pi}\sigma} e^{-t^2/2\sigma^2} \tag{57}$$

$$\epsilon_{2,i}(\omega) = \lim_{\sigma \to 0} (2\pi)^3 \frac{V \hbar^2 e^2}{\pi m^2 \omega^2} \sum_{\mathbf{k}} \sum_{v,c} \frac{e^{-\left(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega\right)^2/2\sigma^2}}{\sqrt{2\pi}\sigma} \left| \sum_{\mathbf{G}} c^*_{\mathbf{k}+\mathbf{G},v} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i \right|^2$$

From the orthonormality of $\Psi_{\mathbf{k},n}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G},n} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$, we know that $c_{\mathbf{k}+\mathbf{G},n}$ has the dimension of $\frac{1}{\sqrt{V}}$. Moreover, $(\mathbf{k}+\mathbf{G})_i$ is in unit of $\frac{2\pi}{a}$. Since the argument of the exp must be dimensionless, σ must have the dimension of energy. Therefore, we write all the previous quantities in an adimensional form:

- $c_{\mathbf{k}+\mathbf{G},n} \to \frac{c_{\mathbf{k}+\mathbf{G},n}}{\sqrt{V}}$
- $(\mathbf{k}+\mathbf{G})_i \to \frac{2\pi}{a}(\mathbf{k}+\mathbf{G})_i \to \frac{2\pi}{a a_B}(\mathbf{k}+\mathbf{G})_i$
- $\sigma \to \sigma$ Ry, $\hbar\omega \to \hbar\omega$ Ry, $\epsilon_n(\mathbf{k}) \to \epsilon_n(\mathbf{k})$ Ry
- $V = N\Omega \to N\Omega a_B^3$

$$\epsilon_{2,i}(\omega) = \lim_{\sigma \to 0} \frac{(2\pi)^5}{a^2 a_B^2} \frac{\hbar^4 e^2}{\underbrace{V}_{N\Omega a_B^3} \pi m^2 (\hbar\omega)^2 \ \mathrm{Ry}^3} \sum_{\mathbf{k}} \sum_{v,c} \frac{e^{-\left(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega\right)^2/2\sigma^2}}{\sqrt{2\pi}\sigma} \left| \sum_{\mathbf{G}} c^*_{\mathbf{k}+\mathbf{G},v} c_{\mathbf{k}+\mathbf{G},c} (\mathbf{k}+\mathbf{G})_i \right|^2$$

The plot of $\epsilon_2(\omega)$ that we have to compare with is in arbitrary units, hence we choose to put $\epsilon_2(\omega)$ in units of:

$$\frac{(2\pi)^5}{a^2 a_B^2}\frac{\hbar^4 e^2}{\Omega a_B^3 \pi m^2\ \mathrm{Ry}^3} = \frac{(2\pi)^5}{a^2\Omega\pi}\underbrace{\frac{\hbar^4}{a_B^4 m^2\ \mathrm{Ry}^3}}_{1/\mathrm{Ry}}\frac{e^2}{a_B} = \underbrace{\frac{(2\pi)^5}{a^2\Omega\pi}}_{\text{adimensional, } \Omega = a^2 c\frac{\sqrt{3}}{2}}\frac{e^2}{a_B\mathrm{Ry}} = \tag{58}$$

$$= \frac{(2\pi)^5}{a^5\sqrt{2}\pi}\frac{e^2}{a_B\mathrm{Ry}} = 0.1138\frac{e^2}{a_B\mathrm{Ry}} \tag{59}$$

And we have :

$$\epsilon_{2,i}(\omega) = \frac{1}{N(\hbar\omega)^2}\lim_{\sigma\to 0}\sum_{\mathbf{k}}\sum_{v,c}\frac{e^{-(\epsilon_c(\mathbf{k})-\epsilon_v(\mathbf{k})-\hbar\omega)^2/2\sigma^2}}{\sqrt{2\pi}\sigma}\underbrace{\left|\sum_{\mathbf{G}} c^*_{\mathbf{k}+\mathbf{G},v}c_{\mathbf{k}+\mathbf{G},c}(\mathbf{k}+\mathbf{G})_i\right|^2}_{|p_{vc}|^2(\text{adimensional})} \tag{60}$$

