Polarons: from Models to Materials to Quantum Simulation

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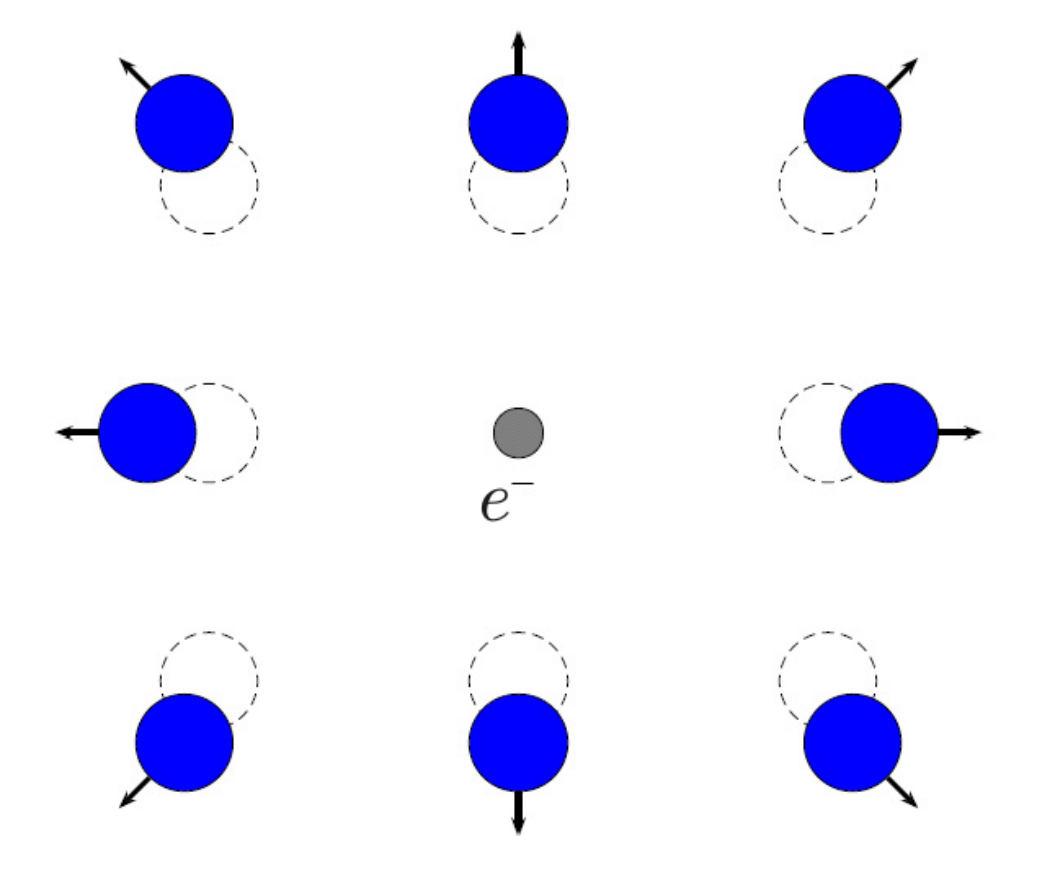
Cavendish Laboratory, Cambridge
November 15, 2012

Small polarons: basics



D. Emin, 1982: "Small polaron is an electron or a hole severely "localized" within a potential well that it creates by displacing the atoms that surround it."

Polaron concept:

L. D. Landau (1933), polar semiconductors (alkali-halides)

Polarons also found in:

transition-metal oxides, glasses, undoped cuprates, some conductive polymers, etc.

main feature:

low-mobility ($\mu < 1\,\mathrm{cm^2/Vs}$), increasing with temperature (at high temperatures)!

Outline of the talk

- Coupled electron-phonon (particle-boson) systems, small polarons
- **MODELS**

  Nonanalyticities in a polaron model and recent corroboration

  VMS and M. Vanević (Uni Basel), PRB **78**, 214301 (2008).
- **MATERIALS**

  Electron-phonon coupling in crystalline organic semiconductors

  N. Vukmirović (SCL, Univ. of Belgrade), C. Bruder, and VMS,
  PRL **109**, 126407 (2012).
- **QUANTUM SIMULATION**

  Quantum simulation of small-polaron formation with trapped ions

  VMS, T. Shi (MPQ), C. Bruder, and J. I. Cirac (MPQ),
  PRL **109**, 250501 (2012).
- Conclusions & Outlook

Generic coupled electron-phonon model

$$\hat{H} = \hat{H}_{\mathrm{e}} + \hat{H}_{\mathrm{ph}} + \hat{H}_{\text{e-ph}}$$

$$\hat{H}_{\mathrm{e}} = -t \sum_{i} (\hat{a}^{\dagger}_{i+1} \hat{a}_i + \mathrm{h.c.})$$

$$\hat{H}_{\mathrm{ph}} = \sum_{q} \omega(q) \hat{b}^{\dagger}_{q} \hat{b}_q$$

translational invariance: $[\hat{H}, \hat{\mathrm{K}}] = 0$ regardless of the form of $\hat{H}_{\text{e-ph}}$

$$\hat{\mathrm{K}} = \sum_{k} k\, \hat{a}^{\dagger}_{k} \hat{a}_k + \sum_{q} q\, \hat{b}^{\dagger}_{q} \hat{b}_q$$

total crystal momentum operator

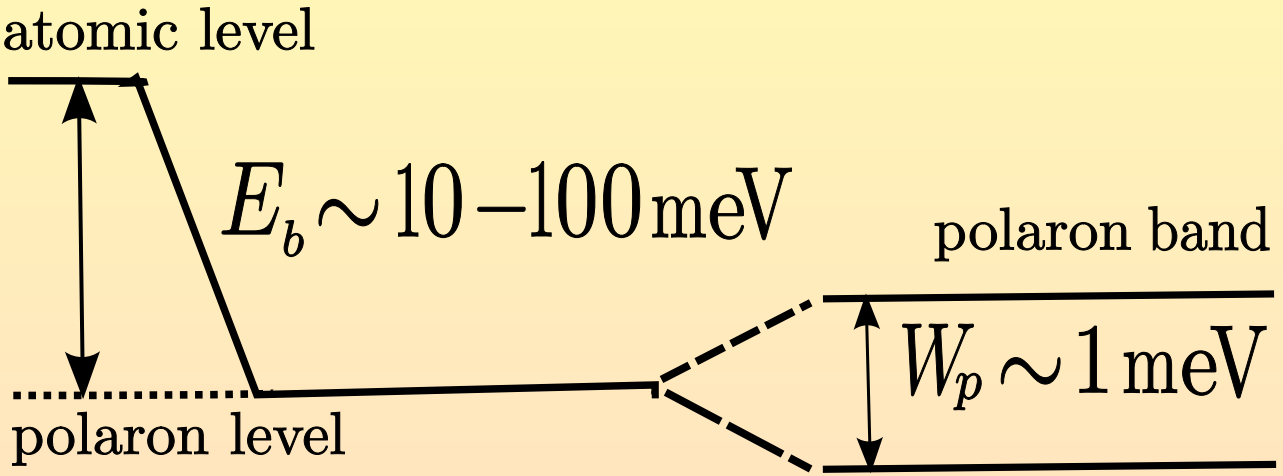
$$\hat{K}|\psi_\kappa\rangle = \kappa\, |\psi_\kappa\rangle$$

$$\hat{H}|\psi_\kappa\rangle = E_\kappa |\psi_\kappa\rangle$$

quasiparticle residue (spectral weight) at quasimomentum $\mathbf{k}$ in band n:

$$Z_n(\mathbf{k}) \equiv |\langle \Psi_{n\mathbf{k}} | \psi_{n\mathbf{k}} \rangle|^2 \qquad (\, 0 < Z_n(\mathbf{k}) < 1 \,)$$

Bare-band electrons vs. small polarons



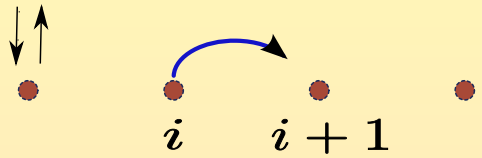
- small-polaron band center is shifted by E_b (binding energy) from that of a bare electron
- small-polaron bandwidth (W_p) is much smaller than W_e

