Ab Initio Finite Temperature Excitons

Andrea Marini

CNISM, and department of physics, Univ. of Rome "Tor Vergata"

MORE 2008

Meeting on Optical Response in Extended Systems

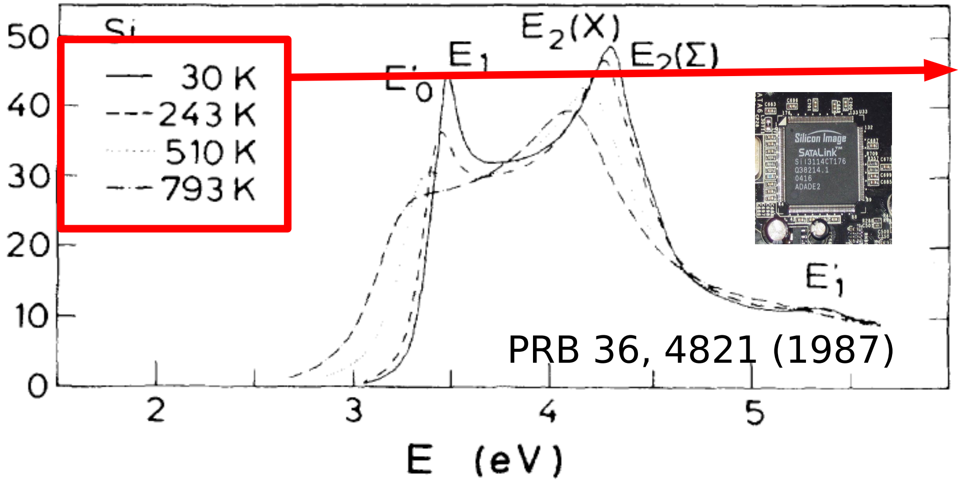
Vienna, 19-21 November 2008

ETSF European Theoretical Spectroscopy Facility

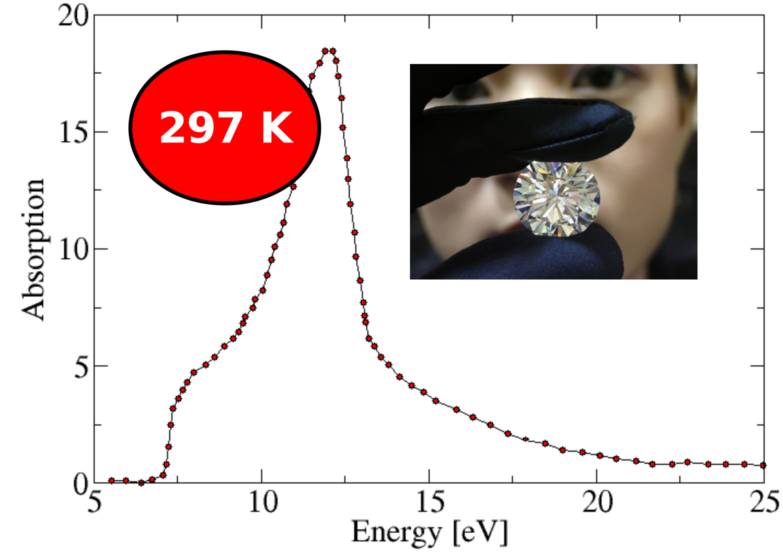
Condensed Matter Theory Group

University of Rome "Tor Vergata"

Real life is at finite temperature (!)



793 K = 68 meV while the QP gap is 1200 meV



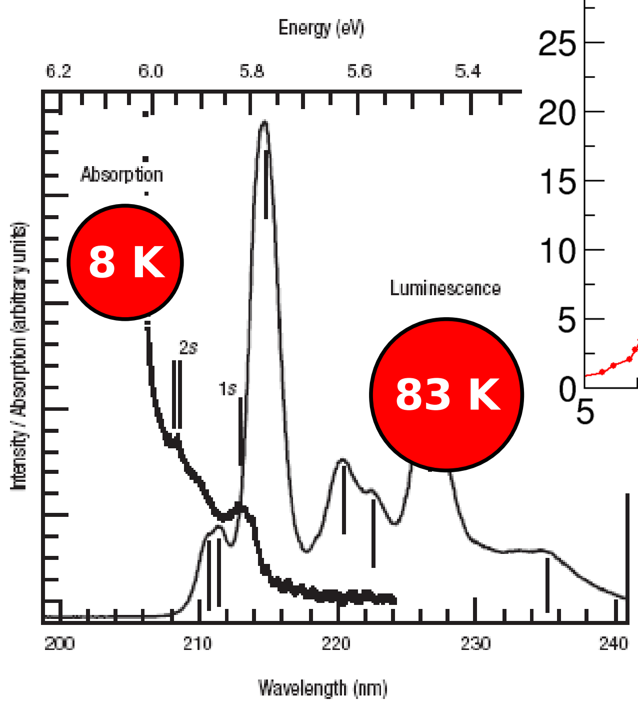
ARTICLES

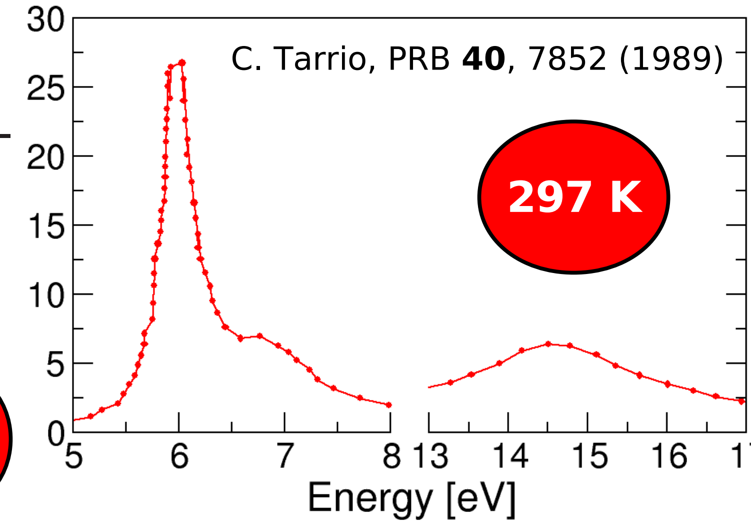
nature materials | VOL 3 | JUNE 2004 | www.nature.com/naturematerials

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

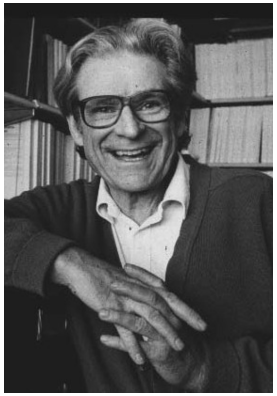
KENJI WATANABE*, TAKASHI TANIGUCHI AND HISAO KANDA

Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Jap
*e-mail: WATANABE.Kenji.aml@nims.go.jp



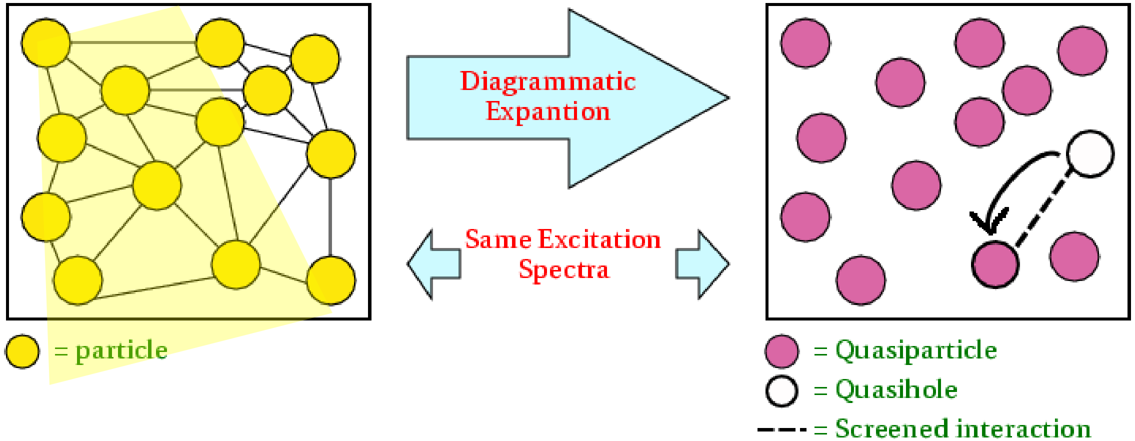


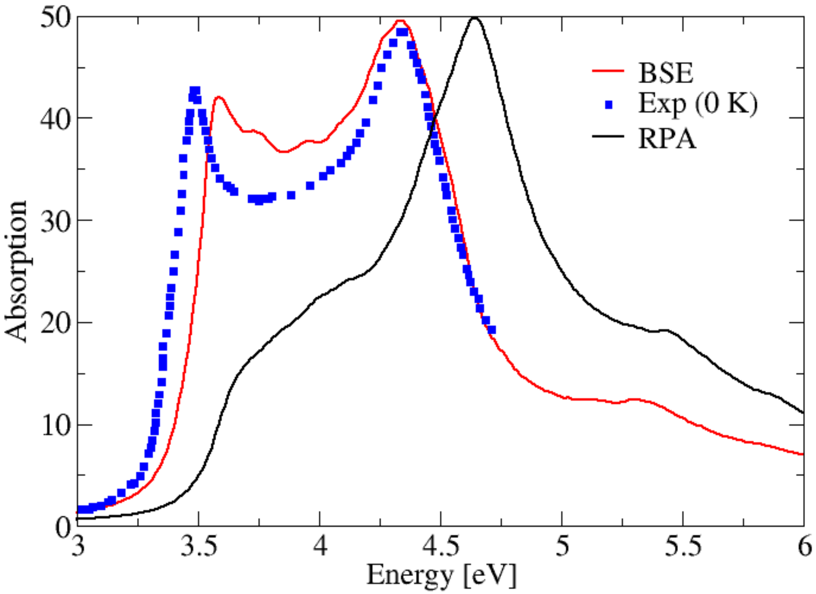
- h-BN is thermally stable
- Wide DIRECT gap insulator

