TB

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Tight-Binding formalism

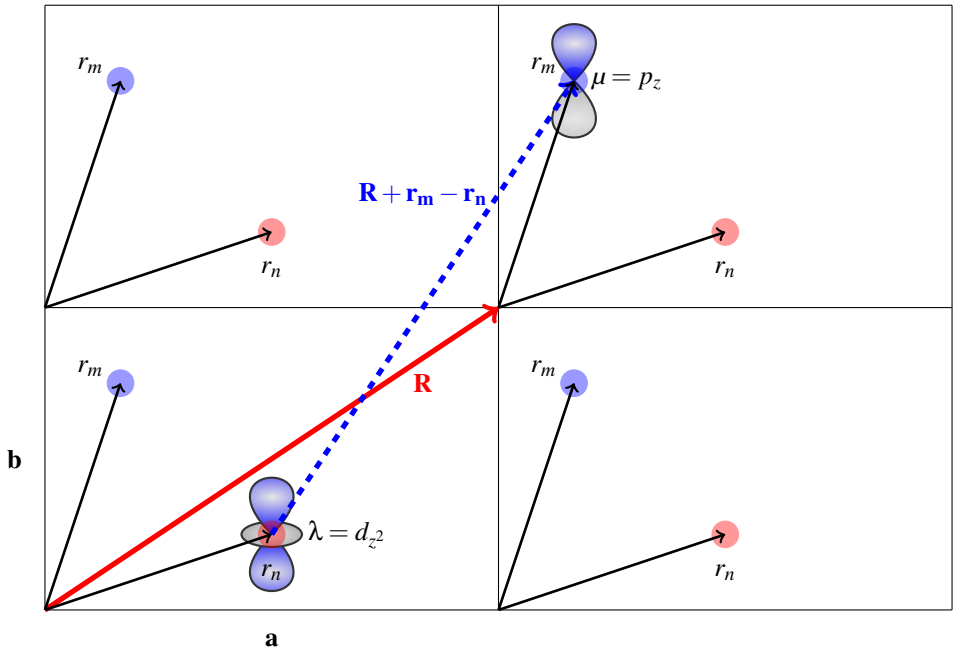

Figure 1: *geometry of the unit-cell and its periodicity*

1 notations

1.1 Geometry

Born von Karman (BVK) conditions are used. BVK: $L_a = N_a \times a,\ L_b = N_b \times b,\ L_c = N_c \times c$.
$N = N_a \times N_b \times N_c$: Total number of cells.
Periodicity along **a**, **b** et **c**. volume of the unit-cell $\omega = \mathbf{a}.(\mathbf{b} \times \mathbf{c})$
$\mathbf{R} = n_a\mathbf{a} + n_b\mathbf{b} + n_c\mathbf{c}$.
Reciprocal vectors $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$. volume of Brillouin zone $\omega^* = \frac{2\Pi^3}{\omega}$
$\mathbf{g} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$.
scalar product: $\mathbf{R}.\mathbf{g} = 2\pi(n_a h + n_b k + n_c l)$
If $\mathbf{R} \in$ Bravais lattice and $\mathbf{g} \in$ Reciprocal lattice then $\mathbf{R}.\mathbf{g} = 2\pi n \Rightarrow e^{i\mathbf{R}.\mathbf{g}} = 1$
n_{at}: number of atoms in the unit-cell.
$\mathbf{R}, \mathbf{R}'$: periodic vectors of the Bravais lattice
$\mathbf{r}_n, \mathbf{r}_m$: position of the atoms in the unit-cell $n = 1 \cdots, n_{at}$.

1.2 Orbitals

λ,μ,ν: orbitals $|s\rangle,|p_x\rangle,|p_y\rangle,|p_z\rangle,|d_{xy}\rangle,|d_{yz}\rangle,|d_{zx}\rangle,|d_{x^2-y^2}\rangle,|d_{3z^2-r^2}\rangle$. l orbitals.
Atomic wave functions of orbital λ centered on site (R,n) .

$$\langle \mathbf{r}|R,n,\lambda\rangle = \phi_\lambda(\mathbf{r}-\mathbf{R}-\mathbf{r}_n)$$

1.3 Hamiltonian

$\hat{H}$ Hamiltonian operator.
$\boldsymbol{H}$ Hamiltonian matrix:

$$\boldsymbol{H}^{\lambda,\mu}_{R,n,R',m} = \langle R,n,\lambda|\hat{H}|R',m,\mu\rangle \quad ; \quad \boldsymbol{S}^{\lambda,\mu}_{R,n,R',m} = \langle Rn,\lambda|\hat{I}|R'm,\mu\rangle$$

2 Bloch Theorem

2.1 notations

$|\alpha,\mathbf{k}\rangle$ Bloch function of index α ($\alpha = 1,\cdots,n_{\text{at}}\times l$) and wave-vector $\mathbf{k}\in$ 1BZ
$\mathbf{k} = k_a\mathbf{a}^* + k_b\mathbf{b}^* + k_c\mathbf{c}^* \in$ 1BZ $\quad k_{i=a,b,c} = (2\times n_i - N_i - 1)/(2N_i) \quad (n_i = 1,\cdots,N_i)$.
We recall some relations:

$$\frac{1}{N}\sum_{\mathbf{R}} e^{i\mathbf{k}.\mathbf{R}} = \delta_{\mathbf{k}} \quad ; \quad \frac{1}{N^2}\sum_{\mathbf{R},\mathbf{R}'} e^{i(\mathbf{k}-\mathbf{k}').(\mathbf{R}-\mathbf{R}')} = \delta_{\mathbf{k},\mathbf{k}'}$$

2.2 Bloch Functions

Expansion of wave functions on atomic orbitals

$$|\Psi_\alpha\rangle = \sum_{\mathbf{R},n,\lambda} C^\alpha_{Rn\lambda}|\mathbf{R},n,\lambda\rangle$$

According to Bloch theorem the function solutions of the Shrodinger equations can be labeled by two indices $\alpha,\mathbf{k}$):

$$C^\alpha_{R,n\lambda} = \frac{1}{\sqrt{N}} e^{i\mathbf{k}.\mathbf{R}} e^{i\mathbf{k}.\mathbf{r}_n} C^\alpha_{n\lambda}(\mathbf{k})$$

So:

$$|\alpha,\mathbf{k}\rangle = \sum_{n,\lambda} C^\alpha_{n\lambda}(\mathbf{k}) \frac{e^{i\mathbf{k}.\mathbf{r}_n}}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}.\mathbf{R}}|\mathbf{R},n,\lambda\rangle$$

Introducing a TB basis adapted to periodicity $|n,\lambda,\mathbf{k}\rangle$ one gets:

$$|\alpha,\mathbf{k}\rangle = \sum_{n,\lambda} C^\alpha_{n\lambda}(\mathbf{k})|n,\lambda,\mathbf{k}\rangle \quad \text{with} \quad |n,\lambda,\mathbf{k}\rangle = \frac{e^{i\mathbf{k}.\mathbf{r}_n}}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}.\mathbf{R}}|\mathbf{R},n,\lambda\rangle$$

The closure relation reads

$$\sum_{\alpha,\mathbf{k}} |\alpha,\mathbf{k}\rangle\langle\alpha,\mathbf{k}| = \hat{I}$$

And the Hamiltonian:

$$\sum_{\alpha,\mathbf{k}} |\alpha,\mathbf{k}\rangle\varepsilon_\alpha(\mathbf{k})\langle\alpha,\mathbf{k}| = \hat{H}$$