Necessary condition for small-polaron formation:

$$E_b \geq W_e/2$$

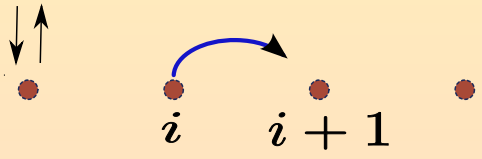
Molecular-crystal model

local (Holstein-type) coupling



$$\epsilon \rightarrow \epsilon + \alpha_{H} u_i$$

non-local (Peierls-type) coupling



$$t \rightarrow t + \alpha_{P} \left(u_{i+1} - u_i\right)$$

dimensionless couplings:

$$\frac{\alpha_{\mathrm{H}}}{\sqrt{2m\omega}} \equiv g\omega$$

$$\frac{\alpha_{\mathrm{P}}}{\sqrt{2m\omega}} \equiv \phi\omega$$

$$\hat{H}_{\mathrm{g}} = g\omega \sum_i \hat{a}_i^\dagger \hat{a}_i (\hat{b}_i^\dagger + \hat{b}_i)$$

$$\hat{H}_{\phi} = \phi\omega \sum_i (\hat{a}_{i+1}^\dagger \hat{a}_i + \mathrm{h.c.})(\hat{b}_{i+1}^\dagger + \hat{b}_{i+1} - \hat{b}_i^\dagger - \hat{b}_i)$$

Momentum dependence and possible nonanalyticities

$$\hat{H}_{\text{e-ph}} = N^{-1/2} \sum_{\mathbf{k},\mathbf{q}} \gamma(\mathbf{k},\mathbf{q})\, \hat{a}^{\dagger}_{\mathbf{k}+\mathbf{q}} \hat{a}_{\mathbf{k}} (\hat{b}^{\dagger}_{-\mathbf{q}} + \hat{b}_{\mathbf{q}})$$

1. **momentum-independent couplings**

   Holstein-type (local) coupling: $\gamma_{\text{H}}(\mathbf{k},\mathbf{q}) = g\omega = \text{const.}$

2. **momentum-dependent couplings**

   Peierls' (SSH) coupling in a one-dimensional or square lattice:

   $$\gamma_{\text{SSH}}(\mathbf{k},\mathbf{q}) \propto \sin(\mathbf{k}\cdot\mathbf{a}) - \sin\left[(\mathbf{k}+\mathbf{q})\cdot\mathbf{a}\right]$$

Gerlach-Löwen theorems [PRB **35**, 4291 & 4297, 1987] rule out any nonanalyticity for momentum-independent and $\mathbf{q}$-dependent couplings!

How about Peierls' coupling? Entanglement measures?

Entanglement measures

bipartite system: $\mathcal{H} = \mathcal{H}_{\mathrm{A}} \otimes \mathcal{H}_{\mathrm{B}}$

the reduced density matrix of system A: $\hat{\rho}_{\mathrm{A}} = \mathrm{Tr}_{\mathrm{B}} \hat{\rho}$

the von Neumann entropy

$$S = -\mathrm{Tr}_{\mathrm{A}}(\hat{\rho}_{\mathrm{A}} \ln \hat{\rho}_{\mathrm{A}})$$

linear entropy (tangle)

$$S_L = 1 - \mathrm{Tr}_{\mathrm{A}}(\hat{\rho}_{\mathrm{A}}^2)$$

Our system: $A \to \mathrm{e}, \quad B \to \mathrm{ph}$

$$\hat{\rho}_{\text{e-ph}} = \frac{|\psi\rangle\langle\psi|}{\langle\psi|\psi\rangle} \implies \hat{\rho}_{\mathrm{e}} = \mathrm{Tr}_{\mathrm{ph}}\left[\hat{\rho}_{\text{e-ph}}\right] \implies S = -\mathrm{Tr}_{\mathrm{e}}(\hat{\rho}_{\mathrm{e}} \ln \hat{\rho}_{\mathrm{e}})$$

inspiration: nonanalyticity of S as a signature of 3D Anderson localization

X. Jia, A. R. Subramaniam, I. A. Gryzberg, and S. Chakravarty,
PRB **77**, 014208 (2008)

PHYSICAL REVIEW B 78, 214301 (2008)

Quantum-entanglement aspects of polaron systems

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(Received 4 September 2008; revised manuscript received 9 November 2008; published 10 December 2008)

We describe quantum entanglement inherent to the polaron ground states of coupled electron-phonon (or, more generally, particle-phonon) systems based on a model comprising both local (Holstein-type) and nonlocal (Peierls-type) couplings. We study this model using a variational method supplemented by the exact numerical diagonalization on a system of finite size. By way of subsequent numerical diagonalization of the reduced density matrix, we determine the particle-phonon entanglement as given by the von Neumann and linear entropies. Our results are strongly indicative of the intimate relationship between the particle localization/delocalization and the particle-phonon entanglement. In particular, we find a compelling evidence for the existence of a nonanalyticity in the entanglement entropies with respect to the Peierls-coupling strength. The occurrence of such nonanalyticity—not accompanied by an actual quantum phase transition—reinforces analogous conclusion drawn in several recent studies of entanglement in the realm of quantum-dissipative systems. In addition, we demonstrate that the entanglement entropies saturate inside the self-trapped region where the small-polaron states are nearly maximally mixed.

DOI: 10.1103/PhysRevB.78.214301 PACS number(s): 71.38.Ht, 03.67.Mn

Toyozawa-type variational Ansatz: inner workings

Y. Toyozawa, Prog. Theor. Phys. **26**, 29 (1961)

Bloch wave-functions (eigenstates of the total crystal momentum):

$$|\psi_\kappa\rangle = N^{-1/2} \sum_n e^{i\kappa n} \, |\psi_\kappa(n)\rangle$$

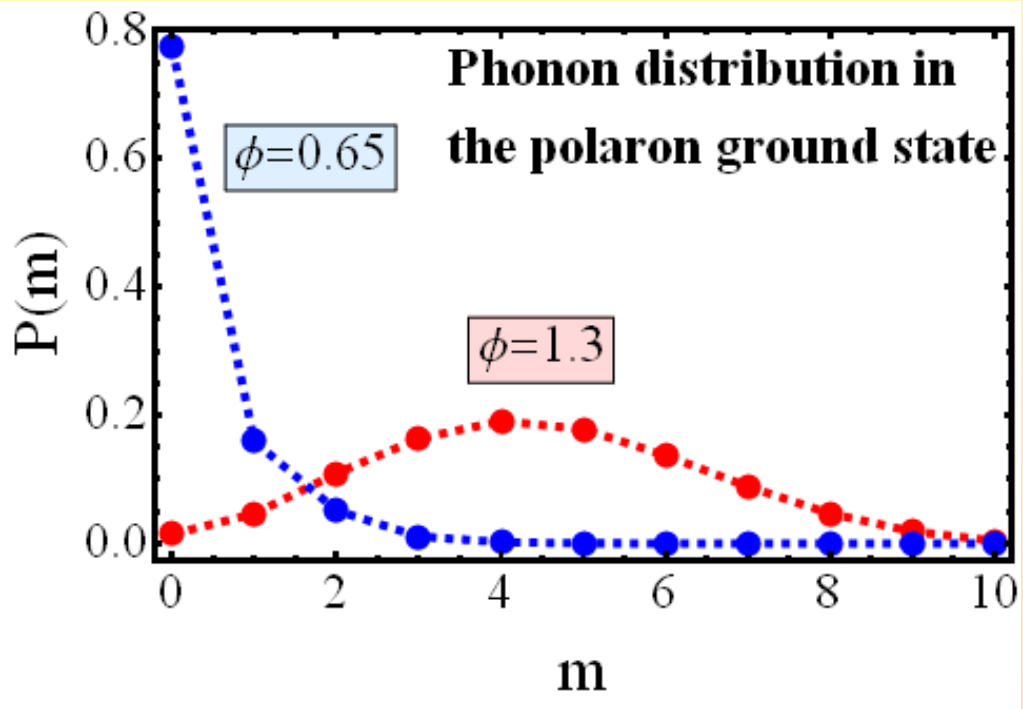
"Wannier-like" function ($4N$ variational parameters):

$$|\psi_\kappa(n)\rangle = \sum_{m=-N/2}^{N/2-1} \Phi_\kappa(m) e^{i\kappa m} a^\dagger_{n+m} |0\rangle_{\mathrm{e}} \otimes |\xi_\kappa(n)\rangle_{\mathrm{ph}} \,,$$

product of phonon coherent states:

$$|\xi_\kappa(n)\rangle_{\mathrm{ph}} \equiv \prod_l \exp\left(v_l^\kappa b^\dagger_{n+l} - v_l^{\kappa *} b_{n+l}\right) |0\rangle_{\mathrm{ph}}$$

