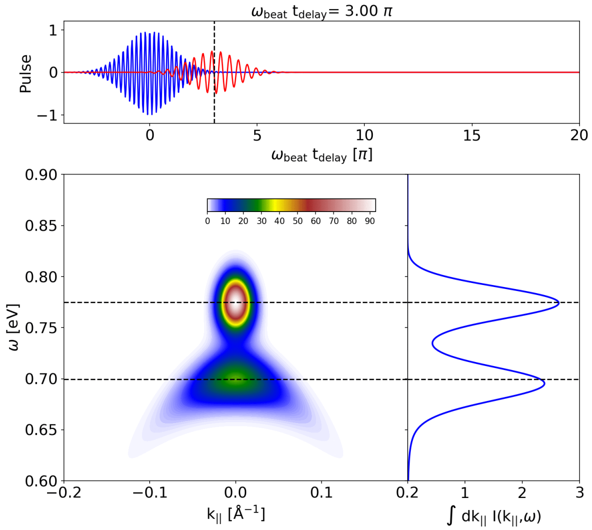
NC STATE

Non-equilibrium spectroscopy of matter: Excitons and correlation functions



<u>Alexander. F. Kemper</u>

North Carolina State University
Department of Physics
https://go.ncsu.edu/kemper-lab

Yale Solid State & Optics Seminar
December 14, 2022

Phys. Rev. B 97, 235310 (2018)
Phys. Rev. B 99, 125303 (2019)
arXiv:2005.08978
J. Elec. Spec. Rel. Phenom. 251, 147104 (2021)

Outline

- Photoemission from excitons and coherences
  - Seeing excitons with time-resolved ARPES
  - Exciton interference
  - Photoemission from coherences inside solids
- Theoretical perspective on non-equilibrium spectroscopy
  - Correlation functions – What do we measure?
  - Non-equilibrium correlation functions – What's different?
  - Non-equilibrium many-body theory
  - Lessons learned

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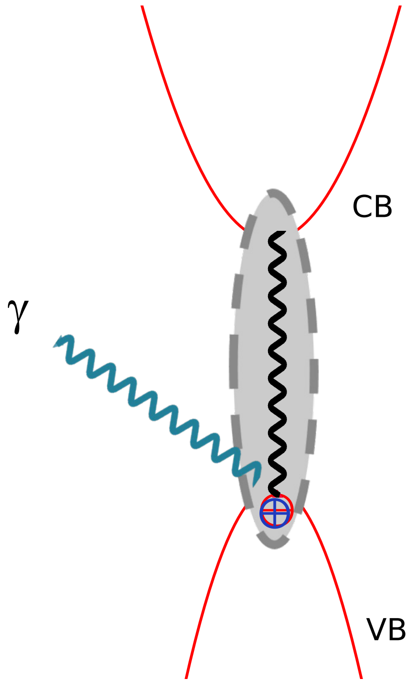
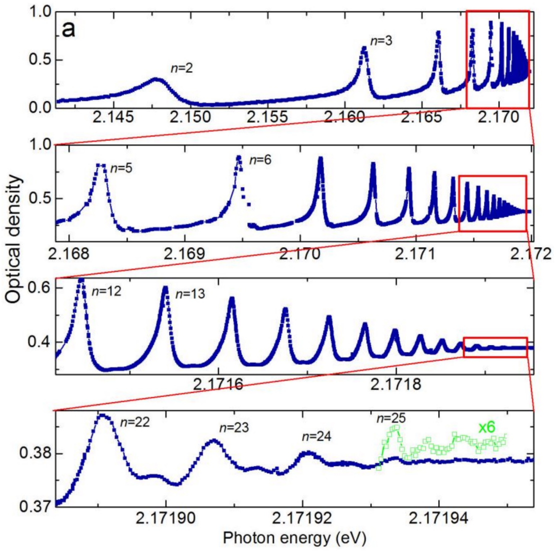
Excitons

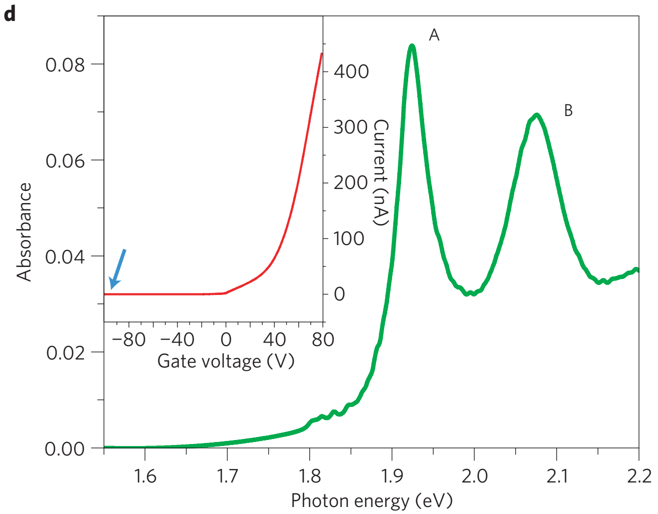


Cu$_2$O



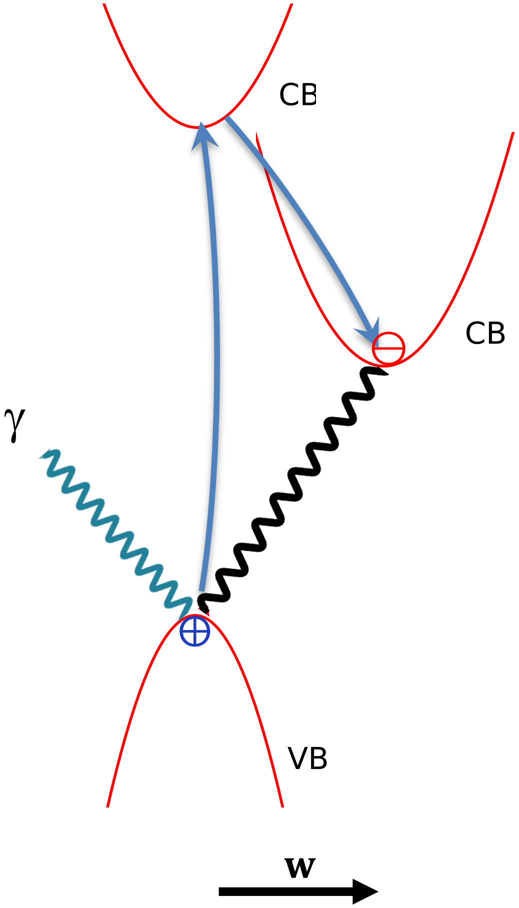
Kazimierczuk, T, et al. *Nature* 514.7522 (2014): 343.

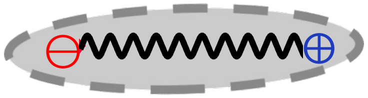
MoS$_2$



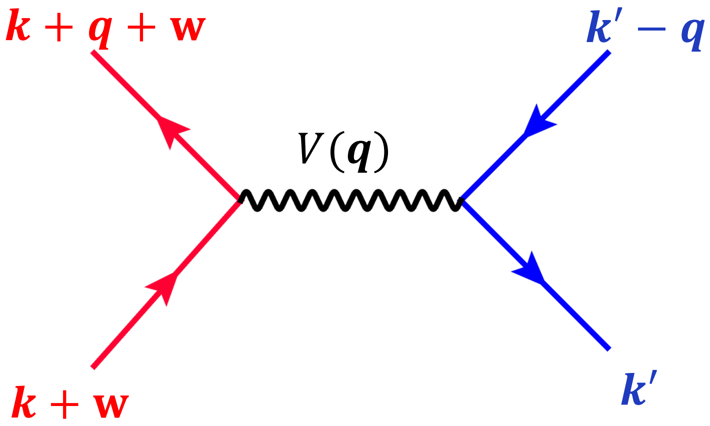
Mak, K. et al. *Nature Materials*, *12*(3), 207-11.

Excitons





Bound electron-hole pair
with binding energy E_λ



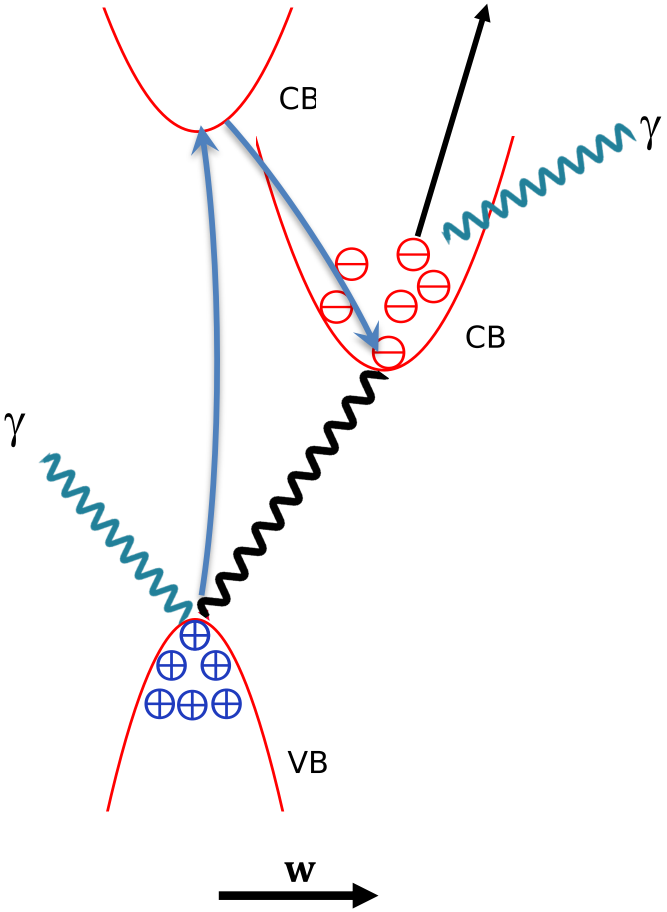
$$\left[\frac{p^2}{2\mu}-E_\lambda\right]\phi_\lambda(\boldsymbol{p},\mathbf{w})=\sum_{\boldsymbol{p}'}V(\boldsymbol{p}-\boldsymbol{p}')\phi_\lambda(\boldsymbol{p}',\mathbf{w})$$

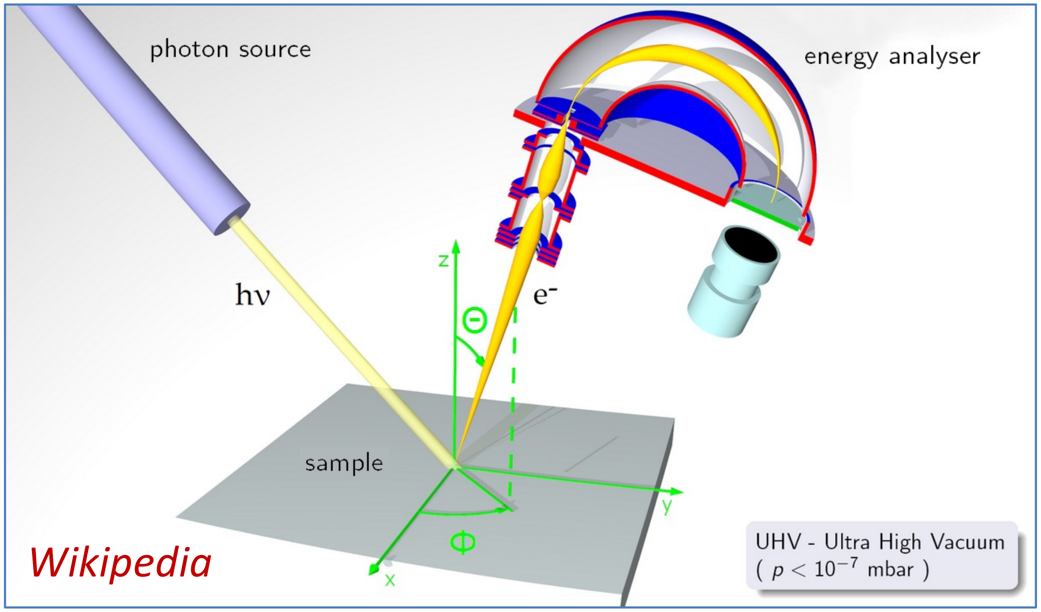
↑

Exciton Wavefunction

Phys. Rev. B 97, 235310 (2018)

Non-equilibrium excitons





Wikipedia

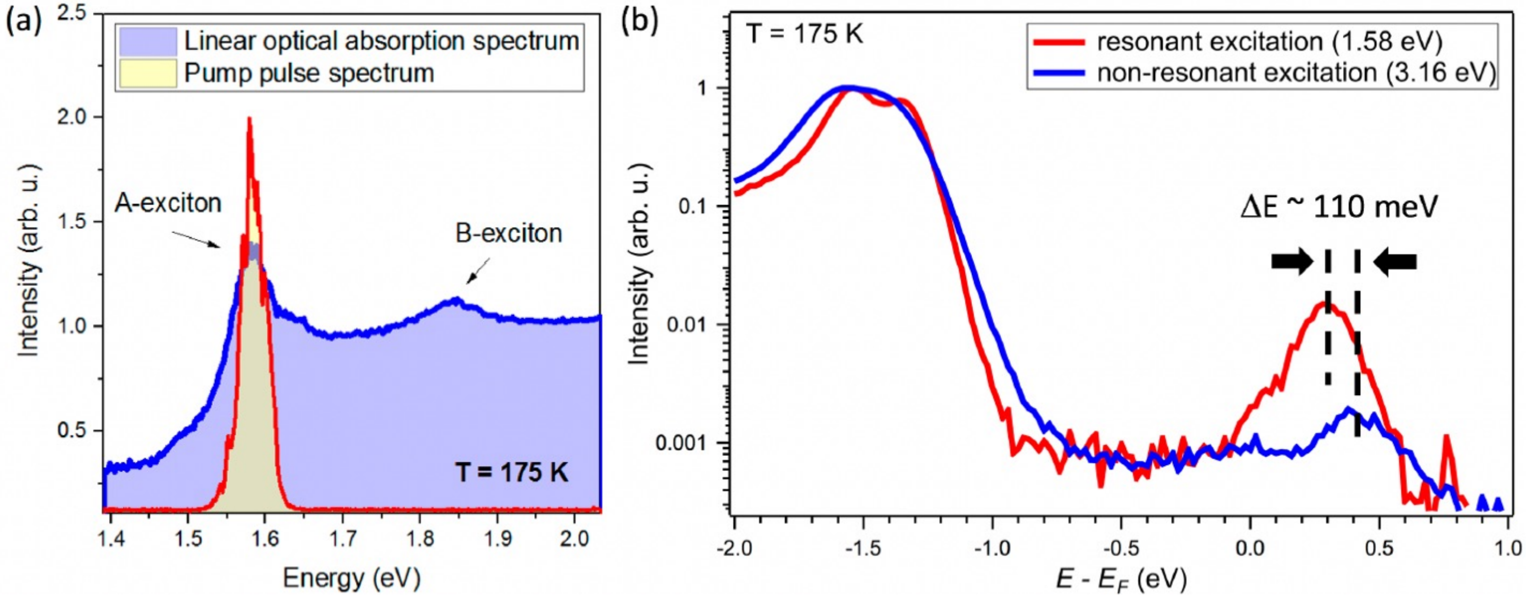
Given a macroscopic occupation of excitons, what should you see in electron spectroscopy?

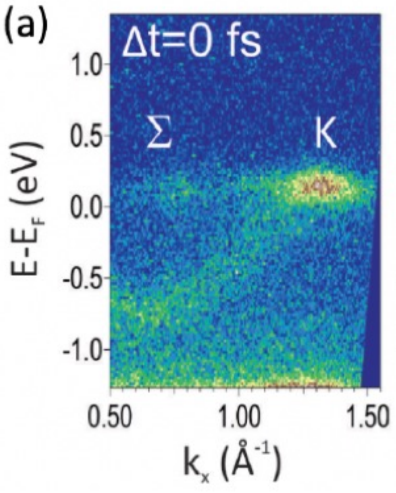
Phys. Rev. B 97, 235310 (2018)

ARPES from Excitons

Bulk $MoSe_2$

Resonant (1.58 eV excitation)
Non-resonant (3.16 eV excitation)





J. Buss et al. CLEO 2017

ARPES from Excitons

Momentum-Resolved Observation of Exciton Formation Dynamics in Monolayer WS_2

Robert Wallauer,* Raul Perea-Causin, Lasse Münster, Sarah Zajusch, Samuel Brem, Jens Güdde, Katsumi Tanimura, Kai-Qiang Lin, Rupert Huber, Ermin Malic,* and Ulrich Höfer

Cite This: *Nano Lett.* 2021, 21, 5867−5873

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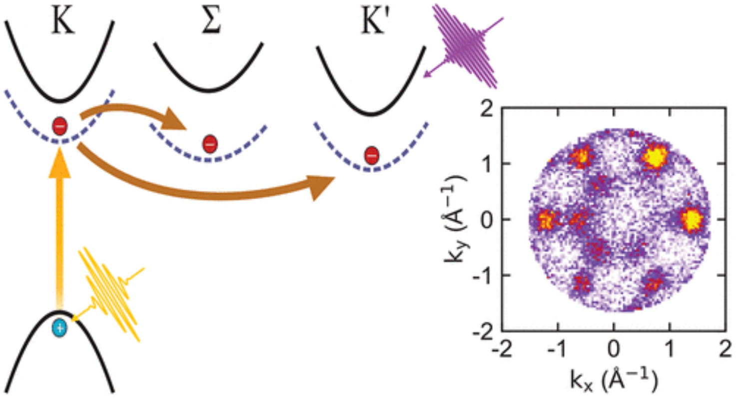
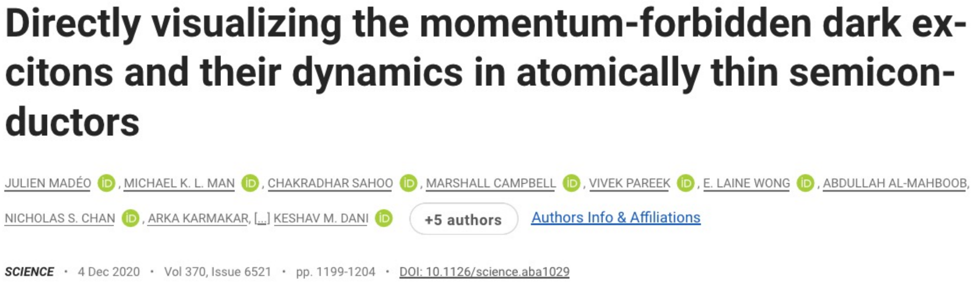
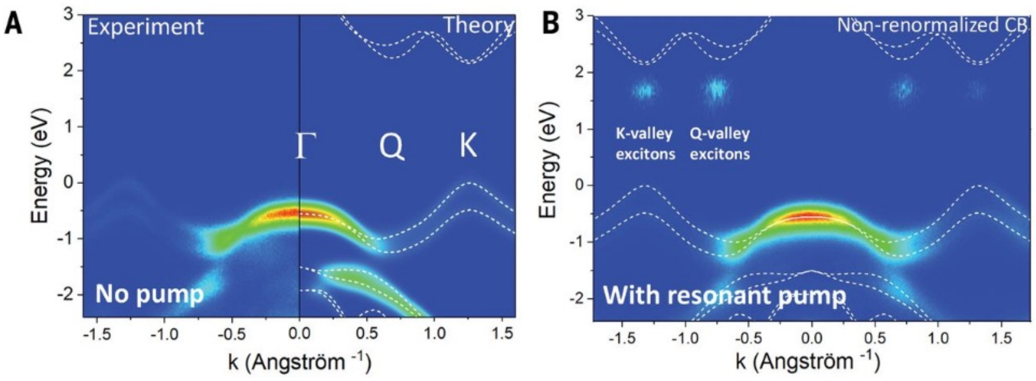




Directly visualizing the momentum-forbidden dark excitons and their dynamics in atomically thin semiconductors

JULIEN MADÉO, MICHAEL K. L. MAN, CHAKRADHAR SAHOO, MARSHALL CAMPBELL, VIVEK PAREEK, E. LAINE WONG, ABDULLAH AL-MAHBOOB, NICHOLAS S. CHAN, ARKA KARMAKAR, [...] KESHAV M. DANI +5 authors Authors Info & Affiliations

SCIENCE • 4 Dec 2020 • Vol 370, Issue 6521 • pp. 1199-1204 • DOI: 10.1126/science.aba1029



ARPES Theory

PHYSICAL REVIEW B **94**, 245303 (2016)

First-principles approach to excitons in time-resolved and angle-resolved photoemission spectra

E. Perfetto,[1,2] D. Sangalli,[2] A. Marini,[2] and G. Stefanucci[1,3]

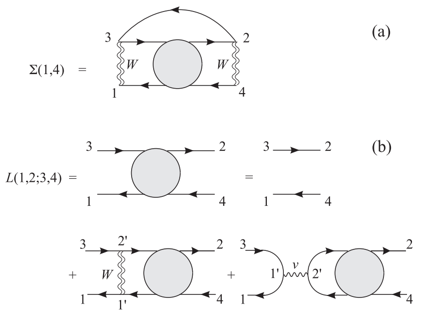


FIG. 2. (a) Diagram for the self-energy. (b) Diagram for L. Wiggly lines denote the bare interaction v and doubly wiggly lines denote the statically screened interaction W.

