

**Notes on the tight binding method in a lattice with a basis**  
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**1 Formulation of the problem.** We want to adapt the linear combination of atomic orbitals to be used within the tight binding method to the case of a lattice with a basis. In the following,  $\Lambda_B$  indicates the number of atoms belonging to the basis, and  $\mathbf{r}_\nu$ ,  $\nu = 1, \dots, \Lambda_B$  identifies their position within the primitive cell. We need to construct the customary Bloch function

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{r} - \mathbf{R}),$$

where  $\mathbf{R}$  are the vectors of the Bravais lattice and

$$\phi(\mathbf{r}) = \sum_{\nu=1}^{\Lambda_B} \sum_n e^{i\mathbf{k}\cdot\mathbf{r}_\nu} b_{n,\nu} \phi_{n,\nu}(\mathbf{r} - \mathbf{r}_\nu),$$

$\phi_{n,\nu}(\mathbf{r})$  being the  $n$ -th atomic orbital of the atom labelled with  $\nu$ , is here a linear combination of atomic orbitals of the various atoms belonging to the basis, with coefficients  $b_{n,\nu}$ . The factors  $e^{i\mathbf{k}\cdot\mathbf{r}_\nu}$ , for a fixed  $\mathbf{k}$ , could be included in the definition of the coefficients  $b_{n,\nu}$ , but the symmetry properties of the lattice can be more easily implemented if these factors are kept explicit.

**2 Deduction of the tight binding equations.** To deduce the tight binding equations, we multiply the Bloch eigenvalue equation  $(\hat{H}_{\text{at}} + \Delta U - \varepsilon_{\mathbf{k}})\psi_{\mathbf{k}}(\mathbf{r}) = 0$  by  $e^{-i\mathbf{k}\cdot\mathbf{r}_\lambda} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda)$  and integrate. We find

$$\begin{aligned} 0 &= \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}_\lambda} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \left( \hat{H}_{\text{at}} + \Delta U - \varepsilon_{\mathbf{k}} \right) \psi_{\mathbf{k}}(\mathbf{r}) \\ &= (E_{\ell,\lambda} - \varepsilon_{\mathbf{k}}) \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}_\lambda} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \psi_{\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}_\lambda} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \Delta U \psi_{\mathbf{k}}(\mathbf{r}), \end{aligned}$$

where we used the fact that  $\phi_{\ell,\lambda}(\mathbf{r} - \mathbf{r}_\lambda)$  is an eigenfunction of the (Hermitian) atomic Hamiltonian  $\hat{H}_{\text{at}}$ , with eigenvalue  $E_{\ell,\lambda}$ . Let us now focus on the two integrals appearing in the last term. After substituting the expression for  $\psi_{\mathbf{k}}$ , the first reads

$$\mathcal{I}_{\ell,\lambda} \equiv \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}_\lambda} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{\nu=1}^{\Lambda_B} \sum_n e^{i\mathbf{k}\cdot(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda)} b_{n,\nu} \int d\mathbf{r} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \phi_{n,\nu}(\mathbf{r} - \mathbf{R} - \mathbf{r}_\nu).$$

There are three kind of terms:  $\mathbf{R} = 0$  and  $\mathbf{r}_\nu = \mathbf{r}_\lambda$  (same cell, same atom);  $\mathbf{R} = 0$  and  $\mathbf{r}_\nu \neq \mathbf{r}_\lambda$  (same cell, different atom);  $\mathbf{R} \neq 0$  (different cells, no need to separate same and different atoms). Then

$$\begin{aligned} \hat{\mathcal{I}}_{\ell,\lambda} &= b_{\ell,\lambda} + \sum_{\nu \neq \lambda} \sum_n e^{i\mathbf{k}\cdot(\mathbf{r}_\nu - \mathbf{r}_\lambda)} b_{n,\nu} \int d\mathbf{r} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \phi_{n,\nu}(\mathbf{r} - \mathbf{R} - \mathbf{r}_\nu) \\ &+ \sum_{\mathbf{R} \neq 0} \sum_{\nu=1}^{\Lambda_B} \sum_n e^{i\mathbf{k}\cdot(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda)} b_{n,\nu} \int d\mathbf{r} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \phi_{n,\nu}(\mathbf{r} - \mathbf{R} - \mathbf{r}_\nu). \end{aligned}$$

