Properties of semiconductors within the tight-binding method

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Key question and Summary

How can we compute properties of semiconductors within the tight-binding method ?

1. State of the art
2. Calculation method
   - Tight-binding method
   - Slater Koster parameter
   - Chadi and Cohen determinant
   - Tetrahedron method and effective mass
3. Results
   - Crystalline structure
   - Silicon
   - AsGa
4. Conclusion

State of the art

- Semiconductors have a band gap between their valence and conduction band
- Very used in industry due to their price and abondance
- Specific properties of Silicon and AsGa : their bands structures, densities of states and hole's masses
- **Tight-Binding approach**

Method - Tight-Binding method

- **Parametrized method**
- Simple model : electron on each site has a probability to hope on neighbours' site
- In this approach the Bloch wave function is a LCAO :

$$\psi_u(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{R_p} e^{i\vec{k}\cdot\vec{R}_p} \phi_u(\vec{r} - \vec{R}_p)$$

- Interactions between two sites :

$$< \psi_u | \hat{H} | \psi_v > = \sum_{R'} e^{i\vec{k}\cdot R'} \int \phi_u^*(x) \hat{H} \phi_v(x - R')$$

- Very complicated !

Method - Slater Koster parameter

Using a local frame to simplify calculation

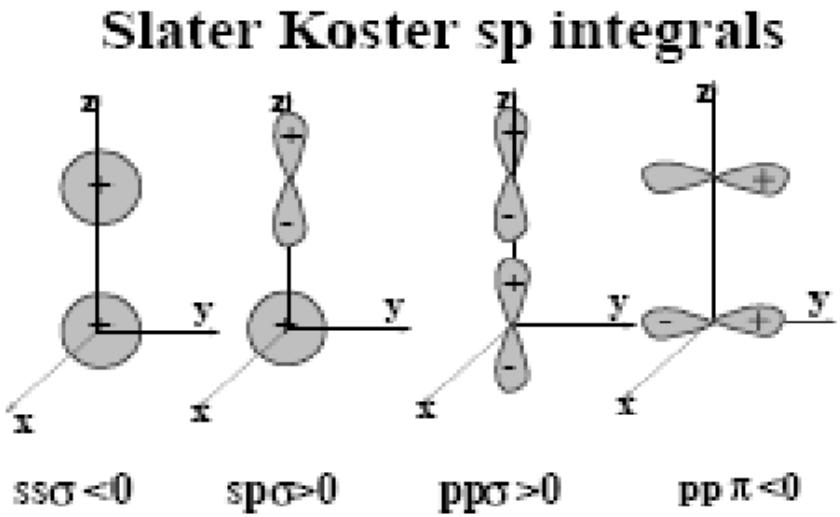


Figure 1: Orbitals' interactions

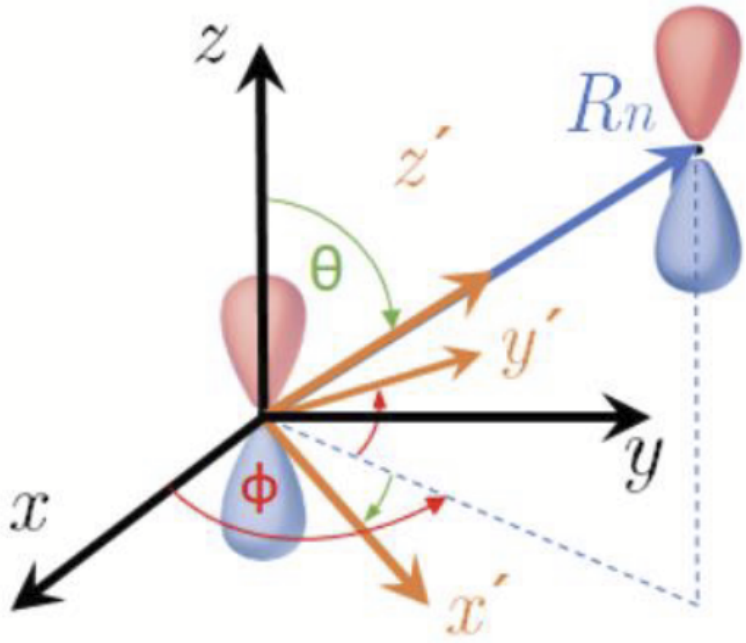


Figure 2: Rotation between global and local frame

Method - Slater Koster parameter

Finally we get our constants to fit[1] :

$E_{s,s}$	$(ss\sigma)$
$E_{s,x}$	$l(sp\sigma)$
$E_{x,x}$	$l^2(pp\sigma)+(1-l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma)-lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma)-ln(pp\pi)$

Figure 3: Energies constants due to interactions

TABLE VI. Energy integrals (in Rydbergs) for diamond, from Herman's calculations.

$E_{s,s}(000)$	−1.37
$E_{x,x}(000)$	−0.378
$E_{s,s}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	−0.325
$E_{x,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.0563
$E_{x,y}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.277
$E_{s,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.122
$E_{s,s}(110)$	0.019
$E_{x,x}(011)$	−0.064
$E_{x,y}(110)$	−0.022
$E_{x,x}(110)$	−0.006
$E_{s,x}(011)$	0.119

Figure 4: Value of the constants

[1] J.C. SLATER and G.F. Koster *Simplified LCAO Method for the Periodic Potential Problem*