If the Bloch coefficient $C^\alpha_{i\lambda}(\mathbf{k})$ are normalized correctly:

$$\langle\alpha,\mathbf{k}|\beta,\mathbf{k}\rangle = \sum_{n\lambda,m\mu} (C^\alpha_{n\lambda}(\mathbf{k}))^\star S^{\lambda,\mu}_{a,b}(\mathbf{k}) C^\beta_{m\mu}(\mathbf{k}) = \delta_{\alpha\beta} \quad \forall\mathbf{k}$$

3 Schrödinger Equation

Schrödinger Equation:

$$\hat{H}|\alpha,\mathbf{k}\rangle = \varepsilon_\alpha(\mathbf{k})|\alpha,\mathbf{k}\rangle$$

Generalized eigenvalue problem:.

$$H(\mathbf{k})C^\alpha(\mathbf{k}) = \varepsilon_\alpha(\mathbf{k})S(\mathbf{k})C^\alpha(\mathbf{k})$$
$$H^{\lambda,\mu}_{n,m}(\mathbf{k}) = \langle n,\lambda,\mathbf{k}|\hat{H}|m,\mu,\mathbf{k}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}.(\mathbf{R}+\mathbf{r}_m-\mathbf{r}_n)}\langle 0,n,\lambda|\hat{H}|\mathbf{R},m,\mu\rangle$$
$$S^{\lambda,\mu}_{n,m}(\mathbf{k}) = \langle n,\lambda,\mathbf{k}|\hat{I}|m,\mu,\mathbf{k}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}.(\mathbf{R}+\mathbf{r}_m-\mathbf{r}_n)}\langle 0,n,\lambda|\hat{I}|\mathbf{R},m,\mu\rangle$$

$$\begin{pmatrix} (\hat{H}_{11}) & \cdots & (\hat{H}_{1m}) & \cdots & (\hat{H}_{1n_{\text{at}}}) \\ \vdots & \ddots & & & \\ (\hat{H}_{n1}) & \cdots & (\hat{H}_{nm}) & \cdots & \\ \vdots & & & \ddots & \\ (\hat{H}_{n_{\text{at}}1}) & & & & (\hat{H}_{n_{\text{at}},n_{\text{at}}}) \end{pmatrix} \begin{pmatrix} (C^\alpha_1) \\ \vdots \\ (C^\alpha_a) \\ \vdots \\ (C^\alpha_{n_a}) \end{pmatrix} = \varepsilon_\alpha(\mathbf{k}) \begin{pmatrix} (S_{11}) & \cdots & (S_{1b}) & \cdots & (S_{1n_a}) \\ \vdots & \ddots & & & \\ (S_{a1}) & \cdots & (S_{ab}) & \cdots & \\ \vdots & & & \ddots & \\ (S_{n_a1}) & & & & (S_{n_an_a}) \end{pmatrix} \begin{pmatrix} (C^\alpha_1) \\ \vdots \\ (C^\alpha_a) \\ \vdots \\ (C^\alpha_{n_a}) \end{pmatrix}$$

(H_{nm}) matrice $l \times l$ with $\left(H_{nm}\right)_{\lambda,\mu} = H^{\lambda\mu}_{nm}(\mathbf{k})$. $H(\mathbf{k})$ matrix of size $(ln_{\text{at}}) \times (ln_{\text{at}})$.
The wave-vector should be normalized:

$$\sum_{n\lambda,m\mu} C^{\alpha\star}_{n\lambda}(\mathbf{k})S^{\lambda,\mu}_{n,m}(\mathbf{k})C^\beta_{m\mu}(\mathbf{k}) = \delta_{\alpha\beta} \quad \forall\mathbf{k}$$

In matrix form:

$${}^tC^{\alpha\star}(\mathbf{k})\mathcal{S}(\mathbf{k})C^\beta(\mathbf{k}) = \delta_{\alpha\beta} \quad \forall\mathbf{k}$$

Setting $\widetilde{C}^\alpha = \mathcal{S}(\mathbf{k})C^\alpha(\mathbf{k})$, one gets:

$${}^tC^{\alpha\star}(\mathbf{k})\widetilde{C}^\beta(\mathbf{k}) = \delta_{\alpha\beta} \quad \forall\mathbf{k}$$

4 Remarks on non-orthogonal basis in Quantum Mechanics

4.1 Dual basis

Let's ignore λ and $\mathbf{k}$ indices. One consider a non-orthogonal basis $|a\rangle$. One defines its dual $|\tilde{a}\rangle$

$$|\tilde{a}\rangle = \sum_b (S^{-1})_{a,b}|b\rangle$$

the following orthogonality relation holds

$$\langle\tilde{b}|a\rangle = \delta_{a,b}$$

And two closure relations:

$$\sum_a |\tilde{a}\rangle\langle a| = \hat{I} \quad ; \quad \sum_a |a\rangle\langle\tilde{a}| = \hat{I}$$

The eigenstates $|\alpha\rangle$ can be decomposed on the $|a\rangle$ basis:

$$|\alpha\rangle = \sum_a C^\alpha_a|a\rangle$$

And the coefficient C^α_a are obtained:

$$C^\alpha_a = \langle\tilde{a}|\alpha\rangle$$

4.2 Matrix expression of an operator in a non-orthogonal basis

Let $\hat{A}$ be an operator. One can define 4 different matrices: A, $\tilde{A}$, $\tilde{A}'$, and $\bar{A}$:

$$A_{ab} = \langle a|\hat{A}|b\rangle \quad ; \quad \tilde{A}_{ab} = \langle \tilde{a}|\hat{A}|b\rangle \quad ; \quad \tilde{A}'_{ab} = \langle a|\hat{A}|\tilde{b}\rangle \quad ; \quad \bar{A}_{ab} = \langle \tilde{a}|\hat{A}|\tilde{b}\rangle$$

One then easily shows that

$$\hat{A}|b\rangle = \sum_a \tilde{A}_{ab}|a\rangle \quad ; \quad \hat{A}|\tilde{b}\rangle = \sum_a \tilde{A}'_{ab}|\tilde{a}\rangle$$

and

$$\hat{A} = \sum_{ab} |a\rangle \bar{A}_{ab} \langle b|$$

The following matrix relations can be easily derived:

$$A = S\bar{A}S \quad ; \quad \bar{A} = S^{-1}AS^{-1} \quad ; \quad \tilde{A} = S^{-1}A = \bar{A}S \quad ; \quad \tilde{A}' = AS^{-1} = S\bar{A}$$

A and $\bar{A}$ are Hermitian contrary to $\tilde{A}$ et $\tilde{A}'$. However $\tilde{A}$ et $\tilde{A}'$ are the matrix representation of the linear operator in basis $|a\rangle$ and $|\tilde{a}\rangle$ respectively. Hence, they have the property of composition of operators:

$$\widetilde{AB} = \tilde{A}\tilde{B} \quad \text{and} \quad \widetilde{AB}' = \tilde{A}'\tilde{B}'$$

Let us also note that the trace of the operator $\hat{A}$ is obtained from the trace of $\tilde{A}$ or $\tilde{A}'$ matrix:

$$\mathrm{Tr}(\hat{A}) = \mathrm{Tr}(\tilde{A}) = \mathrm{Tr}(\tilde{A}') = \sum_a \tilde{A}_{aa} = \sum_a \tilde{A}'_{aa}$$

