Electron and Spin–Phonon Interaction in DNA

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Introduction: Structure of DNA

- B form is the most common form.
- Double right handed helix polymer.
- Nucleotides are the building blocks, which are formed by a base, a sugar and a phosphate group.
- Bases can be Purines (A, G) or Pyrimidines (T, C).
- The sugar is a deoxyribose sugar.
- The phosphate group act as structural support.

Introduction: Structure of DNA

- Self assembly and self recognition
- High transfer rates of charge
- Spin selectivity (CISS Effect)

Introduction: DNA in the context of molecular spintronics

- Spintronics study: Inject, manipulate and detect spin polarization and spin polarized currents.
- Individual molecules.
- DNA properties: spin polarization, spin dependent transport, long distance electron transfer, chiral induced spin selectivity.

Chiral Induced Spin Selectivity! (CISS Effect)

Introduction: DNA in the context of molecular spintronics

Chiral Induced Spin Selectivity! (CISS Effect)

Other amazing applications!

- Quantum information science, quantum computers
- Sensors
- Spin injection through molecules in spintronic devices
- Spin selective chemistry

Introduction: DNA in the context of molecular spintronics

Some open questions!

- Better understanding of the electron transport process (including the spin)
- What is the mechanism for the CISS effect?
- Origin of the high electron and spin transfer, even at room temperature
- Electron and spin-phonon coupling role in modulating and protecting these currents

Chiral Induced Spin Selectivity! (CISS Effect)

Understanding the electron-phonon and spin-phonon interaction is fundamental to understand this effect!

Introduction: DNA in the context of molecular spintronics

Understanding the electron-phonon and spin-phonon interaction is fundamental to understand this effect!

The importance of theoretical, analytical models in this context:

- DFT. Challenging for the number of atoms in the unit cell. Expensive in time. The effect of spin selectivity is underestimated by these calculations.
- Analytical methods (Tight Binding). Atomistic derivations that can derive in Hamiltonians with the relevant interactions.

Outline

- Introduction
- The Model
  - DNA structure model
  - The envelope function approximation
  - Inclusion of the vibrations
- Electron–phonon interaction in DNA
- Spin–phonon interaction in DNA
- Conclusions
The model: DNA structure model

B-DNA

Unpaired electrons at the pz orbitals

“Simple” analytical model

The model: DNA structure model

- B-form DNA with N sites per helix.

Vectors connecting nearest neighbors

\[
\tau_{1}^{A,B} = a\Delta \phi \hat{y} + \frac{b\Delta \phi}{2\pi} \hat{z},
\]

\[
\tau_{2}^{A,B} = -a\Delta \phi \hat{y} - \frac{b\Delta \phi}{2\pi} \hat{z},
\]

\[
\tau_{3} = -2a\hat{x}.
\]
The model: DNA structure model

- Modes in the double-helix DNA model.

Stretching (longitudinal) mode
Breathing (radial) mode
The model: The envelope function approximation

Wave function
\[ \Psi(r) \approx u_\mathbf{k}(r) F(r), \]

Fast oscillating wave function \quad Slowly varying envelope function

Wavefunctions used for the nearest neighbors TB model, in the DNA two-sites system:

\[ \Psi_{A\sigma}(\mathbf{R}_A) = e^{i\mathbf{K} \cdot \mathbf{R}_A} F_{A\sigma}^\mathbf{K}(\mathbf{R}_A) + e^{i\mathbf{K}' \cdot \mathbf{R}_A} F_{A\sigma}^{\mathbf{K}'}(\mathbf{R}_A), \]

\[ \Psi_{B\sigma}(\mathbf{R}_B) = e^{i\mathbf{K} \cdot \mathbf{R}_B} F_{B\sigma}^\mathbf{K}(\mathbf{R}_B) + e^{i\mathbf{K}' \cdot \mathbf{R}_B} F_{B\sigma}^{\mathbf{K}'}(\mathbf{R}_B). \]

\[ K = \frac{\pi}{2R^2}(0, a\Delta \phi, \frac{b\Delta \phi}{2\pi}), \quad K' = -K. \]