Since within the tight binding method one assumes that the difference  $E_{\ell,\lambda} - \varepsilon_{\mathbf{k}}$  is small, small terms implying the overlap of orbitals of different atoms can be neglected when they multiply  $E_{\ell,\lambda} - \varepsilon_{\mathbf{k}}$ , so that one can take  $\mathcal{I}_{\ell,\lambda} \approx b_{\ell,\lambda}$ . The term

$$\begin{aligned} \mathcal{J}_{\ell,\lambda} &\equiv \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}_\lambda} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \Delta U \psi_{\mathbf{k}}(\mathbf{r}) \\ &= \sum_{\mathbf{R}} \sum_{\nu=1}^{\Lambda_B} \sum_n e^{i\mathbf{k}\cdot(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda)} b_{n,\nu} \int d\mathbf{r} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \Delta U \phi_{n,\nu}(\mathbf{r} - \mathbf{R} - \mathbf{r}_\nu) \end{aligned}$$

can be treated in an analogous manner. Here, we only need to distinguish the term  $\mathbf{R} = 0$ ,  $\mathbf{r}_\nu = \mathbf{r}_\lambda$  and  $n = \ell$  (same cell, same atom, same orbital) from all others, so that

$$\mathcal{J}_{\ell,\lambda} = \left[ \int d\mathbf{r} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \Delta U \phi_{\ell,\lambda}(\mathbf{r} - \mathbf{r}_\lambda) \right] b_{\ell,\lambda} - \left( \sum_{\mathbf{R}} \sum_{\nu=1}^{\Lambda_B} \sum_n \right)' \gamma_{\ell,\lambda;n,\nu}(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda) e^{i\mathbf{k}\cdot(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda)} b_{n,\nu},$$

where the prime in the sums appearing in the second term implies that the term with  $\mathbf{R} = 0$ ,  $\mathbf{r}_\nu = \mathbf{r}_\lambda$ ,  $n = \ell$  must be excluded, as it was considered explicitly. The first term is a (small) change of the atomic energy  $E_{\ell,\lambda}$ , and is usually omitted. Hereafter

$$\gamma_{\ell,\lambda;n,\nu}(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda) \equiv - \int d\mathbf{r} \phi_{\ell,\lambda}^*(\mathbf{r} - \mathbf{r}_\lambda) \Delta U \phi_{n,\nu}(\mathbf{r} - \mathbf{R} - \mathbf{r}_\nu)$$

denote the so-called transfer integrals. Then, the problem of determining the eigenvalues and eigenfunctions of the Bloch Hamiltonian translates into the linear homogeneous system

$$(E_{\ell,\lambda} - \varepsilon_{\mathbf{k}}) b_{\ell,\lambda} - \left( \sum_{\mathbf{R}} \sum_{\nu=1}^{\Lambda_B} \sum_n \right)' \gamma_{\ell,\lambda;n,\nu}(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda) e^{i\mathbf{k}\cdot(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda)} b_{n,\nu} = 0,$$

for  $\lambda = 1, \dots, \Lambda_B$  and  $\ell = 1, 2, \dots$

**3 Simplified form of the tight binding equations.** To further simplify the tight binding equations we assume that for each atom in the basis there is only one set of (nearly) degenerate orbitals that participate in the formation of the band. This set can include one  $s$  orbital; one, two, or three  $p$  orbitals; two  $sp$  orbitals; three  $sp^2$  orbitals; four  $sp^3$  orbitals; one to five  $d$  orbitals; and so on. Then, for each  $\nu = 1, \dots, \Lambda_B$  labelling an atom of the basis, there will be a definite set of orbitals,  $n = 1, \dots, N_\nu$ . Hence, the linear problem set by the tight binding equations is a  $\mathcal{N} \times \mathcal{N}$  problem, with

