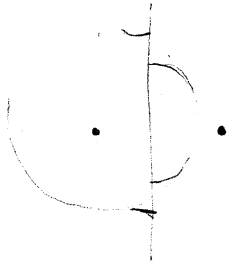


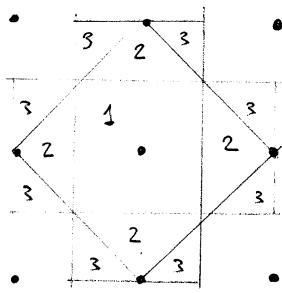
For weak potentials, the Fermi surface can be evaluated starting from the free-electron sphere centered at  $\vec{k}=0$ , and noticing that the latter will be modified near Bragg planes.



the gradient of the energy dispersion is in the Bragg plane  $\rightarrow$  an isosurface must be  $\perp$  to it.

Example: Square lattice

First 3 BZ of a square lattice



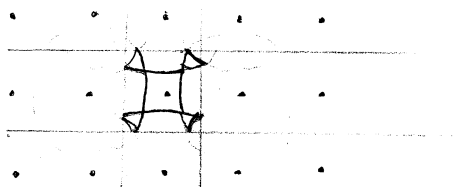
- Bragg planes are the planes bisecting the lines joining the origin and the reciprocal lattice points

-  $n$ BZ is the set of points that can be reached from the 1BZ by crossing  $n-1$  Bragg planes but not fewer

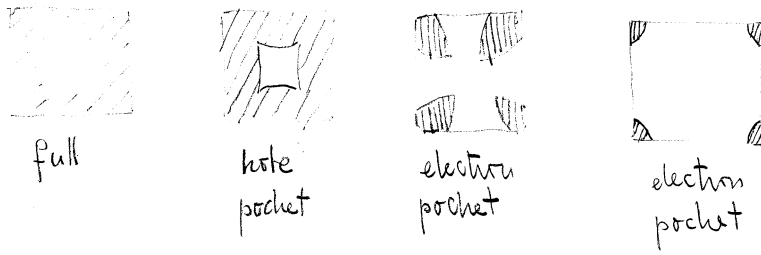
To determine the Fermi surface according to the Horizon construction one fixes a Fermi energy corresponding to a given free electron concentration

$$n_e \rightarrow E_F = \frac{\hbar^2}{2m} (3\pi^2)^{2/3} n_e^{2/3} \rightarrow k_F = (3\pi^2 n_e)^{1/3}$$

and draws free energy Fermi surfaces centered at each reciprocal lattice point. The intricate set of lines obtained in the 1BZ represent a first approximation to the Fermi surface.



In the folded zone scheme one obtains thus, by zone folding from the different zones (equivalently from Fermi surfaces centered around further neighbors



An equivalent result obtained in tight binding would correspond to isolines obtained cutting the surfaces associated to the different bands which originates from the different atomic orbitals.

## 2.7 Alkali and Noble metals

Let us consider the category of monovalent metals. We can find

	Alkali metals (bcc)		Noble metals (fcc)	
Lithium	Li: [He] 2s <sup>1</sup>			
Sodium	Na: [Ne] 3s <sup>1</sup>			
Potassium	K: [Ar] 4s <sup>1</sup>		Cu: [Ar] 3d <sup>10</sup> 4s <sup>1</sup>	Copper
Rubidium	Rb: [Kr] 5s <sup>1</sup>		Ag: [Kr] 4d <sup>10</sup> 5s <sup>1</sup>	Silver
Cesium	Cs: [Xe] 6s <sup>1</sup>		Au: [Xe] 5d <sup>10</sup> 6s <sup>1</sup>	Gold

- Alkali metals: they have 1 valence electron and a bcc crystal structure

$$\frac{k_F^3}{3\pi^2} = n_e = \frac{N_e}{V} = \frac{2}{a^3} \leftarrow \text{bcc lattice can be seen as simple cubic with 2 atoms basis}$$

$$\Rightarrow k_F = 0.620 \frac{2\pi}{a}$$

The minimum distance from  $\Gamma$  to the 1BZ face is in the [110]

$$\Gamma N = \frac{2\pi}{a} \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + 0} = 0.707 \frac{2\pi}{a} > k_F$$

(fcc in reciprocal space) The Fermi surface has almost no distortion from the free particle sphere.

