Influence of vibrational modes on the electronic properties of DNA

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Outline

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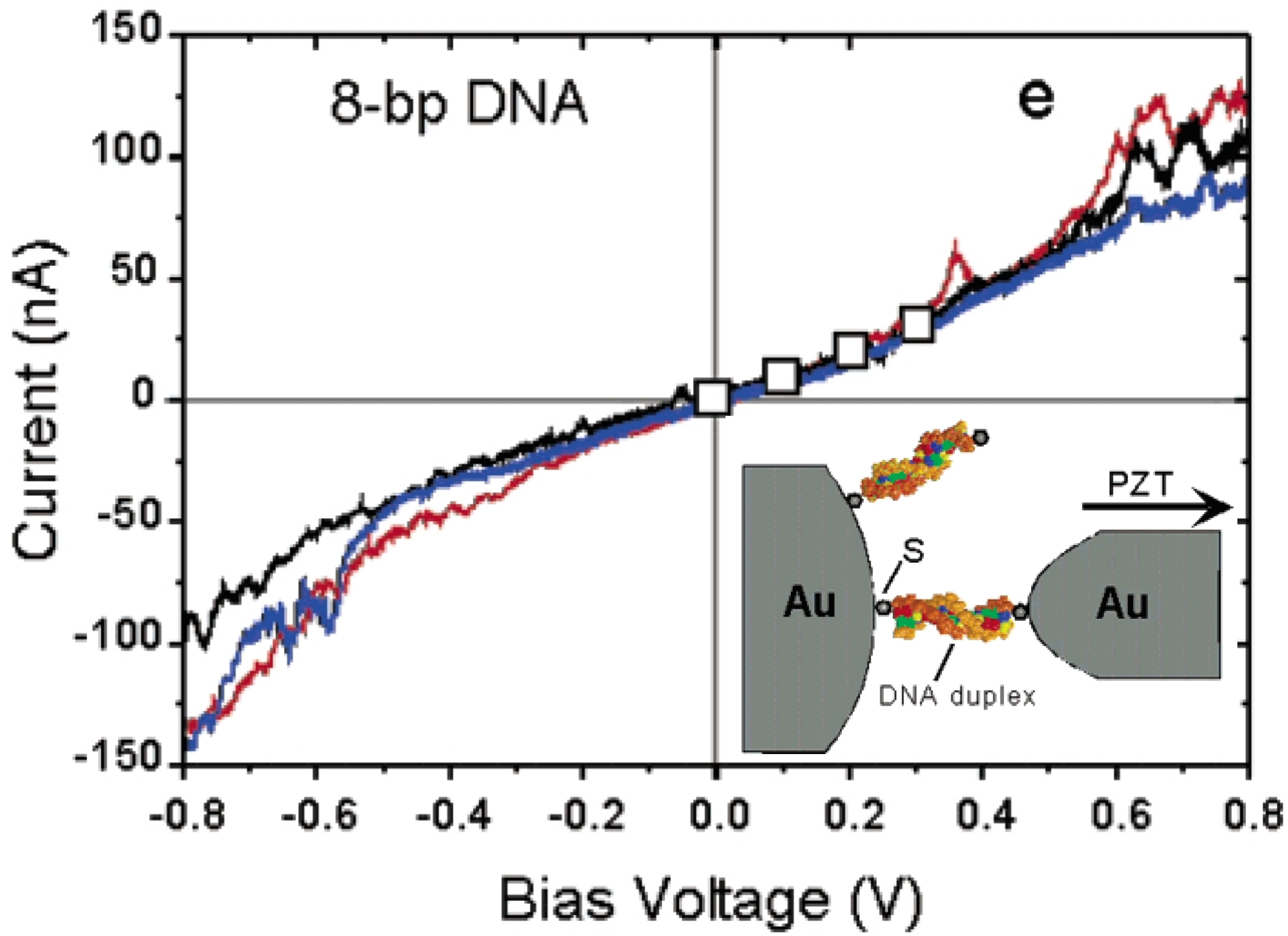
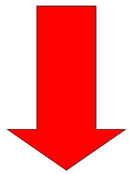
- Technique
- Results
- Conclusion

