Supplementary material to:
P. Marconcini, M. Macucci,
“The $k \cdot p$ method and its application to graphene, carbon nanotubes and graphene nanoribbons: the Dirac equation”

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1. – Note on pp. 518–520

The equation (126) can clearly be obtained also exploiting the completeness relation for the adopted basis functions.

Indeed, if we define |j′m⟩ ≡ ϕ(r - Rj′m) and thus ψj′(Rj′m) = ⟨j′m|ψ⟩ (where j′ = A, B indicates the type of the atom and m specifies the particular atom), equation (120) can be rewritten as

\[ |ψ⟩ = \sum_{j′,m} |j′m⟩⟨j′m|ψ⟩ = \left[ \sum_{j′,m} |j′m⟩⟨j′m|ψ⟩ \right] |ψ⟩. \]

If we insert the relation \( \sum_{j′,m} |j′m⟩⟨j′m| = 1 \) (completeness relation) inside equation (121), we obtain

\[ H \left[ \sum_{j′,m} |j′m⟩⟨j′m|ψ⟩ \right] = E \left[ \sum_{j′,m} |j′m⟩⟨j′m|ψ⟩ \right] \Rightarrow \sum_{j′,m} H|j′m⟩⟨j′m|ψ⟩ = E \sum_{j′,m} |j′m⟩⟨j′m|ψ⟩. \]

If then we left-multiply by ⟨jn|, we arrive at

\[ \sum_{j′,m} ⟨jn|H|j′m⟩⟨j′m|ψ⟩ = E \sum_{j′,m} ⟨jn|j′m⟩⟨j′m|ψ⟩ \Rightarrow \sum_{j′,m} h_{Rj, Rj′m}ψj′(Rj′m) = E \sum_{j′,m} s_{Rj, Rj′m}ψj′(Rj′m), \]

which coincides with the equation (126).
The multiplication by the smoothing function $g(r - R_i)$ (with $i = A$ or $B$) is just an analytical way to attribute each value $F(R_i)$, originally defined only at the lattice point $R_i$, to the region surrounding the point $R_i$, in such a way as to extend the definition domain of the envelope functions to all the points $r$ of the plane.

More in detail, in the following calculations we will first multiply each tight-binding equation by a proper phase term, in such a way as to end up with terms, slowly varying in the space, in which the phase term is absent, and other terms in which a phase term $e^{\pm i(K' - K) \cdot R_i}$ appears and makes them very fast-variable in space. Then, we will sum the resulting equation over $R_i$, using as a weight function the smoothing function $g(r - R_i)$ (with $r$ a generic point of the plane). In this way, we will actually average the values that each term of the equation assumes at the lattice points $R_i$ located inside a neighborhood of $r$. For the terms which not contain the phase factor $e^{\pm i(K' - K) \cdot R_i}$, this procedure makes it possible to define the slowly-variable envelope functions in all the points $r$ of the plane, averaging over the values that it assumes at the lattice points $R_i$ around $r$. Instead, the terms containing the phase factor $e^{\pm i(K' - K) \cdot R_i}$ will disappear. Indeed, averaging, over a sufficiently wide number of lattice points $R_i$, the product of the value of an envelope function $F$, which is very slowly-varying in space, and of a term $e^{\pm i(K' - K) \cdot R_i}$, which over the domain has very rapid variations around a null average value, we obtain a null result.
3. – Extended version of the calculations at pp. 525–531

If we multiply the first of the tight-binding equations (140) by \( g(r - R_A) e^{-iK \cdot R_A} \) and we sum it over \( R_A \), we find

\[
E \sum_{R_A} g(r - R_A) F_A^K(R_A) =
- E i e^{i\theta} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} F_A^{K'}(R_A)
- \sum_{R_A} g(r - R_A) u(R_A) F_A^K(R_A)
+ i e^{i\theta} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} u(R_A) F_A^{K'}(R_A) =
- \gamma_0 \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} F_B^{K'}(R_A - \tau_l);
\]

exploiting the property (144), it becomes

\[
E \sum_{R_A} g(r - R_A) F_A^K(r) - E i e^{i\theta} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} F_A^{K'}(r) =
- \sum_{R_A} g(r - R_A) u(R_A) F_A^K(r)
+ i e^{i\theta} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} u(R_A) F_A^{K'}(r) =
- \gamma_0 \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} F_B^{K'}(r - \tau_l);
\]

For the quantities in the square brackets, we can use the properties (141) and (143), together with the definitions

\[
u_A(r) = \sum_{R_A} g(r - R_A) u(R_A), \quad u'_A(r) = \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} u(R_A),
\]

obtaining:

\[
E F_A^K(r) - u_A(r) F_A^K(r) + i e^{i\theta} u'_A(r) F_A^{K'}(r) =
- \gamma_0 \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} F_B^K(r - \tau_l).
\]
Let us now calculate the value of the sums which appear in the previous expression

\[ \sum_{l=1}^{\infty} e^{-iK \tau_l} F_B^K (r - \tau_l) \approx \sum_{l=1}^{\infty} e^{-iK \tau_l} \left[ F_B^K (r) - \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F_B^K (r) \right] = \left\{ \sum_{l=1}^{\infty} e^{-iK \tau_l} F_B^K (r) - \left[ \sum_{l=1}^{\infty} e^{-iK \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F_B^K (r) \right] \right\}. \]

Expanding the smooth quantity

\[ \left( \sum_{l=1}^{\infty} e^{-iK \tau_l} \right) F_B^K (r) - \left[ \sum_{l=1}^{\infty} e^{-iK \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F_B^K (r) \right]. \]

Let us now calculate the value of the sums which appear in the previous expression

\[ \sum_{l=1}^{\infty} e^{-iK \tau_l} = 1 + e^{-i \frac{2\pi}{3}} + e^{i \frac{2\pi}{3}} = 0; \]

\[ \sum_{l=1}^{\infty} e^{-iK \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = 1 - \frac{a}{\sqrt{3}} \left( \frac{\partial}{\partial x'} - \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) + e^{-i \frac{2\pi}{3}} \frac{a}{\sqrt{3}} \left( \frac{\partial}{\partial x'} + \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) = \frac{a}{\sqrt{3}} \left( -1 + \frac{1}{2} e^{-i \frac{2\pi}{3}} + \frac{e^{i \frac{2\pi}{3}}}{2} \right) \frac{\partial}{\partial x'} + \left( -\frac{\sqrt{3}}{2} e^{-i \frac{2\pi}{3}} + \frac{\sqrt{3}}{2} e^{i \frac{2\pi}{3}} \right) \frac{\partial}{\partial y'} \right). \]

Since

\[ -1 + \frac{1}{2} e^{-i \frac{2\pi}{3}} + \frac{e^{i \frac{2\pi}{3}}}{2} = -1 + \frac{1}{2} \left( e^{-i \frac{2\pi}{3}} + e^{i \frac{2\pi}{3}} \right) = -1 + \frac{1}{2} (1) = -\frac{3}{2} \]

and

\[ -\frac{\sqrt{3}}{2} e^{-i \frac{2\pi}{3}} + \frac{\sqrt{3}}{2} e^{i \frac{2\pi}{3}} = \frac{\sqrt{3}}{2} \left( e^{i \frac{2\pi}{3}} - e^{-i \frac{2\pi}{3}} \right) = \frac{\sqrt{3}}{2} (i \sqrt{3}) = \frac{3}{2}, \]

we have that

\[ \sum_{l=1}^{\infty} e^{-iK \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = \frac{a}{\sqrt{3}} \left( \frac{\partial}{\partial x'} - \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) = -\frac{\sqrt{3}}{2} a(i \dot{k}_{x'} + \dot{k}_{y'}) = -\frac{\sqrt{3}}{2} a(\dot{k}_{x'} - i \dot{k}_{y'}), \]

where we have defined \( \dot{k} = -i \nabla \) and thus

\[ \dot{k}_{x'} = -i \frac{\partial}{\partial x'} \quad \text{and} \quad \dot{k}_{y'} = -i \frac{\partial}{\partial y'}. \]

Substituting these results, eq. (148) becomes

\[ \left[ E F_A^K (r) - u_A (r) F_A^K (r) + i e^{i \theta'} u_A (r) F_A^K (r) \right] \simeq \left[ -\gamma_0 e^{i \theta'} \left( \frac{\sqrt{3}}{2} a(\dot{k}_{x'} - i \dot{k}_{y'}) F_B^K (r) \right) \right] = \frac{\sqrt{3}}{2} \gamma_0 a e^{i \theta'} (\dot{k}_{x'} - i \dot{k}_{y'}) F_B^K (r) = \gamma (\dot{k}_x - i \dot{k}_y) F_B^K (r). \]
where we have passed from the original reference frame $\Sigma' = (\hat{x}', \hat{y}', \hat{z}')$ to a new frame $\Sigma = (\hat{x}, \hat{y}, \hat{z})$, rotated, in the plane $(\hat{x}', \hat{y}')$, around the origin by an angle $\theta'$ (positive in the counterclockwise direction) with respect to the original one (fig. 7) and we have used the fact that

$$e^{i\theta'(\hat{k}_x' - i\hat{k}_y')} = (\cos \theta' + i \sin \theta')(\hat{k}_x' - i\hat{k}_y') =$$

$$(\cos \theta' \hat{k}_x' + \sin \theta' \hat{k}_y') - i(\cos \theta' \hat{k}_y' - \sin \theta' \hat{k}_x') = \hat{k}_x - i\hat{k}_y$$