However the trace of the operator is NOT the trace of A or $\bar{A}$

$$\mathrm{Tr}(\hat{A}) = \mathrm{Tr}(S^{-1}A) = \mathrm{Tr}(AS^{-1}) = \mathrm{Tr}(\bar{A}S) = \mathrm{Tr}(S\bar{A})$$

Let us consider an operator of the form $\hat{A} = F(\hat{H})$[1]. $\hat{H}$ can be diagonalized in eigen-state basis $|\alpha\rangle$:

$$\hat{A} = \sum_\alpha |\alpha\rangle F(\varepsilon_\alpha) \langle\alpha|$$

Using the expression of $|\alpha\rangle$ in the $|a\rangle$ basis:

$$|\alpha\rangle = \sum_a C_a^\alpha |a\rangle$$

we get

$$\hat{A} = \sum_{ab} |a\rangle \bar{A}_{ab} \langle b| \quad \text{with} \quad \bar{A}_{ab} = \sum_\alpha F(\varepsilon_\alpha) C_a^\alpha (C_b^\alpha)^\star$$

Let's consider two important operator, the density operator $\hat{\rho} = f(\hat{H})$ and the Green function operator $\hat{G}(z) = (z\hat{I} - \hat{H})^{-1}$:

$$\bar{\rho}_{ab} = \sum_\alpha f(\varepsilon_\alpha) C_a^\alpha (C_b^\alpha)^\star$$

And for $\hat{G}(z)$ using the identity $(z\hat{I} - \hat{H})\hat{G}(z) = \hat{I}$ we have:

$$\langle a|(z\hat{I} - \hat{H}) \sum_b |b\rangle \langle \tilde{b}|\hat{G}(z)|\tilde{c}\rangle = \delta_{a,c}$$

Hence we have the following matrix relation

$$(zS - H)\bar{G}(z) = Id$$

[1] if F is the Fermi function then $\hat{A}$ the density operator $\hat{\rho}$, or if $F(x) = 1/(z-x)$ then $\hat{A}$ is the Green function $G(z)$, or if Dirac $F(x) = \delta(E-x)$ then we get the density of states

4.3 Tensorial notation

The tensorial can be very useful is some cases:

$$|\phi_a\rangle = |a\rangle \quad ; \quad |\phi^a\rangle = |\tilde{a}\rangle$$

we then have:

$$A_{ab} = \langle\phi_a|\hat{A}|\phi_b\rangle = A_{ab} \quad ; \quad A^{ab} = \langle\phi^a|\hat{A}|\phi^b\rangle = \bar{A}_{ab} \quad ; \quad A^a{}_b = \langle\phi^a|\hat{A}|\phi_b\rangle = \tilde{A}_{ab} \quad ; \quad A_a{}^b = \langle\phi_a|\hat{A}|\phi^b\rangle = (GAb\ _a)^\star$$

And for the overlaps:

$$I_{ab} = \langle\phi_a|\hat{I}|\phi_b\rangle = S_{ab} \quad ; \quad I^{ab} = \langle\phi^a|\hat{I}|\phi^b\rangle = (S^{-1})_{ab} \quad ; \quad I^a{}_b = \langle\phi^a|\hat{I}|\phi_b\rangle = \delta^a_b \quad ; \quad I_a{}^b = \langle\phi_a|\hat{I}|\phi^b\rangle = \delta^b_a$$

With Einstein convention the closure relations reads:

$$|\phi^a\rangle\langle\phi_a| = \hat{I} \quad ; \quad |\phi_a\rangle\langle\phi^a| = \hat{I}$$

The trace of operator $\hat{A}$ reads:

$$\mathrm{Tr}(\hat{A}) = \langle\phi^a|\hat{A}|\phi_a\rangle = A^a{}_a = \langle\phi_a|\hat{A}|\phi^a\rangle = A_a{}^a$$

The trace of the product of two operators $\hat{A}.\hat{B}$

$$\mathrm{Tr}(\hat{A}.\hat{B}) = \langle\phi_a|\hat{A}.\hat{B}|\phi^a\rangle = \langle\phi_a|\hat{A}|\phi_b\rangle\langle\phi^b|\hat{B}|\phi^a\rangle = A_{ab}B^{ba}$$

5 Definition of local quantities in a non-orthogonal basis

5.1 Definition of operators

Let's consider the density operator $\hat{\rho} = f(\hat{H})$ [2] and the density operator $\hat{D}(E) = \delta(E - \hat{H})$:

$$\hat{\rho} = \sum_\alpha |\alpha\rangle f_\alpha \langle\alpha| \quad ; \quad \hat{D}(E) = \sum_\alpha |\alpha\rangle\delta(E - \varepsilon_\alpha)\langle\alpha|)$$

The trace of $\hat{\rho}$ is equal to the number of electrons:

$$\mathrm{Tr}(\hat{\rho}) = N_e = \int_{-\infty}^{+\infty} f(E)D(E)dE = \sum_\alpha f_\alpha)$$

while the trace of $\hat{D}(E)$ is the density of states:

$$D(E) = \mathrm{Tr}(\hat{D}(E)) = \sum_\alpha \delta(E - \varepsilon_\alpha)$$

Let's write the trace of the operator with the TB coefficients $|\alpha\rangle = \sum_a C^\alpha_a |a\rangle$.

$$\mathrm{Tr}(\hat{\rho}) = \sum_a \sum_\alpha \langle\tilde{a}|\alpha\rangle f_\alpha \langle\alpha|a\rangle = \left[\sum_{ab}\left(\sum_\alpha f_\alpha C^\alpha_a (C^\alpha_b)^\star\right) S_{a,b}\right] = \mathrm{Tr}\left(\bar{\rho}S\right)$$

One recognize the general result obtained previously for the trace of an operator applied to $\hat{\rho} = f(\hat{H})$ and its matricial expression $\bar{\rho}$

$$\bar{\rho}_{ab} = \sum_\alpha f_\alpha C^\alpha_a (C^\alpha_b)^\star$$

[2] $f(x) = \frac{1}{1+\exp(\frac{x-E_f}{k_B T})}$

5.2 Local decomposition of density operator

One notes that the previous sum can be decomposed as a sum of partial sums

$$\mathrm{Tr}(\hat{\rho}) = \sum_a \rho_a$$

with:

$$\rho_a = \frac{1}{2}\left[\sum_\alpha f_\alpha \left(\sum_b C_a^{\alpha^\star} S_{a,b} C_b^\alpha + C_a^\alpha S_{a,b}^\star C_b^{\alpha\star}\right)\right] = \frac{1}{2}\left[\langle \tilde{a}|\hat{\rho}|a\rangle + \langle a|\hat{\rho}|\tilde{a}\rangle\right]$$

Or:

$$\rho_a = \Re\left[\sum_\alpha f_\alpha \sum_b C_a^{\alpha^\star} S_{a,b} C_b^\alpha\right] = \Re\left[\bar{\rho} S\right]_{a,a}$$

Setting $\widetilde{C}_a^\alpha = \sum_b S_{ab} C_b^\alpha$ one finally obtains:

$$\rho_a = \Re\left(\sum_\alpha f_\alpha C_a^{\alpha\star} \widetilde{C}_a^\alpha\right)$$

In matrix form:

$$\widetilde{C}^\alpha = \mathcal{S} C^\alpha$$

And the trace of $\hat{\rho}$ gives the total number of electrons:

$$\mathrm{Tr}(\hat{\rho}) = \sum_\alpha f_\alpha \underbrace{{}^t C^{\alpha\star} \widetilde{C}^\alpha}_{=1} = N_e$$

