RKKY interaction in graphene

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Graphene 2004
Graphene sublattices and Brillouin zone
Bonding and anti-bonding

In isolated form, carbon has six electrons in the orbital configuration $1s^22s^22p^2$. When arranged in the honeycomb crystal, two electrons remain in the core $1s$ orbital, while the other orbitals hybridize, forming three $sp^2$ bonds and one $p_z$ orbital. The $sp^2$ orbitals form the $\sigma$ band, which contains three localized electrons. The bonding configuration among the $p_z$ orbitals of different lattice sites generates a valence band, or $\pi$-band, containing one electron, whereas the antibonding configuration generates the conduction band ($\pi^*$), which is empty.
Dirac points and dispersion law

**Figure**: Brillouin zone centered around the Γ point and Dirac cone resulting from the linearization of tight-binding spectrum around the $K$ points (blue circles).
Nearest and next–nearest neighbor hopping model

\[ H = \begin{pmatrix} -t' \sum e^{i \mathbf{k} \cdot \mathbf{a}} & -t \sum \delta_i e^{i \mathbf{k} \cdot \delta_i} \\ -t \sum \delta_i e^{-i \mathbf{k} \cdot \delta_i} & -t' \sum e^{i \mathbf{k} \cdot \mathbf{a}} \end{pmatrix}, \]
Dispersion law

\[ E_{\pm}(\mathbf{k}) = \pm t \sqrt{3 + f(\mathbf{k}) - t'f(\mathbf{k})}, \]

\[ f(\mathbf{k}) = \sum_{\delta_i} e^{ik \cdot \delta_i} = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2} k_y a\right) \cos\left(\frac{3}{2} k_y a\right). \]

At the vertices of the Brillouin zone

\[ \mathbf{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right), \quad \mathbf{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right) \]

\[ f(\mathbf{K}) = f(\mathbf{K}') = -3, \]

hence the Brillouin zones merge there.
The general tight-binding Hamiltonian

\[
H = \begin{vmatrix}
- \sum_a t'(a) e^{ik \cdot a} & - \sum_a t(a + \delta) e^{ik \cdot (a + \delta)} \\
- \sum_a t^*(a + \delta) e^{-ik \cdot (a + \delta)} & - \sum_a t'(a) e^{ik \cdot a}
\end{vmatrix},
\]

where \( a \) is an arbitrary lattice vector, and \( \delta \) is any (fixed) vector connecting two sites of different sub-lattices. The dispersion law thus is given by equation

\[
F(E, k) = 0,
\]

where

\[
F(E, k) = \left[ E + \sum_a t'(a) e^{ik \cdot a} \right]^2 - \left| \sum_a t(a + \delta) e^{ik \cdot (a + \delta)} \right|^2
\]
Merging of the zones

\[ \sum_a t(a + \delta)e^{iK \cdot (a+\delta)} = 0 \]

\( t(a + \delta) \) realizes the \( A_1 \) (unit) representation of the point symmetry group \( C_{3v} \), and \( e^{iK \cdot (a+\delta)} \), \( e^{iK' \cdot (a+\delta)} \) realize \( E \) representation of the group.

On the other hand, generally

\[ \sum_a t'(a)e^{iK \cdot a} \neq 0. \quad (1) \]

This is because \( t'(a) \) realizes the \( A_1 \) representation of the point symmetry group \( C_{6v} \), and \( e^{iK \cdot a} \), \( e^{iK' \cdot a} \) realize representation \( A_1 + B_1 \).
Linear spectrum

In mathematics the Dirac points are called conical points of the surface; if the surface is given by

\[ F(E, k) = 0, \]

the conditions for the conical points are

\[ \frac{\partial F}{\partial E} = 0, \quad \frac{\partial F}{\partial k} = 0. \]

\[ F(E, k) = \left[ E + \sum_{\mathbf{a}} t'(\mathbf{a}) e^{i\mathbf{k} \cdot \mathbf{a}} \right]^2 - \left| \sum_{\mathbf{a}} t(\mathbf{a} + \delta) e^{i\mathbf{k} \cdot (\mathbf{a} + \delta)} \right|^2 \]
History of RKKY

RKKY stands for Ruderman-Kittel-Kasuya-Yosida and refers to a coupling mechanism of nuclear magnetic moments or magnetic ions in a normal metal by means of an exchange interaction with the conduction electrons. The RKKY interaction was originally proposed as a means of explaining unusually broad nuclear spin resonance lines that had been observed in natural metallic silver.
Physical system
RKKY interaction in metals

