Finite temperature calculations of the electronic and optical properties of solids and nanostructures: the role of electron-phonon coupling from an Ab-Initio perspective

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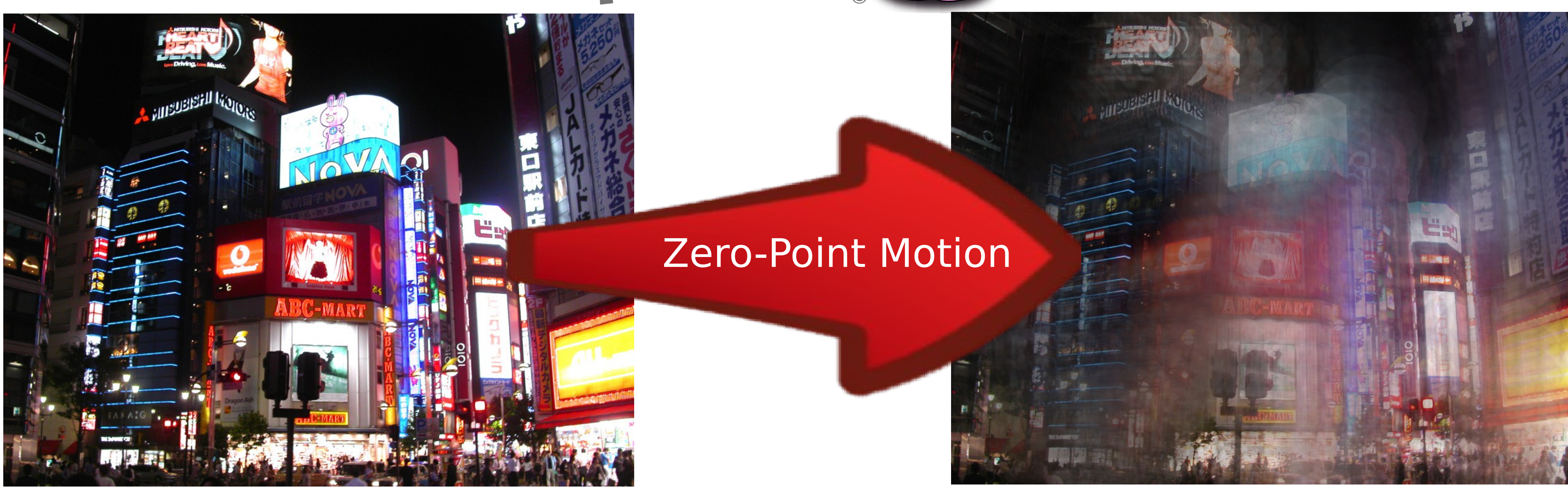
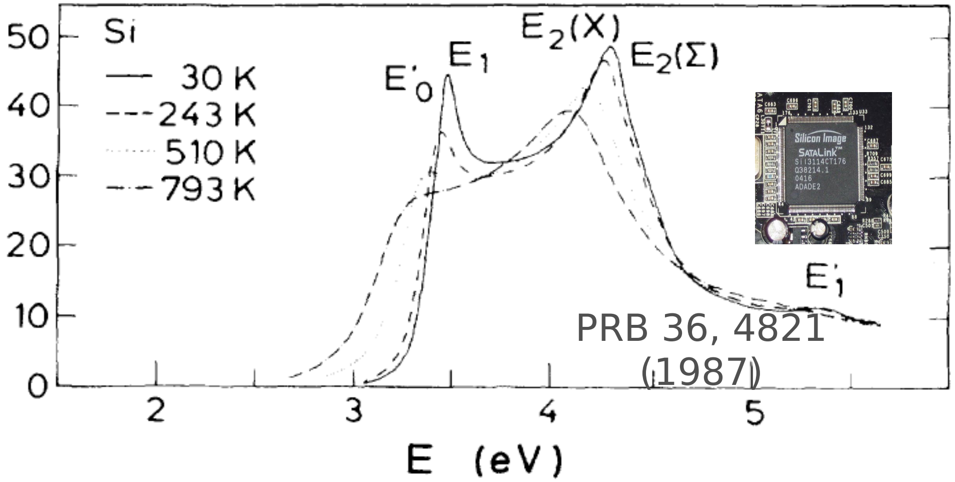
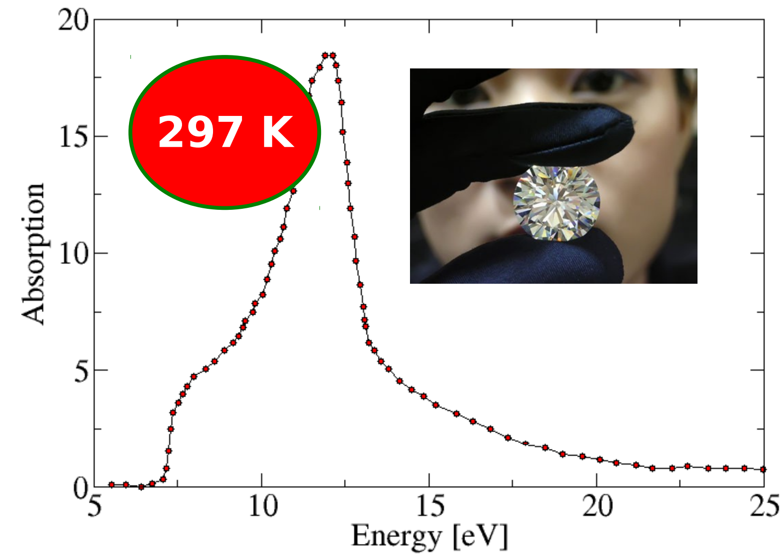
Consiglio Nazionale delle Ricerche



Real life is at finite temperature (I)





ARTICLES

nature materials | VOL 3 | JUNE 2004 | www.nature.com/naturematerials

Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal

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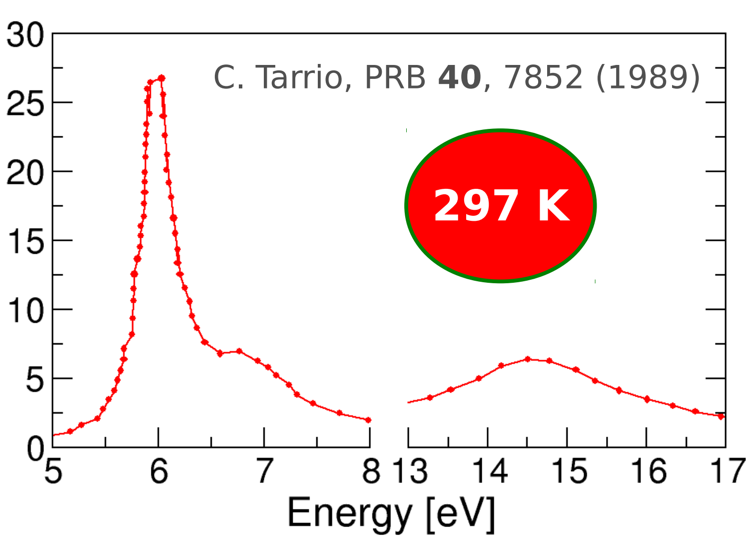
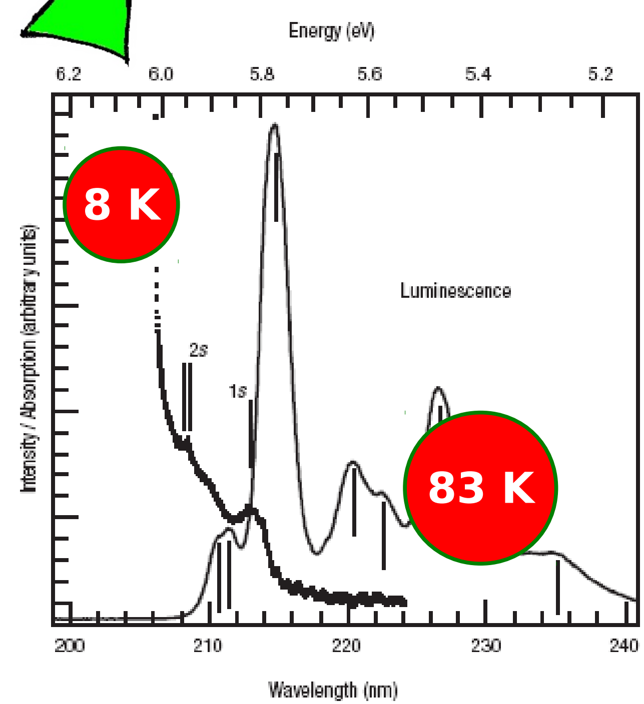




Real life is at finite temperature (II)

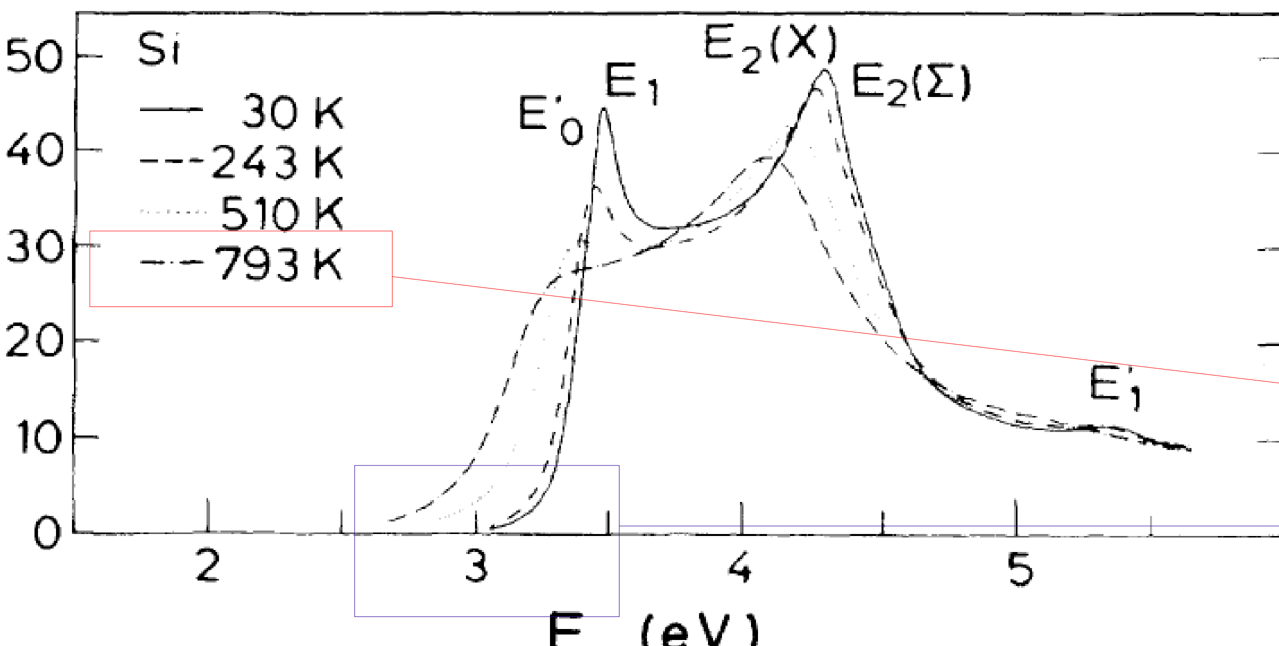
PHYSICAL REVIEW B VOLUME 36, NUMBER 9 15 SEPTEMBER 1987-II

Temperature dependence of the dielectric function and interband critical points in silicon

P. Lautenschlager, M. Garriga, L. Viña,* and M. Cardona
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany
(Received 30 April 1987)

The complex dielectric function $\epsilon(\omega)$ of Si was measured ellipsometrically in the 1.7–5.7-eV photon-energy range at temperatures between 30 and 820 K. The observed structures are analyzed by fitting the second-derivative spectrum $d^2\epsilon/d\omega^2$ with analytic critical-point line shapes. Results for the temperature dependence of the parameters of these critical points, labeled E_0', E_1, E_2, and E_1', are presented. The data show good agreement with microscopic calculations for the energy shift and the broadening of interband transitions with temperature based on the electron-phonon interaction. The character of the E_1 transitions in semiconductors is analyzed. We find that for Si and light III-V or II-VI compounds an excitonic line shape represents best the experimental data, whereas for Ge, α-Sn, and heavy III-V or II-VI compounds a two-dimensional critical point yields the best representation.

"... unfortunately theorists do not even bother to compare their calculations with low-temperature measurements, using more easily accessible room temperature spectra."



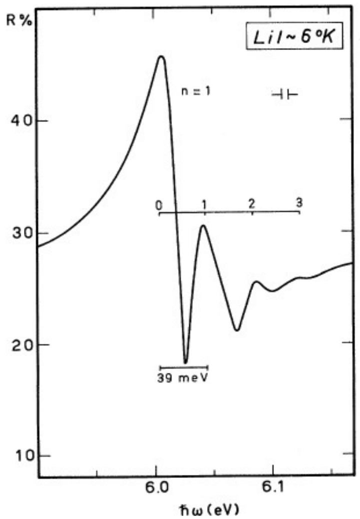
793 K = 68 meV

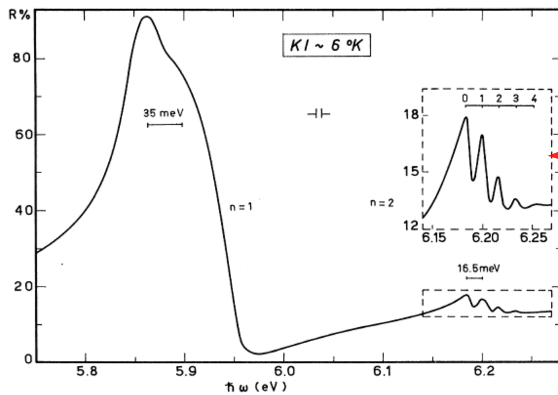
QP gap is 1200 meV

At the absorption threshold the QP lifetime is EXACTLY infinite

YES ! We do need phonons.

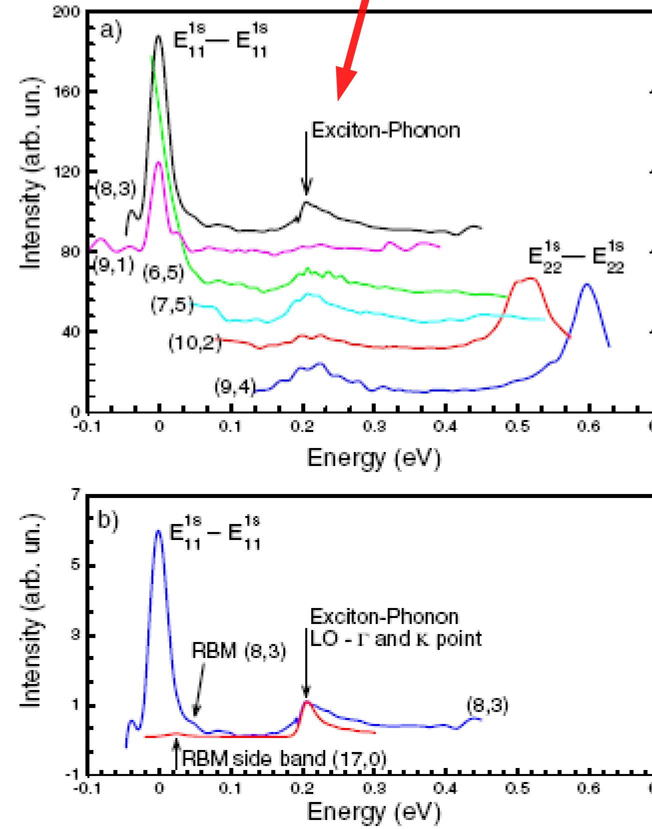
Real life is at finite temperature (III)



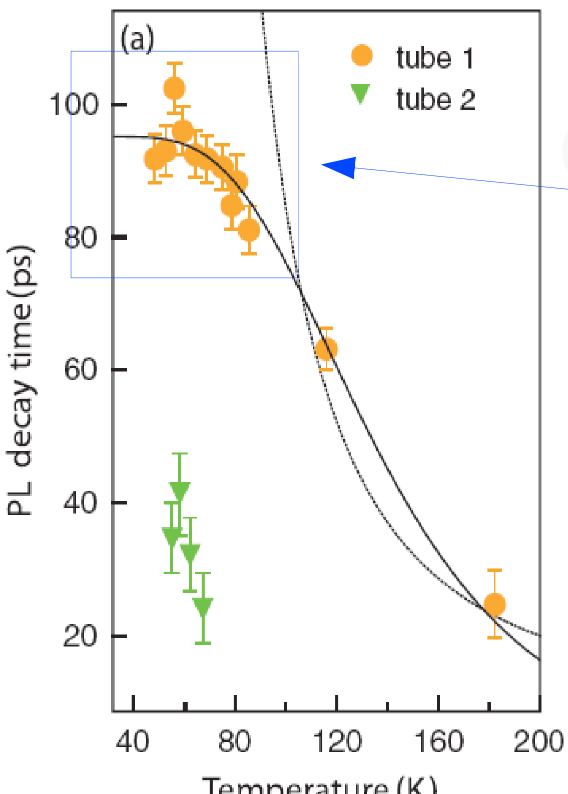


G. Baldini, A. Bosacchi, and B. Bosacchi, PRL, **23**, 846 (1969)

phonon sidebands

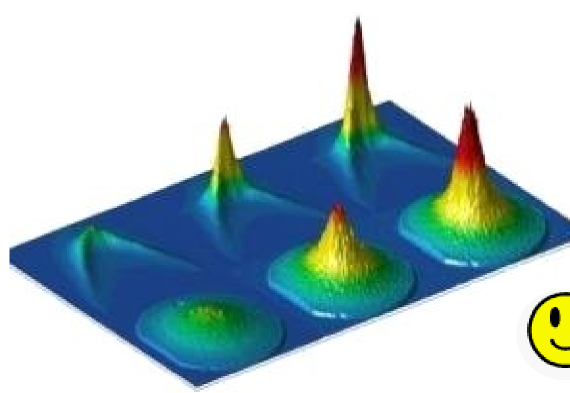


PRL 95, 247401 (2005)



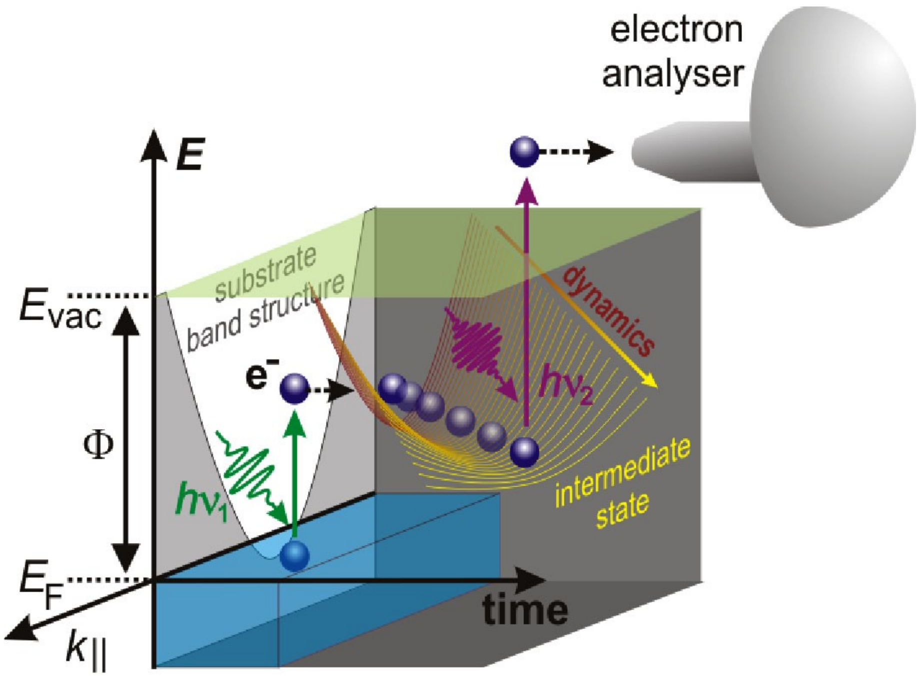
PRL 95, 197401 (2005)

Phonons are responsible for the low-temperature saturation of the excitonic lifetime



There are many different “flavours” of excitons: polaritons, polaronic excitons... whose physical properties are influenced by the exciton-phonon interaction

Electron–phonon today

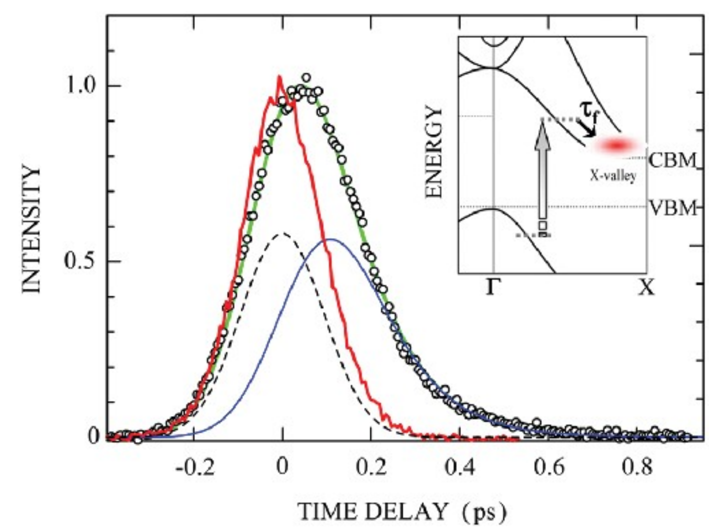


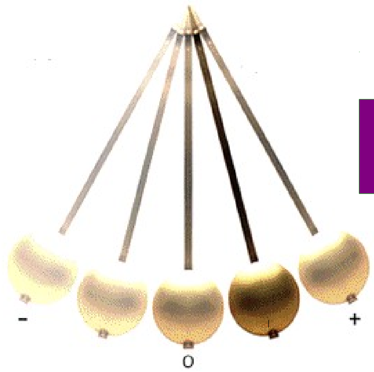
1. An ultra-short laser pulse pumps electrons in the conduction
2. The non-thermal electronic distribution relaxes via e–e and e–ph scatterings
3. The electronic population is probed after varying delays with photoemission

PRL **102**, 087403 (2009) PHYSICAL REVIEW LETTERS week ending 27 FEBRUARY 2009

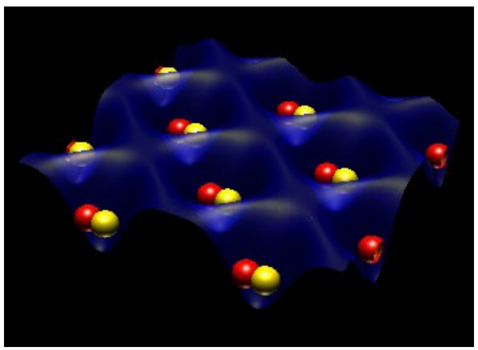
Ultrafast Carrier Relaxation in Si Studied by Time-Resolved Two-Photon Photoemission Spectroscopy: Intravalley Scattering and Energy Relaxation of Hot Electrons

See Monday's talk!