- Noble metals: neglecting the d-electrons (relevant for optical properties) they also have 1 valence electron but fcc crystal structure.

$$\frac{k_F^3}{3\pi^2} = n_e = \frac{4}{a^3} \leftarrow \begin{array}{l} \text{simple cubic cell with} \\ \text{4 atoms basis} \end{array}$$

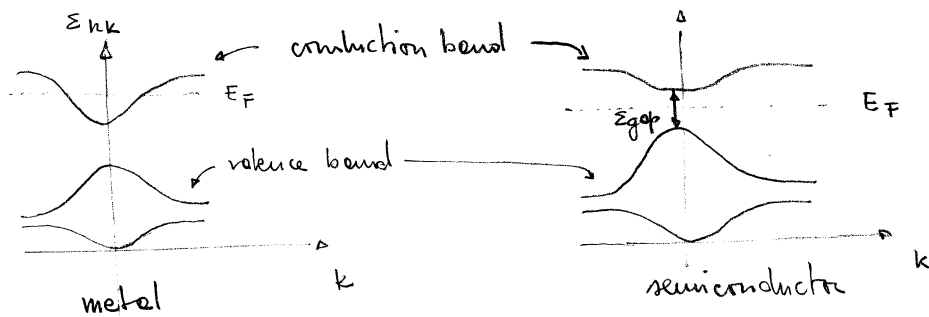
The minimum distance from the  $\Gamma$  point to the 1BZ face is (bcc)

$$\Gamma L = \frac{a\pi}{a} \sqrt{\frac{3}{4}} = \frac{\sqrt{3}}{2} \frac{2\pi}{a} \Rightarrow \frac{k_F}{\Gamma L} = 0.903$$

The Fermi surface touches the 1BZ faces and thus it "opens".

## 2.6 SEMICONDUCTORS

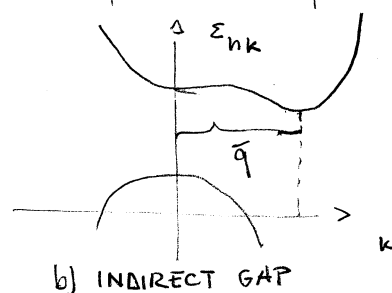
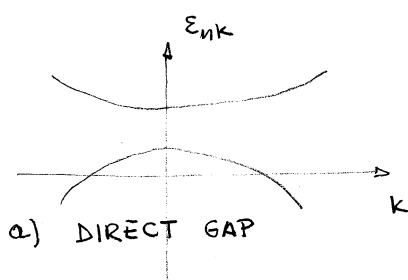
Semiconductors have a tremendous importance in present technological applications. Here we analyze some properties related to their band structure



$$k_B T \quad (T = 300 \text{ K}) = 0.025 \text{ eV}$$

$$E_{\text{gap}}: \quad \text{Ge} = 0.65 \text{ eV} \quad \text{Si} = 1.12 \text{ eV} \quad \text{C (diamond)} = 5.5 \text{ eV} \quad \text{insulator.}$$

The gap in a semicond. can be direct (max of valence band and min of conduction band at the same  $k$ -point.) or indirect (max of valence band and min of conduction band at different  $k$ -points).

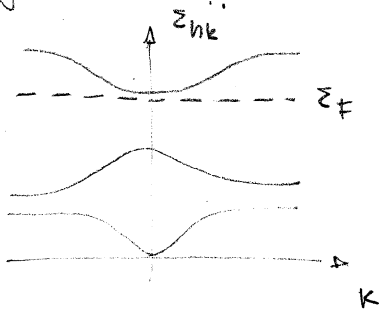


a) for most of the compound semiconductors  $A_3B_5$  and  $A_2B_6$  in the zincblende structure the conduction band minimum is found at the  $\Gamma$  point

b) Homopolar semiconductors eg. Si, Ge are indirect gap semiconductors.

In doped semiconductors the Fermi level is shifted from the middle of the gap to the impurity levels which can be close to the conduction band minimum (n doping) or valence band maximum (p doping)

The thermally excited carriers can follow an applied electric field and carry current.



Near band-edge states determine some of the characteristic properties of semiconductors.