Total Hamiltonian

\[ H_T = H - JS_i \cdot s_i - JS_j \cdot s_j, \]

where \( H \) is the Hamiltonian of free electrons, \( S_i \) is the spins of the impurity and \( s_i \) is the spin of itinerant electrons at site \( i \).

\[ H_{\text{RKKY}} = \frac{J^2}{\mu_0 (g \mu_B)^2} \frac{2k_F R_{ij} \cos(2k_F R_{ij}) - \sin(2k_F R_{ij})}{(2k_F R_{ij})^4} S_i \cdot S_j \]
Adatom

**Figure**: Graphene honeycomb lattice with an adatom sitting on top of carbon atom.
The correction to the thermodynamic potential

\[ H_T = H + H_{\text{int}} \]

\[ \Delta \Omega = -T \ln \left< S \right> \equiv -T \ln \text{tr} \left\{ S \cdot e^{-H/T} / Z \right\} \]

where the \( S \)-matrix is

\[ S = \exp \left\{ - \int_0^{1/T} H_{\text{int}}(\tau) d\tau \right\} \]

\[ H_{\text{int}}(\tau) = e^{\tau(H-\mu \hat{N})} H_{\text{int}} e^{-\tau(H-\mu \hat{N})} \]
Second order term

\[ H_{\text{int}} = -JS_i \cdot s_i - JS_j \cdot s_j, \]

\[ s_i = \frac{1}{2} c_{i\alpha}^\dagger \sigma_{\alpha\beta} c_{i\beta}, \]

the second order term of the expansion is

\[ \Delta \Omega = \frac{J^2}{4} \sum_{\alpha\beta\gamma\delta} T \int_0^{1/T} \int_0^{1/T} d\tau_1 d\tau_2 \left\langle T_{\tau} \left\{ c_{i\alpha}^\dagger(\tau_1) c_{i\beta}(\tau_1) c_{j\gamma}^\dagger(\tau_2) c_{j\delta}(\tau_2) \right\} \right\rangle. \]
Wick theorem

For non-interacting electrons

\[
\langle T_\tau \left\{ c_{i\alpha}(\tau_1) c_{i\beta}(\tau_1) c_{j\gamma}^\dagger(\tau_2) c_{j\delta}(\tau_2) \right\} \rangle
\]

\[
= - \langle T_\tau \left\{ c_{i\beta}(\tau_1) c_{j\gamma}^\dagger(\tau_2) \right\} \rangle \langle T_\tau \left\{ c_{j\delta}(\tau_2) c_{i\alpha}(\tau_1) \right\} \rangle
\]

\[
G_{\beta\gamma}(i, j, \tau_1 - \tau_2) = - \langle T_\tau \left\{ c_{i\beta}(\tau_1) c_{j\gamma}^\dagger(\tau_2) \right\} \rangle
\]

\[
= - \delta_{\beta\gamma} \langle T_\tau \left\{ c_i(\tau_1) c_j^\dagger(\tau_2) \right\} \rangle
\]

is the Matsubara Green’s function.
Spin indices summation

\[
\sum_{\alpha \beta \gamma \delta} S_i \cdot \sigma_{\alpha \beta} S_j \cdot \sigma_{\gamma \delta} = \sum_{\alpha \beta} S_i \cdot \sigma_{\alpha \beta} S_j \cdot \sigma_{\beta \alpha} = S_i \cdot S_j,
\]

\[
\Delta \Omega = -J^2 \chi_{ij} S_i \cdot S_j,
\]

where

\[
\chi_{ij} = -\frac{1}{4} \int_0^{1/T} G(i, j; \tau)G(j, i; -\tau) d\tau
\]
Thus we obtain

\[ H_{\text{RKKY}} = -J^2 \chi_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \]

where \( \chi_{ij} \) is the free electrons static real space spin susceptibility.
Matsubara Green’s function

The Green’s function can be easily written down using representation of eigenvectors and eigenvalues of the operator $H$

$$(H - E_n) u_n = 0.$$ 

It is

$$G(i, j; \tau) = \sum_n u_n^*(i) u_n(j) e^{-\xi_n \tau} \begin{cases} - (1 - n_F(\xi_n)), & \tau > 0 \\ n_F(\xi_n), & \tau < 0 \end{cases},$$

where $\xi_n = E_n - \mu$, and $n_F(\xi) = (e^{\beta \xi} + 1)^{-1}$ is the Fermi distribution function.
Bipartite lattice we’ll understand in the sense, that all the sites can be divided in two sublattices, and there is only inter–sublattice hopping (no intra–sublattice hopping). Thus the Hamiltonian $H$ in matrix representation is

$$H = \begin{pmatrix} 0 & T \\ T^\dagger & 0 \end{pmatrix},$$

where $T$ is some matrix $N \times M$. 
Graphene lattice consists of two sublattices

\[ H = \sum_{\langle ij \rangle} t_{ij} c_i^\dagger c_j. \]
Mathematic preliminaries

\[ \tilde{H} = \begin{pmatrix} 0 & B \\ C & 0 \end{pmatrix}. \]