Motivation



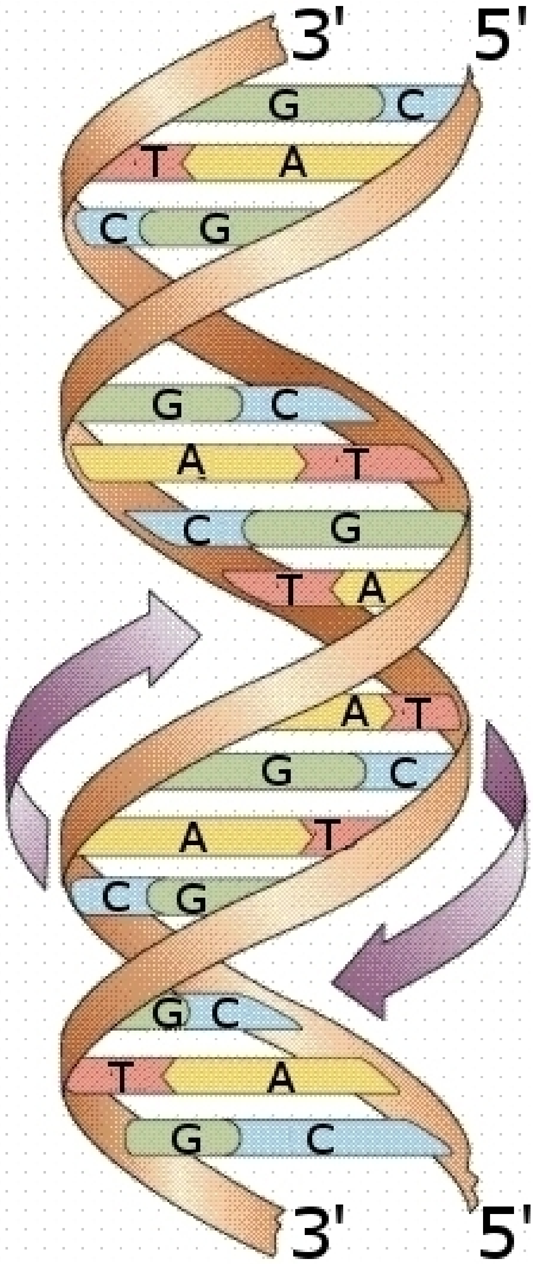
Xu et al., Nano Lett. **4,** 1105 (2004)

various experiments:
- in aqueous solution
- at room temperature



inclusion of vibrations and energy dissipation

Electronic properties of DNA



overlapping π-orbitals → electronic delocalization

- HOMO on guanine and adenine
- LUMO on cytosine and thymine
- large bandgap (~2eV) between HOMO and LUMO

consider hole transport (HOMO)

→ single *tight-binding* site per base pair

Purves et al., Life: The Science of Biology, 4th Edition

Theoretical model: Hamiltonian

$$H = H_{\rm el} + H_{\rm L/R} + H_{\rm T,L} + H_{\rm T,R} + H_{\rm bath} + H_{\rm vib} + H_{\rm el-vib}$$

$H_{\rm el}$: *tight-binding* chain with N elements (i.e. base pairs)
(ϵ_i and t_{ij} from *ab initio* calculations)

$$H_{\rm el} = \sum_i \epsilon_i a_i^\dagger a_i + \sum_{\langle ij \rangle} t_{ij} a_i^\dagger a_j$$

$H_{\rm L/R}$: non-interacting electrodes

$H_{\rm T,L}/H_{\rm T,R}$: hopping from electrode to adjacent base pair with strength $t_{\rm L/R}$ (linewidth: $\Gamma_{\rm L/R} = 2\pi\rho_e|t_{\rm L/R}|^2$)

for details see BBS et al.,Phys. Rev. B **75,** 106711 (2007)