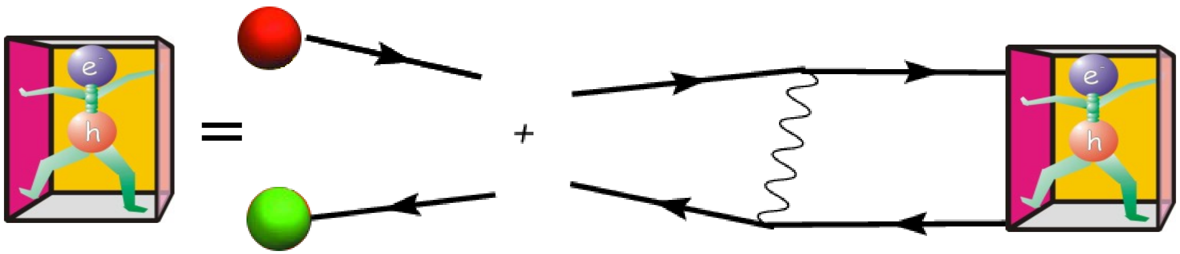



Excitons:
the state-of-the-art

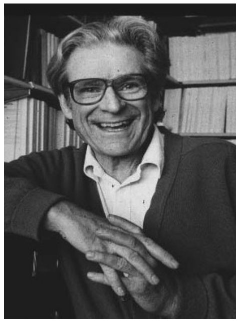
Review: G. Onida, O. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002)

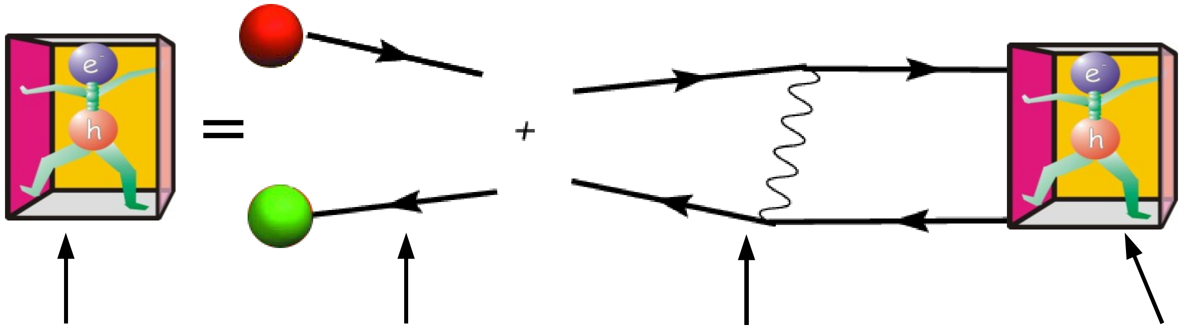






Excitons: the state-of-the-art





Quasi**h**ole and
quasi**e**lectron

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

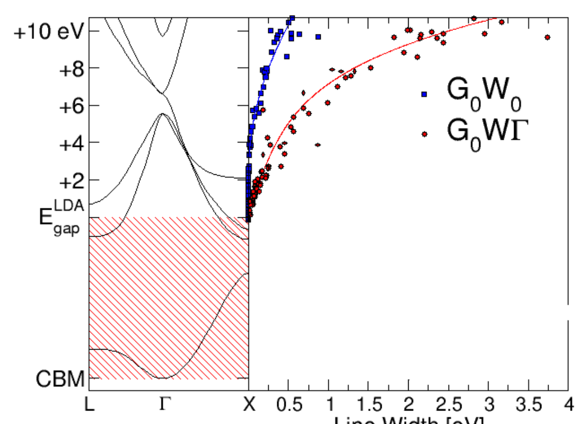
$$\tilde{L}_{K_1,K_2}(\tau) = \tilde{L}^{(0)}_{K_1,K_2}(\tau)\left[\delta_{2,3} + \Pi^{el}_{K_2,K_3}(\tau=0)\right]\tilde{L}_{K_3,K_2}(\tau)$$

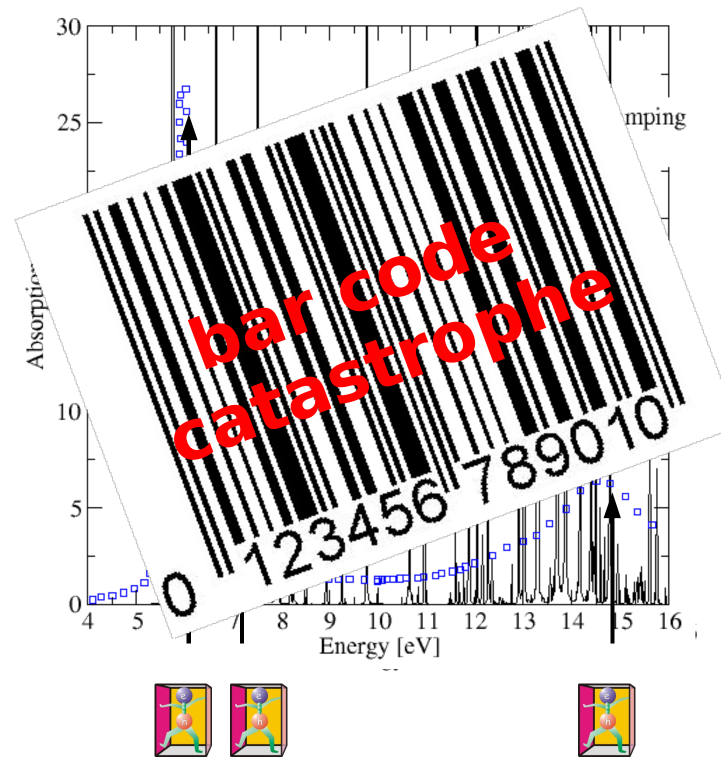
The excitons are the poles of $\tilde{L}$ and eigenstates of the Bethe-Salpeter Hamiltonian

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

Quasiparticle energies are real in the optical range

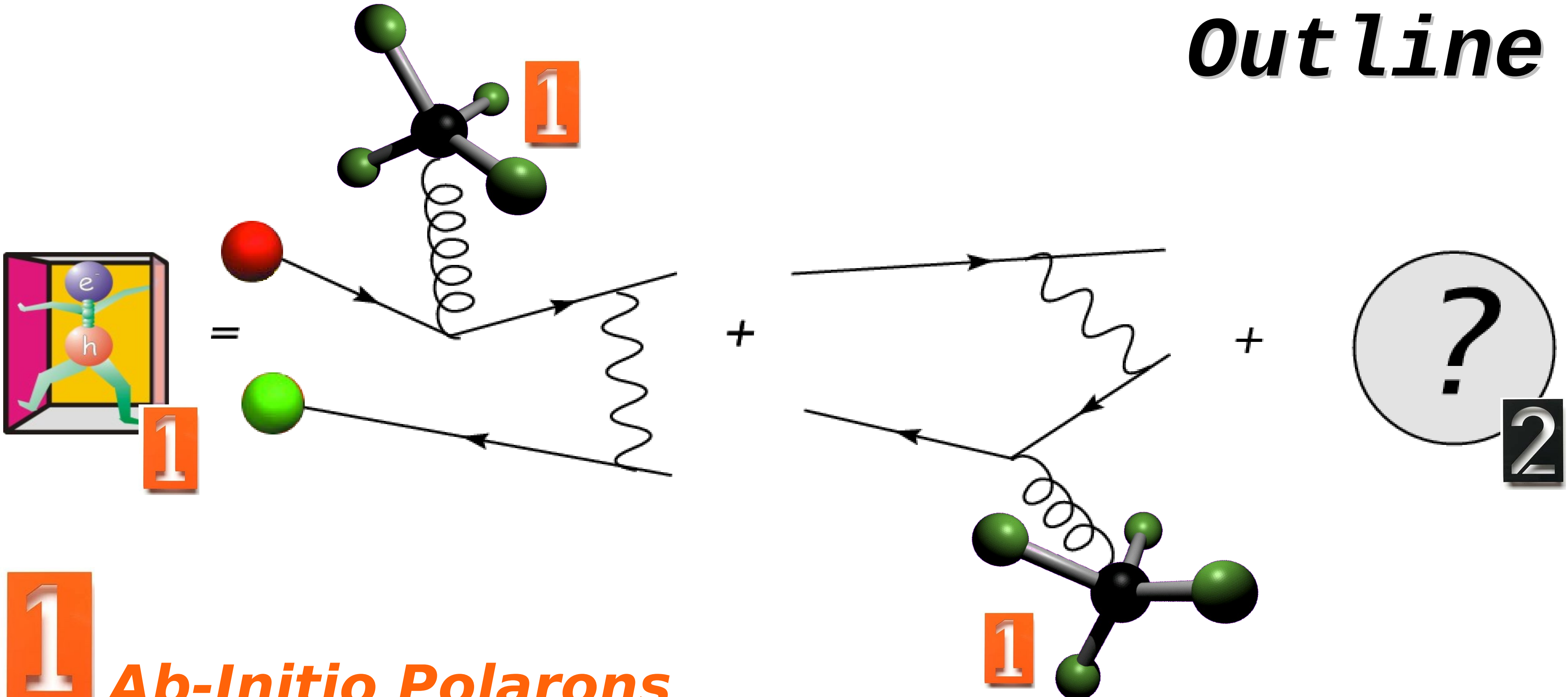
The BS Hamiltonian is Hermitian





Review: *G. Onida, O. Reining, and A. Rubio, Rev. Mod. Phys.* ***74****, 601 (2002)*