In order to describe the dispersion of the energy bands around a given point  $\vec{k}_0$  in the 1BZ let us assume the SE for electrons in a periodic potential to be solved for a given  $\vec{k}_0$ .

$$\hat{h} \psi_{n\vec{k}_0}(\vec{r}) = \left( -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \psi_{n\vec{k}_0}(\vec{r}) = \varepsilon_n(\vec{k}_0) \psi_{n\vec{k}_0}(\vec{r})$$

when  $\psi_{n\vec{k}_0}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}_0 \cdot \vec{r}} u_{n\vec{k}_0}(\vec{r})$  according to the Bloch form.

$\varepsilon_n(\vec{k})$  is the solution of the SE associated to  $\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} u_{n\vec{k}}(\vec{r})$ .

we will look for  $\varepsilon_n(\vec{k})$  within  $\vec{k} \cdot \hat{p}$  method.

$$i) \quad \psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i(\vec{k}-\vec{k}_0) \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}} u_{n\vec{k}}(\vec{r})$$

$$\begin{aligned} \Rightarrow \hat{h} \psi_{n\vec{k}}(\vec{r}) &= e^{i(\vec{k}-\vec{k}_0) \cdot \vec{r}} \varepsilon_n(\vec{k}) \frac{1}{\sqrt{V}} e^{i\vec{k}_0 \cdot \vec{r}} u_{n\vec{k}}(\vec{r}) \\ &= e^{i\vec{k}-\vec{k}_0 \cdot \vec{r}} \left( \frac{\hbar^2}{2m} (\vec{k}-\vec{k}_0)^2 + \frac{\hbar}{m} (\vec{k}-\vec{k}_0) \cdot \hat{p} + \hat{h} \right) \frac{1}{\sqrt{V}} e^{i\vec{k}_0 \cdot \vec{r}} u_{n\vec{k}}(\vec{r}) \end{aligned} \quad (2.54)$$

where  $\hat{p} = -i\hbar\vec{\nabla}$  is the momentum operator.

ii) Use the fact that  $u_{n\vec{k}_0}(\vec{r})$  are a complete orthonormal set, see (2.19) and (2.2)

$$u_{n\vec{k}}(\vec{r}) = \sum_{n'} C_{nn'}(\vec{k}-\vec{k}_0) u_{n'\vec{k}_0}(\vec{r}) \quad (2.55)$$

For what concerns the  $\vec{k}-\vec{k}_0$  dependence of the coefficients  $C_{nn'}$ , it is enough to assume  $u_{n\vec{k}}$  to be analytical. We thus take (2.54) and project it on  $u_{n\vec{k}_0}$ . More explicitly:

$$\begin{aligned} \varepsilon_n(\vec{k}) e^{i\vec{k}_0 \cdot \vec{r}} \sum_{n'} C_{nn'}(\vec{k}-\vec{k}_0) u_{n'\vec{k}_0}(\vec{r}) \\ = \frac{\hbar^2}{2m} |\vec{k}-\vec{k}_0|^2 + \frac{\hbar}{m} (\vec{k}-\vec{k}_0) \cdot \hat{p} + \hat{h} \Big| e^{i\vec{k}_0 \cdot \vec{r}} \sum_{n'} C_{nn'}(\vec{k}-\vec{k}_0) u_{n'\vec{k}_0}(\vec{r}) \end{aligned}$$

we multiply by  $e^{-i\vec{k}_0 \cdot \vec{r}} u_{n\vec{k}_0}^*(\vec{r})$  and integrate over a unit cell:

$$\begin{aligned} \varepsilon_n(\vec{k}) C_{nn}(\vec{k}-\vec{k}_0) = \quad (2.56) \\ = \left( \frac{\hbar^2}{2m} |\vec{k}-\vec{k}_0|^2 + \varepsilon_n(\vec{k}_0) \right) C_{nn}(\vec{k}-\vec{k}_0) + \sum_{n' \neq n} \frac{\hbar}{m} (\vec{k}-\vec{k}_0) \cdot \vec{p}_{nn'} C_{nn'}(\vec{k}-\vec{k}_0) \end{aligned}$$