Vibrations and el-vib coupling

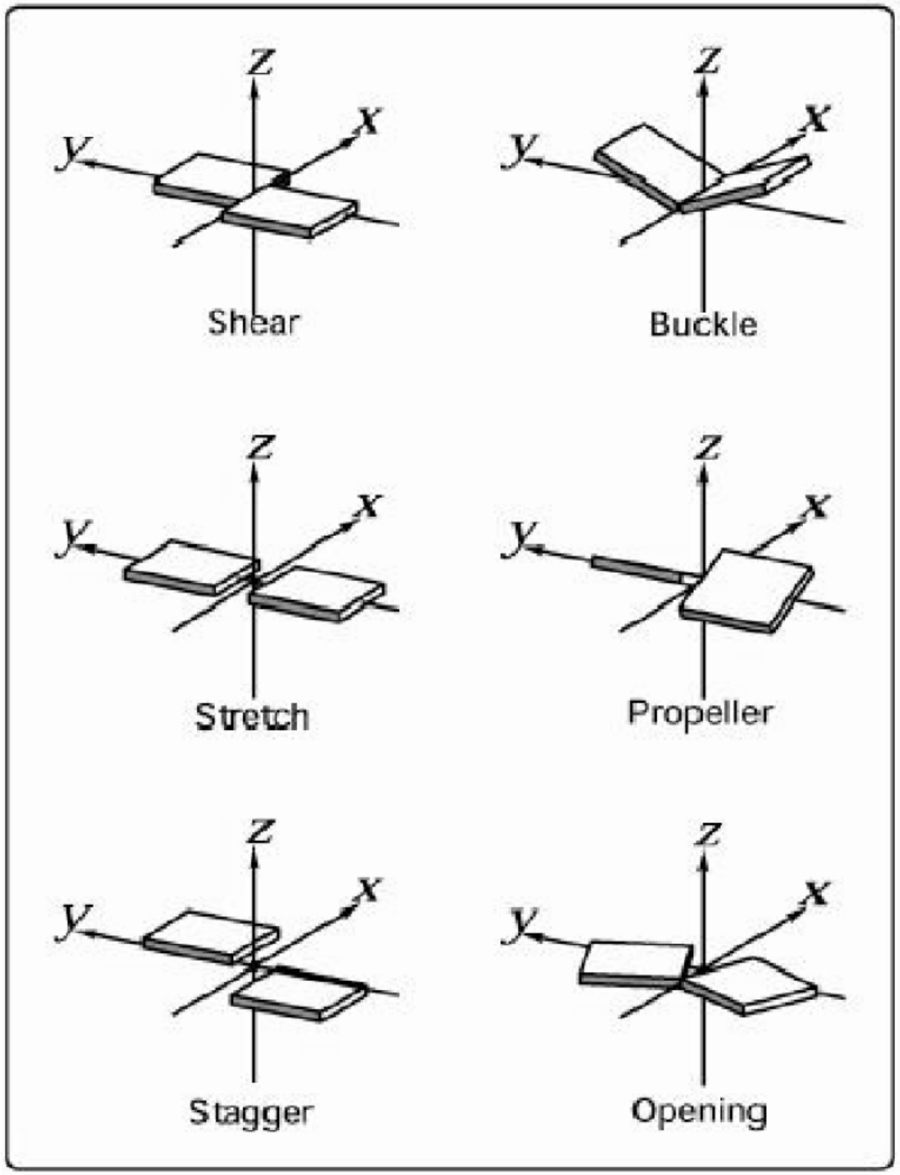
H_{vib}: vibrational modes of DNA-chain

$$H_{\mathrm{vib}} = \sum_{\alpha} \hbar\omega_\alpha B_\alpha^\dagger B_\alpha$$

$H_{\mathrm{el-vib}}$: local *and* non-local coupling of electronic and vibronic degrees of freedom of the DNA

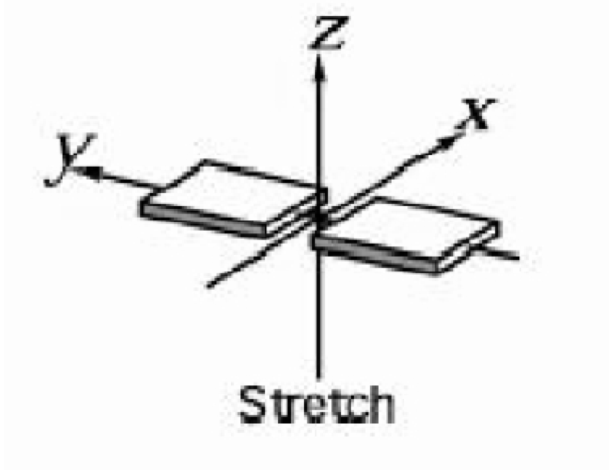
$$\begin{aligned} H_{\mathrm{el-vib}} &= \sum_{i}\sum_{\alpha} \lambda_0 a_i^\dagger a_i \left(B_\alpha + B_\alpha^\dagger\right) \\ &+ \sum_{\langle ij\rangle}\sum_{\alpha} \lambda_1 a_i^\dagger a_j \left(B_\alpha + B_\alpha^\dagger\right) \end{aligned}$$

Vibrational modes in base pairs



E. B. Starikov, Philos. Mag. **85,** 3435 (2005)

examplary mode: Stretch



$\hbar\omega$ = 16 meV (GC)

$\hbar\omega$ = 11 meV (AT)

linear coupling to local energy **ε** and hopping t

→ $|\lambda_0| \approx$ 1-10meV

$|\lambda_1| \approx$ 1-10meV

Bath

H_{bath}: vibrons coupled to (`ohmic') bath with high-frequency cut-off ω_c

- bath allows for dissipation of electronic and vibronic energy
- vibrons change from discrete modes to continuous spectra

spectral function for single vibron with resonance ω_0 :

$$D(\omega) = \frac{1}{\pi}\left(\frac{\eta(\omega)}{(\omega-\omega_0)^2+\eta(\omega)^2} - \frac{\eta(\omega)}{(\omega+\omega_0)^2+\eta(\omega)^2}\right)$$

$\eta(\omega) = 0.05\,\omega\,\theta(\omega_c - \omega)$ (weak coupling to ohmic bath)