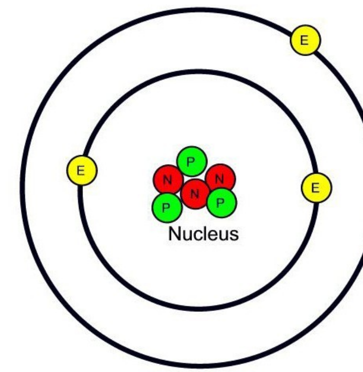


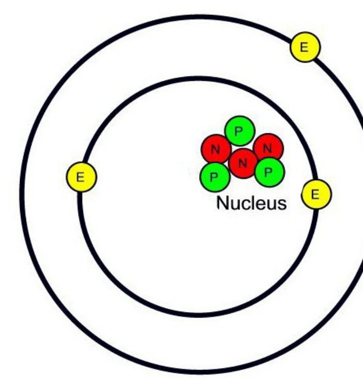


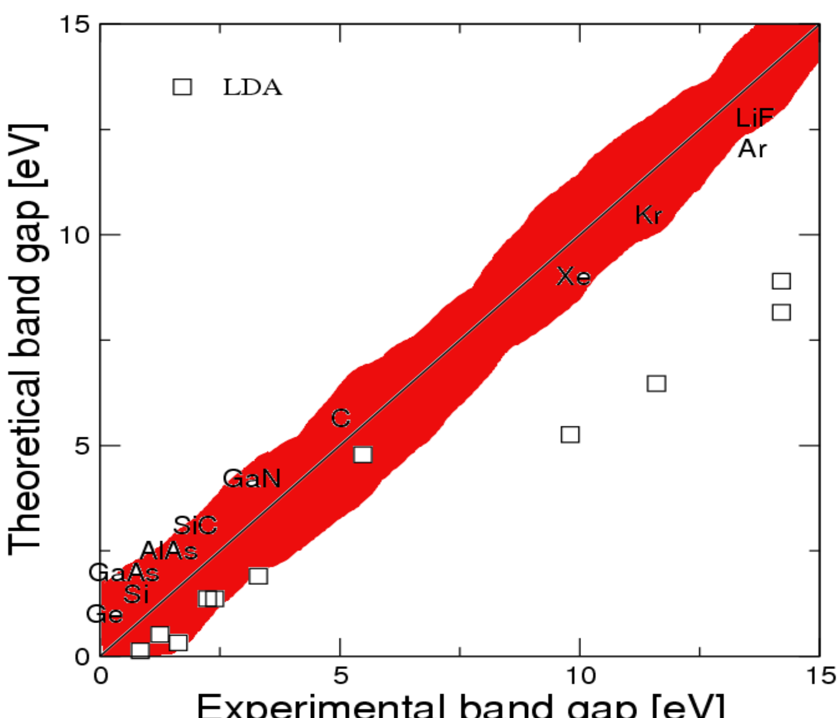
$$\langle u^2(T)\rangle \approx \frac{\hbar}{4M\Omega}\langle 1+2N_{Bose}(T)\rangle$$



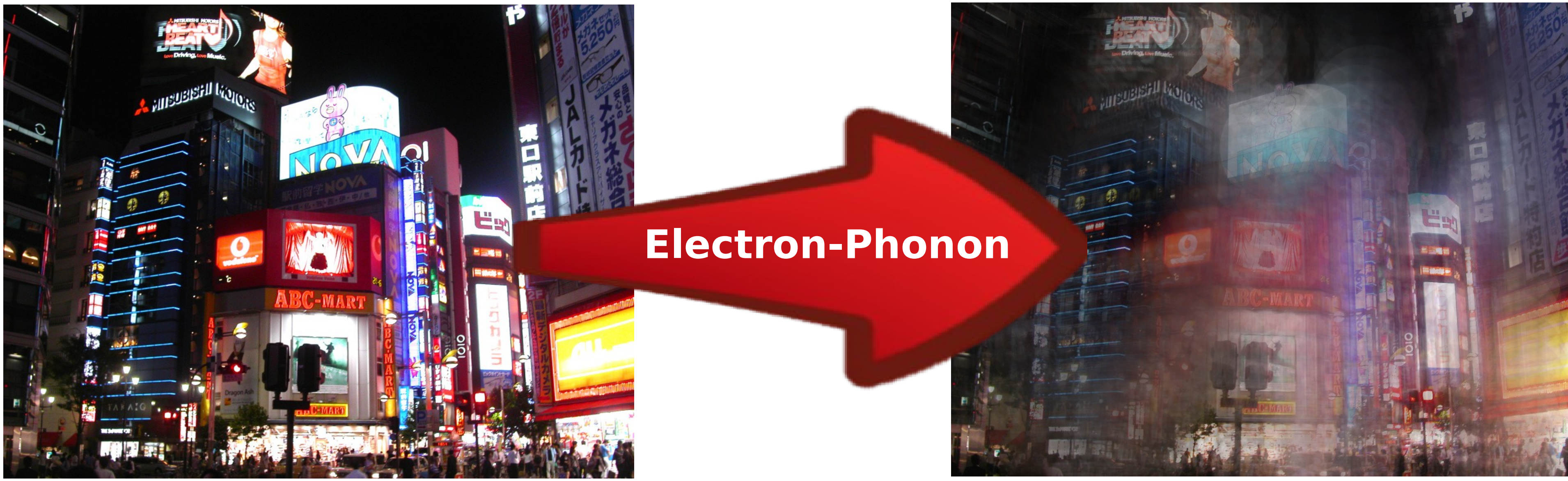
The quantistic zero-point motion effect





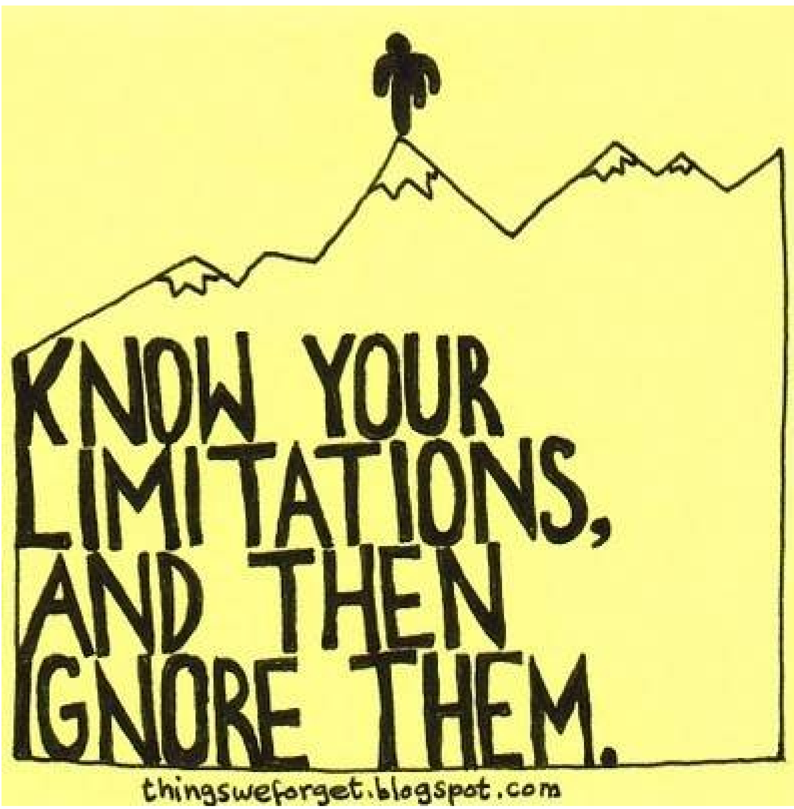


THE Motivation



Are purely electronic theories reliable ???

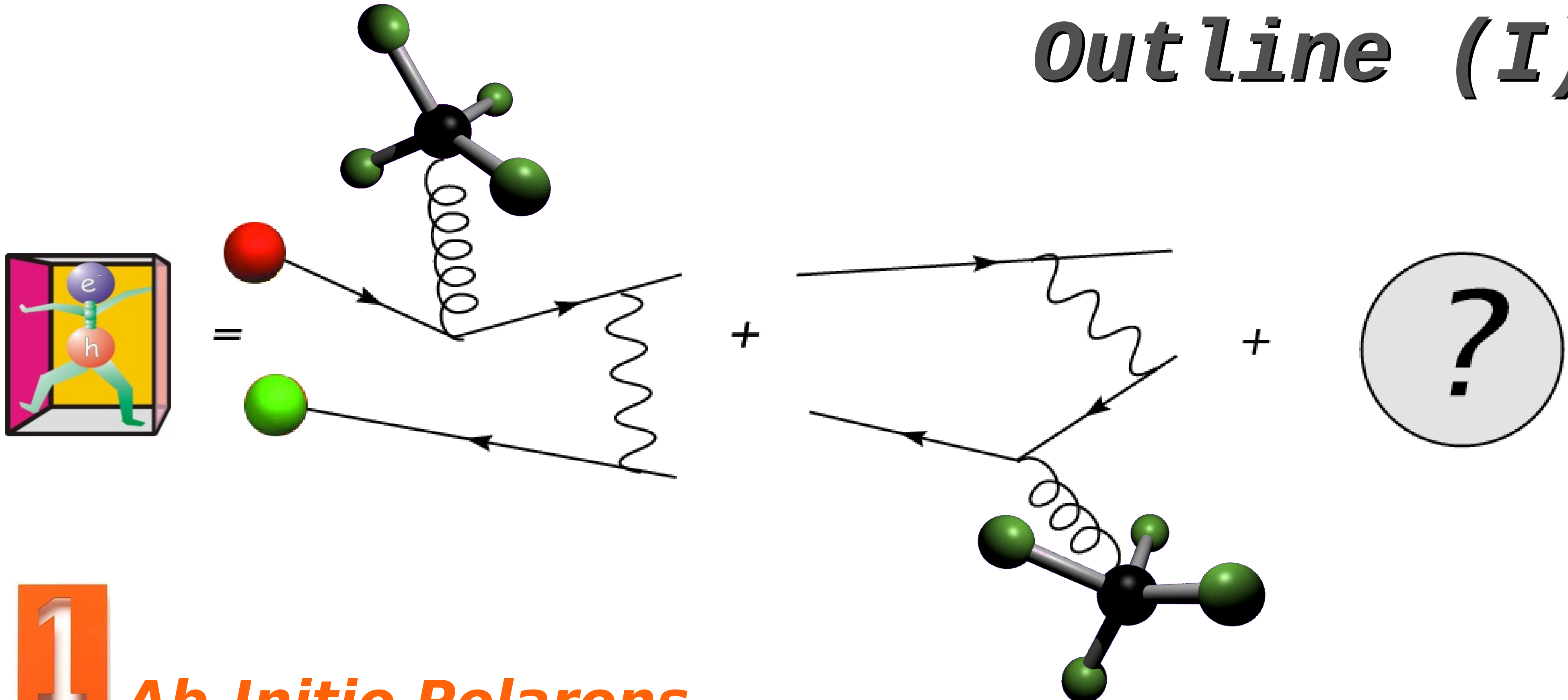
THE limitations...



In this talk ...

- I will not extensively discuss formal aspects (vertex, conserving props., …)
- I will (try) not do extensive and heavy math (see references for that)
- I will not talk about superconductivity, Fröhlich or Holstein Hamiltonians
- I will use LDA or GGA, nothing more complicated (including SC-GW)

Outline (I)



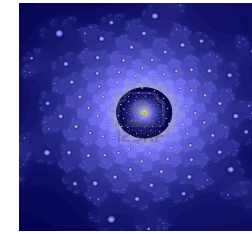
1 *Ab-Initio Polarons*

2 *Finite temperature excitons*

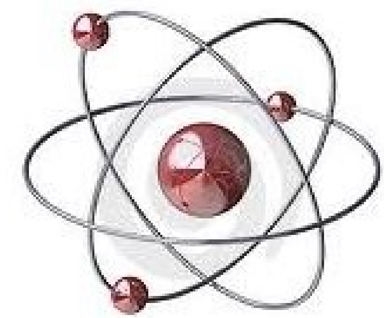
3 *Spectral functions and the QP-approximation*

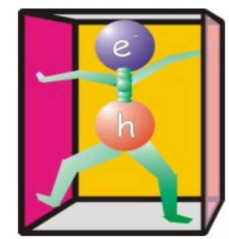
Outline (II)

1 Ab-Initio Polarons



- The Heine-Allen-Cardona Approach (static)
- The Hedin-Lundqvist approach (dynamical)
- The Diagrammatic approach (dynamical)
- Density Functional Perturbation Theory

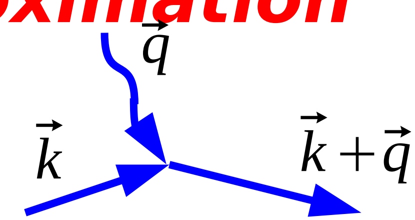




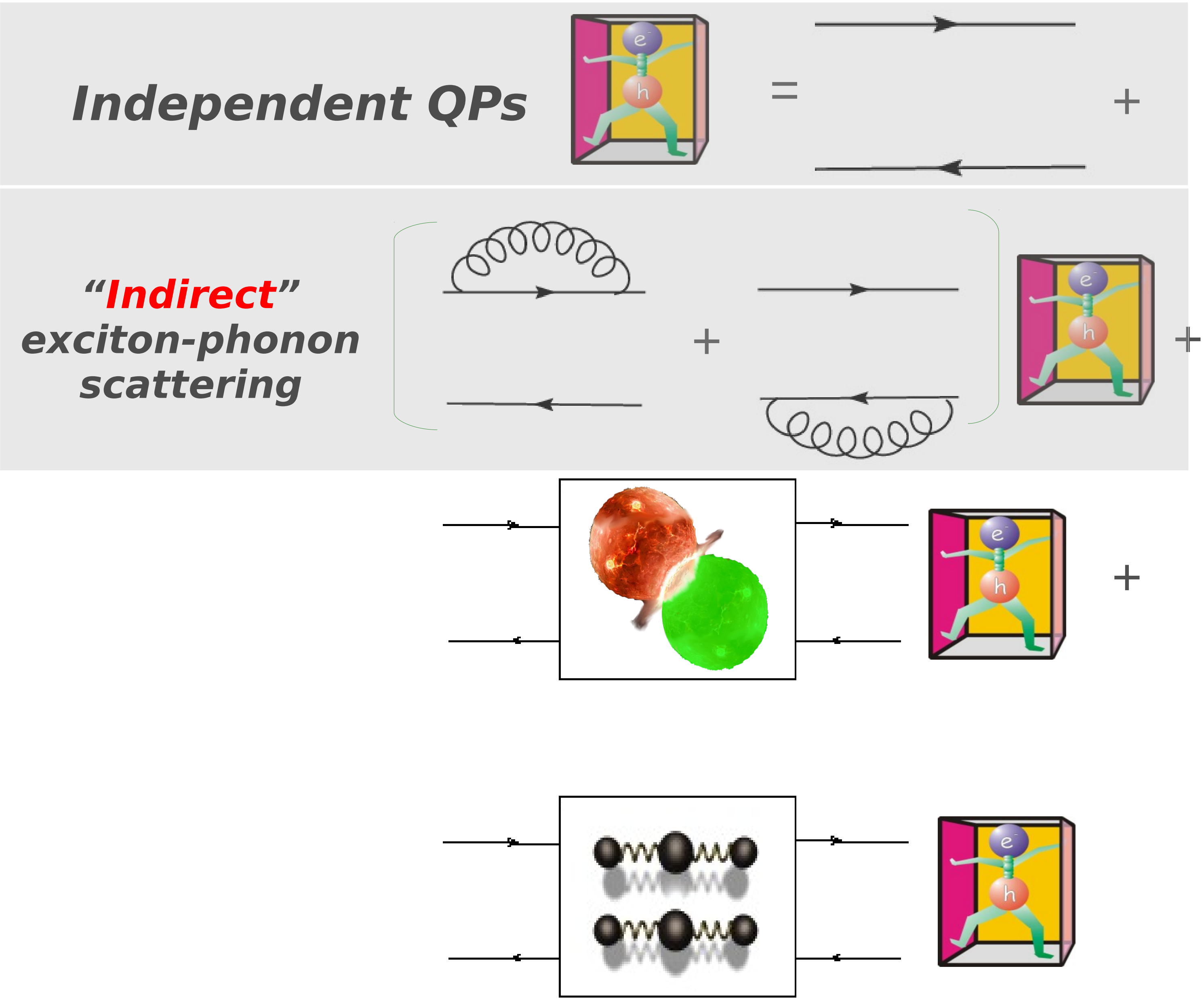
2 Finite temperature excitons

- The Bethe-Salpeter equation in the polaronic basis
- A phonon induced kernel for the Bethe-Salpeter equation
- Finite temperature optical spectra of solids

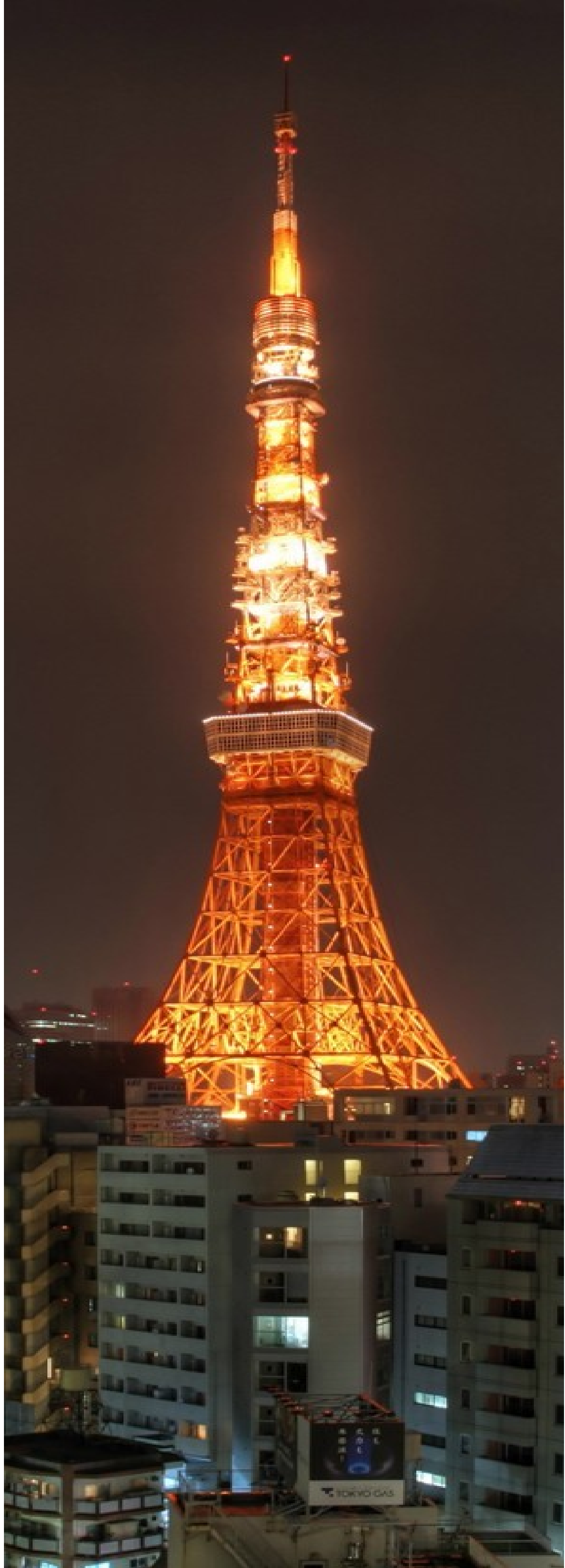
3 Spectral functions and the QP-approximation