Exact diagonalization approach



need truncation (phonons !)
of the original Hilbert space

$$\mathcal{H} = \mathcal{H}_{\rm e} \otimes \mathcal{H}_{\rm ph}$$

to states with the total
of at most M phonons

$$|\Psi\rangle = \sum_{\mathbf{n},\mathbf{m}} C_{\mathbf{n},\mathbf{m}} \, |\mathbf{n}\rangle_{\rm e} \otimes |\mathbf{m}\rangle_{\rm ph}$$

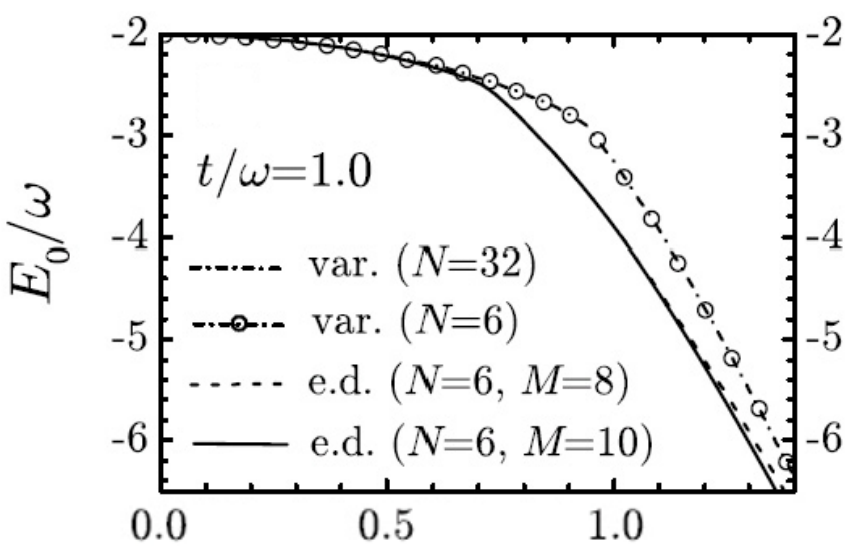
Dimension of the truncated Hilbert space:

$\boldsymbol{N = 6}$ sites, $\boldsymbol{M = 8}$ phonons $\longrightarrow$ $\boldsymbol{D = 7722}$

$\boldsymbol{M = 9}$ phonons $\longrightarrow$ $\boldsymbol{D = 12012}$

$\boldsymbol{M = 10}$ phonons $\longrightarrow$ $\boldsymbol{D = 18018}$

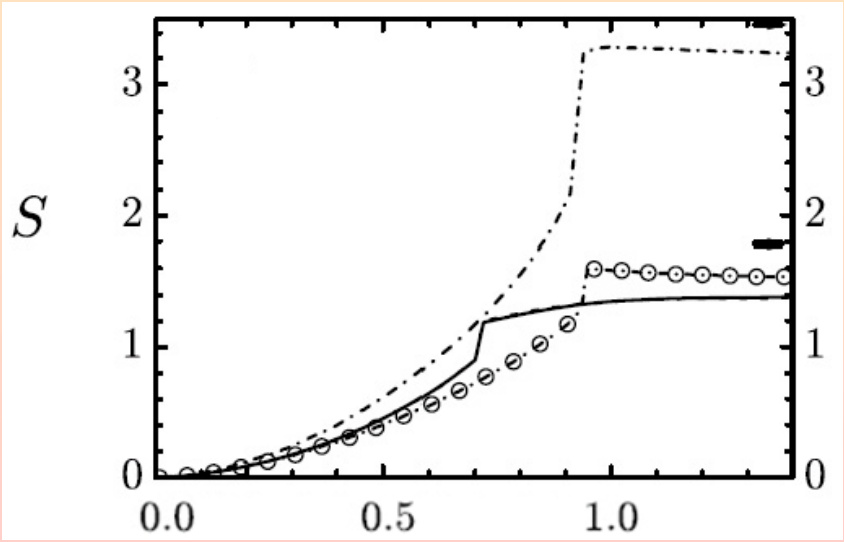
Nonanalyticities with respect to Peierls-type coupling

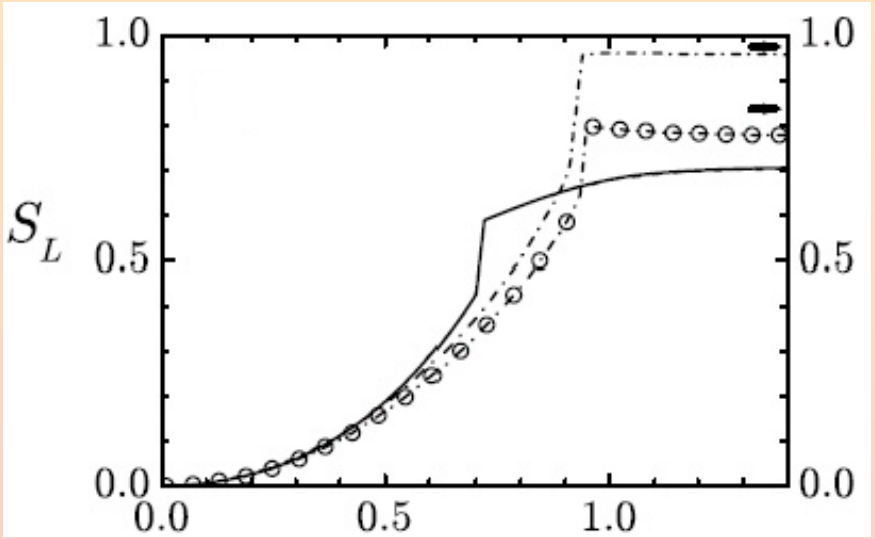


Entanglement entropies show a nonanalytic behavior!

small-polaron band minimum:

