united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

SMR.1511 - 18

Third Stig Lundqvist Conference on Advancing Frontiers of Condensed Matter Physics:

"Fundamental Interactions and Excitations in Confined Systems"

11 - 15 August 2003

Femtosecond decoherence of quasiparticles in the states of surface image potential: Beyond the lifetime effects given by Fermi's golden rule

Branko GUMHALTER
University of Zagreb
Institute of Physics
P.O. Box 304
Bijenicka Cesta 46
10001 Zagreb
CROATIA

Femtosecond decoherence of quasiparticles in the states of surface image potential: Beyond the lifetime effects given by Fermi's golden rule*

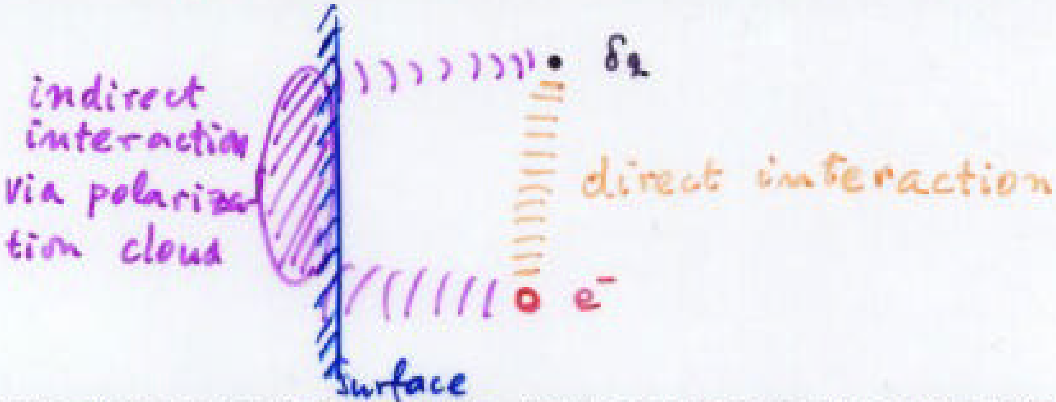
Branko Gumhalter
Institute of Physics of the University,
P.O. Box 304, 10001 Zagreb, Croatia.

---

[*] Work done in part at the *Donostia International Physics Center, San Sebastian, Spain.* See Refs. B. Gumhalter and H. Petek, Surf. Sci. 445(2000)195; B. Gumhalter, Surf. Sci. 518(2002)81

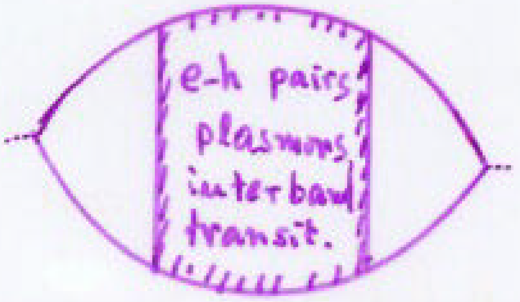
PRELIMINARIES

Electron ⓔ and probe charge δq in front of a metal surface



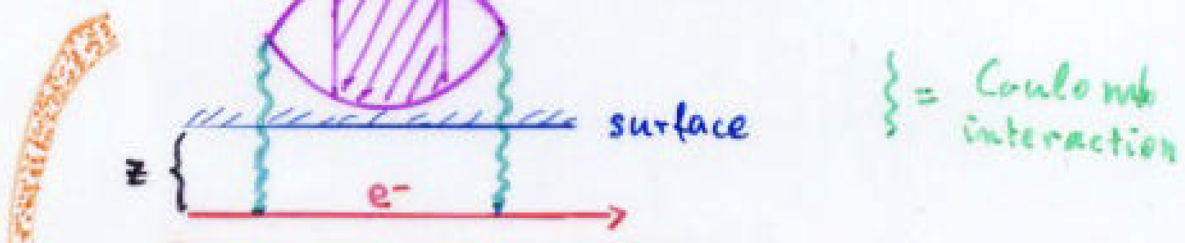
Polarisation properties of the surface described by the linear response function

$R_{\vec q}(\omega) =$



$, \quad S_{\vec q}(\omega) = \frac{1}{\pi}\left|\mathrm{Im}\, R_{\vec q}(\omega)\right|$

Adiabatic interaction of the electron with a flat metal surface gives rise to the **image potential**:

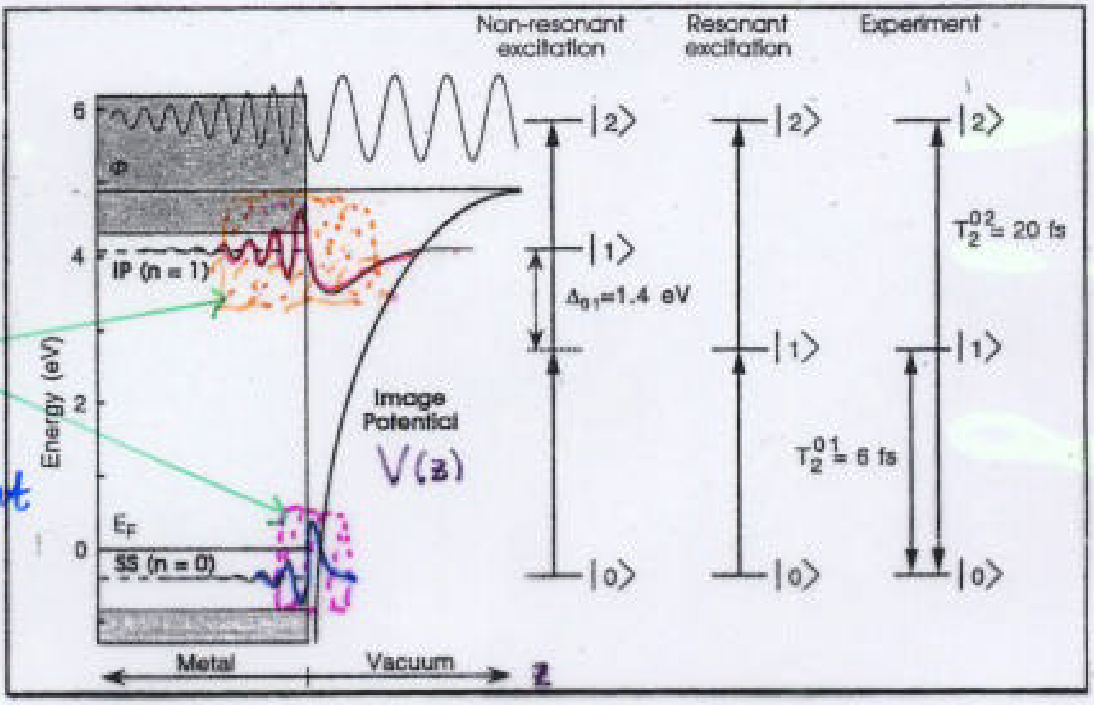


$$\boxed{\lim_{z\gg z_e} V_{im}(z) = -\frac{e^2}{4(z-z_e)}}$$

This in combination with other interactions (one- and many-body) builds up the total potential.