Outline



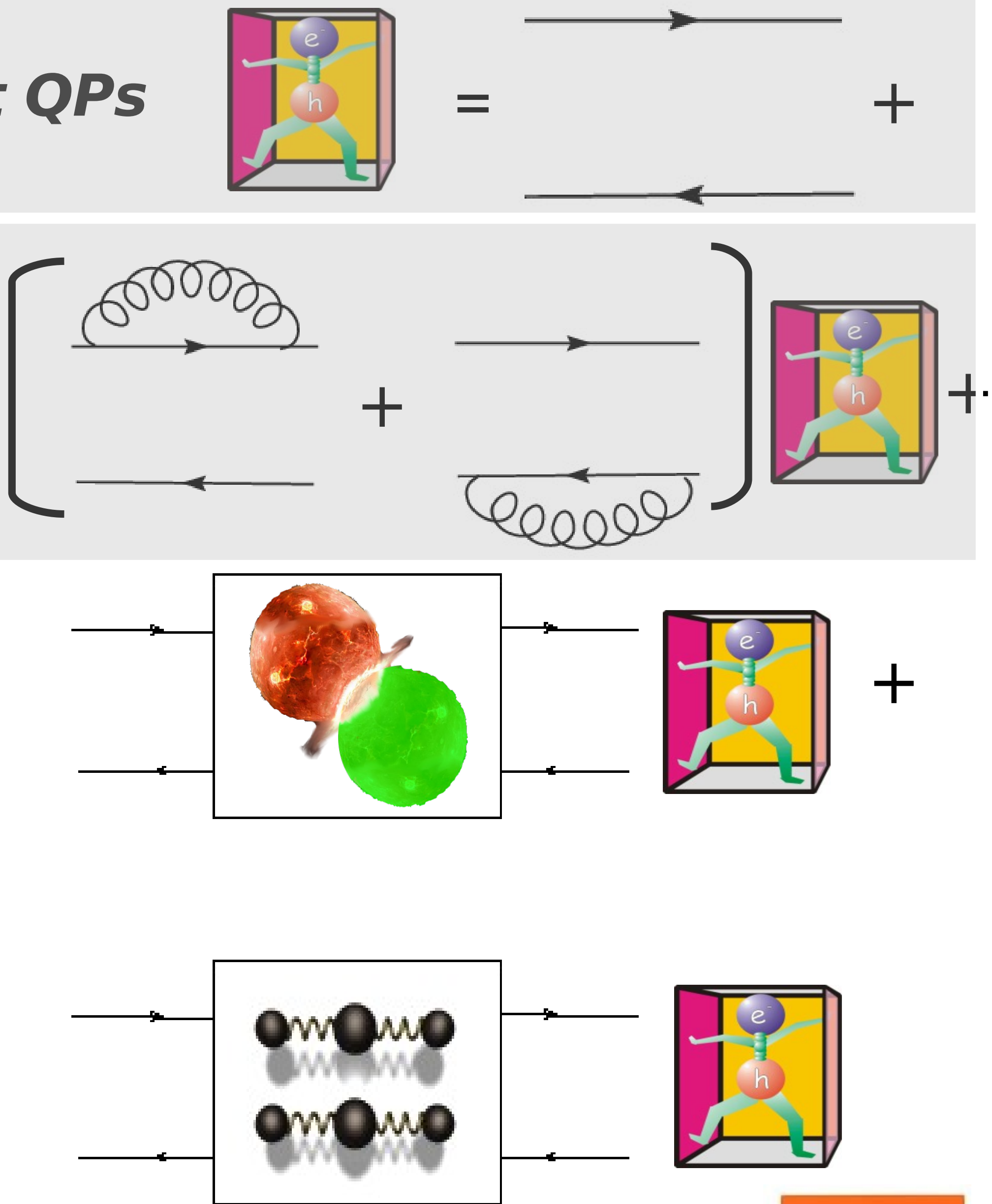
1 *Ab-Initio Polarons*

2 *Finite temperature dynamics for the excitons*

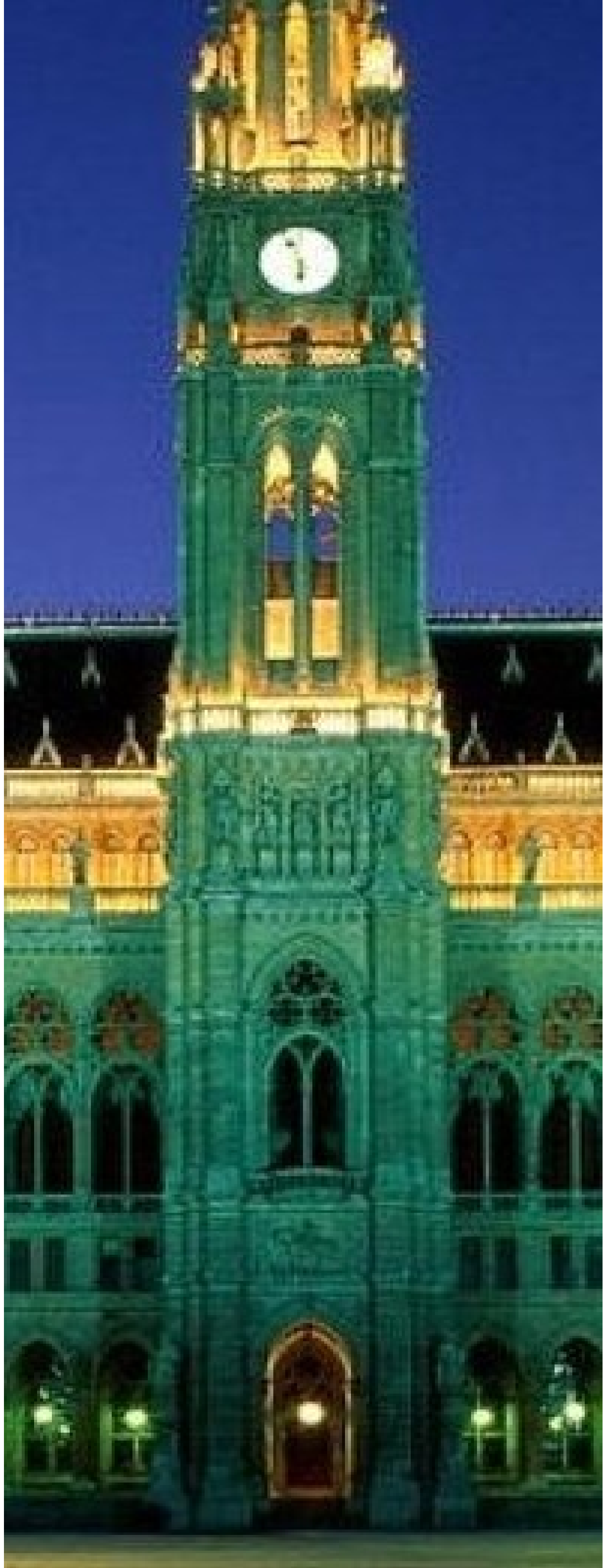
3 *Finite temperature optics*

Independent QPs

“Indirect” exciton-phonon scattering

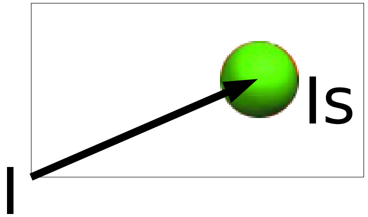


Ab-Initio Polarons



Polarons: the Cardona Allen approach

Solid St. Comm. 133, 3 (2005) ; PRB **23**, 1495 (1981)



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

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

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

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

Debye-Waller

Fan

An-harmonic term

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

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

$$\delta E_{n\mathbf{k}} = \int_0^{\Omega_D} d\Omega \, g^2 F_{n\mathbf{k}}(\Omega) \left[2\langle N_\Omega\rangle + 1\right]$$