Secular equation

\[ \begin{vmatrix} -EI & B \\ C & -EI \end{vmatrix} = 0. \]

Determinant of the block matrix

\[ \begin{vmatrix} A & B \\ C & D \end{vmatrix} = |A| \left| D - CA^{-1}B \right|. \]

\[ \left| E^2 I_{M \times M} - CB \right| = 0. \]
Symmetry of the spectrum and the wave functions

The spectrum is symmetric, that is non-zero eigenvalues of the matrix $H$ are present in pairs $(E, -E)$.

Eigenfunctions equation

$$\begin{pmatrix} -E_n I & T \\ T^\dagger & -E_n I \end{pmatrix} u_n = 0,$$

Hence

$$u_{\bar{n}}(i) = \pm u_n(i),$$

where $u_n$ is the eigenfunction corresponding to $E_n$ and $u_{\bar{n}}$ is the eigenfunction corresponding to $-E_n$, and in the r.h.s. there is $+$ if the site $i$ belongs to one sublattice, and there is $-$ if the site belongs to the opposite sublattice.
Symmetry of the Green’s function

\[
G(i, j; \tau) = \sum_n u_n^*(i)u_n(j)e^{-\xi \tau} \times \begin{cases} 
- (1 - n_F(\xi_n)), & \tau > 0 \\
n_F(\xi_n), & \tau < 0 
\end{cases},
\]

\[
u_{\bar{n}}(i) = \pm u_n(i),
\]

For \( \mu = 0 \)

\[
n_F(\xi_m) = 1 - n_F(\xi_m).
\]
Symmetry of different terms in the Green’s function

\[ G(i, j; \tau) = \sum_n u_n^*(i)u_n(j)e^{-\xi_n \tau} \times \begin{cases} - (1 - n_F(\xi_n)), & \tau > 0 \\ n_F(\xi_n), & \tau < 0 \end{cases}, \]

The terms with non-zero energy are pairwise antisymmetric (with respect to simultaneous transformation \( \tau \rightarrow -\tau, \) \( i \leftrightarrow j \) and complex conjugation) for the sites \( i \) and \( j \) belonging to the same sublattice, and pairwise symmetric for the sites \( i \) and \( j \) belonging to opposite sublattices. The term (terms) with \( E = 0 \) is antisymmetric with respect to the above mentioned transformation, no matter which sublattices the sites belong to.
Symmetry of the Green’s function

For the sites $i$ and $j$ belonging to the same sublattice

$$G(j, i; -\tau) = -G^*(i, j; \tau).$$

For the sites $i$ and $j$ belonging to different sublattices

$$G(j, i; -\tau) = G^*(i, j; \tau),$$

provided there are no zero energy states, or we can neglect there contribution to the Green’s function.
Symmetry of the RKKY interaction

\[ G(j, i; -\tau) = \mp G^*(i, j; \tau). \]

\[ \chi_{ij} = -\frac{1}{4} \int_0^{1/T} G(i, j; \tau)G(j, i; -\tau) d\tau \]

The RKKY interaction on the bipartite lattice at half filling is ferromagnetic between impurities on the same sublattice and is antiferromagnetic between impurities on opposite sublattices (under the above stated restriction).
Graphene wave functions

The wave function for the momentum around Dirac points

$$\psi_{\nu, k}(k) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta_k/2} \\ \nu e^{i\theta_k/2} \end{pmatrix},$$  \hspace{1cm} (2)$$

$$\psi_{\nu, k'}(k) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\theta_k/2} \\ \nu e^{-i\theta_k/2} \end{pmatrix},$$  \hspace{1cm} (3)$$

where $$\alpha = \pm 1$$ corresponds to electron and hole band respectively.
Graphene Green’s functions

\[ G(i,j;\tau) = \sum_n u_n^*(i)u_n(j)e^{-\xi_n\tau} \begin{cases} -(1 - n_F(\xi_n)), & \tau > 0 \\ n_F(\xi_n), & \tau < 0 \end{cases}, \]

the \( \sum_n \) turns into \( \frac{a^2}{(2\pi)^2} \int d^2p \)

\[ u_n(i) = e^{ip\cdot R_i}\psi_p, \]

where \( \psi_p \) is the appropriate component of spinor electron wave-function (depending upon which sublattice the magnetic adatom belongs to) in momentum representation.
Graphene Green’s functions