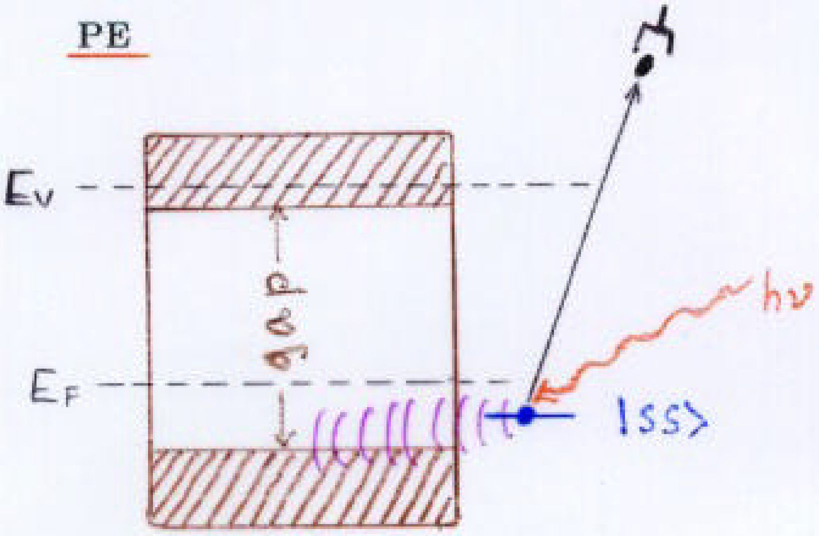
Electron confinement in Q-2D surface bands

gion
f
finement

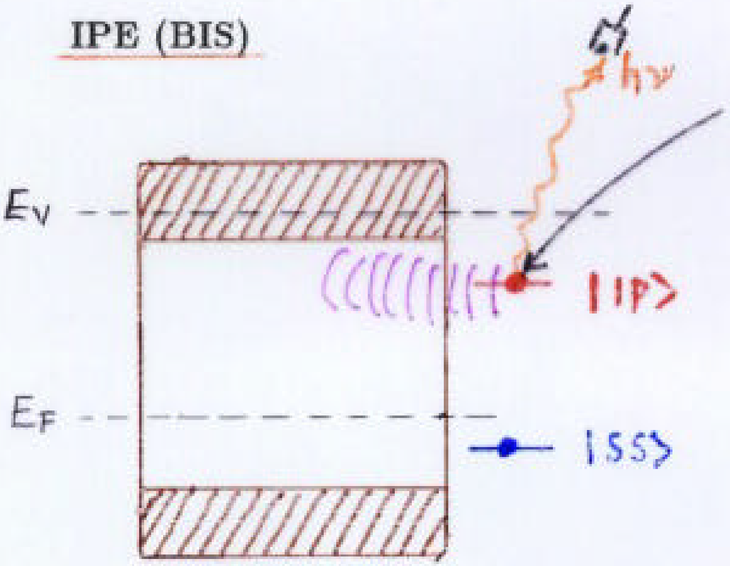


Final state interactions in PE, IPE and 2PPE from Q 2D surface bands

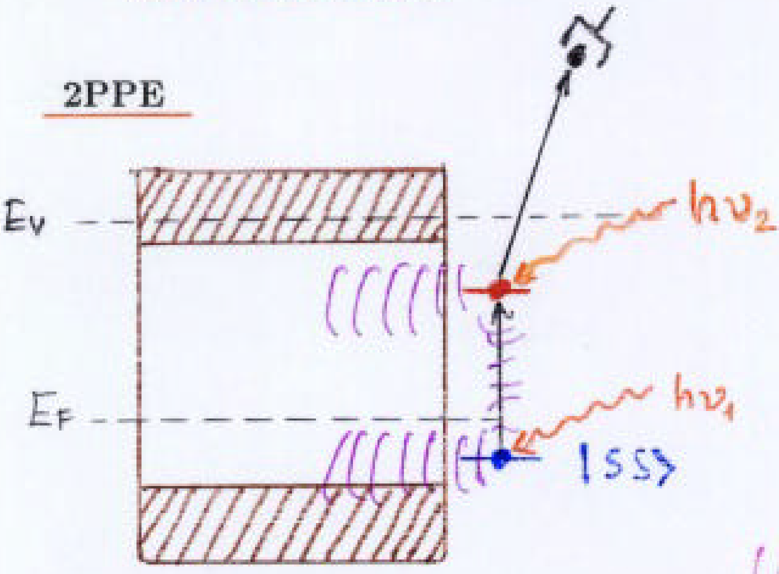
PE



IPE (BIS)



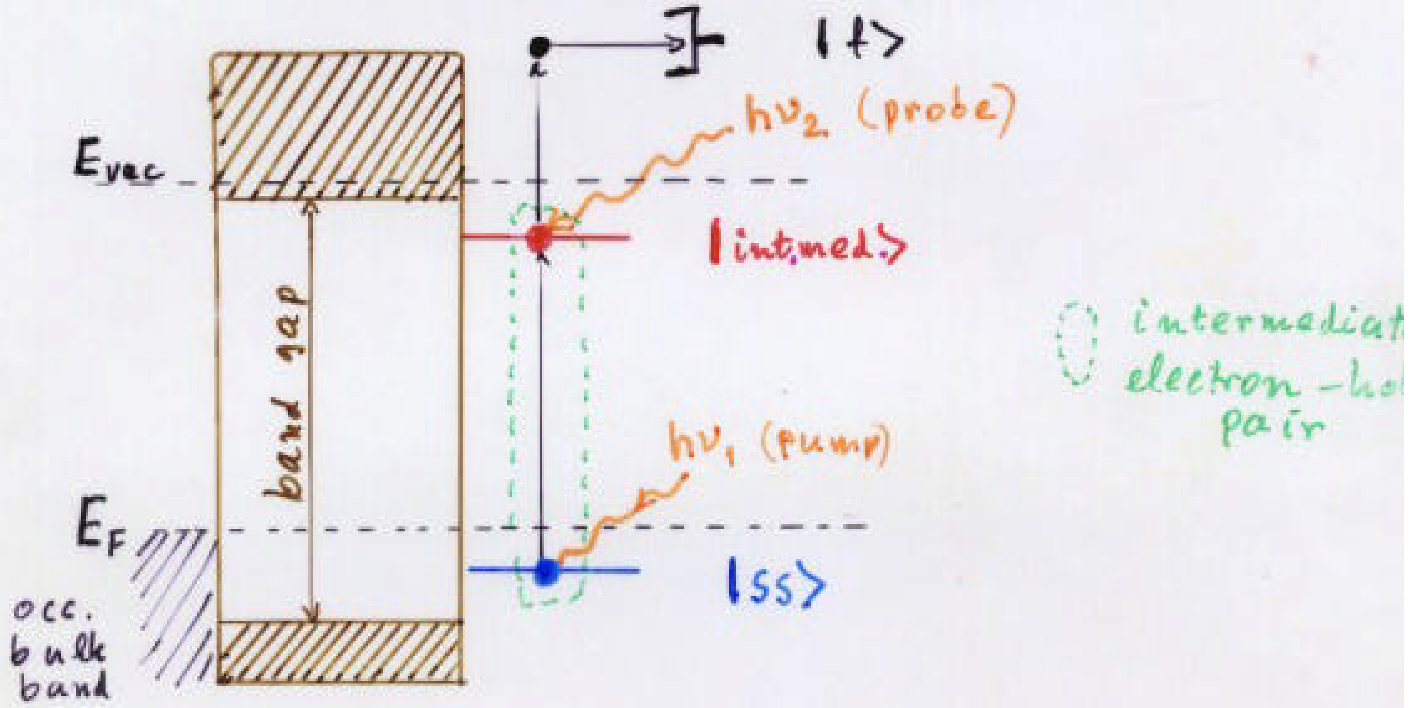
2PPE



((((((Transient interactions !