- Quasiparticles and spectral functions
- Polarons as entangled electron-phonon states



Ab-Initio Polarons

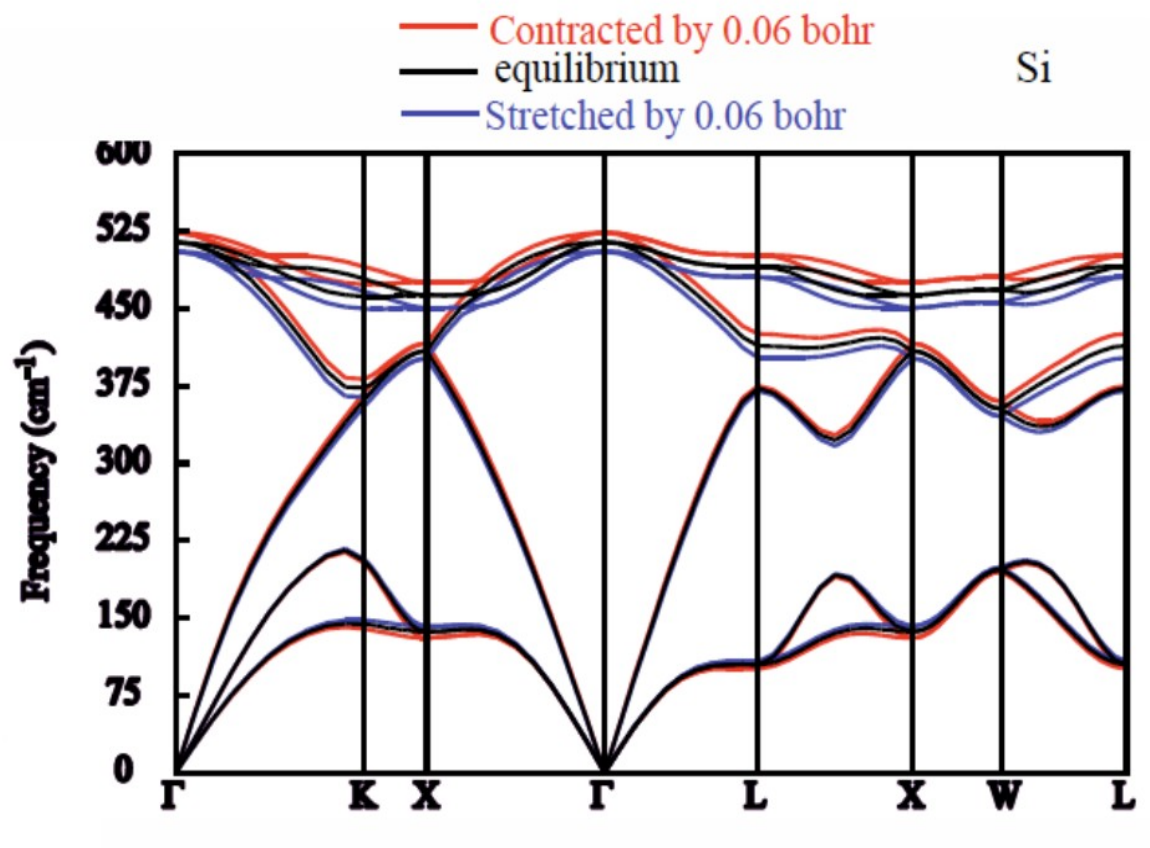


The quasi-harmonic approximation

$$\left(\frac{\partial \varepsilon_{n\vec{k}}}{\partial T}\right)_P = \left(\frac{\partial \varepsilon_{n\vec{k}}}{\partial T}\right)_V + \left(\frac{\partial \varepsilon_{n\vec{k}}}{\partial \ln V}\right)_T \alpha_P(T)$$

Phonon population

Thermal expansion



$$\gamma_{m\vec{q}} = -\frac{\partial(\ln \omega_{m\vec{q}})}{\partial(\ln V)}$$

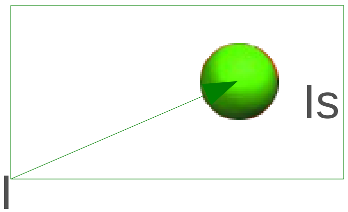
Grüneisen parameters

$$\alpha(T) = \frac{V}{3B}\sum_{\vec{q},m}\frac{1}{\hbar\omega_{m\vec{q}}}\gamma_{m\vec{q}}\frac{\partial n(\omega_{m\vec{q}})}{\partial T}$$

It can be easily calculated using DFT and finite-differences

The Heine–Allen–Cardona Approach (I)

For a review see M. Cardona, Solid State Commun. **133**, 3 (2005).



$$H = T + V_{SCF}(\{\mathbf{R}_{Is}\})$$

$$\mathbf{R}_{Is} = \mathbf{R}_{Is} + \mathbf{u}_{Is}$$

$$\delta H = \delta H^{(1)} + \delta H^{(2)}$$

$$\delta H^{(1)} = \sum_{Is} \frac{\partial V_{SCF}}{\partial \mathbf{R}_{Is}} \mathbf{u}_{Is}$$

$$\delta H^{(2)} = \frac{1}{2} \sum_{IsJt} \frac{\partial^2 V_{SCF}}{\partial \mathbf{R}_{Is} \partial \mathbf{R}_{Jt}} \mathbf{u}_{Is} \mathbf{u}_{Jt}$$

Using standard 1st and 2nd order perturbation theory and the fact that $E_{n\mathbf{k}} \equiv \langle n\mathbf{k}|H|n\mathbf{k}\rangle$

$$\delta E_{n\mathbf{k}} = \sum_{IsJt} \left[\underbrace{\frac{1}{2} \langle \frac{\partial^2 V_{SCF}}{\partial \mathbf{R}_{Is} \partial \mathbf{R}_{Jt}} \rangle}_{\text{Debye-Waller}} + \underbrace{\sum_{m\mathbf{p}} (E_{n\mathbf{k}} - E_{m\mathbf{p}})^{-1} \langle \frac{\partial V_{SCF}}{\partial \mathbf{R}_{Is}} |m\mathbf{p}\rangle \langle m\mathbf{p}| \frac{\partial V_{SCF}}{\partial \mathbf{R}_{Jt}} \rangle}_{\text{Fan}} \right] \mathbf{u}_{Is} \mathbf{u}_{Jt}$$

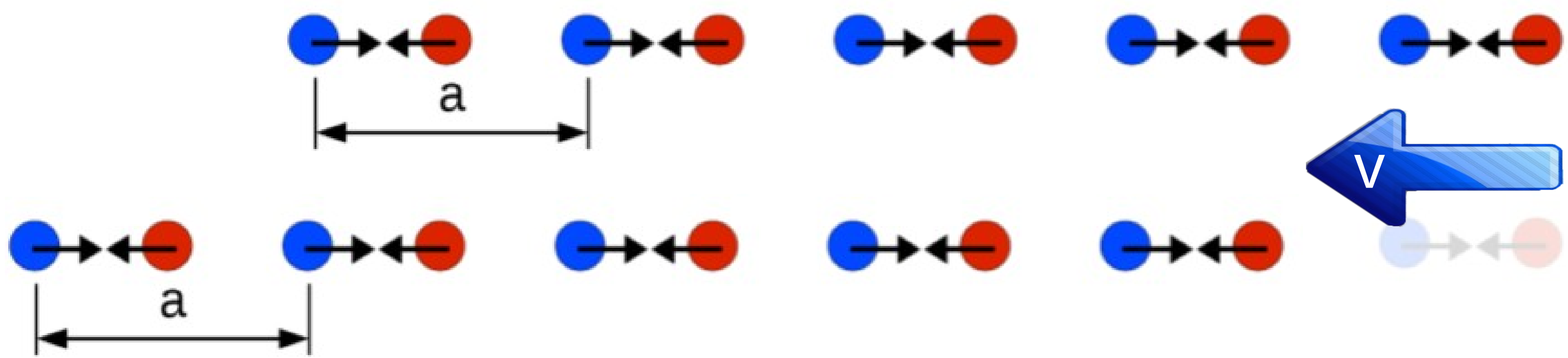
Now we can rewrite the displacement operator using the canonical operators

$$\sum_{Is} \mathbf{u}_{Is} \langle n'\mathbf{k} + \mathbf{q}| \frac{\partial V_{SCF}}{\partial \mathbf{R}_{Is}} |n\mathbf{k}\rangle = \sum_{\mathbf{q}\lambda} g^{\mathbf{q}\lambda}_{n'n\mathbf{k}} \left(b^{\dagger}_{\mathbf{q}\lambda} + b_{\mathbf{q}\lambda} \right)$$

$$\langle (b^{\dagger}_{\mathbf{q}\lambda} + b_{\mathbf{q}\lambda})(b^{\dagger}_{\mathbf{q}\lambda} + b_{\mathbf{q}\lambda}) \rangle = 2N_{\mathbf{q}\lambda} + 1$$

$$\boxed{\delta E_{n\mathbf{k}} = \sum_{\mathbf{q}\lambda m} \frac{\left| g^{\mathbf{q}\lambda}_{n'n\mathbf{k}} \right|^2}{E_{n\mathbf{k}} - E_{m\mathbf{k}+\mathbf{q}}} (2N_{\mathbf{q}\lambda} + 1)}$$

The Heine-Allen-Cardona Approach (II)



By imposing an *"acoustic sum rule"* $\delta E_{n\mathbf{k}}\left[\{\mathbf{u}_{Is}+\mathbf{v}\}\right] = \delta E_{n\mathbf{k}}\left[\{\mathbf{u}_{Is}\}\right]$

$$\boxed{\langle \frac{\partial^2 V_{SCF}}{\partial \mathbf{R}_{Is}\partial \mathbf{R}_{Jt}} \rangle = \sum_m \left(E_{n\mathbf{k}} - E_{m\mathbf{k}}\right)^{-1} F\left[\langle n\mathbf{k}|\frac{\partial V_{SCF}}{\partial \mathbf{R}_{Is}}|m\mathbf{p}\rangle\right]}$$

$$\boxed{\delta E_{n\mathbf{k}} = \sum_{\mathbf{q}\lambda m}\left[\frac{|g^{\mathbf{q}\lambda}_{n'n\mathbf{k}}|^2}{E_{n\mathbf{k}} - E_{m\mathbf{k}+\mathbf{q}}} - \frac{\Lambda^{\mathbf{q}\lambda}_{n'n\mathbf{k}}}{E_{n\mathbf{k}} - E_{m\mathbf{k}}}\right]\left(2\langle N_{\mathbf{q}\lambda}\rangle + 1\right)}$$

Non-Diagonal DW corrections can be important in isolated systems like molecules

$$\delta H^{(2)} = \frac{1}{2}\sum_{IsJt} \frac{\partial^2 V_{SCF}}{\partial \mathbf{R}_{Is}\partial \mathbf{R}_{Jt}} \mathbf{u}_{Is}\mathbf{u}_{Jt}$$

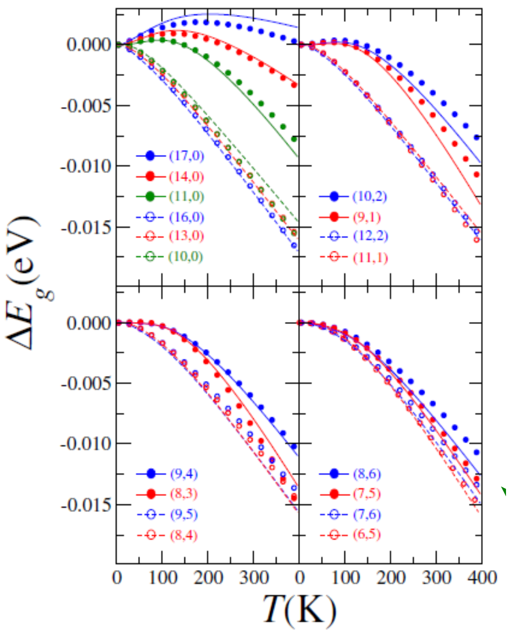
X. Gonze et al, Annalen der Physik **523**, 168 (2011)

Clear dependence on the temperature

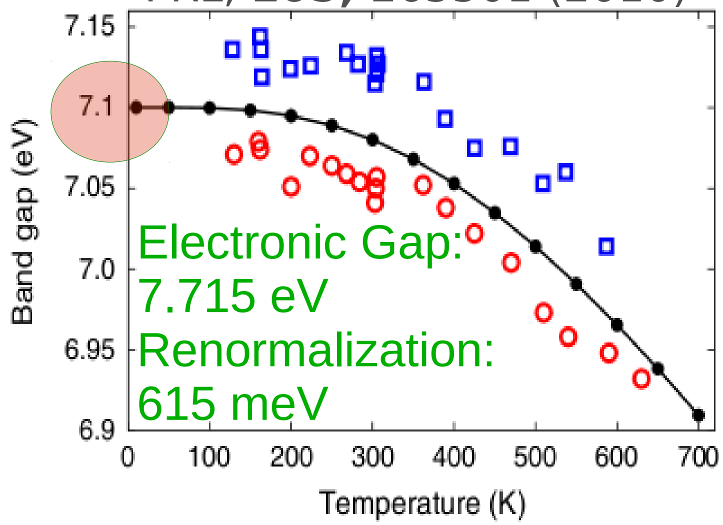
Polaron damping neglected

The Heine-Allen-Cardona Approach (III)

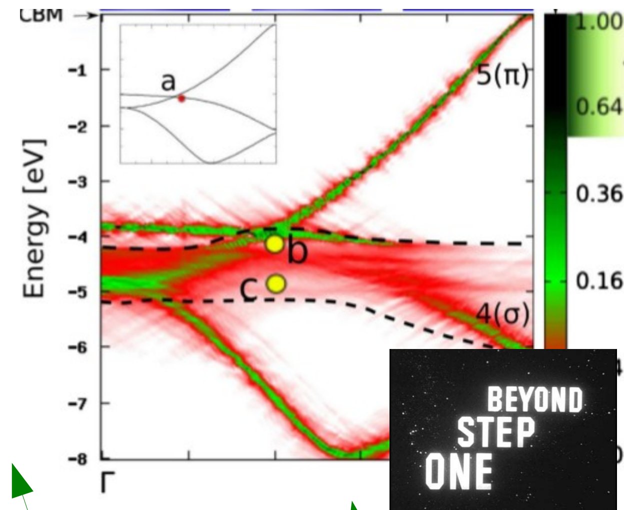
R. B. Capaz *et al.* PRL. **94**, 36801 (2005)



F. Giustino, *et al.*
PRL, **105,** 265501 (2010)



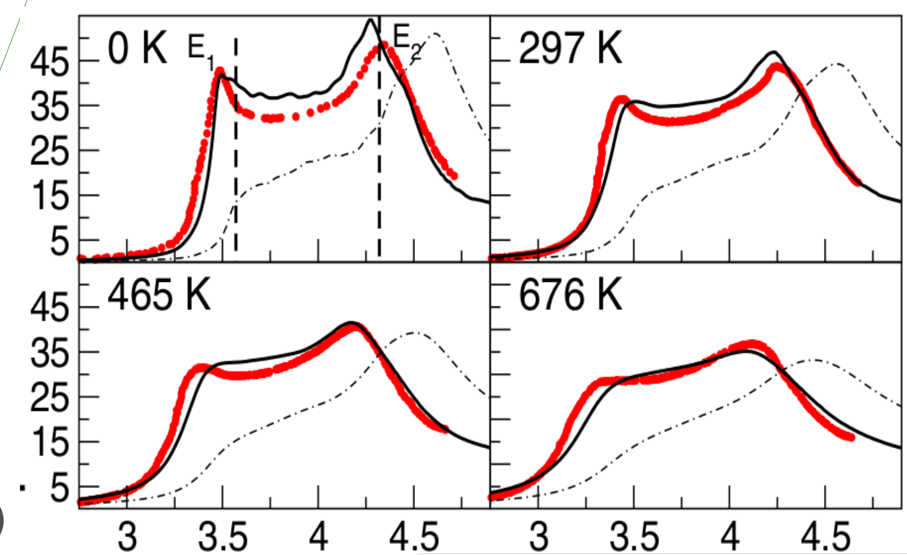
E. Cannuccia
PRL **107**, 255501 (2011)



State	Mass	SE	DW	Total
$\Gamma_{25'}(v)$	12.00	0.0	0.0	0.0
$\Gamma_{15}(c)$	12.00	−547.8	−130.1	−677.9

S. Zollner *et al.*
PRB **45**, 3376 (1992)

A. Marini
PRL **101**, 106405 (2008)



Green's functions: an (over)simplified picture (I)

G. Strinati, Nuovo Cimento **11**, 1 (1988)

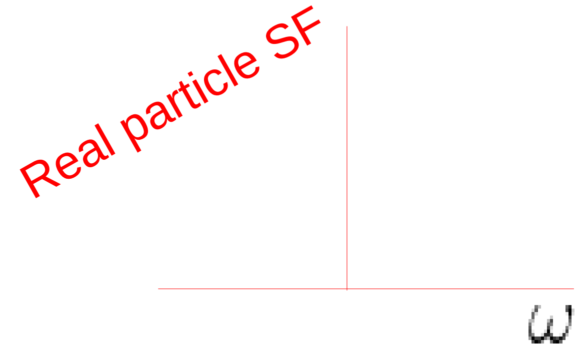
$$G_{n\mathbf{k}} = \langle n\mathbf{k} \mid (\omega - H)^{-1} \mid n\mathbf{k} \rangle$$

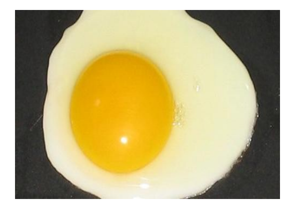
$$G_{n\mathbf{k}}(\omega) = \sum_I \left| \langle \Psi \mid c^\dagger_{n\mathbf{k}} \mid I\mathbf{k} \rangle \right|^2 (\omega - E_{I\mathbf{k}})^{-1}$$

$$\boxed{E_{I\mathbf{k}} \rightarrow A_{n\mathbf{k}}(\omega) = \sum_I \left| \langle \Psi \mid c^\dagger_{n\mathbf{k}} \mid I\mathbf{k} \rangle \right|^2 \delta(\omega - E_{I\mathbf{k}})}$$

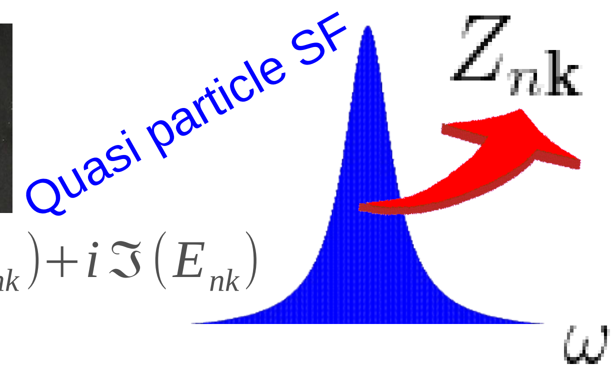
Spectral Functions

$E_{Ik} = \epsilon_{nk}$



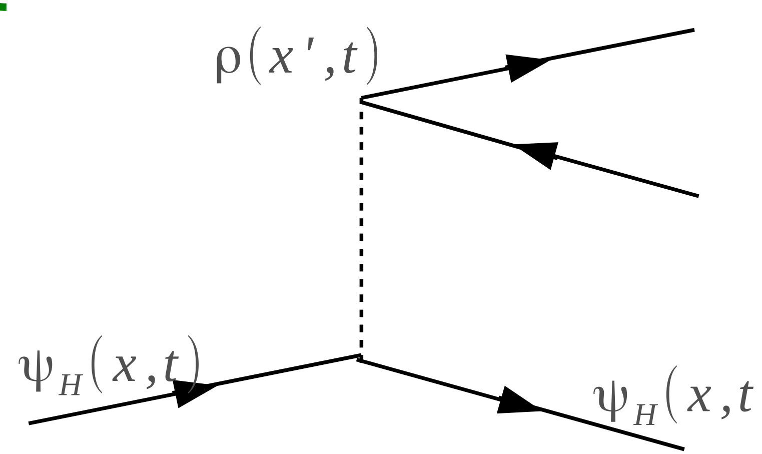


$E_{Ik} = \Re(E_{nk}) + i\,\Im(E_{nk})$



$$G(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2) \equiv (-i) \langle T\{\hat{\psi}_H(\mathbf{x}_1, t_1)\, \hat{\psi}^\dagger_H(\mathbf{x}_1, t_1)\}\rangle$$