Method - Chadi and Cohen determinant

Determinant of the hamiltonian representing nearest-neighbours interactions between 2 atoms[2] :

$$
\begin{array}{c|cccccccc}
 & s_0 & s_1 & x_0 & y_0 & z_0 & x_1 & y_1 & z_1 \\
\hline
s_0 & E_{s_0}-E(\boldsymbol{k}) & V_{ss}g_0 & 0 & 0 & 0 & V_{s_0p}g_1 & V_{s_0p}g_2 & V_{s_0p}g_3 \\
s_1 & V_{ss}g_0^* & E_{s_1}-E(\boldsymbol{k}) & -V_{s_1p}g_1^* & -V_{s_1p}g_2^* & -V_{s_1p}g_3^* & 0 & 0 & 0 \\
x_0 & 0 & -V_{s_1p}g_1 & E_{p_0}-E(\boldsymbol{k}) & 0 & 0 & V_{xx}g_0 & V_{xy}g_3 & V_{xy}g_2 \\
y_0 & 0 & -V_{s_1p}g_2 & 0 & E_{p_0}-E(\boldsymbol{k}) & 0 & V_{xy}g_3 & V_{xx}g_0 & V_{xy}g_1 \\
z_0 & 0 & -V_{s_1p}g_3 & 0 & 0 & E_{p_0}-E(\boldsymbol{k}) & V_{xy}g_2 & V_{xy}g_1 & V_{xx}g_0 \\
x_1 & V_{s_0p}g_1^* & 0 & V_{xx}g_0^* & V_{xy}g_3^* & V_{xy}g_2^* & E_{p_1}-E(\boldsymbol{k}) & 0 & 0 \\
y_1 & V_{s_0p}g_2^* & 0 & V_{xy}g_3^* & V_{xx}g_0^* & V_{xy}g_1^* & 0 & E_{p_1}-E(\boldsymbol{k}) & 0 \\
z_1 & V_{s_0p}g_3^* & 0 & V_{xy}g_2^* & V_{xy}g_1^* & V_{xx}g_0^* & 0 & 0 & E_{p_1}-E(\boldsymbol{k})
\end{array}
= 0 .
$$

Figure 5: Determinant for interactions

[2] D. J. CHADI and M. L. COHEN *Tight-Binding Calculations of the Valence Bands of Diamond and Zincblende Crystals*

Tetrahedron method and effective mass

- Analytical formula for density of states $g(E)$:

$$g_n(E)dE = \frac{1}{4\pi^3} \int_{S_n(E)} \frac{dS}{|\nabla E_{nk}|}$$

- Effective mass :

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}$$

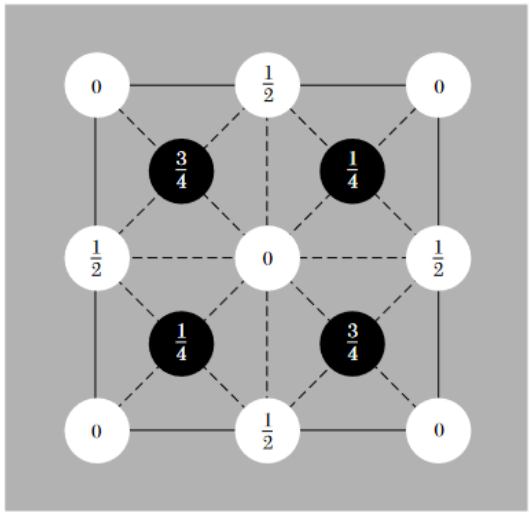
- Conduction mass m_c^* :

$$\frac{3}{m_c^*} = \frac{1}{m_L^*} + \frac{2}{m_T^*}$$

with m_L^* and m_T^* longitudinal and transverse masses

Results - Crystalline structure

- Si ($3s^2 3p^2$) and AsGa (As :$4s^2 4p^3$, Ga :$4s^2 4p^1$) have diamond structures :



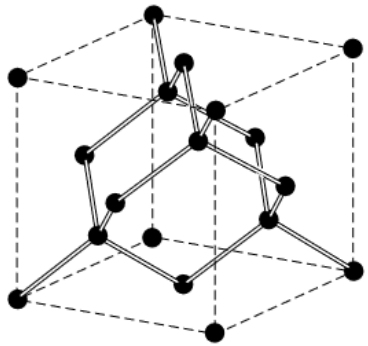
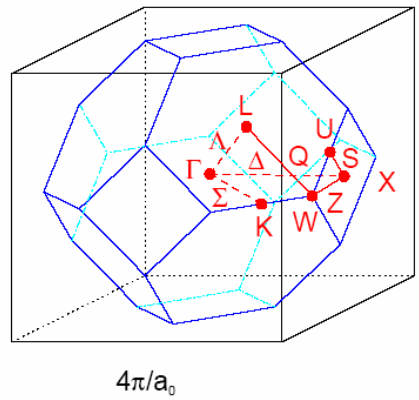


Figure 6: Silicon's Bands structure with orbitals' contribution



$\Gamma = \frac{2\pi}{a_0}[0,0,0]$ $\quad U = \frac{2\pi}{a_0}[1,\frac{1}{4},\frac{1}{4}]$

$X = \frac{2\pi}{a_0}[1,0,0]$ $\quad W = \frac{2\pi}{a_0}[1,\frac{1}{2},0]$

$L = \frac{2\pi}{a_0}[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ $\quad K = \frac{2\pi}{a_0}[\frac{3}{4},\frac{3}{4},0]$

$\Delta = \frac{2\pi}{a_0}[\xi,0,0],$ $\quad 0 \leq \xi \leq 1$

$\Lambda = \frac{2\pi}{a_0}[\xi,\xi,\xi],$ $\quad 0 \leq \xi \leq \frac{1}{2}$

$\Sigma = \frac{2\pi}{a_0}[\xi,\xi,0],$ $\quad 0 \leq \xi \leq \frac{3}{4}$

$Z = \frac{2\pi}{a_0}[1,\xi,0],$ $\quad 0 \leq \xi \leq \frac{1}{2}$

$Q = \frac{2\pi}{a_0}[1-\xi,\frac{1}{2},\xi],$ $\quad 0 \leq \xi \leq \frac{1}{2}$

$S = \frac{2\pi}{a_0}[1,\xi,\xi],$ $\quad 0 \leq \xi \leq \frac{1}{4}$

Figure 7: First Brillouin zone

Results - Silicon : Bands and DOS

Considering only first neighbours and using :
$E_s = 0, E_p = 7.20, V_{ss} = -8.13, V_{sp} = 5.88, V_{xx} = 3.17, V_{xy} = 7.51$
(units : eV)