I. INTRODUCTION TO 2PPE DYNAMCS

Typical experimental tool for probing the structure of 2D electronic bands at metal surfaces is two-photon photoemission spectroscopy (2PPE).



The first step of 2PPE from an occupied surface state is characterized by excitation of an electron-hole pair in the surface region.

Absorption of a pump pulse photon induces transitions of the system from its ground state to an excited state:

$$| 0_{syst}\rangle \to |\underbrace{\ldots \overbrace{0_{\mathbf{K},SS}, \ldots, \mathbf{k_F}, 0..1_{\mathbf{K}}}^{h\text{-}e}, Q.}_{e\text{-}h \text{ pair over ground state}}\rangle \tag{1}$$

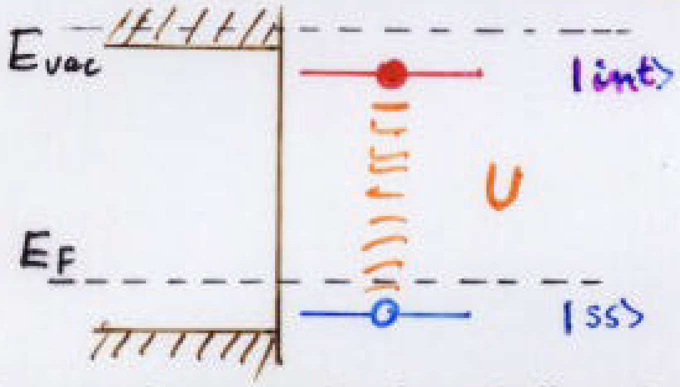
One can distinguish several time scales typical of the evolutuion and dephasing of an optically excited electron-hole pair!

(i) $t < \tau_{screen} \approx \omega_s^{-1}$ $(\hbar\omega_s \approx 10\ \text{eV})$

In this time interval an e-h pair excited over the ground (charge equilibrium) state of the system cannot be affected by the electronic response of the metal.

⇓

The only interaction that can act between the two uncompensated charges is the instantaneous and therefore unscreened Coulomb interaction U.



Owing to this interaction the optically excited e-h pair may form during this time interval a transient "excitonic state" with the lowest excitation energy

$$\Delta E = E_1 - E_0 \approx -\mu\left(\frac{1}{n_1^2} - \frac{1}{n_0^2}\right)\text{Ryd} = \frac{3\mu}{4}\text{Ryd}, \tag{2}$$

where $\mu = \frac{m_e m_h}{(m_e + m_h)}$ is the reduced mass of the excited electron-hole pair. For effective masses typical of the SS-band on Cu(111) surface:

$$\Delta E \approx 4.5eV. \tag{3}$$

This transient or intermediate state will decay fast with the switching on of the coupling of uncompensated charges of the excited e-h pair to the substrate response.

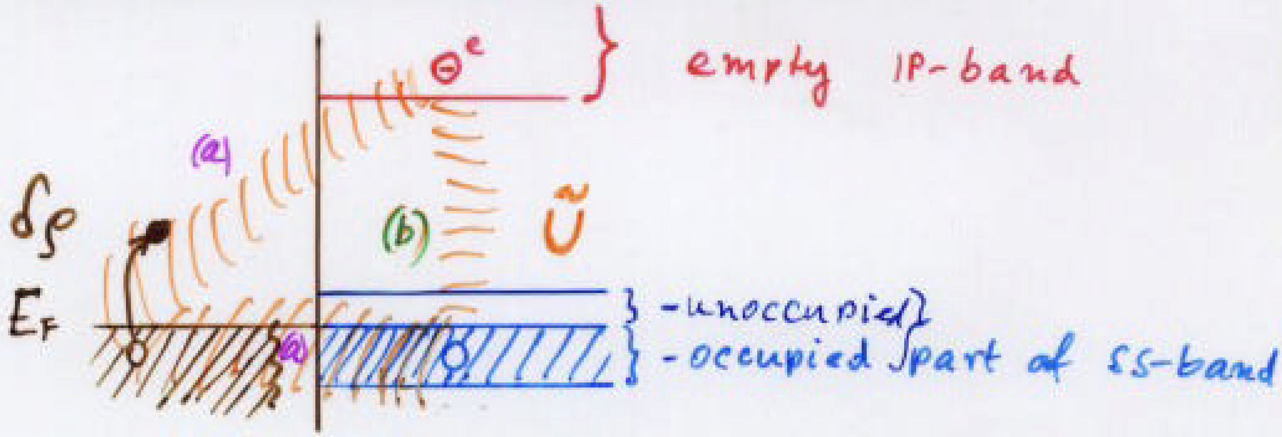
(ii) $t > \tau_{screen} \approx \omega_s^{-1}$

In this time interval the "fast" component of the substrate response (plasmons and high energy interband transitions) could have adiabatically responded to develop images of both constituent charges of the excited e-h pair.

The excited electron and the hole start their propagation in the 2D bands of the surface image potential in a coherent state:

$$| i_{\mathbf{K}}\rangle = | \ldots 0_{\mathbf{K},SS}, \ldots, \mathbf{k_F}, \ldots 1_{\mathbf{K},IP}, \ldots\rangle \tag{4}$$

The decoherence or dephasing of the excited state $| i_{\mathbf{K}}\rangle$ is caused by interactions giving rise to inelastic scattering out of the coherent state:



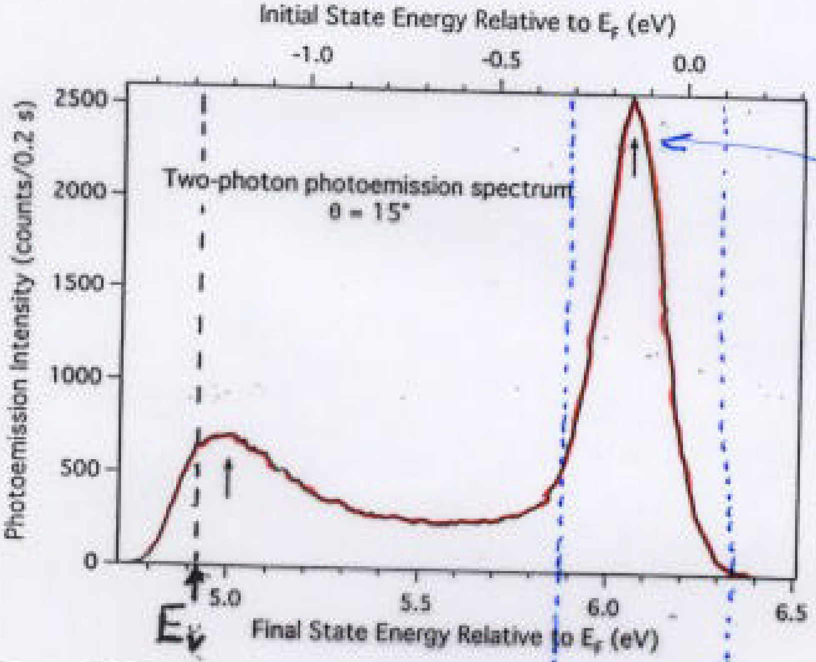
Transient interactions switched on with the creation of IP-SS pair:

(a) Interactions of IP-electron and SS-hole with substrate charge density fluctuations (intraband e-h pairs, plasmons and interband e-h excitations),

(b) Direct dynamically screened Coulomb interaction $\tilde{U}$ between the IP-electron and SS-hole.