5.3 Average operator

5.3.1 Average of any operator $\hat{A}$

The average of $\hat{A}$ reads:

$$\langle \hat{A}\rangle = \mathrm{Tr}(\hat{\rho}.\hat{A}) = \sum_\alpha f_\alpha \langle \alpha|\hat{A}|\alpha\rangle$$

Writing the Bloch $|\alpha\rangle$ in the basis $|a\rangle$ one gets:

$$\langle \hat{A}\rangle = \sum_{ab}\left(\sum_\alpha f_\alpha C_a^\alpha (C_b^\alpha)^\star\right)\langle b|\hat{A}|a\rangle$$

$\langle \hat{A}\rangle$ can be written in matrix form:

$$\langle \hat{A}\rangle = \mathrm{Tr}\left[\bar{\rho} A\right]$$

with as usual:

$$\bar{\rho}_{ab} = \sum_\alpha f_\alpha C_a^\alpha (C_b^\alpha)^\star$$

Note that the summation can be re-organized in a different manner:

$$\langle \hat{A}\rangle = \sum_\alpha f_\alpha \, {}^t C^{\alpha\star} A C^\alpha$$

5.4 Average of an operator of the form $\hat{A} = g(\hat{H})$

If $\hat{A} = g(\hat{H})$, using $\hat{H}|\alpha\rangle = \varepsilon_\alpha|\alpha\rangle$ one gets:

$$\langle\hat{A}\rangle = \mathrm{Tr}(\hat{\rho}g(\hat{H})) = \sum_{ab}\left(\sum_\alpha f_\alpha g(\varepsilon_\alpha)C_b^\alpha (C_a^\alpha)^\star\right)S_{a,b}$$

In matrix form:

$$\langle\hat{A}\rangle = \mathrm{Tr}\left[\overline{\rho A}S\right]$$

with:

$$\overline{\rho A}_{ab} = \sum_\alpha f_{E_f}(\varepsilon_\alpha)g(\varepsilon_\alpha)C_a^\alpha (C_b^\alpha)^\star$$

Reorganizing the sum one obtains the "trivial" result:

$$\langle\hat{A}\rangle = \sum_\alpha f_\alpha g(\varepsilon_\alpha)\underbrace{{}^tC^{\alpha\star}\widetilde{C}^\alpha}_{=1} = \sum_\alpha f_\alpha g(\varepsilon_\alpha)$$

One can as-well define the local component

$$A_a = \frac{1}{2}\left[\sum_\alpha f_\alpha g(\varepsilon_\alpha)\left(\sum_b C_a^{\alpha^\star}S_{a,b}C_b^\alpha + \sum_b C_a^\alpha S_{a,b}^\star C_b^{\alpha\star}\right)\right]$$

or

$$A_a = \Re\left[\sum_\alpha f_\alpha g(\varepsilon_\alpha)\sum_b C_a^{\alpha\star}S_{a,b}C_b^\alpha\right]$$

In a more compact form:

$$A_a = \Re\left[\sum_\alpha f_\alpha g(\varepsilon_\alpha)C_a^{\alpha\star}\widetilde{C}_a^\alpha\right] = \frac{1}{2}\left[\langle\tilde{a}|\hat{\rho}.\hat{G}|a\rangle + \langle a|\hat{\rho}.\hat{G}|\tilde{a}\rangle\right]$$

5.4.1 Total energy

In the case of the total energy $\hat{A} = \hat{H}$ so $G(x) = x$

$$E^{tot} = \langle\hat{H}\rangle = \sum_\alpha f_\alpha\varepsilon_\alpha\underbrace{{}^tC^{\alpha\star}\widetilde{C}^\alpha}_{=1} = \sum_\alpha f_\alpha\varepsilon_\alpha$$

Using previous section one can define the local decomposition of the energy:

$$E_a^{tot} = \Re\left[\sum_\alpha f_\alpha\varepsilon_\alpha C_a^{\alpha\star}\widetilde{C}_a^\alpha\right]$$

6 Back to the periodic case, Bloch theorem

6.1 TB basis in "real" space and its dual

$\widetilde{|R,n,\lambda\rangle} = \sum_{R',m,\mu}(S^{-1})^{\lambda,\mu}_{Rn,R'm}|R',m,\mu\rangle$ dual basis verifying the relation $\widetilde{\langle R',m,\mu|}R,n,\lambda\rangle = \delta_{R,R'}\delta_{n,m}\delta_{\lambda,\mu}$

Closure relation: $\sum_{R,n,\lambda}\widetilde{|R,n,\lambda\rangle}\langle R,n,\lambda| = \hat{I}$

$$|\Psi_\alpha\rangle = \sum_{\mathbf{R},n,\lambda}C_{Rn\lambda}^\alpha|\mathbf{R},n,\lambda\rangle$$

TB coefficients: $\widetilde{\langle R,n,\lambda|}\alpha,\mathbf{k}\rangle = C_{R,n,\lambda}^\alpha = \frac{1}{\sqrt{N}}e^{i\mathbf{k}.\mathbf{R}}e^{i\mathbf{k}.\mathbf{r}_n}C_{n\lambda}^\alpha(\mathbf{k})$

6.2 TB Bloch basis and its dual

We recall

$$|n,\lambda,\mathbf{k}\rangle = \frac{e^{i\mathbf{k}.\mathbf{r}_n}}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}.\mathbf{R}} |\mathbf{R},n,\lambda\rangle$$

The dual basis is naturally defined as:

$$\widetilde{|n,\lambda,\mathbf{k}\rangle} = \sum_{m,\mu} (S^{-1}(\mathbf{k}))^{\lambda,\mu}_{n,m} |m,\mu,\mathbf{k}\rangle$$

the orthogonality relation holds: $\widetilde{\langle n,\mu,\mathbf{k}|}m,\lambda,\mathbf{k}\rangle = \delta_{n,m}\delta_{\lambda,\mu}$. As well as the closure relation: $\sum_{n,\lambda,\mathbf{k}} \widetilde{|n,\lambda,\mathbf{k}\rangle}\langle n,\lambda,\mathbf{k}| = \hat{I}$

And the TB coefficients $\widetilde{\langle n,\lambda,\mathbf{k}|}\alpha,\mathbf{k}\rangle = C^{\alpha}_{n,\lambda}(\mathbf{k})$

6.3 Charge and local density

6.3.1 Density operator

The density operator $\hat{\rho}$ and the density of states operator $\hat{D}(E)$ (which trace gives the density of stats):

$$\hat{\rho} = f(\hat{H}) \quad [3] \quad ; \quad \hat{D}(E) = \delta(E-H) \quad ; \quad D(E) = \mathrm{Tr}\hat{D}(E)$$

$$\rho = \sum_{\alpha\mathbf{k}} |\alpha,\mathbf{k}\rangle w_{\mathbf{k}} f_\alpha(\mathbf{k}) \langle\alpha,\mathbf{k}| \quad ; \quad \boldsymbol{D}(E) = \sum_{\alpha\mathbf{k}} |\alpha,\mathbf{k}\rangle w_{\mathbf{k}} \delta(E-\varepsilon_\alpha(\mathbf{k})) \langle\alpha,\mathbf{k}| \quad ; \quad D(E) = \sum_{\alpha\mathbf{k}} w_{\mathbf{k}} \delta(E-\varepsilon_\alpha(\mathbf{k}))$$