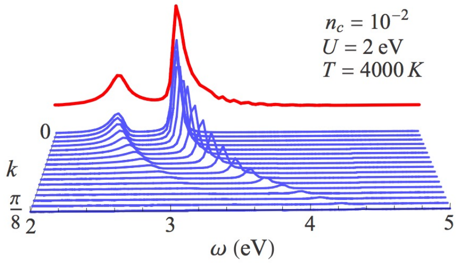
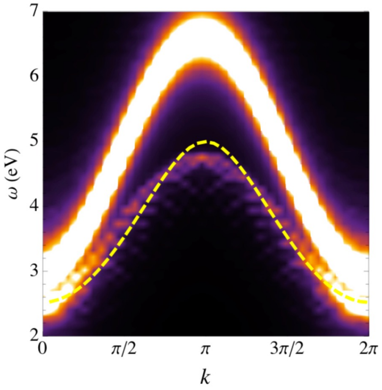


FIG. 7. Lesser Green's function $-iG^{<}_{cc,k}(\omega)$ (in arbitrary units) for different momenta k of the conduction electron. The (red) curve in the background is the integrated quantity $-i\int dkG^{<}_{cc,k}(\omega)$.



Also:

Hiromasa Ohnishi, Norikazu Tomita, and Keiichiro Nasu, *Int. J. Mod. Phys. B* https://doi.org/10.1142/S0217979218500947

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ARPES Theory

Equilibrium $H|\Psi_n\rangle = E_n|\Psi_n\rangle$

Time evolution Operator $U(t,t_0) = T_t \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 H_{pump}(t_1)\right)$

Assume a steady-state distribution of excitons

With Pump + Probe $H \rightarrow H_{pump}(t) + H_{probe}(t)$

Time evolution Operator $\bar{U}(t,t_0) = T_t \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 \left[H_{pump}(t_1) + H_{probe}(t_1)\right]\right)$

Linearize this assuming weak probe

Probability to find photoelectron with momenta $\boldsymbol{k}$ $= \lim_{t\to\infty} \frac{k^2 dk d\Omega_k}{(2\pi)^3} P(t); \quad P(t) = \sum_{n,m} \rho_n |\langle \Psi_m; \boldsymbol{k}|\Psi_n^F(t)\rangle|^2$

Probe photoemits an electron $H_{probe}(t) = s(t)e^{-i\omega_0 t} M_{fc}(\boldsymbol{k},\boldsymbol{k}')f^\dagger(\boldsymbol{k})b(\boldsymbol{k}' - \mathbf{w})$

Free electron CB electron

ARPES Theory

Assuming Gaussian probe pulse with temporal width σ:

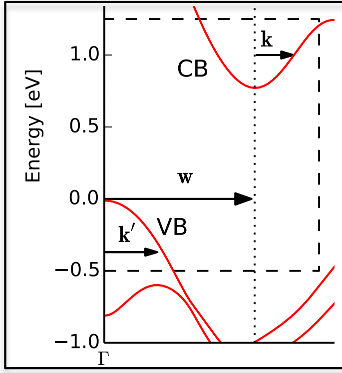
$$P(t_d) \propto |M|^2 \sum_{\lambda,\mathbf{Q}} \rho_{\lambda,\mathbf{Q}} |\phi_\lambda(\mathbf{k}' - \mathbf{w} - \alpha\mathbf{Q})|^2 \times \exp\left(-\sigma^2[-\omega + E_{\lambda,\mathbf{Q}} + \epsilon_{v,\mathbf{k}'-\mathbf{w}-\mathbf{Q}}]^2\right)$$

Exciton Distribution

Exciton Wavefunction

Energy Conservation

Valence band dispersion!



Indirect gap nature shows up through momentum conservation and **w** in the expression

Phys. Rev. B 97, 235310 (2018)

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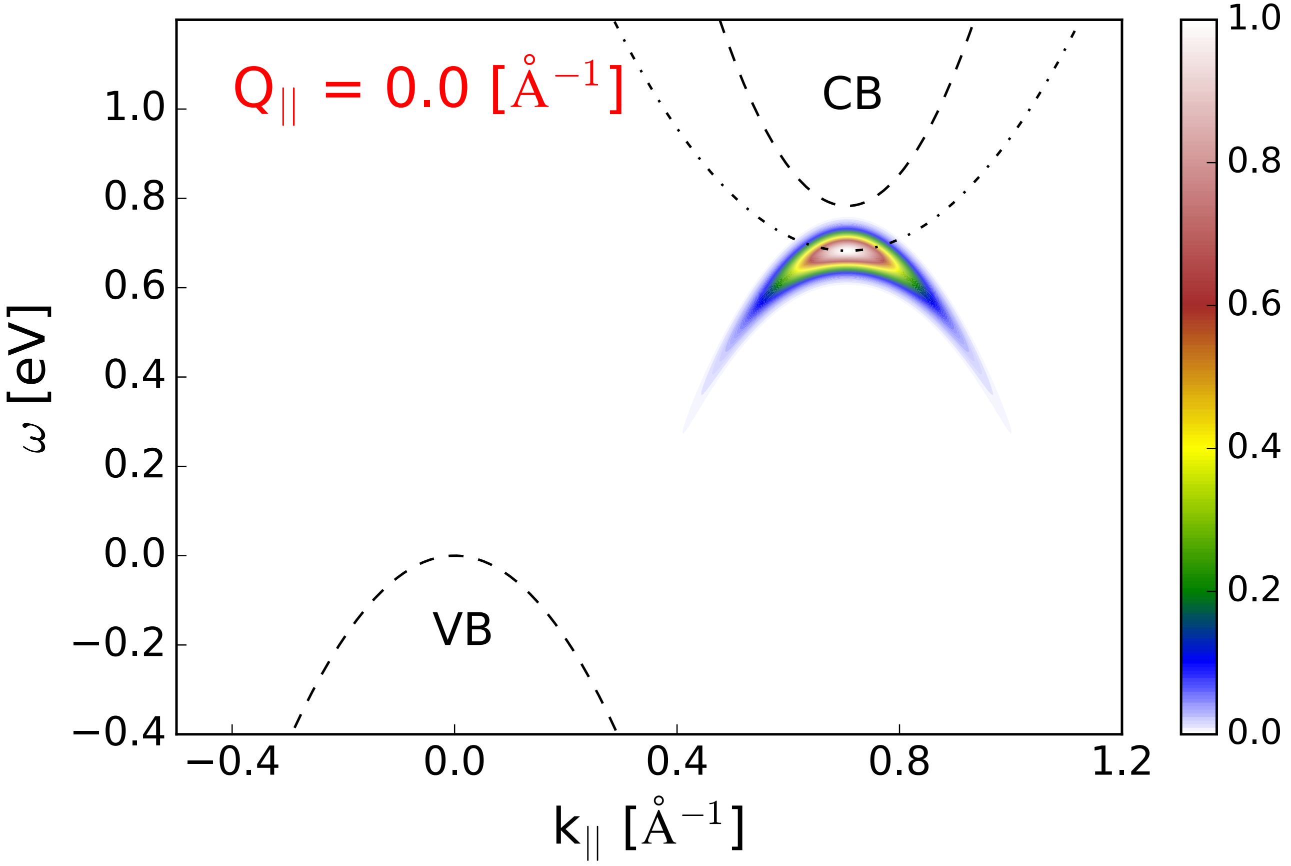
Results: Infinitely Sharp Exciton ρ



With only Q=0 excitons:

ARPES shows

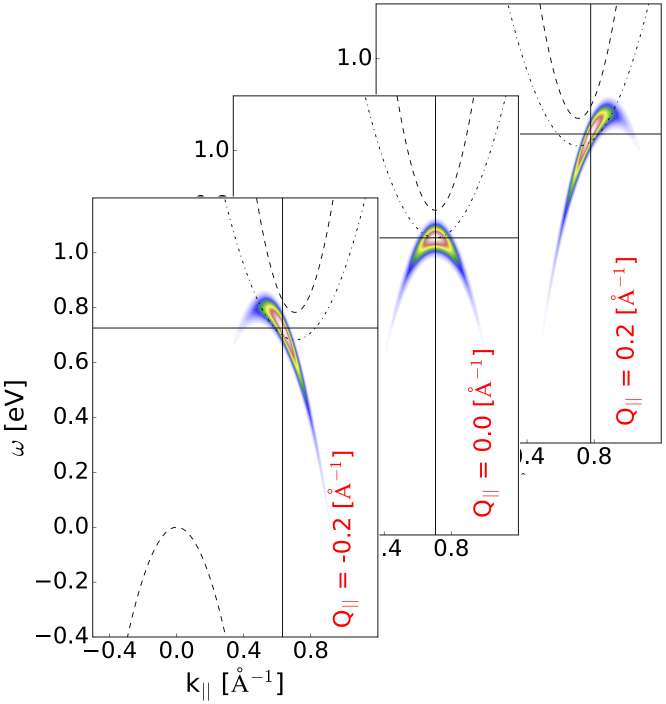
- Replica of the valence band dispersion
- Near conduction band
- Offset by exciton E_b

Phys. Rev. B 97, 235310 (2018)

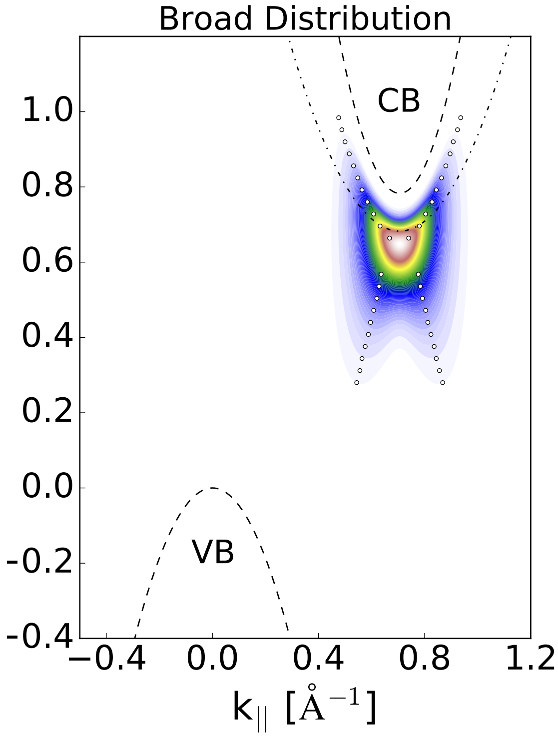
Results

$$P(t_d) \propto |M|^2 \sum_{\lambda,\mathbf{Q}} \rho_{\lambda,\mathbf{Q}} |\phi_\lambda(\mathbf{k}' - \mathbf{w} - \alpha\mathbf{Q})|^2 \times \exp\left(-\sigma^2[-\omega + E_{\lambda,\mathbf{Q}} + \epsilon_{v,\mathbf{k}'-\mathbf{w}-\mathbf{Q}}]^2\right)$$

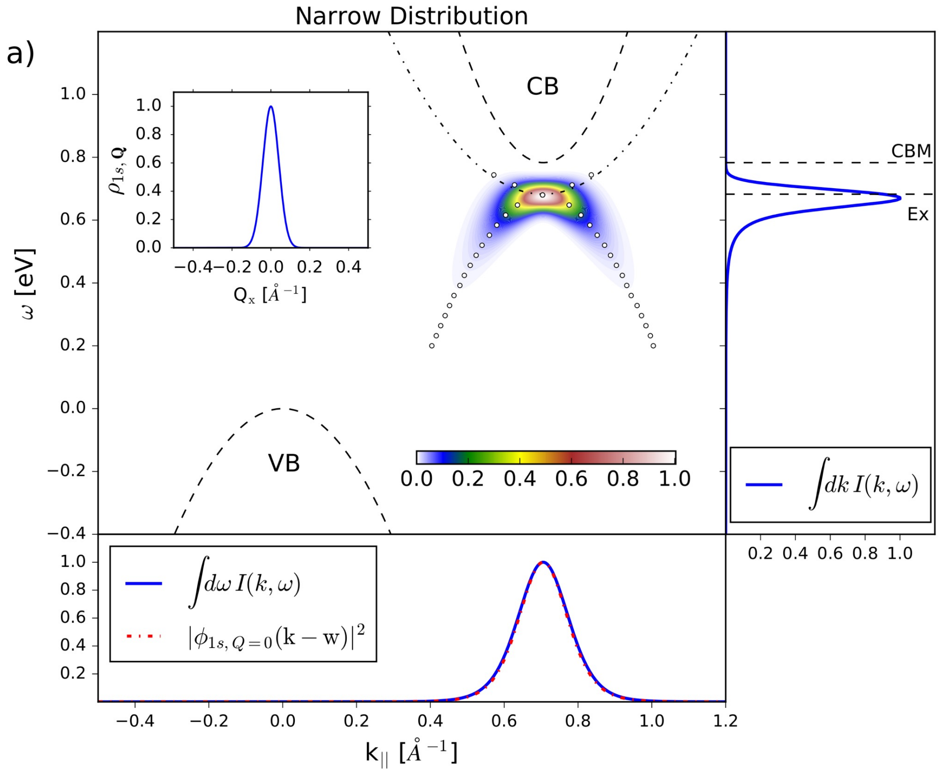
↑ Exciton Distribution



Boltzmann Weighted →


Broad Distribution

Phys. Rev. B 97, 235310 (2018)



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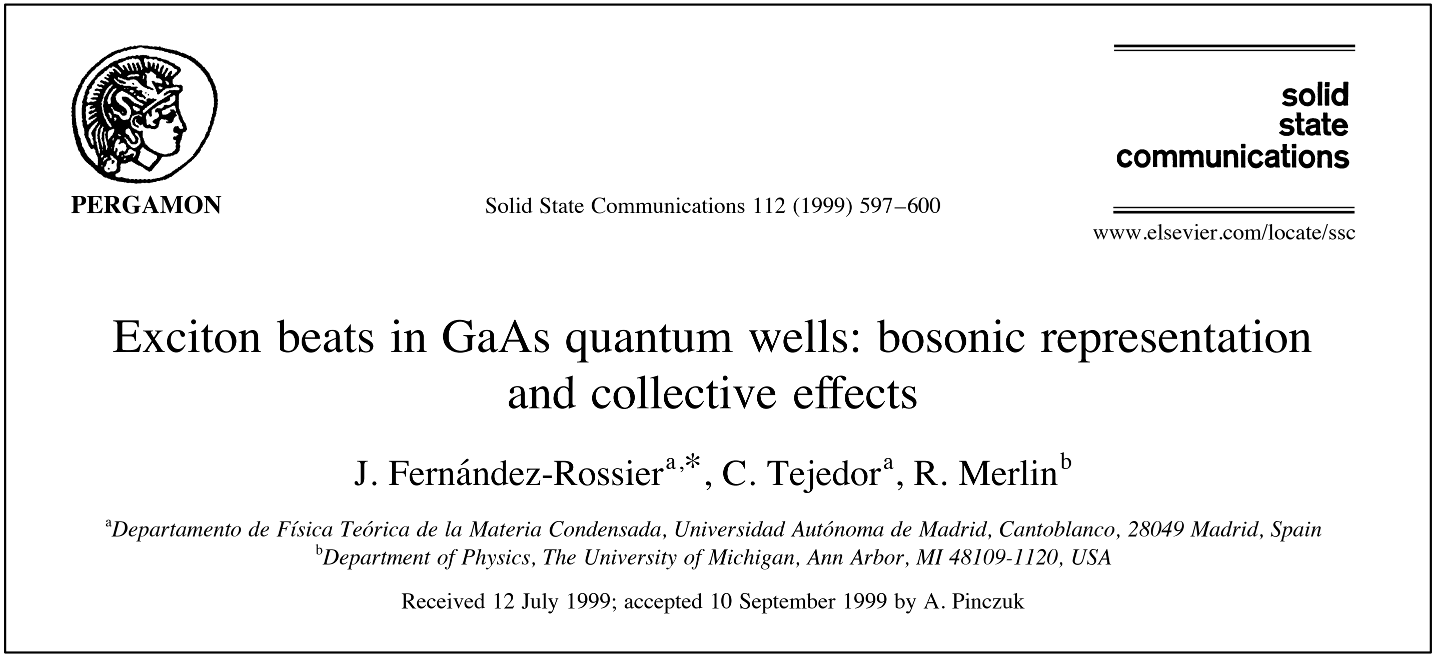
Exciton coherences



PERGAMON

Solid State Communications 112 (1999) 597–600

solid
state
communications

www.elsevier.com/locate/ssc

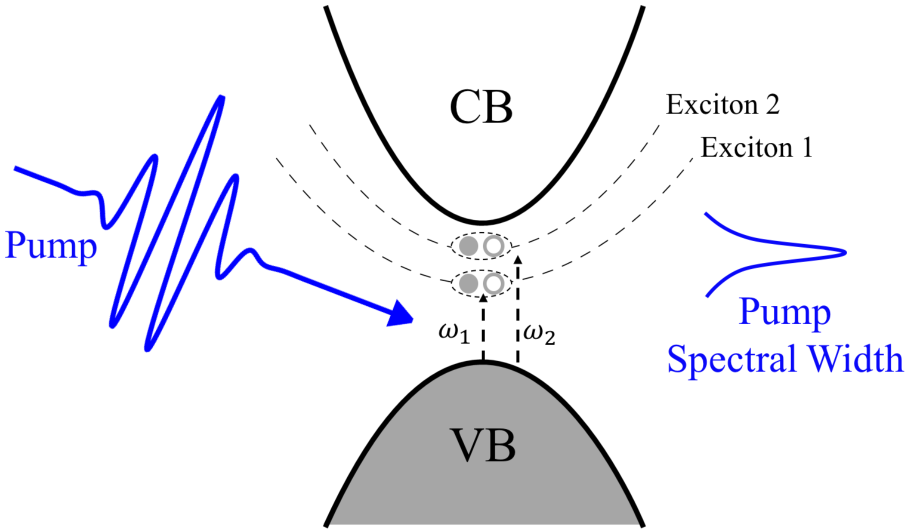
Exciton beats in GaAs quantum wells: bosonic representation and collective effects

J. Fernández-Rossier[a,*], C. Tejedor[a], R. Merlin[b]

[a]*Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain*
[b]*Department of Physics, The University of Michigan, Ann Arbor, MI 48109-1120, USA*