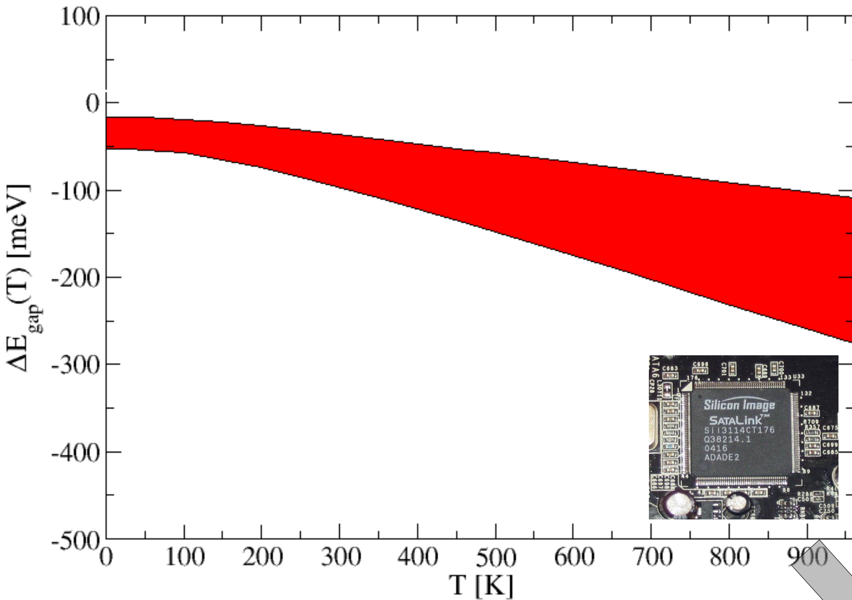
"Generalized" Eliashberg function

Energy corrections do not vanish when T → 0

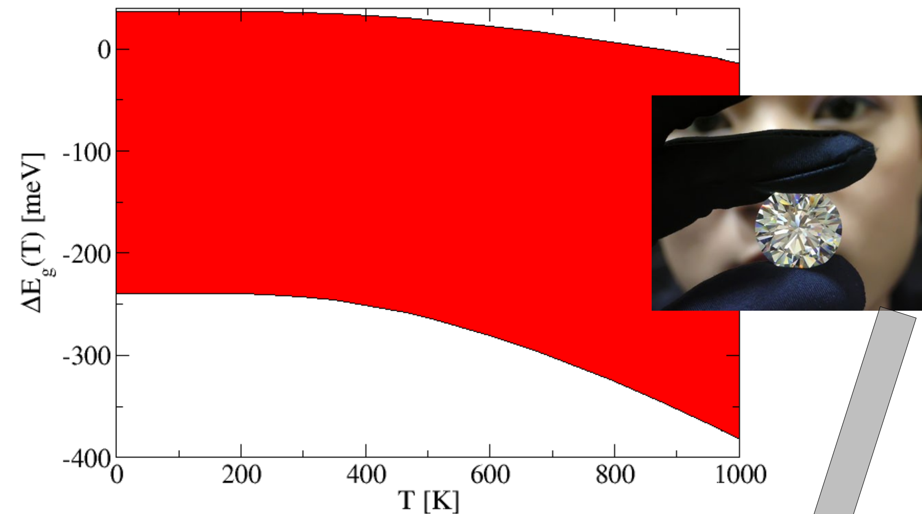
DFPT is used to calculate phonons and electron-phonon coupling coefficients.

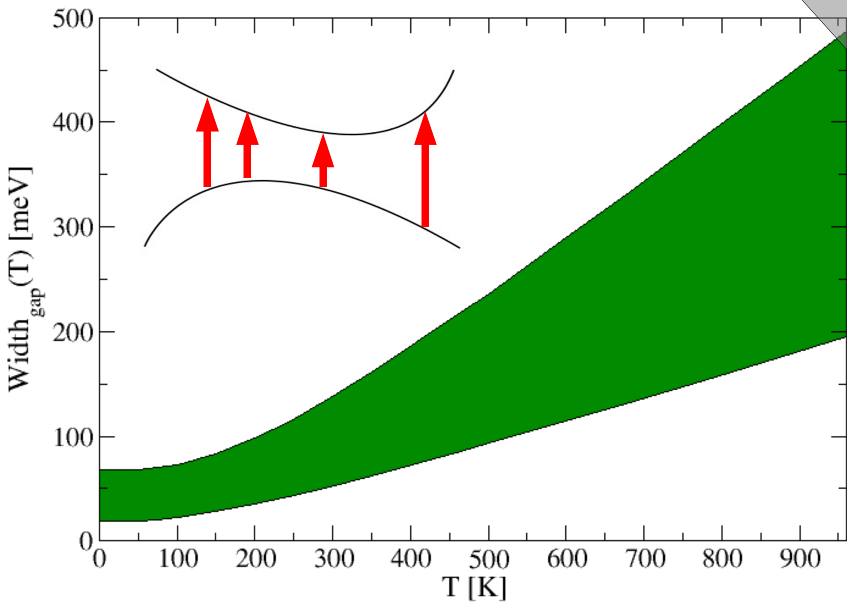
http://www.pwscf.org

Ab-Initio Polarons: Silicon and Diamond

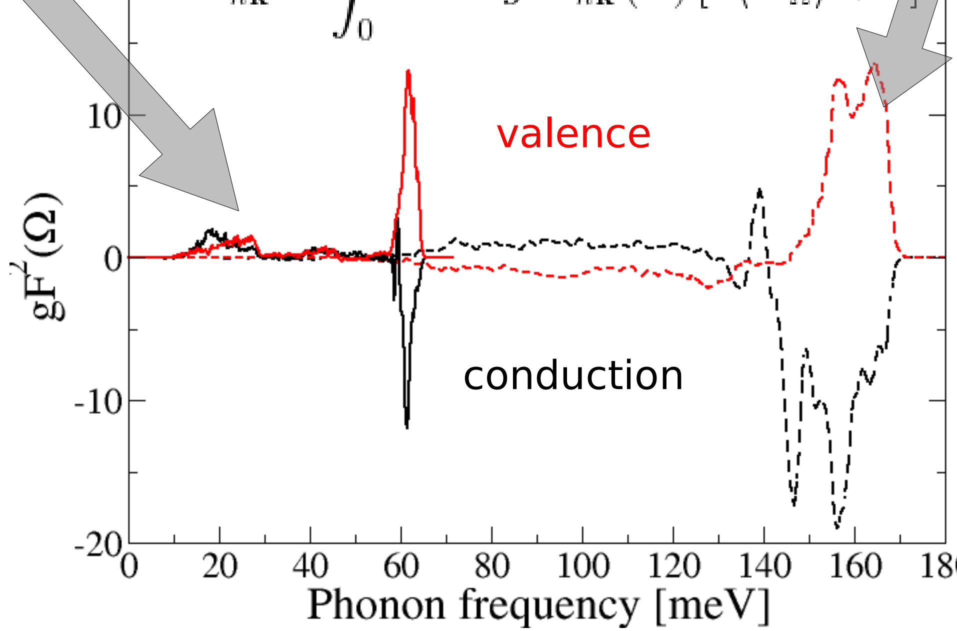


Phonon induced gap correction can be as large as 0.1 eV at room temperature (15% of the QP correction)



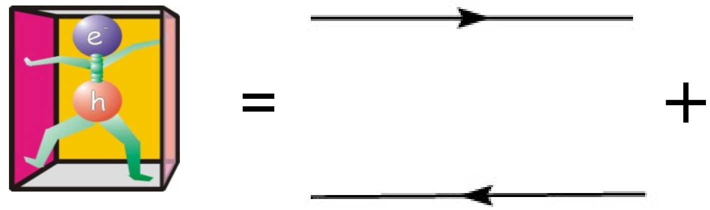


$$\delta E_{n\mathbf{k}} = \int_0^{\Omega_D} d\Omega\, g^2F_{n\mathbf{k}}(\Omega)\left[2\langle N_\Omega\rangle + 1\right]$$

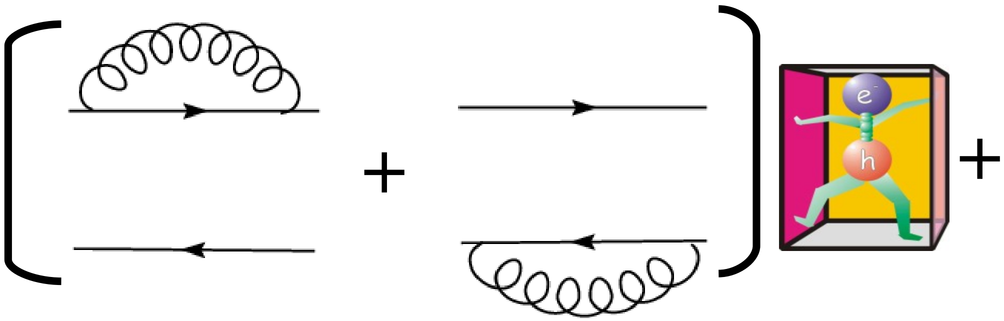


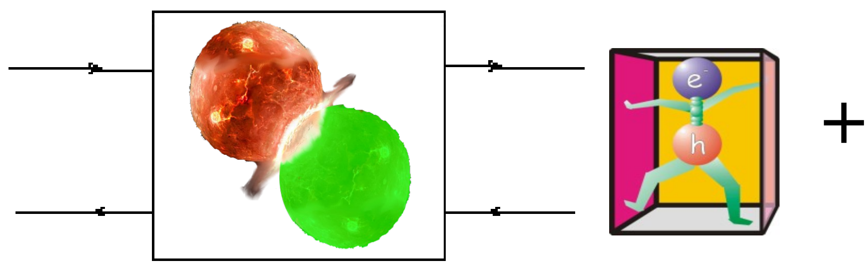
Optical electron-hole pair widths are 30 meV at T=0 and 150 meV at room-temperature.