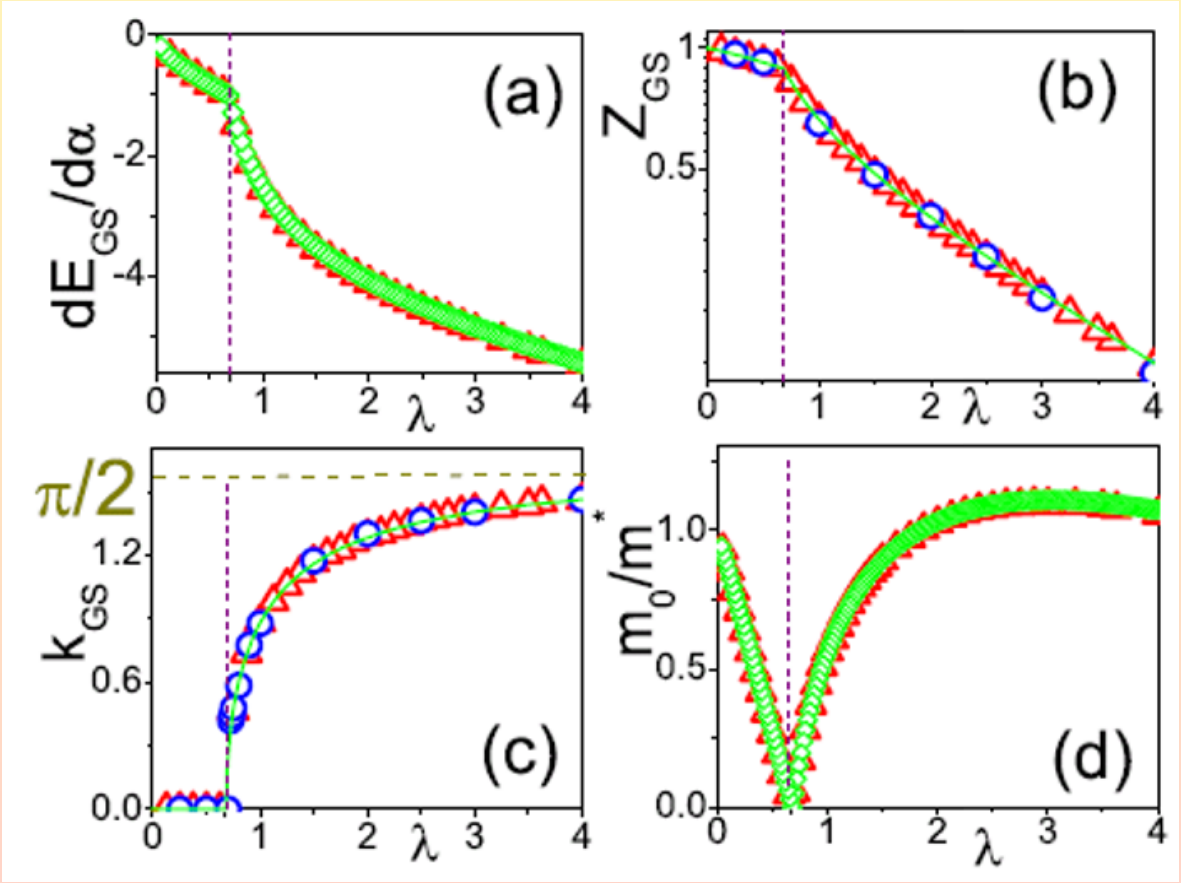
$$\boldsymbol{\kappa = 0 \;\rightarrow\; \kappa = -k_{\mathrm{GS}}, k_{\mathrm{GS}}}$$





2010 corroboration

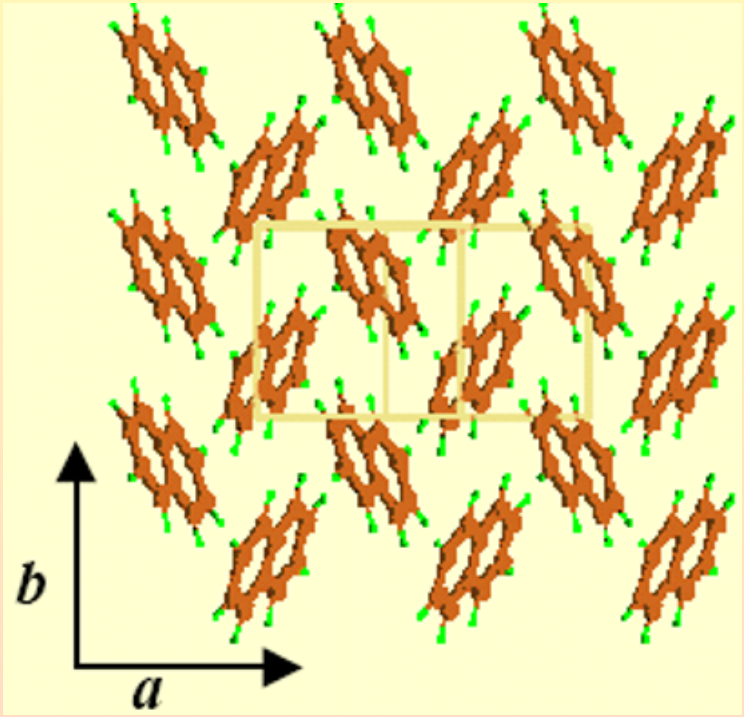
D. J. J. Marchand, G. De Filippis, V. Cataudella, M. Berciu, N. Nagaosa, N. V. Prokof'ev, A. S. Mischenko, and P. C. E. Stamp, PRL **105**, 266605 (2010)



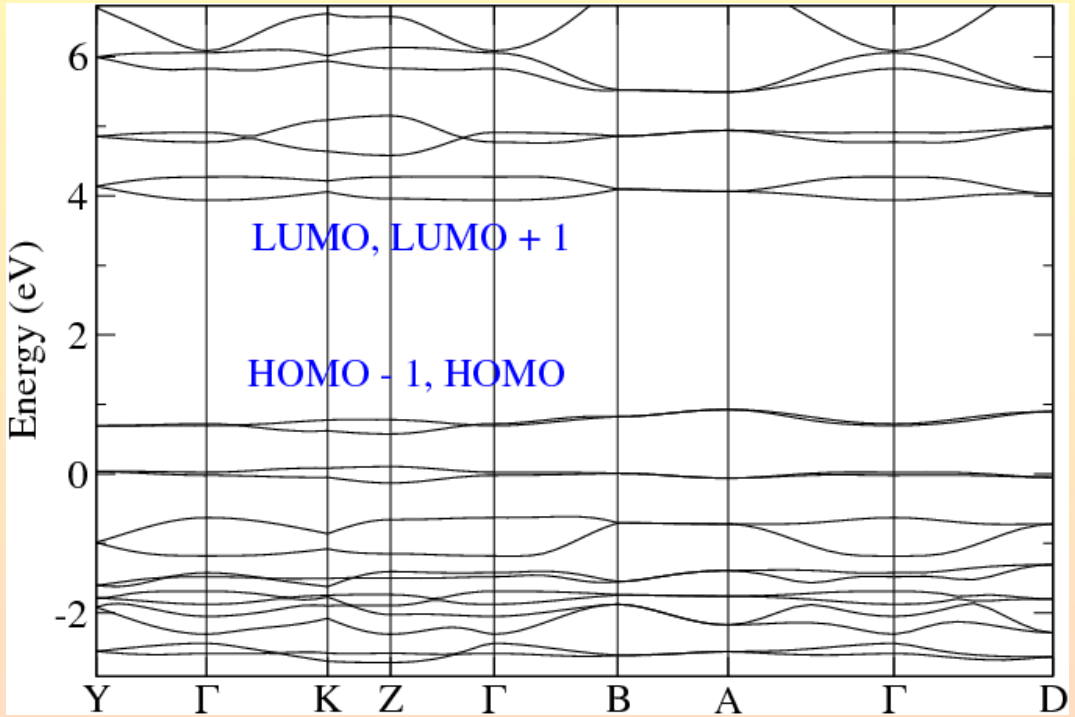
$$\lambda \equiv 2\phi^2 \frac{\omega}{t}$$

Crystalline organic semiconductors: polyacenes (oligoacenes)

See, e.g., K. Hannewald, VMS, *et al.*, PRB **69**, 075211 (2004)