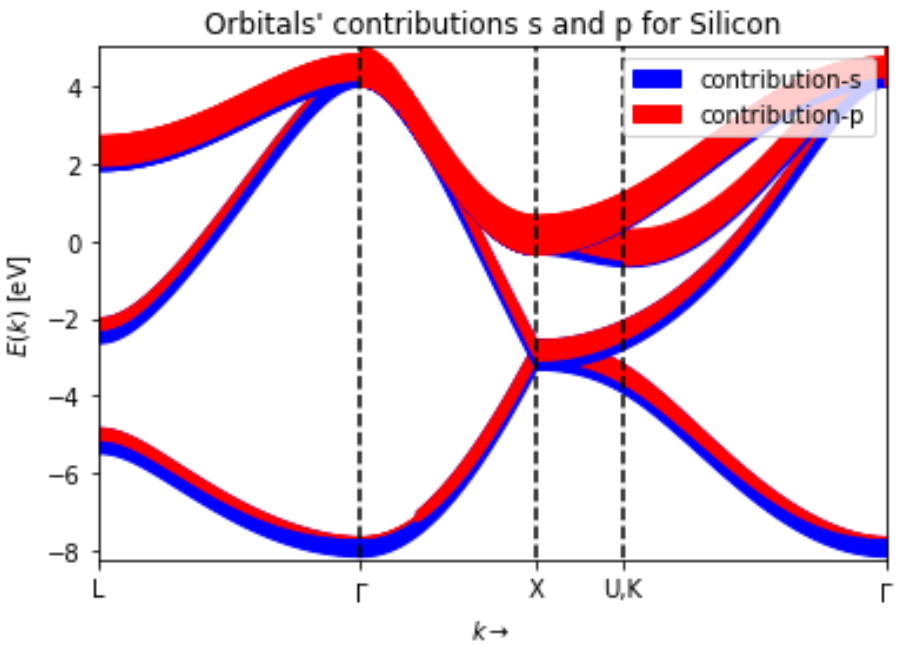


Figure 8: Silicon's Bands structure with orbitals' contribution

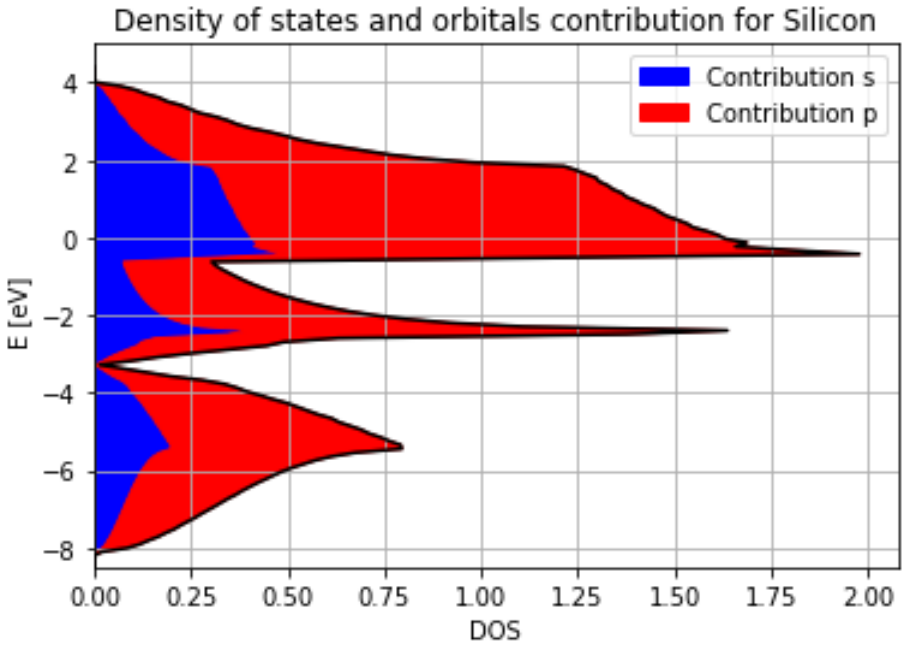


Figure 9: Silicon's density of states

Results - Silicon : Ligth and heavy holes

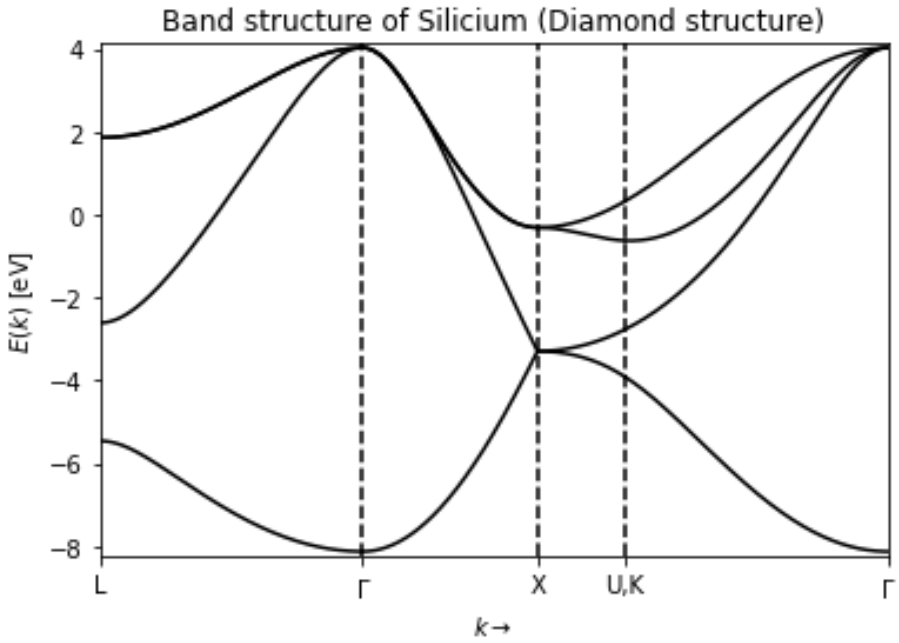


Figure 10: Silicon's Bands structure

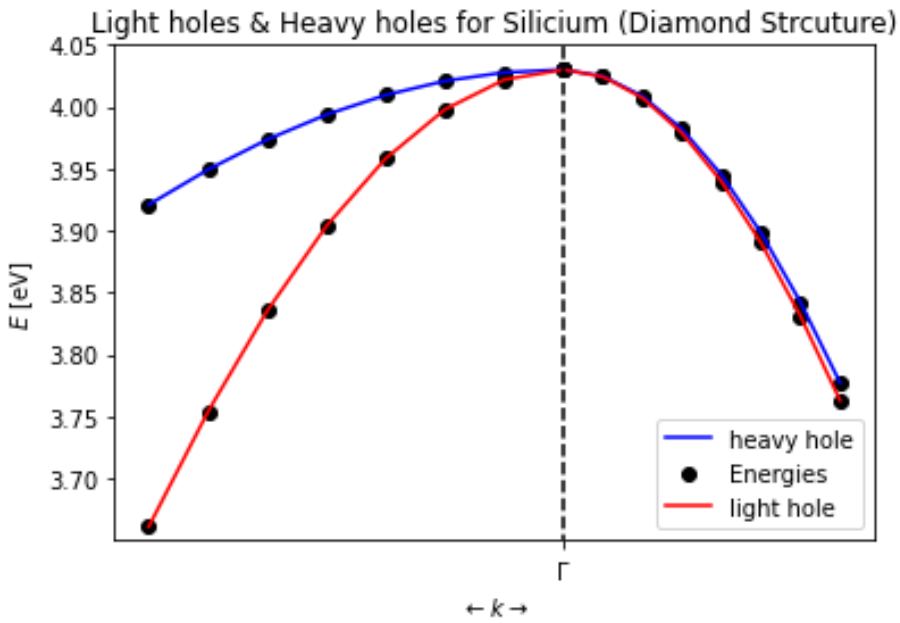


Figure 11: Fit near Γ point

We found $m_{hh} = 0.34$ and $m_{lh} = 0.16$ (in atomic units $\hbar = m_0 = 1$) while experiments[3] measured : $m_{hh} = 0.49$ and $m_{lh} = 0.16$

[3] *Solid State Physics*, Giuseppe Grosso and Giuseppe Pastori Parravicini, Table 13.1

Results - AsGa : Bands and DOS

Considering only first neighbours and using :
$V_{ss} = -7.00, V_{s_0 p} = 7.28, V_{s_1 p} = 3.70, V_{xx} = 0.93, V_{xy} = 4.72,$
$E_{s_0} = -6.01, E_{s_1} = -4.79, E_{p_0} = 0.19, E_{p_1} = 4.59$ (units : eV)