The model: The envelope function approximation

\[ \varepsilon \Psi_{A\sigma}(R_A) = \sum_{l=1}^{2} t_{R_{A\sigma},(R_A+\tau^A_l)}^{in} \Psi_{A\sigma}(R_A + \tau^A_l) \]

\[ + \sum_{l=1}^{2} V_{R_{A\sigma},(R_A+\tau^A_l)\sigma'}^{in} \Psi_{A\sigma'}(R_A + \tau^A_l) \]

\[ + t_{R_{A\sigma},(R_A+\tau^A_3)\sigma}^{out} \Psi_{B\sigma}(R_A + \tau^A_3), \]

\[ \varepsilon \Psi_{B\sigma}(R_B) = \sum_{l=1}^{2} t_{R_{B\sigma},(R_B+\tau^B_l)}^{in} \Psi_{B\sigma}(R_B + \tau^B_l) \]

\[ + \sum_{l=1}^{2} V_{R_{B\sigma},(R_B+\tau^B_l)\sigma'}^{in} \Psi_{B\sigma'}(R_B + \tau^B_l) \]

\[ + t_{R_{B\sigma},(R_B-\tau^B_3)\sigma}^{out} \Psi_{A\sigma}(R_B - \tau^B_3). \]

The model: Inclusion of the vibrations

\[ \varepsilon \Psi_{A\sigma}(\mathbf{R}_A) = \sum_{l=1}^{2} t^{\text{in}}_{R_A\sigma}(\mathbf{R}_A + \mathbf{\tau}_l^A) \Psi_{A\sigma}(\mathbf{R}_A + \mathbf{\tau}_l^A) \]

\[ + \sum_{l=1}^{2} V^{\text{in}}_{R_A\sigma}(\mathbf{R}_A + \mathbf{\tau}_l^A) \Psi_{A\sigma}(\mathbf{R}_A + \mathbf{\tau}_l^A) \]

\[ + t^{\text{out}}_{R_A\sigma}(\mathbf{R}_A + \mathbf{\tau}_3) \Psi_{B\sigma}(\mathbf{R}_A + \mathbf{\tau}_3), \]

\[ \varepsilon \Psi_{B\sigma}(\mathbf{R}_B) = \sum_{l=1}^{2} t^{\text{in}}_{R_B\sigma}(\mathbf{R}_B + \mathbf{\tau}_l^B) \Psi_{B\sigma}(\mathbf{R}_B + \mathbf{\tau}_l^B) \]

\[ + \sum_{l=1}^{2} V^{\text{in}}_{R_B\sigma}(\mathbf{R}_B + \mathbf{\tau}_l^B) \Psi_{B\sigma}(\mathbf{R}_B + \mathbf{\tau}_l^B) \]

\[ + t^{\text{out}}_{R_B\sigma}(\mathbf{R}_B - \mathbf{\tau}_3) \Psi_{A\sigma}(\mathbf{R}_B - \mathbf{\tau}_3). \]

How to include phonons?

These hopping parameters depend on the hybridization between atomic orbitals of different atoms involved in the process, and therefore, they depend on the distances between atoms.

 Atomic vibrations modulate the hopping parameters

The model: Inclusion of the vibrations

\[ \varepsilon \Psi_{A\sigma}(\mathbf{R}_A) = \sum_{l=1}^{2} \left( t_{A\sigma}^{in}(\mathbf{R}_A + \mathbf{\tau}_l^{A}) \Psi_{A\sigma}(\mathbf{R}_A + \mathbf{\tau}_l^{A}) \right. \]

\[ + \sum_{l=1}^{2} V_{A\sigma}^{in}(\mathbf{R}_A + \mathbf{\tau}_l^{A}) \Psi_{A\sigma'}(\mathbf{R}_A + \mathbf{\tau}_l^{A}) \]

\[ + t_{A\sigma}^{out}(\mathbf{R}_A + \mathbf{\tau}_3) \Psi_{B\sigma}(\mathbf{R}_A + \mathbf{\tau}_3), \]

\[ \varepsilon \Psi_{B\sigma}(\mathbf{R}_B) = \sum_{l=1}^{2} \left( t_{B\sigma}^{in}(\mathbf{R}_B + \mathbf{\tau}_l^{B}) \Psi_{B\sigma}(\mathbf{R}_B + \mathbf{\tau}_l^{B}) \right. \]

\[ + \sum_{l=1}^{2} V_{B\sigma}^{in}(\mathbf{R}_B + \mathbf{\tau}_l^{B}) \Psi_{B\sigma'}(\mathbf{R}_B + \mathbf{\tau}_l^{B}) \]

\[ + t_{B\sigma}^{out}(\mathbf{R}_B - \mathbf{\tau}_3) \Psi_{A\sigma}(\mathbf{R}_B - \mathbf{\tau}_3). \]