Experimental 2PPE spectrum from Cu(111)

(Ogawa et al., PRL 78(1997)1339)



from |SS⟩

$\hbar\omega_x = 3.1$ e

FIG. . 2PP spectrum measured at $k_\parallel = 0.15$ Å^{-1} ($\Theta = 15°$) from Cu(111).

The 2PPE SS-peak affected by the coherence of the intermediate ("excitonic") state.

Information on the properties of "excitonic" state is deducible from the response function $\mathcal{R}(t)$ of the system describing the quadratic response to the applied electromagnetic field. This object is much easier to calculate than the $(3-j)$ or $(5-j)$ correlation functions:

$$\mathcal{R}(t) = i\langle 0 \mid T[H_x(t), H_x(0)] \underbrace{\mid 0\rangle}_{\text{initial ground state}} \qquad (2)$$

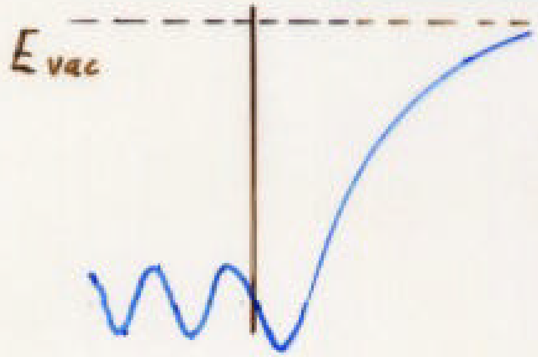
II. DESCRIPTION OF DEPHASING OR DECOHERENCE OF IP-SS E-H PAIRS IN TERMS OF QUASIPARTICLE LIFETIMES

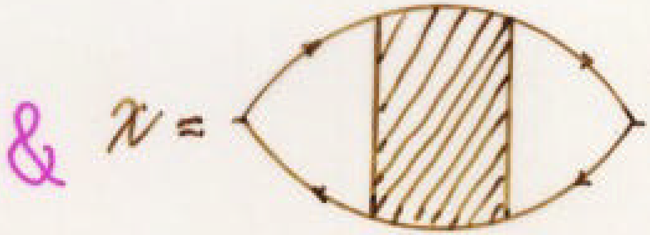
San Sebastian School:

Calculate lifetimes of electrons in IP-bands and holes in SS-band separately

$$\tau_{SS}, \qquad \tau_{IP}, \tag{5}$$

starting from Fermi's Golden Rule and adiabatic assumption, and using accurate forms of the surface (image) potential and substrate response function.





Compare the obtained results with experimental data from PE, IPE and 2PPE spectroscopies.

Note: !

The final states of PE, IPE and 2PPE are the excited states of the system which arose as a result of action of suddenly switched on perturbation! All these cases are characterized by **final state interactions** *of the uncompensated charges of the hole (PE), electron (IPE) or e-h (2PPE) with the surface response.*

Q.1: Is it justified to interpret the results of 2PPE experiments by calculating separately the lifetimes of **SS** and **IP** states using Fermi's Golden rule and adiabatic assumption?

Q.2: What is the role of **IP**-electron-**SS**-hole interaction (vertex corrections) in the dephasing of the state $| i_{\mathbf{K}} \rangle = | \ldots 0_{\mathbf{K},SS}, \ldots, \mathbf{k_F}, \ldots 1_{\mathbf{K},IP}, \ldots \rangle$?

Answers to these questions deduced from the properties of the response function $\mathcal{R}(t)$ describing evolution of an e-h pair created by photon absorption!

Definition of the response function for optical absorption

$$\mathcal{R}(t) = i \langle \tilde{0} \mid T \left(H_x(t) H_x(0) \right) \mid \tilde{0} \rangle, \tag{6}$$

ground state with
adiabatically formed
image potential

where in the second quantization form

$$H_x = \sum_{\mathbf{K}} f_{\mathbf{K}} c^{\dagger}_{\mathbf{K},IP} c_{\mathbf{K},SS} e^{-i\omega_x t} + h.c. \tag{7}$$

and the amplitude of transitions is measured by the oscillator strength $f_{\mathbf{K}}$.

Substituting (~~22~~ 7) into (~~21~~ 6) we get:

$$\mathcal{R}(t) = \sum_{\mathbf{K'},\mathbf{K}} f^{*}_{\mathbf{K'}} f_{\mathbf{K}} \mathcal{R}(\mathbf{K'}, \mathbf{K}, t) e^{i\omega_x t}, \tag{8}$$

where the momentum resolved response function $\mathcal{R}(\mathbf{K'}, \mathbf{K}, t)$ is:

$$\boxed{\mathcal{R}(\mathbf{K'}, \mathbf{K}, t) = i \langle \tilde{0} \mid T \left(c^{\dagger}_{\mathbf{K'},SS}(t) c_{\mathbf{K'},IP}(t) c^{\dagger}_{\mathbf{K},IP}(0) c_{\mathbf{K},SS}(0) \right) \mid \tilde{0} \rangle.} \tag{9}$$

Coherent propagation: $K = k'$!

Coherent propagation of e-h pairs - lifetime effects

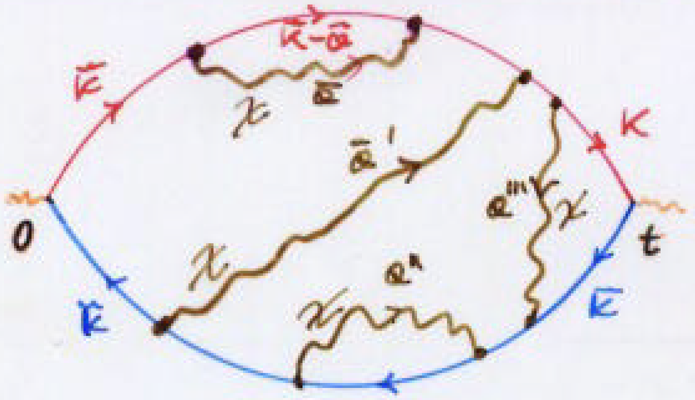
The amplitude of coherent spatio-temporal propagation of an IP-SS electron-hole pair is given by the *diagonal* electron-hole Green's function:

$$\mathcal{R}(\mathbf{K},\mathbf{K},t) = i\langle\bar{0} \mid T\left(c^{\dagger}_{\mathbf{K},SS}(t)c_{\mathbf{K},IP}(t)c^{\dagger}_{\mathbf{K},IP}(0)c_{\mathbf{K},SS}(0)\right) \mid \bar{0}\rangle. \tag{10}$$