Independent QPs

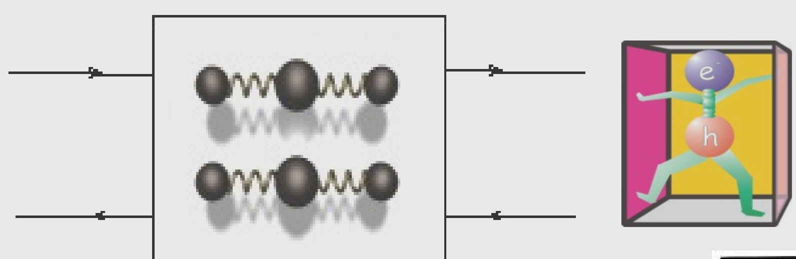


"Indirect" exciton-phonon scattering

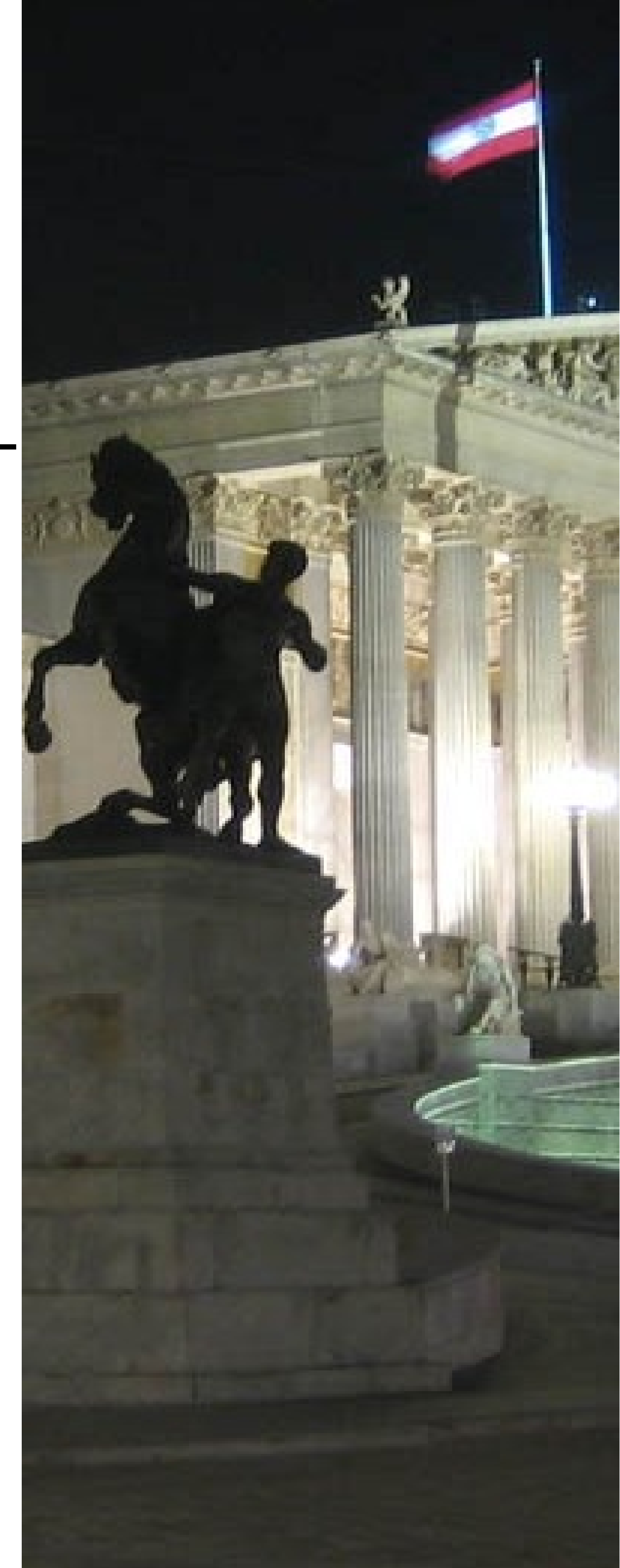




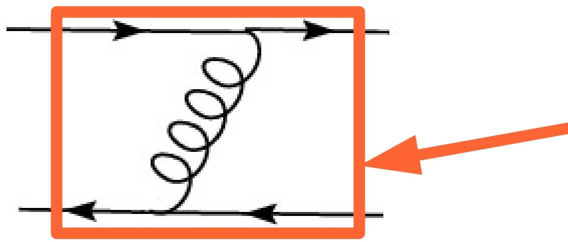
"Direct" exciton-phonon scattering



Finite temperature dynamics for the excitons



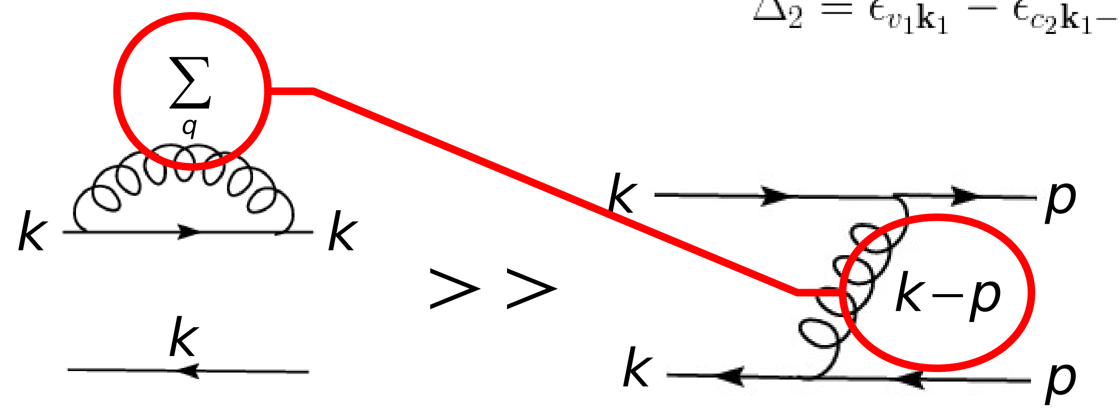
The dynamical BSE: the phonon term



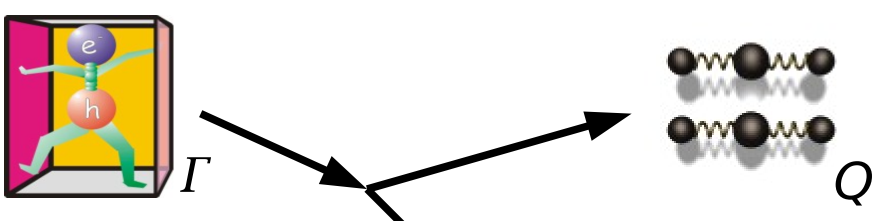
$$\Pi^{ph}_{\mathbf{K}_1,\mathbf{K}_2}(i\omega) = -\sum_{\lambda} g^{\mathbf{q}\lambda}_{c_2 c_1 \mathbf{k}_1} \left(g^{\mathbf{q}\lambda}_{v_2 v_1 \mathbf{k}_1}\right)^* \sum_{I} \left[\frac{1+\langle N_{\mathbf{q}\lambda}\rangle}{i\omega + \Delta_I - \omega_{\mathbf{q}\lambda}} + \frac{\langle N_{\mathbf{q}\lambda}\rangle}{i\omega + \Delta_I + \omega_{\mathbf{q}\lambda}} \right]$$

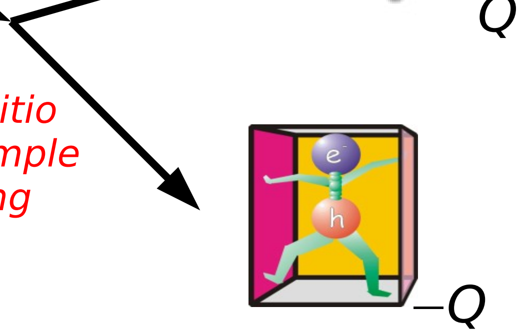
$$\Delta_1 = \epsilon_{v_2 \mathbf{k}_1 - \mathbf{q}} - \epsilon_{c_1 \mathbf{k}_1}$$
$$\Delta_2 = \epsilon_{v_1 \mathbf{k}_1} - \epsilon_{c_2 \mathbf{k}_1 - \mathbf{q}}$$

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

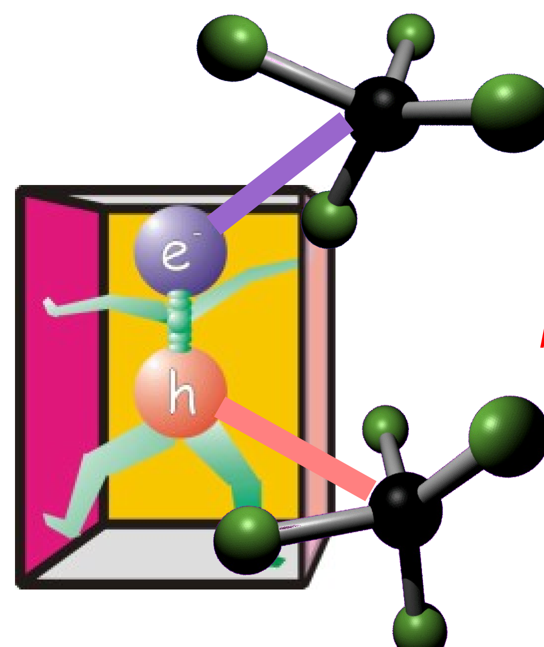


The momenta conservation makes the polaronic (indirect) term dominant



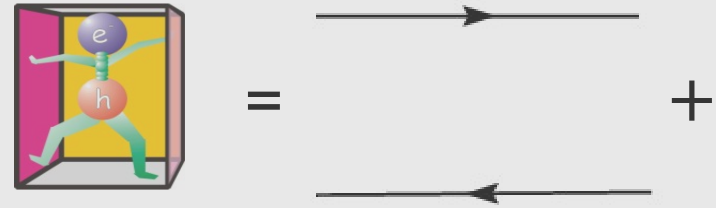


"There is no Ab-Initio giustification for simple bosonic scattering pictures"