naphthalene crystal

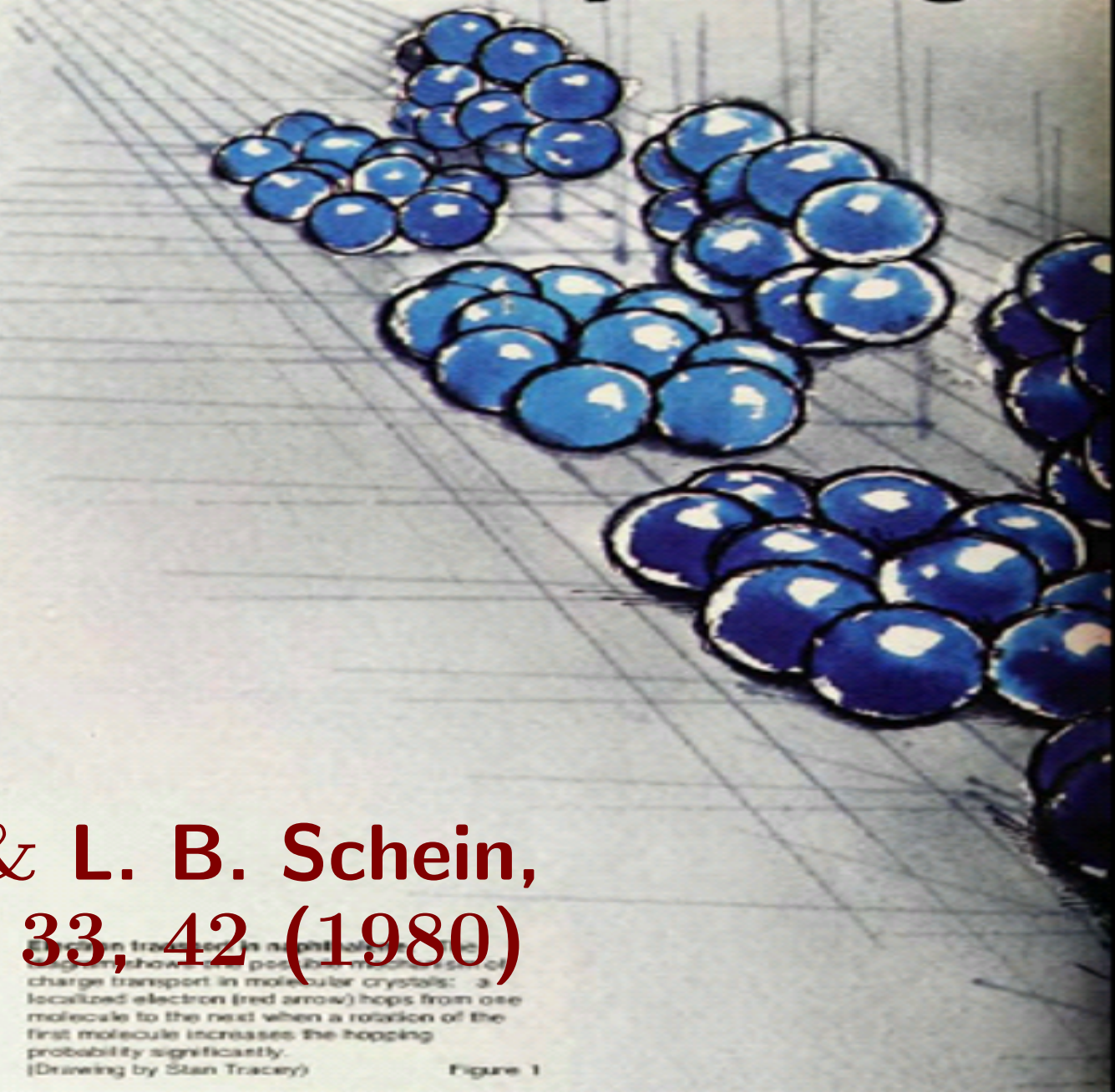


naphthalene band structure

naphthalene, anthracene, tetracene, pentacene

highly anisotropic van der Waals bonded solids,
with narrow bands ($W = 0.1 - 0.4$ eV)

Organic solids: is energy-band theory enough?



The study of the electronic properties of organic solids is a major new frontier in solid state physics. On the practical side, organic solids provide electronic and optical materials whose properties can be tailored to suit specific applications. They also pose continuing challenges to fundamental concepts because they afford unique model systems for establishing the bounds of validity for the traditional energy-band models that have proven so successful in describing the electronic properties of inorganic metals and semiconductors.

In addition to their interesting optical, transport and photochemical properties, organic solids are versatile in their mechanical behavior and are easy to fabricate for a wide range of uses. Once relegated to a fairly narrow spectrum of applications in electronics (as dielectrics) and photochemistry (for lithography), organic solids are finding a host of new uses. Among these are:

- photo and electron-beam resists for microelectronics
- radiation-cured (solventless) coatings
- electromechanical and thermoelectric transducers
- photodielectrics
- insulators and encapsulants for microelectronics
- photoconductors and developer materials for electrophotography

Organic polymers also show promise for future uses as

- electrical conductors and perhaps even superconductors
- optical light pipes, waveguides and nonlinear circuit elements

These applications have provided the impetus for research into the electronic, photoelectronic and photochemical properties of organic solids.

In a recent article in Physics Today (December 1978, page 44), Philip Allen and William Butler argue that electronic conduction in metals at very low and high temperatures still poses a challenge to the transport theory based on Felix Bloch's work. In this article we develop a similar argument that organic solids constitute an

charge transport in molecular crystals: a localized electron (red arrow) hops from one molecule to the next when a rotation of the first molecule increases the hopping probability significantly.
(Drawing by Stan Tracey)

Figure 1

C. B. Duke & L. B. Schein,
Phys. Today 33, 42 (1980)

Organic solids: is energy-band theory enough?

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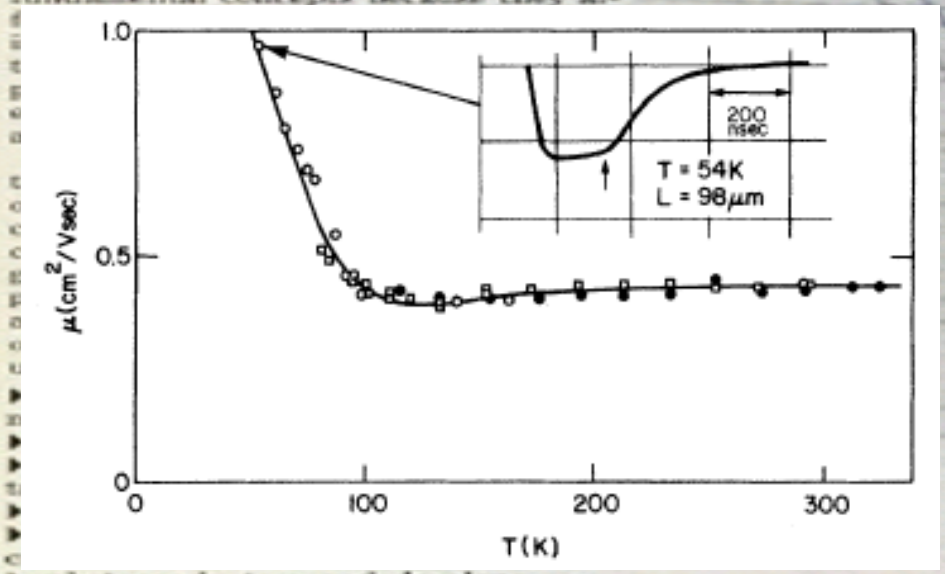

▶ photoconductors and developer materials for electrophotography

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Figure 1

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Charge carriers in polyacenes: small polarons or not?

- Electron(hole)-phonon coupling more important than in inorganic semiconductors, but is it strong enough for polaronic behavior?
- coupling becomes weaker with increasing molecular size, while the bands (HOMO, LUMO) become wider;
- coupling weaker for holes (HOMO) than for electrons (LUMO)!

Idea: Extract electron-phonon coupling functions in momentum space using ab-initio approach

Methodology: F. Giustino *et. al.*, PRB **76**, 165108 (2007)

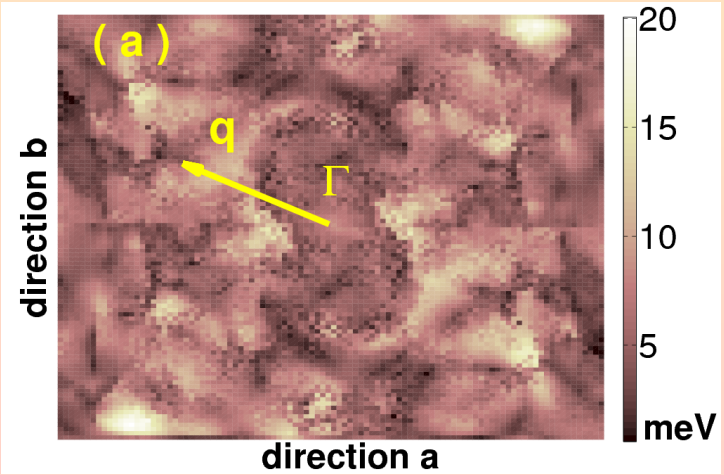
Challenge: System size $\geq$ 36 atoms per unit cell!