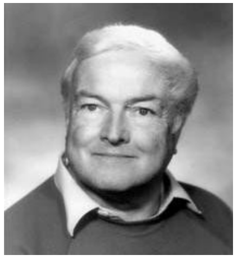
$$i\partial_t \hat{\psi}_H(\mathbf{x}, t) = (\ldots) + \int d\mathbf{x}' \frac{\rho(\mathbf{x}', t)}{|\mathbf{x} - \mathbf{x}'|} \hat{\psi}_H(\mathbf{x}, t)$$

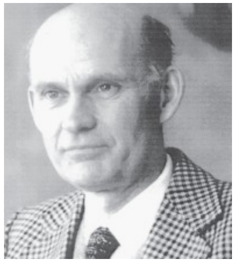


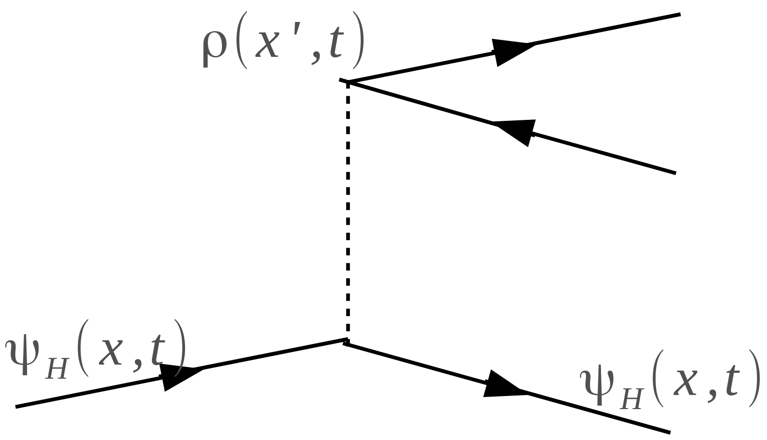
$\rho(x', t)$ Electronic & Nuclear density

Diagrammatic vs Hedin-Lundqvist approach (I)

LH and SL, Solid. State Phys. **23**, 1 (1969); RvL, PRB **69**, 115110 (2004)







Feynmann diagrams

Equation of motion

$$H \rightarrow H + \int \phi(x)\rho(x,t)$$

$$\psi_H(x,t) \rightarrow \psi_{H,\phi}(x,t)$$

$$\frac{\delta\psi_H(x,t)}{\delta\phi} \sim \rho(x',t)\psi_H(x,t)$$

$$[i\partial_t - h(1)]G(1,2) = \delta(1,2) + \int dr\,\Sigma(1,3)G(3,2)$$

$$\Sigma(1,2) \sim \iint d3\,d4\,v(1,3)G(1,4)\frac{\delta G^{-1}(4,5)}{\delta\phi(3)}$$

Green's functions: an (over)simplified picture (II)

$$[i\partial_t - h(1)]G(1,2) = \delta(1,2) + \int dr\, \Sigma(1,3) G(3,2)$$

Time Fourier transformation

$$G_{n\mathbf{k}}(\omega) = \frac{1}{\omega - \epsilon_{n\mathbf{k}} - \Sigma_{n\mathbf{k}}(\omega) + i\eta}$$

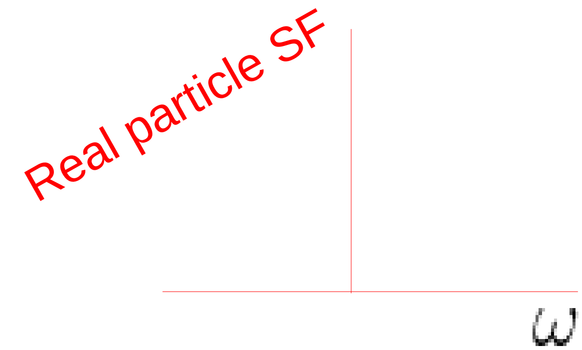
Linear expansion

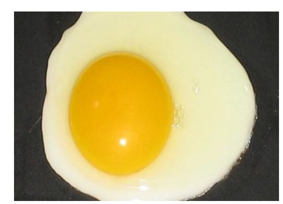
$$E_{nk} = \epsilon_{nk} + \Sigma(\epsilon_{nk}) + \Sigma'(\epsilon_{nk})(E_{nk} - \epsilon_{nk})$$

QP approximation

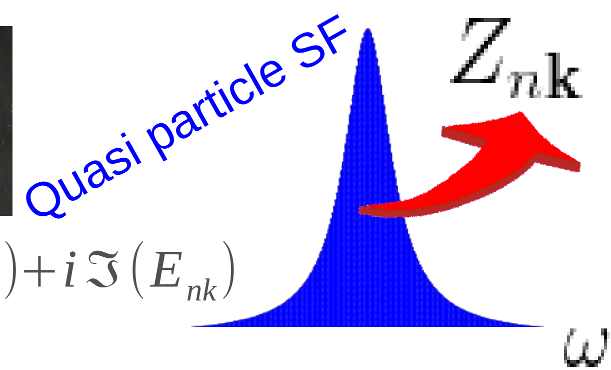
$$\boxed{G_{nk}(\omega) = \frac{Z_{nk}}{(\omega - E_{nk})} \qquad Z_{nk} = \frac{1}{(1 - \Sigma'(\epsilon_{nk}))}}$$

$E_{Ik} = \epsilon_{nk}$





$E_{Ik} = \Re(E_{nk}) + i\Im(E_{nk})$

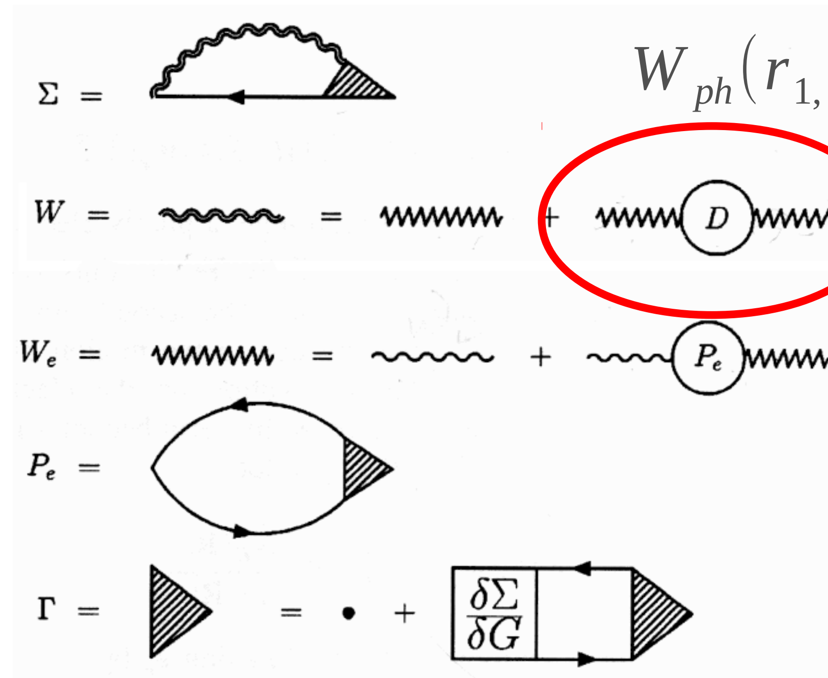


Hedin-Lundqvist approach (II)

RvL, PRB **69**, 115110 (2004)

$$\frac{\delta n(x,t)}{\delta\phi(x',t')} \sim P_e(x,t;x',t)$$

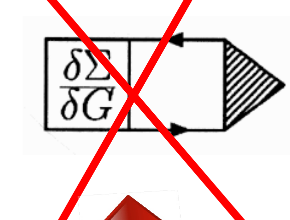
$$\boxed{\frac{\delta N(x,t)}{\delta\phi(x',t')} \sim D(x,t;x',t)}$$



$W_{ph}(r_1, r_2, w)$

$$= W_{ph}(\mathbf{r}_1,\mathbf{r}_2,i\omega) = \sum_{\mathbf{q}\lambda} \frac{2\omega_{\mathbf{q}\lambda}}{\omega^2+\omega^2_{\mathbf{q}\lambda}} g_{\mathbf{q}\lambda}(\mathbf{r}_1,i\omega)\, g^*_{\mathbf{q}\lambda}(\mathbf{r}_2,i\omega)$$

&

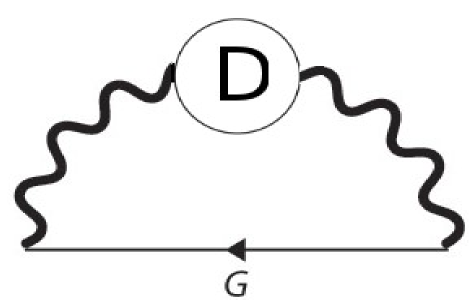


+

$$g_{\mathbf{q}\lambda}(\mathbf{r},i\omega) \propto \omega_{\mathbf{q}\lambda}^{-1/2} \sum_{Is} \int d\mathbf{r}_1 \epsilon_e^{-1}(\mathbf{r},\mathbf{r}_1;i\omega)\, \epsilon(\mathbf{q}\lambda|s)\cdot\nabla V_{ion}(\mathbf{r}_1)\, e^{i\mathbf{q}\cdot(\mathbf{R}_I+\tau_s)}$$

=

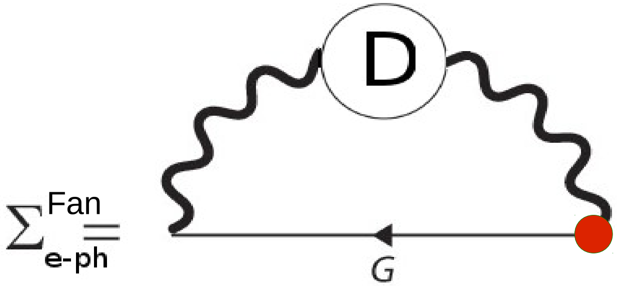
Fan self-energy $\Sigma^{\text{Fan}}_{\text{e-ph}} =$



$$\Gamma \sim \left(\frac{m_{electron}}{M_{atom}}\right)^{1/2}$$

Migdal's theorem

Hedin-Lundqvist approach (III): the FAN self-energy



(ω=0)

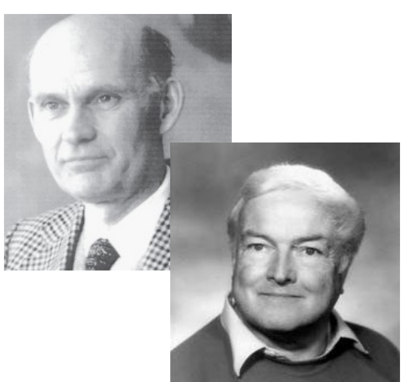
$$\sum_{atoms} \int dr_1 \epsilon^{-1}(r, r_1) \vec{\epsilon} . \nabla V_{ion}(r_1)$$ (LH)

$$V_{SCF}(r)$$ (HAC)

$$G_{n\mathbf{k}}(\omega) = \frac{1}{\omega - \epsilon_{n\mathbf{k}} - \Sigma_{n\mathbf{k}}(\omega) + i\eta}$$

$$\Sigma^{Fan}_{n\mathbf{k}}(\omega) = \sum_{\mathbf{q}\lambda} \frac{1}{N_{\mathbf{q}}} \sum_{n'} |\, g^{\mathbf{q},\lambda}_{n'n\mathbf{k}} \,|^2 \left[\frac{N_{q\lambda} + 1 - f_{n'\mathbf{k}-\mathbf{q}}}{\omega - \epsilon_{n'\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}\lambda} - i0^+} + \frac{N_{q\lambda} + f_{n'\mathbf{k}-\mathbf{q}}}{\omega - \epsilon_{n'\mathbf{k}-\mathbf{q}} + \omega_{\mathbf{q}\lambda} - i0^+} \right]$$ (LH)

$$\delta E_{n\mathbf{k}} = \sum_{\mathbf{q}\lambda m} \left[\frac{|g^{\mathbf{q}\lambda}_{n'n\mathbf{k}}|^2}{E_{n\mathbf{k}} - E_{m\mathbf{k}+\mathbf{q}}} - \frac{\Lambda^{\mathbf{q}\lambda}_{n'n\mathbf{k}}}{E_{n\mathbf{k}} - E_{m\mathbf{k}}} \right] (2\langle N_{\mathbf{q}\lambda}\rangle + 1)$$ (HAC)



STATIC & ADIABATIC limit

$\omega \approx \epsilon_{nk}$

$|\epsilon_{nk} - \epsilon_{n'k-q}| \gg \omega_{q\lambda}$

Fan term in Heine-Allen-Cardona Theory

Density Functional Perturbation Theory

[S. Baroni, REVIEWS OF MODERN PHYSICS, 2001 , 73, 515]

$$\frac{\partial V_{xc}}{\partial \mu} = \frac{dV_{xc}}{d\rho}\frac{\partial \rho(\mathbf{r})}{\partial \mu} \qquad \frac{\partial V_H}{\partial \mu} = \int \frac{1}{|\mathbf{r}-\mathbf{r}'|}\frac{\partial \rho(\mathbf{r}')}{\partial \mu} d^3 r'$$

DFPT is composed by a self-consistent linear system

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i\right] P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} = -P_c \frac{\partial V_{KS}}{\partial \mu}\psi_i(\mathbf{r})$$

$$\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_H}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu}$$

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_i P_c \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu}\psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu}$$

Dynamical Matrix

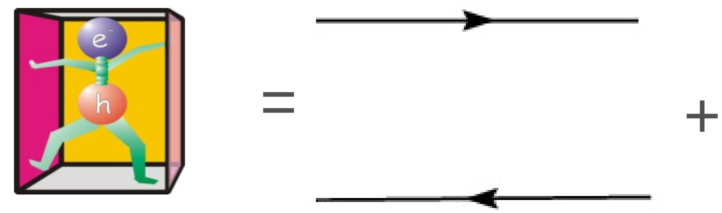
$$\omega_{q\lambda}$$

El-Ph matrix elements

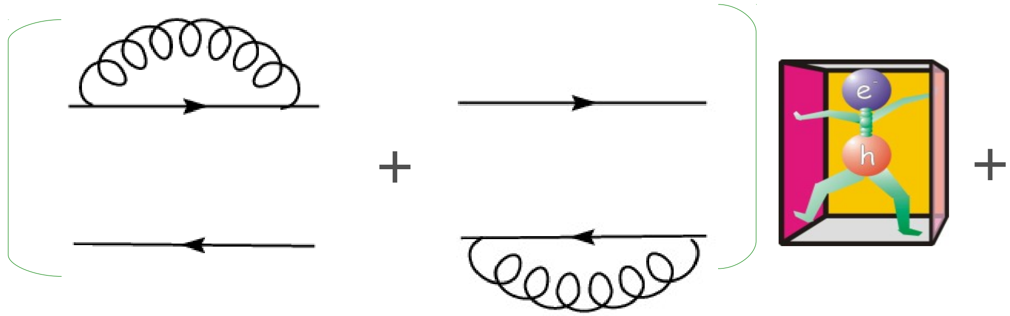
$$g_{nn'k}^{q\lambda} \sim (M\omega_{q\lambda})^{-1} \langle nk | \frac{dV_{KS}}{du_{q\lambda}} | n'k-q \rangle$$

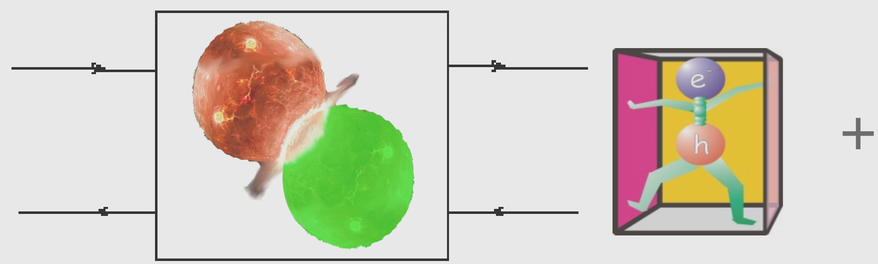
By working out the DFPT definition of the KS potential it is possible to link DFPT to the static limit of the electron-phonon potential defined in MBPT

Independent QPs

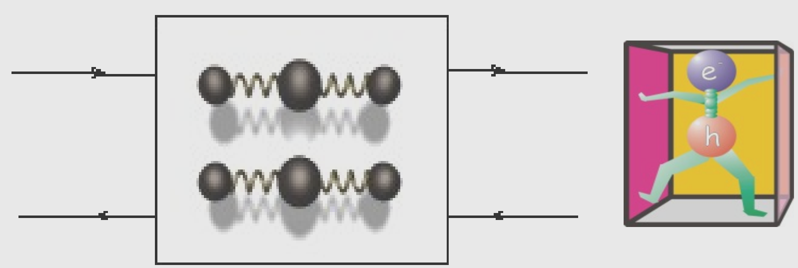


“Indirect” exciton-phonon scattering

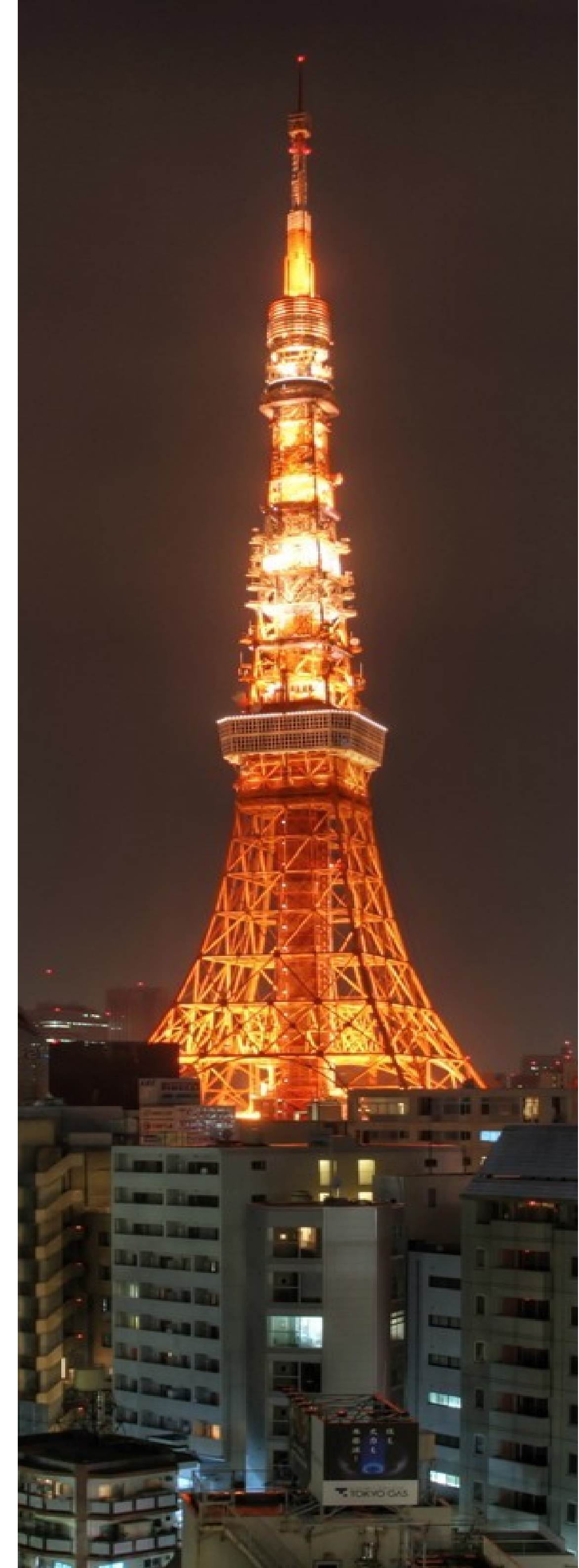




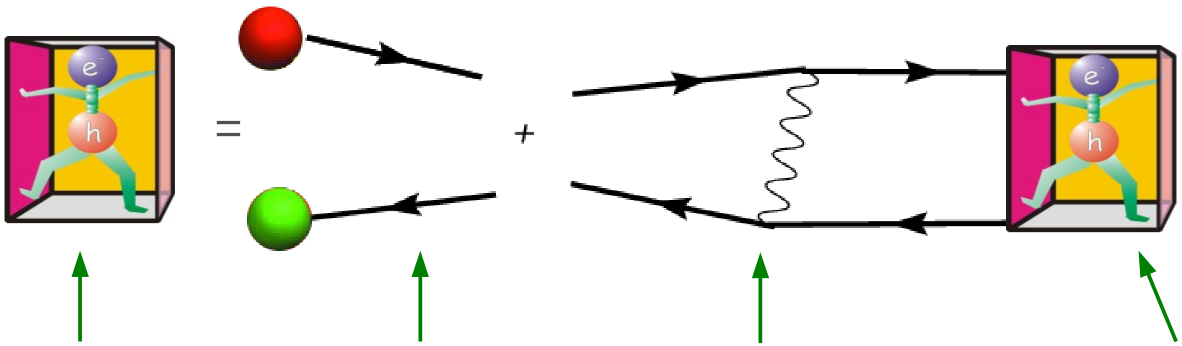
“Direct” exciton-phonon scattering

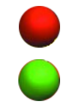


Finite temperature excitons



Excitons: the polaronic picture





Quasihole and
quasielectron

$$\mathbf{K}\equiv(n_e,n_h,\mathbf{k})$$

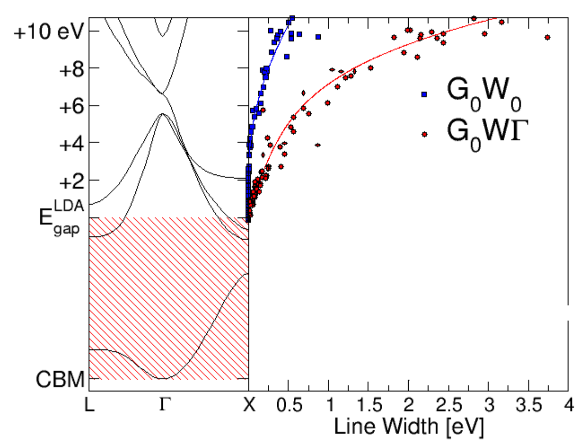
$$\tilde{L}_{K_1,K_2}(\tau)=\tilde{L}^{(0)}_{K_1,K_2}(\tau)[\delta_{2,3}+\Pi^{el}_{K_2,K_3}(\tau=0)]\tilde{L}_{K_3,K_2}(\tau)$$