Received 12 July 1999; accepted 10 September 1999 by A. Pinczuk

Exciton coherences

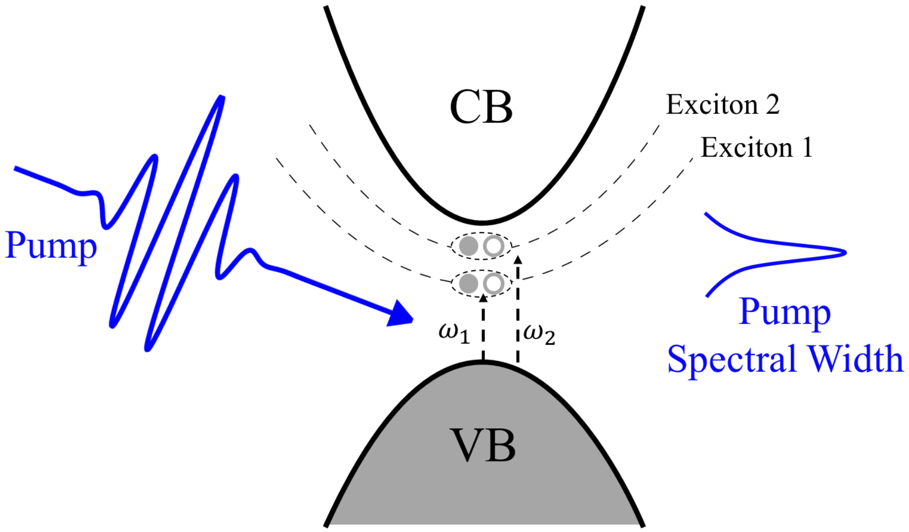


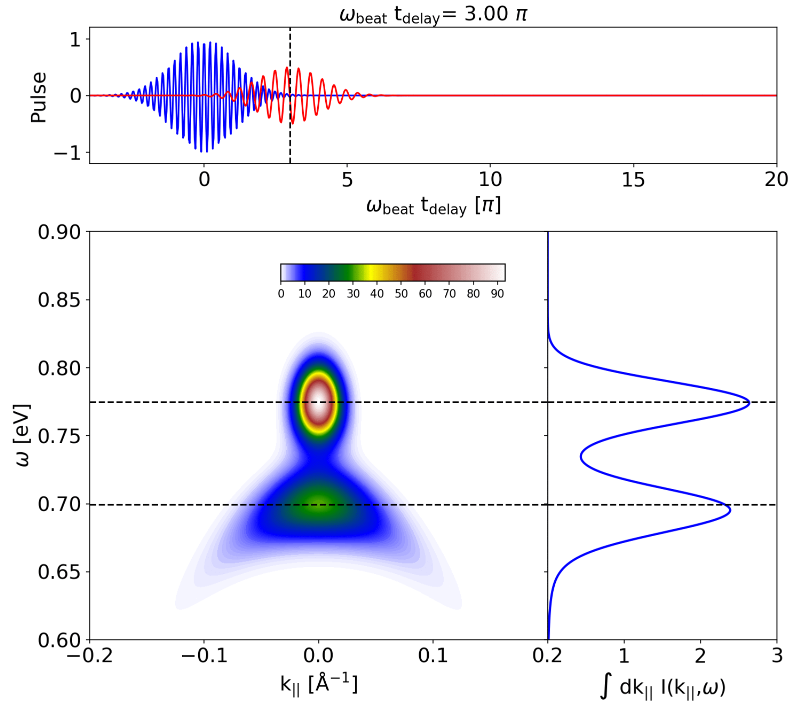
Coherent state formalism

$$\begin{aligned}|\Psi(t)\rangle &= Ne^{-iH_0 t}e^{iK_1 A_1^\dagger}e^{iK_2 A_2^\dagger}|0\rangle \\ &= N\sum_{n_1,n_2}\frac{(i\bar{K}_1(t))^{n_1}}{\sqrt{n_1!}}\frac{(i\bar{K}_2(t))^{n_2}}{\sqrt{n_2!}}|n_1;n_2\rangle \\ &= Ne^{i\bar{K}_1(t)A_1^\dagger}e^{i\bar{K}_2(t)A_2^\dagger}|0\rangle\end{aligned}$$

Phys. Rev. B 99, 125303 (2019)

Exciton coherences





Coherent state formalism

$$
\begin{aligned}
|\Psi(t)\rangle &= N e^{-iH_0 t} e^{iK_1 A_1^\dagger} e^{iK_2 A_2^\dagger} |0\rangle \\
&= N \sum_{n_1, n_2} \frac{(i\bar{K}_1(t))^{n_1}}{\sqrt{n_1!}} \frac{(i\bar{K}_2(t))^{n_2}}{\sqrt{n_2!}} |n_1; n_2\rangle \\
&= N e^{i\bar{K}_1(t) A_1^\dagger} e^{i\bar{K}_2(t) A_2^\dagger} |0\rangle
\end{aligned}
$$

Phys. Rev. B 99, 125303 (2019)

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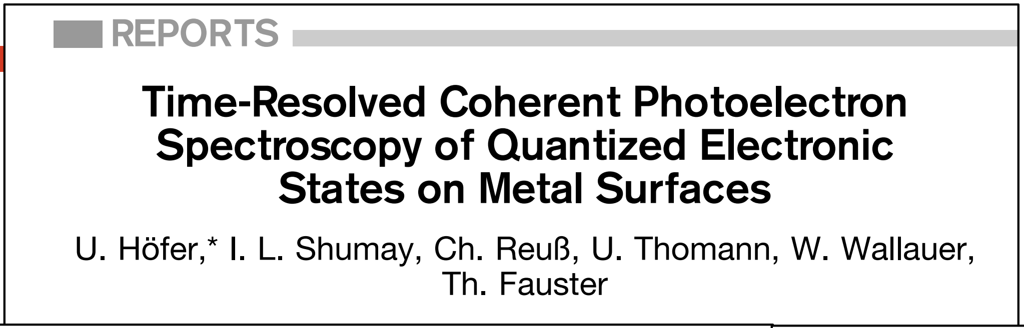


REPORTS

Time-Resolved Coherent Photoelectron Spectroscopy of Quantized Electronic States on Metal Surfaces

U. Höfer,* I. L. Shumay, Ch. Reuß, U. Thomann, W. Wallauer,
Th. Fauster

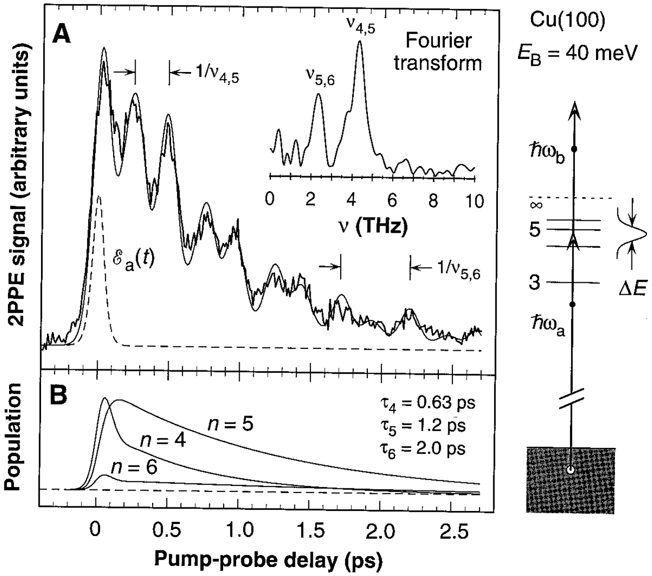
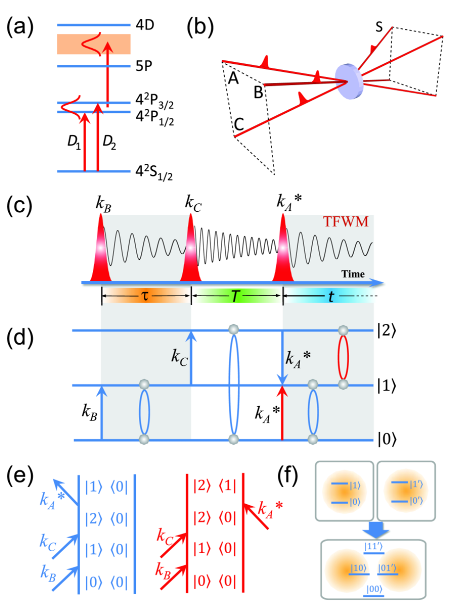


Fig. 3. Quantum beats observed after the coherent excitation of image-potential states with quantum numbers $n = 4$, 5, and 6 ($E_B \simeq 40$ meV). (**A**) The thick curve corresponds to the measured 2PPE signal as function of pump-probe delay. The thin line is the result of the density matrix calculation for the two-photon excitation depicted schematically on the right side of the figure. The dashed line shows the envelope $\mathscr{E}_a(t)$ of the exciting UV pulse. The Fourier transform was obtained after subtraction of a smooth exponential decay from the measured data and directly gives the beating frequencies $\nu_{4,5} = (E_5 - E_4)/h$ and $\nu_{5,6} = (E_6 - E_5)/h$ between the excited states. (**B**) Relative population of the individual levels resulting from the calculation and corresponding decay times τ_n. The coherent peaks visible for $n = 4$ and $n = 6$ are caused by off-resonant excitation of these levels from the continuum of initial states in the metal.

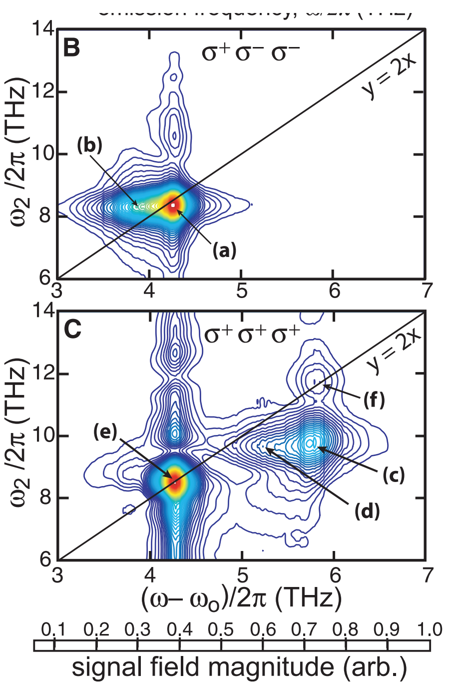
Solids (Image Potential States):
Petek, Weinelt

Atoms, Molecules & Quantum Wells:
Long storied history of coherence-related studies with both optics & photoemission

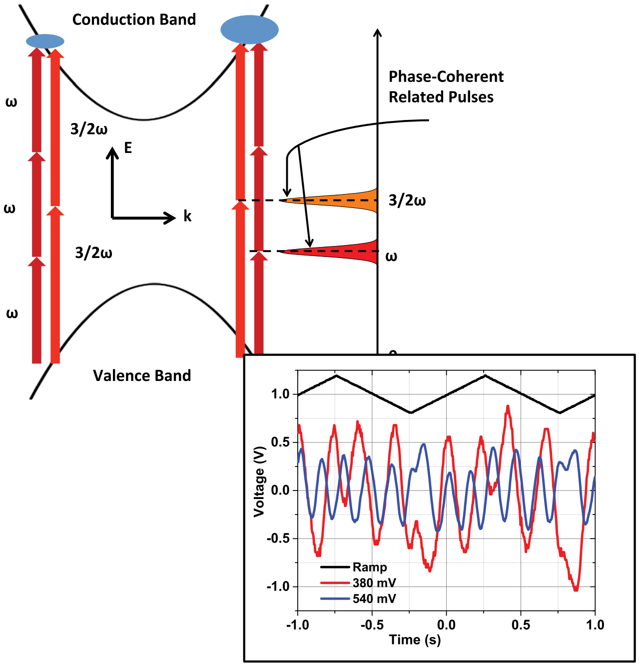
Q: Can we observe coherences inside the material?



Dai, *PRL* 2012 – Na vapor



Stone, *Science* 2009 – GaAs QW



Wang, *PRL* 2019 – AlGaAs

Theoretical approaches to time-resolved ARPES

Wavefunctions (Höfer)

$$I(t) \propto |a_n(t)\Psi_n(t) + a_{n+1}(t)\Psi_{n+1}(t)|^2 \quad (2a)$$

$$\propto a_n^2 + a_{n+1}^2 + 2a_n a_{n+1}\cos(\omega_{n,n+1}t) \quad (2b)$$

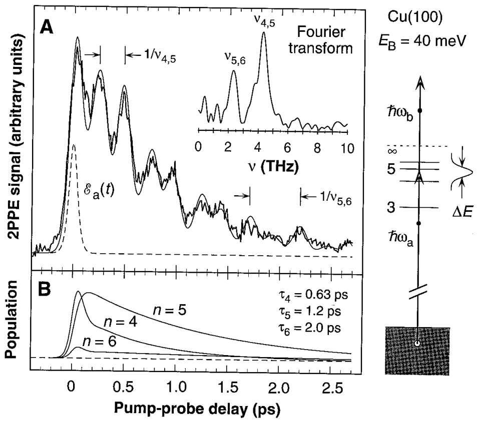


Fig. 3. Quantum beats observed after the coherent excitation of image-potential states with quantum numbers $n = 4$, 5, and 6 ($E_B \simeq 40$ meV). (**A**) The thick curve corresponds to the measured 2PPE signal as function of pump-probe delay. The thin line is the result of the density matrix calculation for the two-photon excitation depicted schematically on the right side of the figure. The dashed line shows the envelope $\mathcal{E}_a(t)$ of the exciting UV pulse. The Fourier transform was obtained after subtraction of a smooth exponential decay from the measured data and directly gives the beating frequencies $\nu_{4,5} = (E_5 - E_4)/h$ and $\nu_{5,6} = (E_6 - E_5)/h$ between the excited states. (**B**) Relative population of the individual levels resulting from the calculation and corresponding decay times τ_n. The coherent peaks visible for $n = 4$ and $n = 6$ are caused by off-resonant excitation of these levels from the continuum of initial states in the metal.

Theoretical approaches to time-resolved ARPES of coherences

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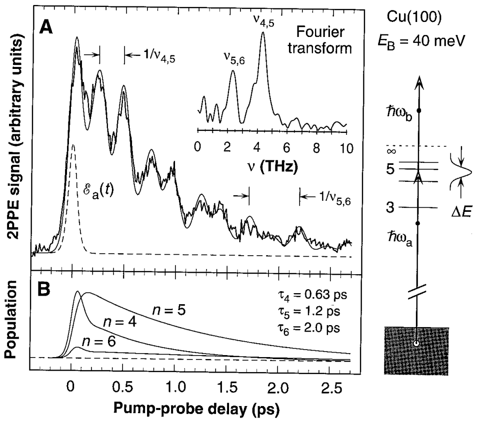

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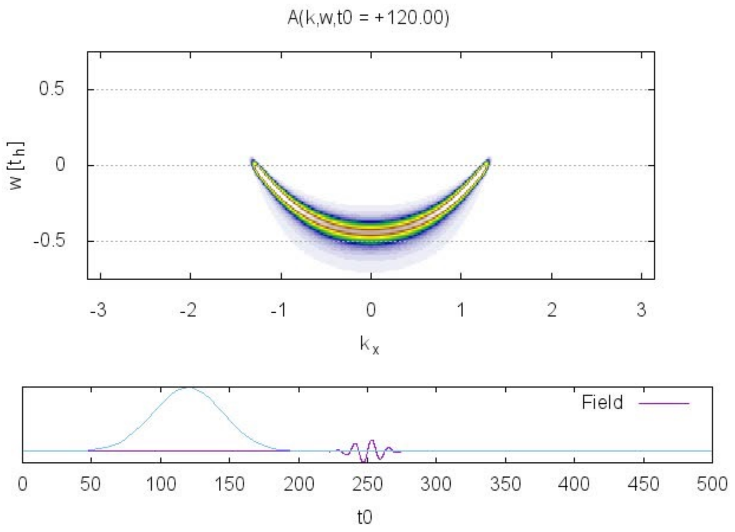
Green's functions (Freericks PRL 2009)

$$G^<_{\mathbf{k}}(t,t') = i\langle \hat{c}^\dagger_{\mathbf{k}}(t')\hat{c}_{\mathbf{k}}(t)\rangle.$$

$$\mathcal{I}(\mathbf{k},\omega,t_0) = -i\iint dt\,dt'\,s(t)s(t')e^{i\omega(t-t')}G^<_{\mathbf{k}}(t,t').$$



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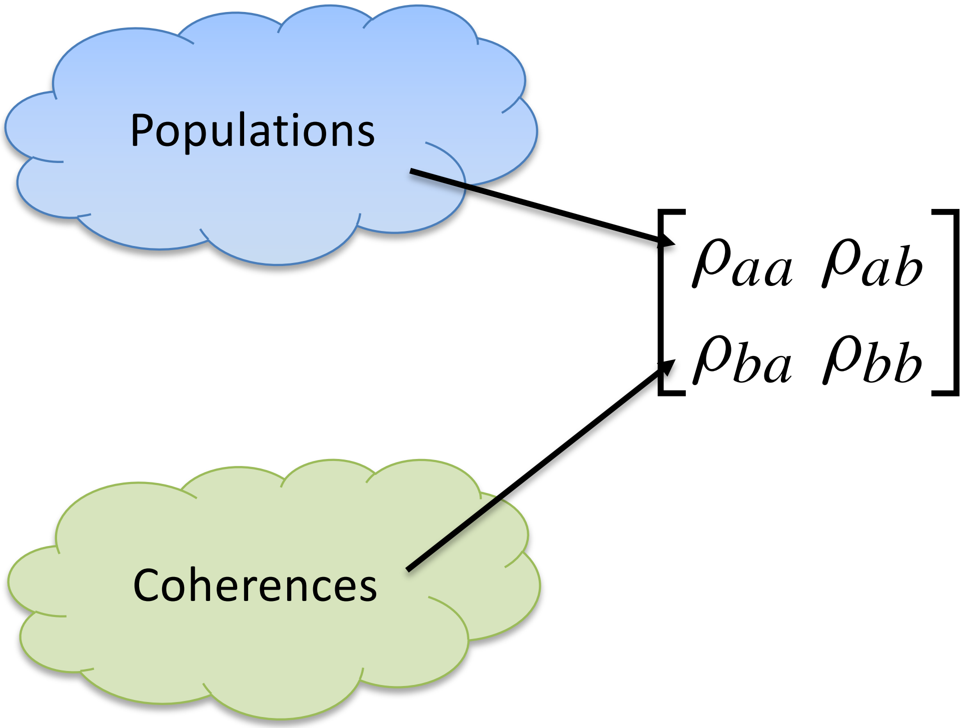
Theoretical approaches to time-resolved ARPES of coherences

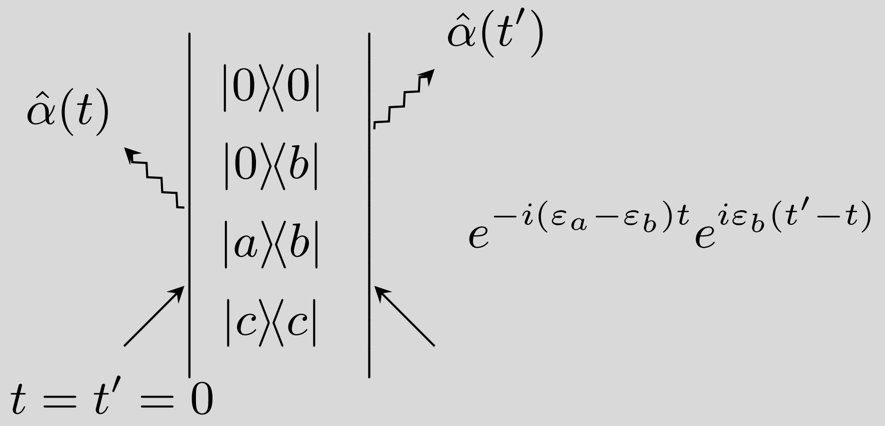
Density Matrix (Mukamel,Tokmakoff)

$$G^{<}_{\mathbf{k}}(t,t') = i\langle \hat{c}^{\dagger}_{\mathbf{k}}(t')\hat{c}_{\mathbf{k}}(t)\rangle. \longrightarrow G^{<}_{\mathbf{k}}(t,t') = i\,\mathrm{Tr}\{\hat{c}^{\dagger}_{\mathbf{k}}(t')\hat{c}_{\mathbf{k}}(t)\rho\},$$



$$\begin{bmatrix} \rho_{aa} & \rho_{ab} \\ \rho_{ba} & \rho_{bb} \end{bmatrix}$$

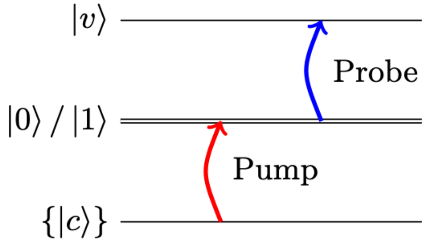
Two-sided Feynman pathway diagrams for photoemission & ARPES



$$e^{-i(\varepsilon_a-\varepsilon_b)t}e^{i\varepsilon_b(t'-t)}$$

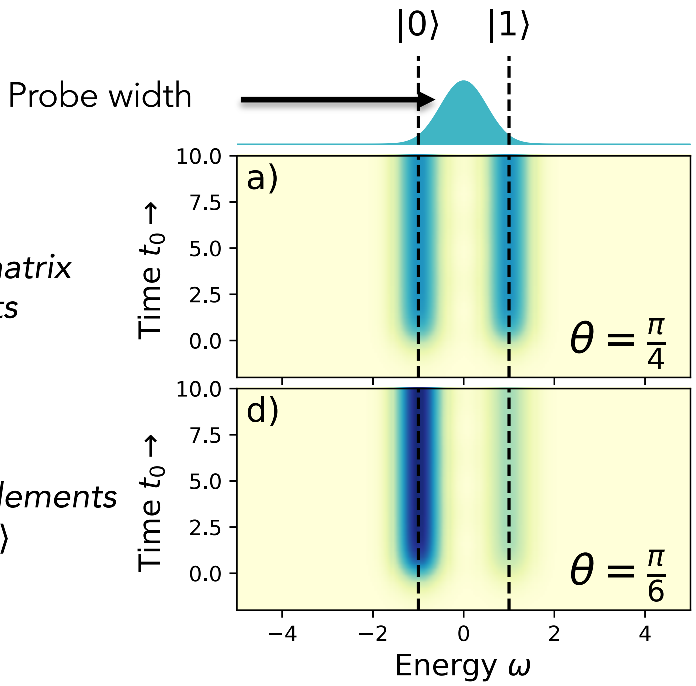
arXiv:2005.08978

Photoemission from coherences inside solids



$$\varepsilon_{\text{coherence}} = \frac{1}{2}\left(\varepsilon_0 + \varepsilon_1\right)$$

$$\mathcal{I}_{\text{coherence}}(t) \sim \cos\left(\left(\varepsilon_0 - \varepsilon_1\right) t\right)$$