Atomic vibrations modulate the hopping parameters

\[ t_{in,\sigma}^{in,\sigma}(\mathbf{R}_I, I + \mathbf{\tau}_l) = t_{0}^{in,\sigma} - \frac{\beta_{in,\sigma}^{in,\sigma}}{c^2} \mathbf{\tau}_l \]

\[ \cdot [\mathbf{u}_I(\mathbf{R}_I) - \mathbf{u}_I(\mathbf{R}_I + \mathbf{\tau}_l)], \]

\[ V_{in,\sigma}^{in,\sigma}(\mathbf{R}_I, I + \mathbf{\tau}_l) = V_{0}^{in} - \frac{\eta_{in} V_{0}^{in}}{c^2} \mathbf{\tau}_l \]

\[ \cdot [\mathbf{u}_I(\mathbf{R}_I) - \mathbf{u}_I(\mathbf{R}_I + \mathbf{\tau}_l)], \]

\[ c = |\mathbf{\tau}_l| \quad \text{Equilibrium distance between atoms} \]

\[ \beta_{in,\sigma}^{in,\sigma} = -\frac{c}{t_{0}^{in,\sigma}} \frac{\partial}{\partial c} t_{0}^{in,\sigma}, \quad \eta_{in} = -\frac{c}{V_{0}^{in}} \frac{\partial}{\partial c} V_{0}^{in}, \]

The model: Inclusion of the vibrations

\[ t_{in,out}^{R_I,R_I+\tau_l} = t_0^{in,out} - \frac{\beta_{in,out}}{c^2} t_0^{in,out} \tau_l^I \]
\[ \cdot [u_I(R_I) - u_I(R_I + \tau_l^I)], \]
\[ V_{in}^{R_I,R_I+\tau_l^I} = V_0^{in} - \eta^{in} V_0^{in} \frac{\tau_l^I}{c^2} \]
\[ \cdot [u_I(R_I) - u_I(R_I + \tau_l^I)], \]
\[ c = |\tau_l^I| \quad \text{Equilibrium distance between atoms} \]

\[ \beta_{in,out} = -c t_0^{in,out} \frac{\partial}{\partial c} t_0^{in,out} \]
\[ \eta^{in} = -c V_0^{in} \frac{\partial}{\partial c} V_0^{in}, \]

Optical and acoustical amplitudes

\[ \alpha^{ac} u(r) = u_A(r) + u_B(r), \]
\[ \alpha^{op} v(r) = u_A(r) - u_B(r), \]

Intra–helix displacement

\[ \varepsilon \psi_{\sigma}(R_A) = \sum_{l=1}^{2} t_{in}^{R_A,\sigma,(R_A+\tau_l^A)} \psi_{\sigma}(R_A + \tau_l^A) \]
\[ + \sum_{l=1}^{2} V_{in}^{R_A,\sigma,(R_A+\tau_l^A)} \psi_{\sigma}(R_A + \tau_l^A) \]
\[ + t_{out}^{R_A,\sigma,(R_A+\tau_l^A)} \psi_{\sigma}(R_A + \tau_l^A), \]

Inter–helix displacement

\[ \varepsilon \psi_{\sigma}(R_B) = \sum_{l=1}^{2} t_{in}^{R_B,\sigma,(R_B+\tau_l^B)} \psi_{\sigma}(R_B + \tau_l^B) \]
\[ + \sum_{l=1}^{2} V_{in}^{R_B,\sigma,(R_B+\tau_l^B)} \psi_{\sigma}(R_B + \tau_l^B) \]
\[ + t_{out}^{R_B,\sigma,(R_B+\tau_l^B)} \psi_{\sigma}(R_B + \tau_l^B). \]