Technique

Lang-Firsov transformation:

$$\bar{H} = e^S H e^{-S} \; ; \; S = -\sum_{i\alpha} \frac{\lambda_0}{\omega_\alpha} a_i^\dagger a_i \left[B_\alpha - B_\alpha^\dagger \right]$$

transformed Hamiltonian:

$$\begin{aligned} \bar{H} &= \sum_i (\epsilon_i - \Delta) a_i^\dagger a_i - \sum_{i,j;i\neq j} t_{ij} a_i^\dagger a_j + H_{\mathrm{T,L}} + H_{\mathrm{T,R}} + H_{\mathrm{L}} + H_{\mathrm{R}} \\ &+ \sum_\alpha \sum_{i,j;i\neq j} \lambda_{1\alpha} \, a_i^\dagger a_j (B_\alpha + B_\alpha^\dagger) + H_{\mathrm{vib}} + H_{\mathrm{bath}} \\ \Delta &= \int d\omega D(\omega) \frac{{\lambda_0}^2}{\omega} \, . \quad \text{(polaron shift)} \end{aligned}$$

Equation of Motion

<u>retarded Green function:</u>

$$G^{\mathrm{ret}}_{kl}(t) = -i\theta(t)\left\langle\left\{a_k(t)\chi(t), a_l^\dagger\chi^\dagger\right\}\right\rangle_{\bar{H}}$$

$$\chi = \exp\left[\sum_\alpha \frac{\lambda_0}{\omega_\alpha}\left(B_\alpha - B_\alpha^\dagger\right)\right]$$

<u>equation of motion:</u>

$$i\frac{\partial}{\partial t}G^{\mathrm{ret}}_{kl}(t) = \delta(t)\delta_{kl} - i\theta(t)\left\langle\left\{\left[a_k(t)\chi(t), \bar{H}\right], a_l^\dagger\chi^\dagger\right\}\right\rangle_{\bar{H}}$$

- hierarchy of higher order Green functions
- truncated at first level (first order in λ_1)

Calculation of the current

general relation by Meir and Wingreen (PRL **68**, 2512 (1992))
can be split into two parts:

$$I_{\mathrm{el}}(V) = \frac{e}{h}\int dE\,(f_{\mathrm{L}}(E) - f_{\mathrm{R}}(E))\,\mathrm{Tr}\left\{\Gamma_{\mathrm{L}} G^{\mathrm{ret}} \Gamma_{\mathrm{R}} G^{\mathrm{adv}}\right\}$$

$$I_{\mathrm{inel}}(V) = \frac{ie}{4h}\int dE\,(f_{\mathrm{L}}(E) - f_{\mathrm{R}}(E))\,\mathrm{Tr}\left\{(\Gamma_{\mathrm{L}} + \Gamma_{\mathrm{R}})\, G^{\mathrm{ret}} \left(\Sigma^{\mathrm{ret}}_{\mathrm{vib}} - \Sigma^{\mathrm{adv}}_{\mathrm{vib}}\right) G^{\mathrm{adv}}\right\}$$

Galperin/Ratner/Nitzan J. Chem. Phys **121**, 11968 (2004)

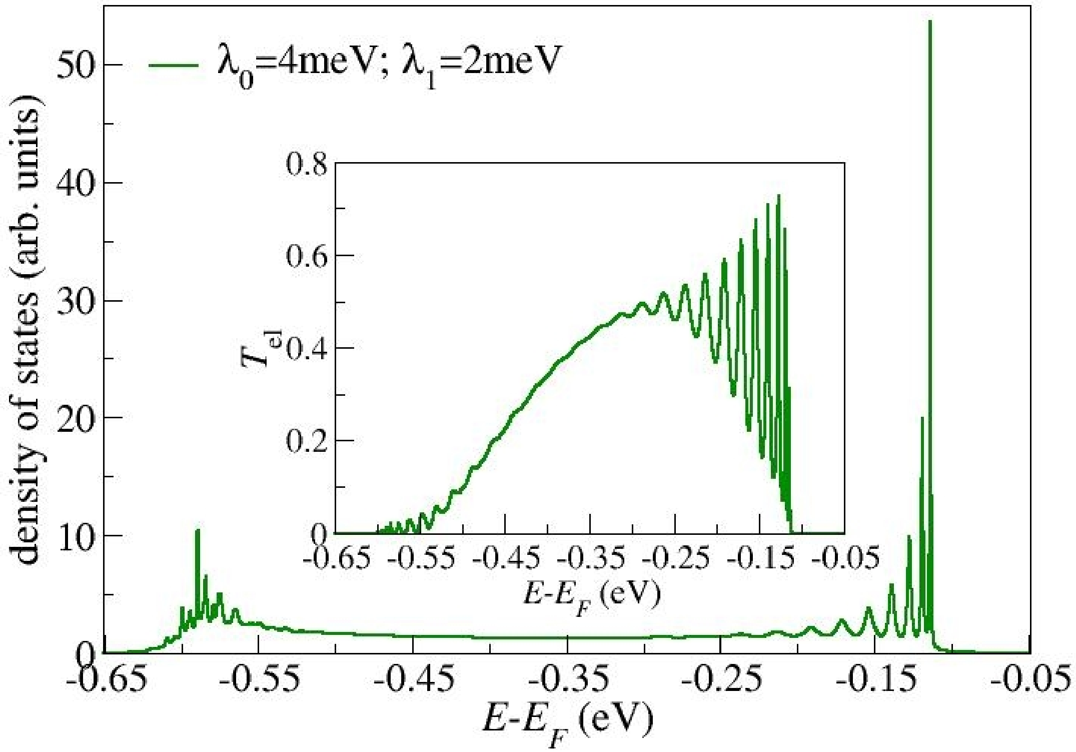
`elastic transmission'
$$T_{\mathrm{el}}(E) = \mathrm{Tr}\left\{\Gamma_{\mathrm{L}} G^{\mathrm{ret}} \Gamma_{\mathrm{R}} G^{\mathrm{adv}}\right\}$$