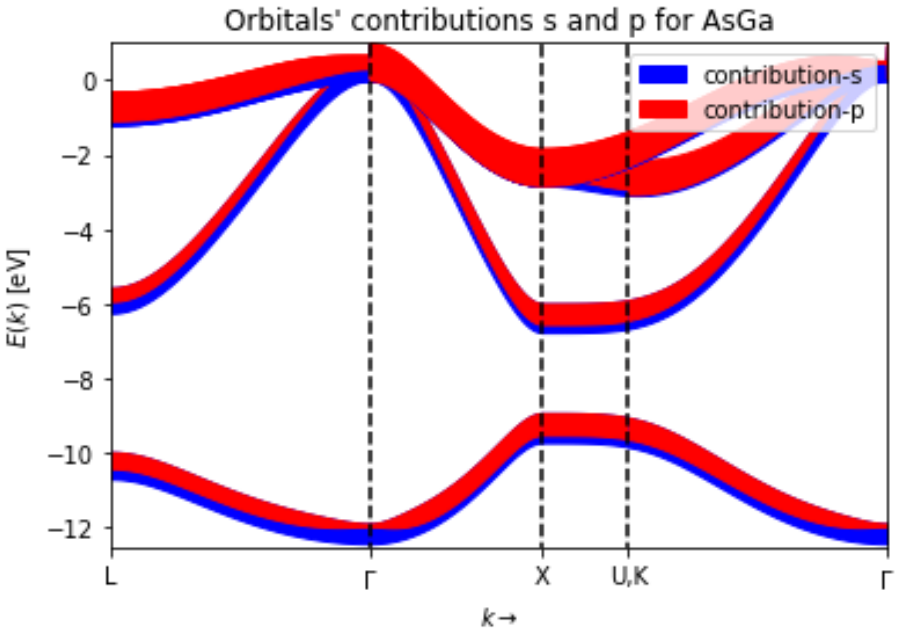


Figure 12: AsGa's Bands structure with orbitals' contribution

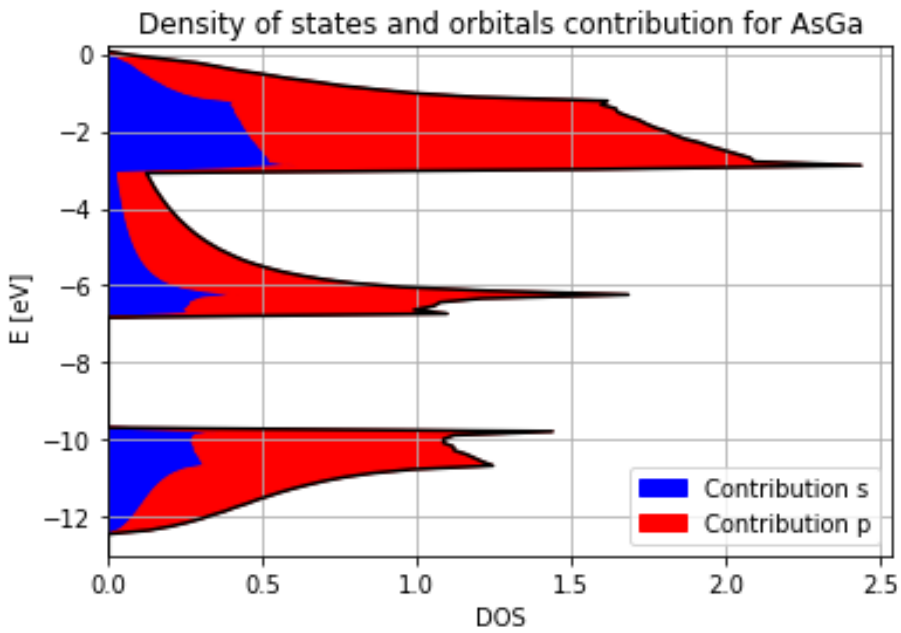


Figure 13: AsGa's density of states

Results - AsGa : Ligth and heavy holes

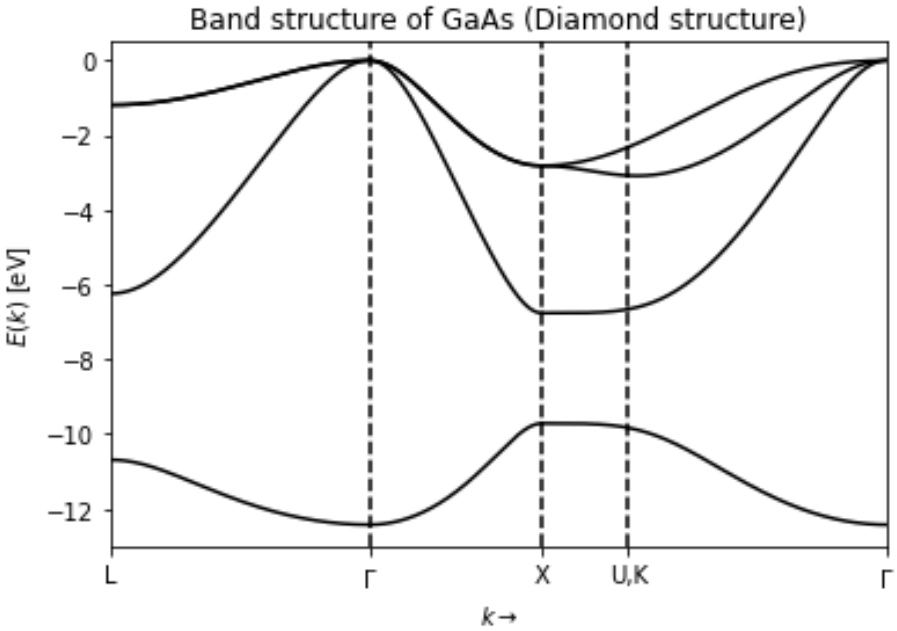


Figure 14: AsGa's Bands structure

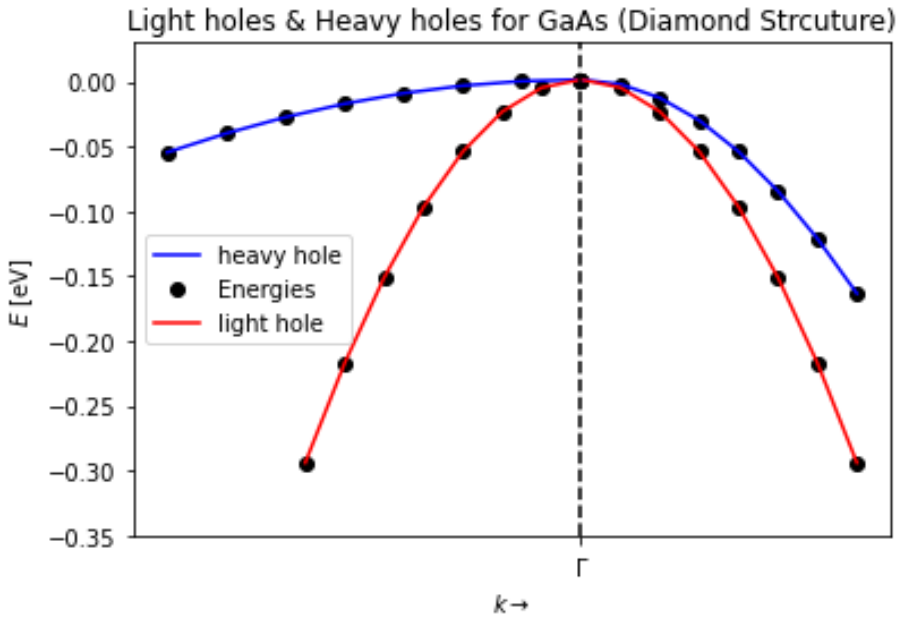


Figure 15: Fit near Γ point

We found $m_{hh} = 0.54$ and $m_{lh} = 0.14$ (in atomic units $\hbar = m_0 = 1$) while experiments[4] measured : $m_{hh} = 0.48$ and $m_{lh} = 0.09$

[4] *Solid State Physics*, Giuseppe Grosso and Giuseppe Pastori Parravicini, Table 13.1

Conclusion

- Learn how to compute band structure and others properties
- Above our approach...

Conclusion

- Learn how to compute band structure and others properties

- Above our approach...
  - Relativistic effects
  - Spin-orbit coupling
  - Optical transition

Bibliography


D. J. CHADI and M. L. COHEN *Tight-Binding Calculations of the Valence Bands of Diamond and Zincblende Crystals*,phys. stat. sol. (b) 68, 405 (1975), https://inst.eecs.berkeley.edu/~ee230/sp08/chadi%20and%20cohen.pdf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M.ALOUANI *M2's lessons*