$w_{\mathbf{k}}$ is the weight of wave-vector $\mathbf{k}$, in practice the summation over $\mathbf{k}$ is discrete and involves special $\mathbf{k}$ points. The summation is normalized such that:

$$\sum_{\mathbf{k}} w_{\mathbf{k}} = 1 = \frac{\omega}{8\pi^3} \int_{\mathrm{BZ}} d\mathbf{k}$$

By definition the trace of $\hat{\rho}$ is equal to the number of electrons:

$$\mathrm{Tr}(\hat{\rho}) = N_e = \int_{-\infty}^{+\infty} f(E) D(E) dE = \sum_{\alpha}(\mathbf{k}) w_{\mathbf{k}} f_\alpha(\mathbf{k})$$

Let's write the trace of $\hat{\rho}$ using the TB coefficient:

$$\mathrm{Tr}(\hat{\rho}) = \sum_{\alpha\mathbf{k}} w_{\mathbf{k}} \langle\alpha,\mathbf{k}|f_\alpha(\mathbf{k})|\alpha,\mathbf{k}\rangle = \sum_{\mathbf{k}} w_{\mathbf{k}} \left[\sum_{\substack{n\lambda \\ m\mu}} \left(\sum_{\alpha} f_\alpha(\mathbf{k}) C^{\alpha}_{m\mu}(\mathbf{k}) (C^{\alpha}_{n\lambda}(\mathbf{k}))^\star \right) S^{\lambda,\mu}_{n,m}(\mathbf{k}) \right]$$

One recognize the result of the previous section in matricial form of $\hat{\rho} = f(\hat{H})$ in TB basis:

$$\mathrm{Tr}(\hat{\rho}) = \sum_{\mathbf{k}} w_{\mathbf{k}} \mathrm{Tr}\left[\bar{\rho}(\mathbf{k}) S(\mathbf{k})\right]$$

With

$$\bar{\rho}^{\lambda\mu}_{nm}(\mathbf{k}) = \sum_{\alpha} f_\alpha(\mathbf{k}) C^{\alpha}_{n\lambda}(\mathbf{k}) (C^{\alpha}_{m\mu}(\mathbf{k}))^\star$$

[3] $f(x) = \frac{1}{1+\exp(\frac{x-E_f}{k_B T})}$

6.3.2 Local decomposition

One notes that the previous summation can be decomposed in local components:

$$\mathrm{Tr}(\hat{\rho}) = \sum_{n\lambda} \rho_{n\lambda}$$

where $\rho_{n\lambda}$ is the charge on site n and orbital λ:

$$\rho_{n\lambda} = \frac{1}{2}\left[\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k}) \sum_{m\mu} C^{\alpha\star}_{n\lambda}(\mathbf{k}) S^{\lambda,\mu}_{n,m}(\mathbf{k}) C^{\alpha}_{m\mu}(\mathbf{k}) + \sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k}) \sum_{m\mu} C^{\alpha}_{n\lambda}(\mathbf{k}) S^{\lambda,\mu\star}_{n,m}(\mathbf{k}) C^{\alpha\star}_{n\mu}(\mathbf{k})\right]$$

Or:

$$\rho_{n\lambda} = \Re\left[\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k}) \sum_{m\mu} C^{\alpha\star}_{n\lambda}(\mathbf{k}) S^{\lambda,\mu}_{n,m}(\mathbf{k}) C^{\alpha}_{m\mu}(\mathbf{k})\right]$$

Setting $\widetilde{C}^{\alpha}_{n\lambda} = \sum_{m\mu} S^{\lambda\mu}_{nm}(\mathbf{k}) C^{\alpha}_{m\mu}(\mathbf{k})$ One gets

$$\rho_{n,\lambda} = \Re\left(\sum_{\alpha,\mathbf{k}} f_\alpha(\mathbf{k}) w_{\mathbf{k}} C^{\alpha\star}_{n\lambda}(\mathbf{k}) \widetilde{C}^{\alpha}_{n\lambda}(\mathbf{k})\right)$$

Or in matrix form:

$$\widetilde{C}^{\alpha}(\mathbf{k}) = S(\mathbf{k}) C^{\alpha}(\mathbf{k})$$

Hence the trace of the operator $\hat{\rho}$ reads:

$$\mathrm{Tr}(\hat{\rho}) = \sum_{\alpha\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k})^t C^{\alpha\star}(\mathbf{k}) \widetilde{C}^{\alpha}(\mathbf{k}) = N_e$$

6.4 Average operator

6.4.1 Average value of the operator $\hat{A}$

The average of $\hat{A}$ reads:

$$\langle \hat{A} \rangle = \mathrm{Tr}(\hat{\rho}\hat{A}) = \sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k}) \langle \alpha, \mathbf{k} | \boldsymbol{A} | \alpha, \mathbf{k} \rangle$$

Unsing the expansion of the Bloch $|\alpha, \mathbf{k}\rangle$ on the TB basis $|n, \lambda, \mathbf{k}\rangle$ gives:

$$\langle \hat{A} \rangle = \sum_{\substack{n\lambda \\ m\mu}} \left(\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k}) C^{\alpha}_{n\lambda}(\mathbf{k}) (C^{\alpha}_{m\mu}(\mathbf{k}))^\star\right) \langle m\mu, \mathbf{k} | \boldsymbol{A} | n\lambda, \mathbf{k} \rangle$$

$\langle \hat{A} \rangle$ can be written as the trace of a matrix product:

$$\langle \hat{A} \rangle = \sum_{\mathbf{k}} w_{\mathbf{k}} \mathrm{Tr}\left[\bar{\rho}(\mathbf{k}) A(\mathbf{k})\right]$$

With:

$$\bar{\rho}^{\lambda\mu}_{nm}(\mathbf{k}) = \sum_{\alpha} f_\alpha(\mathbf{k}) C^{\alpha}_{n\lambda}(\mathbf{k}) (C^{\alpha}_{m\mu}(\mathbf{k}))^\star$$

Note that the summation can be re-organized in a slightly different way:

$$\langle \hat{A} \rangle = \sum_{\alpha\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k})^t C^{\alpha\star}(\mathbf{k}) A(\mathbf{k}) C^{\alpha}(\mathbf{k})$$

6.4.2 Average of an operator of the form $\hat{A} = g(\hat{H})$

Let's consider $\hat{A} = g(\hat{H})$ then:

$$\langle \hat{A} \rangle = \mathrm{Tr}(\hat{\rho} F(\hat{H})) = \sum_{\mathbf{k}} \sum_{\substack{n\lambda \\ m\mu}} \left(\sum_{\alpha} w_{\mathbf{k}} f_{\alpha}(\mathbf{k}) g(\varepsilon_{\alpha}(\mathbf{k})) C^{\alpha}_{m\mu}(\mathbf{k}) (C^{\alpha}_{n\lambda}(\mathbf{k}))^{\star} \right) S^{\lambda,\mu}_{n,m}(\mathbf{k})$$

In matrix form:

$$\langle \hat{A} \rangle = \sum_{\mathbf{k}} w_{\mathbf{k}} \mathrm{Tr} \left[(\overline{FG})(\mathbf{k}) S(\mathbf{k}) \right]$$

with

$$\overline{FG}^{\lambda\mu}_{nm}(\mathbf{k}) = \sum_{\alpha} f_{\alpha}(\mathbf{k}) g(\varepsilon_{\alpha}(\mathbf{k})) C^{\alpha}_{n\lambda}(\mathbf{k}) (C^{\alpha}_{m\mu}(\mathbf{k}))^{\star}$$