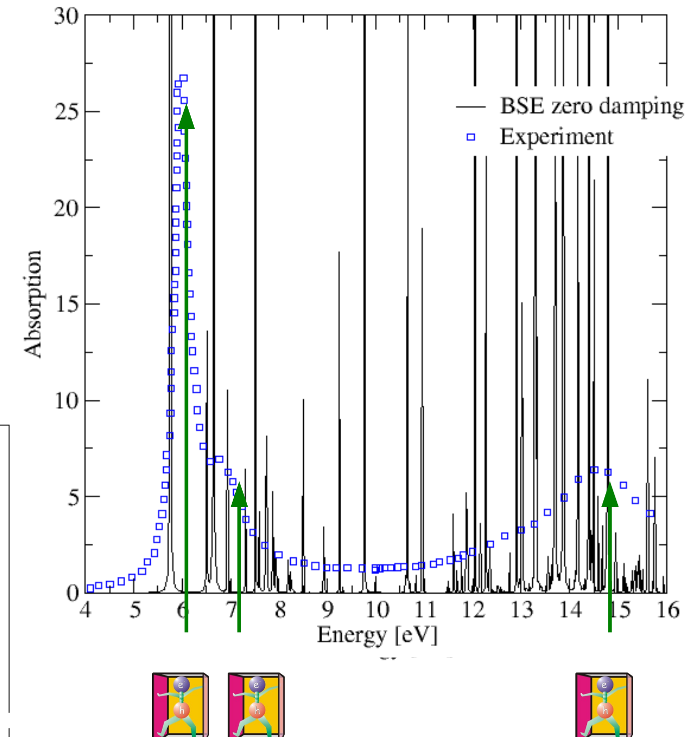
The excitons are the poles of $\tilde{L}$ and eigenstates of the Bethe-Salpeter Hamiltonian

$$H^{el}_{K,K'}=(\epsilon_e-\epsilon_h)\delta_{K,K'}+\Pi^{el}_{K_1,K_2}$$

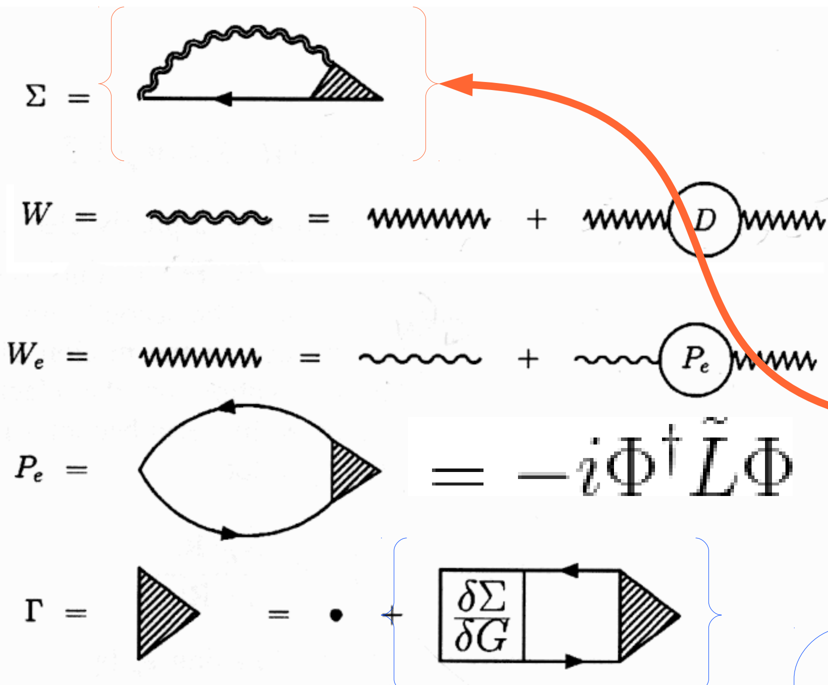
Quasiparticle energies are real in the optical range

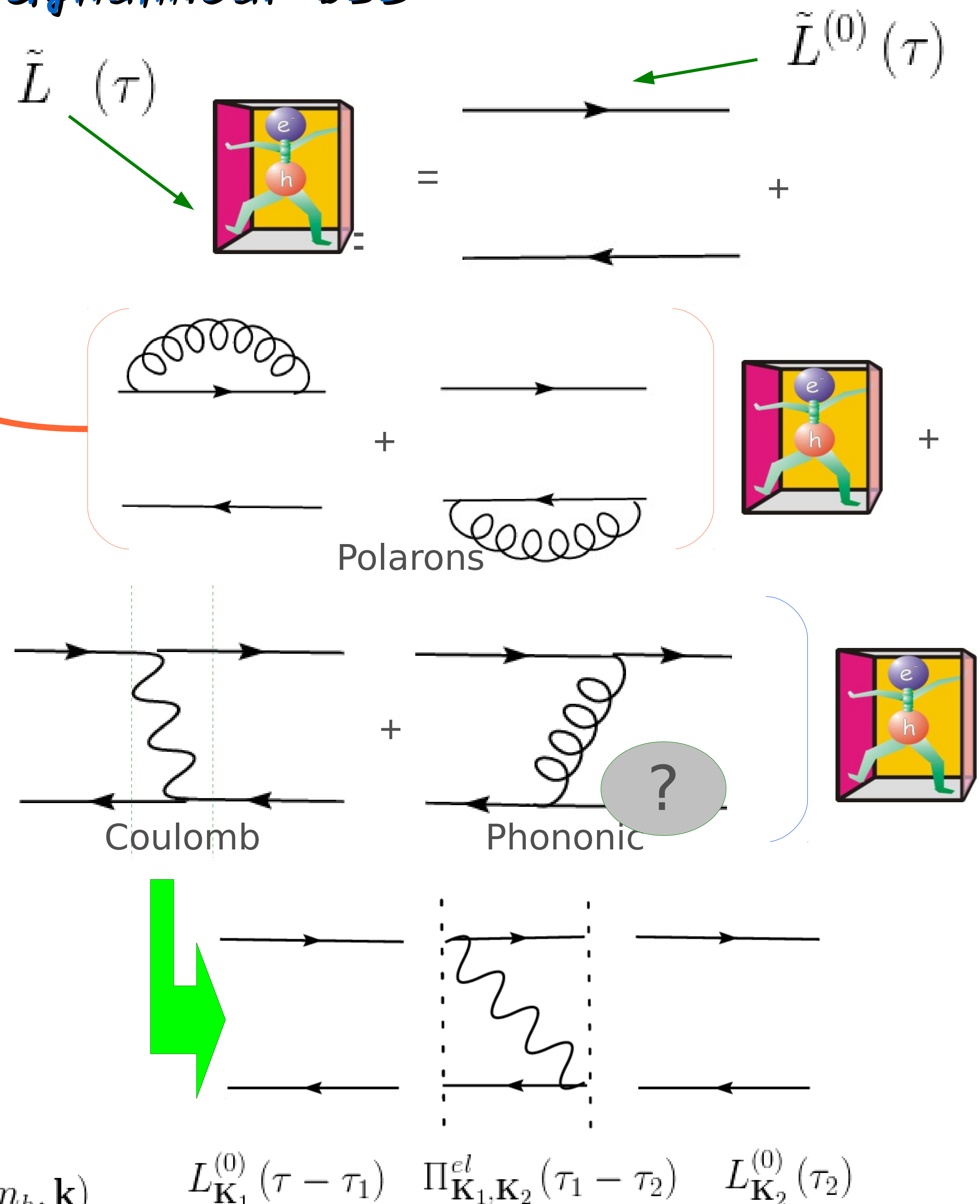
The BS Hamiltonian is Hermitian





The dynamical BSE



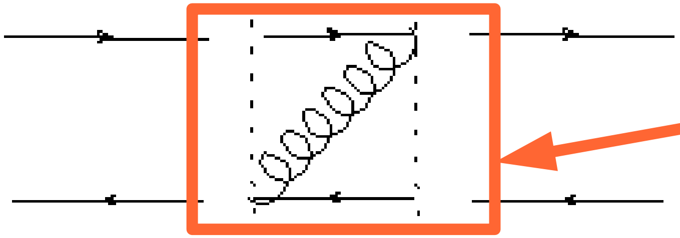


$$\boxed{\epsilon\,(i\omega) \equiv 1 - 4\pi P_e\,(i\omega)}$$

The dynamical BSE [AM, R. Del Sole, PRL **91**, 176402 (2003)] was introduced to sum the frequency dependent Coulomb interaction

$$\mathbf{K} \equiv (n_e, n_h, \mathbf{k})$$

The dynamical BSE II: the phonon term



$$\Pi^{ph}_{\mathbf{K}_1,\mathbf{K}_2}(i\omega) = -\sum_{\lambda} g^{\mathbf{q}\lambda}_{c_2c_1\mathbf{k}_1}\left(g^{\mathbf{q}\lambda}_{v_2v_1\mathbf{k}_1}\right)^* \sum_I \left[\frac{1+\langle N_{\mathbf{q}\lambda}\rangle}{i\omega+\Delta_I-\omega_{\mathbf{q}\lambda}} + \frac{\langle N_{\mathbf{q}\lambda}\rangle}{i\omega+\Delta_I+\omega_{\mathbf{q}\lambda}}\right]$$

$$\Delta_1 = \epsilon_{v_2\mathbf{k}_1-\mathbf{q}} - \epsilon_{c_1\mathbf{k}_1}$$
$$\Delta_2 = \epsilon_{v_1\mathbf{k}_1} - \epsilon_{c_2\mathbf{k}_1-\mathbf{q}}$$

Partial summation of the electronic part

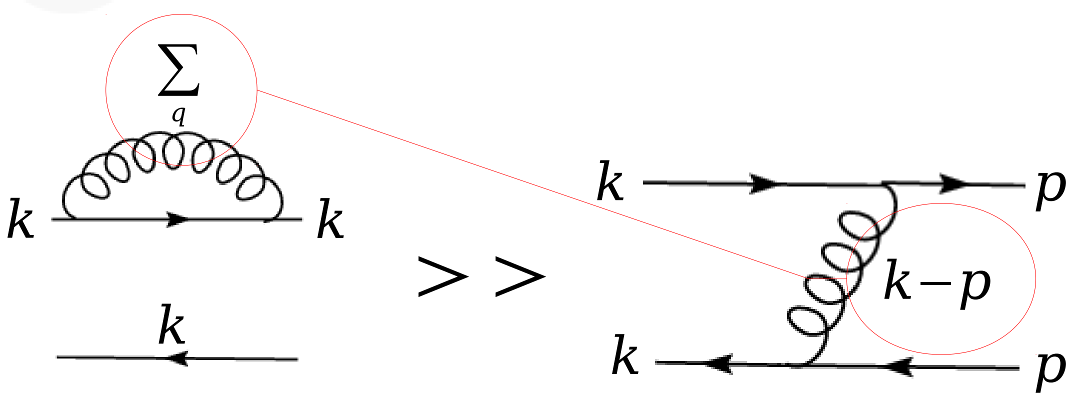
$$\tilde{L}(i\omega) = \tilde{L}^{(0)}(i\omega)\left[1+\left(\Pi^{el}(i\omega)+\Pi^{ph}(i\omega)\right)\tilde{L}(i\omega)\right] = \tilde{L}^{el}(i\omega)\left[1+\Pi^{ph}(i\omega)\tilde{L}(i\omega)\right]$$

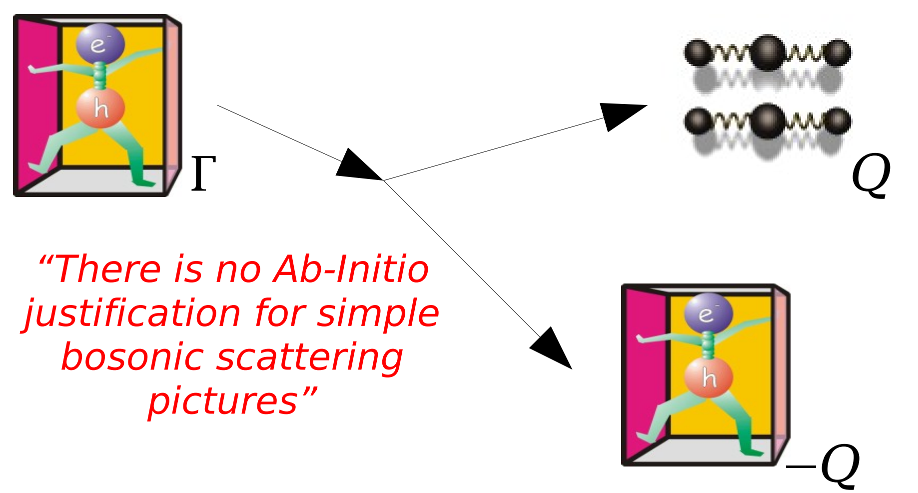
with $\tilde{L}^{el}(i\omega) = \tilde{L}^{(0)}(i\omega)\left[1+\Pi^{el}(i\omega)\tilde{L}^{el}(i\omega)\right]$

Excitonic "Self-Energy"

The phononic part of the Bethe-Salpeter kernel reduces to a "self-energy-like" operator (without introducing bosonic coordinates)

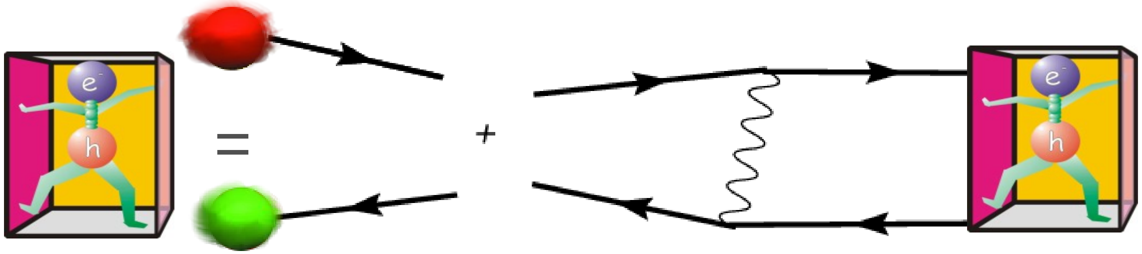
The momenta conservation makes the polaronic (indirect) term dominant





"There is no Ab-Initio justification for simple bosonic scattering pictures"

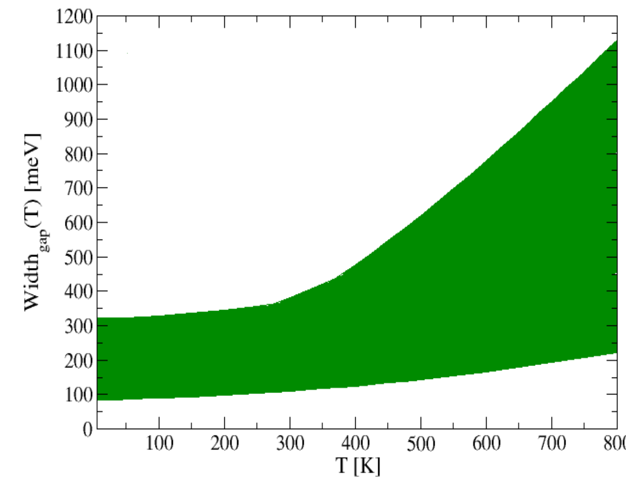
Excitons: the polaronic picture



Quasihole and quasielectron **polarons**

$$\mathbf{K} \equiv (n_e, n_h, \mathbf{k})$$

$$H_{\mathbf{K},\mathbf{K}'}(T) = [E_e(T) - E_h(T)] + i\,\boxed{[\Gamma_e(T) - \Gamma_h(T)]} + \Pi^{el}_{\mathbf{K}_1,\mathbf{K}_2}$$