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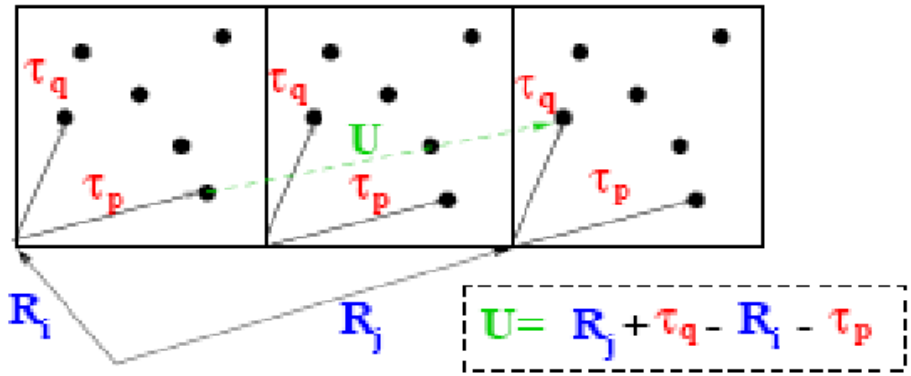
Tight-Binding wave function

For a crystal with Na atoms per unit cell the crystal wave function can be written as:

$$|\psi_{nk}\rangle = \frac{1}{\sqrt{N}} \sum_{t,lm} c_{t,lm,nk} \sum_{R_j} e^{ik(R_j+\tau_t)} \, |j,t,lm\rangle$$

with $N=N_a \times N_{cell}$



The Bloch wave function of each sub-lattice of atom located at τ_t is given by

$$|\phi^k_{tlm}\rangle \frac{1}{\sqrt{N_{cell}}} \sum_{R_j} e^{ik(R_j+\tau_t)} \, |j,t,lm\rangle$$

Tight-Binding wave function

$$< \psi_n|\hat{H}|\psi_m >= \frac{1}{N}\sum_{R_i}\sum_{R_j} e^{i\vec{k}\cdot(\vec{R}_j-\vec{R}_i)} \int \phi_n^*(\vec{r}-\vec{R}_i)\hat{H}\phi_m(\vec{r}-\vec{R}_j)$$

Let's put $x = r - R_i$:

$$< \psi_n|\hat{H}|\psi_m >= \frac{1}{N}\sum_{R_i}\sum_{R_j} e^{i\vec{k}\cdot(\vec{R}_j-\vec{R}_i)} \int \phi_n^*(x)\hat{H}\phi_m(x-(R_j-R_i))$$

Let's put : $R' = R_j - R_i$, R' is a lattice's vector.

$$< \psi_n|\hat{H}|\psi_m >= \frac{1}{N}\sum_{R_i}\sum_{R'} e^{i\vec{k}\cdot R'} \int \phi_n^*(x)\hat{H}\phi_m(x-R')$$

Sum over R_i simplifies $1/N$ and we get :

$$< \psi_n|\hat{H}|\psi_m >= \sum_{R'} e^{i\vec{k}\cdot R'} \int \phi_n^*(x)\hat{H}\phi_m(x-R')$$

Reciprocal space

- Bloch's theorem : $\psi_{nk} = e^{i\vec{k}\cdot\vec{r}} u_{nk}(\vec{r})$ with $u_{nk}(\vec{r}+\vec{R}) = u_{nk}(\vec{r})$
- Born-Von Karman BC : we can take box of length L big enough to have $\psi(\vec{r}+\vec{L}) = \psi(\vec{r})$
- Bloch + BVK : $\psi(\vec{r}) = \psi(\vec{r}+\vec{L})e^{i\vec{k}\vec{L}} \Rightarrow e^{i\vec{k}\vec{L}} = 1$ with $L = N_i a_i$
- Quantification of $\vec{k}$: $e^{iN_i\vec{k}\cdot\vec{a}_i} = 1 \Rightarrow \vec{k} = \sum_i \frac{m_i \vec{b}_i}{N_i}$ with m an integer and $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$
- Definition of $\vec{b}$:$\vec{b_i} = 2\pi \frac{\vec{a_{i+1}} \times \vec{a_{i+2}}}{\vec{a_1}\cdot(\vec{a_2}\times\vec{a_3})}$.

Reciprocal space

- Make our problem easier
- Periodic potential
- Hamiltonian is bloc diagonal for each point k

Slater Koster parameter - Details

We use, spherical coordinate and by using usual rotation matrices around y and z axis we have :

$$R(l,m,n) = \begin{pmatrix} \frac{ln}{\sqrt{1-n^2}} & -\frac{m}{\sqrt{1-n^2}} & l \\ \frac{mn}{\sqrt{1-n^2}} & \frac{l}{\sqrt{1-n^2}} & m \\ -\sqrt{1-n^2} & 0 & n \end{pmatrix}$$

with $l = \frac{x}{r}$, $m = \frac{y}{r}$ and $n = \frac{z}{r}$
Example of simplification :

$$\begin{aligned} < x|\hat{H}|x > &\simeq < x|\hat{V}|x > \\ &= < R_{11}x' + R_{12}y' + R_{13}z'|\hat{V}|R_{11}x' + R_{12}y' + R_{13}z' > \\ &= R_{11}^2 pp\pi + R_{12}^2 pp\pi + R_{13}^2 pp\sigma \\ &= (R_{11}^2 + R_{12}^2)pp\pi + R_{13}^2 pp\sigma \\ &= (1 - l^2)pp\pi + l^2 pp\sigma \end{aligned}$$

Determinant of $\hat{H}$ - Details

For diamond structure crystals $E_{s_0} = E_{s_1}$, $E_{p_0} = E_{p_1}$, and $V_{s_0 p} = V_{s_1 p}$, and from this point we will drop the subscripts for these crystals. The functions g_0, g_1, g_2, and g_3 in (6) are given by

$$g_0(\boldsymbol{k}) = \cos\pi\frac{k_1}{2}\cos\pi\frac{k_2}{2}\cos\pi\frac{k_3}{2} - i\sin\pi\frac{k_1}{2}\sin\pi\frac{k_2}{2}\sin\pi\frac{k_3}{2}, \quad (7)$$

$$g_1(\boldsymbol{k}) = -\cos\pi\frac{k_1}{2}\sin\pi\frac{k_2}{2}\sin\pi\frac{k_3}{2} + i\sin\pi\frac{k_1}{2}\cos\pi\frac{k_2}{2}\cos\pi\frac{k_3}{2}, \quad (8)$$

$$g_2(\boldsymbol{k}) = -\sin\pi\frac{k_1}{2}\cos\pi\frac{k_2}{2}\sin\pi\frac{k_3}{2} + i\cos\pi\frac{k_1}{2}\sin\pi\frac{k_2}{2}\cos\pi\frac{k_3}{2}, \quad (9)$$

$$g_3(\boldsymbol{k}) = -\sin\pi\frac{k_1}{2}\sin\pi\frac{k_2}{2}\cos\pi\frac{k_3}{2} + i\cos\pi\frac{k_1}{2}\cos\pi\frac{k_2}{2}\sin\pi\frac{k_3}{2}, \quad (10)$$

where $\boldsymbol{k} = (2\pi/a)\,(k_1, k_2, k_3)$.