$$\mathcal{N} = \sum_{\nu=1}^{\Lambda_B} N_\nu.$$

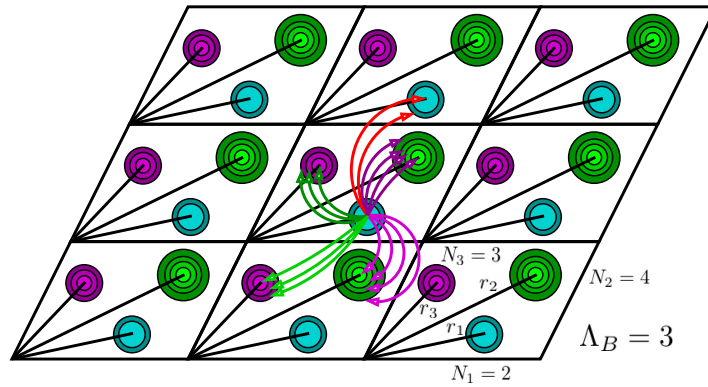


FIG. 1: Example of a Bravais lattice with a three-atom basis,  $\Lambda_B = 3$ . With respect to the tight binding method, let us assume that the atom located at  $\mathbf{r}_1$  contributes with  $N_1 = 2$  orbitals (the different shades of cyan); the atom located at  $\mathbf{r}_2$  contributes with  $N_2 = 4$  orbitals (the different shades of green); the atom located at  $\mathbf{r}_3$  contributes with  $N_3 = 3$  orbitals (the different shades of magenta). After choosing one primitive cell as the starting point, for each atom ( $\lambda = 1, \dots, \Lambda_B$ ) and for each orbital of the chosen atom ( $\ell = 1, \dots, N_\lambda$ ), connect the selected orbital of the chosen atom to all possible orbitals ( $n = 1, \dots, N_\lambda$ ) of the same atom in different primitive cells (red arrows), to define the coefficients  $\gamma_{\ell;n}^\lambda(\mathbf{R})$  ( $\mathbf{R}$  is the Bravais lattice locating the final primitive cell relative to the one adopted as a starting point); then, connect the selected orbital of the chosen atom to all possible orbitals of all the different atoms ( $\nu \neq \lambda$ ,  $n = 1, \dots, N_\nu$ ) in the same ( $\mathbf{R} = 0$ , dark magenta and dark green arrows) and different ( $\mathbf{R} \neq 0$ , light magenta and light green arrows) primitive cells, to define the coefficients  $\gamma_{\ell;n}^{\lambda;\nu}(\mathbf{R})$ . Each connection carries a factor  $e^{i\mathbf{k}\cdot(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda)}$ . Whenever two connections are characterized by values of  $\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda$  that are related by a symmetry of the lattice, the corresponding  $\gamma$ 's should be identified, up to an overall sign that depends on the relative phase of the overlapping orbitals that are involved in the transfer integral. Since  $\mathcal{N} = \sum_{\nu=1}^{\Lambda_B} N_\nu = 9$  in the example depicted in the figure, the related Bloch problem translates into a  $9 \times 9$  system of homogeneous equations, yielding 9 eigenvalues  $\varepsilon_{\mathbf{k},s}$ ,  $s = 1, \dots, 9$  (bands).

The  $\gamma$ 's with  $\mathbf{R} = 0$ ,  $\mathbf{r}_\nu = \mathbf{r}_\lambda$  and  $n \neq \ell$  couple different nearly degenerate orbitals on the same atom (if  $N_\nu > 1$ ). These terms do not give rise to a band dispersion, since  $\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda = 0$ , and only redefine the form of the orthogonal

orbitals on a given atom once the lattice potential  $\Delta U$  is taken into account. They can be neglected if we attribute to each atomic eigenvalue  $E_{\ell,\lambda}$  the value corresponding to this re-orthogonalisation of the atomic basis. In any case, this effect is small, because the lattice correction  $\Delta U$  is negligible inside an atom and only become sizable in the interatomic region, where the overlap of orbitals belonging to different atoms contribute to the formation of the bands, allowing for electrons to be transferred from one atom to the next and become a delocalized Bloch wave.