Code: Im. part of dielectric constant

We discuss the part of the code that computes the immaginary part of dieletric constant. This is very similar to the program to calculate the DOS, but in a case of not zero potential (that we can approach using subroutines of CB program that we have seen). The main changes from the DOS + CB program that I made are the following: in the *input_ cb* subroutine I put a new variable *pol* to be inserted in input which is the polarization that it can be 1,2 or 3 in order to compute $\epsilon_{2,pol}(\omega)$. Moreover, in *cb_ permittivity* we have implemented the formulas eq.(60). We sum over a mesh of k points which are generated thanks to the subroutine *kgen(nk1, nk2, nk3, bg).* I have coded two cycles over the valence (8 in total) and conduction bands ($(nbnd-8)$ in total) which contain an implementation of $|p_{vc}|^2$ (in adimensional units) multiplied by the gaussian generated by the subroutine $gaussian(x, sigma)$. p_{vc} is easily computed observing that $c_{\mathbf{k}+\mathbf{G},n}$ are stored in the eigenvector matrix *evc(..,..)* which is filled in the *diagonalize()* subroutine.

Comparing plots of Im. part of dielectric constant

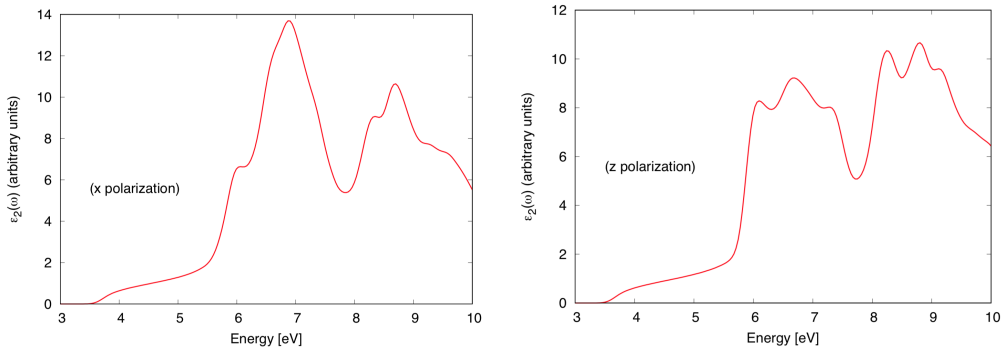

Figure 7: On the left, we have $\epsilon_2(\omega)$ with perpendicular polarization, while on the right parallel polarization. (The parameters used are $nbnds = 17$, $E_{CUT} = 16.0$ in units of $\mathrm{Ry}(2\pi/a)^2$, $\sigma = 0.1$ eV, a grid of $59 \times 59 \times 59$ k points. The computation was realized over $[3.0, 10.0]$ eV using 200 points in this interval.)

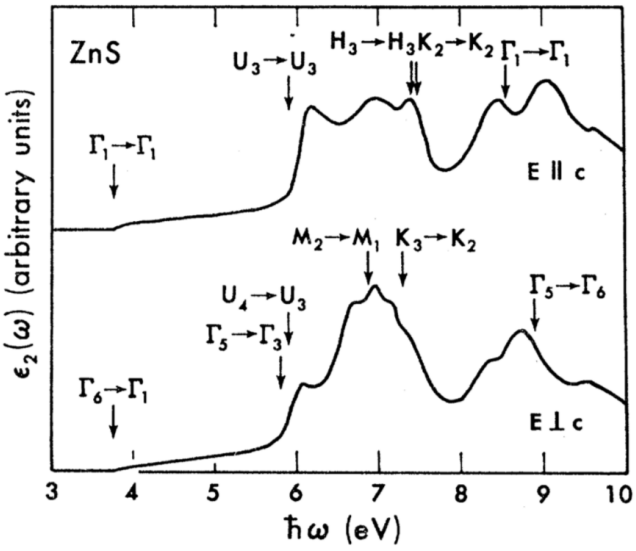

Figure 8: $\epsilon_2(\omega)$ in the reference in arbitrary units as a function of ω in eV for hexagonal ZnS.