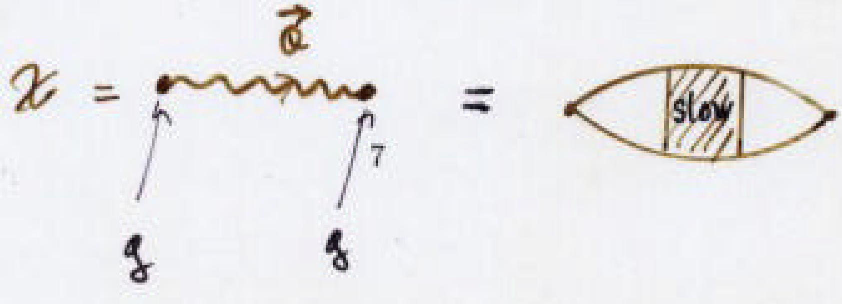
The temporal variation of $\mathcal{R}(\mathbf{K},\mathbf{K},t)$ encompasses information on lifetime effects or the decay of the state $\mid i_{\mathbf{K}}\rangle = \mid ...0_{\mathbf{K},SS},...,\mathbf{k_F},...1_{\mathbf{K},IP},...\rangle$.

Note: The amplitude of incoherent evolution of the IP-SS electron-hole pair is given by the off diagonal *components* $\mathcal{R}(\mathbf{K}' \neq \mathbf{K},t)$ *of the response function (24).*

Diagrammatic representation of $\mathcal{R}(\mathbf{K},\mathbf{K},t)$:

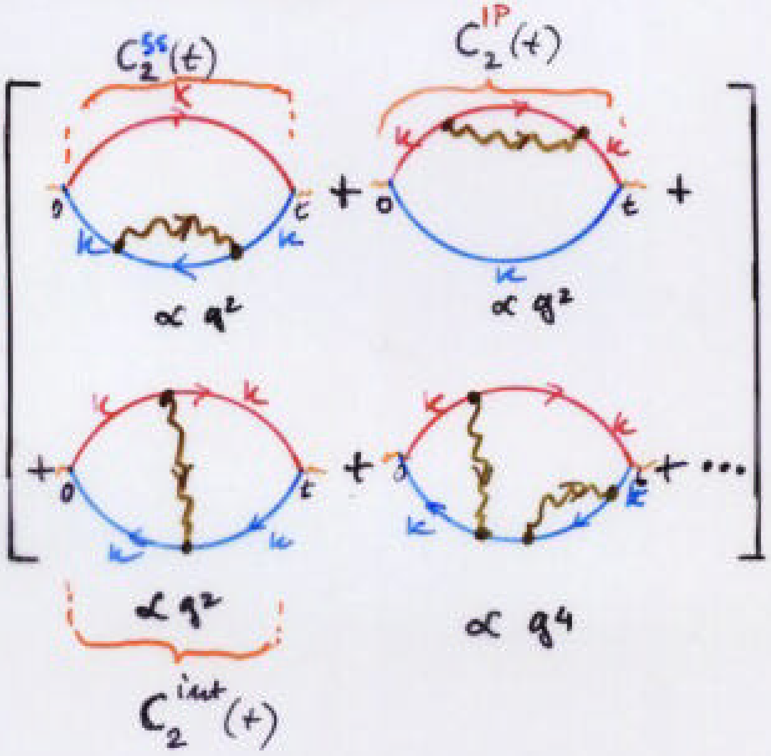


(Here, for the sake of our studies of intraband decoherence of IP-SS pairs the wavy line includes only low energy e-h pair excitations in the substrate but not plasmons)



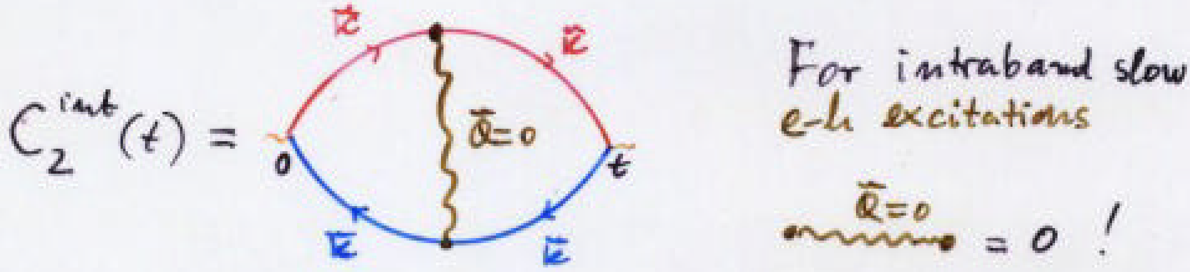
Systematic expansion of $\mathcal{R}(\mathbf{K},\mathbf{K},t)$ in powers of the coupling constant g is carried out using cumulant expansion:

$$\mathcal{R}(\mathbf{K},\mathbf{K},t) = \exp \qquad (11)$$



Important!

Due to parallel momentum conservation the low energy component of the substrate response (intraband e-h excitations in the substrate) give **zero** contribution to second order vertex diagram:

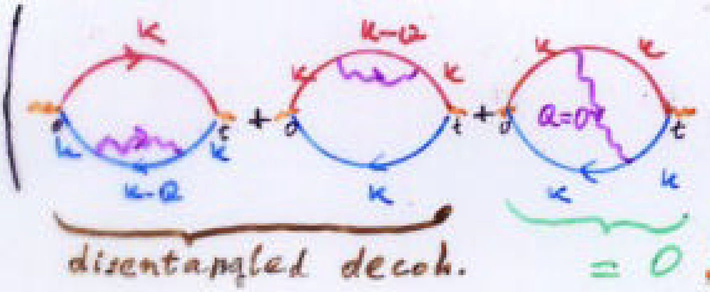


For intraband slow e-h excitations

Hence, up to the order $O(g^4)$ only the second order self-energy corrections required in the description of coherent motion of an IP-SS electron-hole pair!

Disentangled decoherence in diagonal IP-SS e-h propagator

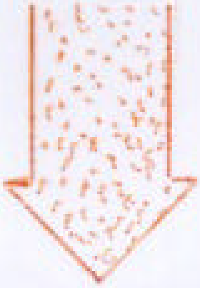
The decoherence effects contained in the *diagonal* IP-SS electron-hole pair propagator are disentangled up to $\mathcal{O}(g^4)$.



$$\mathcal{R}_1(\mathbf{K},\mathbf{K},t) = \exp\left(\quad + \quad + \quad + \mathcal{O}(g^4) \right) \qquad (12)$$

⇒Disentangled decoherence arises from renormalized SS- and IP-single particle propagators.

⇒Up to $\mathcal{O}(g^4)$ only the disentangled decoherence characterizes the lifetimes in PE, IPE and 2PPE.



Same type of disentangled relaxation processes determine lowest order decoherence of excited electrons and holes in PE, IPE & 2PPE.