We are then left only with genuine transfer integrals, involving the same atom in different primitive cells ( $\mathbf{R} \neq 0$ ,  $\mathbf{r}_\nu = \mathbf{r}_\lambda$ ), or different atoms in the same ( $\mathbf{R} = 0$ ,  $\mathbf{r}_\nu \neq \mathbf{r}_\lambda$ ) or different  $\mathbf{R} \neq 0$ ,  $\mathbf{r}_\nu \neq \mathbf{r}_\lambda$  primitive cells. In the following we adopt the simplified notation

$$\gamma_{\ell;n}^\lambda(\mathbf{R}) \equiv \gamma_{\ell,\lambda;n,\lambda}(\mathbf{R})$$

for transfer integrals coupling the same atom in different primitive cells, and

$$\gamma_{\ell;n}^{\lambda;\nu}(\mathbf{R}) \equiv \gamma_{\ell,\lambda;n,\nu}(\mathbf{R} + \mathbf{r}_\nu - \mathbf{r}_\lambda)$$

for transfer integrals coupling different atoms ( $\mathbf{r}_\nu \neq \mathbf{r}_\lambda$ ) in the same ( $\mathbf{R} = 0$ ) or different ( $\mathbf{R} \neq 0$ ) primitive cells. To work out the general form of the band structure for a given lattice, we must face the problem of assigning values to the  $\gamma$ 's that do not violate the symmetry of the lattice, to define all the coefficients of the linear problem

$$(E_{\ell,\lambda} - \varepsilon_{\mathbf{k}}) b_{\ell,\lambda} - \sum_{\mathbf{R} \neq 0} \sum_{n=1}^{N_\lambda} \gamma_{\ell;n}^\lambda(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} b_{n,\lambda} - \sum_{\mathbf{R}} \sum_{\nu \neq \lambda} \sum_{n=1}^{N_\nu} \gamma_{\ell;n}^{\lambda;\nu}(\mathbf{R}) e^{i\mathbf{k}\cdot(\mathbf{R}+\mathbf{r}_\nu-\mathbf{r}_\lambda)} b_{n,\nu} = 0,$$

for  $\lambda = 1, \dots, \Lambda_B$ ,  $\ell = 1, \dots, N_\lambda$  (see FIG. 1). The sum over  $\mathbf{R}$  is restricted to a finite number of Bravais lattice vector,  $|\mathbf{R}| \leq R_{\text{cut}}$ , defining nearest, next-to-nearest, ..., primitive cells.

**4 Examples.** Some examples should clarify how to implement the procedure described so far.

a. Consider a one-dimensional lattice described by the vectors  $\mathbf{R} = a \hat{\mathbf{i}}$ , where  $\hat{\mathbf{i}}$  is the unit vector along the  $x$  axis (see FIG. 2). Consider the primitive cell highlighted by the box and a two-atom ( $\Lambda_B = 2$ ) basis  $\mathbf{r}_1 = a_1 \hat{\mathbf{i}}$  (cyan circle) and  $\mathbf{r}_2 = a_2 \hat{\mathbf{i}}$  (magenta circle), with  $a_1 < a_2 < a$ . The wave-vector labelling Bloch states is  $\mathbf{k} = k \hat{\mathbf{i}}$ . Each atom contributes to the bands with a single  $s$  orbital ( $N_1 = N_2 = 1$ ).

Choosing the primitive cell highlighted by the box as the starting point, we connect (red arrows) the cyan atom located at  $\mathbf{r}_1$  to the nearest cyan atoms in the two primitive cells nearby, located at  $(a_1 \pm a) \hat{\mathbf{i}}$ , and call  $\gamma_{11}$  the common value of the two transfer integrals, attaching to them the factors  $e^{\pm ika}$ . Then, we connect (blue arrows) this atom to the two neighboring magenta atoms, located at  $a_2 \hat{\mathbf{i}}$  and  $(a_2 - a) \hat{\mathbf{i}}$ , and call  $\gamma_{12}$  and  $\tilde{\gamma}_{12}$  the two (generically inequivalent) transfer integrals, attaching to them the factors  $e^{ik(a_2-a_1)}$  and  $e^{ik(a_2-a-a_1)}$ , respectively. The two transfer integrals become equivalent by symmetry if  $a_2 = a_1 + \frac{1}{2}a$ , i.e., if the two magenta atoms are equidistant from the cyan atom.