We can observe that the positions of the peaks of our plots are in agreement with the ones in the reference figure.
As shown in the following, I have checked my results increasing the number of k points in the grid keeping fixed the other variables, increasing the number of bands keeping fixed the other variables and decreasing σ. We show the results we obtained, for example, for parallel polarization.

Increasing the number of k-points

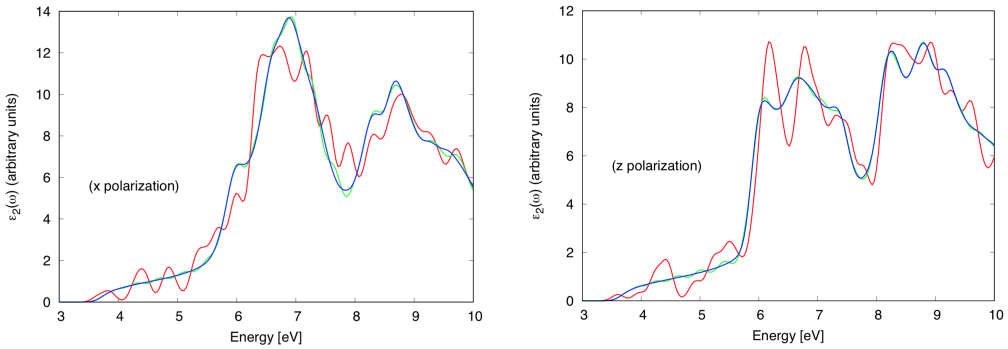

Figure 9: $\epsilon_2(\omega)$ with perpendicular polarization on the left, while on the right parallel polarization. Red line for $10 \times 10 \times 10$ k points, Green line for $28 \times 28 \times 28$ k points, Blue line for $59 \times 59 \times 59$ k points, (The parameters used are: $nbnds = 17$, $E_{CUT} = 16.0$ in units of $\mathrm{Ry}(2\pi/a)^2$, $\sigma = 0.1$ eV. The computation was realized over $[3.0, 10.0]$ eV using 200 points in this interval.)

Increasing the number of bands

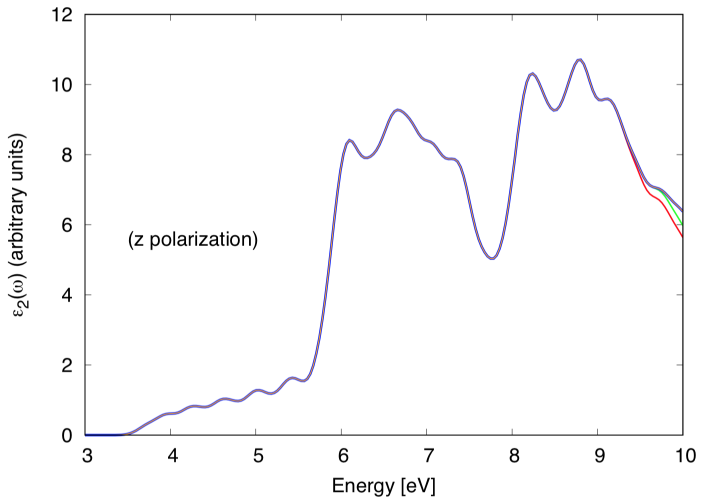

Figure 10: $\epsilon_2(\omega)$ with parallel polarization. Red line for 14 bands, Green line for 15 bands, Blue line for 17 bands, Orange line for 22 bands. (The parameters used are: $E_{CUT} = 22.0$ in units of $\mathrm{Ry}(2\pi/a)^2$, $\sigma = 0.1$ eV, a grid of $28 \times 28 \times 28$ k points. The computation was realized over $[3.0, 10.0]$ eV using 200 points in this interval.) As expected, the curves start to be different only at high energy.