Reorganizing the summation gives:

$$\langle \hat{A} \rangle = \sum_{\alpha\mathbf{k}} w_{\mathbf{k}} f_{\alpha}(\mathbf{k}) g(\varepsilon_{\alpha}(\mathbf{k}))^{t} C^{\alpha\star}(\mathbf{k}) \widetilde{C}^{\alpha}(\mathbf{k})$$

And the local component

$$A_{n\lambda} = \frac{1}{2} \left[\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_{\alpha}(\mathbf{k}) g(\varepsilon_{\alpha}(\mathbf{k})) \left(\sum_{m\mu} C^{\alpha^{\star}}_{n\lambda}(\mathbf{k}) S^{\lambda,\mu}_{nm}(\mathbf{k}) C^{\alpha}_{m\mu}(\mathbf{k}) + \sum_{m\mu} C^{\alpha}_{n\lambda}(\mathbf{k}) S^{\lambda,\mu\star}_{n,m}(\mathbf{k}) C^{\alpha\star}_{m\mu}(\mathbf{k}) \right) \right]$$

So that

$$A_{n\lambda} = \Re \left[\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_{\alpha}(\mathbf{k}) g(\varepsilon_{\alpha}(\mathbf{k})) \sum_{m\mu} C^{\alpha\star}_{n\lambda}(\mathbf{k}) S^{\lambda,\mu}_{n,m}(\mathbf{k}) C^{\alpha}_{m\mu}(\mathbf{k}) \right]$$

Or in a more compact form:

$$A_{n\lambda} = \Re \left[\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_{\alpha}(\mathbf{k}) g(\varepsilon_{\alpha}(\mathbf{k})) C^{\alpha\star}_{n\lambda}(\mathbf{k}) \widetilde{C}^{\alpha}_{n\lambda}(\mathbf{k}) \right]$$

6.4.3 Total energy

In the case of the total energy $\hat{A} = \hat{H}$ so that $g(x) = x$

$$E_{tot} = \langle \hat{H} \rangle = \sum_{\alpha\mathbf{k}} w_{\mathbf{k}} f_{\alpha}(\mathbf{k}) \varepsilon_{\alpha}(\mathbf{k})^{t} C^{\alpha\star}(\mathbf{k}) \widetilde{C}^{\alpha}(\mathbf{k})$$

The local component of the energy is defined as:

$$E^{\mathrm{tot}}_{n\lambda} = \Re \left[\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_{\alpha}(\mathbf{k}) \varepsilon_{\alpha}(\mathbf{k}) C^{\alpha\star}_{n\lambda}(\mathbf{k}) \widetilde{C}^{\alpha}_{n\lambda}(\mathbf{k}) \right]$$

6.4.4 Group velocity

Let's consider the groupe velocity $\mathbf{v}_{\mathbf{k},\alpha}$, of band α at $\mathbf{k}$:

$$\hbar \mathbf{v}_{\mathbf{k},\alpha} = \nabla_{\mathbf{k}} \varepsilon_{\alpha}(\mathbf{k})$$

For component $d = x, y, z$

$$\hbar v^{d}_{\mathbf{k},\alpha} = \frac{\partial}{\partial k_d} \langle \alpha\mathbf{k} | \hat{H} | \alpha\mathbf{k} \rangle$$

Using the expansion of the Bloch function in TB basis as well as the generalized eigenvalue equation and normalization of eigenvectors one gets:

$$\hbar v^d_{\mathbf{k},\alpha} =^t C^{\alpha\star}(\mathbf{k}) \left[\frac{\partial}{\partial k_d} H(\mathbf{k}) - \varepsilon_\alpha(\mathbf{k}) \frac{\partial}{\partial k_d} S(\mathbf{k}) \right] C^\alpha(\mathbf{k})$$

Hence we have to calculate the derivative the Hamiltonian matrix

$$\frac{\partial}{\partial k_d} H^{\lambda,\mu}_{n,m}(\mathbf{k}) = i \sum_{\mathbf{R}} (\mathbf{R}^d + \mathbf{r}^d_m - \mathbf{r}^d_n) e^{i\mathbf{k}.(\mathbf{R}+\mathbf{r}_m-\mathbf{r}_n)} \langle 0,n,\lambda|\hat{H}|\mathbf{R},m,\mu\rangle$$

and overlap

$$\frac{\partial}{\partial k_d} S^{\lambda,\mu}_{n,m}(\mathbf{k}) = i \sum_{\mathbf{R}} (\mathbf{R}^d + \mathbf{r}^d_m - \mathbf{r}^d_n) e^{i\mathbf{k}.(\mathbf{R}+\mathbf{r}_m-\mathbf{r}_n)} \langle 0,n,\lambda|\hat{I}|\mathbf{R},m,\mu\rangle$$

7 What about spin!

7.1 Local and global basis

One can choose a global spin basis linked to the crystal lattice or a local basis linked to the orientation of the spin magnetization. For the global basis $\sigma = \uparrow, \downarrow$ diagonalize σ_z operator while for the local basis $\sigma'' = \uparrow, \downarrow$ diagonalize $\sigma_{z''}$. The global basis is indentical for each atom of the system, while in case of non-collinear magnetization the local basis can change from site to site! We will use the global basis in the following.

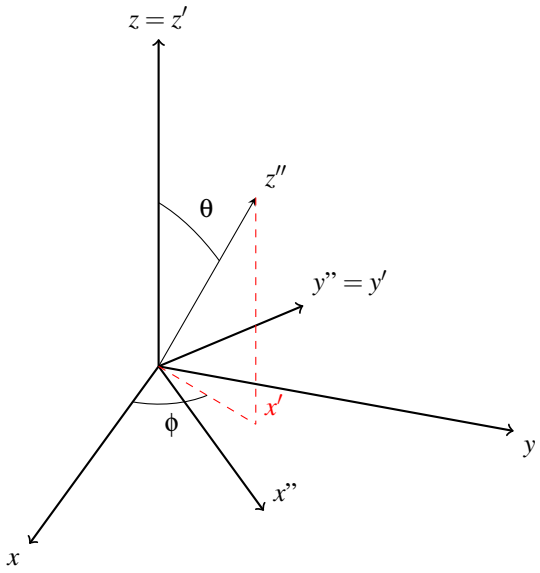

Figure 2: *Definition of the spin basis in spherical coordinates*

7.2 TB basis and Bloch theorem with spinors

Let's introduce the spin variable σ, we define the TB basis with an additionnal index:

$$|\mathbf{R},n,\lambda,\sigma\rangle = |\mathbf{R},n,\lambda\rangle \otimes |\sigma\rangle$$

In the TB basis adapted to the periodic conditions $|n,\lambda,\sigma,\mathbf{k}\rangle$

$$|n,\lambda,\sigma,\mathbf{k}\rangle = \frac{e^{i\mathbf{k}.\boldsymbol{r}_n}}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}.\mathbf{R}} |\mathbf{R},n,\lambda,\sigma\rangle$$

And the Bloch function:

$$|\alpha,\mathbf{k}\rangle = \sum_{n,\lambda,\sigma} C^{\alpha}_{n\lambda\sigma}(\mathbf{k})|n,\lambda,\sigma,\mathbf{k}\rangle$$

Note that if the Hamiltonian does NOT possess term that "mix" up and down spins the coefficients $C^{\alpha}_{a\lambda\sigma}(\mathbf{k})$ can be separated in "up" ($\sigma=\uparrow$) and "down" ($\sigma=\downarrow$). This situation occurs when the magnetization is collinear without spin-orbit coupling.