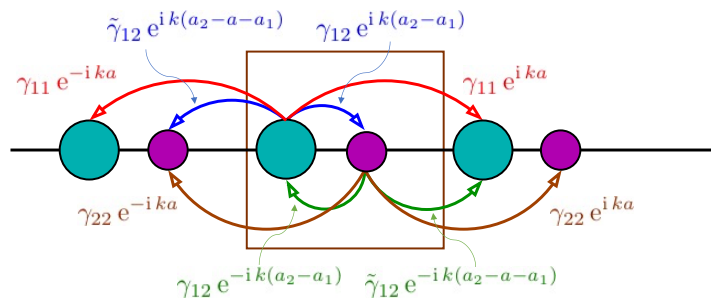


FIG. 2: One-dimensional lattice described by the vectors  $\mathbf{R} = a \hat{\mathbf{i}}$ , where  $\hat{\mathbf{i}}$  is the unit vector along the  $x$  axis, with a two-atom basis. The two inequivalent atoms are located at  $\mathbf{r}_1 = a_1 \hat{\mathbf{i}}$  (cyan circle) and  $\mathbf{r}_2 = a_2 \hat{\mathbf{i}}$  (magenta circle), with  $a_1 < a_2 < a$ . Both participate in the band formation with an  $s$  orbital. The primitive cell chosen as the starting point is highlighted by a box. The arrows define the various transfer integrals (see text).

Now let us pick the magenta atom, located at  $\mathbf{r}_2$  in the primitive cell selected as the starting point, and connect (brown arrows) it with the the nearest magenta atoms in the two primitive cells nearby, located at  $(a_2 \pm a) \hat{\mathbf{i}}$ . We call  $\gamma_{22}$  the common value of the two transfer integrals, attaching to them the factors  $e^{\pm ika}$ . Then, we connect

(green arrows) this atom to the two neighboring cyan atoms, located at  $a_1 \hat{\mathbf{i}}$  and  $(a_1 + a) \hat{\mathbf{i}}$ . By symmetry, the corresponding transfer integrals are again  $\gamma_{12}$  and  $\tilde{\gamma}_{12}$ , respectively. We must attach to them the factors  $e^{-ik(a_2-a_1)}$  and  $e^{-ik(a_2-a-a_1)}$ , respectively.

Let us call the atomic energies with  $E_1$  and  $E_2$ . Then, in the present case,  $\mathcal{N} = \sum_{\nu=1}^{\Lambda_B} N_\nu = 2$  and the tight binding equations correspond to the  $2 \times 2$  homogeneous problem

$$\begin{aligned} [E_1 - 2\gamma_{11} \cos(ka) - \varepsilon_k] b_1 - (\gamma_{12} + \tilde{\gamma}_{12} e^{-ika}) e^{ik(a_2-a_1)} b_2 &= 0, \\ [E_2 - 2\gamma_{22} \cos(ka) - \varepsilon_k] b_2 - (\gamma_{12} + \tilde{\gamma}_{12} e^{ika}) e^{ik(a_1-a_2)} b_1 &= 0. \end{aligned}$$

To determine the two bands, we must set to zero the determinant

$$\begin{vmatrix} E_1 - 2\gamma_{11} \cos(ka) - \varepsilon_k & -(\gamma_{12} + \tilde{\gamma}_{12} e^{-ika}) e^{ik(a_2-a_1)} \\ -(\gamma_{12} + \tilde{\gamma}_{12} e^{ika}) e^{ik(a_1-a_2)} & E_2 - 2\gamma_{22} \cos(ka) - \varepsilon_k \end{vmatrix}$$

finding the equation

$$[E_1 - 2\gamma_{11} \cos(ka) - \varepsilon_k] [E_2 - 2\gamma_{22} \cos(ka) - \varepsilon_k] - [\gamma_{12}^2 + \tilde{\gamma}_{12}^2 + 2\gamma_{12}\tilde{\gamma}_{12} \cos(ka)] = 0.$$