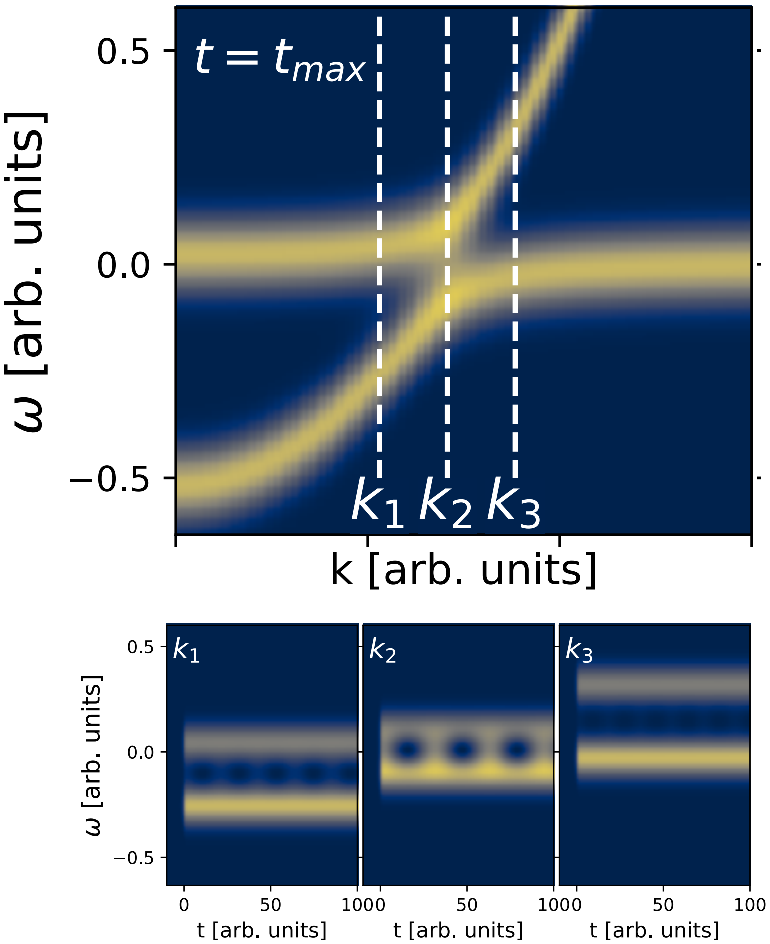


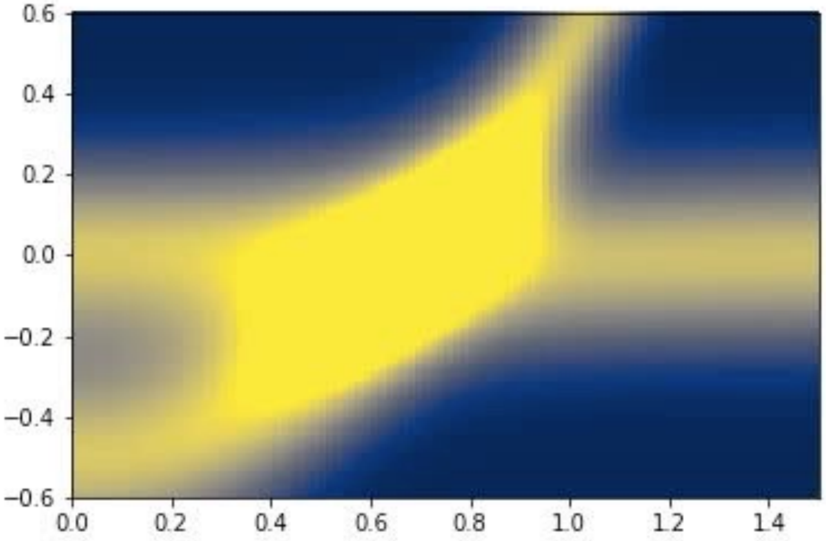
Equal matrix elements

Matrix elements favor |0⟩

arXiv:2005.08978

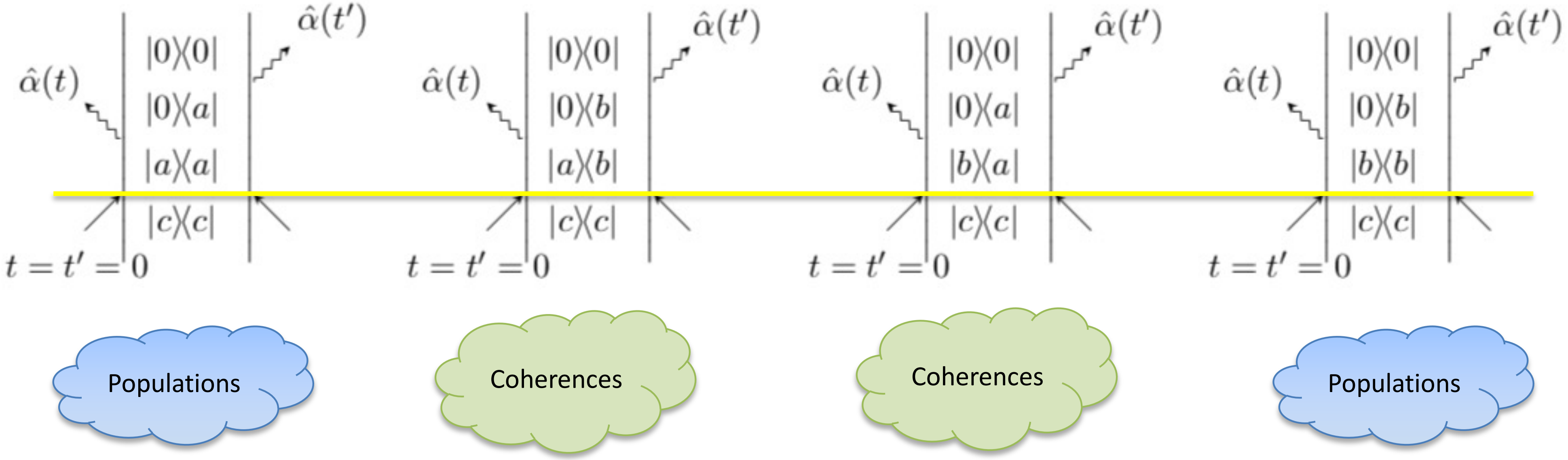
Photoemission from coherences inside solids





arXiv:2005.08978

Theoretical approaches to time-resolved ARPES of coherences



Populations

Coherences

Coherences

Populations

arXiv:2005.08978

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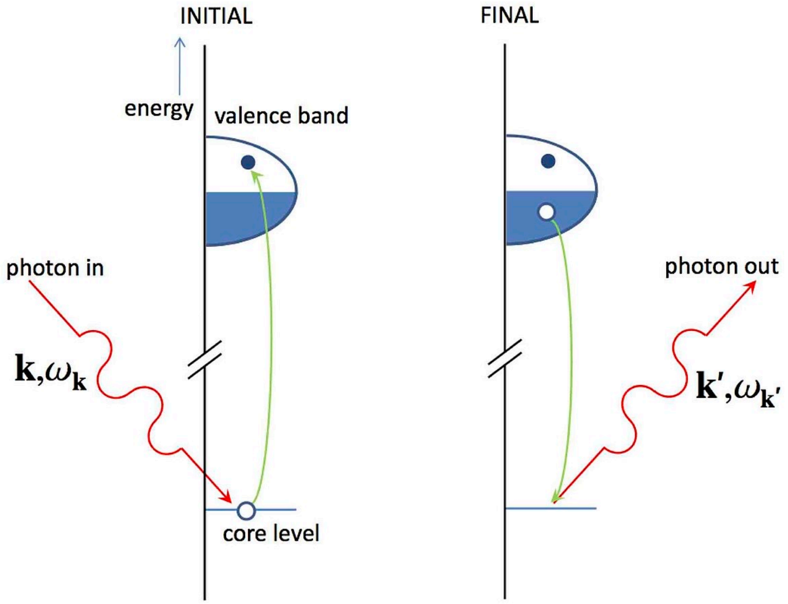
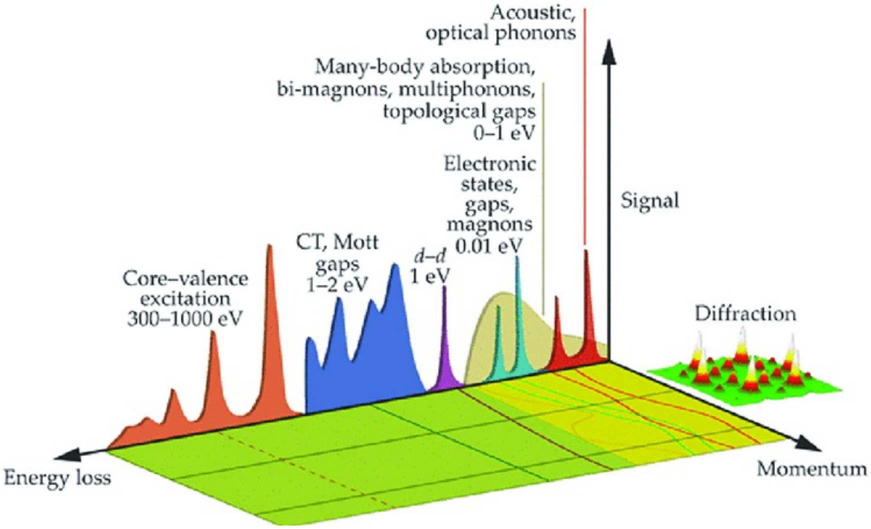
Theoretical approaches to time-resolved ARPES of coherences





$$
\begin{aligned}
J^{(2)\mathrm{RIXS}}_{\boldsymbol{q}_\mathrm{f}\boldsymbol{e}_\mathrm{f}} &= \sum_{m,n}\int_{-\infty}^{\infty}dt_2\int_{-\infty}^{t_2}dt_1\int_{-\infty}^{\infty}dt'_2\int_{-\infty}^{t'_2}dt'_1 s(t'_1)s(t'_2)s(t_2)s(t_1)\\
&\times\langle\mathcal{U}(-\infty,t'_1)\mathcal{D}^\dagger_{n\boldsymbol{\varepsilon}'}(t'_1)\mathcal{U}(t'_1,t'_2)\mathcal{D}_{n\boldsymbol{\varepsilon}}(t'_2)\mathcal{U}(t'_2,t_2)\mathcal{D}^\dagger_{m\boldsymbol{e}'}(t_2)\mathcal{U}(t_2,t_1)\mathcal{D}_{m\boldsymbol{e}}(t_1)\mathcal{U}(t_1,-\infty)\rangle\\
&\times\sum_{\substack{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}'_2,\boldsymbol{k}'_1\\ \boldsymbol{e},\boldsymbol{e}',\boldsymbol{\varepsilon},\boldsymbol{\varepsilon}'}} e^{i(\boldsymbol{k}_1-\boldsymbol{k}_2)\cdot\boldsymbol{r}_m+i(\boldsymbol{k}'_2-\boldsymbol{k}'_1)\cdot\boldsymbol{r}_n}\langle a^\dagger_{\boldsymbol{k}'_1\boldsymbol{\varepsilon}'}(t'_1)a_{\boldsymbol{k}'_2\boldsymbol{\varepsilon}}(t'_2)a^\dagger_{\boldsymbol{q}_\mathrm{f}\boldsymbol{e}_\mathrm{f}}a_{\boldsymbol{q}_\mathrm{f}\boldsymbol{e}_\mathrm{f}}a^\dagger_{\boldsymbol{k}_2\boldsymbol{e}'}(t_2)a_{\boldsymbol{k}_1\boldsymbol{e}}(t_1)\rangle_\mathrm{ph},
\end{aligned}
$$

10.1103/RevModPhys.83.705

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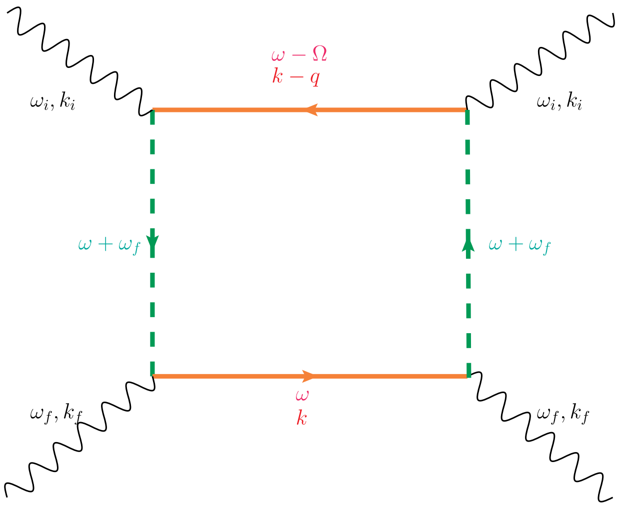
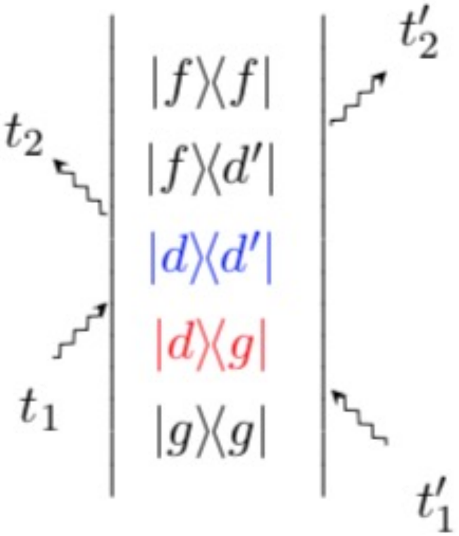
Theoretical approaches to time-resolved ARPES of coherences





$$J^{(2)\mathrm{RIXS}}_{\boldsymbol{q}_\mathrm{f}\boldsymbol{e}_\mathrm{f}} = \sum_{m,n} \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{t_2} dt_1 \int_{-\infty}^{\infty} dt_2' \int_{-\infty}^{t_2'} dt_1' s(t_1') s(t_2') s(t_2) s(t_1)$$
$$\times \langle \mathcal{U}(-\infty, t_1') \mathcal{D}^\dagger_{n\boldsymbol{\varepsilon}'}(t_1') \mathcal{U}(t_1', t_2') \mathcal{D}_{n\boldsymbol{\varepsilon}}(t_2') \mathcal{U}(t_2', t_2) \mathcal{D}^\dagger_{m\boldsymbol{e}'}(t_2) \mathcal{U}(t_2, t_1) \mathcal{D}_{m\boldsymbol{e}}(t_1) \mathcal{U}(t_1, -\infty) \rangle$$
$$\times \sum_{\substack{\boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_2', \boldsymbol{k}_1' \\ \boldsymbol{e}, \boldsymbol{e}', \boldsymbol{\varepsilon}, \boldsymbol{\varepsilon}'}} e^{i(\boldsymbol{k}_1 - \boldsymbol{k}_2)\cdot \boldsymbol{r}_m + i(\boldsymbol{k}_2' - \boldsymbol{k}_1')\cdot \boldsymbol{r}_n} \langle a^\dagger_{\boldsymbol{k}_1' \boldsymbol{\varepsilon}'}(t_1') a_{\boldsymbol{k}_2' \boldsymbol{\varepsilon}}(t_2') a^\dagger_{\boldsymbol{q}_\mathrm{f} \boldsymbol{e}_\mathrm{f}} a_{\boldsymbol{q}_\mathrm{f} \boldsymbol{e}_\mathrm{f}} a^\dagger_{\boldsymbol{k}_2 \boldsymbol{e}'}(t_2) a_{\boldsymbol{k}_1 \boldsymbol{e}}(t_1) \rangle_\mathrm{ph},$$

PHYS. REV. X 6, 041019 (2016)

To conclude Part 1…

- Photoemission from excitons

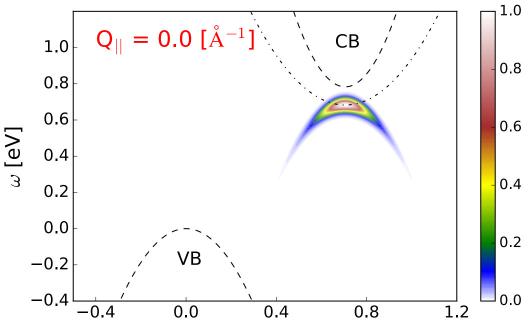
  Phys. Rev. B 97, 235310 (2018)

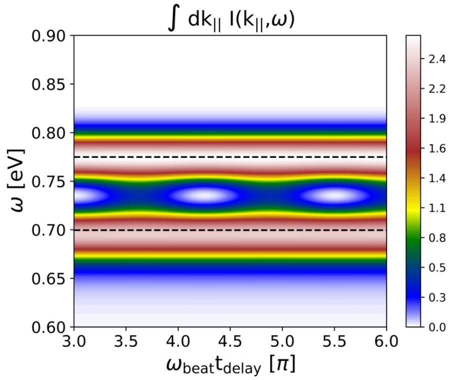
- Exciton interference & coherence

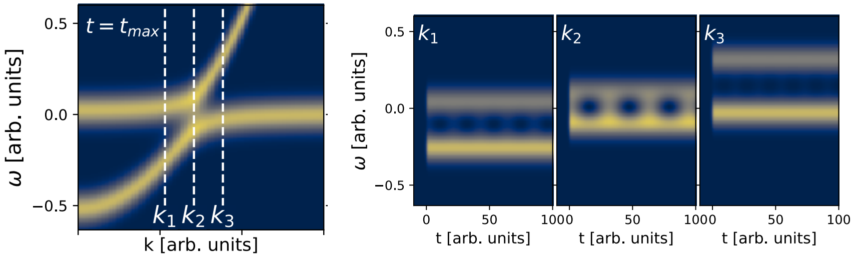
  Phys. Rev. B 99, 125303 (2019)