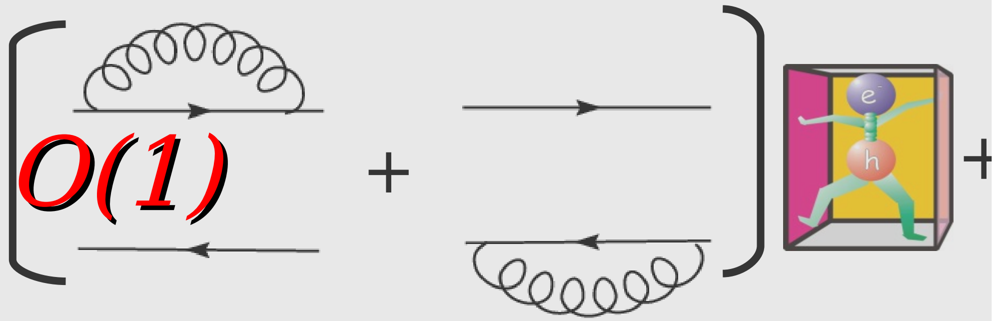


"Excitons-phonon interaction is dictated by the internal structure of the excitonic state."

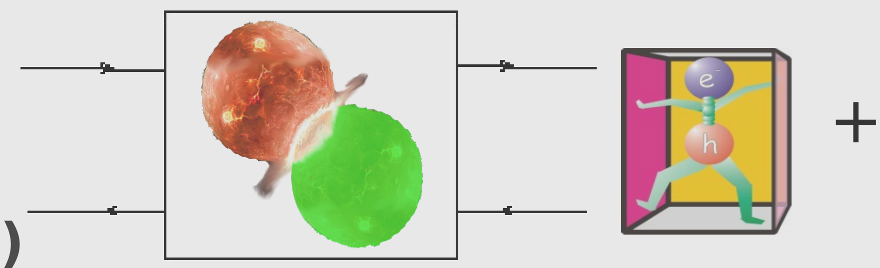
Independent QPs



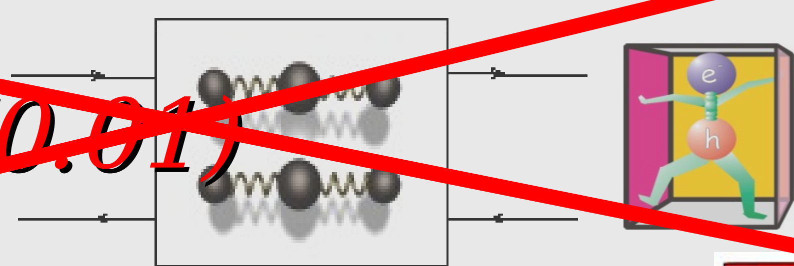
“Indirect” exciton-phonon scattering



Electron-Hole Columbian scattering (binding process)

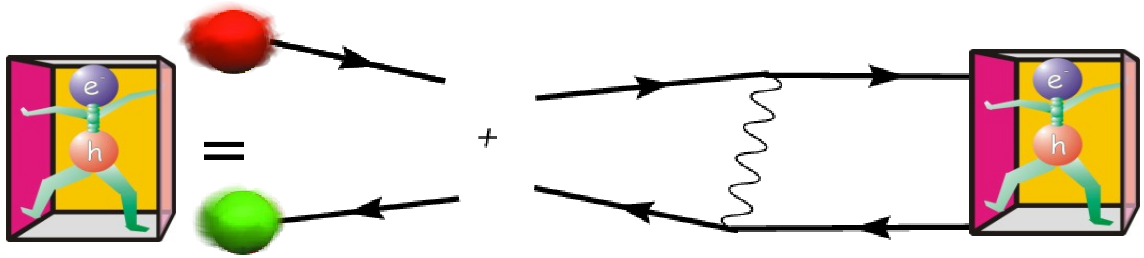


“Direct” exciton phonon scattering



Finite temperature optics

Excitons: the polaronic picture

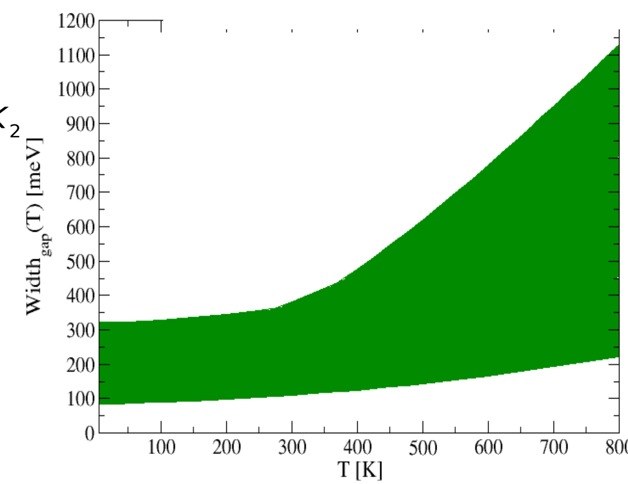


Quasihole and quasielectron **polarons**

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

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

$$H_{K,K'}(T) = \left[(E_e(T) - E_h(T)) + i(\Gamma_e(T) - \Gamma_h(T))\right]\delta_{K,K'} + \Pi^{el}_{K_1,K_2}$$



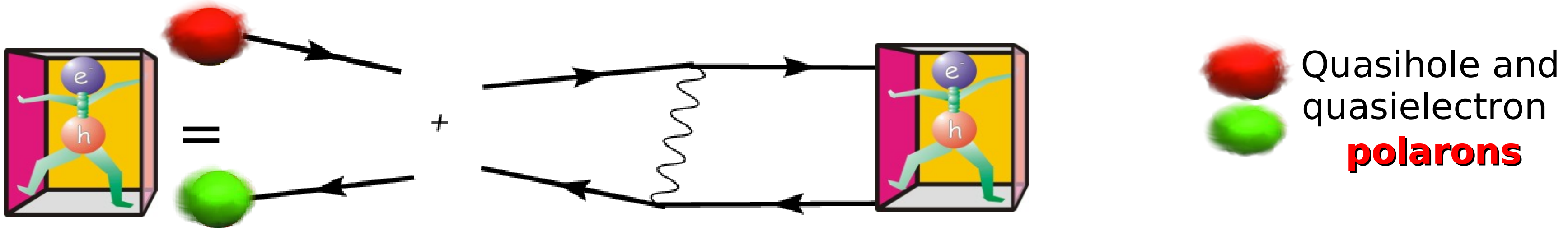
The BS Hamiltonian is
NOT Hermitian

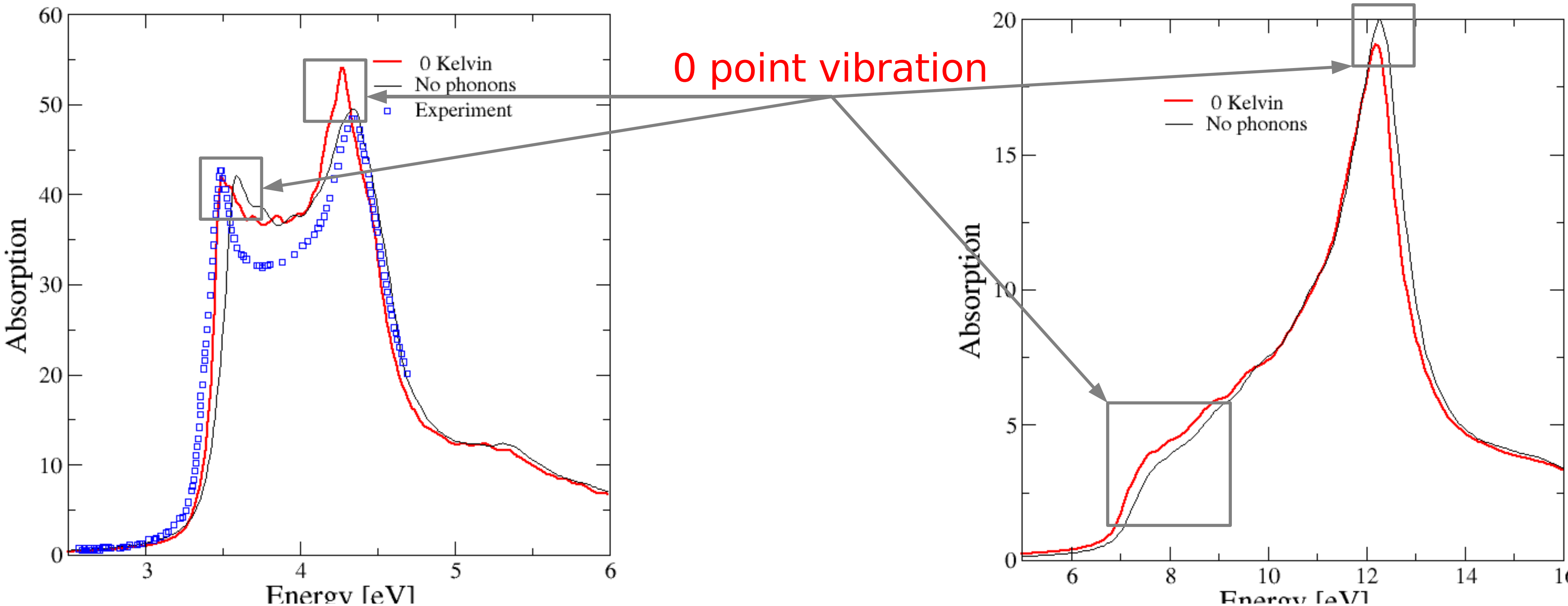
$$H_{K,K'}(T)\lambda_{K'}(T) = E_\lambda(T)\lambda_K(T)$$