(due to the relations between old and new coordinates), with

$$\hat{k}_x = -i \frac{\partial}{\partial x} \quad \text{and} \quad \hat{k}_y = -i \frac{\partial}{\partial y}.$$

Indeed, it is a well-known result that, for a rotation by $\theta'$ of the reference frame, the relations between the new and the old coordinates are $x = x' \cos \theta' + y' \sin \theta'$ and $y = y' \cos \theta' - x' \sin \theta'$. Therefore we have that

$$\frac{\partial F(x, y)}{\partial x'} = \frac{\partial F(x, y)}{\partial x} \frac{\partial x}{\partial x'} + \frac{\partial F(x, y)}{\partial y} \frac{\partial y}{\partial x'} = \frac{\partial F(x, y)}{\partial x} \cos \theta' = \frac{\partial F(x, y)}{\partial y} \sin \theta' \cos \theta'$$

and that

$$\frac{\partial F(x, y)}{\partial y'} = \frac{\partial F(x, y)}{\partial x} \frac{\partial x}{\partial y'} + \frac{\partial F(x, y)}{\partial y} \frac{\partial y}{\partial y'} = \frac{\partial F(x, y)}{\partial x} \sin \theta' + \frac{\partial F(x, y)}{\partial y} \cos \theta' \sin \theta'.$$

As a consequence, we have that

$$\frac{\partial F(x, y)}{\partial x'} (\cos \theta' \hat{k}_x' + \sin \theta' \hat{k}_y') = \cos \theta' \left( -i \frac{\partial F(x, y)}{\partial x'} \right) + \sin \theta' \left( -i \frac{\partial F(x, y)}{\partial y'} \right) =$$

$$- i \left[ \frac{\partial F(x, y)}{\partial x} \cos^2 \theta' - \frac{\partial F(x, y)}{\partial y} \cos \theta' \sin \theta' \right. \right.$$

$$+ \left. \frac{\partial F(x, y)}{\partial x} \sin^2 \theta' + \frac{\partial F(x, y)}{\partial y} \sin \theta' \cos \theta' \right] =$$

$$- i \frac{\partial F(x, y)}{\partial x} (\cos^2 \theta' + \sin^2 \theta') = - i \frac{\partial F(x, y)}{\partial x} = \hat{k}_x F(x, y)$$

and that

$$\frac{\partial F(x, y)}{\partial x'} (\cos \theta' \hat{k}_y' - \sin \theta' \hat{k}_x') = \cos \theta' \left( -i \frac{\partial F(x, y)}{\partial y'} \right) - \sin \theta' \left( -i \frac{\partial F(x, y)}{\partial x'} \right) =$$

$$- i \left[ \frac{\partial F(x, y)}{\partial x} \sin \theta' \cos \theta' + \frac{\partial F(x, y)}{\partial y} \cos^2 \theta' - \right. \right.$$

$$- \left. \frac{\partial F(x, y)}{\partial x} \cos \theta' \sin \theta' + \frac{\partial F(x, y)}{\partial y} \sin^2 \theta' \right] =$$

$$- i \frac{\partial F(x, y)}{\partial y} (\cos^2 \theta' + \sin^2 \theta') = - i \frac{\partial F(x, y)}{\partial y} = \hat{k}_y F(x, y),$$

from which we obtain eq. (154).
Analogously, if we multiply the second of the tight-binding equations (140) by \( g(r - R_B) \) and we sum it over \( R_B \), we find

\[
E \sum_{R_B} g(r - R_B) f_B^K(R_B) - E i e^{-i \theta'} \sum_{R_B} g(r - R_B) e^{i(K' - K) R_B} f_B^{K'}(R_B)
\]

\[
- \sum_{R_B} g(r - R_B) u(R_B) f_B^K(R_B)
\]

\[
+ i e^{-i \theta'} \sum_{R_B} g(r - R_B) e^{i(K' - K) R_B} u(R_B) f_B^{K'}(R_B) =
\]

\[
\gamma_0 i e^{-i \theta'} \sum_{l=1}^3 e^{iK_T l} \sum_{R_B} g(r - R_B) f_A^K(R_B + \tau l)
\]

\[
+ \gamma_0 \sum_{l=1}^3 e^{iK_T l} \sum_{R_B} g(r - R_B) e^{i(K' - K) R_B} f_A^{K'}(R_B + \tau l);
\]

exploiting the property (144), it becomes

\[
E \left[ \sum_{R_B} g(r - R_B) \right] f_B^K(r) - E i e^{-i \theta'} \left[ \sum_{R_B} g(r - R_B) e^{i(K' - K) R_B} \right] f_B^{K'}(r)
\]

\[
- \left[ \sum_{R_B} g(r - R_B) u(R_B) \right] f_B^K(r)
\]

\[
+ i e^{-i \theta'} \left[ \sum_{R_B} g(r - R_B) e^{i(K' - K) R_B} u(R_B) \right] f_B^{K'}(r) =
\]

\[
\gamma_0 i e^{-i \theta'} \sum_{l=1}^3 e^{iK_T l} \left[ \sum_{R_B} g(r - R_B) \right] f_A^K(r + \tau l)
\]

\[
+ \gamma_0 \sum_{l=1}^3 e^{iK_T l} \left[ \sum_{R_B} g(r - R_B) e^{i(K' - K) R_B} \right] f_A^{K'}(r + \tau l).
\]
For the quantities in the square brackets, we can use the properties (141) and (143), together with the definitions

\( u_B(r) = \sum_{R_B} g(r - R_B) u(R_B), \quad u'_B(r) = \sum_{R_B} g(r - R_B) e^{i(K' \cdot K)} R_B u(R_B), \)

obtaining

\[
E F_B^K(r) - u_B(r) F_B^K(r) + i e^{-i\theta'} u'_B(r) F_B^{K'}(r) = \gamma_0 i e^{-i\theta'} \sum_{l=1}^{3} e^{iK \tau_l} F_A^K(r + \tau_l).
\]

Expanding the smooth quantity \( F_A^K(r + \tau_l) \) to the first order in \( \tau_l \), we have that

\[
\sum_{l=1}^{3} e^{iK \tau_l} F_A^K(r + \tau_l) \simeq \sum_{l=1}^{3} e^{iK \tau_l} \left[ F_A^K(r) + \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F_A^K(r) \right] = \sum_{l=1}^{3} e^{iK \tau_l} \left( F_A^K(r) \right).
\]

Let us now calculate the value of the sums which appear in the previous expression

\[
\sum_{l=1}^{3} e^{iK \tau_l} = 1 + e^{i\frac{2\pi}{3}} + e^{-i\frac{2\pi}{3}} = 0;
\]

\[
\sum_{l=1}^{3} e^{iK \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = \frac{a}{\sqrt{3}} \left( -\frac{\partial}{\partial x'} \right)
\]

\[
+ e^{i\frac{2\pi}{3}} \frac{a}{\sqrt{3}} \left( \frac{1}{2} \frac{\partial}{\partial x'} - \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) + e^{-i\frac{2\pi}{3}} \frac{a}{\sqrt{3}} \left( \frac{1}{2} \frac{\partial}{\partial x'} + \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) = \frac{a}{\sqrt{3}} \left( -1 + e^{i\frac{2\pi}{3}} + e^{-i\frac{2\pi}{3}} \right) \frac{\partial}{\partial x'} + \left( -\frac{\sqrt{3}}{2} e^{i\frac{2\pi}{3}} + \frac{\sqrt{3}}{2} e^{-i\frac{2\pi}{3}} \right) \frac{\partial}{\partial y'}.
\]