For \( i \) and \( j \) belonging to the same sublattice

\[
G^{AA}(i,j; \tau > 0) = -\frac{1}{2} \left[ e^{iK \cdot R_{ij}} + e^{iK' \cdot R_{ij}} \right] \frac{a^2}{(2\pi)^2} \int d^2k e^{-E_+(k)\tau},
\]

and for \( i \) and \( j \) belonging to different sublattices

\[
G^{AB}(i,j; \tau > 0) = \frac{1}{2} \frac{a^2}{(2\pi)^2} \int d^2k e^{-E_+(k)\tau} \times \left[ e^{i(K+k) \cdot R_{ij}-i\theta_k} + e^{i(K'+k) \cdot R_{ij}+i\theta_k} \right].
\]

For \( \tau < 0 \) we should change the sign of the Green’s functions and substitute \( E_- \) for \( E_+ \).
Angle integration

For isotropic dispersion law $E(k) = E(k)$

$$
\int d^2 k e^{i \mathbf{k} \cdot \mathbf{R}_{ij} - E(k) \tau} = \int_0^\infty d k k J_0(k R) e^{-E(k) \tau}
$$

$$
\int d^2 k e^{i \mathbf{k} \cdot \mathbf{R}_{ij} \pm i \theta_k - E(k) \tau} = \int_0^\infty d k k J_1(k R) e^{-E(k) \tau}
$$

($J_0$ and $J_1$ are the Bessel function of zero and first order respectively.)
Linear dispersion $E_{\pm}(k) = \pm v_F k$

Using mathematical identity

$$\int_0^{\infty} x^{n-1} e^{-px} J_\nu(cx) \, dx = (-1)^{n-1} c^{-\nu} \frac{\partial^{n-1}}{\partial p^{n-1}} \left( \frac{\sqrt{p^2 + c^2} - p}{\sqrt{p^2 + c^2}} \right)^\nu,$$

after simple calculus we obtain

$$\chi^{AA}(R_{ij}) = \frac{a^4}{256v_F R^3} \left[ 1 + \cos((K - K') \cdot R_{ji}) \right]$$

$$\chi^{AB}(R_{ij}) = -\frac{3a^4}{256v_F R^3} \left[ 1 + \cos((K - K') \cdot R_{ji} - 2\theta_R) \right],$$

where $\theta_R$ is the angle between the vectors $K - K'$ and $R_{ij}$.

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Bilayer graphene: Bernal ($\tilde{A} - B$) stacking.
Bilayer graphene: Bernal ($\bar{A} - B$) stacking.

a) Top view of a graphene bilayer; white and black circles: top layer carbon atoms; gray and red: bottom layer.
b) four-band spectrum of the bilayer, $\pm E_{\gamma}(p)$, with $\gamma = \pm$ near the corner of the Brillouin zone.
c) Brillouin zone with high symmetry points.
d) Illustration of the four band spectrum around the $K$ point.
Low–energy modes

The low–energy modes are localized on $A$ and $\tilde{B}$ sites, we consider RKKY interaction of the magnetic adatoms siting on top of carbon atom in $A$ and/or $\tilde{B}$ sites.

$$E_{\pm}(k) = \pm \frac{k^2}{2m}$$

and wave functions

$$\psi_{\nu, k}(k) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta_k} \\ e^{i\theta_k} \end{pmatrix}$$

$$\psi_{\nu, k'}(k) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\theta_k} \\ e^{-i\theta_k} \end{pmatrix}.$$
RKKY interaction in bilayer graphene

\[ \int_0^\infty J_0(x) \exp(-px^2) x dx = \frac{1}{2p} \exp \left( -\frac{1}{4p} \right). \]

After simple calculus we obtain

\[ \chi^{AA}(\mathbf{R}_{ji}) = \frac{ma^2}{16\pi^2 R^2} \left[ 1 + \cos((\mathbf{K} - \mathbf{K}') \cdot \mathbf{R}_{ji}) \right]. \]
Frequency representation of Matsubara Green’s function

\[
\chi_{ij} = \frac{T}{4} \sum_{n,m} u_n^*(i) u_m(i) u_n(j) u_m^*(j) \sum_{\omega} \frac{1}{i\omega - \xi_n} \frac{1}{i\omega - \xi_m}
\]

where \( \omega = \pi T (2l + 1) \) (l is an integer) is Matsubara frequency.