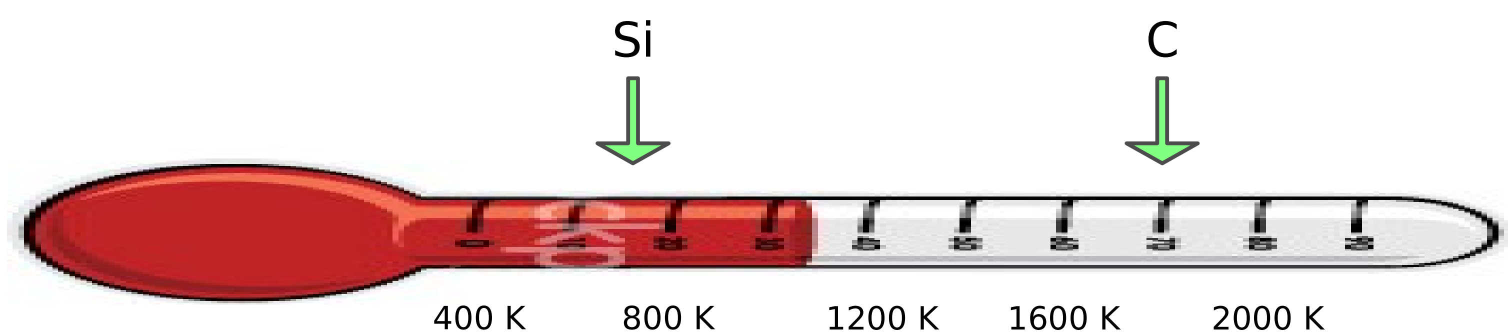
$$\epsilon_2(\omega, T) \propto \sum_\lambda S_\lambda(T)(\omega - E_\lambda)^{-1}$$

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

Finite T optics: Si and diamond

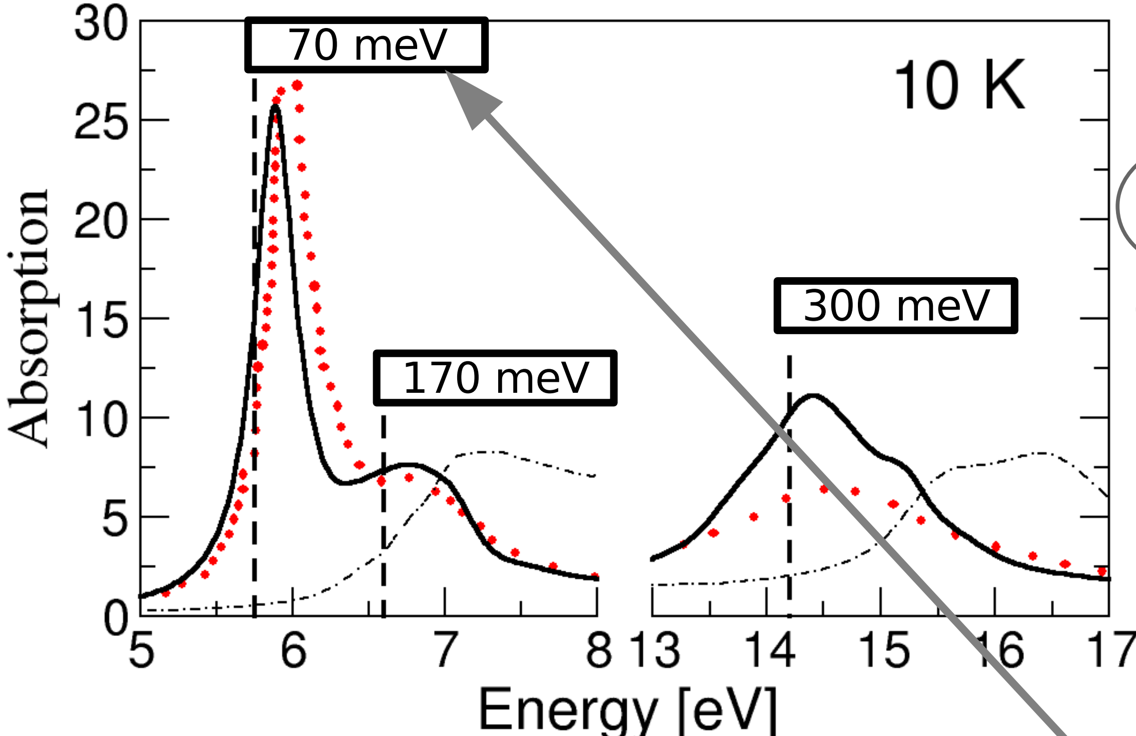


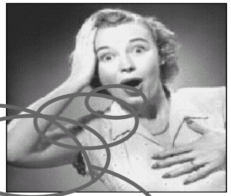




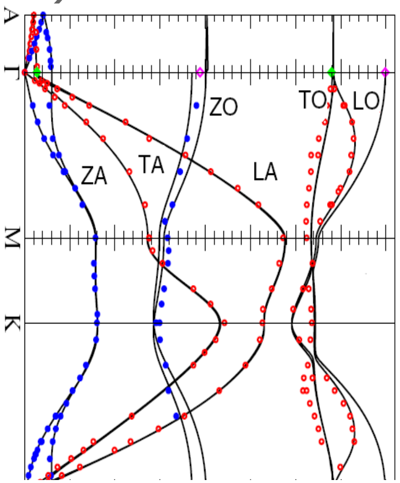
Hexagonal-BN: optics

B. Arnaud PRL. **96**, 026402 (2006); C. Tarrio, PRB **40**, 7852 (1989)





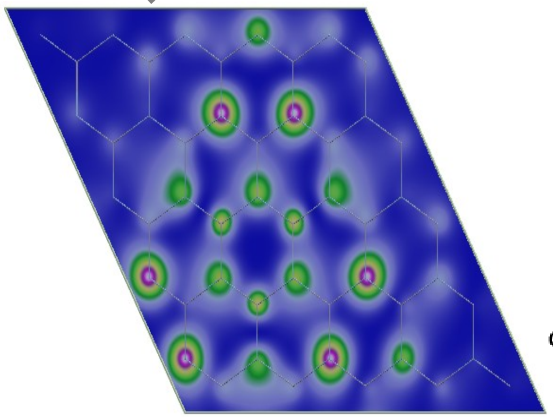
- **Huge blue-shift** (zero-point vibrations) of the excitonic energies
- Lowest energy peak **binding energy reduced by 200 meV** (30%)

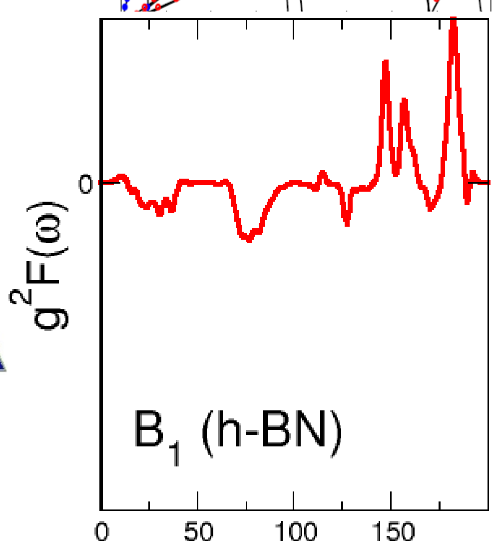


$$\delta E_{e,h} = \int_0^{\Omega_D} d\Omega \, g^2 F_{e,h}(\Omega) \left[2\langle N_\Omega \rangle + 1\right]$$

$$g^2 F_\lambda(\omega) \equiv \sum_{e,h} |\langle e,h|\lambda\rangle|^2 \left[g^2 F_e(\omega) - g^2 F_h(\omega)\right]$$