Since

\[-1 + e^{i\frac{2\pi}{3}} + e^{-i\frac{2\pi}{3}} = -1 + \frac{1}{2} (e^{i\frac{2\pi}{3}} + e^{-i\frac{2\pi}{3}}) = -1 + \frac{1}{2}(-1) = -\frac{3}{2}\]

and

\[-\frac{\sqrt{3}}{2} e^{i\frac{2\pi}{3}} + \frac{\sqrt{3}}{2} e^{-i\frac{2\pi}{3}} = -\frac{\sqrt{3}}{2} (e^{i\frac{2\pi}{3}} - e^{-i\frac{2\pi}{3}}) = -\frac{\sqrt{3}}{2}(i\sqrt{3}) = -\frac{3}{2},\]

we have that

\[
\sum_{l=1}^{3} e^{iK \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = \frac{a}{\sqrt{3}} \frac{3}{2} \left( \frac{\partial}{\partial x'} + i \frac{\partial}{\partial y'} \right) = -\frac{\sqrt{3}}{2} a(i\kappa_x' - \kappa_y').
\]
Substituting these results, eq. (162) becomes

\[
E F^K_B(r) - u_B(r) F^K_B(r) + i e^{-i\phi} u'_B(r) F^K'_B(r) = \\
\gamma_0 i e^{-i\phi} \left( -\frac{\sqrt{3}}{2} a(\hat{k}_x' + i\hat{k}_y') \right) F^K_A(r) = \\
\frac{\sqrt{3}}{2} \gamma_0 a e^{-i\phi}(\hat{k}_x' + i\hat{k}_y') F^K_A(r) = \gamma(\hat{k}_x + i\hat{k}_y) F^K_A(r),
\]

where we have made use of the relation

\[
e^{-i\phi}(\hat{k}_x' + i\hat{k}_y') = (\cos \theta' - i \sin \theta')(\hat{k}_x' + i\hat{k}_y') = \\
(\cos \theta' \hat{k}_x' + \sin \theta' \hat{k}_y') + i(\cos \theta' \hat{k}_y' - \sin \theta' \hat{k}_x') = \hat{k}_x + i\hat{k}_y.
\]

Instead, if we multiply the first of the tight-binding equations (140) by \(g(r - R_A)\times (i e^{-i\phi} e^{-iK' R_A})\) and we sum it over \(R_A\), we find

\[
E i e^{-i\phi} \sum_{R_A} g(r - R_A)e^{i(K - K') R_A} F^K_A(R_A) + E \sum_{R_A} g(r - R_A) F^K'_A(R_A) \\
- i e^{-i\phi} \sum_{R_A} g(r - R_A)e^{i(K - K') R_A} u(R_A) F^K_A(R_A) \\
- \sum_{R_A} g(r - R_A)u(R_A) F^K'_A(R_A) = \\
\gamma_0 \sum_{l=1}^3 e^{-iK' \tau_i} \sum_{R_A} g(r - R_A)e^{i(K - K') R_A} F^K_B(R_A - \tau_l) \\
- \gamma_0 i e^{-i\phi} \sum_{l=1}^3 e^{-iK' \tau_i} \sum_{R_A} g(r - R_A) F^K'_B(R_A - \tau_l);
\]

exploiting the property (144), it becomes

\[
E i e^{-i\phi} \left[ \sum_{R_A} g(r - R_A)e^{i(K - K') R_A} F^K_A(r) \right] + E \left[ \sum_{R_A} g(r - R_A) F^K'_A(r) \right] \\
- i e^{-i\phi} \left[ \sum_{R_A} g(r - R_A)e^{i(K - K') R_A} u(R_A) F^K_A(r) \right] \\
- \left[ \sum_{R_A} g(r - R_A)u(R_A) \right] F^K'_A(r) = \\
\gamma_0 \sum_{l=1}^3 e^{-iK' \tau_i} \left[ \sum_{R_A} g(r - R_A)e^{i(K - K') R_A} F^K_B(r - \tau_l) \right] \\
- \gamma_0 i e^{-i\phi} \sum_{l=1}^3 e^{-iK' \tau_i} \left[ \sum_{R_A} g(r - R_A) F^K'_B(r - \tau_l) \right].
\]
For the quantities in the square brackets, we can use the properties (141) and (143), in the form
\[
\sum_{R_A} g(r - R_A) e^{i(K - K')} R_A = \left( \sum_{R_A} g(r - R_A) e^{i(K - K')} R_A \right)^* = 0,
\]
obtaining
\[
EF_A^{K'}(r) - i e^{-i\theta} u_A^* (r) F_A^K (r) - u_A(r) F_A^{K'} (r) =
- \gamma_0 i e^{-i\theta} \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} F_B^{K'} (r - \tau_l).
\]
Expanding the smooth quantity \( F_B^{K'} (r - \tau_l) \) to the first order in \( \tau_l \), we have that
\[
\sum_{l=1}^{3} e^{-iK' \cdot \tau_l} F_B^{K'} (r - \tau_l) \simeq \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \left[ F_B^{K'} (r) - \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F_B^{K'} (r) \right] =
\left( \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \right) F_B^{K'} (r) - \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F_B^{K'} (r).
\]
Let us now calculate the value of the sums which appear in the previous expression
\[
\sum_{l=1}^{3} e^{-iK' \cdot \tau_l} = 1 + e^{i\frac{2\pi}{3}} + e^{-i\frac{2\pi}{3}} = 0;
\]
\[
\sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = \frac{a}{\sqrt{3}} \left( - \frac{\partial}{\partial x'} \right);
\]
\[
e^{i\frac{2\pi}{3}} \frac{a}{\sqrt{3}} \left( \frac{1}{2} \frac{\partial}{\partial x'} \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) + e^{-i\frac{2\pi}{3}} \frac{a}{\sqrt{3}} \left( \frac{1}{2} \frac{\partial}{\partial x'} + \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) =
\frac{a}{\sqrt{3}} \left( -1 + \frac{1}{2} e^{i\frac{2\pi}{3}} + \frac{1}{2} e^{-i\frac{2\pi}{3}} \right) \frac{\partial}{\partial x'} + \left( - \frac{\sqrt{3}}{2} e^{i\frac{2\pi}{3}} + \frac{\sqrt{3}}{2} e^{-i\frac{2\pi}{3}} \right) \frac{\partial}{\partial y'}.
\]
Since
\[
-1 + \frac{1}{2} e^{i\frac{2\pi}{3}} + \frac{1}{2} e^{-i\frac{2\pi}{3}} = -1 + \frac{1}{2} (e^{i\frac{2\pi}{3}} + e^{-i\frac{2\pi}{3}}) = -1 + \frac{1}{2} (-1) = -\frac{3}{2}
\]
and
\[
- \frac{\sqrt{3}}{2} e^{i\frac{2\pi}{3}} + \frac{\sqrt{3}}{2} e^{-i\frac{2\pi}{3}} = - \frac{\sqrt{3}}{2} e^{i\frac{2\pi}{3}} - e^{-i\frac{2\pi}{3}} = - \frac{\sqrt{3}}{2} (i \sqrt{3}) = - i \frac{3}{2},
\]
we have that
\[
\sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = - \frac{a}{\sqrt{3}} \left( \frac{\partial}{\partial x'} + i \frac{\partial}{\partial y'} \right) =
- \frac{\sqrt{3}}{2} a (i \kappa_x' - \kappa_y') = - i \frac{\sqrt{3}}{2} a ( \kappa_x' + i \kappa_y').
\]
Substituting these results, eq. (167) becomes

\[ EF_A^{K'}(r) - i e^{-i\theta'} u_A^*(r) F_A^K(r) - u_A(r) E_K(r) \approx \]
\[ -\gamma_0 i e^{-i\theta'} \left( \frac{\sqrt{3}}{2} a(\hat{k}_x' + i\hat{k}_y') F_B^{K'}(r) \right) = \]
\[ \frac{\sqrt{3}}{2} \gamma_0 a e^{-i\theta'} (\hat{k}_x' + i\hat{k}_y') F_B^{K'}(r) = \gamma (\hat{k}_x + i\hat{k}_y) F_B^{K'}(r), \]

where we have exploited the relation (166).