- Photoemission from coherences inside solids

  arXiv:2005.08978



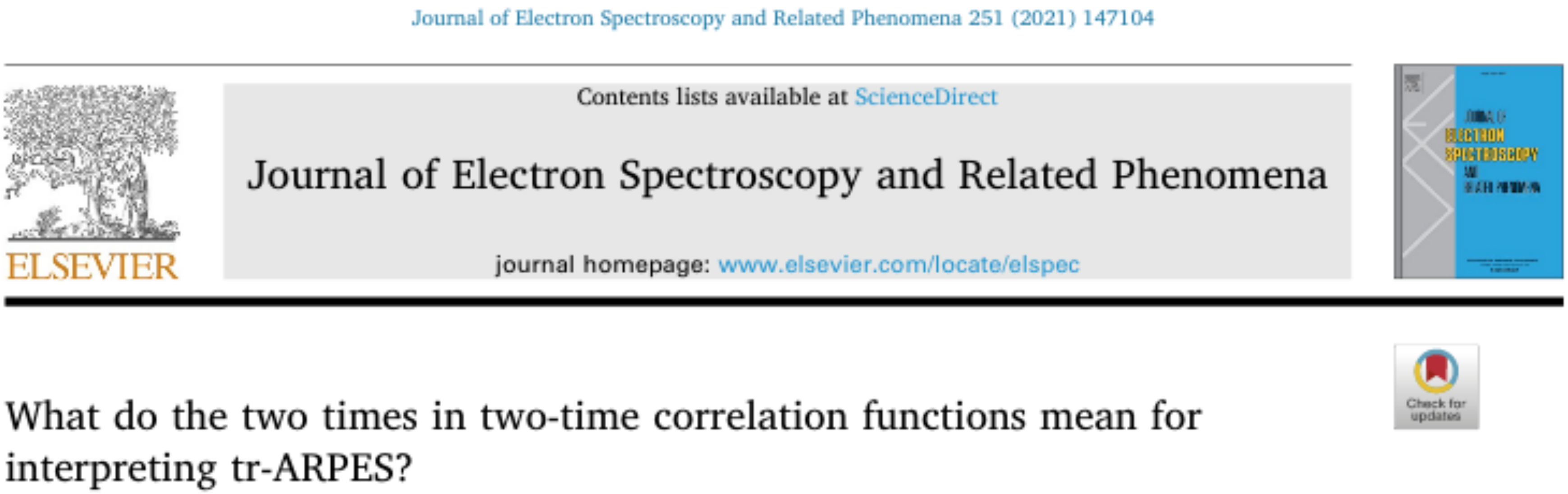




Outline

- Photoemission from excitons and coherences
  - Seeing excitons with time-resolved ARPES
  - Exciton interference
  - Photoemission from coherences inside solids

- Theoretical perspective on non-equilibrium spectroscopy
  - Correlation functions – What do we measure?
  - Non-equilibrium correlation functions – What’s different?
  - Non-equilibrium many-body theory
  - Lessons learned



Journal of Electron Spectroscopy and Related Phenomena 251 (2021) 147104

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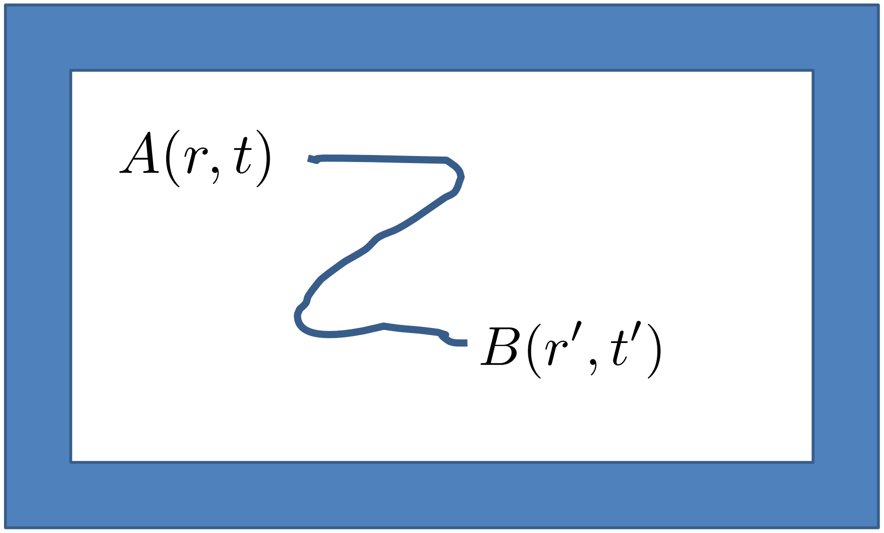
What do the two times in two-time correlation functions mean for interpreting tr-ARPES?

Correlation functions

$$\langle A(r,t)B(r',t')\rangle$$

Given some (observable) operator B at (r',t'), what is the likelihood of some (observable) operator A at (r,t)?



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Correlation functions

Conductivity

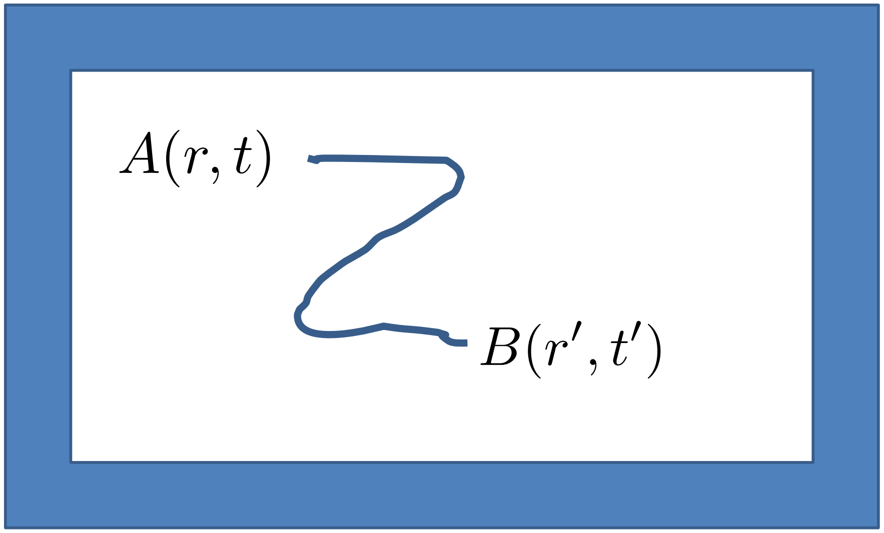
$$\langle j(r,t) j(r',t') \rangle$$

Single-particle spectra (ARPES)

$$\langle c(r,t) c^\dagger(r',t') \rangle$$

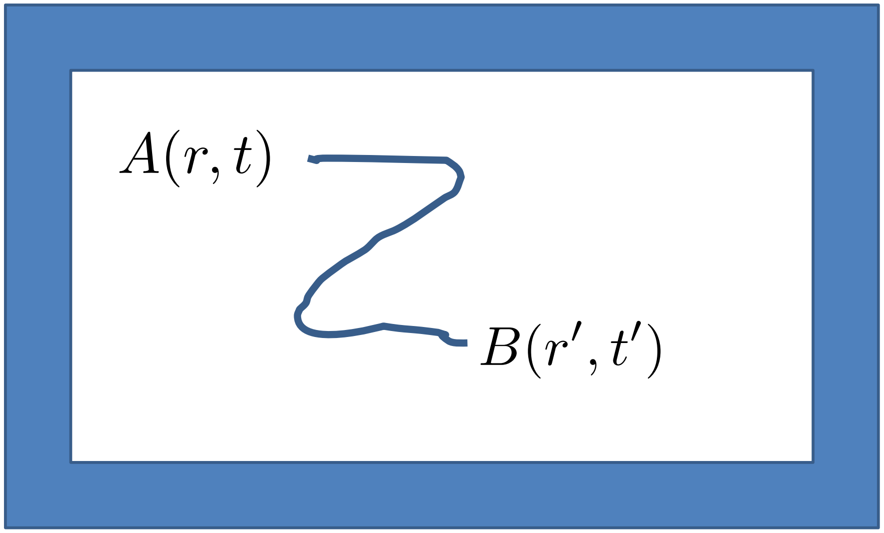
Spin-resolved neutron scattering

$$\sigma_{\alpha\beta}^{x,y,z} \langle S_\alpha(r,t) S_\beta(r',t') \rangle$$



Correlation functions

$$\langle A(r,t)B(r',t')\rangle$$



Time-translation invariance:

$$\langle A(r,t_{relative})B(r',0)\rangle$$

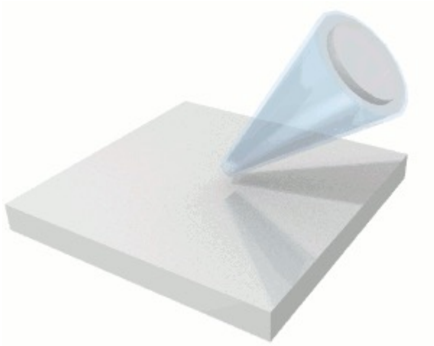
We typically Fourier transform and work in the frequency (energy) domain:

$$\chi(\omega) = \int_{-\infty}^{\infty} \langle A(r,t_{relative})B(r',0)\rangle e^{i\omega t_{relative}} dt_{relative}$$

Correlation functions – an example: ARPES

$$G^{<}(r,t;r',t') = i\langle c^{\dagger}(r',t')c(r,t)\rangle/\mathcal{Z}$$

(Plus a few steps)



Damascelli, Rev. Mod. Phys. 75, 473 (2003)
Freericks, et al., PRL ***102****, 136401 (2009)*

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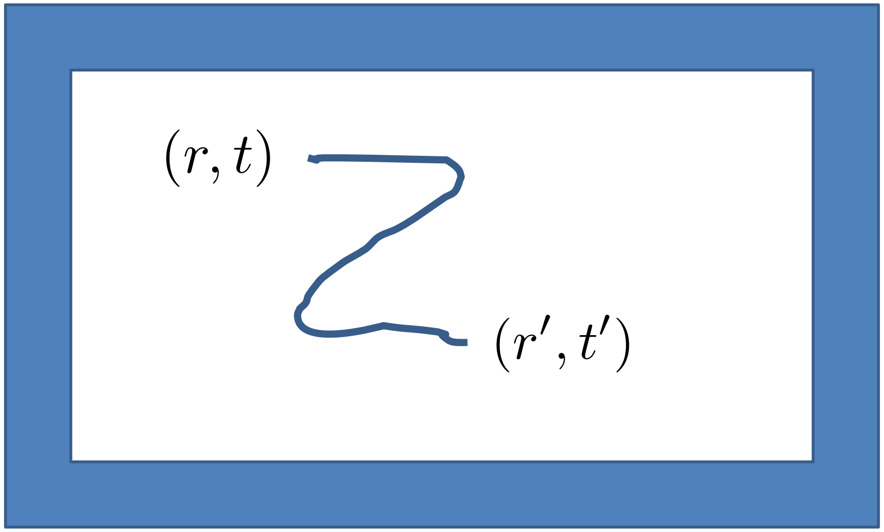
Correlation functions – an example: ARPES

$$G^{<}(r,t;r',t') = i\langle c^{\dagger}(r',t')c(r,t)\rangle/\mathcal{Z}$$

Given that I create a single particle excitation at (r,t), what is the probability that I may find it at (r',t')?

Space-translation invariance: go into Bloch basis with quasi-momentum

$$G_k^{<}(t,t') = i\langle c_k^{\dagger}(t')c_k(t)\rangle/\mathcal{Z}$$



Correlation functions – an example: ARPES

$$\begin{aligned} G_k^<(t,t') &= i\langle c_k^\dagger(t')c_k(t)\rangle/\mathcal{Z} \\ &= -i\sum_\gamma \rho_\gamma \langle\Psi_\gamma|c_k^\dagger(t')c_k(t)|\Psi_\gamma\rangle \end{aligned}$$

Density matrix

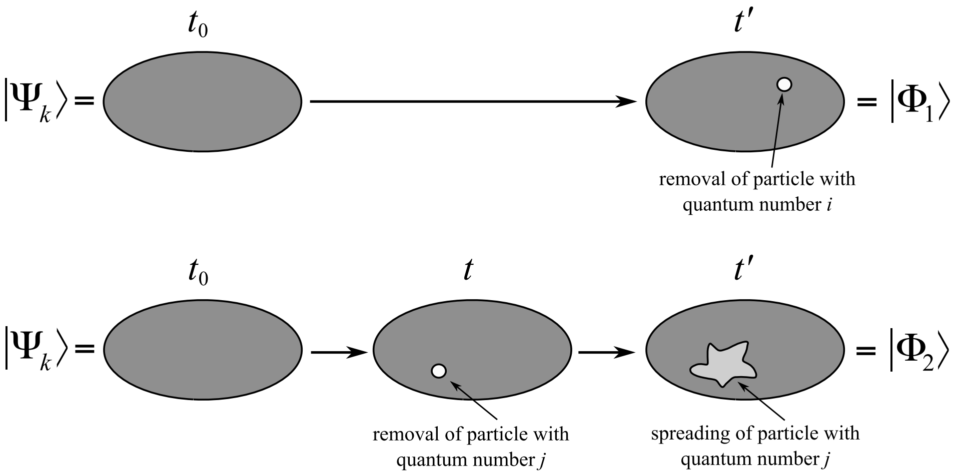
Eigenstates

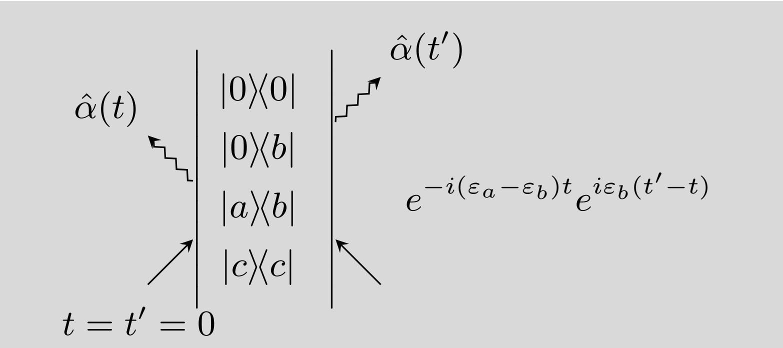
$$\langle\Psi_\gamma|c_k^\dagger(t')c_k(t)|\Psi_\gamma\rangle = \langle\Psi_\gamma|U(t_0,t')c_k^\dagger U(t',t)c_k U(t,t_0)|\Psi_\gamma\rangle$$

Time evolution operators

Correlation functions – an example: ARPES

$$\langle\Psi_\gamma|c_k^\dagger(t')c_k(t)|\Psi_\gamma\rangle = \underbrace{\langle\Psi_\gamma|U(t_0,t')c_k^\dagger}_{|\Phi_1\rangle^\dagger}\underbrace{U(t',t)c_kU(t,t_0)|\Psi_\gamma\rangle}_{|\Phi_2\rangle}$$





arXiv:2005.08978

Correlation functions – an example: ARPES

$$\langle\Psi_\gamma|c_k^\dagger(t')c_k(t)|\Psi_\gamma\rangle = \langle\Psi_\gamma|\underbrace{U(t_0,t')c_k^\dagger}_{|\Phi_1\rangle^\dagger}\underbrace{U(t',t)c_kU(t,t_0)}_{|\Phi_2\rangle}|\Psi_\gamma\rangle$$

When there is no explicit time dependence in the Hamiltonian,

$$= \langle\Psi_\gamma|e^{i\mathcal{H}(t'-t_0)}c_k^\dagger e^{-i\mathcal{H}(t'-t)}c_k e^{-i\mathcal{H}(t-t_0)}|\Psi_\gamma\rangle$$

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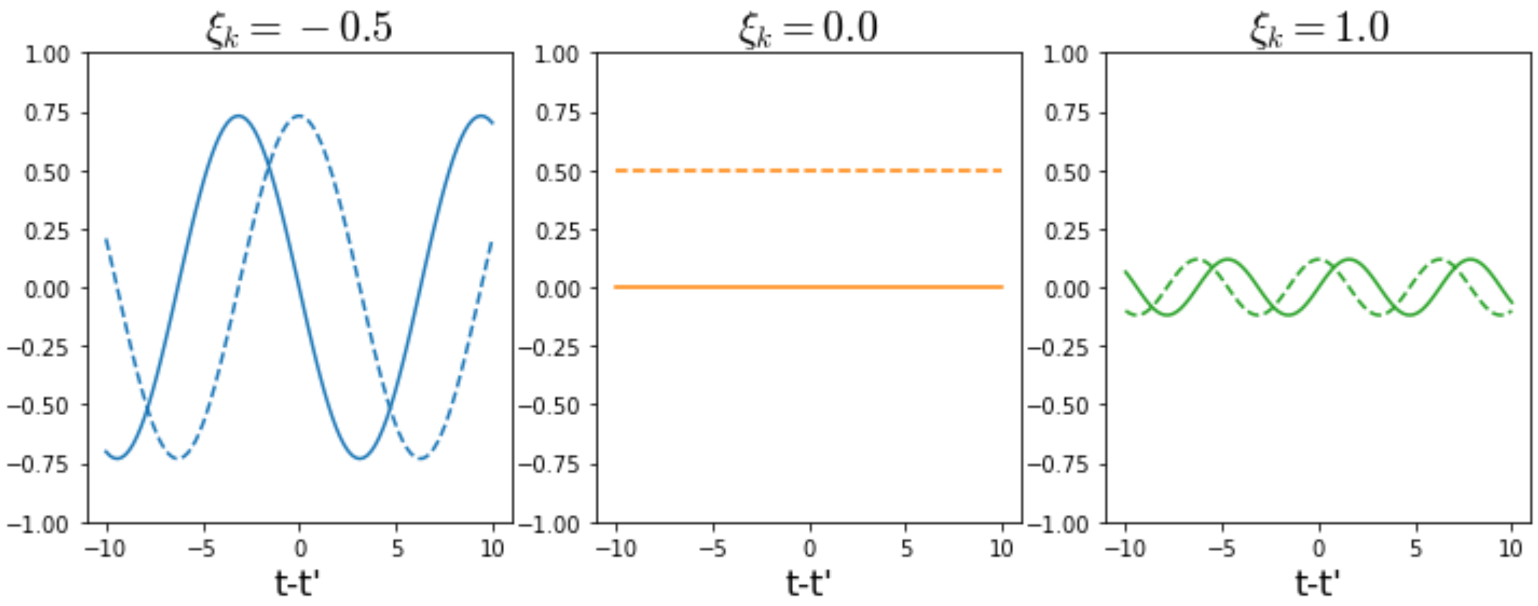
Correlation functions – an example: ARPES

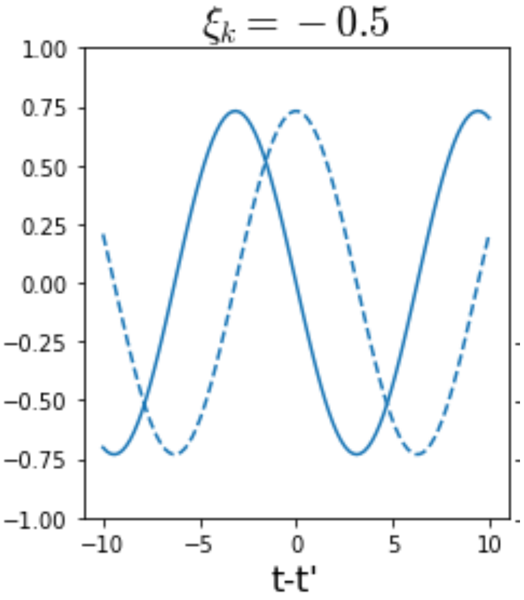
Assuming the single-particle excitation is an eigenstate,

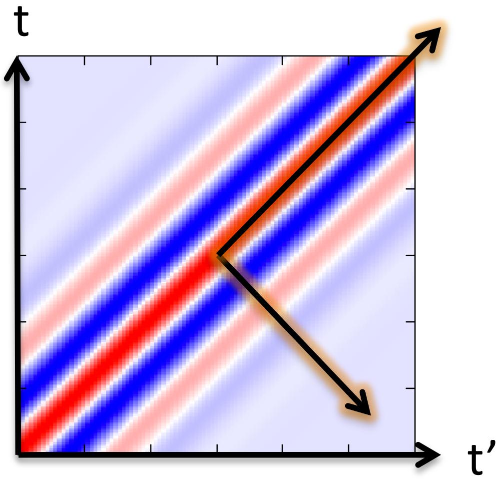
$$G^{<}(t,t') = i f(\xi_k) e^{-i\xi_k (t-t')}$$