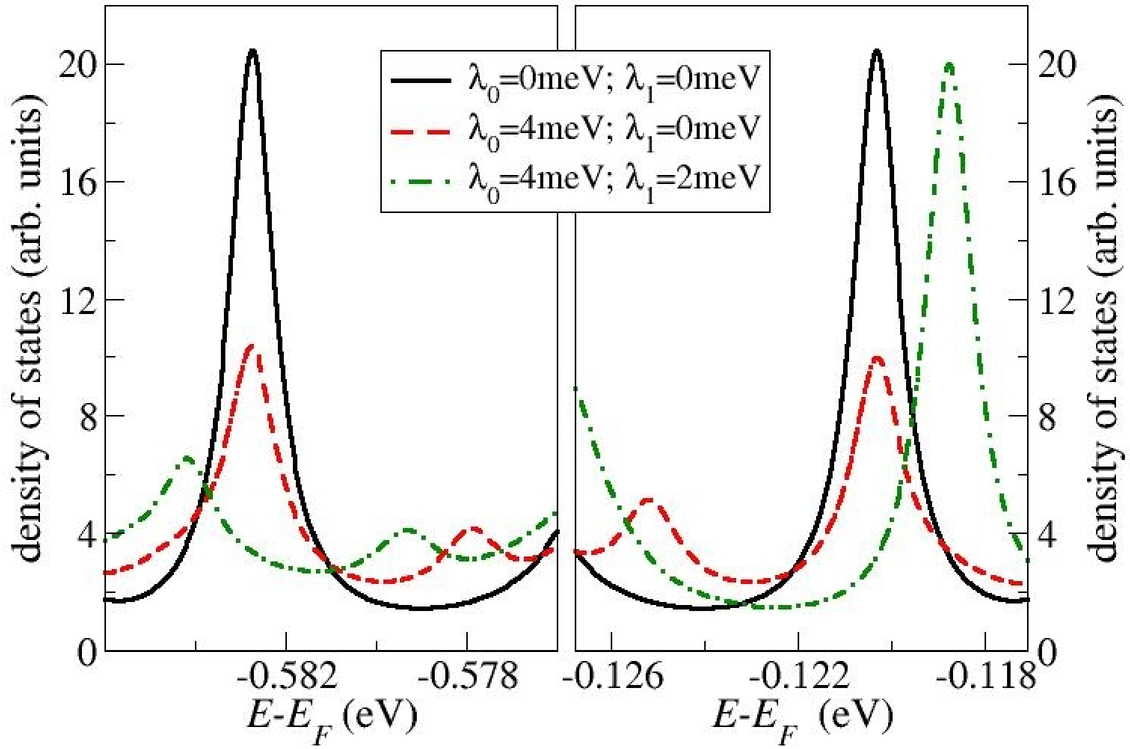
for inelastic current
use approximation
$$\Sigma^{<}_{\mathrm{vib}} = -\frac{f_{\mathrm{L}}(E) + f_{\mathrm{R}}(E)}{2}\left(\Sigma^{\mathrm{ret}}_{\mathrm{vib}} - \Sigma^{\mathrm{adv}}_{\mathrm{vib}}\right)$$

Results: homogeneous DNA

Poly(G-C) (26 base pairs)

- local energy: ε_G = -0.35eV
- Fermi energy: E_F = 0eV
- temperature: T = 300K
- vibrational energy: $\hbar\omega_0$=10meV
- linewidth: Γ=100meV