where  $\vec{p}_{nn'} \equiv \frac{1}{V_{\text{cell}}} \int_{V_{\text{cell}}} d\vec{r} u_{n\vec{k}_0}^*(\vec{r}) \hat{p} e^{i\vec{k}_0 \cdot \vec{r}} u_{n'\vec{k}_0}(\vec{r})$ . In other terms

one obtains the secular problem:

$$\sum_{n'} \left[ \left( \varepsilon_n(\vec{k}) - \varepsilon_n(\vec{k}_0) - \frac{\hbar^2}{2m} |\vec{k}-\vec{k}_0|^2 \right) \delta_{nn'} + \frac{\hbar}{m} (\vec{k}-\vec{k}_0) \cdot \vec{p}_{nn'} \right] C_{nn'}(\vec{k}-\vec{k}_0) = 0,$$

that can be solved treating  $\frac{\hbar}{m} (\vec{k}-\vec{k}_0) \cdot \vec{p}_{nn'}$  as a perturbation.

For example:  $\vec{k}_0 = \Gamma$  point and ionic potential with inversion symmetry

$$V(\vec{r}) = V(-\vec{r}).$$

$$\varepsilon_n(\vec{k}) = \varepsilon_n(\vec{0}) + \frac{\hbar^2}{2m} \left( k^2 + \frac{2}{m} \sum_{n' \neq n} \frac{(\vec{k} \cdot \vec{p}_{nn'}) (\vec{k} \cdot \vec{p}_{n'n})}{\varepsilon_n(\vec{0}) - \varepsilon_{n'}(\vec{0})} \right) \quad (2.57)$$

since  $\int d\vec{r} u_{n\vec{0}}^*(\vec{r}) \hat{p} u_{n\vec{0}}(\vec{r}) = 0$  for a system with inversion symmetry.

It is thus convenient to define the effective mass tensor for the band  $n$

$$\left( \frac{1}{m^*(n)} \right)_{\alpha\alpha'} \equiv \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon_n(\vec{k})}{\partial k_\alpha \partial k_{\alpha'}} = \frac{1}{m} \left( \delta_{\alpha\alpha'} + \frac{2}{m} \sum_{n' \neq n} \frac{p_{\alpha,nn'} p_{\alpha',n'n}}{\varepsilon_n(\vec{0}) - \varepsilon_{n'}(\vec{0})} \right), \quad (2.58)$$

such that 
$$\varepsilon_n(\vec{k}) = \varepsilon_n(\vec{0}) + \frac{\hbar^2}{2} \sum_{\alpha\alpha'} \left( \frac{1}{m(n)} \right)_{\alpha\alpha'} k_\alpha k_{\alpha'} \quad (2.59)$$

- If  $m^*$  is diagonal and isotropic, one obtains the same dispersion as for free particles but with modified mass.

- The effective mass can be very different from  $m$  and even become negative, e.g. by maxima of  $\varepsilon_n$ . Natural interpretation in terms of holes.

Example: conduction band edge at the  $\Gamma$ -point. (GeAs, InSb)

Set  $n=c$  for the lowest conduction band, with the Bloch factor ( $\equiv$  with the Bloch function at  $\vec{k}=0$ )  $u_{c\vec{k}=0}(\vec{r}) \equiv \langle \vec{r} | S \rangle$  arising from the  $s$  anti-bonding orbital.

This state is strongly coupled to  $p$  anti-bonding  $|n'\rangle = |X_c\rangle, |Y_c\rangle, |Z_c\rangle$  and to bonding (valence band)  $p$  states  $|n'\rangle = |X_v\rangle, |Y_v\rangle, |Z_v\rangle$ .

To lowest order one finds:

$$\varepsilon_c(\vec{k}) = \varepsilon_c(\vec{0}) + \frac{\hbar^2}{2m} \left( k^2 + \frac{2}{m} \sum_{n'} \frac{|\langle S | \vec{k} \cdot \hat{p} | n' \rangle|^2}{\varepsilon_c(\vec{0}) - \varepsilon_{n'}(\vec{0})} \right)$$