7.3 Expression of an operator in the TB basis

$\hat{A}$ hermitian operator can be written in the TB basis $|n,\lambda,\sigma,\mathbf{k}\rangle$:

$$A^{\lambda\sigma,\mu,\sigma'}_{n,m}(\mathbf{k}) = \langle n,\lambda,\sigma,\mathbf{k}|\hat{A}|m,\mu,\sigma'\mathbf{k}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}.(\mathbf{R}+\mathbf{r}_m-\mathbf{r}_n)}\langle 0,n,\lambda,\sigma|\hat{A}|\mathbf{R},m,\mu,\sigma'\rangle$$

If $\hat{A}$ is independent of spin:

$$A^{\lambda\sigma,\mu\sigma'}_{n,m}(\mathbf{k}) = A^{\lambda,\mu}_{n,m}(\mathbf{k})\otimes\boldsymbol{\sigma}_0$$

This result applies to the component of the Hamiltonian that does not depend on spin H_0:

$$H^{0,\lambda\sigma,\mu\sigma'}_{n,m}(\mathbf{k}) = H^{0,\lambda,\mu}_{n,m}(\mathbf{k})\otimes\boldsymbol{\sigma}_0 \quad \text{and} \quad S^{\lambda\sigma,\mu\sigma'}_{n,m}(\mathbf{k}) = S^{\lambda,\mu}_{n,m}(\mathbf{k})\otimes\boldsymbol{\sigma}_0$$

The TB magnetic Hamiltonian contains four terms H_0, H_{LCN}, H_{Stoner} and H_{SOC} [4]:

$$H = H_0\otimes\boldsymbol{\sigma}_0 + \sum_{\substack{n,\lambda\\ m\mu}} U_{n,\lambda}(\rho_{n,\lambda}-\rho^0_{n,\lambda})\delta_{n,\lambda,b\mu}\otimes\boldsymbol{\sigma}_0 - \frac{1}{2}\sum_{\substack{n,\lambda\\ m\mu}} I_{n,\lambda}\delta_{n,\lambda,m\mu}\mathbf{m}_{n\lambda}.\boldsymbol{\sigma} + \sum_{\substack{n,\lambda,\sigma\\ m,\mu,\sigma'}}\xi_{n,\lambda}\delta_{n,m}\langle\lambda,\sigma|\mathbf{l}.\sigma|\mu,\sigma'\rangle$$

7.4 Average operators

7.4.1 Pauli operator

The average of the spin operator is expressed as follows $\boldsymbol{\sigma}$ [5]:

$$\langle\boldsymbol{\sigma}\rangle = \sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_{\alpha}(\mathbf{k})\langle\alpha,\mathbf{k}|\boldsymbol{\sigma}|\alpha,\mathbf{k}\rangle$$

Let's use the definition of $|\alpha,\mathbf{k}\rangle$ and the fact that $\boldsymbol{\sigma}$ acts only on spin variables:

$$|\alpha,\mathbf{k}\rangle = \sum_{n,\lambda,\sigma} C^{\alpha}_{n\lambda\sigma}(\mathbf{k})|n,\lambda,\sigma,\mathbf{k}\rangle \quad ; \quad \boldsymbol{\sigma}|n,\lambda,\sigma',\mathbf{k}\rangle = \sum_{\sigma\sigma'}\boldsymbol{\sigma}_{\sigma\sigma'}|n,\lambda,\sigma',\mathbf{k}\rangle$$

$$\langle\boldsymbol{\sigma}\rangle = \text{Tr}(\hat{\rho}\boldsymbol{\sigma}) = \sum_{\sigma\sigma'}\left[\sum_{\substack{n\lambda\\ m\mu}}\left(\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_{\alpha}(\mathbf{k}) C^{\alpha}_{m\mu\sigma'}(\mathbf{k})(C^{\alpha}_{n\lambda\sigma}(\mathbf{k}))^{\star}\right) S^{\lambda,\mu}_{a,b}(\mathbf{k})\right]\boldsymbol{\sigma}_{\sigma\sigma'}$$

Let's introduce the density matrix $\bar{\rho}$ de:

$$\bar{\rho}^{\sigma\sigma'} = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{\substack{a\lambda\\ b\mu}}\left(\sum_{\alpha} f_{\alpha}(\mathbf{k}) C^{\alpha}_{m\mu\sigma}(\mathbf{k})(C^{\alpha}_{n\lambda\sigma'}(\mathbf{k}))^{\star}\right) S^{\lambda,\mu}_{n,m}(\mathbf{k})$$

$$\bar{\rho} = \begin{pmatrix} \rho^{\uparrow\uparrow} & \rho^{\uparrow\downarrow} \\ \rho^{\downarrow\uparrow} & \rho^{\downarrow\downarrow} \end{pmatrix}$$

[4] For more details aboit the Hamiltonian see "Comptes Rendus Physique 17 406-429 (2016)."

[5] $\boldsymbol{\sigma} = (\sigma_x,\sigma_y,\sigma_z)$ est formé des 3 matrices de Pauli et $\boldsymbol{\sigma}_{\sigma\sigma'}$ représente les coefficients de ces matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Hence we have:

$$\langle \boldsymbol{\sigma} \rangle = \sum_{\sigma\sigma'} \bar{\rho}^{\sigma'\sigma} \boldsymbol{\sigma}_{\sigma\sigma'} = \mathrm{Tr}(\tilde{\rho}\boldsymbol{\sigma})$$

Le calcul montre donc que:

$$\begin{array}{rcl} \langle \sigma_x \rangle & = & \bar{\rho}^{\downarrow\uparrow} + \bar{\rho}^{\uparrow\downarrow} = 2\Re(\bar{\rho}^{\uparrow\downarrow}) \\ \langle \sigma_y \rangle & = & i(\bar{\rho}^{\uparrow\downarrow} - \bar{\rho}^{\downarrow\uparrow}) = -2\Im(\bar{\rho}^{\uparrow\downarrow}) \\ \langle \sigma_z \rangle & = & \bar{\rho}^{\uparrow\uparrow} - \bar{\rho}^{\downarrow\downarrow} \\ \langle \sigma_0 \rangle & = & \bar{\rho}^{\uparrow\uparrow} + \bar{\rho}^{\downarrow\downarrow} \end{array}$$

Inverting these formula one gets:

$$\begin{array}{rcl} \bar{\rho}^{\uparrow\uparrow} & = & \frac{1}{2}[\langle \sigma_0 \rangle + \langle \sigma_z \rangle] \\ \bar{\rho}^{\downarrow\downarrow} & = & \frac{1}{2}[\langle \sigma_0 \rangle - \langle \sigma_z \rangle] \\ \bar{\rho}^{\uparrow\downarrow} & = & \frac{1}{2}[\langle \sigma_x \rangle - i\langle \sigma_y \rangle] \\ \bar{\rho}^{\downarrow\uparrow} & = & \frac{1}{2}[\langle \sigma_x \rangle + i\langle \sigma_y \rangle] \end{array}$$

7.4.2 Local quantities

One can défine a local density:

$$\bar{\rho}^{\sigma\sigma'}_{n\lambda} = \frac{1}{2}\left[\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k}) \left(\sum_{m\mu} C^{\alpha\star}_{n\lambda\sigma'}(\mathbf{k}) S^{\lambda,\mu}_{n,m}(\mathbf{k}) C^{\alpha}_{m\mu\sigma}(\mathbf{k}) + \sum_{m\mu} C^{\alpha}_{n\lambda\sigma}(\mathbf{k}) S^{\lambda,\mu\star}_{n,m}(\mathbf{k}) C^{\alpha\star}_{m\mu\sigma'}(\mathbf{k}) \right) \right]$$