asymmetry and change in bandwidth due to non-local coupling

Results: zero bias conductance

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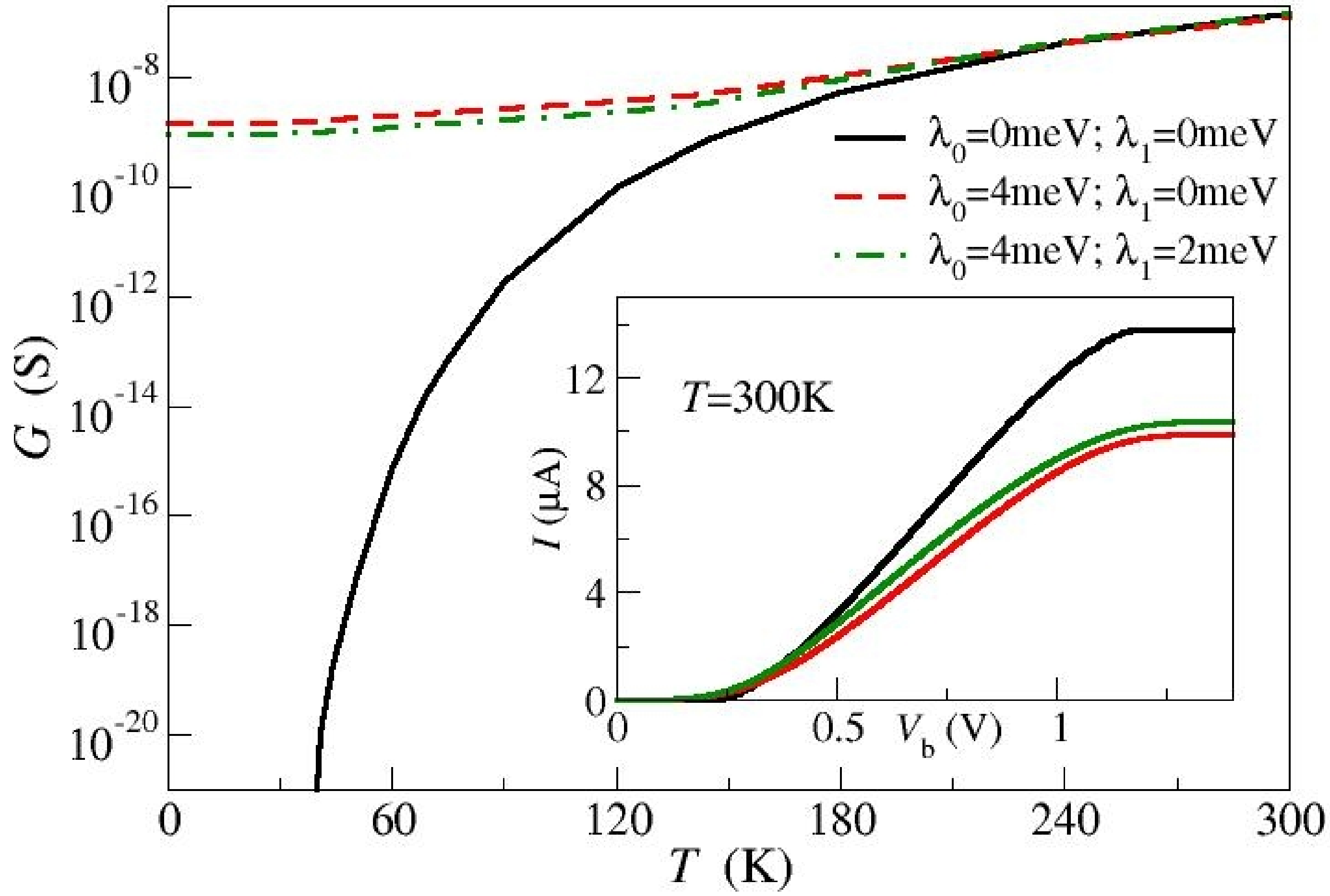
Poly(G-C) (26 base pairs)