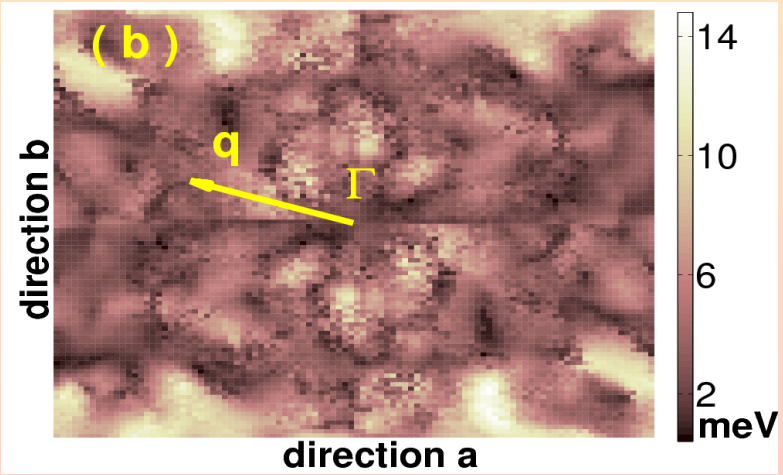
Momentum-dependent coupling (vertex) functions

$$\hat{H}_{\text{e-ph}} = N^{-1/2} \sum_{nn',\mathbf{k},\mathbf{q},\lambda} \gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q})\, \hat{a}^{\dagger}_{n',\mathbf{k}+\mathbf{q}} \hat{a}_{n,\mathbf{k}} (\hat{b}^{\dagger}_{-\mathbf{q},\lambda} + \hat{b}_{\mathbf{q},\lambda})$$

$$\gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q}) = \sqrt{\frac{\hbar}{2\omega_{\lambda,\mathbf{q}}}} \sum_{S\alpha} e^{(\lambda)}_{S\alpha}(\mathbf{q}) \frac{1}{\sqrt{M_S}} \left\langle \psi_{n',\mathbf{k}+\mathbf{q}} \left| \frac{\partial U_{\text{scf}}}{\partial u_{\mathbf{q}S\alpha}} \right| \psi_{n,\mathbf{k}} \right\rangle$$

codes used: `Quantum-ESPRESSO`, `EPW`, `Wannier90`

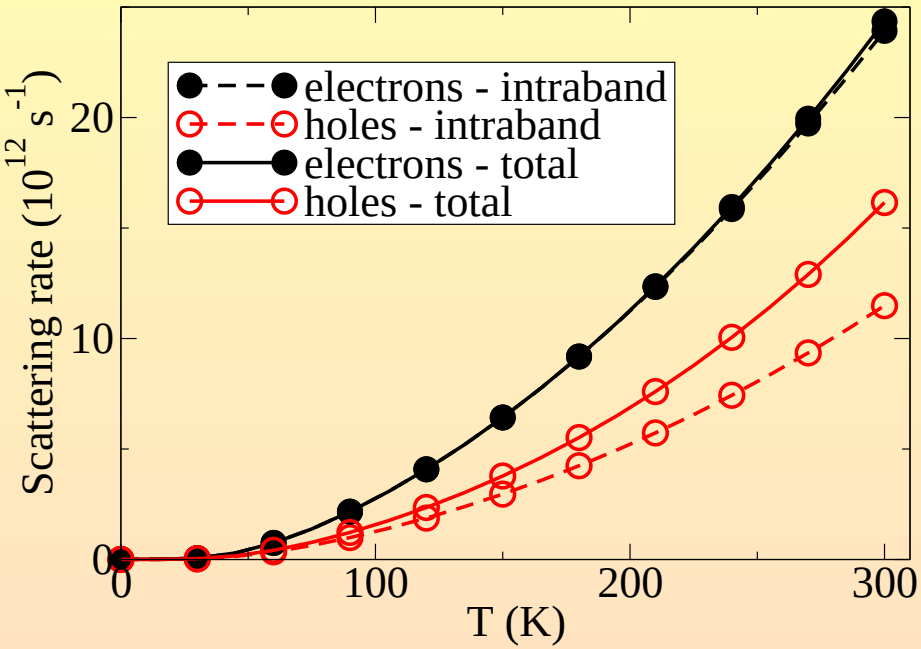




$\mathbf{e}^-$ @ LUMO-band bottom

$\mathbf{h}^+$ @ HOMO-band top

"Sanity check": HOMO and LUMO inelastic scattering rates



averaged vertex functions
(over phonon branches and momenta):
$\approx \mathbf{7.8}$ meV ($\mathbf{6.8}$ meV) for LUMO-band electrons (HOMO-band holes),

much smaller than the respective bandwidths ($> \mathbf{200}$ meV)!

inelastic scattering rates – Fermi golden rule expression:

$$\left(\frac{1}{\tau}\right)_{n\mathbf{k}} = \frac{2\pi}{N\hbar} \sum_{n',\mathbf{q},\lambda} |\gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q})|^2 \left(\Delta^{\lambda,-}_{n'n} + \Delta^{\lambda,+}_{n'n}\right)$$

$$\Delta^{\lambda,\pm}_{n'n} \equiv (n_{\lambda,\mathbf{q}} + 1/2 \pm 1/2)\delta(\varepsilon_{n',\mathbf{k}+\mathbf{q}} - \varepsilon_{n,\mathbf{k}} \pm \hbar\omega_{\lambda,\mathbf{q}})$$

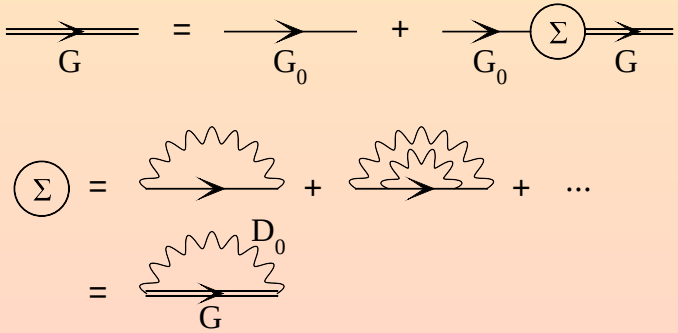
Nonpolaronic character of carriers

Rayleigh-Schrödinger (RS) perturbation theory

$$Z_n^{-1}(\mathbf{k}) = 1 + \frac{1}{N} \sum_{n',\mathbf{q},\lambda} \frac{|\gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q})|^2}{\left[\varepsilon_n(\mathbf{k}) - \varepsilon_{n'}(\mathbf{k}+\mathbf{q}) - \hbar\omega_{\lambda,\mathbf{q}}\right]^2}$$

yields $Z_\mathrm{e} \approx 0.74$ and $Z_\mathrm{h} \approx 0.78$!

binding energy $E_\mathrm{b} = 68.7$ meV (58.8 meV) for electrons (holes)
$\Rightarrow$ small-polaron condition $E_b \geq W/2$ not satisfied!



$$Z_n^{-1}(\mathbf{k}) = 1 - \frac{\partial}{\partial\omega} \mathrm{Re}\,\Sigma_n(\mathbf{k},\omega)|_{\omega=E_n(\mathbf{k})}$$

self-consistent Born approximation (SCBA):