For a cubic lattice it holds  $\langle S | \hat{p}_x | X_{n'} \rangle = \langle S | \hat{p}_y | Y_{n'} \rangle = \langle S | \hat{p}_z | Z_{n'} \rangle \equiv p_{n'}$   
 on the other hand  $\langle S | \hat{p}_i | J \rangle = 0$  if  $i \neq J$ . It follows that

$$\frac{2}{m} \sum_{n'} \frac{|\langle S | \vec{k} \cdot \hat{p} | n' \rangle|^2}{\varepsilon_c(\vec{0}) - \varepsilon_{n'}(\vec{0})} = \frac{2k^2}{m} \sum_{n'} \frac{p_{n'}^2}{\varepsilon_c(\vec{0}) - \varepsilon_{n'}(\vec{0})} \quad n' = C, X, Y, Z$$

Electrons behave as free electrons but with an effective mass  $m^*$ :

$$\frac{m}{m^*} = 1 + \frac{2}{m} \sum_{n'} \frac{p_{n'}^2}{\varepsilon_c(\vec{0}) - \varepsilon_{n'}(\vec{0})} \quad (2.60)$$

For example:

$$\frac{m^*}{m} = 0.067 \quad \text{GaAs} \quad \varepsilon_{\text{gap}} = 1.52 \text{ eV}$$

$$\frac{m^*}{m} = 0.0135 \quad \text{InSb} \quad \varepsilon_{\text{gap}} = 0.25 \text{ eV}$$

A thumb rule can be given:  $m_c^* \propto \frac{m}{1 + \frac{20 \text{ eV}}{\varepsilon_{\text{gap}}}}$

Example: conduction band edge of indirect gap semicond. (ex. Ge, Si)

The minimum of the conduction band along the  $\Delta$  axis. This implies, asymmetries of the  $p$  matrix elements  $\perp$  or  $\parallel$  to  $\vec{\Delta}$  consequently one distinguishes  $m_{\perp}^*$  and  $m_{\parallel}^*$ .

- One speaks about "heavy" or "light" holes when referring to the valence  $p$ -bands of semiconductors due to the different curvature of the bands.

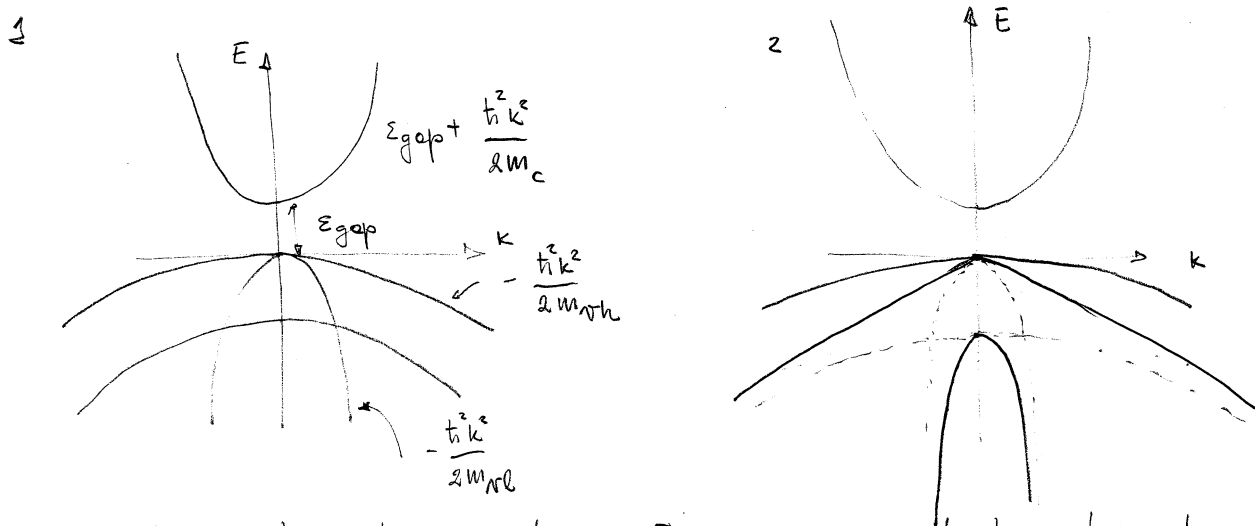
- Spin-orbit coupling (SOC) plays a crucial role in the physics of semiconductors. SOC is a relativistic effect. It occurs since the electron "moves" around the positively charged nucleus at relativistic speeds and the electric field of the nucleus Lorentz-transforms to a magnetic field seen by the electrons

$$\vec{B} = -\frac{1}{2} \frac{(\vec{r} \times \vec{E})/c^2}{\sqrt{1 - \frac{v^2}{c^2}}} \approx -\frac{1}{2} \frac{\vec{r} \times \vec{E}}{c^2}$$