The BS Hamiltonian is NOT Hermitian

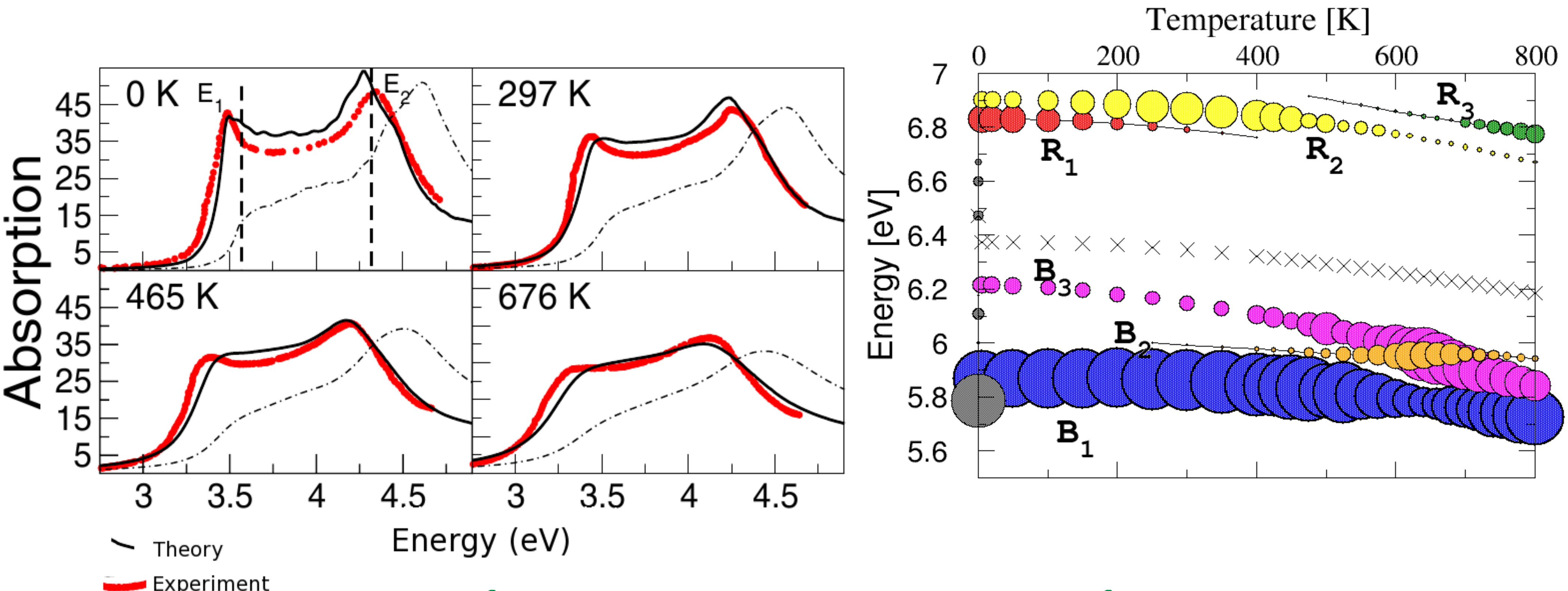
$$H_{\mathbf{K},\mathbf{K}'}(T)\,\lambda_{\mathbf{K}'}(T) = E_\lambda(T)\,\lambda_{\mathbf{K}}(T)$$

$$\epsilon_2(\omega, T) \propto \sum_\lambda S_\lambda(T)\left(\omega - E_\lambda(T)\right)^{-1}$$

$$\tau^\lambda(T) = \left[2\,\Im\left(E_\lambda(T)\right)\right]^{-1}$$

Finite T excitons

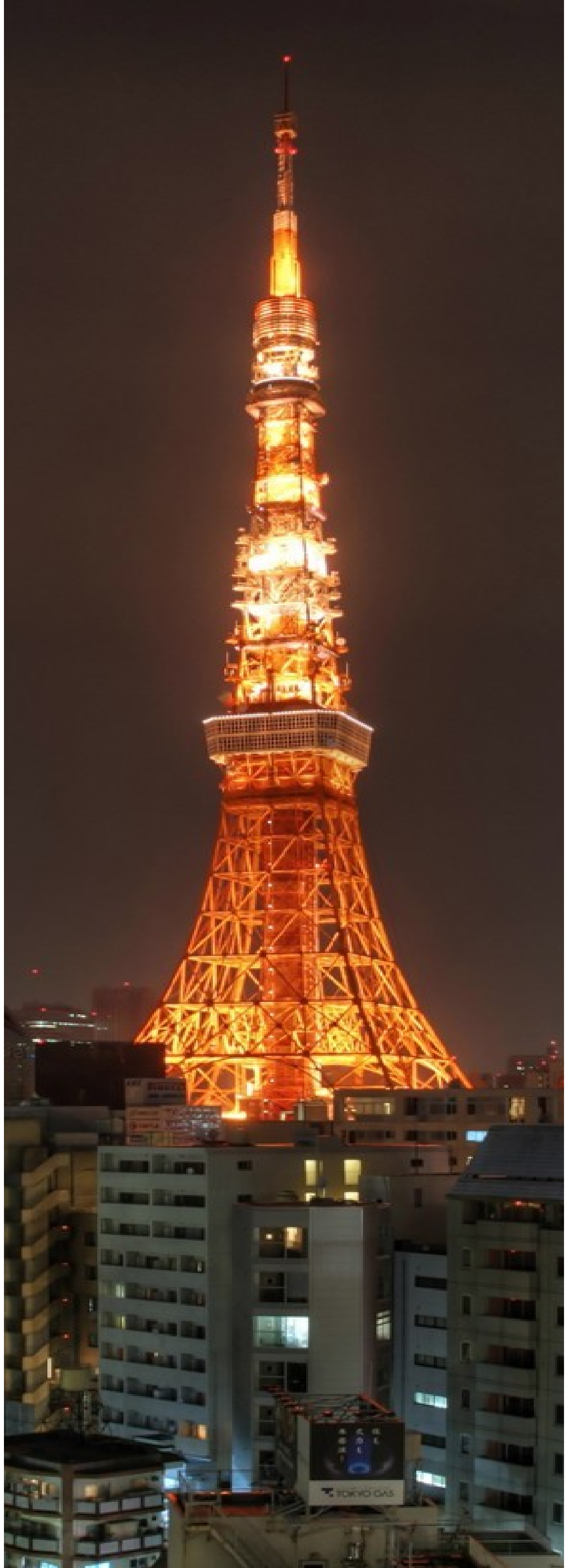
AM, *Phys. Rev. Lett.* **101**, 106405 (2008)



Bright to dark (and vice versa) transitions

...gradual worsening of optical efficiency

$$\Re\left[\Delta E_{\lambda}(T)\right] = \underbrace{\left[\langle \lambda(T) | \mathbf{H}^{FA} | \lambda(T)\rangle - \langle \lambda_{FA} | \mathbf{H}^{FA} | \lambda_{FA}\rangle\right]}_{\text{CHANGE in the excitonic state}} + \underbrace{\int d\omega\, \Re\left[g^2 F_{\lambda}(\omega, T)\right]\left[N(\omega, T) + 1/2\right]}_{\text{INCOHERENT contribution}}$$



Giant polaronic effects in nanostructures

Spectral Functions and QP picture

$$G_{n\mathbf{k}}(\omega) = \frac{1}{\omega - \epsilon_{n\mathbf{k}} - \Sigma_{n\mathbf{k}}(\omega) + i\eta}$$

$$G_{n\mathbf{k}} = \langle n\mathbf{k} \mid (\omega - H)^{-1} \mid n\mathbf{k} \rangle$$

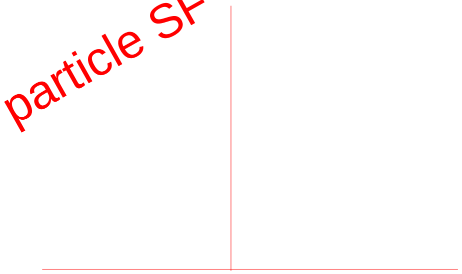
$$G_{n\mathbf{k}}(\omega) = \sum_I \mid \langle \Psi \mid c^{\dagger}_{n\mathbf{k}} \mid I\mathbf{k} \rangle \mid^2 (\omega - E_{I\mathbf{k}})^{-1}$$

$$\boxed{E_{I\mathbf{k}} \rightarrow A_{n\mathbf{k}}(\omega) = \sum_I \mid \langle \Psi \mid c^{\dagger}_{n\mathbf{k}} \mid I\mathbf{k} \rangle \mid^2 \delta(\omega - E_{I\mathbf{k}})}$$

Spectral Functions

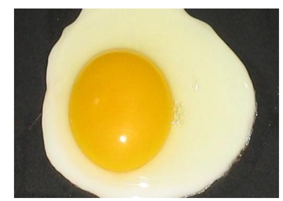
Expanding in eigenstates of the total Hamiltonian the QP picture holds when there is a **dominant (and sharp!) pole that collects most of electronic charge**

Real particle SF

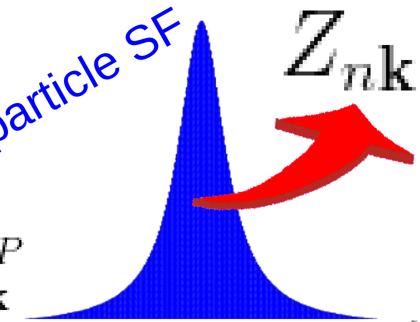


$$E_{I\mathbf{k}} = E^{(0)}_{n\mathbf{k}}$$

ω

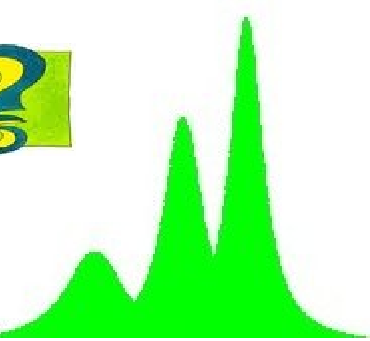


Quasi particle SF



$$E_{I\mathbf{k}} = E^{QP}_{n\mathbf{k}} + i\Gamma^{QP}_{n\mathbf{k}}$$

ω



$$E_{I\mathbf{k}} = \ldots$$

ω

Spectral Functions in the HEG (I)

PHYSICAL REVIEW VOLUME 131, NUMBER 3 1 AUGUST 1963

Coupled Electron-Phonon System*

S. ENGELSBERG
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey
AND
J. R. SCHRIEFFER
University of Pennsylvania, Philadelphia, Pennsylvania
(Received 26 March 1963)

$$\Sigma_{n\mathbf{k}}^{Fan}(\omega) = \sum_{\mathbf{q}\lambda} \frac{1}{N_{\mathbf{q}}} \sum_{n'} | g_{n'n\mathbf{k}}^{\mathbf{q},\lambda} |^2 \left[\frac{B(\omega_{\mathbf{q}\lambda}) + 1 - f_{n'\mathbf{k}-\mathbf{q}}}{\omega - \epsilon_{n'\mathbf{k}-\mathbf{q}} - \omega_{\mathbf{q}\lambda} - i0^+} + \frac{B(\omega_{\mathbf{q}\lambda}) + f_{n'\mathbf{k}-\mathbf{q}}}{\omega - \epsilon_{n'\mathbf{k}-\mathbf{q}} + \omega_{\mathbf{q}\lambda} - i0^+} \right]$$

Debye Model in the HEG
At zero temperature

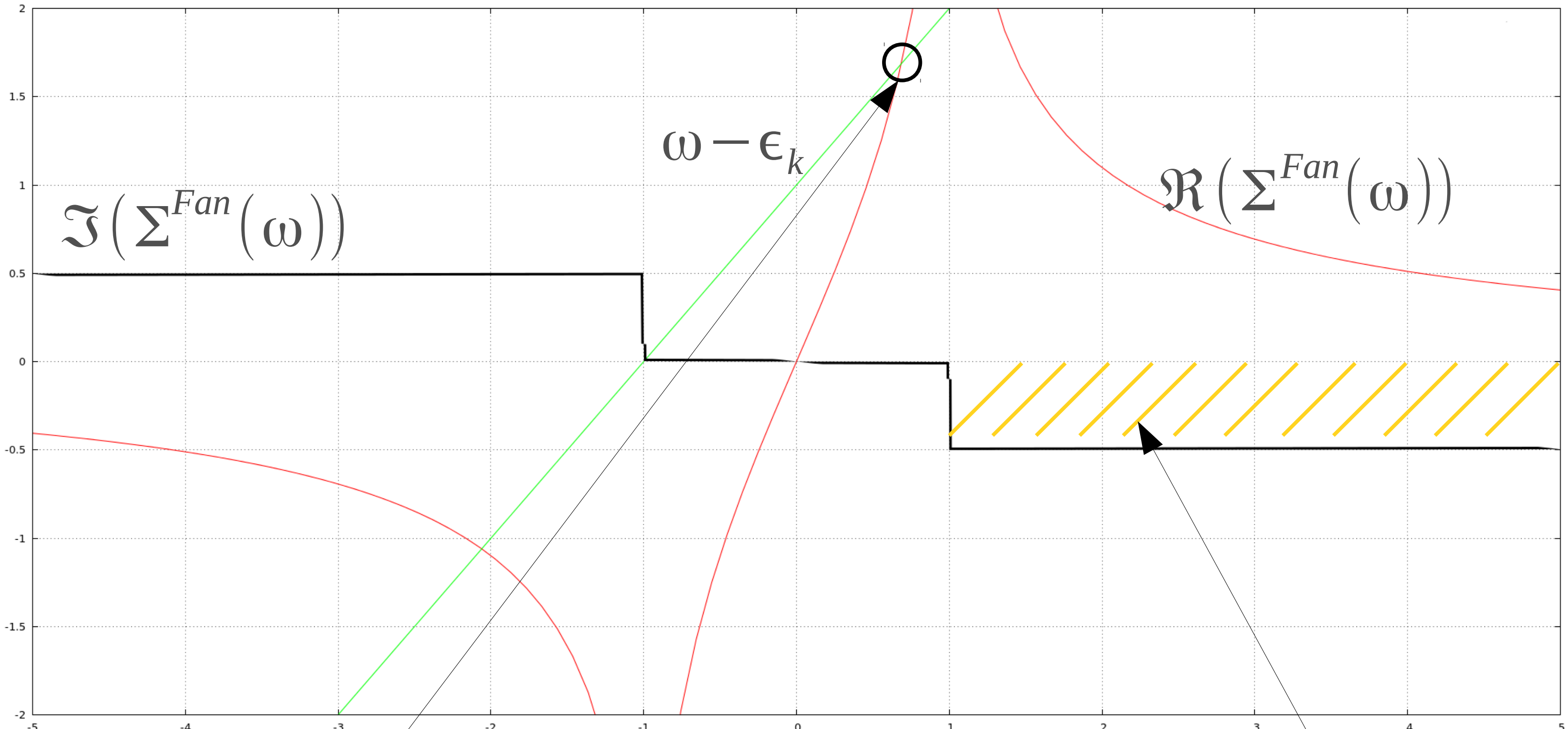
$$\omega_{q\lambda} \sim \omega \qquad g_{nn'k}^{q\lambda} \sim g$$

$$\epsilon_{nk} = \epsilon_k \sim \frac{k^2}{2}$$

$$\Sigma^{Fan}(\omega) = i g^2 \int d^4 k (2\pi)^{-4} D(p-k) G(k)$$

$$D(p-k) = ((p_0 - k_0)^2 - \omega^2 + i\eta)^{-1} \qquad G(k) = (k_0 - \epsilon_k \pm i\eta)^{-1}$$

Spectral Functions in the HEG (II)



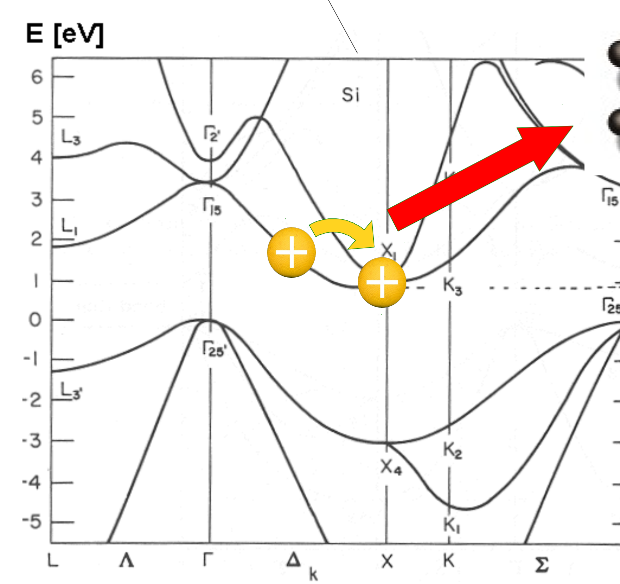
$$E_k=\epsilon_k+\Sigma_k(E_k)$$

QP

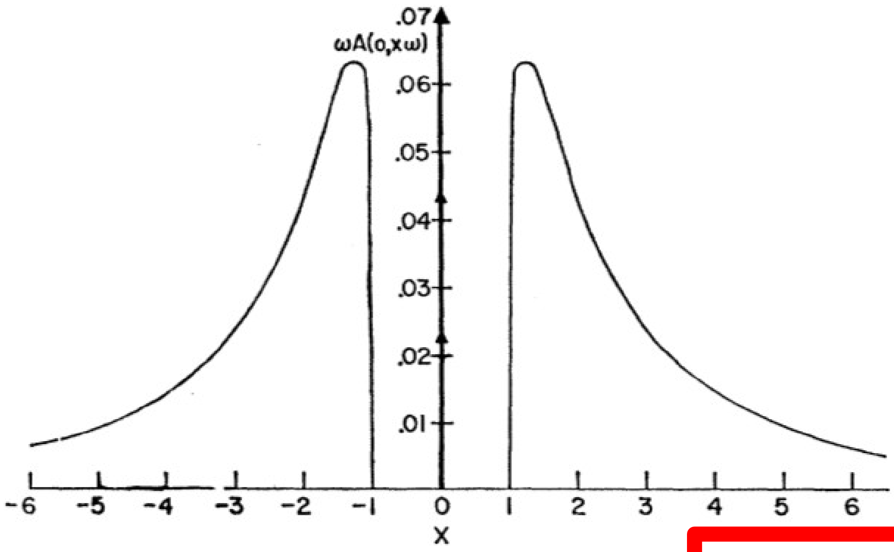
$$E_k=\frac{\epsilon_k}{(1+g^2 N\omega^{-2})}$$

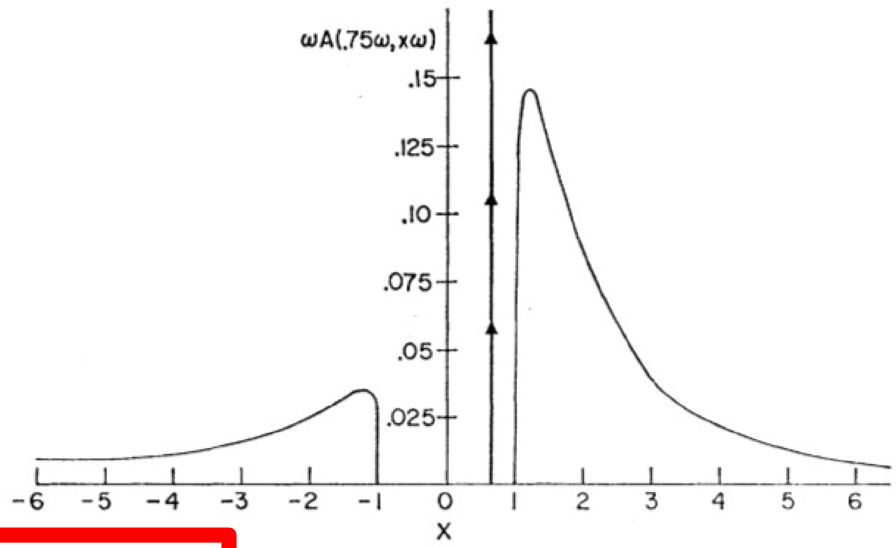
$$G_{nk}(\omega)=\frac{Z_{nk}}{(\omega-E_{nk})}$$

$$Z_{nk}=\frac{1}{(1-\Sigma'(\epsilon_{nk}))}$$

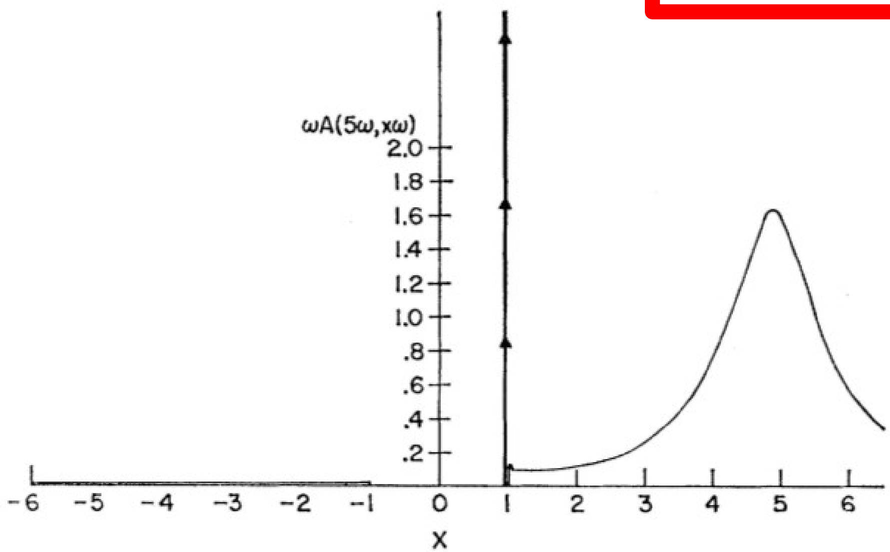


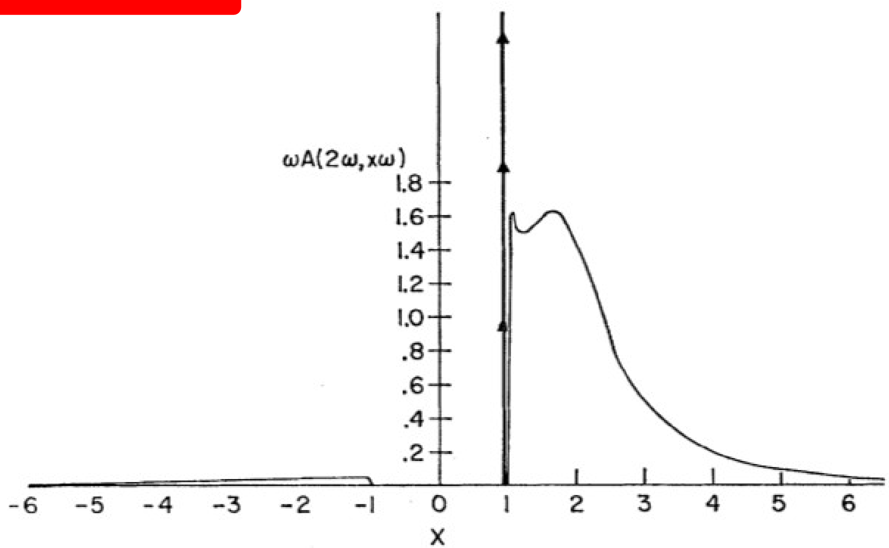
Spectral Functions in the HEG (III)