For diamond structure crystals, the parameters appearing in (6) are related to those of Slater and Koster [6] by

$$\left.\begin{aligned} E_s &= E_{s,s}\,(000)\,, & E_p &= E_{x,x}\,(000)\,, \\ V_{ss} &= 4E_{s,s}\,(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\,, & V_{xx} &= 4E_{x,x}\,(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\,, \\ V_{xy} &= 4E_{x,y}\,(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\,, & V_{sp} &= 4V_{s,x}\,(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})\,. \end{aligned}\right\} \quad (11)$$

Determinant of $\hat{H}$ - Details

TABLE V. Matrix components of energy for diamond structure.

$(s/s)_{11}=(s/s)_{22}$	$E_{s,s}(000)+4E_{s,s}(110)(\cos\xi\cos\eta+\cos\eta\cos\zeta+\cos\xi\cos\zeta)$
$(x/x)_{11}=(x/x)_{22}$	$E_{x,x}(000)+4E_{x,x}(110)(\cos\xi\cos\eta+\cos\xi\cos\zeta)+4E_{x,x}(011)\cos\eta\cos\zeta$
$(s/s)_{12}=(s/s)_{21}^*$	$4E_{s,s}(\frac{1}{2}\frac{1}{2}\frac{1}{2})(\cos\frac{1}{2}\xi\cos\frac{1}{2}\eta\cos\frac{1}{2}\zeta-i\sin\frac{1}{2}\xi\sin\frac{1}{2}\eta\sin\frac{1}{2}\zeta)$
$(s/x)_{12}=-(s/x)_{21}^*$	$4E_{s,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})(i\sin\frac{1}{2}\xi\cos\frac{1}{2}\eta\cos\frac{1}{2}\zeta-\cos\frac{1}{2}\xi\sin\frac{1}{2}\eta\sin\frac{1}{2}\zeta)$
$(s/x)_{11}=-(s/x)_{22}^*$	$-4E_{s,x}(011)\sin\xi\sin\eta+4iE_{s,x}(110)(\sin\xi\cos\eta+\sin\xi\cos\zeta)$
$(x/x)_{12}=(x/x)_{21}^*$	$4E_{x,x}(\frac{1}{2}\frac{1}{2}\frac{1}{2})(\cos\frac{1}{2}\xi\cos\frac{1}{2}\eta\cos\frac{1}{2}\zeta-i\sin\frac{1}{2}\xi\sin\frac{1}{2}\eta\sin\frac{1}{2}\zeta)$
$(x/y)_{12}=(x/y)_{21}^*=(y/x)_{12}$	$4E_{x,y}(\frac{1}{2}\frac{1}{2}\frac{1}{2})(i\cos\frac{1}{2}\xi\cos\frac{1}{2}\eta\sin\frac{1}{2}\zeta-\sin\frac{1}{2}\xi\sin\frac{1}{2}\eta\cos\frac{1}{2}\zeta)$
$(x/y)_{11}=(x/y)_{22}^*$	$-4E_{x,y}(110)\sin\xi\sin\eta-4iE_{x,y}(011)(\sin\xi\cos\zeta-\sin\eta\cos\zeta)$

Figure 16: Interaction element of the Hamiltonian's determinant

DOS - Details

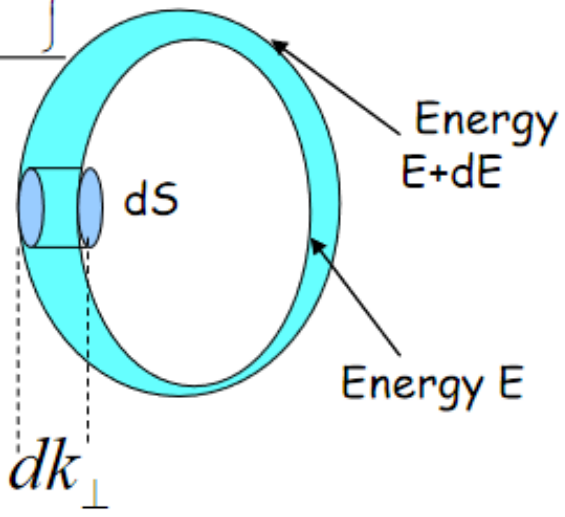
As in the free-electron case, the density of states for the energy levels E_{nk} between E and E+dE for the band n is given by the volume of k-space primitive cell with

$E \le E_{nk} \le E + dE$ divided by the volume $(2\pi)^3/V$ per allowed wave vector.

spins

Density per unit volume

$$g_n(E)\,dE = \frac{2}{V}\frac{\int d^3k \begin{cases} 1, & E \le E_{nk} \le E + dE \\ 0, & \text{otherwise} \end{cases}}{(2\pi)^3/V}$$



$$dE = |\nabla E_{nk}|\,dk_\perp \quad \text{and} \quad d^3k = dS \cdot dk_\perp$$

The density of states is therefore given by:

$$g_n(E) = \frac{1}{4\pi^3}\int_{S_n(E)} \frac{dS}{|\nabla E_{nk}|} \qquad (2.11)$$