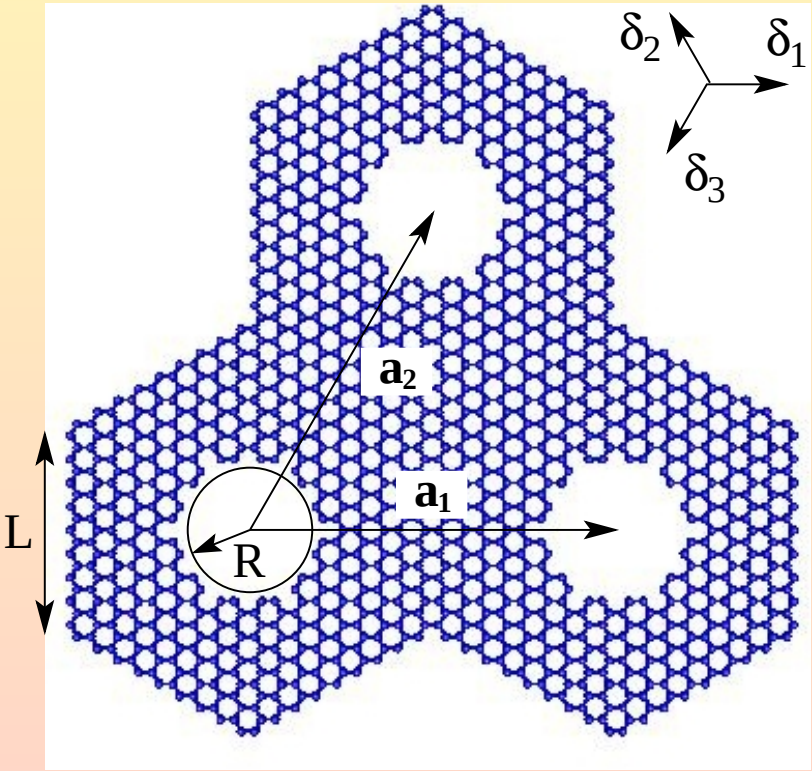
$$\Sigma_n(\mathbf{k},\omega) = \frac{1}{N} \sum_{\lambda,\mathbf{q}} \frac{|\gamma^{\lambda}_{nn}(\mathbf{k},\mathbf{q})|^2}{\omega - \omega_{\lambda,\mathbf{q}} - \varepsilon_n(\mathbf{k}+\mathbf{q}) - \Sigma_n(\mathbf{k}+\mathbf{q},\omega-\omega_{\lambda,\mathbf{q}}) + i\delta}$$

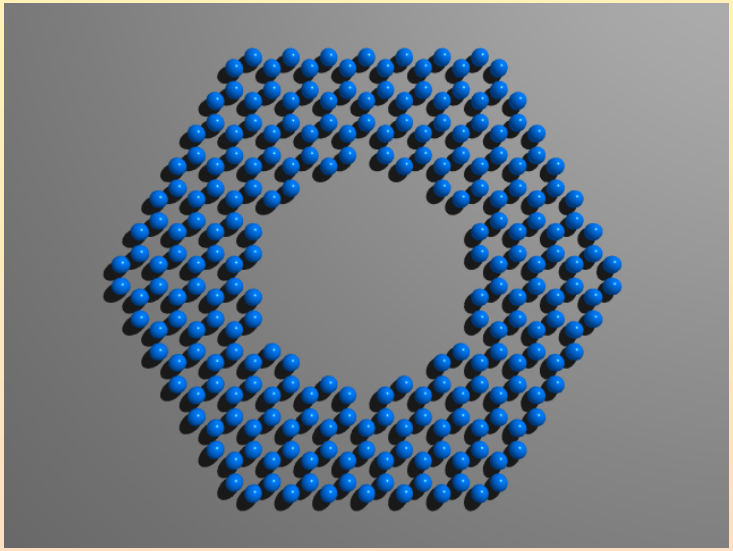
results on a $6 \times 6 \times 6$ grid: $Z_\mathrm{e}^{\mathrm{SCBA}} \approx 0.78$ ($Z_\mathrm{e}^{\mathrm{RS}} \approx 0.77$)

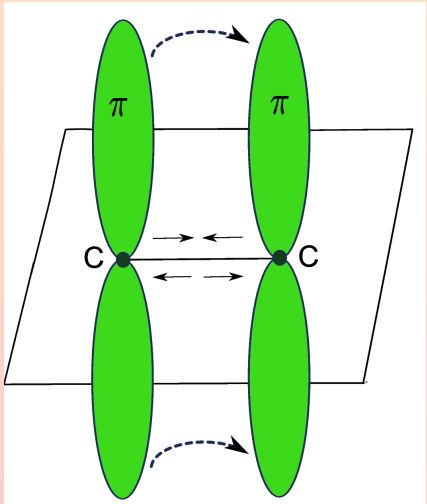
Polarons on demand: graphene antidot lattices

VMS, N. Vukmirović, and C. Bruder, PRB **82**, 165410 (2010)

N. Vukmirović, VMS, and M. Vanević, PRB **81**, 041408(R) (2010)



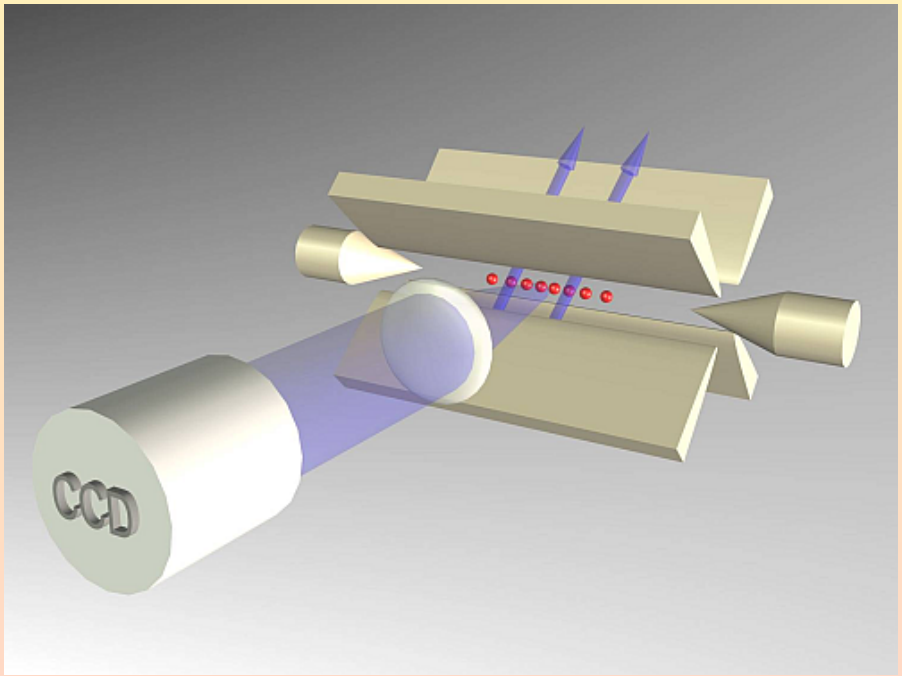




semiconducting counterparts of graphene with tunable bandwidths

Analog quantum simulations with trapped ions

IDEA: (Feynman '81, Lloyd '96; see J. I. Cirac and P. Zoller, Nature Phys. 2012)
Simulate the dynamics of a quantum system of interest using another system that is easier to control and measure



Source: R. Blatt's group (Innsbruck)

Trapped ions as a platform for quantum simulation:

- easy for trapping and cooling
- high-precision measurements
- internal states $\longrightarrow$ pseudospins

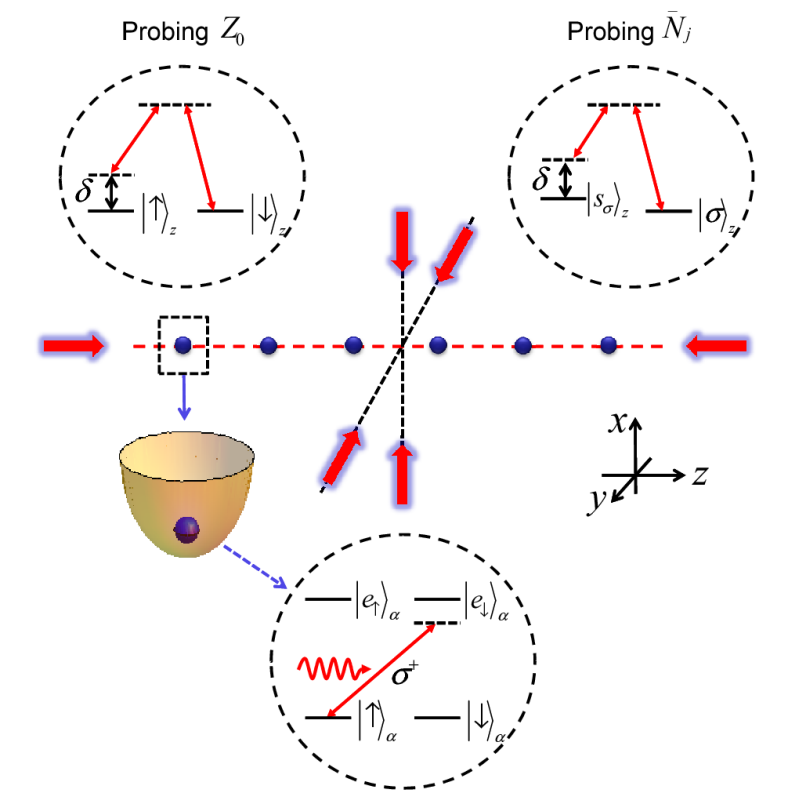
Review: R. Blatt and C. F. Roos, Nature Phys. **8**, 277 (2012)

Recent development: 2D ion trap lattices

Quantum simulation of small Holstein polaron formation

Goal: simulate the strong-coupling regime of the Holstein model using a linear array of ion microtraps

Previous proposal: J. P. Hague and C. MacCormick, NJP **14**, 033019 (2012)



Important points to address:

- Can we realize strictly local coupling of a single excitation to phonons?
- Can we make phonons dispersionless?
- Can we reach strong coupling with realistic values of system parameters?