Correlation functions – an example: ARPES

$$G^<(t,t') = i f(\xi_k) e^{-i\xi_k (t-t')}$$





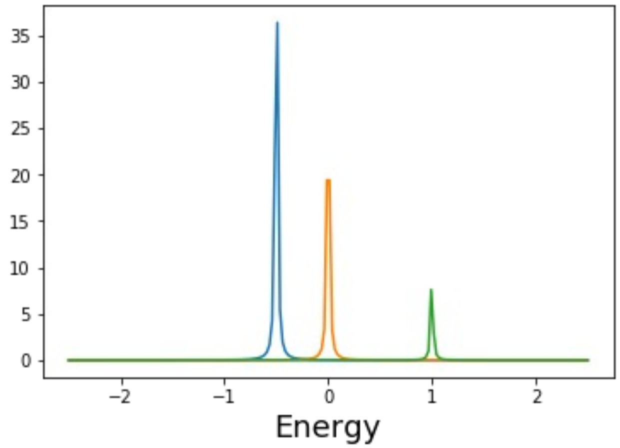
Average (measurement) time
$t_{\mathrm{ave}} = \frac{1}{2}(t+t')$

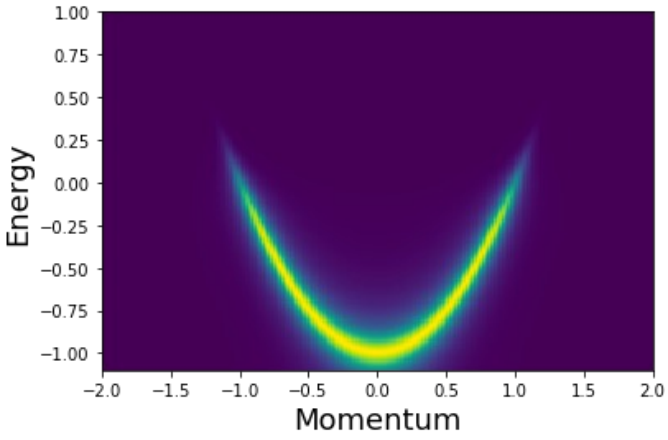
Relative time
$t_{\mathrm{rel}} = t - t'$

Correlation functions – an example: ARPES

$$G^{<}(\omega) = \int_{-\infty}^{\infty} d(t-t')\left[i f(\xi_k) e^{-i\xi_k (t-t')} \right]$$

$$= 2\pi i f(\xi_k)\delta(\omega - \xi_k)$$





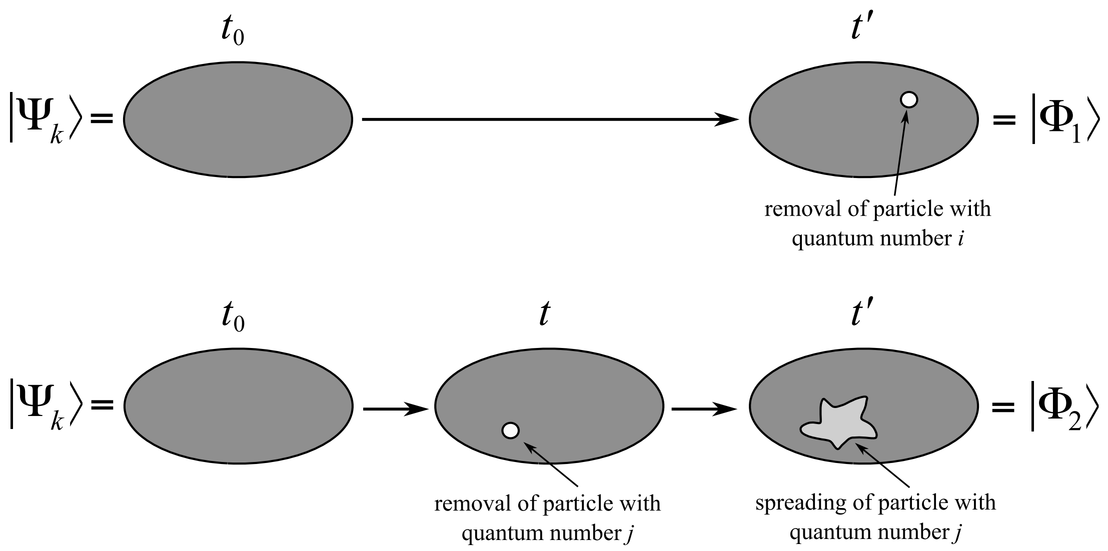
Correlation functions – an example: ARPES

Okay, but most systems are interacting?!

Correlation functions – an example: ARPES

Recall that the ARPES correlation function involved

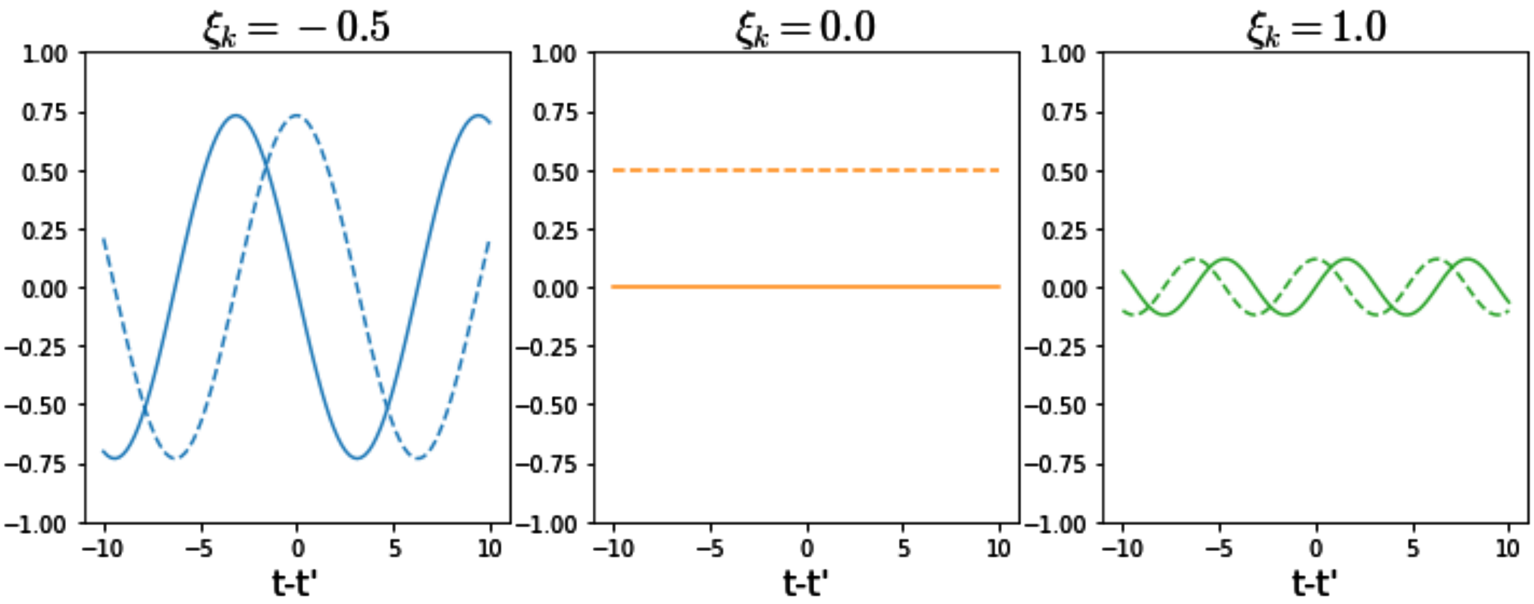
$$\langle\Psi_\gamma|\underbrace{U(t_0,t')c_k^\dagger}_{|\Phi_1\rangle^\dagger}\underbrace{U(t',t)c_kU(t,t_0)}_{|\Phi_2\rangle}|\Psi_\gamma\rangle$$



Since the single-particle basis is *not* the eigenbasis, the bottom situation spreads out and we may expect the overlap to decay as $|t-t'|\to\infty$

Correlation functions – an example: ARPES

$$G^{<}(t,t') = i f(\xi_k) e^{-i\xi_k (t-t')} e^{-\Gamma|t-t'|}$$



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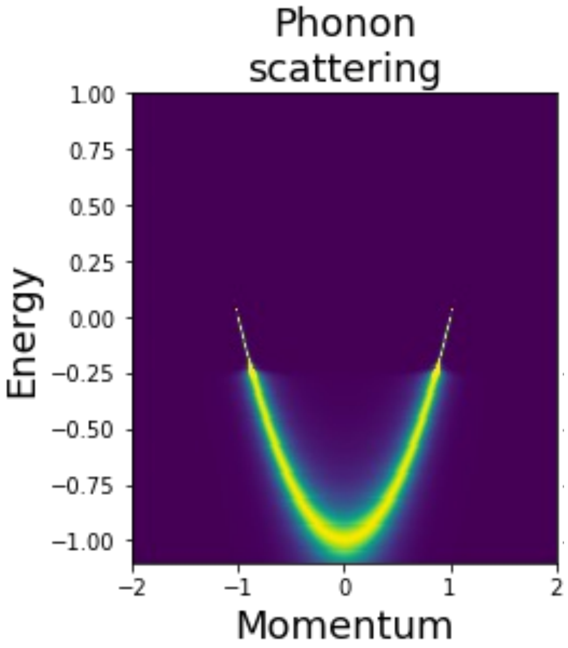
Correlation functions – an example: ARPES

$$G^<(\omega,k) = -2if(\omega)\mathrm{Im}\frac{1}{\omega-\xi_k-\boxed{\Sigma(\omega,k)}}$$



The *self-energy* $\Sigma(\omega,k)$ encodes the effect of interactions on the single-particle Green’s function.

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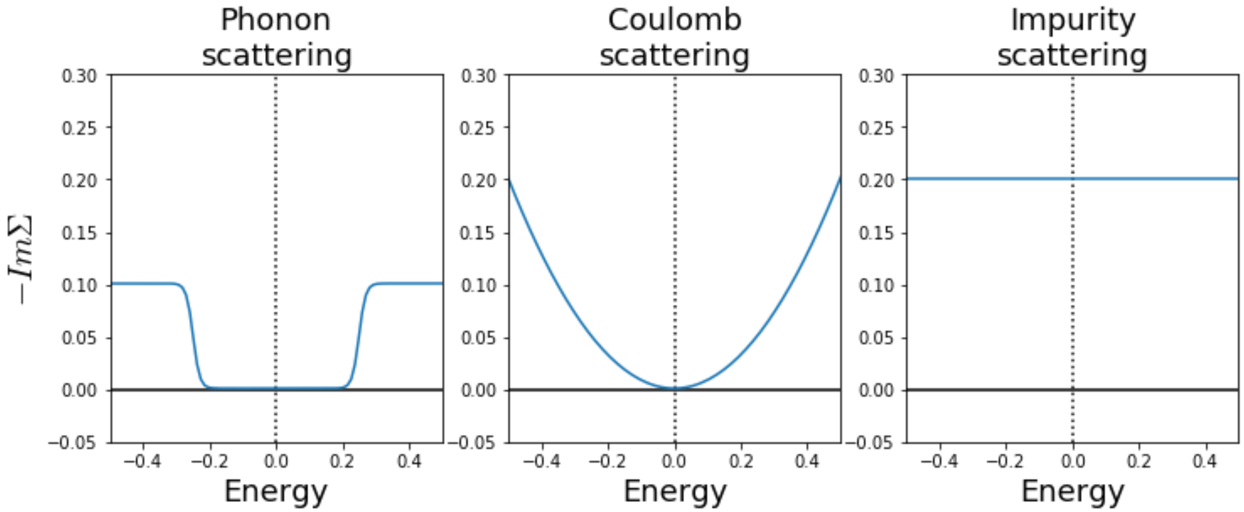
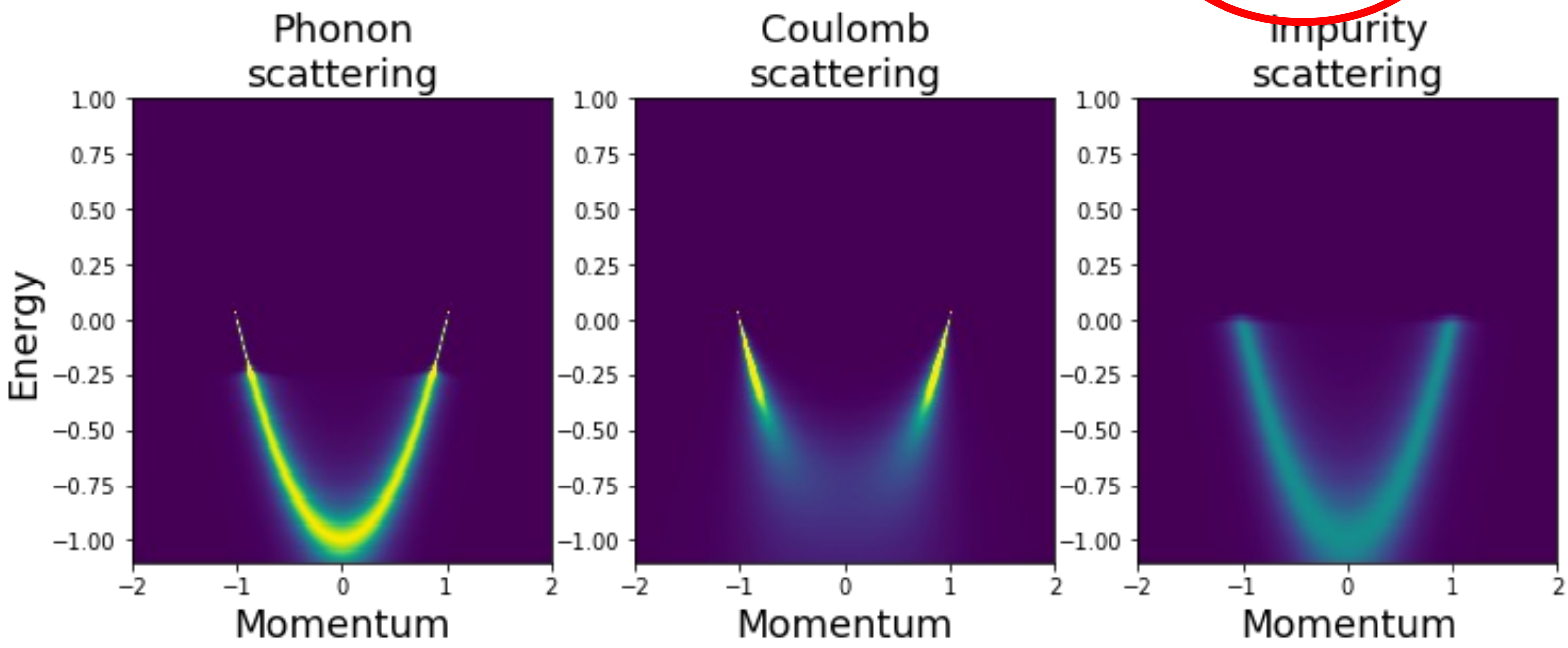
Correlation functions – an example: ARPES

The energy dependence of $\Sigma(\omega)$ is characteristic for a few different processes.



Correlation functions – an example: ARPES

$$G^{<}(\omega, k) = -2if(\omega)\mathrm{Im}\frac{1}{\omega - \xi_k - \Sigma(\omega, k)}$$

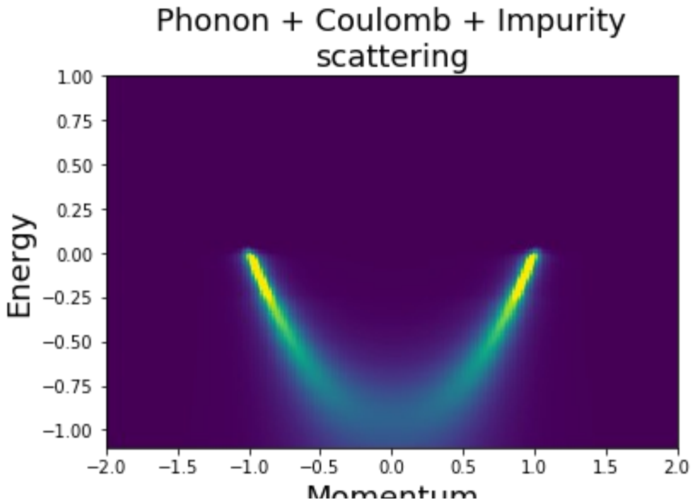


Correlation functions – an example: ARPES

$$G^{<}(\omega,k) = -2if(\omega)\mathrm{Im}\frac{1}{\omega-\xi_k-\Sigma(\omega,k)}$$

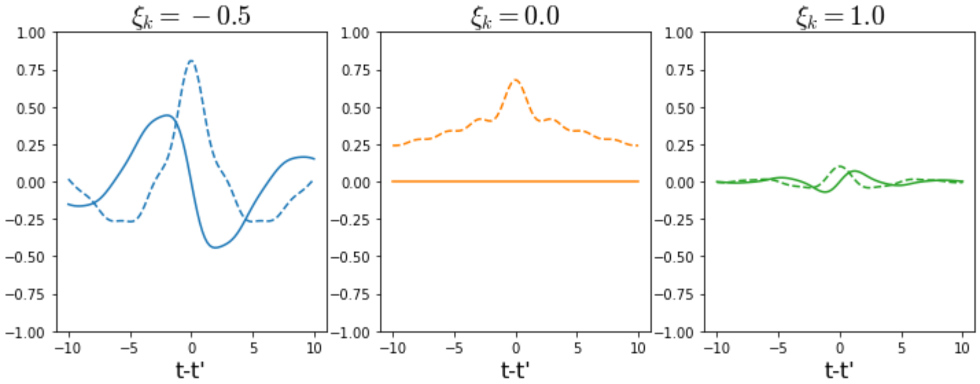
To first order, the self-energies are additive (known as *Matthiessen’s rule)*:

$$\Sigma = \Sigma_{phonon} + \Sigma_{Coulomb} + \Sigma_{impurity}$$



Going back to the time domain, the correlation function decay time is related to the self-energy via

$$\boxed{1/\tau = -2\mathrm{Im}\Sigma}$$



Correlation functions – an example: ARPES

- Depend on time differences (relative times)
- The correlation functions decay due to spreading in state space through interactions
- The self-energy encodes the interactions and gives rise to the correlation function decay (or line width in frequency)

$$\langle A(r, t_{relative}) B(r', 0) \rangle$$

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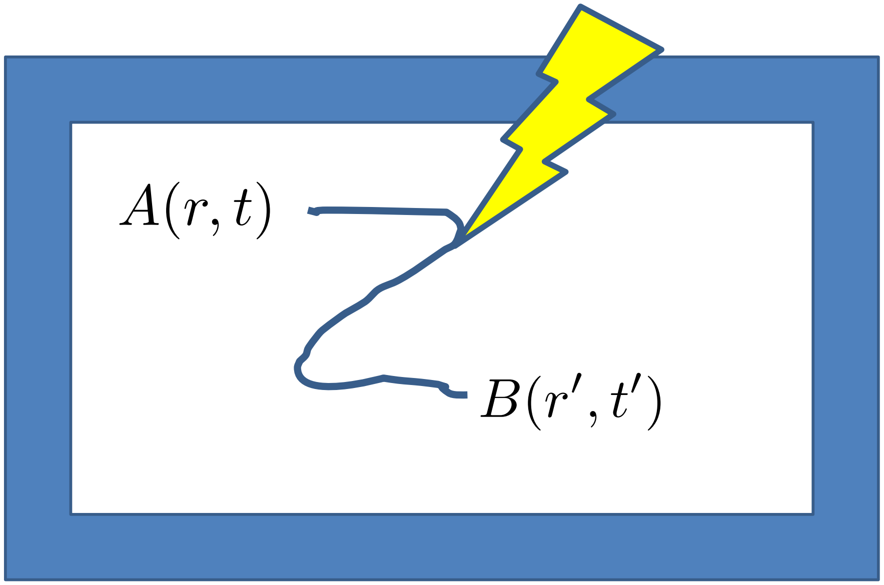
Non-equilibrium Correlation functions

$$\langle A(r,t)B(r',t')\rangle$$

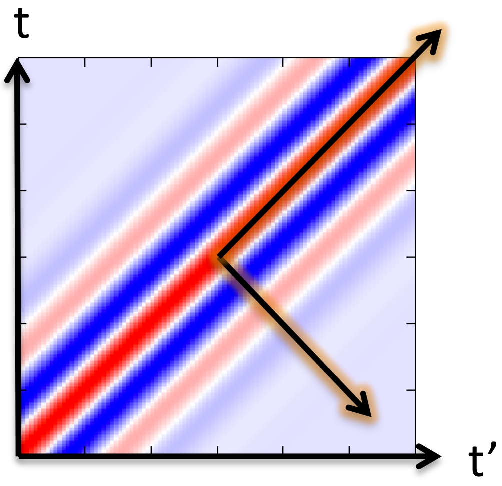
Given some (observable) operator B at (r',t'), what is the likelihood of some (observable) operator A at (r,t)?