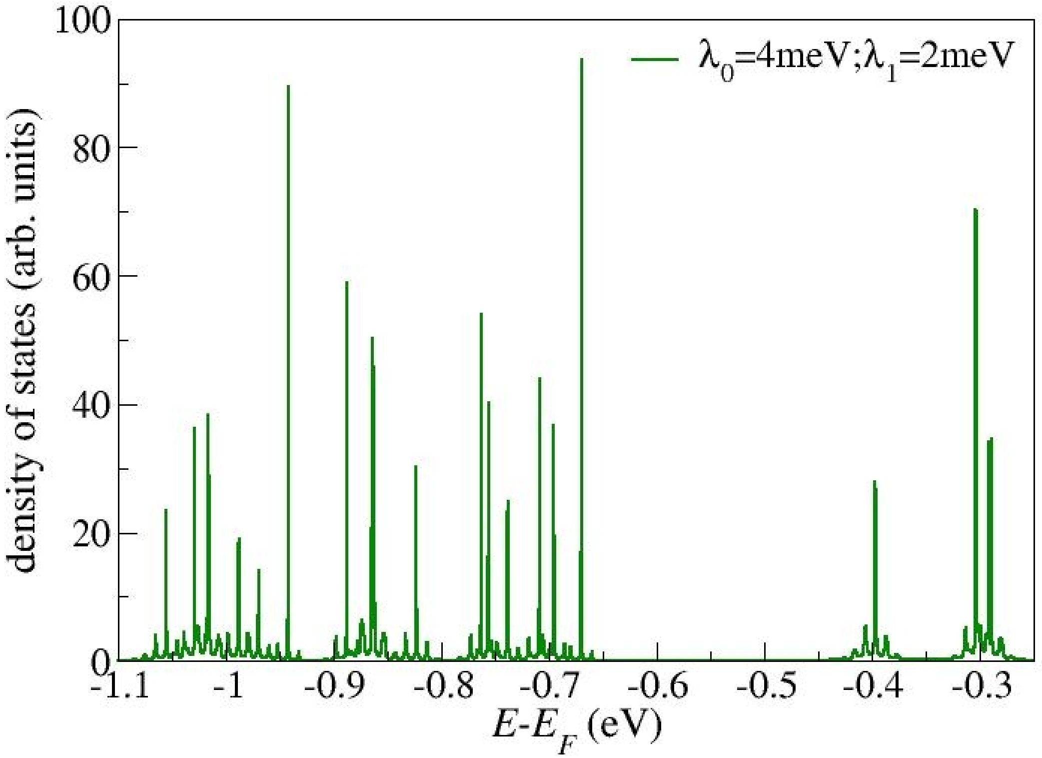
coupling to vibrations →

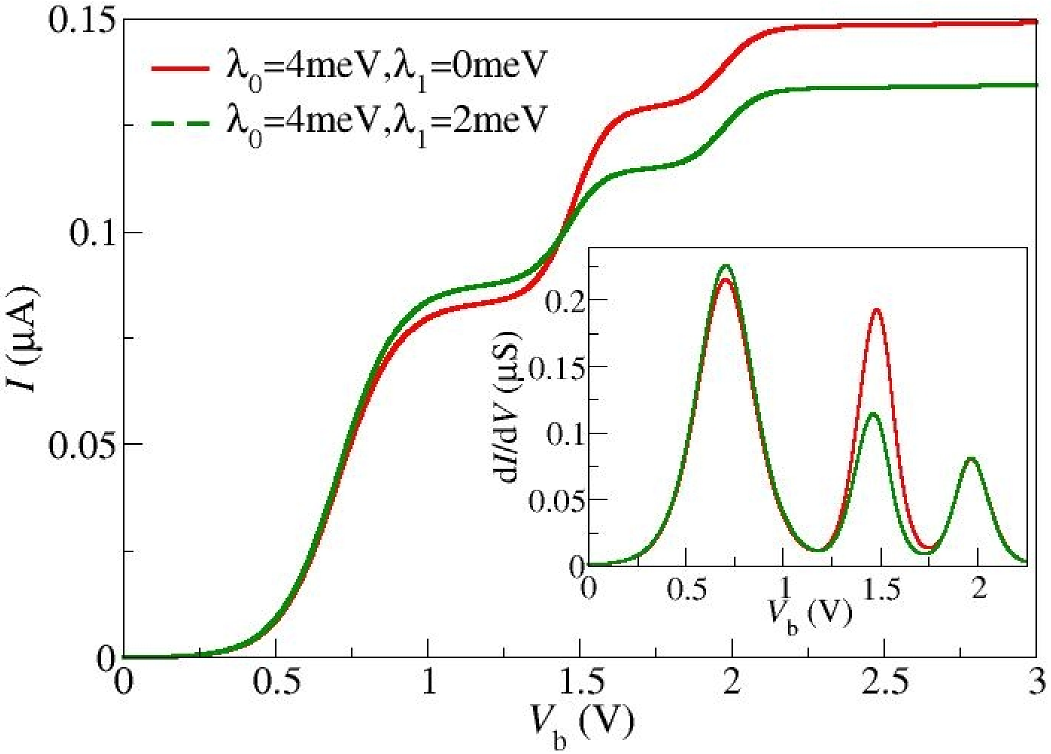
- increase of conductance at low temperatures
- decrease of conductance at high temperatures

Results: inhomogeneous DNA

5' - CAT TAA TGC TAT GCA GAA AAT CTT AG - 3'

- local energy: ε_G= -0.35eV, ε_A= -0.86eV
- Fermi energy: E_F= 0eV
- temperature: T = 300K
- vibrational energy: $\hbar\omega_0$=10meV
- linewidth: Γ=100meV