Coupling internal states to motion in a nutshell

foundations: D. Porras and J. I. Cirac, PRL **92**, 207901 (2004)

basic mechanism: standing laser wave, detuned from a transition leads to a position and state-dependent conservative potential (**a.c.-Stark shift**)

$$\boxed{V(x_\alpha) \propto \Omega^2(x_\alpha)/\Delta_\alpha}$$ detuning: $$\boxed{\Delta_\alpha \equiv \omega_{L,\alpha} - \omega_0}$$

Lamb-Dicke regime ($a \ll d_0$):
linear expansion of $\Omega^2(x_\alpha)$ around the ion equilibrium positions

$$\Longrightarrow \boxed{H_I = \sum_{i,\alpha} F_\alpha q_i^\alpha (1+\sigma_i^\alpha)}$$ "pushing" force: $F_\alpha \propto G_\alpha^2 k_\alpha / 2\Delta_\alpha$

$\Longrightarrow$ coupling of an excitation $(1+\sigma_i^z \to 2c_i^\dagger c_i)$ to longitudinal phonons

$(q_i^z \propto b_i + b_i^\dagger)$ is Holstein-like (local): $$\boxed{H_{\mathrm{e-ph}} \propto \sum_i c_i^\dagger c_i (b_i + b_i^\dagger)}$$

Character of phonon modes and e-ph coupling

vibrational modes (transverse and longitudinal) result from:
trapping potentials + Coulomb repulsion between ions

stiff limit: $\beta_\alpha \equiv \dfrac{e^2}{m\omega_\alpha^2 d_0^3} \ll 1$ (well localized modes in direction α)

eliminate high-energy transverse phonons $\Longrightarrow$ for longitudinal ones (RWA)

$$H_L = \tilde{\omega}_z \sum_i b_i^\dagger b_i - \sum_{i \neq j} \frac{\tilde{\beta}_z \tilde{\omega}_z}{2\,|i-j|^3} (b_j^\dagger b_i + \text{H.c.}) \qquad (\,\tilde{\omega}_z \approx \omega_z\,)$$

nearly dispersionless (completely local) phonons $\Longrightarrow$ $J \ll \tilde{\omega}_z$

$$H_{\mathrm{e-ph}} = g\tilde{\omega}_z \textstyle\sum_i c_i^\dagger c_i (b_i + b_i^\dagger)$$

$$g = \frac{4\pi}{\tilde{\omega}_z} \frac{G_z^2}{\Delta_z} \times \frac{a}{d_0}$$

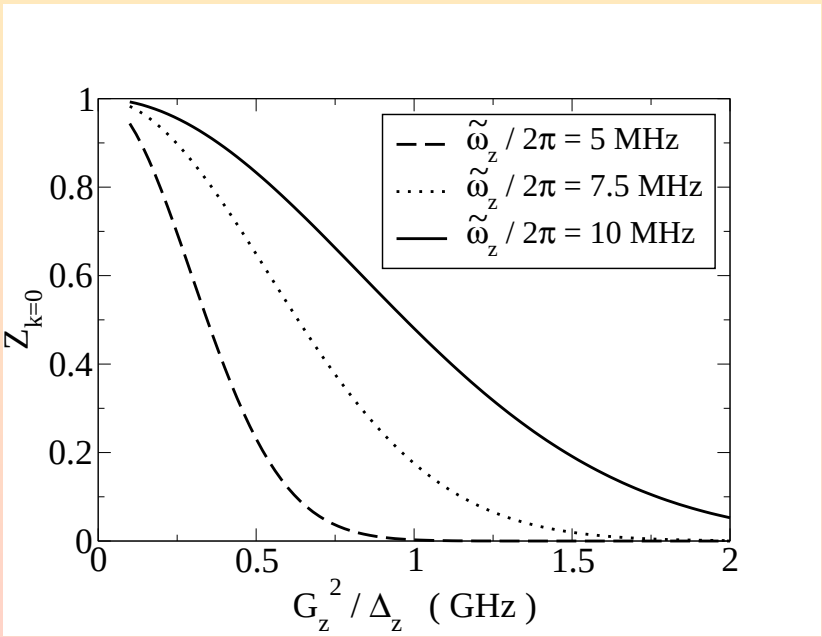
typical values:
$\omega_z/2\pi = 1 - 20$ MHz
$\Delta_z = 1000$ GHz,
$G_z = 10 - 100$ GHz

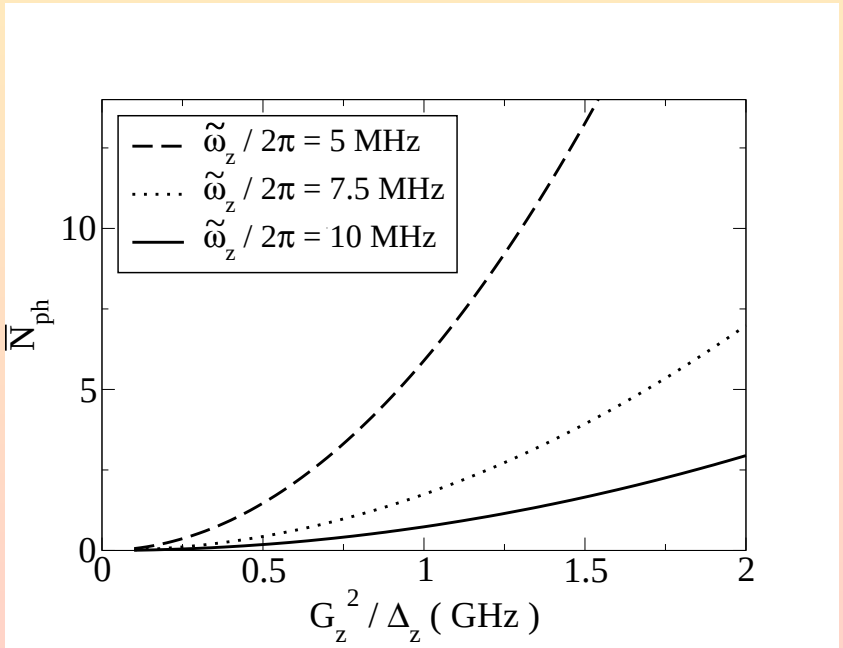
Polaron crossover

strength: ability to reach controllably the strong-coupling regime (small polarons)

limitation: ability to simulate only the anti-adiabatic case of the Holstein model

results from Toyozawa-Ansatz calculation on $N = 32$ sites:





$$Z_{k=0} \equiv \frac{|\langle \Psi_{k=0} | \psi_{k=0} \rangle|^2}{\langle \psi_{k=0} | \psi_{k=0} \rangle}$$

$$\bar{N}_{ph} \equiv \langle \psi_{k=0} | \sum_i b_i^\dagger b_i \, | \psi_{k=0} \rangle$$

Conclusions and Outlook

- Single-particle SSH model (Peierls' coupling) shows a nonanalytic behavior at a critical coupling strength!
- Charge carriers in crystalline organic semiconductors are NOT (small) polarons!
- Small (Holstein) polaron formation can be simulated with trapped ions. In the multiple-excitation regime, study density-driven destabilization of small polarons