Different smearing of gaussians for different k grid dimensions and energy values

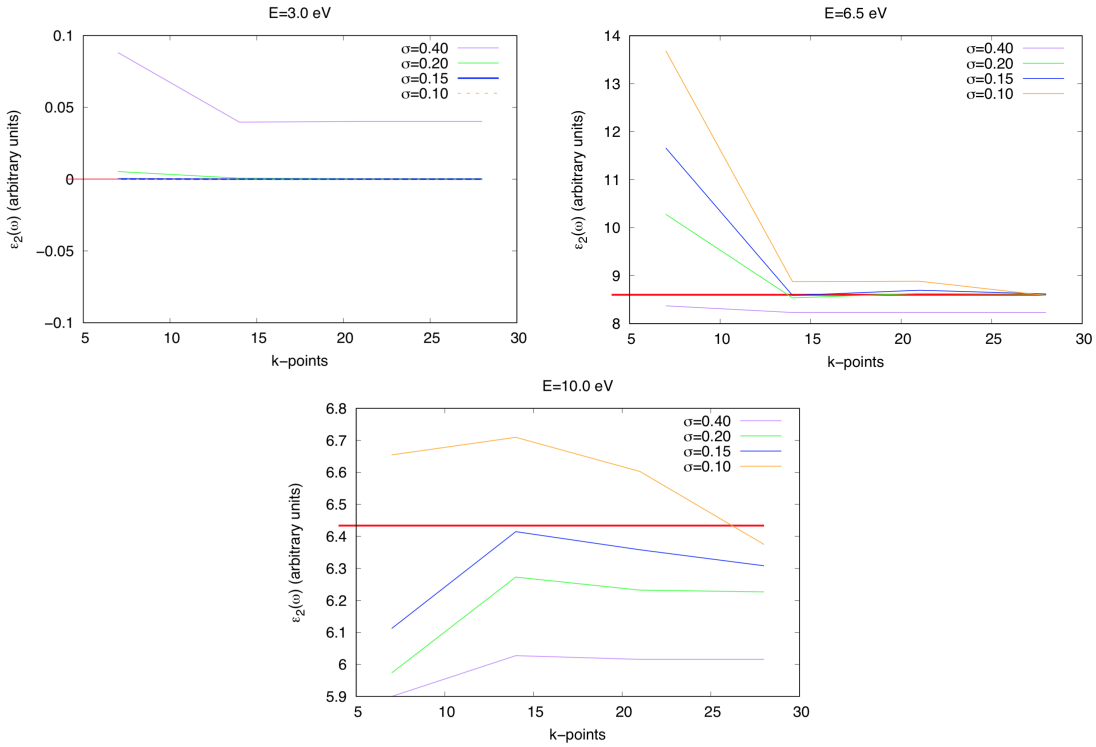

Figure 11: The case of E=3.0 eV , E=6.5 eV and E=10.0 eV are shown. The figures show the convergence of imaginary part of dielectric constant (z-polarization) for different values of grid dimensions $nk \times nk \times nk$ (nk = 7, 14, 21, 28) on the x axis and different values of sigma (σ = 0.4, 0.2, 0.15, 0.1 eV). The red line indicates the value that I got using a mesh of 59x59x59 k points and σ = 0.1 eV. (The parameters used are: $nbnds = 17$, $E_{CUT} = 16.0$ in units of $\mathrm{Ry}(2\pi/a)^2$. The computation was realized over $[3.0, 10.0]$ eV.)