Figure 17: Analytical formula for DOS

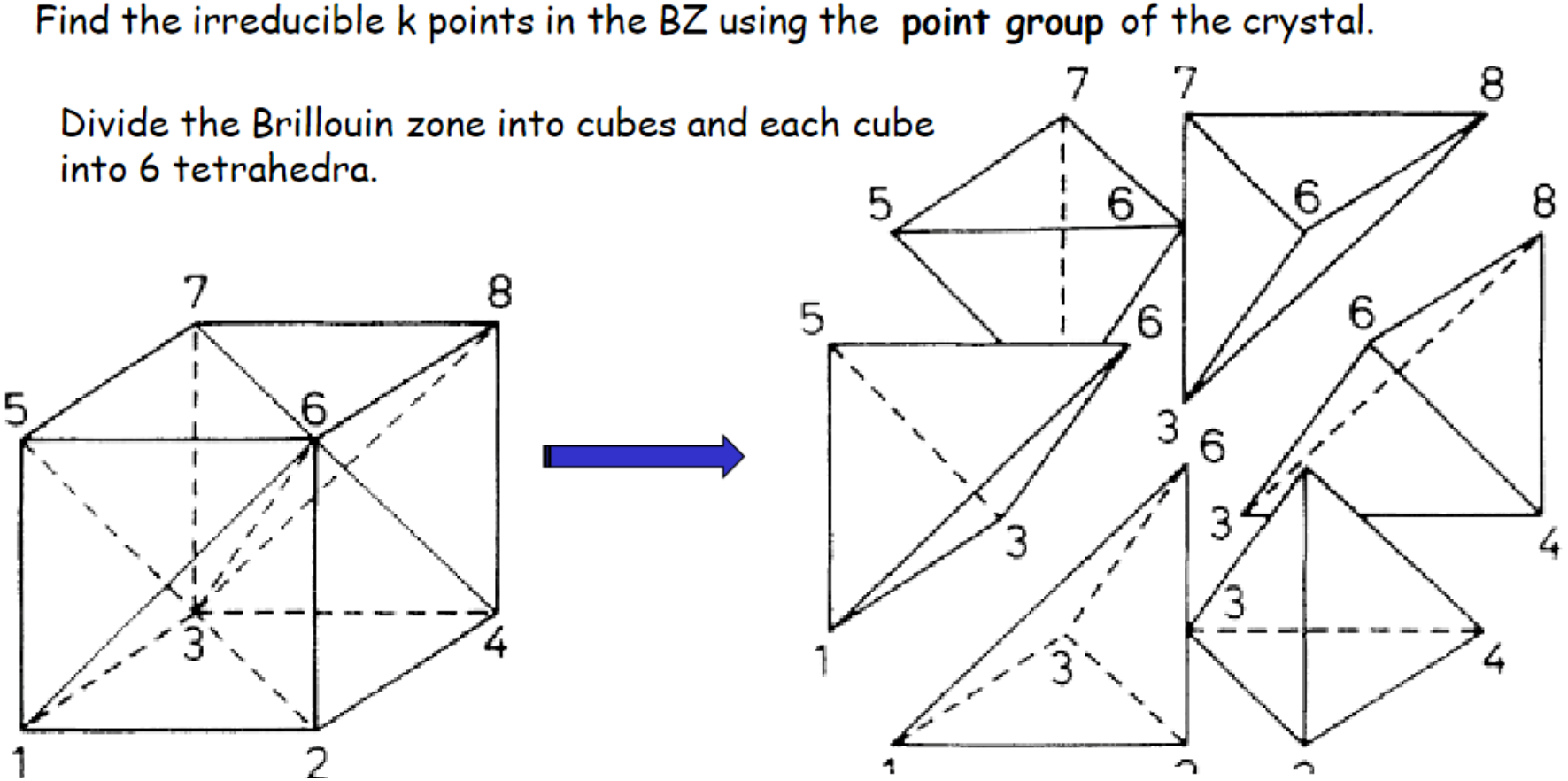


Figure 18: The tetrahedron method

DOS - Details

1. Order the energies ε_i of the corners and the associated k-points
2. Subtract the energy ε_0 at the first corner to get $\Delta\varepsilon_i$
3. Get the energy for which you calculate the DOS and remove ε_0
4. Find the values of k that give the intersection with the tetrahedron
5. Compute the area of the intersection and divide it by the gradient of ε

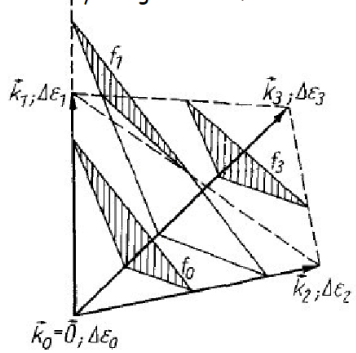


Figure 19: Algorithm

1. $\varepsilon < \varepsilon_1$ and $\varepsilon > \varepsilon_4$: $D_T(\epsilon) = 0$

2. $\varepsilon_1 < \varepsilon < \varepsilon_2$: $$D_T(\epsilon) = \frac{V_T}{V_G}\frac{3(\epsilon-\epsilon_1)^2}{\epsilon_{21}\epsilon_{31}\epsilon_{41}}$$

3. $\varepsilon_2 < \varepsilon < \varepsilon_3$: $$D_T(\epsilon) = \frac{V_T}{V_G}\frac{1}{\epsilon_{31}\epsilon_{41}}\left[3\epsilon_{21} + 6(\epsilon-\epsilon_2) - 3\frac{(\epsilon_{31}+\epsilon_{42})(\epsilon-\epsilon_2)^2}{\epsilon_{32}\epsilon_{42}}\right]$$

4. $\varepsilon_3 < \varepsilon < \varepsilon_4$: $$D_T(\epsilon) = \frac{V_T}{V_G}\frac{3(\epsilon_4-\epsilon)^2}{\epsilon_{41}\epsilon_{42}\epsilon_{43}}$$

Figure 20: Contribution of one tetrahedron to the DOS[6]

[6] *Improved tetrahedron method for Brillouin-zone integrations*,Peter E. Blöch , O.Jepsen and O.K. Andersen, 15 June 1994