\[
\chi_{ij} = \frac{1}{4} \sum_{n,m} u_n^*(i) u_m(i) u_n(j) u_m^*(j) \frac{n_F(\xi_m) - n_F(\xi_n)}{\xi_n - \xi_m}
\]
The way the analytic calculations shouldn’t be done

\[ \chi(q) = \sum_{\nu, \nu', p} M_{\nu, \nu', p, q} \frac{n_F [E_{\nu'}(p + q)] - n_F [E_{\nu}(p)]}{E_{\nu}(p) - E_{\nu'}(p + q)}, \]

where \( E_{\nu}(p) \) is the graphene spectrum, and \( \nu = \pm 1 \) labels the conduction and valence band.

\[ \chi(R_{ij}) = \frac{a^2}{(2\pi)^2} \int d^2q \chi(q) e^{i q \cdot R_{ij}}. \]
The way the analytic calculations can be done

\[\chi^{AA}(R_{ij}) = \frac{a^4}{4\pi^2 v_F R^3} \left[ 1 + \cos((K - K') \cdot R_{ij}) \right] \]
\[\int_0^\infty dxx J_0(x) \int_0^\infty dx' x' J_0(x') \frac{1}{x + x'} \]

\[\chi^{AB}(R_{ij}) = -\frac{a^4}{4\pi^2 v_F R^3} \left[ 1 + \cos((K - K') \cdot R_{ij}) \right] \]
\[\int_0^\infty dxx J_1(x) \int_0^\infty dx' x' J_1(x') \frac{1}{x + x'} \]
Convergence of the integrals

\[ \int_0^\infty \frac{x^\nu}{x + z} J_\nu(cx) \, dx = \frac{\pi z^\nu}{2 \cos \nu \pi} \left[ \mathbf{H}_{-\nu}(cz) - Y_{-\nu}(cz) \right], \]

\( \mathbf{H}_\nu(z) \) is the Struve function and \( Y_\nu(z) \) is the Neumann function

\[ \frac{\pi}{2} \int_0^\infty dxx^2 J_0(x) \left[ Y_0(x) - \mathbf{H}_0(x) + \frac{2}{\pi x} \right] \]

\[ \frac{\pi}{2} \int_0^\infty dxx^2 J_1(x) [Y_{-1}(x) - \mathbf{H}_{-1}(x)]. \]

The divergence of the integrals is guaranteed by the asymptotics

\( \mathbf{H}_\nu(x) - Y_\nu(x) \rightarrow \frac{1}{\sqrt{\pi \Gamma \left( \nu + \frac{1}{2} \right)}} \left( \frac{x}{2} \right)^{\nu - 1} + O \left( \left( x/2 \right)^{\nu - 3} \right) . \)
For the case of substitutional impurities

\[ \chi^{S_AS_A}(\mathbf{R}_{ij}) = \frac{\chi^{S_AS_A}}{v_F R^7} \left[ 1 + \cos((\mathbf{K} - \mathbf{K}') \cdot \mathbf{R}_{ij}) \right] \]

\[ \chi^{S_AS_B}(\mathbf{R}_{ij}) = -\frac{\chi^{S_AS_B}}{v_F R^7} \left[ 1 - \cos((\mathbf{K} - \mathbf{K}') \cdot \mathbf{R}_{ij} - 6\theta_R) \right]. \]
From Anderson to Kondo model

Figure: Intersection of the Dirac cone spectrum, $E(k) = \pm v|k|$, with the localized level $E_f = \varepsilon_0$: (b) $\varepsilon_0 > 0$, (c) $\varepsilon_0 < 0$.

$$H_{hyb} = \sum_{\lambda,\alpha,i \in \mathcal{P}} \left( v_i^\lambda c_{i\alpha}^\dagger f_{\lambda\alpha} + h.c. \right),$$

$$H_{pd} = - \sum_{\lambda,\alpha,\beta,i,j \in \mathcal{P}} J v_i^\lambda v_j^{\lambda*} S \cdot \sigma_{\alpha\beta} c_{i\alpha}^\dagger c_{j\beta}.$$
The RKKY interaction on the bipartite lattice at half filling is ferromagnetic between impurities on the same sublattice and is antiferromagnetic between impurities on opposite sublattices. The latter is true, provided there are no zero energy states.

\[ H_{RKKY} = -J^2 \chi_{ij} S_i \cdot S_j, \]

\[ \chi^{AA} (R_{ij}) = \frac{a^4}{256 v_F R^3} \left[ 1 + \cos((K - K') \cdot R_{ji}) \right] \]

\[ \chi^{AB} (R_{ij}) = -\frac{3a^4}{256 v_F R^3} \left[ 1 + \cos((K - K') \cdot R_{ji} - 2\theta_R) \right]. \]