Finally, if we multiply the second of the tight-binding equations (140) by \( g(r - R_B) \times e^{-iK' R_B} \) and we sum it over \( R_B \), we find

\[
E i e^{i\theta'} \sum_{R_B} g(r - R_B) e^{i(K - K') R_B} F_B^K(R_B) + E \sum_{R_B} g(r - R_B) F_B^{K'}(R_B) \\
\quad - i e^{i\theta'} \sum_{R_B} g(r - R_B) e^{i(K - K') R_B} u(R_B) F_B^K(R_B) \\
\quad - \sum_{R_B} g(r - R_B) u(R_B) F_B^{K'}(R_B) = \\
\quad -\gamma_0 \sum_{l=1}^3 e^{iK' \tau_l} \sum_{R_B} g(r - R_B) e^{i(K - K') R_B} F_A^K(R_B + \tau_l) \\
\quad + \gamma_0 i e^{i\theta'} \sum_{l=1}^3 e^{iK' \tau_l} \sum_{R_B} g(r - R_B) F_A^{K'}(R_B + \tau_l); \\
\]

exploiting the property (144) it becomes

\[
E i e^{i\theta'} \left[ \sum_{R_B} g(r - R_B) e^{i(K - K') R_B} F_B^K(r) \right] + E \left[ \sum_{R_B} g(r - R_B) \right] F_B^{K'}(r) \\
\quad - i e^{i\theta'} \left[ \sum_{R_B} g(r - R_B) e^{i(K - K') R_B} u(R_B) \right] F_B^K(r) \\
\quad - \left[ \sum_{R_B} g(r - R_B) u(R_B) \right] F_B^{K'}(r) = \\
\quad -\gamma_0 \sum_{l=1}^3 e^{iK' \tau_l} \left[ \sum_{R_B} g(r - R_B) e^{i(K - K') R_B} \right] F_A^K(r + \tau_l) \\
\quad + \gamma_0 i e^{i\theta'} \sum_{l=1}^3 e^{iK' \tau_l} \left[ \sum_{R_B} g(r - R_B) \right] F_A^{K'}(r + \tau_l). \\
\]

For the quantities in the square brackets, we can use the properties (141) and (143), in the form

\[
\sum_{R_B} g(r - R_B) e^{i(K - K') R_B} = \left( \sum_{R_B} g(r - R_B) e^{i(K' - K) R_B} \right)^* = 0, \\
\]
obtaining

\begin{equation}
E F_B^{K'}(r) - i e^{iθ'} u_B^*(r) F_B^K(r) - u_B(r) F_B^{K'}(r) =
\gamma_0 i e^{iθ} \sum_{l=1}^{3} e^{iK' \cdot \tau_l} F_A^{K'}(r + \tau_l).
\end{equation}

Expanding the smooth quantity $F_A^{K'}(r + \tau_l)$ to the first order in $\tau_l$, we have that

\begin{equation}
\sum_{l=1}^{3} e^{iK' \cdot \tau_l} F_A^{K'}(r + \tau_l) \simeq \sum_{l=1}^{3} e^{iK' \cdot \tau_l} \left[ F_A^{K'}(r) + \left( \tau_l \cdot \frac{∂}{∂r} \right) F_A^{K'}(r) \right] =
\left( \sum_{l=1}^{3} e^{iK' \cdot \tau_l} \right) F_A^{K'}(r) + \left[ \sum_{l=1}^{3} e^{iK' \cdot \tau_l} \left( \tau_l \cdot \frac{∂}{∂r} \right) \right] F_A^{K'}(r).
\end{equation}

Let us now calculate the value of the sums which appear in the previous expression

\begin{equation}
\sum_{l=1}^{3} e^{iK' \cdot \tau_l} = 1 + e^{-i \frac{2π}{3}} + e^{i \frac{2π}{3}} = 0;
\end{equation}

\begin{equation}
\sum_{l=1}^{3} e^{iK' \cdot \tau_l} \left( \tau_l \cdot \frac{∂}{∂r} \right) = \frac{a}{\sqrt{3}} \left( \frac{∂}{∂x'} \right);
\end{equation}

\begin{equation}
+ e^{-i \frac{2π}{3}} \frac{a}{\sqrt{3}} \left( \frac{1}{2} \frac{∂}{∂x'} - \sqrt{3} \frac{∂}{∂y'} \right) + e^{i \frac{2π}{3}} \frac{a}{\sqrt{3}} \left( \frac{1}{2} \frac{∂}{∂x'} + \sqrt{3} \frac{∂}{∂y'} \right) =
\frac{a}{\sqrt{3}} \left( -1 + \frac{1}{2} e^{-i \frac{2π}{3}} + \frac{1}{2} e^{i \frac{2π}{3}} \right) \frac{∂}{∂x'} + \left( -\frac{3}{2} e^{-i \frac{2π}{3}} + \frac{3}{2} e^{i \frac{2π}{3}} \right) \frac{∂}{∂y'} ,
\end{equation}

Since

\(-1 + \frac{1}{2} e^{-i \frac{2π}{3}} + \frac{1}{2} e^{i \frac{2π}{3}} = -1 + \frac{1}{2} (e^{-i \frac{2π}{3}} + e^{i \frac{2π}{3}}) = -1 + \frac{1}{2}(-1) = -\frac{3}{2} \)

and

\(-\frac{3}{2} e^{-i \frac{2π}{3}} + \frac{3}{2} e^{i \frac{2π}{3}} = \frac{3}{2} (e^{i \frac{2π}{3}} - e^{-i \frac{2π}{3}}) = \frac{3}{2} (i \sqrt{3}) = \frac{i 3}{2}.\)

we have that

\begin{equation}
\sum_{l=1}^{3} e^{iK' \cdot \tau_l} \left( \tau_l \cdot \frac{∂}{∂r} \right) = -\frac{a}{\sqrt{3}} \frac{3}{2} \left( \frac{∂}{∂x'} - i \frac{∂}{∂y'} \right) =
- \frac{\sqrt{3}}{2} a(i \hat{κ}_x + \hat{κ}_y) = -i \frac{\sqrt{3}}{2} a(\hat{κ}_x - i \hat{κ}_y).\)
Substituting these values, eq. (171) becomes

\begin{equation}
E F^K_B(r) - i e^{i\theta'} u^*_B(r) F^K_B(r) - u_B(r) F^K_B(r) = \\
\gamma_0 i e^{i\theta'} \left(-i\frac{\sqrt{3}}{2} a(\kappa_x - i\kappa_y)\right) F^K_B(r) = \\
\frac{\sqrt{3}}{2} \gamma_0 a e^{i\theta'}(\kappa_x - i\kappa_y) F^K_B(r) = \gamma(\kappa_z - i\kappa_y) E F^K_B(r),
\end{equation}

where we have exploited the relation (154).

In this way, we have obtained the four equations (153), (165), (170) and (174), that we can summarize

\begin{equation}
\begin{cases}
  u_A(r) F^K_A(r) + \gamma(\kappa_x - i\kappa_y) F^K_B(r) - i e^{i\theta'} u'_A(r) F^K_B(r) = E F^K_A(r), \\
  \gamma(\kappa_x + i\kappa_y) F^K_A(r) + u_B(r) F^K_B(r) - i e^{-i\theta'} u'_B(r) F^K_B(r) = E F^K_A(r), \\
  i e^{-i\theta'} u^*_A(r) F^K_A(r) + u_A(r) F^K_B(r) + \gamma(\kappa_x + i\kappa_y) F^K_B(r) = E F^K_B(r), \\
  i e^{i\theta'} u^*_B(r) F^K_B(r) + \gamma(\kappa_x - i\kappa_y) F^K_A(r) + u_B(r) F^K_A(r) = E F^K_B(r),
\end{cases}
\end{equation}

and write in matrix form

\begin{equation}
E \begin{bmatrix}
  u_A(r) \\
  \gamma(\kappa_x - i\kappa_y) \\
  \gamma(\kappa_x + i\kappa_y) \\
  i e^{-i\theta'} u^*_A(r) \\
  0 \\
  i e^{i\theta'} u^*_B(r)
\end{bmatrix}
\begin{bmatrix}
  F^K_A(r) \\
  F^K_B(r) \\
  F^K_A(r) \\
  F^K_B(r) \\
  F^K_A(r) \\
  F^K_B(r)
\end{bmatrix}
= \begin{bmatrix}
  \gamma(\kappa_x - i\kappa_y) u_B(r) \\
  \gamma(\kappa_x + i\kappa_y) u_A(r) \\
  0 \\
  \gamma(\kappa_x - i\kappa_y) u_B(r) \\
  \gamma(\kappa_x + i\kappa_y) u_A(r) \\
  0
\end{bmatrix},
\end{equation}

which is the $k \cdot p$ equation of graphene.
4. – Extended version of the calculations at p. 537

If we move to the momentum representation (see eq. (111)) and enforce

\[
\text{(202)} \quad \det \left\{ \begin{array}{cc} 0 & \gamma(k_x + i\kappa y) \\ \gamma(k_x - i\kappa y) & 0 \end{array} \right\} - E \left[ \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right] = 0,
\]

we find the dispersion relations

\[
\text{(203)} \quad E_{s}^{K'}(\kappa) = s\gamma\sqrt{\kappa_x^2 + \kappa_y^2} = s\gamma|\kappa|,
\]

where \(s\) can assume the values +1 or −1.