The renormalized pair propagator exhibits two distinct behaviours:

(i) Gaussian-like decay in the very short initial time interval:

$$\boxed{\mathcal{R}_{\mathbf{K},\mathbf{K}}(t) = \boxed{\mathcal{R}^{0}_{\mathbf{K}}(t)}\, e^{-\sigma^2_{\mathbf{K}} t^2}, \qquad t < \frac{\Gamma_{\mathbf{K}}}{\hbar\sigma^2_{\mathbf{K}}} < 10^{-1} fs,} \tag{12}$$

where the "free" or un re normalized IP-SS pair propagator is given by:

$$\boxed{\mathcal{R}^{0}_{\mathbf{K}}(t)} = i e^{-i(\epsilon_{\mathbf{K},IP} - \epsilon_{\mathbf{K},SS})t/\hbar}\, \Theta(t). \tag{13}$$

(ii) For longer times the evolution of $\mathcal{R}_{\mathbf{K},\mathbf{K}}(t)$ is described by:

$$\boxed{\mathcal{R}_{\mathbf{K},\mathbf{K}}(t) = \mathcal{R}^{0}_{\mathbf{K}}(t) \exp[\underbrace{-i\Lambda_{\mathbf{K}} t - \Gamma_{\mathbf{K}} t}_{\text{exp. decay}} - z_{\mathbf{K}}(t)], \qquad t > \frac{\Gamma_{\mathbf{K}}}{\hbar\sigma^2_{\mathbf{K}}}.} \tag{14}$$

Characteristic parameters:

—Relaxation shift of the level(s):

$$\Lambda_{\mathbf{K}} = \Lambda^{IP}_{\mathbf{K}} + \Lambda^{SS}_{\mathbf{K}}, \tag{15}$$

—Lifetime of the coherent state(s) up to $O(g^4)$:

exp. decay

$$\Gamma_{\mathbf{K}} = \Gamma^{IP}_{\mathbf{K}} + \Gamma^{SS}_{\mathbf{K}}, \tag{16}$$

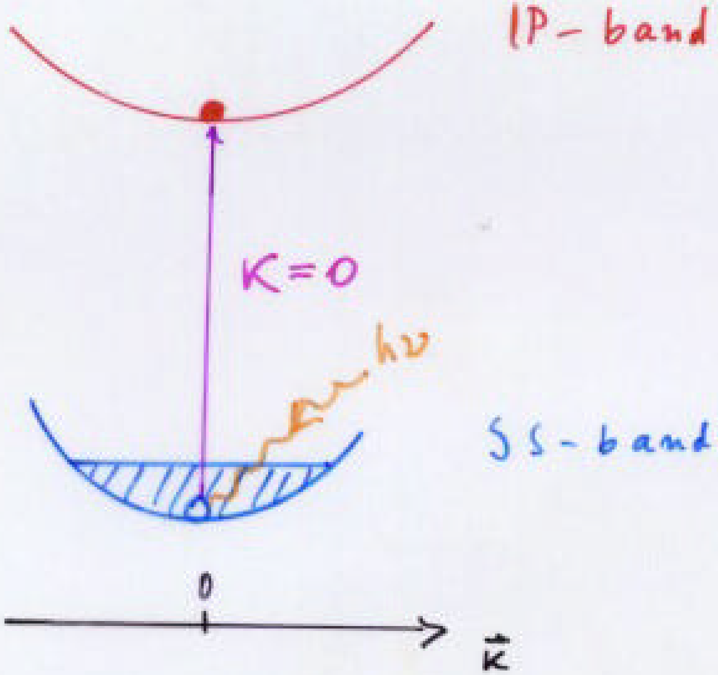
—Transient corrections (leading to the DWF) ⟹ Deviation from exp. decay:

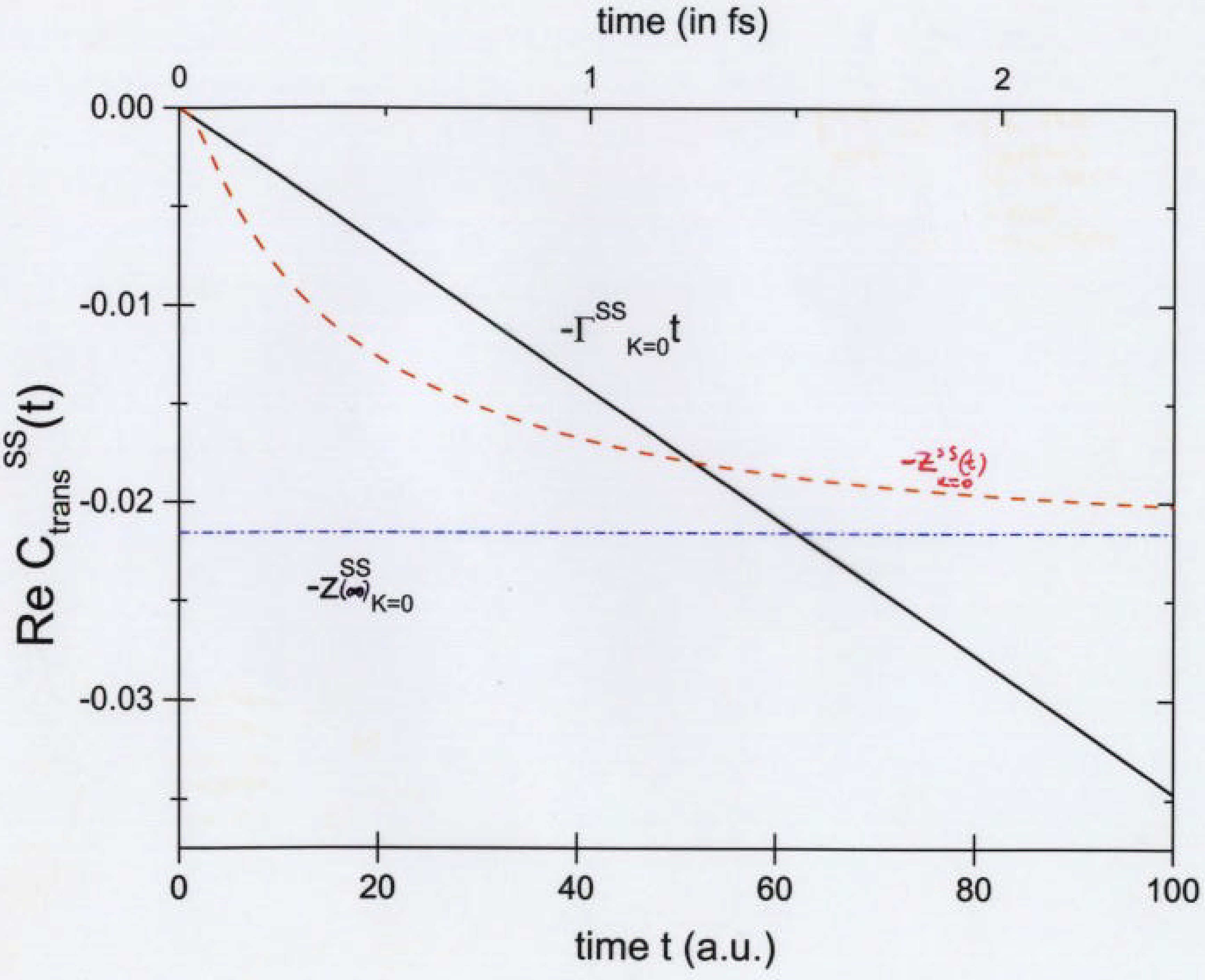
$$z_{\mathbf{K}}(t) = z^{IP}_{\mathbf{K}}(t) + z^{SS}_{\mathbf{K}}(t). \quad , \quad z_k(\infty) \neq 0 \tag{17}$$