Electron–Photon Interaction in DNA

\[ \epsilon F_A(\mathbf{r}) \mathbf{l} = -t_{o}^{\text{in}} 2 R \nu k_y F_A(\mathbf{r}) + t_{o}^{\text{out}} (1 - 2aik_x + \frac{4\beta^{\text{out}}}{c^2} (a^2 \partial_x (\alpha^{ac} u_x - \alpha^{op} v_x) + a\alpha^{op} v_x)) 1 F_B(\mathbf{r}) \]

\[ \epsilon F_B(\mathbf{r}) \mathbf{l} = -t_{o}^{\text{in}} 2 R \nu k_y F_B(\mathbf{r}) + t_{o}^{\text{out}} (1 + 2aik_x + \frac{4\beta^{\text{out}}}{c^2} (a^2 \partial_x (\alpha^{ac} u_x - \alpha^{op} v_x) + a\alpha^{op} v_x)) 1 F_A(\mathbf{r}) \]

\[ \mathcal{H} \mathbf{F}(\mathbf{r}) = \epsilon \mathbf{F}(\mathbf{r}) \quad \mathbf{F}(\mathbf{r}) = (F^K(\mathbf{r}), F^{K'}(\mathbf{r})) \]

\[ \mathcal{H} = \begin{pmatrix} \mathcal{H}^K & 0 \\ 0 & \mathcal{H}^{K'} \end{pmatrix} \quad \mathcal{H}^{K,K'} = \begin{pmatrix} A & B \\ B & -t_{o}^{\text{in}} 2 R \nu k_y \end{pmatrix} \]

The stretching modes are decoupled from the electron transmission (at 1st order)

Breathing modes are predominant

No coupling with phonons in the intra helix elements of the Hamiltonian!

Spin–Phonon Interaction in DNA

\[ \mathcal{H}_{K,K'} = \begin{pmatrix} \mathbf{A}^\uparrow & \mathbf{A}^\downarrow \\ \mathbf{B}^\uparrow & \mathbf{B}^\downarrow \end{pmatrix} = \begin{pmatrix} -2t_0^\text{in}f^\text{in}(k)\nu & 2i\lambda_{SO}^\text{in}\gamma^\text{in}\nu \\ -2i\lambda_{SO}^\text{in}\gamma^\text{in}\nu & -2t_0^\text{in}f^\text{in}(k)\nu \\ t_0^\text{out}(f^\text{out}(k))^* & 0 \\ 0 & t_0^\text{out}(f^\text{out}(k))^* \end{pmatrix} \]

At this order we can see that the spin is coupled to the stretching modes, while breathing modes are coupled to the non–spin–flipping elements of the Hamiltonian.

\[ \gamma^\text{in} \equiv 1 + \frac{\eta^\text{in}\Delta\phi^2}{c^2} [a^2(\alpha^{ac}\partial_yu_y + \alpha^{op}\partial_yv_y) + \frac{ab}{2\pi}(\alpha^{ac}\partial_yu_z + \alpha^{op}\partial_yv_z + \alpha^{ac}\partial_zu_y + \alpha^{op}\partial_zv_y) + \frac{b^2}{4\pi^2}(\alpha^{ac}\partial_zv_z + \alpha^{op}\partial_zv_z)], \]

\[ \gamma^\text{out} \equiv \frac{2\beta^\text{out}}{c^2}(a(\alpha^{ac}\partial_xu_x - \alpha^{op}\partial_xv_x) + \alpha^{op}v_x), \]

\[ f^\text{in}(k) \equiv \Delta\phi(ak_y + \frac{b}{2\pi}k_z), \]

\[ f^\text{out}(k) \equiv 1 - 2iak_x + 2a\gamma_A^\text{out}. \]
Conclusions

- Intra-helix non spin-flip coupling only includes a second order kinetic term.
- Electron-phonon interaction is only present between helices (In the breathing modes)
- Spin-phonon interaction appears for inter helix elements
- Breathing and stretching modes participating in ET

Future work

- To include the Rashba spin orbit interaction in the model
- Calculate transport properties including the electron and spin phonon interactions
- This model can be used to describe electron transfer in other organic molecules
Collaborators and students

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TB description of the electron–phonon and spin-phonon interactions in electron transfer in DNA

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Collaborators and students

Andrés Hidalgo
Electronic Properties of Li and K on Graphene: Top, Hollow and Bridge Configurations

Dennis Alejandro Freire
Analytical Tight Binding Hamiltonian for 2D Black Phosphorus

Cristina Vaca
Quantum capacitance in graphene with adsorbed Alkali metals

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TB description of the electron–phonon and spin-phonon interactions in electron transfer in DNA

Ricardo Vera
Calculation of the differential conductance of a Graphene based Superlattice/superconductor junction using Green’s functions