We can no longer just work with relative time because time-translation-invariance is broken.

Non-equilibrium Correlation functions

$$\langle A(r,t)B(r',t')\rangle$$

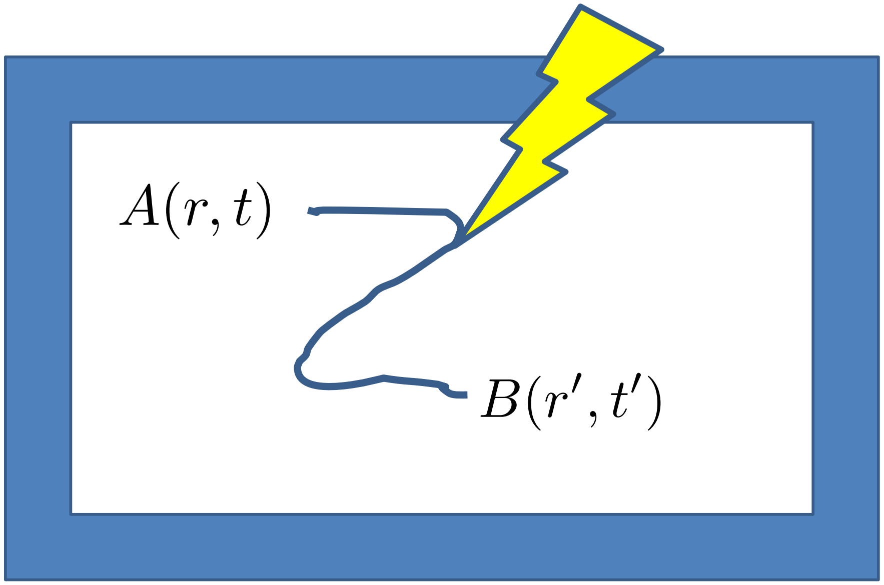


Average (measurement) time

$$t_{\mathrm{ave}} = \frac{1}{2}(t+t')$$

Relative time

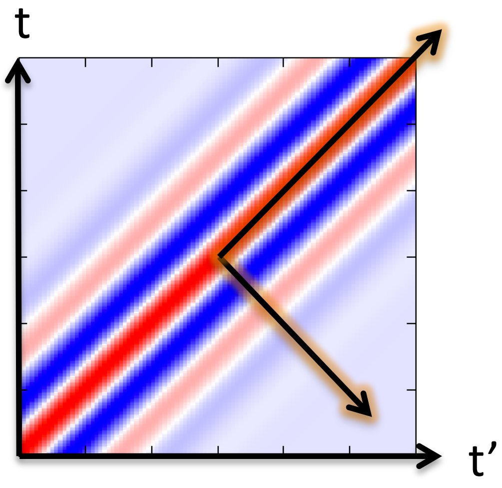
$$t_{\mathrm{rel}} = t - t'$$



$$\langle A(r,t_{ave}+t_{rel}/2)B(r',t_{ave}-t_{rel}/2)\rangle$$

Non-equilibrium Correlation functions

$$\langle A(r,t)B(r',t')\rangle$$



Average (measurement) time

$$t_{\text{ave}} = \frac{1}{2}(t+t')$$

Relative time

$$t_{\text{rel}} = t - t'$$

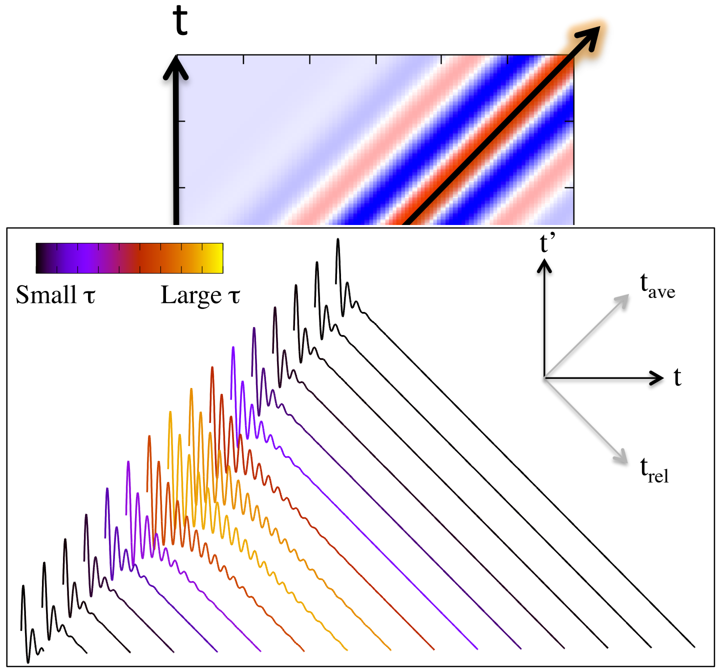
1. In equilibrium, there is <u>no</u> dynamics along the average time direction. This steady state is achieved through a balance of scattering rates.

2. Out of equilibrium, the dynamics along average time need not be the same as those along relative time – in general, they are not.

How do we make some progress?

Non-equilibrium Correlation functions

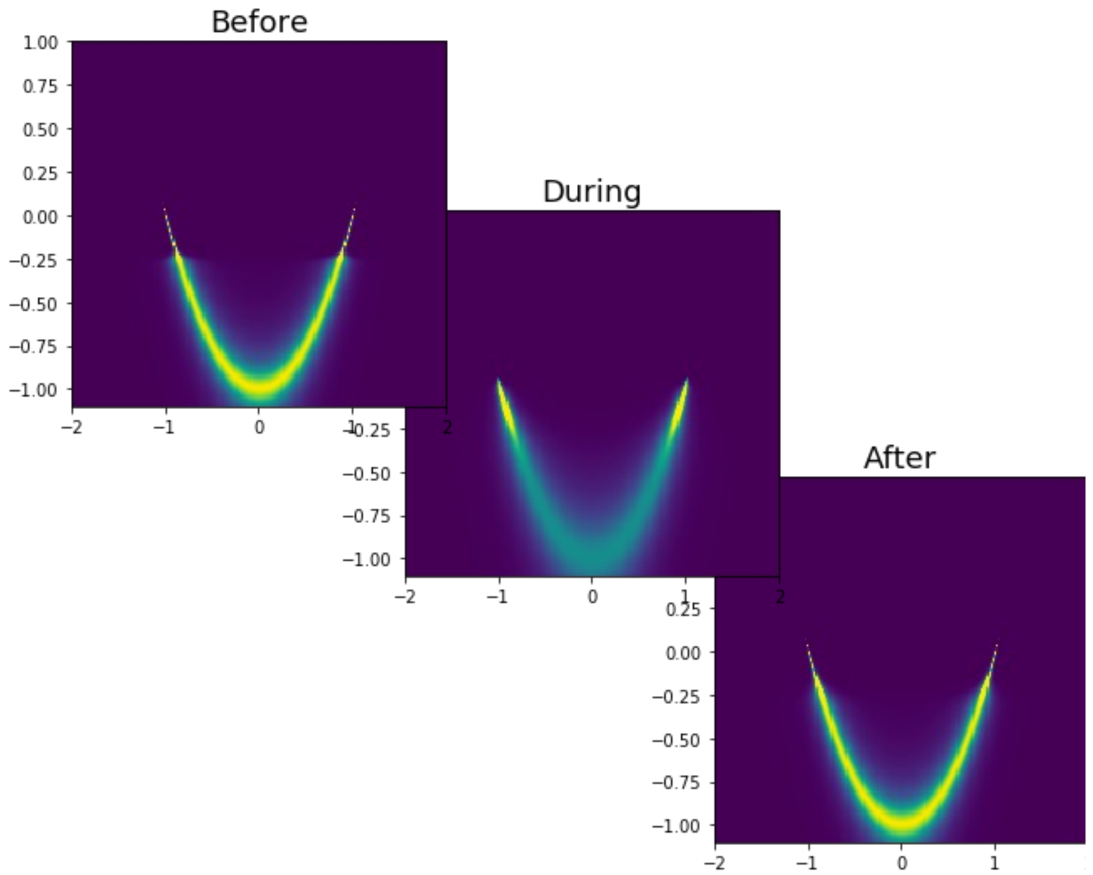
- Suppose that
  1. We are making measurements long after the pump
  2. The average (measurement) time-dependence is slow compared to the time dependence in t_{rel} (which we called Γ).
- Then we may (carefully) map the time dependence onto the parameters of the correlation function



$$G^{<}(t,t') = if(\xi_k)e^{-i\xi_k(t_{rel})}e^{-|t_{rel}|/\tau(t_{ave})}$$

Non-equilibrium Correlation functions

- Suppose that
  1. We are making measurements long after the pump
  2. The average (measurement) time-dependence is slow compared to the time dependence in t_{rel} (which we called Γ).
- Then we may (carefully) map the time dependence onto the parameters of the correlation function and Fourier transform along t_{rel}



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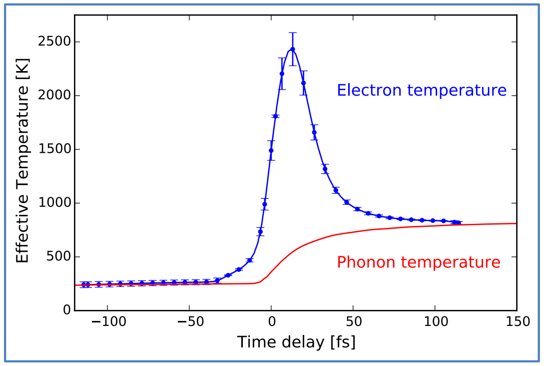
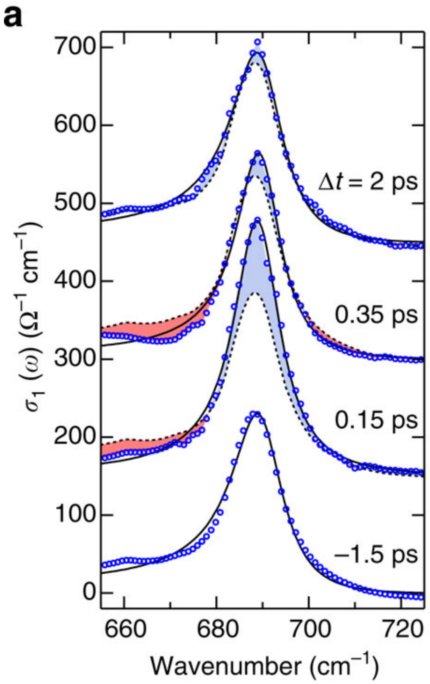
Non-equilibrium Correlation functions

- Example parameters that are modeled to change with *average* time:
  - System temperature
  - Drude scattering rates
  - Coupling constants
  - Order parameters (e.g. superconducting gaps)





G. Coslovich, Nature Communications 4, 2643 (2013).

PHYSICAL REVIEW X **7,** 041013 (2017)

Ultrafast Gap Dynamics and Electronic Interactions in a Photoexcited Cuprate Superconductor

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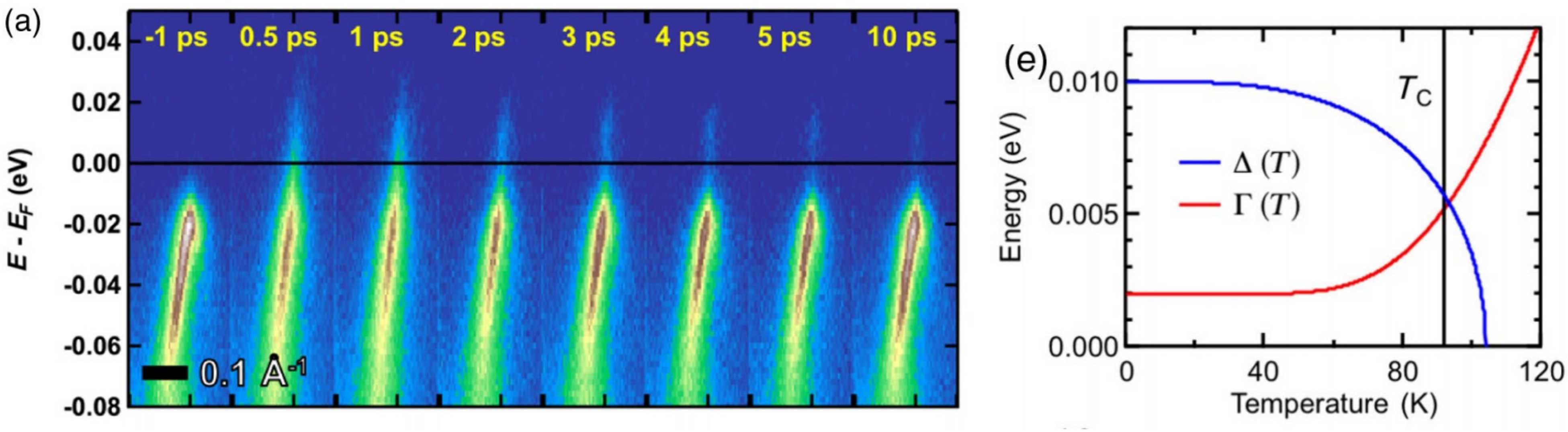
R. D. Zhong,[2] G. D. Gu,[2] and D. S. Dessau[1,3]



Non-equilibrium Correlation functions

Changing parameters as a function of time

PROS:

- Easy to understand and communicate
- We can rely on our equilibrium intuition and knowledge

CONS:

- We only rely on our equilibrium intuition and knowledge
- Difficult to tell when it's appropriate and when it isn't

How can we do better?

Outline

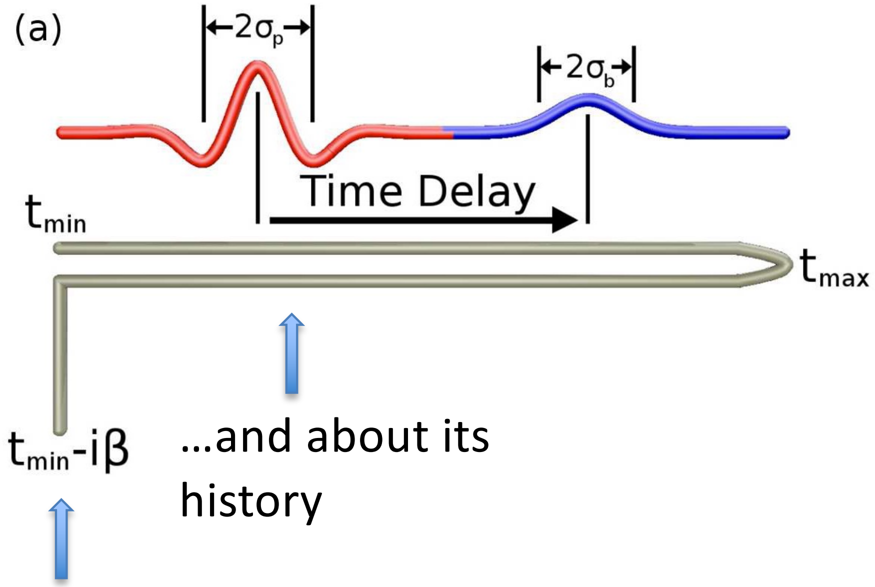
- Photoemission from excitons and coherences
  - Seeing excitons with time-resolved ARPES
  - Exciton interference
  - Photoemission from coherences inside solids

- Theoretical perspective on non-equilibrium spectroscopy
  - Correlation functions – What do we measure?
  - Non-equilibrium correlation functions – What’s different?
  - Non-equilibrium many-body theory
  - Lessons learned

Non-Equilibrium Many-Body Theory

$$G_{\mathbf{k}}(t,t') = G^0_{\mathbf{k}}(t,t') + \oint dt_1\, dt_2\, G^0_{\mathbf{k}}(t,t_1)\,\Sigma(t_1,t_2)\,G_{\mathbf{k}}(t_2,t')$$

$$G_k(\omega) = G^0_k(\omega) + G^0_k(\omega)\,\underline{\Sigma(\omega)}\,G_k(\omega)$$



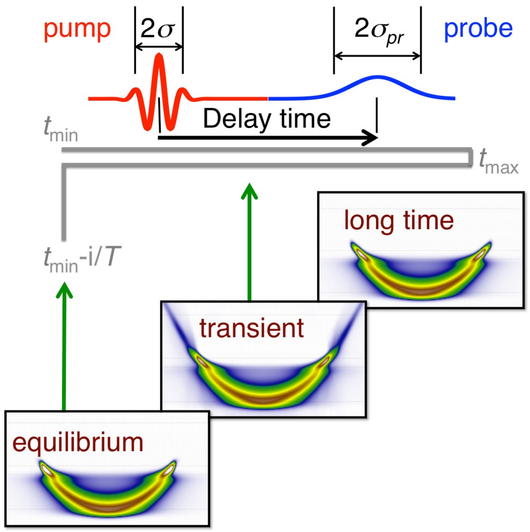
…and about its history

System knows about its thermal initial state…

Include the effects of strong driving field through Peierls substitution

$$\boldsymbol{k} \rightarrow \boldsymbol{k} - e\mathbf{A}(t)$$

Time-resolved ARPES



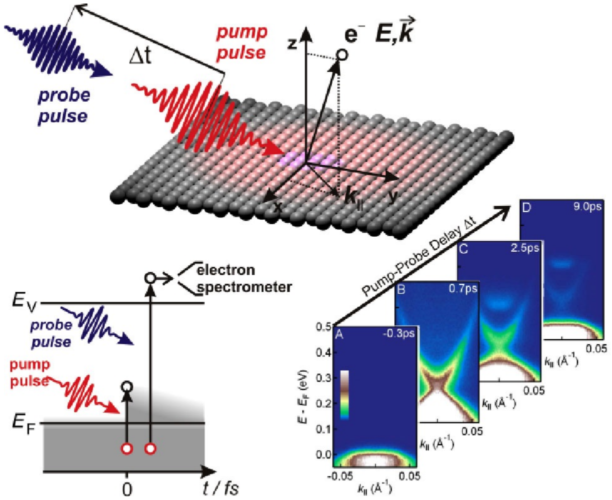
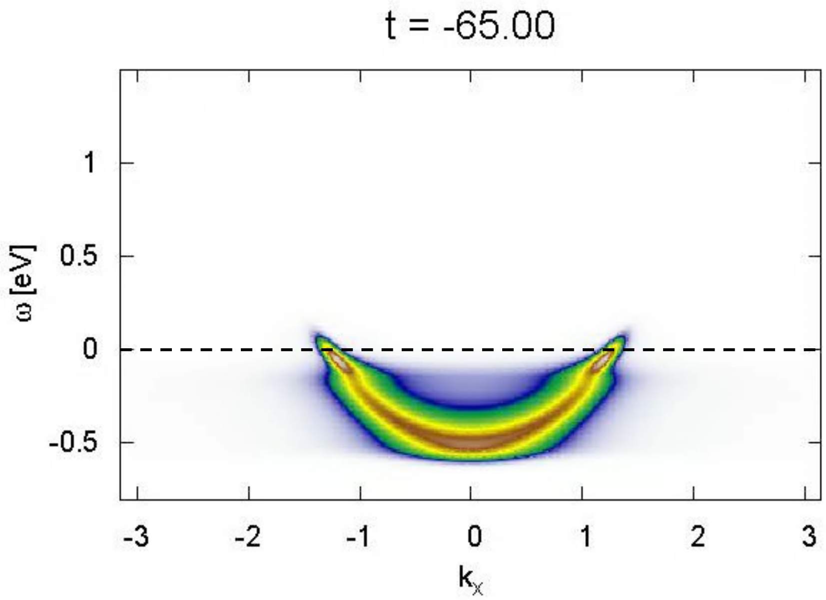


Image source: FHI Berlin

$$\boxed{A_{\mathbf{k}}(\omega,t_0) = \mathrm{Im}\,\frac{1}{2\pi\sigma^2}\int dtdt\,\boxed{G^{<}_{\mathbf{k}}(t,t')}\boxed{e^{-(t-t_0)^2/2\sigma^2}e^{-(t'-t_0)^2/2\sigma^2}e^{i\omega(t-t')}}}$$