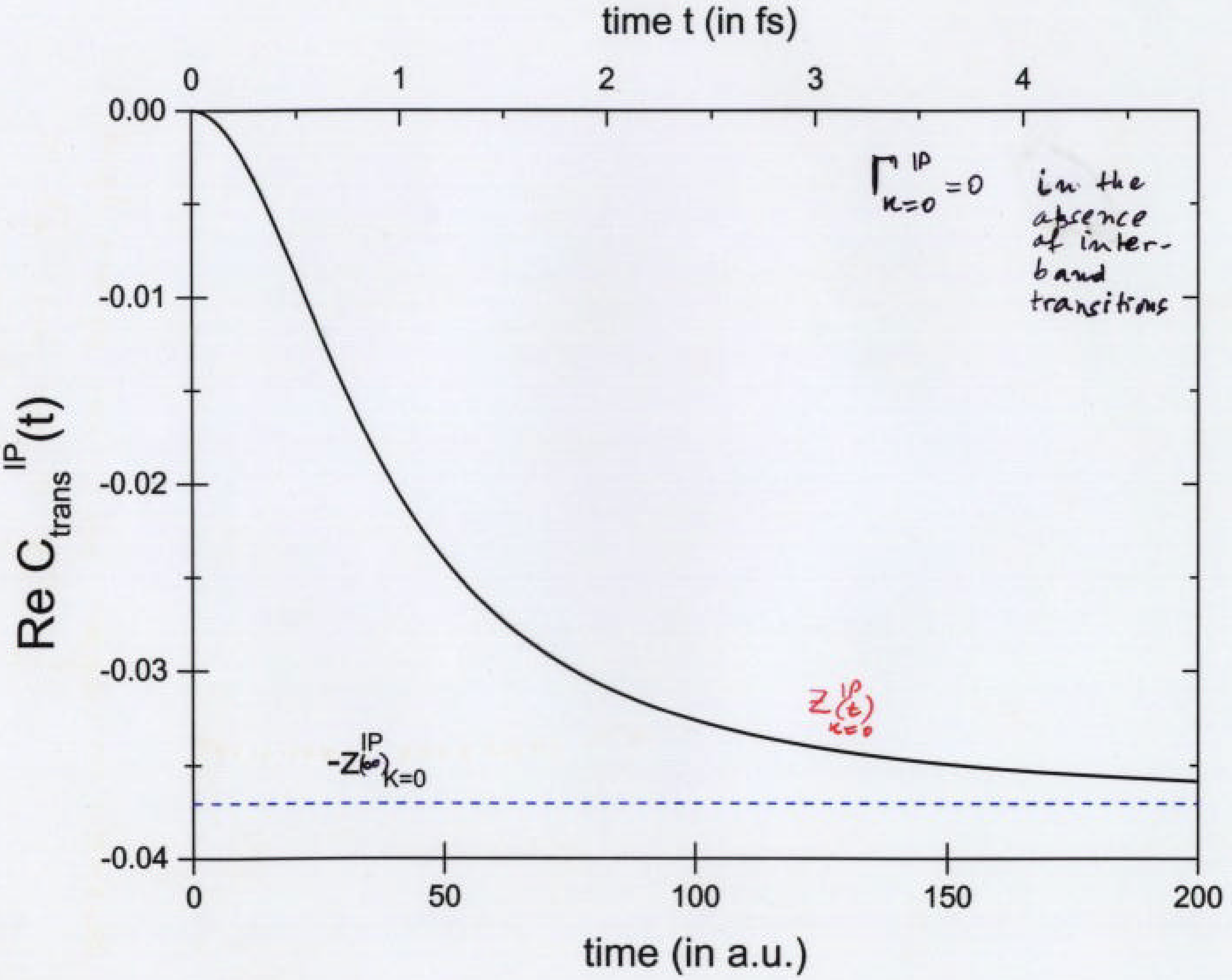
All these quantities additive in the absence of vertex corrections!

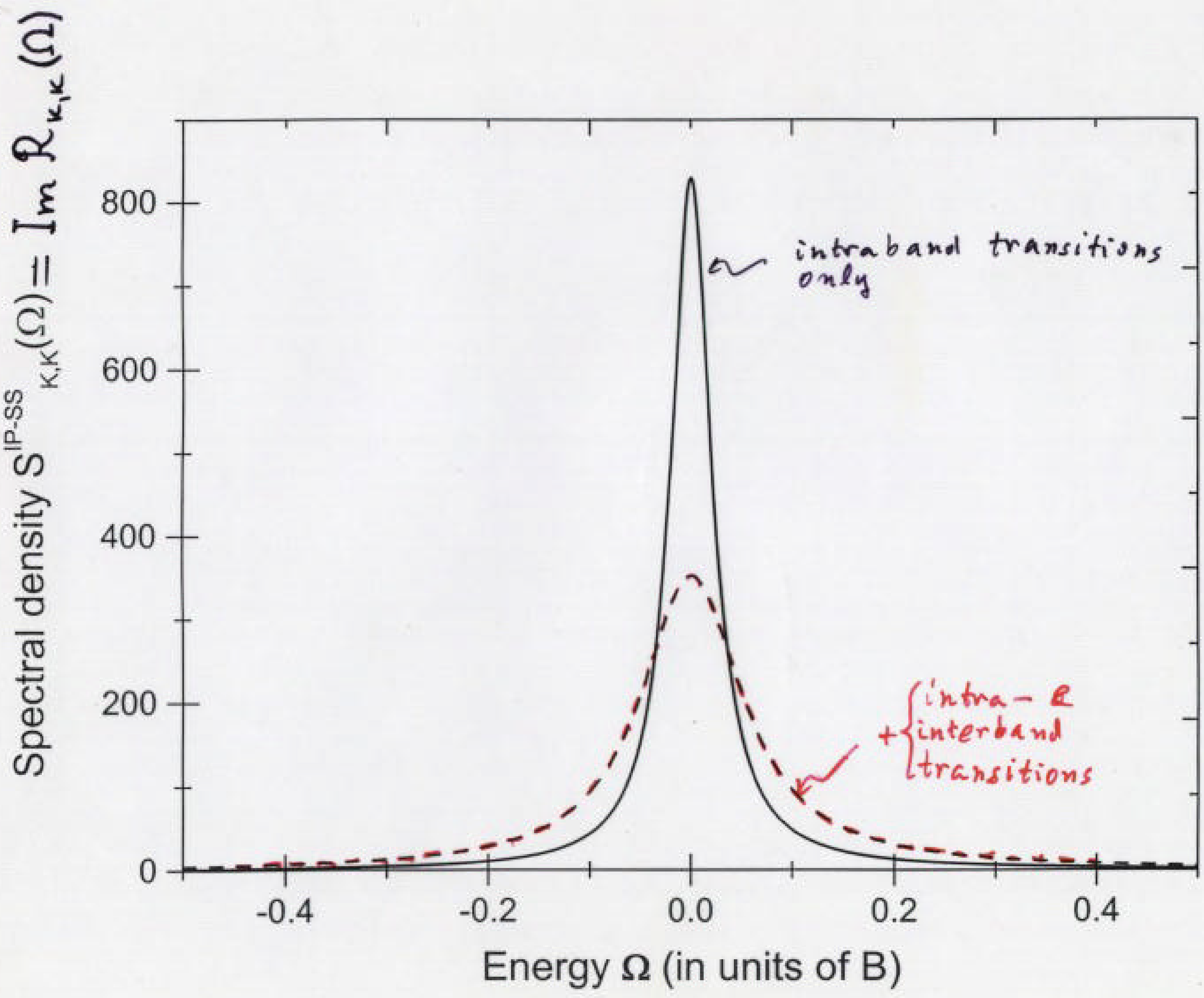
III. APPLICATION TO SS→IP TRANSITIONS IN 2PPE FROM CU(111) SURFACES