The corresponding envelope functions are

\[
\text{(204)} \quad F_{s}^{K'}(r) = \frac{1}{\sqrt{2\Omega}} e^{i\kappa \cdot r} e^{i\tilde{\phi}_s(\kappa)} R(\alpha(\kappa)) |\bar{s}\rangle,
\]

with \(\tilde{\phi}_s(\kappa)\) an arbitrary phase factor and

\[
\text{(205)} \quad |\bar{s}\rangle = \frac{1}{\sqrt{2}} \left[ \begin{array}{c} is \\ 1 \end{array} \right].
\]

This result is easily verified noting that

\[
\gamma \left[ \begin{array}{cc} 0 & \hat{k}_x + i\hat{k}_y \\ \hat{k}_x - i\hat{k}_y & 0 \end{array} \right] F_{s}^{K'}(r) =
\gamma \left[ \begin{array}{cc} 0 & \hat{k}_x + i\hat{k}_y \\ \hat{k}_x - i\hat{k}_y & 0 \end{array} \right] \frac{1}{\sqrt{2\Omega}} e^{i\kappa \cdot r} e^{i\tilde{\phi}_s(\kappa)} R(\alpha(\kappa)) |\bar{s}\rangle =
\gamma \left[ \begin{array}{cc} 0 & i|\kappa|e^{ia} \\ -i|\kappa|e^{-ia} & 0 \end{array} \right] \left( \frac{1}{\sqrt{2\Omega}} e^{i\kappa \cdot r} e^{i\tilde{\phi}_s(\kappa)} \left[ \begin{array}{cc} e^{i\frac{\pi}{2}} & 0 \\ 0 & e^{-i\frac{\pi}{2}} \end{array} \right] \frac{1}{\sqrt{2}} \left[ \begin{array}{c} is \\ 1 \end{array} \right] \right) =
\frac{1}{2\sqrt{\Omega}} \gamma e^{i\kappa \cdot r} e^{i\tilde{\phi}_s(\kappa)} \left[ \begin{array}{cc} 0 & is|\kappa| e^{i\frac{\pi}{2}} \\ -i|\kappa| e^{-i\frac{\pi}{2}} & 0 \end{array} \right] \left[ \begin{array}{c} is \\ 1 \end{array} \right] =
\frac{1}{2\sqrt{\Omega}} e^{i(\kappa \cdot r + \tilde{\phi}_s(\kappa))} \left[ \begin{array}{c} is|\kappa| e^{i\frac{\pi}{2}} \\ |\kappa| e^{-i\frac{\pi}{2}} \end{array} \right]
\]

and that also

\[
E_{s}^{K'} F_{s}^{K'}(r) = s\gamma|\kappa| \left( \frac{1}{\sqrt{2\Omega}} e^{i\kappa \cdot r} e^{i\tilde{\phi}_s(\kappa)} \left[ \begin{array}{cc} e^{i\frac{\pi}{2}} & 0 \\ 0 & e^{-i\frac{\pi}{2}} \end{array} \right] \frac{1}{\sqrt{2}} \left[ \begin{array}{c} is \\ 1 \end{array} \right] \right) =
\frac{1}{2\sqrt{\Omega}} \gamma e^{i(\kappa \cdot r + \tilde{\phi}_s(\kappa))} \left[ \begin{array}{c} e^{i\frac{\pi}{2}} is|\kappa| e^{i\frac{\pi}{2}} \\ |\kappa| e^{-i\frac{\pi}{2}} \end{array} \right] =
\frac{1}{2\sqrt{\Omega}} e^{i(\kappa \cdot r + \tilde{\phi}_s(\kappa))} \left[ \begin{array}{c} is|\kappa| e^{i\frac{\pi}{2}} \\ |\kappa| e^{-i\frac{\pi}{2}} \end{array} \right].
\]
From these functions $F^K_A$, $F^K_B$, $F^{K'}_A$, and $F^{K'}_B$, we can find the functions $\psi_A$ and $\psi_B$ and thus the electron wave function $\psi$ in the absence of an external potential, using the relations (134) and (120).
5. – Extended version of the calculations at pp. 539–540

However the terms containing the phase factors \( e^{i(K' - K) \cdot R_A}, e^{i(K' - K) \cdot R_B}, \) or their complex conjugates are negligible with respect to the others.

Indeed, using the smoothing function \( g(r) \), we know from the property (141) with \( r = R_A \) that \( \sum_{R_A} g(R_A - R'_A) = 1 \). Therefore we can insert this sum into the term

\[
\sum_{R_A} \left[ e^{i(K' - K) \cdot R_A} F_A^{K'}(R_A) F_A^K(R_A) \right],
\]

obtaining

\[
\sum_{R_A} \left\{ \left[ \sum_{R'_A} g(R_A - R'_A) \right] e^{i(K' - K) \cdot R_A} F_A^{K'}(R_A) F_A^K(R_A) \right\},
\]

that can be rewritten, as a result of the point-symmetry of the function \( g \) with respect to its center and thus of the fact that \( g(R_A - R'_A) = g(-(R_A - R'_A)) \), in this way:

\[
\sum_{R_A} \sum_{R'_A} g(R'_A - R_A) e^{i(K' - K) \cdot R_A} F_A^{K'}(R_A) F_A^K(R_A).
\]

If then we use the property (144) with \( r = R'_A \) and in particular the fact that

\[
g(R'_A - R_A) F_A^{K'}(R_A) = g(R'_A - R_A) F_A^{K'}(R'_A)
\]

(due to the smoothness of the envelope functions), the term becomes

\[
\sum_{R'_A} \left[ \sum_{R_A} g(R'_A - R_A) e^{i(K' - K) \cdot R_A} \left. F_A^{K'}(R'_A) F_A^K(R_A) \right] \right.
\]

and, by way of the property (143) with \( r = R'_A \), we conclude that the quantities between square brackets, and thus the overall term, are very small.

Analogously, we can see that the terms

\[
\sum_{R_A} \left[ e^{-i(K' - K) \cdot R_A} F_A^{K'}(R_A) F_A^K(R_A) \right] = \\
\sum_{R_A} \left\{ \left[ \sum_{R'_A} g(R_A - R'_A) \right] e^{-i(K' - K) \cdot R_A} F_A^{K'}(R_A) F_A^K(R_A) \right\} = \\
\sum_{R_A} \sum_{R'_A} g(R'_A - R_A) e^{-i(K' - K) \cdot R_A} F_A^{K'}(R_A) F_A^K(R_A) = \\
\sum_{R_A} \left[ \sum_{R'_A} g(R'_A - R_A) e^{-i(K' - K) \cdot R_A} \left. F_A^{K'}(R'_A) F_A^K(R_A) \right] \right.
\]
\[
\sum_{R_B} \left[ e^{i(K' - K) \cdot R_B} F_B^{K^*}(R_B) F_B^K(R_B) \right] = \\
\sum_{R_B} \left\{ \left[ \sum_{R_B'} g(R_B - R_B') e^{i(K' - K) \cdot R_B} F_B^{K^*}(R_B) F_B^K(R_B) \right] \right\} = \\
\sum_{R_B} \sum_{R_B'} g(R_B' - R_B) e^{i(K' - K) \cdot R_B} F_B^{K^*}(R_B) F_B^K(R_B) = \\
\sum_{R_B} \left[ \sum_{R_B'} g(R_B' - R_B) e^{i(K' - K) \cdot R_B} F_B^{K^*}(R_B') F_B^K(R_B') \right],
\]

and

\[
\sum_{R_B} \left[ e^{-i(K' - K) \cdot R_B} F_B^{K'^*}(R_B) F_B^K(R_B) \right] = \\
\sum_{R_B} \left\{ \left[ \sum_{R_B'} g(R_B - R_B') e^{-i(K' - K) \cdot R_B} F_B^{K'^*}(R_B) F_B^K(R_B) \right] \right\} = \\
\sum_{R_B} \sum_{R_B'} g(R_B' - R_B) e^{-i(K' - K) \cdot R_B} F_B^{K'^*}(R_B) F_B^K(R_B) = \\
\sum_{R_B} \left[ \sum_{R_B'} g(R_B' - R_B) e^{-i(K' - K) \cdot R_B} F_B^{K'^*}(R_B') F_B^K(R_B') \right],
\]

are negligible. Since \( g(r) \) has non negligible values only within a few lattice constants from its center, the previous considerations are approximately valid also if we limit the sums to the atoms contained in the area \( S \).
Multiplying the second equation of (245) by \( g(r - R_B)(-ie^{-i\theta'}e^{-iK'R_B}) \), summing it over \( R_B \) and then using the properties of the function \( g \), we find analogously

\[
e^{iK'C_h} \sum_{R_B} g(r - R_B) F^K_B (r + C_h) \]

\[
- ie^{-i\theta'} e^{iK'C_h} \sum_{R_B} g(r - R_B) e^{i(K' - K)R_B} F^{K'}_B (R_B + C_h) = \]

\[
\sum_{R_B} g(r - R_B) F^K_B (R_B) - ie^{-i\theta'} \sum_{R_B} g(r - R_B) e^{i(K' - K)R_B} F^{K'}_B (R_B) \Rightarrow \]

\[
e^{iK'C_h} \sum_{R_B} g(r - R_B) F^K_B (r + C_h) \]

\[
- ie^{-i\theta'} e^{iK'C_h} \left[ \sum_{R_B} g(r - R_B) e^{i(K' - K)R_B} \right] F^{K'}_B (r + C_h) = \]

\[
\left[ \sum_{R_B} g(r - R_B) F^K_B (r) - ie^{-i\theta'} \left[ \sum_{R_B} g(r - R_B) e^{i(K' - K)R_B} \right] \right] F^{K'}_B (r) \Rightarrow \]

\[
e^{iK'C_h} F^K_B (r + C_h) = F^K_B (r). \]