E.g. for Hydrogen in its ground state  $v \approx \alpha c = \frac{1}{137} c \Rightarrow B \sim 12T$  for an orbit with radius  $r_0 \sim 0.5 \text{ \AA}$ . In semiconductors it mostly affects the valence bands since they are associated to atomic levels closest to the nucleus. Moreover SOC is larger the heavier the nucleus since there is a larger E-field. Indeed  $\text{SOC} \propto Z_{\text{at}}^4$ .

Effects on the band structure (for example of GeAs)

1. The SOC splits the degenerate 2 heavy holes and 2 light-holes p-valence bands at the  $\Gamma$  point
2. Split away heavy hole band mixes with the light hole.



Since most transport and optical properties of semiconductors depend just on the states close to the band edges, free particle models with effective mass tensors are mostly applied.



## CHAPTER 3 : LATTICE DYNAMICS

So far we have treated the ions as fixed at the positions  $\{\vec{R}_{0\alpha}\}$  of the underlying lattice. In this chapter we study the basic properties of ionic vibrations.

Under the assumption that the ions perform small oscillations about their equilibrium positions, the set of coupled equations for the interacting ions can be diagonalized, yielding the so called normal modes of vibrations.

We shall see that, even for the classical case of the normal modes of a guitar string, one can represent each normal mode as a harmonic oscillator with a given dispersion relation  $\omega_{\vec{k}}(\vec{k})$ .

The quantized vibrations are denoted phonons, a name pointing at the connection between sound waves and lattice vibration.

- Phonons are analogous to photons, being the latter quanta of electromagnetic waves. With photons they share also the polarization index.
- As Bloch electrons are characterized by the energy dispersion  $\varepsilon_n(\vec{k})$ , with the vector  $\vec{k}$  restricted to the 1BZ, also for phonons  $\vec{k} \in 1BZ$  of the underlying lattice.
- Phonons play a fundamental role in our understanding of sound, specific heat, elasticity and electrical resistivity of solids. Moreover, the electron-phonon coupling is at the origin of conventional superconductivity.

### 3.1 Harmonic approximation, dynamical matrix and normal coordinates

According to the Born-Oppenheimer approximation we have already obtained, for the ionic dynamics the equation:

$$\left[ \hat{T}_{\text{ion}} + \varepsilon_{el, \kappa}(\{\vec{R}_\alpha\}) \right] \chi_{k,m} = E_{k,m} \chi_{k,m} \quad (1.10a)$$

where  $\varepsilon_{el, \kappa}(\{\vec{R}_\alpha\})$  is the energy of the electronic configuration  $\kappa$  and depends on the ionic positions  $\{\vec{R}_\alpha\}$ . Since for the ionic dynamics this represents an effective potential, we introduce  $V_{\text{eff}}(\{\vec{R}_\alpha\}) = \varepsilon_{el, \kappa}(\{\vec{R}_\alpha\})$ , neglecting for a moment the electronic index  $\kappa$ .

#### • Classical analysis

Let us consider a system of  $N$  atoms in equilibrium at position  $\{\vec{R}_\alpha^0\}$ . Small deviation from the equilibrium (the absolute minimum of  $V_{\text{eff}}(\{\vec{R}_\alpha\})$ ) can be described with a Taylor expansion of the potential

$$V_{\text{eff}}(\{\vec{R}_\alpha\}) = V_{\text{eff}}(\{\vec{R}_\alpha^0\}) + \sum_{\alpha, l} \left. \frac{\partial V_{\text{eff}}}{\partial R_{\alpha, l}} \right|_{\{\vec{R}_\alpha^0\}} \cdot u_{l\alpha} + \frac{1}{2} \sum_{\substack{\alpha, \beta \\ l, m}} \left. \frac{\partial^2 V_{\text{eff}}}{\partial R_{\alpha, l} \partial R_{\beta, m}} \right|_{\{\vec{R}_\alpha^0\}} u_{l\alpha} u_{m\beta} \quad (3.1)$$