Consider optically induced transitions from the bottom of SS-band to the bottom of IP-band, i.e. for the case $\mathbf{K} = \mathbf{0}$:



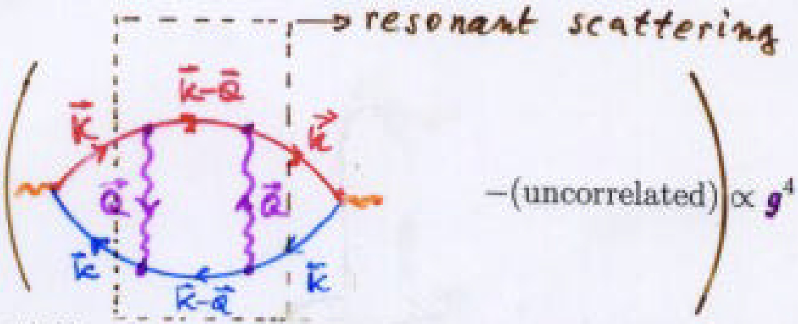

time (in fs)
0
1
2
0.00
-0.01
-0.02
-0.03
Re $C_{trans}^{SS}(t)$
$-\Gamma^{SS}_{K=0}t$
$-Z^{SS}_{K=0}(t)$
$-Z^{SS}_{K=0}(\infty)$
0
20
40
60
80
100
time t (a.u.)


time t (in fs)
0
1
2
3
4
0.00
-0.01
-0.02
-0.03
-0.04
$\mathrm{Re}\ C_{trans}^{IP}(t)$
$\Gamma_{k=0}^{IP} = 0$
in the absence of inter-band transitions
$Z_{k=0}^{IP}(t)$
$-Z_{K=0}^{IP}(\infty)$
0
50
100
150
200
time (in a.u.)


Spectral density $S^{IP\text{-}SS}_{K,K}(\Omega) \equiv \mathrm{Im}\, R_{K,K}(\Omega)$
800
600
400
200
0
-0.4
-0.2
0.0
0.2
0.4
Energy Ω (in units of B)
intraband transitions only
intra- & interband transitions

Entangled decoherence of **IP-SS** electron-hole pairs

Entangled decoherence affecting the lifetime of IP-SS e-h pairs arises in higher order processes of the type:



$$C_4^{ladd} = \left(\qquad -(\text{uncorrelated}) \right) \propto g^4 \qquad (19)$$

Note: $C_2^{SS,IP}$ and C_4^{ladd} embody the same type of interaction matrix elements (i.e. same type of Z-dependence in matrix elements under the $\Sigma_{\mathbf{Q}}$ sign).

⇒ Relevant estimate of the magnitude of C_4^{ladd} is the magnitude of the *first order off-diagonal* vertex correction:

$$\left| \sum_{\mathbf{Q}} \mathcal{R}_1(\mathbf{K}, \mathbf{K}-\mathbf{Q}, t) \Big|_{\mathbf{K}=0} \right|^2 = \left| \qquad \right|^2 \propto g^4 \qquad (20)$$

This correction is controlled by the integral of the type:

spatial vs. temporal cut-off

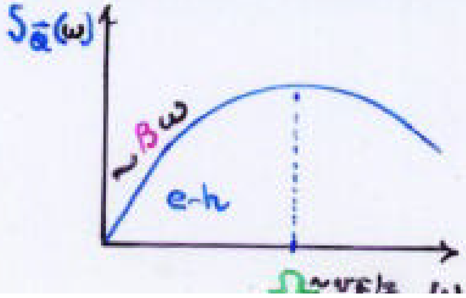
$$2\int_0^\infty dQ \frac{Qe^{-QZ}e^{-i(QZ)^2\frac{t}{\tau}}}{Q^2 + i(\frac{\tau}{t})/Z^2} = 2\int_0^\infty dx \frac{xe^{-x\sqrt{\frac{\tau}{t}}}e^{-ix^2}}{x^2+i}, \qquad (21)$$

where $\tau = 2\mu Z^2/\hbar$ with $\mu = \frac{m_S m_P}{(m_S - m_P)}$ ⇒ IP-SS decoherence sensitive to $(m_P - m_S)$!
This gives:

$$\sum_{\mathbf{Q}} \mathcal{R}_1(\mathbf{K}, \mathbf{K}-\mathbf{Q}, t > \tau) \Big|_{\mathbf{K}=0} \simeq \frac{2\mu e^2 \beta\Omega}{\hbar^2} \times [\mathcal{O}(1)] \sim 1. \quad ! \qquad (22)$$

where $\tau \sim 3$ fs for Cu(111) (same range as in the decay of $z_{\mathbf{K}=0}(t)$!).

Note: In the limit $t > \tau$ the Z-dependence enters the leading term (22) only through the cut-off of the substrate e-h excitation spectrum $\Omega \sim v_F/Z$!



IV. CONCLUSIONS (ANSWERING Q.1 & Q.2)

1. Transient effects due to the sudden (nonadiabatic) switching of the coupling of excited e-h pairs to the substrate response manifest themselves in the time interval

   $$t < \tau_{trans} \sim 3-4 \quad \text{fs.} \tag{18}$$

   !

2. For $t > \tau_{trans}$ the dephasing of a coherent IP-SS e-h pair is dominated by exponential decay characterized by the inverse lifetime:

   $$\Gamma_{\mathbf{K}} = \Gamma_{\mathbf{K}}^{IP} + \Gamma_{\mathbf{K}}^{SS}, \tag{19}$$

   !

   that can be calculated from Fermi's golden rule. This result holds up to $O(g^4)$ at which stage the vertex corrections invalidate the simple additive property (19).

3. High energy *interband* transitions contribute to $\Gamma_{\mathbf{K}}$ but not to $z_{\mathbf{K}}(t)$. !

4. The effects of higher order vertex corrections leading to *resonant IP-SS electron-hole pair scattering* remain to be examined.(entangled de-coherence). !