The basis vectors have disappeared from the final equation, making it evident that the related phase factors can indeed be reabsorbed in the definition of the coefficients of the linear combination of atomic orbitals, as they do not intervene in the final expression of the two bands

$$\varepsilon_{k,\pm} = \frac{E_1 + E_2}{2} - (\gamma_{11} + \gamma_{22}) \cos(ka) \pm \sqrt{\left[ \frac{E_1 - E_2}{2} - (\gamma_{11} - \gamma_{22}) \cos(ka) \right]^2 + \gamma_{12}^2 + \tilde{\gamma}_{12}^2 + 2\gamma_{12}\tilde{\gamma}_{12} \cos(ka)}.$$

The various limiting cases ( $\gamma_{12} = \tilde{\gamma}_{12} = 0$ ;  $\gamma_{11} = \gamma_{22} = 0$  and  $\gamma_{12} = \tilde{\gamma}_{12} \neq 0$ ) yield simpler expressions.

b. Consider a one-dimensional lattice described by the vectors  $\mathbf{R} = a \hat{\mathbf{i}}$ , where  $\hat{\mathbf{i}}$  is the unit vector along the  $x$  axis (see FIG. 3). Consider the primitive cell highlighted by the box and a two-atom ( $\Lambda_B = 2$ ) basis  $\mathbf{r}_1 = a_1 \hat{\mathbf{i}}$  (cyan and red lobes) and  $\mathbf{r}_2 = a_2 \hat{\mathbf{i}}$  (magenta circle), with  $a_1 < a_2 < a$ . The wave-vector labelling Bloch states is  $\mathbf{k} = k \hat{\mathbf{i}}$ . The first atom contributes to the bands with a single  $p_x$  orbital (the two shades indicating the different signs of the two lobes of a  $p_x$  orbital), the second atom contributes with a single  $s$  orbital ( $N_1 = N_2 = 1$ ).

Choosing the primitive cell highlighted by the box as the starting point, we connect (red arrows) the cyan-red atom located at  $\mathbf{r}_1$  to the nearest cyan-red atoms in the two primitive cells nearby, located at  $(a_1 \pm a) \hat{\mathbf{i}}$  and call  $-\gamma_{11}$  the common value of the two transfer integrals, attaching to them the factors  $e^{\pm ika}$ . The minus sign in front of the transfer integrals comes from the fact that a given (say, positive) lobe of the  $p_x$  orbital is closer to the lobe with opposite sign belonging to the other atom. Then, we connect (blue arrows) this atom to the two neighboring magenta atoms, located at  $a_2 \hat{\mathbf{i}}$  and  $(a_2 - a) \hat{\mathbf{i}}$ , and call  $\gamma_{12}$  and  $-\tilde{\gamma}_{12}$  the two transfer integrals, attaching to them the factors  $e^{ik(a_2-a_1)}$  and  $e^{ik(a_2-a-a_1)}$ , respectively. The two opposite signs of the transfer integrals result from the fact that the  $s$  orbital of the magenta atom is closer to the positive and negative lobes of the two cyan-red atoms nearby, respectively. The two transfer integrals have the same absolute value by symmetry if  $a_2 = a_1 + \frac{1}{2}a$ , i.e., if the two magenta atoms are equidistant from the cyan-red atom.

Now let us pick the magenta atom, located at  $\mathbf{r}_2$  in the primitive cell selected as a starting point, and connect (brown arrows) it with the the nearest magenta atoms in the two primitive cells nearby, located at  $(a_2 \pm a) \hat{\mathbf{i}}$ . We call  $\gamma_{22}$  the common value of the two transfer integrals, attaching to them the factors  $e^{\pm ika}$ . Then, we connect (green arrows) this atom to the two neighboring cyan atoms, located at  $a_1 \hat{\mathbf{i}}$  and  $(a_1 + a) \hat{\mathbf{i}}$ . By symmetry, the corresponding transfer integrals are again  $\gamma_{12}$  and  $-\tilde{\gamma}_{12}$ , respectively. We must attach to them the factors  $e^{-ik(a_2-a_1)}$  and  $e^{-ik(a_2-a-a_1)}$ , respectively.