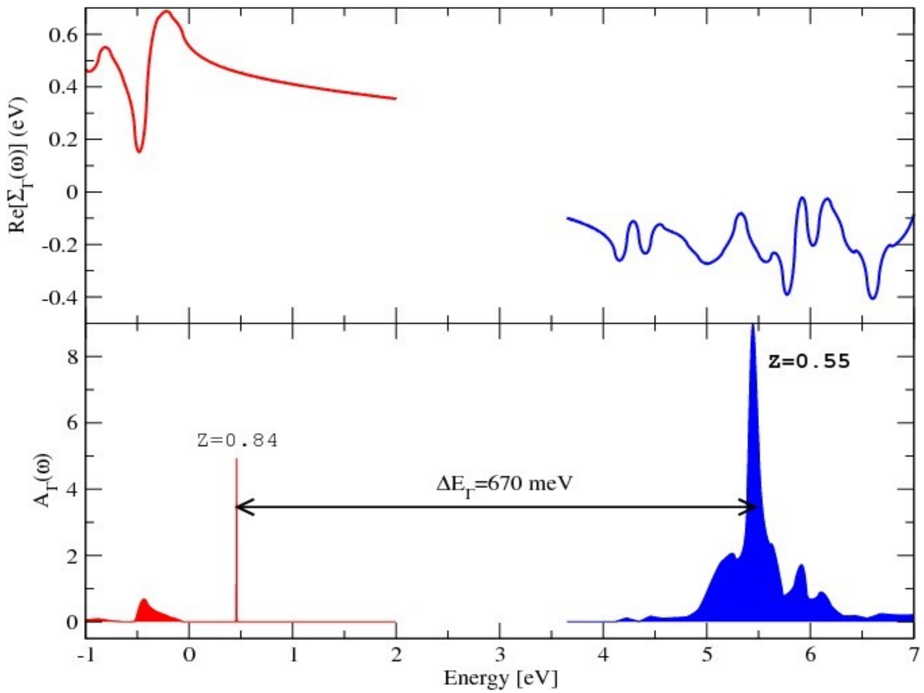
$$g^2 N \omega^{-2} = .5$$

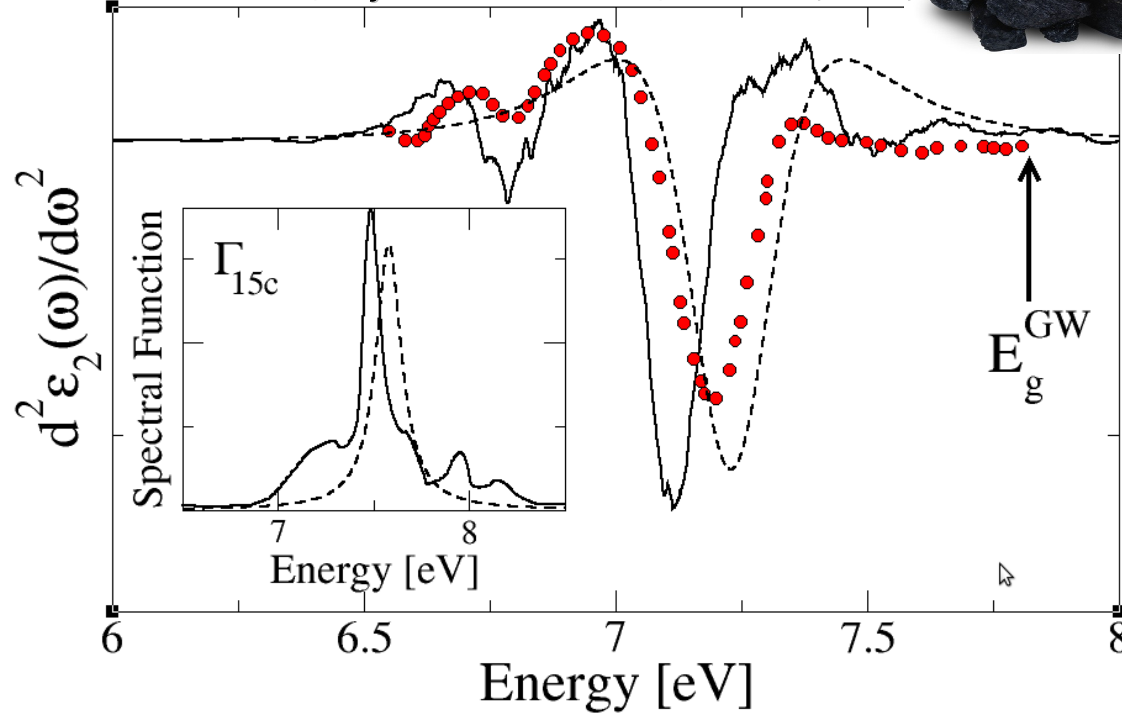


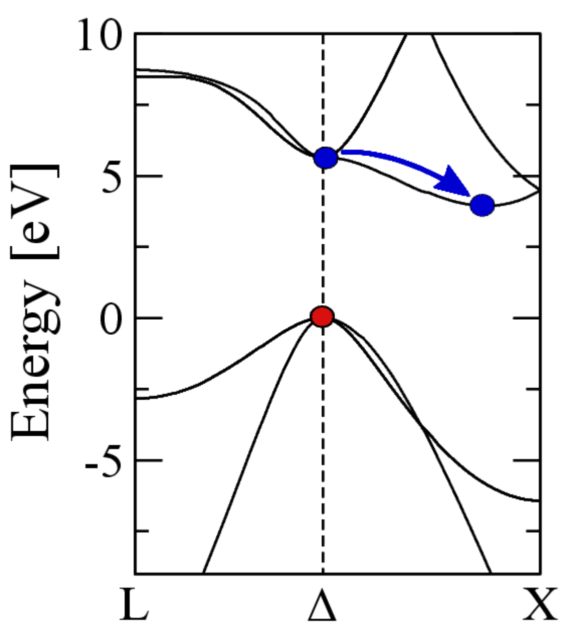


Dynamical effects in Diamond !

E. Cannuccia, *Phys. Rev. Lett.* **107**, 255501 (2011)







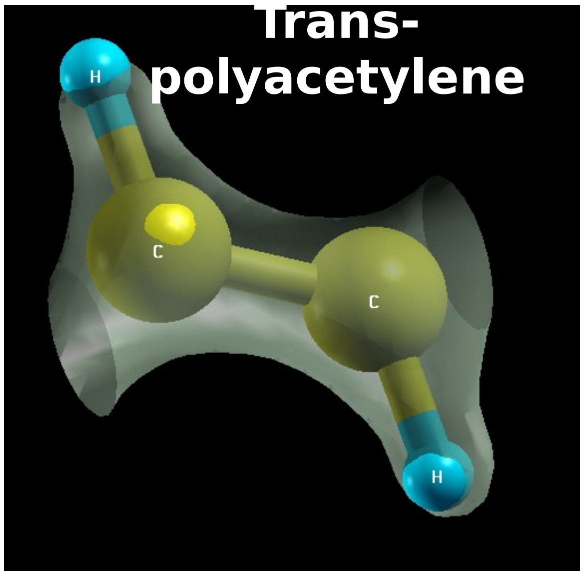
$$\epsilon_2(\omega) \approx \int d\omega' \Im[G_{\Gamma_{15c}}(\omega-\omega')] \Im[G_{\Gamma'_{25c}}(\omega')]$$

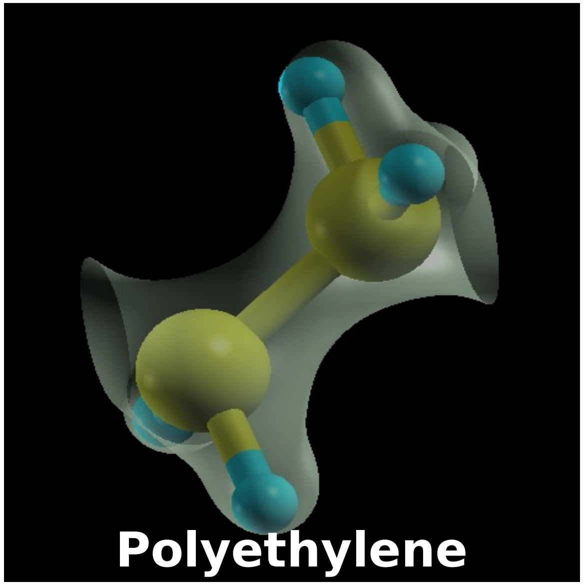
$$\Delta E_g(T \rightarrow 0)$$

On-Mass shell (HAC)
620 meV
(**615** meV in F. Giustino, S.G. Louie and M.L. Cohen, PRL **105**, 265501 (2010))

Quasiparticle approximation
670 meV

C-based nanostructures: polymers



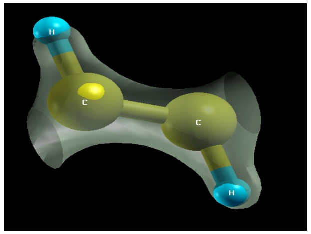


$$\langle u^2(T)\rangle \simeq \frac{\hbar}{4M_s\Omega}\langle 1+2\mathcal{N}_{bose}(T)\rangle$$

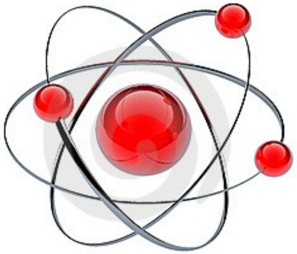
$$\sqrt{\langle u^2\rangle}\approx 0.1\,a.u.$$

$$\sqrt{\langle u_C^2\rangle}\approx 0.2\,a.u.$$

$$\sqrt{\langle u_H^2\rangle}\approx 0.3\,a.u.$$



$$\sqrt{\langle u^2\rangle}\approx 0.4\,a.u.$$



Integrated Optoelectronic Devices Based on Conjugated Polymers

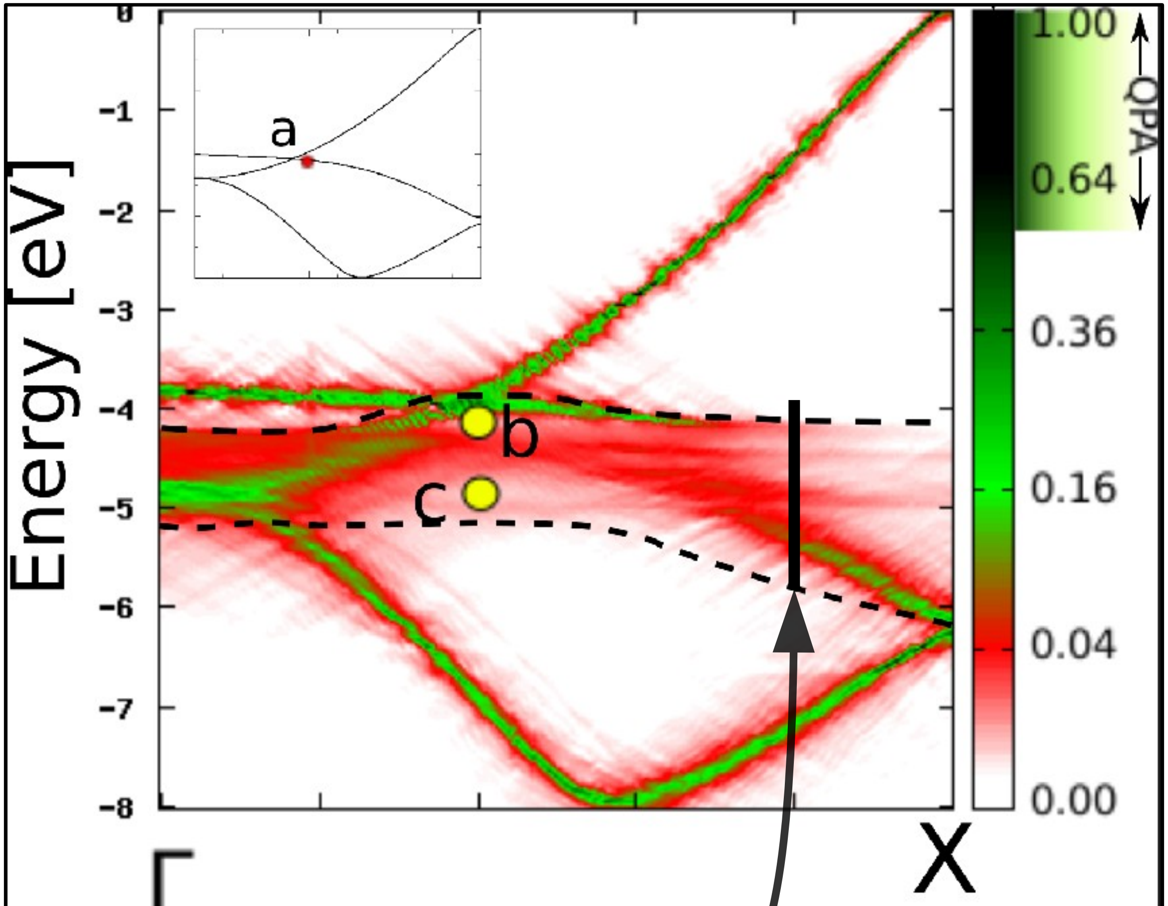
Henning Sirringhaus,* Nir Tessler, Richard H. Friend*

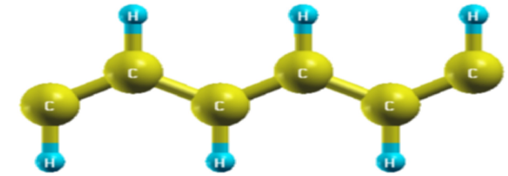
Science **280** 1741 (1998)

An all-polymer semiconductor integrated device is demonstrated with a high-mobility conjugated polymer field-effect transistor (FET) driving a polymer light-emitting diode (LED) of similar size. The FET uses regioregular poly(hexylthiophene). Its performance approaches that of inorganic amorphous silicon FETs, with field-effect mobilities of 0.05 to 0.1 square centimeters per volt second and ON-OFF current ratios of $>10^6$. The high mobility is attributed to the formation of extended polaron states as a result of local self-organization, in contrast to the variable-range hopping of self-localized polarons found in more disordered polymers. The FET-LED device represents a step toward all-polymer optoelectronic integrated circuits such as active-matrix polymer LED displays.

Breakdown of the QP picture

E. Cannuccia, *Phys. Rev. Lett.* **107**, 255501 (2011)

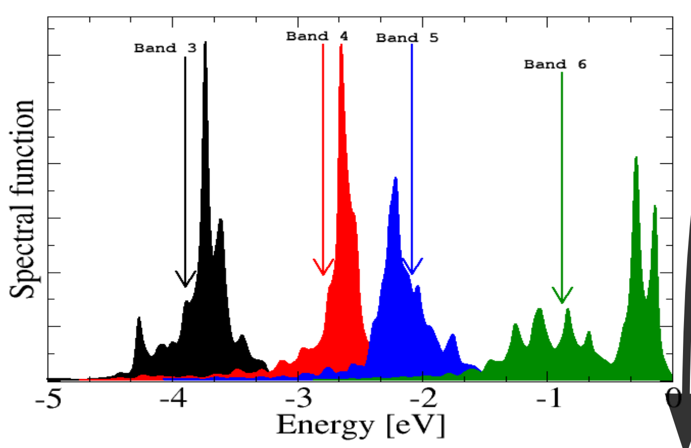


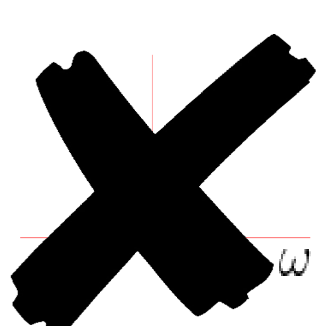


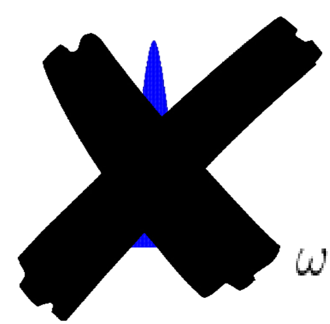
$$A\left(k,\omega\right) \equiv \sum_n \frac{1}{\pi} \left|\Im\left[G_{nk}\left(\omega\right)\right]\right|$$

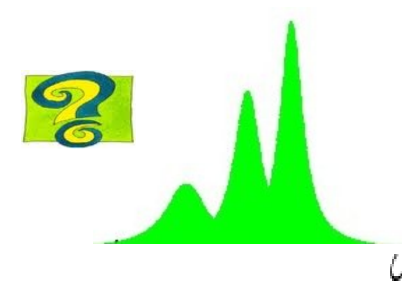
$$\Delta Z \equiv A\left(k,\omega\right)\Delta\omega$$

$$\Delta\omega = 50\, meV.$$



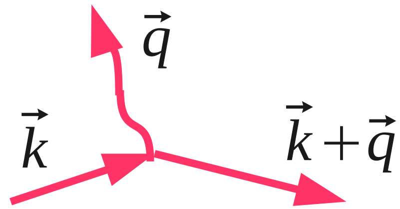


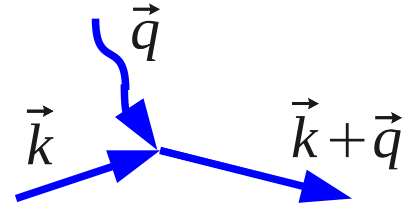




Polarons in an Hamiltonian representation (I)

$$H = H_e + H_{ph} + \frac{1}{N_{\mathbf{q}}} \sum_{n'\mathbf{q}\lambda} g^{\mathbf{q}\lambda}_{n'n\mathbf{k}} c^{\dagger}_{n'\mathbf{k}+\mathbf{q}} c_{n\mathbf{k}} \left(b^{\dagger}_{\mathbf{q}\lambda} + b_{-\mathbf{q}\lambda} \right)$$





Phonon population:

$$N_{ph} = \left(e^{\beta \omega_{\mathbf{q}\lambda}} - 1 \right)^{-1}$$

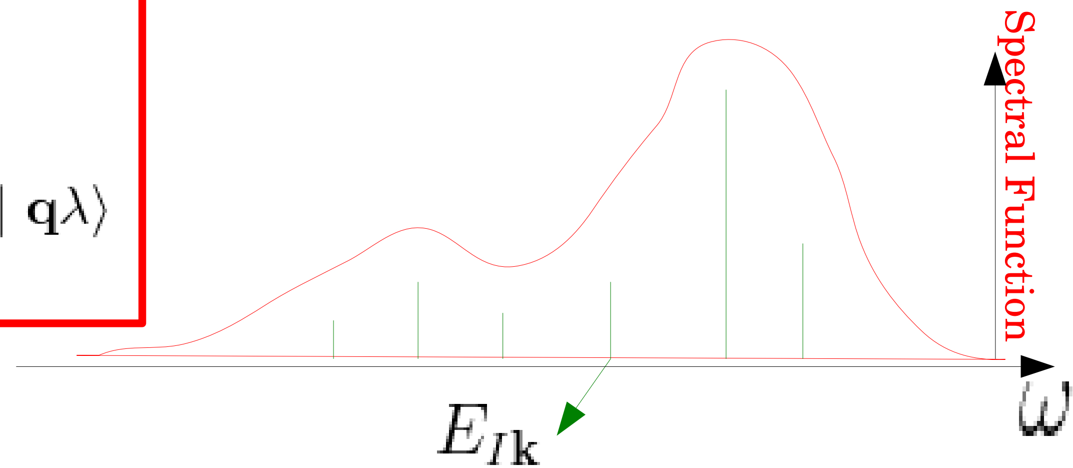
Basis set

T = 0 °K

$$G_{n\mathbf{k}}(\omega) = \sum_I |\langle \Psi \mid c^{\dagger}_{n\mathbf{k}} \mid I\mathbf{k} \rangle|^2 \frac{1}{\omega - E_{I\mathbf{k}}}$$

$$|\, n\mathbf{k} \rangle \otimes |\, vac \rangle \xrightarrow{\text{H}} |\, n\mathbf{k} \rangle \otimes |\, vac \rangle, |\, n\mathbf{k} - \mathbf{q} \rangle \otimes |\, \mathbf{q}\lambda \rangle$$

$$\boxed{\begin{gathered} H \mid I\mathbf{k} \rangle = E_{I\mathbf{k}} \mid I\mathbf{k} \rangle \\ |\, I\mathbf{k} \rangle = A_{n\mathbf{k}} \mid n\mathbf{k} \rangle + \sum_{n\mathbf{q}\lambda} B_{n\mathbf{q}\lambda} \mid n\mathbf{k} - \mathbf{q} \rangle \otimes |\, \mathbf{q}\lambda \rangle \end{gathered}}$$



$$G_{n\mathbf{k}}(\omega) = \frac{G^0_{n\mathbf{k}}(\omega)}{G^0_{n\mathbf{k}}(\omega)^{-1} - \Sigma_{n\mathbf{k}}(\omega)}$$

!