Substituting the value of \( e^{iK'C_h} \), we can rewrite this boundary condition in the form

\[
e^{\frac{2\pi}{3}i\nu} F^K_B (r + C_h) = F^K_B (r) \]

or, equivalently

\[
F^K_B (r + C_h) = e^{-\frac{2\pi}{3}i\nu} F^K_B (r). \]
7. – Extended version of the calculations at pp. 551–553

We can proceed analogously for the boundary conditions near $K'$. Indeed, multiplying the first equation of (245) by $g(r-R_A)(ie^{-i\theta'}e^{-iK'R_A})$, summing it over $R_A$ and then using the properties of the function $g$, we find

$$\begin{align*}
&ie^{-i\theta'}e^{iK'C_h} \sum_{R_A} g(r-R_A)e^{i(K-K')R_A} F_K^A (r+C_h) \\
&+ e^{iK'C_h} \sum_{R_A} g(r-R_A)F_{K'}^A (r+C_h) = \\
&ie^{-i\theta'} \sum_{R_A} g(r-R_A)e^{i(K-K')R_A} F_K^A (r) + \sum_{R_A} g(r-R_A)F_{K'}^A (r) \\
&\Rightarrow ie^{-i\theta'}e^{iK'C_h} \left[ \sum_{R_A} g(r-R_A) \right] F_K^A (r+C_h) \\
&+ e^{iK'C_h} \left[ \sum_{R_A} g(r-R_A) \right] F_{K'}^A (r) = \\
&ie^{-i\theta'} \sum_{R_A} g(r-R_A)e^{i(K-K')R_A} F_K^A (r) + \sum_{R_A} g(r-R_A)F_{K'}^A (r) \\
&\Rightarrow e^{iK'C_h} F_{K'}^A (r+C_h) = F_{K'}^A (r).
\end{align*}$$

The scalar product between $K'$ and $C_h$ is equal to

$$K' \cdot C_h = -\frac{2\pi}{3} (m-n) = -2\pi \tilde{N} - \frac{2\pi \nu}{3},$$

where we have used the previously introduced relation $m-n = 3\tilde{N} + \nu$ with $\nu = 0$ or $\pm 1$ and $\tilde{N}$ a proper integer. Thus we have that

$$e^{iK'C_h} = e^{-i2\pi \tilde{N}}e^{-i2\pi \frac{\nu}{3}} = e^{-i\frac{2\pi \nu}{3}}$$

and consequently the boundary condition near $K'$ is

$$e^{-i\frac{2\pi \nu}{3}} F_{K'}^A (r+C_h) = F_{K'}^A (r),$$

or, equivalently

$$F_{K'}^A (r+C_h) = e^{i\frac{2\pi \nu}{3}} F_{K'}^A (r).$$

On the other hand, multiplying the second equation of (245) by $g(r-R_B)e^{-iK'R_B}$,
summing it over $R_B$ and then using the properties of the function $g$, we find

$$
(277) \quad i e^{iK'c_h} \sum_{R_B} g(r - R_B) e^{i(K' - K)\cdot R_B} F^K_B (R_B + C_h) + e^{iK' c_h} \sum_{R_B} g(r - R_B) F^{-K'}_B (R_B + C_h) =
$$

$$
 i e^{iK' c_h} \sum_{R_B} g(r - R_B) e^{i(K' - K)\cdot R_B} F^K_B (R_B) + \sum_{R_B} g(r - R_B) F^{K'}_B (R_B) \Rightarrow
$$

$$
 i e^{iK' c_h} \sum_{R_B} g(r - R_B) e^{i(K' - K)\cdot R_B} F^K_B (r + C_h) + e^{iK' c_h} \sum_{R_B} g(r - R_B) F^{K'}_B (r + C_h) =
$$

$$
 i e^{iK' c_h} \sum_{R_B} g(r - R_B) e^{i(K' - K)\cdot R_B} F^K_B (r) + \sum_{R_B} g(r - R_B) F^{K'}_B (r) \Rightarrow
$$

$$
e^{iK' c_h} F^{K'}_B (r + C_h) = F^{K'}_B (r).$$

Substituting the value of $e^{iK' c_h}$, we can rewrite this second boundary condition near $K'$ in the form

$$
(278) \quad e^{-\frac{2\pi i}{3}} F^{K'}_B (r + C_h) = F^{K'}_B (r),
$$

or, equivalently

$$
(279) \quad F^{K'}_B (r + C_h) = e^{\frac{2\pi i}{3}} F^{K'}_B (r).
$$

Thus the overall periodic boundary condition near $K'$ is

$$
(280) \quad \begin{bmatrix} F^K_A (r + C_h) \\ F^K_B (r + C_h) \end{bmatrix} = e^{\frac{2\pi i}{3}} \begin{bmatrix} F^K_A (r) \\ F^K_B (r) \end{bmatrix},
$$

which can be written in a compact form

$$
(281) \quad F^{K'} (r + C_h) = e^{\frac{2\pi i}{3}} F^{K'} (r).
$$

Substituting the form that, in the absence of an external potential, the envelope functions have near $K'$ (eq. (204))

$$
(282) \quad F_{sk}^{K'} (r) = \frac{1}{\sqrt{2Ld}} e^{ikr} e^{i\hat{\phi}_s (\kappa)} R(\alpha(\kappa)) |\tilde{s}\rangle = \frac{1}{\sqrt{2Ld}} e^{i(k_x x + k_y y)} e^{i\hat{\phi}_s (\kappa)} R(\alpha(\kappa)) |\tilde{s}\rangle,
$$

the periodic boundary condition becomes

$$
(283) \quad \frac{1}{\sqrt{2Ld}} e^{ikr} e^{i\hat{\phi}_s (\kappa)} R(\alpha(\kappa)) |\tilde{s}\rangle = e^{\frac{2\pi i}{3}} \frac{1}{\sqrt{2Ld}} e^{ikr} e^{i\hat{\phi}_s (\kappa)} R(\alpha(\kappa)) |\tilde{s}\rangle,
$$

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or, equivalently

\[ e^{i\kappa \cdot \mathbf{C}_h} = e^{i\frac{2\pi \kappa}{3}}. \]  

This can be rewritten in the form

\[ e^{i\kappa \cdot \mathbf{L}} = e^{i\frac{2\pi \kappa}{3}} = e^{i\frac{2\pi \kappa}{3}} e^{i2\pi \tilde{N}}, \]

or, equivalently

\[ \kappa \cdot \mathbf{C}_h = \frac{2\pi \nu}{3} + 2\pi \tilde{N} \]

and thus

\[ \kappa = \frac{2\pi}{L} \left( \frac{\pi + \frac{\nu}{3}}{3} \right) = \kappa_\nu(\pi), \]

with \( \pi \) integer.

Analogously to what we have done near \( \mathbf{K} \), this condition on \( \kappa \) can be found also setting

\[ e^{i\mathbf{k} \cdot \mathbf{C}_h} = 1 \]

or, equivalently

\[ \mathbf{k} \cdot \hat{\mathbf{C}}_h = \kappa_x = (\mathbf{K}')_x + \kappa_x = \frac{2\pi}{L} \tilde{m}, \]

which (using eq. (274)) becomes

\[ \kappa_x = \frac{2\pi}{L} \tilde{m} - (\mathbf{K}')_x = \frac{2\pi}{L} \tilde{m} - \mathbf{K}' \cdot \mathbf{C}_h = \frac{2\pi}{L} \tilde{m} + \frac{2\pi}{L} \tilde{N} + \frac{2\pi}{3L} \nu = \frac{2\pi}{L} (\tilde{m} + \tilde{N} + \frac{\nu}{3}) = \frac{2\pi}{L} (\tilde{\pi} + \frac{\nu}{3}) = \kappa_\nu(\tilde{\pi}) \]

(with \( \tilde{\pi} \equiv \tilde{m} + \tilde{N} \)).

If we substitute this condition on \( \kappa_x \) in the dispersion relations of graphene, we find

\[ E_{s,\pi}(\kappa_y) = s\gamma |\kappa| = s\gamma \sqrt{\kappa_x^2 + \kappa_y^2} = s\gamma \sqrt{\tilde{\kappa}_\nu(\tilde{\pi})^2 + \kappa_y^2}, \]

where \( \kappa_y \) now is the wave vector \( \mathbf{k} \) of the nanotube and \( \kappa_y \) is the difference between the wave vector \( \mathbf{k} \) of the nanotube and the component of \( \mathbf{K}' \) along \( y \).