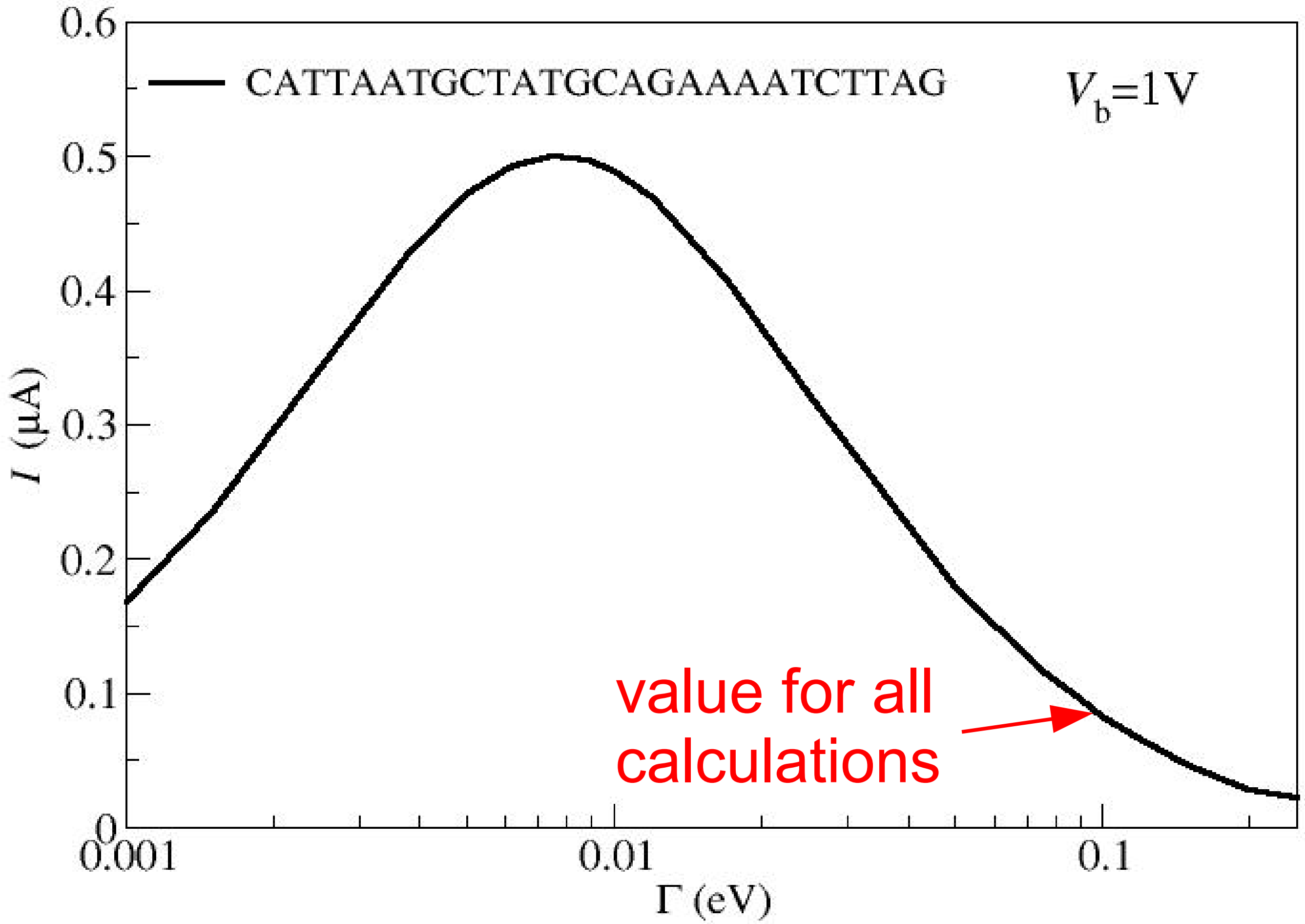




BBS et al., Phys. Rev. B **75,** 106711 (2007)

change in the IV-characteristics due to non-local coupling

Results: dependence on Γ



non-monotonic dependence of current on Γ

$\Gamma_{max} = \mathrm{Im}\{\Sigma_{vib}\} \approx 0.01\,\mathrm{eV}$

Conclusion

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- current dominated by:
  elastic contribution ⟷ homogeneous DNA
  inelastic contribution ⟷ inhomogeneous DNA

- electron-vibron coupling:
  increase of conductance at low temperatures
  decrease of conductance at high temperatures

- non-local electron-vibron coupling:
  asymmetry and increase in bandwidth
  inhomogeneous DNA ⟷ change of IV-characteristics

- non-monotonic dependence of current on Γ

higher order Green functions

for example:

$$\left\langle a_j(t) B_\alpha(t) \chi(t) a_l^\dagger \chi^\dagger \right\rangle \approx F_\alpha(t) \left\langle a_j(t) \chi(t) a_l^\dagger \chi^\dagger \right\rangle$$

assuming no el-vib coupling:

$$\left\langle a_j(t) B_\alpha(t) \chi(t) a_l^\dagger \chi^\dagger \right\rangle_{H_0} = F_\alpha(t) \left\langle a_j(t) \chi(t) a_l^\dagger \chi^\dagger \right\rangle_{H_0}$$

where

$$F_\alpha(t) = (N(\Omega_\alpha) + 1) e^{-i\Omega_\alpha t} - N(\Omega_\alpha) e^{i\Omega_\alpha t}$$