It is useful to introduce $C^\alpha_\sigma(\mathbf{k})$ as a sub-vector of $C^\alpha(\mathbf{k})$. Similarly one defines $\widetilde{C}^\alpha_\sigma(\mathbf{k}) = S(\mathbf{k}) C^\alpha_\sigma(\mathbf{k})$. The local density reads:

$$\bar{\rho}^{\sigma\sigma'}_{n\lambda} = \frac{1}{2}\left[\sum_{\alpha,\mathbf{k}} w_{\mathbf{k}} f_\alpha(\mathbf{k}) \left(C^{\alpha\star}_{n\lambda\sigma'}(\mathbf{k}) \widetilde{C}^{\alpha}_{n\lambda\sigma}(\mathbf{k}) + C^{\alpha}_{n\lambda\sigma}(\mathbf{k}) \widetilde{C}^{\alpha\star}_{n\lambda\sigma'}(\mathbf{k}) \right) \right]$$

$$\bar{\rho}_{n,\lambda} = \begin{pmatrix} \rho^{\uparrow\uparrow}_{n\lambda} & \rho^{\uparrow\downarrow}_{n\lambda} \\ \rho^{\downarrow\uparrow}_{n\lambda} & \rho^{\downarrow\downarrow}_{n\lambda} \end{pmatrix}$$

and we have :

$$\begin{array}{rcl} \langle \sigma_x \rangle_{n\lambda} & = & \rho^{\downarrow\uparrow}_{n\lambda} + \rho^{\uparrow\downarrow}_{n\lambda} = 2\Re(\rho^{\uparrow\downarrow}_{n\lambda}) \\ \langle \sigma_y \rangle_{n\lambda} & = & i(\rho^{\uparrow\downarrow}_{n\lambda} - \rho^{\downarrow\uparrow}_{n\lambda}) = -2\Im(\rho^{\uparrow\downarrow}_{n\lambda}) \\ \langle \sigma_z \rangle_{n\lambda} & = & \rho^{\uparrow\uparrow}_{n\lambda} - \rho^{\downarrow\downarrow}_{n\lambda} \\ \langle \sigma_0 \rangle_{n\lambda} & = & \rho^{\uparrow\uparrow}_{n\lambda} + \rho^{\downarrow\downarrow}_{n\lambda} \end{array}$$

7.5 Average of an operator

7.5.1 General case

$\hat{A}$ Hermitian operator:

$$A^{\lambda\sigma,\mu\sigma'}_{nm}(\mathbf{k}) = \langle n,\lambda,\sigma,\mathbf{k}|\boldsymbol{A}|m,\mu,\sigma'\mathbf{k}\rangle$$

Its average reads:

$$\langle A \rangle = \sum_{\mathbf{k}} w_{\mathbf{k}} \mathrm{Tr}\left[\bar{\rho}(\mathbf{k}) A(\mathbf{k})\right]$$

Where $\hat{\rho}(\mathbf{k})$:

$$\bar{\rho}^{\sigma\sigma'}_{n\lambda m\mu}(\mathbf{k}) = \sum_{\alpha} f_{\alpha}(\mathbf{k}) C^{\alpha}_{n\lambda\sigma}(\mathbf{k}) (C^{\alpha}_{m\mu\sigma'}(\mathbf{k}))^{\star}$$

7.5.2 Orbital moment

Let $\hat{L_d}$ be the oribital moment operator ($d = x, y, z$). Its expression in the TB basis $|\mathbf{R}, n, \mu, \sigma\rangle$ is:

$$\hat{L}_d |\mathbf{R}, n, \lambda, \sigma\rangle = \sum_{\mu} L_d^{\lambda\mu} |\mathbf{R}, n\mu\sigma\rangle$$

This is a "local" operator that do not depend on spin its expression in the $|n, \lambda, \mathbf{k}\rangle$ basis reads:

$$L^{\lambda\sigma,\mu\sigma'}_{d,nm} = \langle n, \lambda, \sigma, \mathbf{k} | \hat{L_d} | m, \mu, \sigma' \mathbf{k} \rangle = \sum_{\nu} S^{\lambda\nu}_{nm}(\mathbf{k}) L_d^{\nu\mu} \delta_{\sigma\sigma'}$$

The local component of the orbital moment is:

$$\langle \hat{L}_d \rangle_n = \Re \left[\sum_{\alpha\mathbf{k}} f_{\alpha}(\mathbf{k}) w_{\mathbf{k}} \sum_{m\lambda\mu\sigma} C^{\alpha\star}_{n\lambda\sigma}(\mathbf{k}) L_d^{\lambda\mu} S^{\lambda\mu}_{nm}(\mathbf{k}) C^{\alpha}_{m\mu\sigma}(\mathbf{k}) \right]$$

Let us give the expression of the orbital operator in the p and d orbital basis.

• p orbitals: $\lambda = \{p_x, p_y, p_z\}$

$$L_x^{(p)} = \hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad L_y^{(p)} = \hbar \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix} \quad L_z^{(p)} = \hbar \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

• d orbitals $\lambda = \{d_{xy}, d_{yz}, d_{xz}, d_{x^2-y2}, d_{z2}\}$

$$L_x^{(d)} = \hbar \begin{pmatrix} 0 & 0 & -i & 0 & 0 \\ 0 & 0 & 0 & -i & -i\sqrt{3} \\ i & 0 & 0 & 0 & 0 \\ 0 & i & 0 & 0 & 0 \\ 0 & i\sqrt{3} & 0 & 0 & 0 \end{pmatrix} \quad L_y^{(d)} = \hbar \begin{pmatrix} 0 & i & 0 & 0 & 0 \\ -i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i & i\sqrt{3} \\ 0 & 0 & i & 0 & 0 \\ 0 & 0 & -i\sqrt{3} & 0 & 0 \end{pmatrix} \quad L_z^{(d)} = \hbar \begin{pmatrix} 0 & 0 & 0 & 2i & 0 \\ 0 & 0 & i & 0 & 0 \\ 0 & -i & 0 & 0 & 0 \\ -2i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

References

[1] *Magnetism of iron: from the bulk to the monatomic wire* Gabriel Autès, Cyrille Barreteau, Daniel Spanjaard and Marie-Catherine Desjonquères J. Phys.: Condens. Matter **18** 6785-6813 (2006) .

[2] *Magnetocrystalline anisotropy energy of Fe(001) and Fe(110) slabs and nanoclusters: A detailed local analysis within a tight-binding model* D. Li, A. Smogunov, C. Barreteau, F. Ducastelle, and D. Spanjaard Phys. Rev. B **88** 214413 (2013).

[3] *An efficient magnetic tight-binding method for transition metals and alloys* C. Barreteau, D. Spanjaard, MC Desjonqueres Comptes Rendus Physique **17** 406-429 (2016).

[4] *Magnetocrystalline anisotropy of Fe, Co, and Ni slabs from density functional theory and tight-binding models* Ludovic Le Laurent, Cyrille Barreteau, and Troels Markussen Phys. Rev. B **100**, 174426 (2019).

[5] *Spin dynamics from a constrained magnetic tight-binding model* Ramon Cardias, Cyrille Barreteau, Pascal Thibaudeau, and Chu Chun Fu Phys. Rev. B **103**, 235436 (2021).