Let us call the atomic energies with  $E_1$  and  $E_2$ . Again,  $\mathcal{N} = \sum_{\nu=1}^{\Lambda_B} N_\nu = 2$  and the tight binding equations correspond now to the  $2 \times 2$  homogeneous problem

$$\begin{aligned} [E_1 + 2\gamma_{11} \cos(ka) - \varepsilon_k] b_1 - (\gamma_{12} - \tilde{\gamma}_{12} e^{-ika}) e^{ik(a_2-a_1)} b_2 &= 0, \\ [E_2 - 2\gamma_{22} \cos(ka) - \varepsilon_k] b_2 - (\gamma_{12} - \tilde{\gamma}_{12} e^{ika}) e^{ik(a_1-a_2)} b_1 &= 0. \end{aligned}$$

To determine the two bands, we must set to zero the determinant

$$\begin{vmatrix} E_1 + 2\gamma_{11} \cos(ka) - \varepsilon_k & -(\gamma_{12} - \tilde{\gamma}_{12} e^{-ika}) e^{ik(a_2-a_1)} \\ -(\gamma_{12} - \tilde{\gamma}_{12} e^{ika}) e^{ik(a_1-a_2)} & E_2 - 2\gamma_{22} \cos(ka) - \varepsilon_k \end{vmatrix}$$

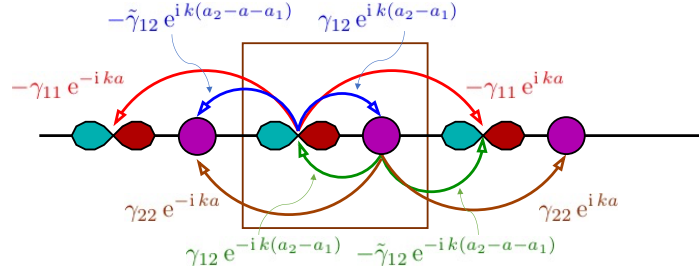


FIG. 3: One-dimensional lattice described by the vectors  $\mathbf{R} = a \hat{\mathbf{i}}$ , where  $\hat{\mathbf{i}}$  is the unit vector along the  $x$  axis, with a two-atom basis. The two inequivalent atoms are located at  $\mathbf{r}_1 = a_1 \hat{\mathbf{i}}$  (cyan and red lobes) and  $\mathbf{r}_2 = a_2 \hat{\mathbf{i}}$  (magenta circle), with  $a_1 < a_2 < a$ . The first atom participates in the band formation with a  $p_x$  orbitals and the two colors represent the negative (cyan) and positive (red) lobes of the  $p_x$  orbital, the second atom participates in the band formation with an  $s$  orbital. The primitive cell chosen as the starting point is highlighted by a box. The arrows define the various transfer integrals (see text).

finding the equation

$$[E_1 + 2\gamma_{11} \cos(ka) - \varepsilon_k] [E_2 - 2\gamma_{22} \cos(ka) - \varepsilon_k] - [\gamma_{12}^2 + \tilde{\gamma}_{12}^2 - 2\gamma_{12}\tilde{\gamma}_{12} \cos(ka)] = 0.$$

Again, the basis vectors have disappeared from the final equation. The final expression of the two bands is

$$\varepsilon_{k,\pm} = \frac{E_1 + E_2}{2} + (\gamma_{11} - \gamma_{22}) \cos(ka) \pm \sqrt{\left[ \frac{E_1 - E_2}{2} + (\gamma_{11} + \gamma_{22}) \cos(ka) \right]^2 + \gamma_{12}^2 + \tilde{\gamma}_{12}^2 - 2\gamma_{12}\tilde{\gamma}_{12} \cos(ka)}.$$

The various limiting cases ( $\gamma_{12} = \tilde{\gamma}_{12} = 0$ ;  $\gamma_{11} = \gamma_{22} = 0$  and  $\gamma_{12} = \tilde{\gamma}_{12} \neq 0$ ) yield simpler expressions.