where:  $\vec{R}_\alpha = \vec{R}_\alpha^0 + \vec{u}_\alpha$ . The harmonic approximation consists in stopping the Taylor expansion of the effective potential to the second order. Since  $\{\vec{R}_\alpha^0\}$  is an absolute minimum for  $V_{\text{eff}}$ , the linear in Eq.(3.1) vanishes exactly. The coefficients of the second order term

$$\Phi_{\alpha l, \beta m} = \left. \frac{\partial^2 V_{\text{eff}}}{\partial R_{\alpha l} \partial R_{\beta m}} \right|_{\{\vec{R}_\alpha^0\}} \quad (3.2)$$

are a positive definite, symmetric matrix of size  $dN \times dN$

where  $N$  is the number of atoms in the system and  $d$  the number of possible independent vibration directions for each atom.

- the symmetry of the matrix  $\Phi$  follows from the invariance of the derivative under site exchange
- the positivity of  $\Phi$  stems instead from the assumption that  $V_{\text{eff}}(\{\vec{R}_\alpha\})$  is an absolute minimum. If just one of the eigenvalues of  $\Phi$  would be negative there would be a direction (the corresponding eigenvector) in the space of deformations  $\{\vec{u}_\alpha\}$  along which  $V_{\text{eff}}$  would decrease, in contradiction with the assumptions.

The Hamilton function associated to the operators in (2.10a) reads, in the harmonic approximation:

$$H_{\text{harm}} = \sum_{\alpha l} \frac{p_{\alpha l}^2}{2M_\alpha} + \sum_{\substack{\alpha\beta \\ l,m}} \frac{1}{2} u_{\alpha l} \Phi_{\alpha l \beta m} u_{\beta m} \quad (3.3)$$

It is useful to introduce the new variables  $\tilde{u}_{\alpha l} = \sqrt{M_\alpha} u_{\alpha l}$ ,  $\tilde{p}_{\alpha l} = \frac{1}{\sqrt{M_\alpha}} p_{\alpha l}$

such that

$$H_{\text{harm}} = \frac{1}{2} \tilde{\mathbf{p}}^t \cdot \tilde{\mathbf{p}} + \tilde{\mathbf{u}}^t \cdot \underline{\underline{\mathbf{D}}} \cdot \tilde{\mathbf{u}} \quad (3.4)$$

where  $t$  in the apex represents the transpose and

$$(\underline{\underline{\mathbf{D}}})_{\alpha l \beta m} = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{\alpha l \beta m} \quad (3.5)$$

is the symmetric and positive definite dynamical matrix.

$\Delta$  is diagonalized by an orthogonal transformation

$$\underline{\underline{C}} \cdot \underline{\underline{\Delta}} \underline{\underline{C}}^T = \underline{\underline{\Omega}} = \begin{pmatrix} \omega_1^2 & & & 0 \\ & \ddots & & \\ & & 0 & \\ & & & \omega_{Nd}^2 \end{pmatrix} \quad (3.6)$$

Such that  $\underline{\underline{C}} \underline{\underline{C}}^T = \underline{\underline{C}}^T \underline{\underline{C}} = \underline{\underline{1}}$ . By the variable transformation

$$\underline{\underline{\bar{p}}} = \underline{\underline{C}} \underline{\underline{\bar{p}}}, \quad \underline{\underline{\bar{u}}} = \underline{\underline{C}} \underline{\underline{\tilde{u}}} \quad (3.7)$$

one obtains a new set of canonically conjugated variables in which the ions hamilton function reads

$$H_{\text{ham}} = \frac{1}{2} (\underline{\underline{\bar{p}}}^t \cdot \underline{\underline{\bar{p}}} + \underline{\underline{\bar{u}}}^t \cdot \underline{\underline{\Omega}} \cdot \underline{\underline{\bar{u}}}) = \frac{1}{2} \sum_{i=1}^{Nd} (\bar{p}_i^2 + \omega_i^2 \bar{u}_i^2) \quad (3.8)$$

That is, the Hamilton function of a set of independent harmonic oscillators with frequencies  $\omega_i$  and normal coordinate  $\bar{u}_i = \sum_{\alpha l} \frac{1}{\sqrt{M_\alpha}} c_{i,\alpha l} u_{\alpha l}$