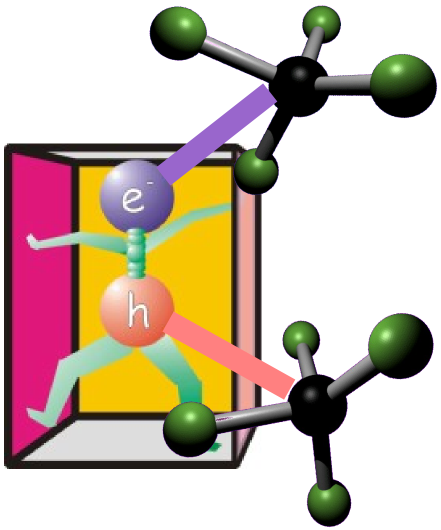
$$\delta E_{e,h} \sim \int_0^{\Omega_D} d\Omega \, g^2 F_\lambda(\Omega) \left[2\langle N_\Omega \rangle + 1\right]$$





http://babbage.sissa.it/abs/0712.3365

Exciton-phonon interaction: weak vs strong coupling regime



$$H_{\substack{ee'\\hh'}}(T) = H^{FA}_{\substack{ee'\\hh'}} + \left[\Delta E_e(T) - \Delta E_h(T)\right]\delta_{eh,e'h'},$$

$$\delta E_{e,h} = \int_0^{\Omega_D} d\Omega\, g^2 F_{e,h}(\Omega)\left[2\langle N_\Omega\rangle + 1\right]$$

$$g^2 F_\lambda(\omega) \equiv \sum_{e,h} |\langle e,h|\lambda\rangle|^2 \left[g^2 F_e(\omega) - g^2 F_h(\omega)\right]$$

$$\Im\left[E_\lambda(T)\right] = \int d\omega\, \Im\left[g^2 F_\lambda(\omega,T)\right]\left[N(\omega,T) + 1/2\right]$$

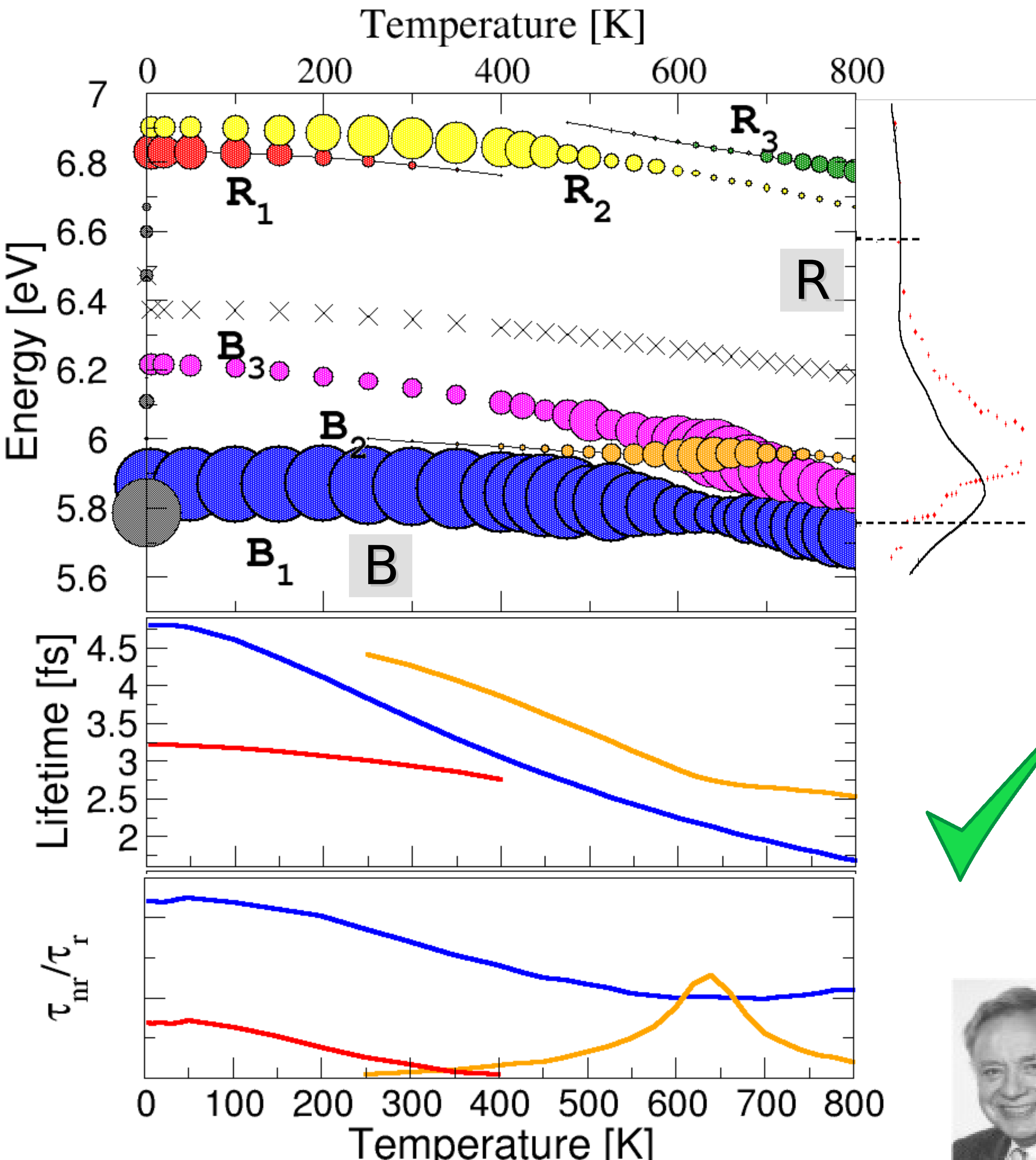
$$\Re\left[\Delta E_\lambda(T)\right] = \left[\langle\lambda(T)|\mathbf{H}^{FA}|\lambda(T)\rangle - \langle\lambda_{FA}|\mathbf{H}^{FA}|\lambda_{FA}\rangle\right] + \int d\omega\, \Re\left[g^2 F_\lambda(\omega,T)\right]\left[N(\omega,T) + 1/2\right]$$

coherent term | incoherent term

weak regime: coherent term << incoherent term (silicon, diamond)

strong regime: coherent and incoherent terms of the same order (hBN ?)

Hexagonal-BN: fine structure



Bright to dark (and vice versa) transitions

The microscopical mechanism of the bright to dark (and vice versa) transitions is a transfer of optical strength between energetically close excitonic states

Thermal stability of excitonic energies, but...

...gradual worsening of optical efficiency

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

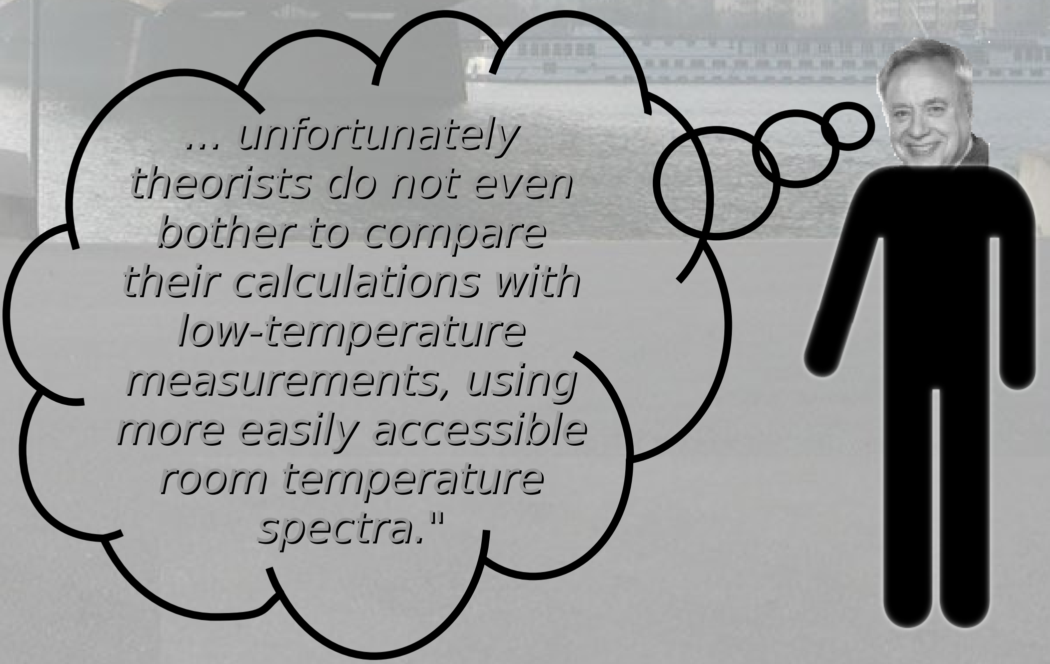
Conclusions...

The finite temperature optical properties of semiconductors with resonant and bound excitons can be described with the standard BSE in the polaronic picture

The excitonic damping and zero-point motion effect are in excellent agreement with the experiment.

The non-radiative lifetime and the optical efficiency of the excitonic states as photo-emitters are slowly decreasing functions of the temperature

The thermal evolution of the excitonic states shows the existence of bright to dark (and vice versa) transitions.



...and...

Codes and People...

Yambo©

http://www.yambo-code.org

***Yambo*: an *ab initio* tool for excited state calculations**, AM, C. Hogan, M. Grüning, D. Varsano, arXiv:0810.3118

Ludger Wirtz
Paul boulanger

Xavier Gonze
Antonio Sanna

:: project

PWscf Plane-Wave Self-Consistent Field

"The computer is a tool for clear thinking"
Freeman J. Dyson

http://www.pwscf.org

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