On the other hand, if, starting from eq. (204), we choose as arbitrary phase \( \tilde{\phi}_s = \alpha/2 \) and then we enforce the condition on \( \kappa_x \), we find as envelope functions in the carbon
nanotube near $K^\prime$: 

\begin{equation}
F_{s\kappa}^{K^\prime}(r) = \frac{1}{\sqrt{2L\ell}} e^{i\kappa_x x + i\kappa_y y} e^{i\tilde{\phi}_s} \begin{bmatrix} e^{i\frac{\tilde{\phi}_s}{2}} & 0 \\ 0 & e^{-i\frac{\tilde{\phi}_s}{2}} \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} i s \\ 1 \end{bmatrix} =
\end{equation}

\begin{equation}
= \frac{1}{2\sqrt{L\ell}} e^{i(\kappa_x x + \kappa_y y)} \begin{bmatrix} is e^{i\frac{\tilde{\phi}_s}{2}} \\ e^{-i\frac{\tilde{\phi}_s}{2}} \end{bmatrix} = \frac{1}{2\sqrt{L\ell}} e^{i(\kappa_x x + \kappa_y y)} \begin{bmatrix} i s e^{i\alpha} \\ 1 \end{bmatrix} =
\end{equation}

\begin{equation}
= \frac{1}{2\sqrt{L\ell}} \begin{bmatrix} s e^{i(\frac{\pi}{2} + \alpha)} \\ 1 \end{bmatrix} e^{i\kappa_x x + i\kappa_y y} =
\end{equation}

\begin{equation}
= \frac{1}{2\sqrt{L\ell}} \begin{bmatrix} s\tilde{b}_\nu(\tilde{\pi}, \kappa_y) \\ 1 \end{bmatrix} e^{i\tilde{\mu}_\nu(\tilde{\pi}) x + i\kappa_y y} = F_{s\kappa\nu}^{K^\prime}(r),
\end{equation}

where (using the definition of the angle $\alpha$: see eq. (193))

\begin{equation}
\tilde{b}_\nu(\tilde{\pi}, \kappa_y) = e^{i(\frac{\pi}{2} + \alpha)} = \frac{\kappa_x + i\kappa_y}{\sqrt{\kappa_x^2 + \kappa_y^2}} = \frac{\tilde{\kappa}_\nu(\tilde{\pi}) + i\kappa_y}{\sqrt{\tilde{\kappa}_\nu(\tilde{\pi})^2 + \kappa_y^2}}.
\end{equation}
8. – Extended version of the calculations at pp. 564–565

Let us now enforce the boundary conditions on $\Phi_B^K(y)$ and $\Phi_A^K(y)$:

\begin{align}
(325) \quad \Phi_B^K(0) = 0 \Rightarrow C + D = 0 \Rightarrow D = -C; \\
\Phi_A^K(\bar{W}) = 0 \Rightarrow \frac{\gamma}{\mathcal{E}}((\kappa'_x + z')Ce^{z'\bar{W}} + (\kappa'_x - z')De^{-z'\bar{W}}) = 0 \Rightarrow \\
(k'_x + z')Ce^{z'\bar{W}} - (k'_x - z')Ce^{-z'\bar{W}} = 0 \Rightarrow \\
e^{-2z'\bar{W}} = \frac{k'_x + z'}{k'_x - z'} = \frac{(-k'_x) - z'}{(-k'_x) + z'},
\end{align}

which is equal to eq. (307) if we substitute $\kappa_x$ with $-\kappa'_x$.

Here we consider again real values of $\kappa'_x$.

If we graphically represent (fig. 11, with $z$ substituted with $z'$, $\kappa_x$ with $-\kappa'_x$, and $-\kappa_x$ with $\kappa'_x$) the two functions $f_1(z') = e^{-2z'\bar{W}}$ and $f_2(z') = ((-\kappa'_x) - z')/((-\kappa'_x) + z')$, we see that (apart from $z' = 0$, which corresponds to identically null $\Phi$'s) there is an intersection between $f_1$ and $f_2$ for a real value of $z'$ (and thus eq. (325) has a real solution $z'$) only if $-\kappa'_x > 0$ (i.e. if $\kappa'_x < 0$) and if $f_1(z')$ is steeper than $f_2(z')$ in $z' = 0$, i.e. if

\begin{align}
&\left| \left[ \frac{d}{dz'} f_1(z') \right]_{z'=0} \right| > \left| \left[ \frac{d}{dz'} f_2(z') \right]_{z'=0} \right| \\
&\left| -2\bar{W}e^{-2z'\bar{W}} \right|_{z'=0} > \left| \left[ \frac{1}{(-\kappa'_x) + z'} - \frac{(-\kappa'_x) - z'}{((-\kappa'_x) + z')^2} \right]_{z'=0} \right| = \\
&\left| \frac{(-\kappa'_x) + z' + (-\kappa'_x) - z'}{((-\kappa'_x) + z')^2} \right|_{z'=0} = \left| \left[ \frac{2(-\kappa'_x)}{((-\kappa'_x) + z')^2} \right]_{z'=0} \right| = 2\bar{W} > \frac{2(-\kappa'_x)}{(-\kappa'_x)^2} \Rightarrow \bar{W} > \frac{1}{-\kappa'_x} \Rightarrow -\kappa'_x > \frac{1}{\bar{W}} \Rightarrow \kappa'_x < -\frac{1}{\bar{W}}.
\end{align}

If instead $\kappa'_x > -1/\bar{W}$, eq. (325) does not have real solutions $z'$ (apart from $z' = 0$).

In the case of real $z'$, from eq. (325) we can find that

\begin{align}
(326) \quad e^{-2z'\bar{W}} = \frac{(-\kappa'_x) - z'}{(-\kappa'_x) + z'} \Rightarrow (-\kappa'_x)e^{-2z'\bar{W}} + z'e^{-2z'\bar{W}} = (-\kappa'_x) - z' \Rightarrow \\
(-\kappa'_x)(1 - e^{-2z'\bar{W}}) = z'(1 + e^{-2z'\bar{W}}) \Rightarrow \\
-k'_x = \frac{z'}{1 - e^{-2z'\bar{W}}} = \frac{z'e^{z'\bar{W}} + e^{-z'\bar{W}}}{e^{z'\bar{W}} - e^{-z'\bar{W}}} = \frac{z'}{\tanh(z'\bar{W})} \Rightarrow \\
\kappa'_x = -\frac{z'}{\tanh(z'\bar{W})},
\end{align}

($z' = 0$ does not have to be considered) and thus

\begin{align}
\kappa'_x = -\frac{z'}{\tanh(z'\bar{W})}.
\end{align}
We can write (exploiting what we have found from the boundary conditions) that

\[
\Phi_K(y) = \frac{\gamma}{E} \left( (\kappa' + z')Ce^{z'y} + (\kappa' - z')De^{-z'y} \right) = \\
\frac{\gamma}{E} \left( (\kappa' + z')Ce^{z'y} - (\kappa' - z')Ce^{-z'y} \right) = \\
\frac{\gamma}{E} \left( \kappa'(e^{z'y} - e^{-z'y}) + z'(e^{z'y} + e^{-z'y}) \right) = \\
\frac{\gamma}{E} 2C (\kappa'_x \sinh(z'y) + z' \cosh(z'y)) = \\
2C \frac{\gamma}{E} z' \frac{\cosh(z'\tilde{W}) \sinh(-z'y) + \sinh(z'\tilde{W}) \cosh(-z'y)}{\sinh(z'\tilde{W})} = \\
2C \left( \frac{\gamma}{E} z' \frac{\sinh(z'(\tilde{W} - y))}{\sinh(z'\tilde{W})} \right),
\]

where in the last step we have exploited the fact that, due to eq. (327), the product between \(\gamma/E\) and \(z'/\sinh(z'\tilde{W})\) can only be equal to +1 (if the two quantities have the same sign) or −1 (if they have opposite signs).

Moreover we have that

\[
\Phi_K'(y) = Ce^{z'y} + De^{-z'y} = Ce^{z'y} - C(e^{z'y} - e^{-z'y}) = 2C \sinh(z'y).
\]

These are edge states, each one exponentially localized on one edge of the ribbon.