Polarons in an Hamiltonian representation (II)

$$G_{n\mathbf{k}}(\omega) = \sum_I |\langle \Psi \mid c^{\dagger}_{n\mathbf{k}} \mid I\mathbf{k}\rangle|^2 \frac{1}{\omega - E_{I\mathbf{k}}}$$

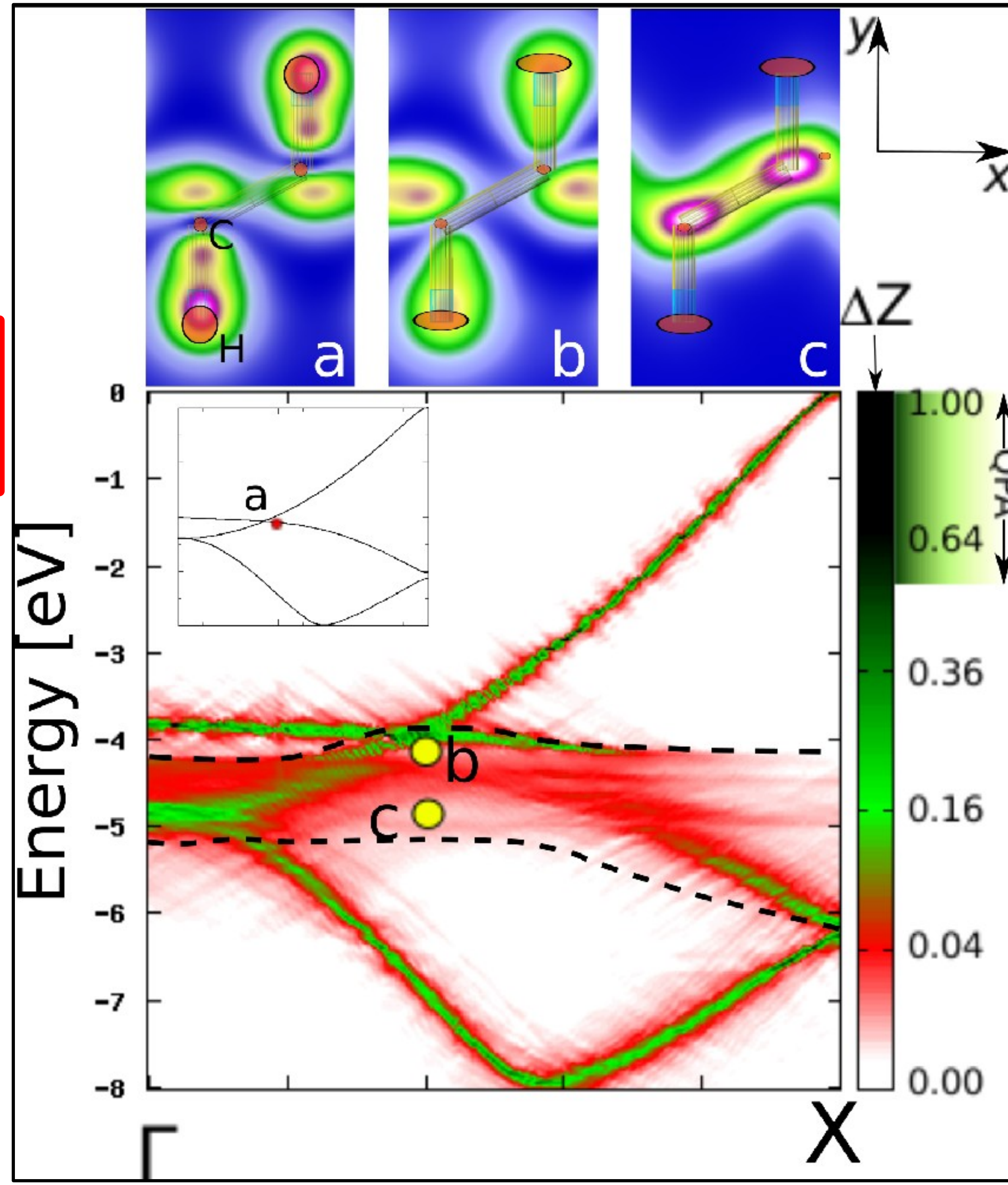
$$\boxed{\mid I\mathbf{k}\rangle = A_{n\mathbf{k}} \mid n\mathbf{k}\rangle + \sum_{n\mathbf{q}\lambda} B_{n\mathbf{q}\lambda} \mid n\mathbf{k}-\mathbf{q}\rangle \otimes \mid \mathbf{q}\lambda\rangle}$$

$$\mid \langle \vec{r} \mid I\mathbf{k}\rangle \mid^2$$

The polaronic wave-function

$$\langle Ik|u^2|Ik\rangle$$

The atomic indetermination IN the polaronic state



Are polymers an isolated case ?

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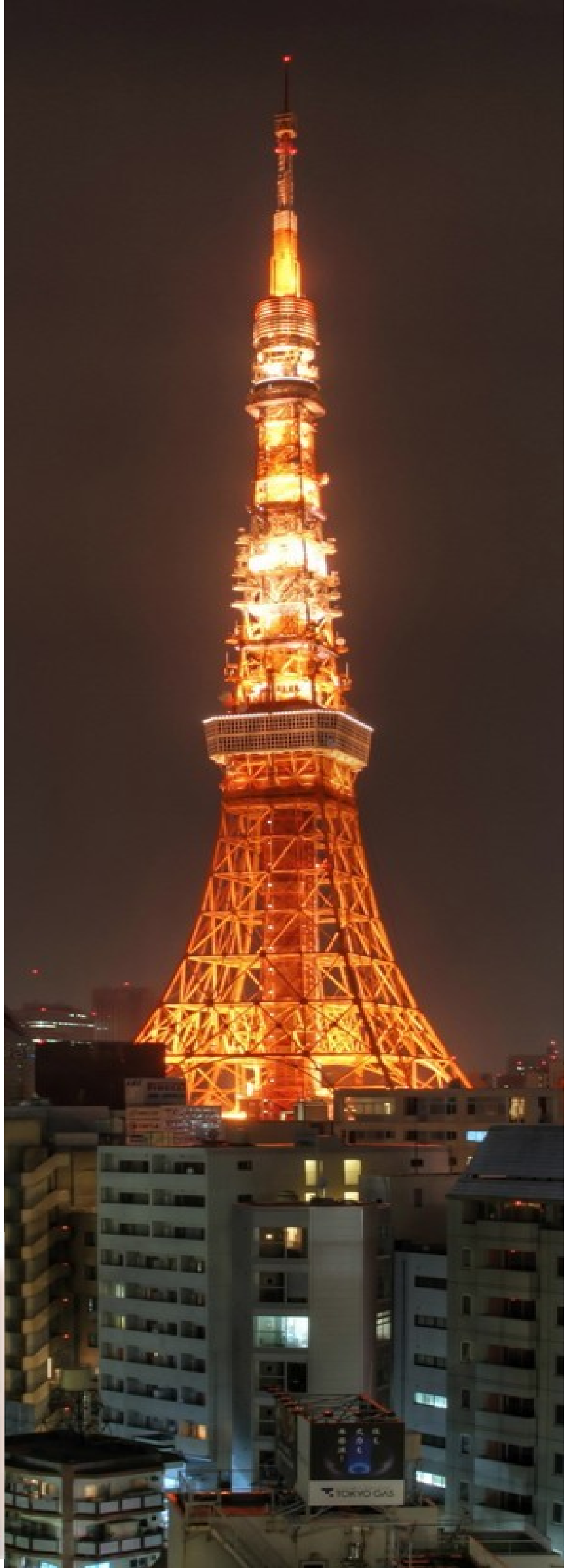
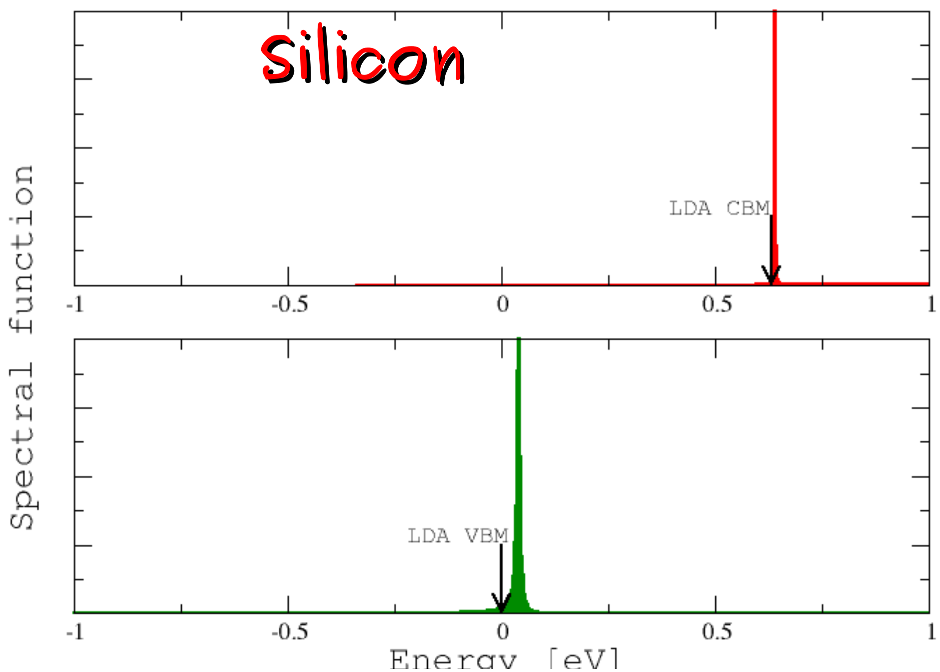
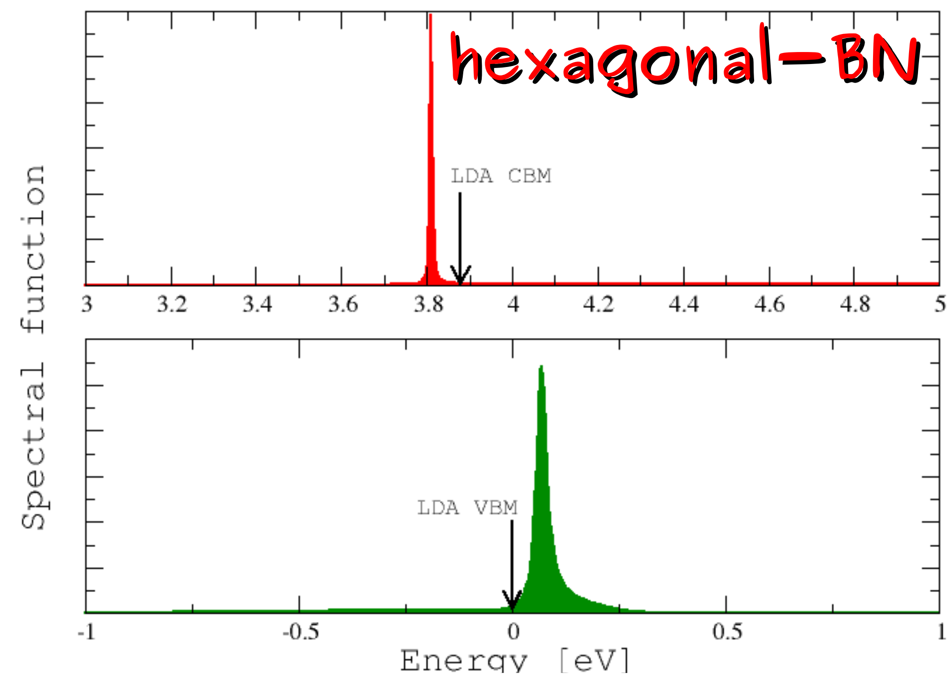
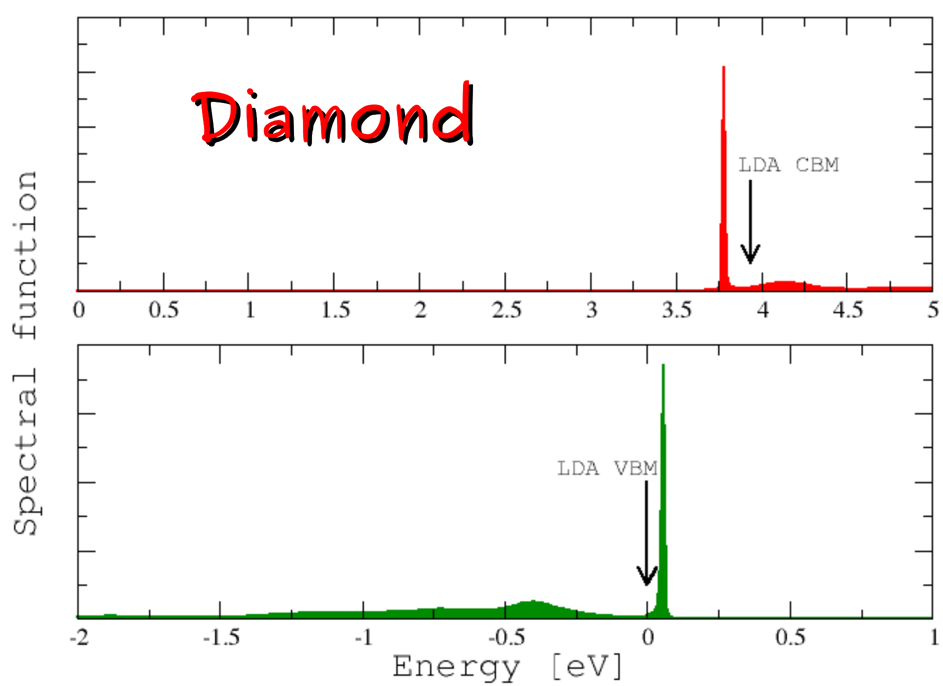
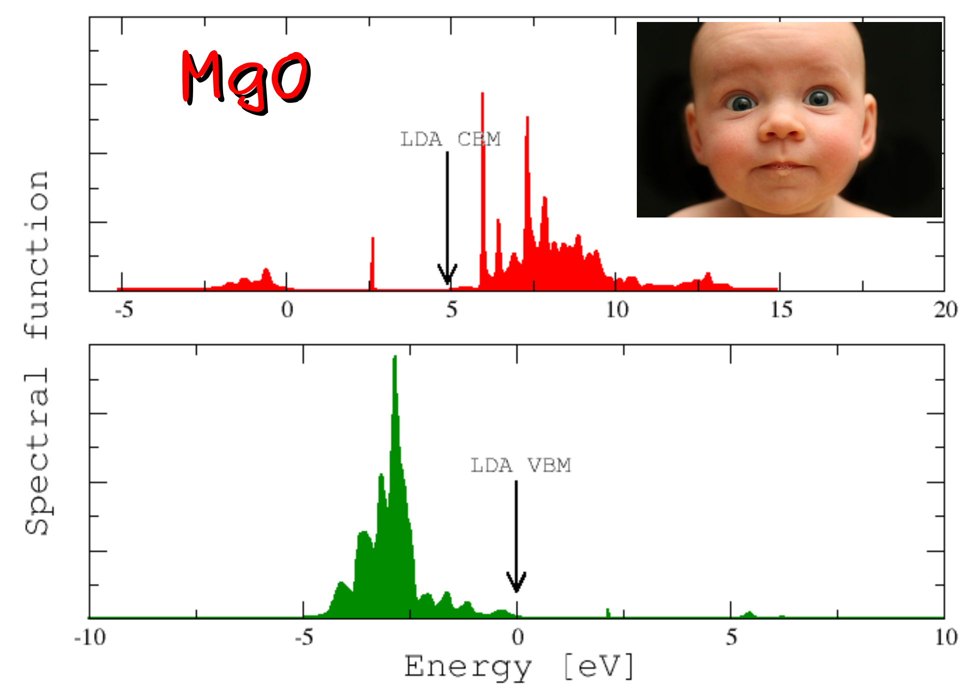


Spectral Functions solids @ the CBM and VBM










TOKYO GAS

Yambo: an ab-initio tool for excited state calculations

Theory&approximations

Many-Body Perturbation Theory

Time-dependent density functional theory

Interfaces

Planewave- Pseudopotential codes:

abinit.org PWscf

Developers

Properties

GPL:
Quasiparticles
Optical absorption
Electron energy loss
Dynamical polarizability

Develop/pre-GPL:
magnetic properties
non-equilibrium dynamics
total energies
electron-phonon effects

Support & reach-out

Dedicated users forum
Online documentation/tutorials
Schools & workshops

Community

about 170 users
(mostly from EU, USA, China)

Publications

more than 120 publications

www.yambo-code.org

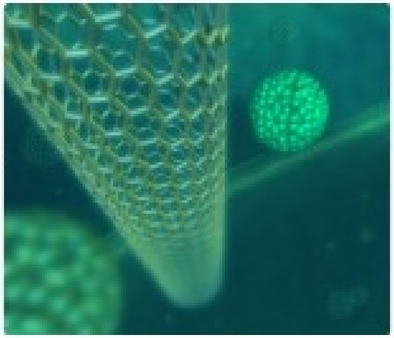
Yambo: an ab-initio tool for R&D

Material Science

applications to
e.g. photovoltaics,
lithium batteries,
microelectronics

Nano Science

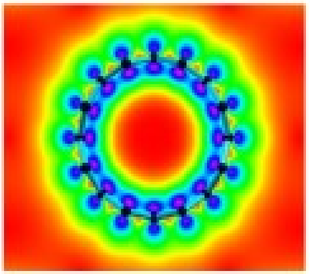
applications to
e.g. nanophotonics,
nanoelectronics



Biology

studies of
photoactive
molecules
and molecular
complexes

Physics



fundamental
understanding
of physical
processes

Yambo©

Optimal MPI (and, shortly, OpenMP) Paralellization

Improved and efficient memory distribution

Interfaced to common and well-known ground-state GPL codes: abinit, QEspresso, CPMD

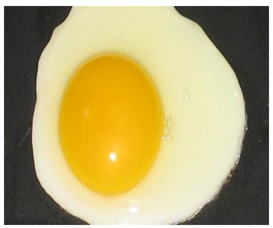
Development work-in-progress within the PRACE (Partnership for Advanced Computing in Europe) in collaboration with the Italian and Portughese Super-Computing centers

***Yambo*: an *ab-initio* tool for excited state calculations**,
Andrea Marini, Conor Hogan, Myrta Grüning, Daniele Varsano,
Comp. Phys. Comm. **180**, 1392 (2009)

Conclusions

Electronic Correlation

Real Particles

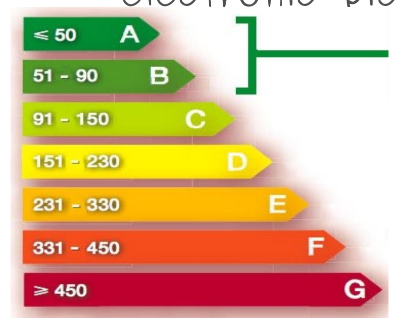


Quasi Particles

Multi-component particles

Electron-Phonon Coupling

Polaronic–induced effect can be HUGE. They can even lead to the breakdown of the electronic picture



The weak correlation is counterbalanced by the low–energy activation process (~Debye energy)

Potential ground–breaking consequences on mobility, optical properties, transport...

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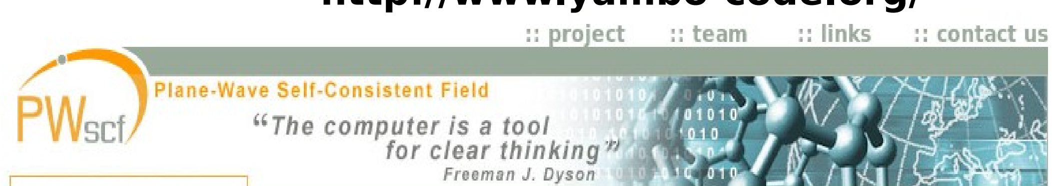
http://www.yambo-code.org/



http://www.pwscf.org

Critical re–examination of ALL purely electronic band–structure calculations on C–based nanostructures ?

People and references...

PhD Thesis (2011)

Giant polaronic effects in polymers: breakdown of the quasiparticle picture

Elena Cannuccia

http://www.yambo-code.org/papers/Thesis_Elena_Cannuccia.pdf

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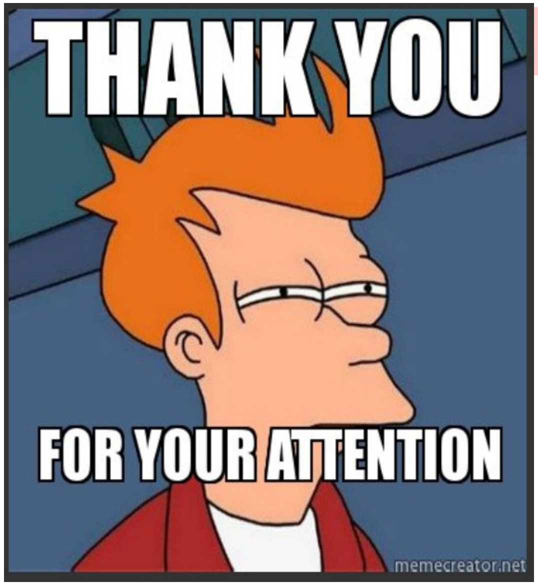
AM ¨*Ab-Initio Finite Temperature Excitons*¨, Phys. Rev. Lett. **101**, 106405 (2008)



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