Also in this case, these edge states correspond to bands flattened towards \(E = 0\). Since the Dirac point \(K'\), folded into the Brillouin zone \((-\pi/a, \pi/a)\) of the zigzag nanoribbon, corresponds to \(k_x = 4\pi/(3a) - 2\pi/a = -2\pi/(3a)\), the condition \(\kappa'_x < -1/\tilde{W}\) is equivalent to \(\kappa'_x = K'_x + \kappa'_x < -2\pi/(3a) - 1/\tilde{W}\). Therefore also in the region \(-\pi/a < k_x < -2\pi/(3a) - 1/\tilde{W}\) we have two bands flattened towards \(E = 0\), which confirms the metallic nature of zigzag nanoribbons.
Let us now instead consider the imaginary solutions \( z' = \imath \kappa'_n \) (with \( \kappa'_n \) real) of eq. (325). In this case the dispersion relation \( E = \pm \gamma \sqrt{\kappa'_x^2 - z'^2} \) becomes \( E = \pm \gamma \sqrt{\kappa'_x^2 + \kappa'_n^2} \). The solutions are given by

\[
(329) \quad e^{-2z' \tilde{W}} = \frac{\kappa'_x + z'}{\kappa'_x - z'} \Rightarrow \\
e^{-i2\kappa'_n \tilde{W}} = \frac{\kappa'_x + i\kappa'_n}{\kappa'_x - i\kappa'_n} = \frac{\sqrt{\kappa'_x^2 + \kappa'_n^2}}{e^{i2\tilde{W}(\kappa'_x + i\kappa'_n)}} = \frac{e^{i2\tilde{W}(\kappa'_x + i\kappa'_n)}}{e^{-i2\tilde{W}(\kappa'_x + i\kappa'_n)}} = \\
k'_n \tilde{W} = -\tilde{W}(\kappa'_x + i\kappa'_n) - \pi m \Rightarrow \tan(k'_n \tilde{W}) = \frac{\kappa'_n}{k'_x} = -\frac{k'_n}{\tan(k'_n \tilde{W})}
\]

(with \( m \) integer); \( \kappa'_n = 0 \) corresponds to identically null \( \Phi \)'s and thus does not have to be considered. We have that

\[
(330) \quad \left( \frac{E}{\gamma} \right)^2 = \kappa'_x^2 + \kappa'_n^2 = \left( -\frac{\kappa'_n}{\tan(k'_n \tilde{W})} \right)^2 + \kappa'_n^2 = \left( \cos^2 (k'_n \tilde{W}) + 1 \right) \frac{1}{\tan(k'_n \tilde{W})} = \\
\frac{\cos^2 (k'_n \tilde{W}) + \sin^2 (k'_n \tilde{W})}{\sin^2 (k'_n \tilde{W})} \Rightarrow |E| = \left| \frac{\kappa'_n}{\tan(k'_n \tilde{W})} \right|,
\]

since (for the properties of the sin function) \( |\sin(k'_n \tilde{W})| < |k'_n \tilde{W}| = |k'_n| \tilde{W} \), we see that now

\[
\left| \frac{E}{\gamma} \right| |\kappa'_n| \tilde{W} = 1
\]

In this case we can write (exploiting what we have found from the boundary conditions) that

\[
(331) \quad \Phi_A(y) = \frac{\gamma}{E} \left( (k'_x + i\kappa'_n)Ce^{i\kappa'_n y} + (k'_x - i\kappa'_n)De^{-i\kappa'_n y} \right) = \\
\frac{\gamma}{E} \left( (k'_x + i\kappa'_n)Ce^{i\kappa'_n y} - (k'_x - i\kappa'_n)Ce^{-i\kappa'_n y} \right) = \\
\frac{\gamma}{E} C \left( k'_x(e^{i\kappa'_n y} - e^{-i\kappa'_n y}) + i\kappa'_n(e^{i\kappa'_n y} + e^{-i\kappa'_n y}) \right) = \\
\frac{\gamma}{E} 2iC(\kappa'_x \sin(k'_n y) + \kappa'_n \cos(k'_n y)) = \\
2iC \frac{\gamma}{E} \left( -\frac{\kappa'_n}{\tan(k'_n \tilde{W})} \sin(k'_n y) + \kappa'_n \cos(k'_n y) \right) = \\
2iC \frac{\gamma}{E} \left( \frac{\kappa'_n}{\sin(k'_n \tilde{W})} \sin(k'_n (\tilde{W} - y)) \right) = \\
2iC \frac{\gamma}{E} \left( \frac{\kappa'_n}{\sin(k'_n \tilde{W})} \sin(k'_n (\tilde{W} - y)) \right),
\]
where in the last step we have taken advantage of the fact that, due to eq. (330), the product between $\gamma/E$ and $\kappa_n'/\sin(\kappa_n' W)$ can only be equal to $+1$ (if the two quantities have the same sign) or $-1$ (if they have opposite signs).

Moreover we have that

$$\Phi^{K'}_B(y) = Ce^{i\kappa_n'y} + De^{-i\kappa_n'y} = Ce^{i\kappa_n'y} - Ce^{-i\kappa_n'y} = C(e^{i\kappa_n'y} - e^{-i\kappa_n'y}) = C2i\sin(\kappa_n'y).$$

These are confined states extending all over the ribbon.

Obviously, once the expressions of the functions $\Phi$ have been obtained, the overall wave function is given by the equations (296), (297) and (299).
Case II-C

Finally, eqs. (360) are satisfied also if

\[
\begin{align*}
B &= 0, \\
\sinh(\kappa_{ni}\tilde{W})\cos((\kappa_{nr} - K)\tilde{W}) - i\cosh(\kappa_{ni}\tilde{W})\sin((\kappa_{nr} - K)\tilde{W}) &= 0.
\end{align*}
\]

If we separately equate to zero the real and imaginary part of the second equation, we find

\[
\begin{align*}
B &= 0, \\
\sinh(\kappa_{ni}\tilde{W})\cos((\kappa_{nr} - K)\tilde{W}) &= 0, \\
\cosh(\kappa_{ni}\tilde{W})\sin((\kappa_{nr} - K)\tilde{W}) &= 0.
\end{align*}
\]

Since the hyperbolic cosine is never equal to zero, these become

\[
\begin{align*}
B &= 0, \\
\sinh(\kappa_{ni}\tilde{W}) \cos((\kappa_{nr} - K)\tilde{W}) &= 0, \\
\sin((\kappa_{nr} - K)\tilde{W}) &= 0.
\end{align*}
\]

However, when the sine of an angle is equal to zero, the cosine of that angle is certainly different from zero; therefore the previous equations become

\[
\begin{align*}
B &= 0, \\
\sinh(\kappa_{ni}\tilde{W}) &= 0, \\
\sin((\kappa_{nr} - K)\tilde{W}) &= 0.
\end{align*}
\]

Since the hyperbolic sine is null only when its argument is null, we conclude that in this case:

\[
\begin{align*}
B &= 0, \\
\kappa_{ni} &= 0, \\
\sin((\kappa_{nr} - K)\tilde{W}) &= 0, \\
\Rightarrow \\
B &= 0, \\
\kappa_n &\text{ real}, \\
\sin((\kappa_n - K)\tilde{W}) &= 0.
\end{align*}
\]

Due to the fact that $B = 0$, also $C = -iB = 0$ (while $D = -iA$).

Instead the consequence of the condition on $\sin((\kappa_n - K)\tilde{W})$ is

\[
\begin{align*}
\sin((\kappa_n - K)\tilde{W}) &= 0 \Rightarrow (\kappa_n - K)\tilde{W} = n\pi \Rightarrow \\
\kappa_n - K &= n\frac{\pi}{\tilde{W}} \Rightarrow \kappa_n = n\frac{\pi}{\tilde{W}} + K.
\end{align*}
\]
In this case the Φ functions (346) are equal to

\[
\begin{align*}
\Phi^K_A(y) &= \frac{\gamma}{E} ((\kappa_x - i\kappa_n)Ae^{i\kappa_n y} + (\kappa_x + i\kappa_n)Be^{-i\kappa_n y}) = \\
\Phi^K_B(y) &= Ae^{i\kappa_n y} + Be^{-i\kappa_n y} = Ae^{i\kappa_n y} = Ae^{-i\kappa_n y}, \\
\Phi^{K'}_A(y) &= \frac{\gamma}{E} ((\kappa_x + i\kappa_n)Ce^{i\kappa_n y} + (\kappa_x - i\kappa_n)De^{-i\kappa_n y}) = \\
&= -\frac{2}{E} (\kappa_x - i\kappa_n)iAe^{-i\kappa_n y} = -\frac{\gamma}{E} (\kappa_x + i\kappa_n)iAe^{i\kappa_n y}, \\
\Phi^{K'}_B(y) &= Ce^{i\kappa_n y} + De^{-i\kappa_n y} = -iAe^{-i\kappa_n y} = -iAe^{i\kappa_n y},
\end{align*}
\]

with

\[
\tilde{\kappa}_n = -\kappa_n = -\left(n \pi W + K\right) = -n \pi W - K = \tilde{n} \pi W - K
\]

(383) where \(\tilde{n} = -n\) is an integer. Clearly, if \(\kappa_n\) satisfies \(E = \pm \gamma \sqrt{\kappa_x^2 + \kappa_n^2}\), also \(\tilde{\kappa}_n = -\kappa_n\) satisfies \(E = \pm \gamma \sqrt{\kappa_x^2 + \kappa_n^2}\)