Freericks, et al., PRL ***102****, 136401 (2009); Freericks, et al., Physica Scripta* ***2015*** *T165 014012 (2015); Freericks and Krishnamurthy, Photonics* ***3*** *58 (2016)*

Electron-boson coupling



Phys. Rev. X 3, 041033

Lessons learned

1. You can assign a time-dependence to a parameter, but be careful to which one.

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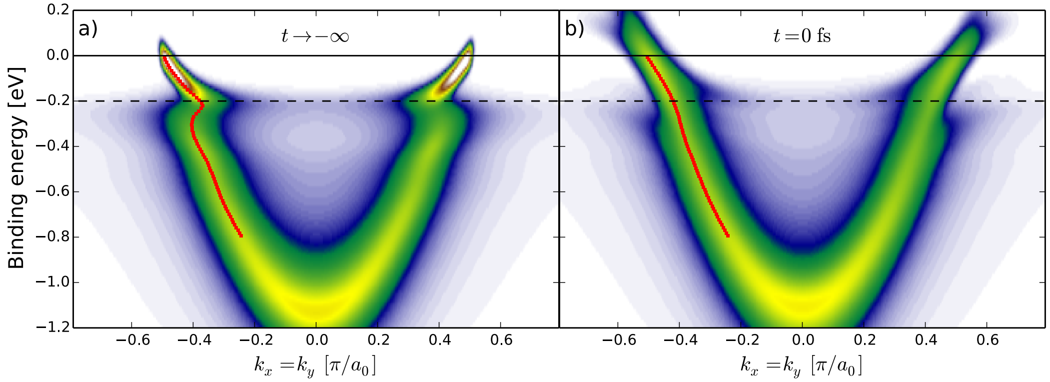
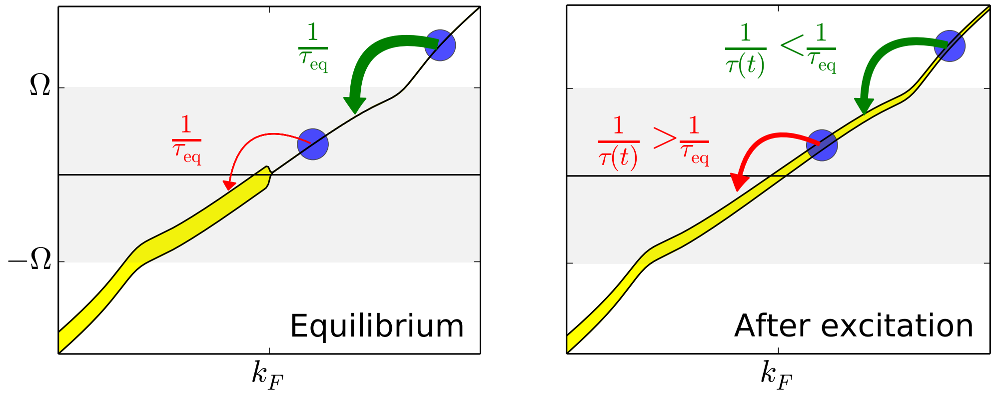
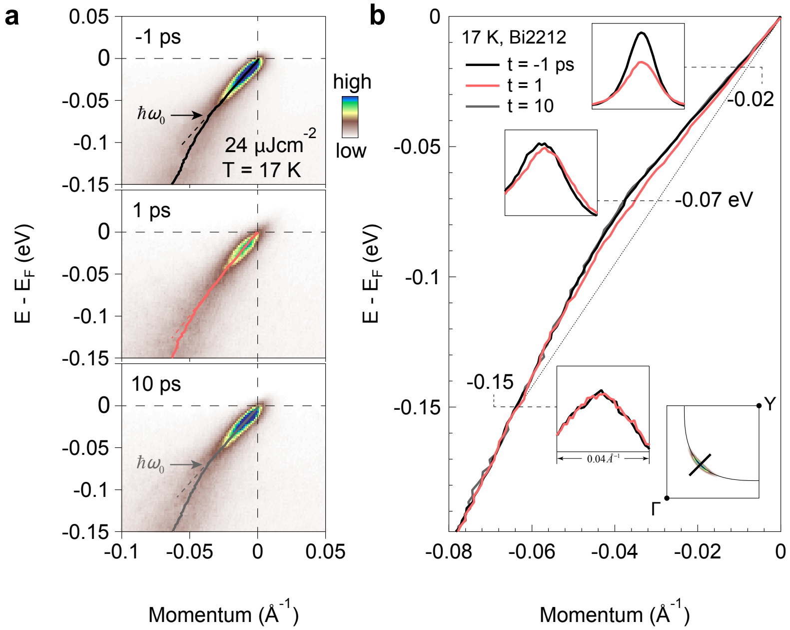
Increased effective temperature looks like decreased coupling







AFK et al PRB 2014

Zhang, Nature Comm. (2014)

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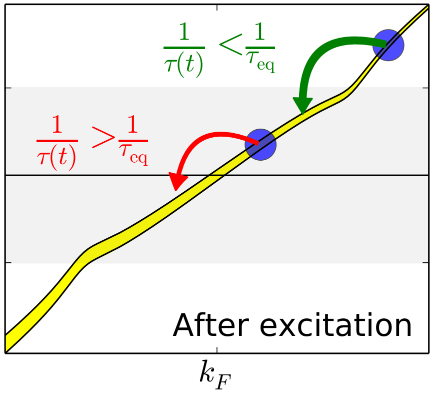
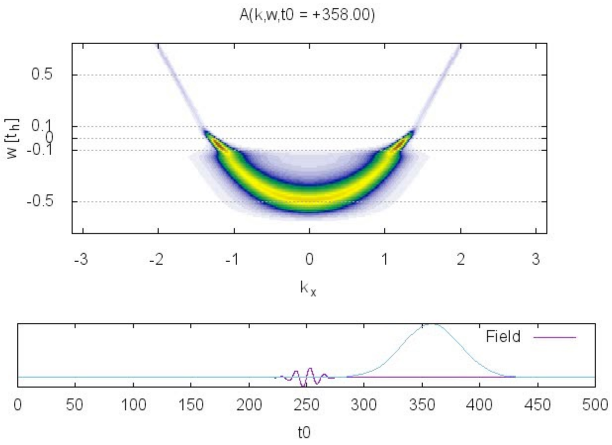
Lessons learned

1. You can assign a time-dependence to a parameter, but be careful to which one.
2. Just because there is scattering, that does not mean there is dynamics.

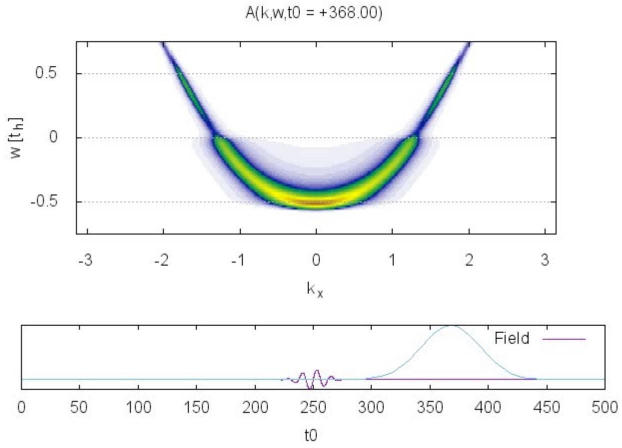


Although there is a linewidth (relative time), there may not be dynamics in average time

Electron-phonon



Impurity



arXiv:1708.05725

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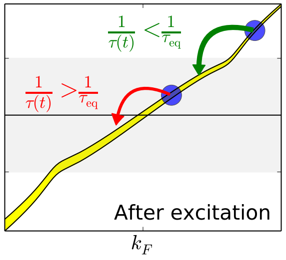
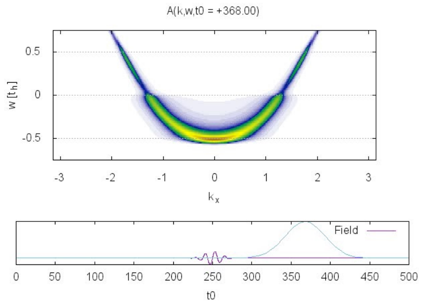
Lessons learned

1. You can assign a time-dependence to a parameter, but be careful to which one.

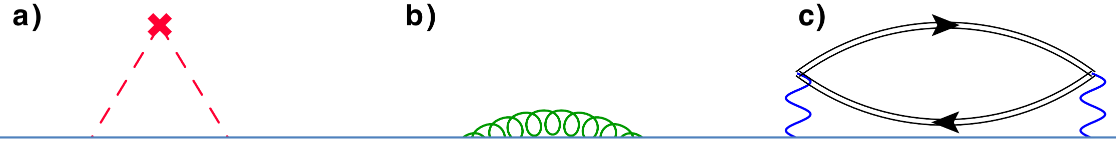
2. Just because there is scattering, that does not mean there is dynamics.

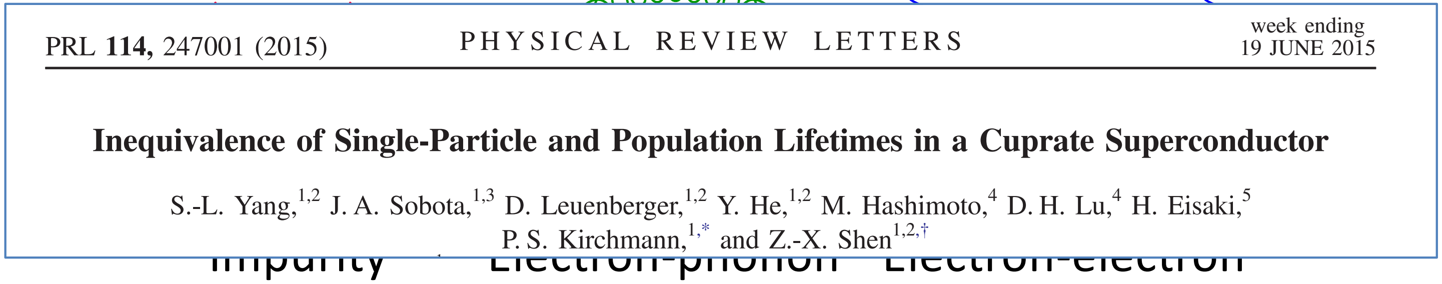
3. Because the dynamics are determined by a balance in rates, sub-interactions can switch on and off





All interactions are not equal




PRL **114,** 247001 (2015) PHYSICAL REVIEW LETTERS week ending 19 JUNE 2015

Inequivalence of Single-Particle and Population Lifetimes in a Cuprate Superconductor

S.-L. Yang,[1,2] J. A. Sobota,[1,3] D. Leuenberger,[1,2] Y. He,[1,2] M. Hashimoto,[4] D. H. Lu,[4] H. Eisaki,[5]
P. S. Kirchmann,[1,*] and Z.-X. Shen[1,2,†]

For equilibrium measurements (e.g. line width), these processes are *equivalent.*

Mathiessen's rule: For weak interactions, scattering rates *add*.

$$\frac{1}{\tau} = \frac{1}{\tau_{e-imp}} + \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_{e-e}}$$

For population dynamics, this is not true.

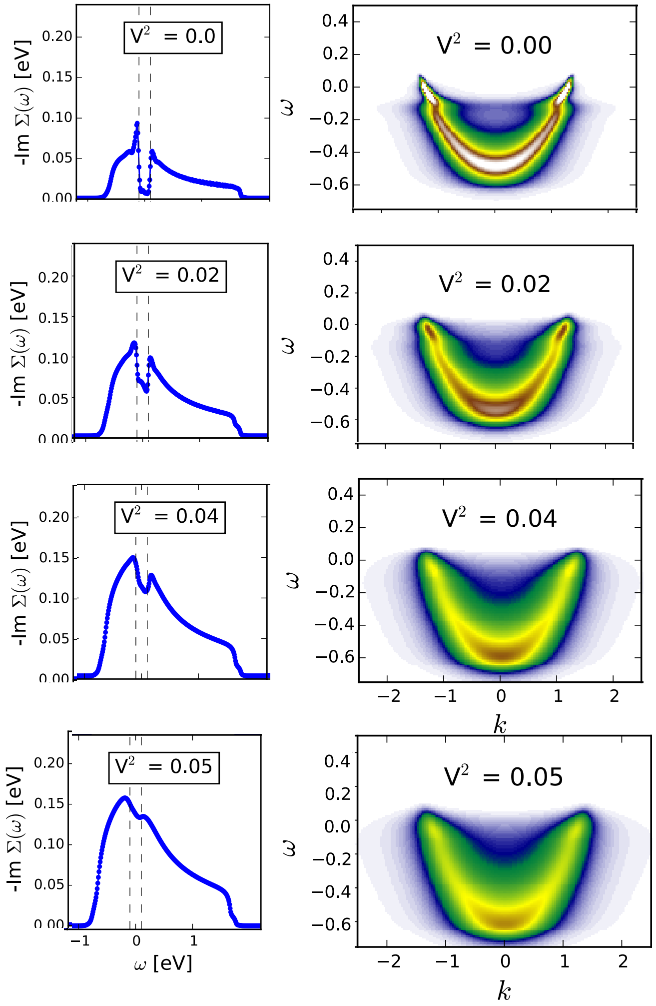
All interactions are not equal

$$\begin{aligned}\frac{dn_{\mathbf{k}}(t_{\text{ave}})}{dt_{\text{ave}}} &= \int_{-\infty}^{\infty} d\omega 2i\mathrm{Im}\Sigma^{R}_{imp}(t_{\text{ave}},\omega)G^{<}_{\mathbf{k}}(t_{\text{ave}},\omega) - \int_{-\infty}^{\infty} d\omega 2i\mathrm{Im}G^{R}_{\mathbf{k}}(t_{\text{ave}},\omega)\Sigma^{<}_{imp}(t_{\text{ave}},\omega)\\ &+ \int_{-\infty}^{\infty} d\omega 2i\mathrm{Im}\Sigma^{R}_{phonon}(t_{\text{ave}},\omega)G^{<}_{\mathbf{k}}(t_{\text{ave}},\omega) - \int_{-\infty}^{\infty} d\omega 2i\mathrm{Im}G^{R}_{\mathbf{k}}(t_{\text{ave}},\omega)\Sigma^{<}_{phonon}(t_{\text{ave}},\omega)\\ &+ \int_{-\infty}^{\infty} d\omega 2i\mathrm{Im}\Sigma^{R}_{el-el}(t_{\text{ave}},\omega)G^{<}_{\mathbf{k}}(t_{\text{ave}},\omega) - \int_{-\infty}^{\infty} d\omega 2i\mathrm{Im}G^{R}_{\mathbf{k}}(t_{\text{ave}},\omega)\Sigma^{<}_{el-el}(t_{\text{ave}},\omega)\end{aligned}$$

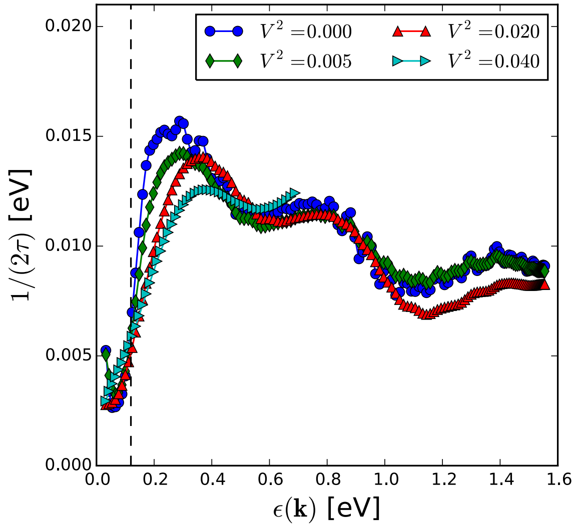
Individual subsets can (and do) cancel out, leading to effective disappearance of the interaction in dynamics.

$$\Sigma_{\text{imp}} \propto G_{\mathbf{k}}$$

Equilibrium: quasiparticle



Non-equilibrium: population



The rate of relaxation is not precisely the self-energy.

All interactions are not equal

$$\begin{aligned}\frac{dn_{\mathbf{k}}(t_{\text{ave}})}{dt_{\text{ave}}} &= \int_{-\infty}^{\infty} d\omega 2i\text{Im}\Sigma^R_{imp}(t_{\text{ave}},\omega)G^<_{\mathbf{k}}(t_{\text{ave}},\omega) - \int_{-\infty}^{\infty} d\omega 2i\text{Im}G^R_{\mathbf{k}}(t_{\text{ave}},\omega)\Sigma^<_{imp}(t_{\text{ave}},\omega)\\ &+ \int_{-\infty}^{\infty} d\omega 2i\text{Im}\Sigma^R_{phonon}(t_{\text{ave}},\omega)G^<_{\mathbf{k}}(t_{\text{ave}},\omega) - \int_{-\infty}^{\infty} d\omega 2i\text{Im}G^R_{\mathbf{k}}(t_{\text{ave}},\omega)\Sigma^<_{phonon}(t_{\text{ave}},\omega)\\ &+ \int_{-\infty}^{\infty} d\omega 2i\text{Im}\Sigma^R_{el-el}(t_{\text{ave}},\omega)G^<_{\mathbf{k}}(t_{\text{ave}},\omega) - \int_{-\infty}^{\infty} d\omega 2i\text{Im}G^R_{\mathbf{k}}(t_{\text{ave}},\omega)\Sigma^<_{el-el}(t_{\text{ave}},\omega)\end{aligned}$$

Individual subsets can (and do) cancel out, leading to effective disappearance of the interaction in dynamics.

$$\Sigma^<_{\text{el}-\text{el}} = f_\omega \text{Im}\Sigma^R_{el-el}$$

$$G^<_{\text{el}-\text{el}} = f_\omega \text{Im}G^R_{el-el}$$

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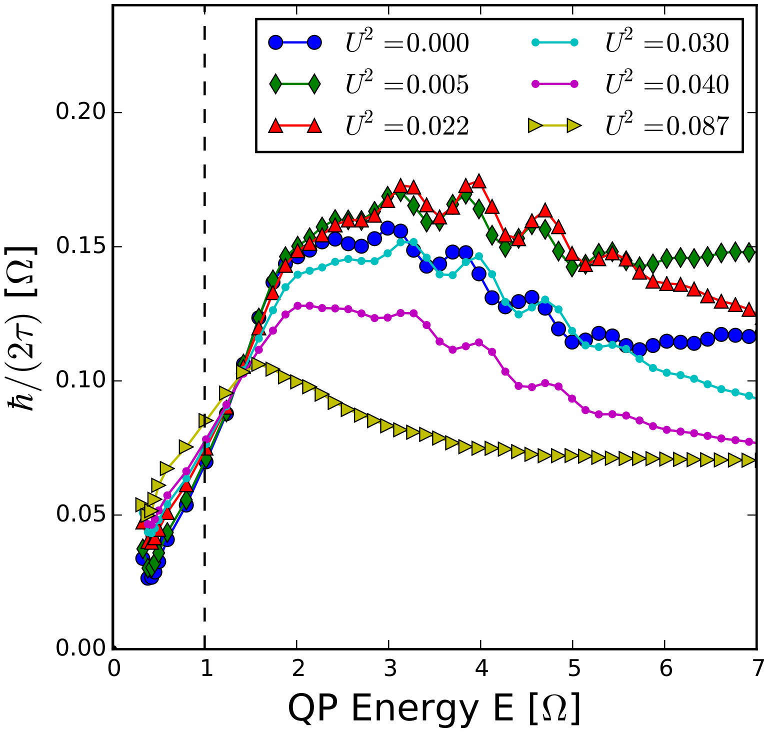
Combining electron-electron and electron-phonon scattering

Nature Communications 7, 13761 (2016)



$$g^2 = 0.02$$

Step in lifetimes remains visible

Competition between e-p and e-e scattering

Matthiessen’s rule, *“Scattering rates add for small interaction strength”* does not hold here.

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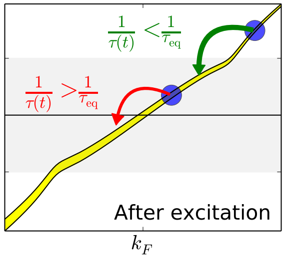

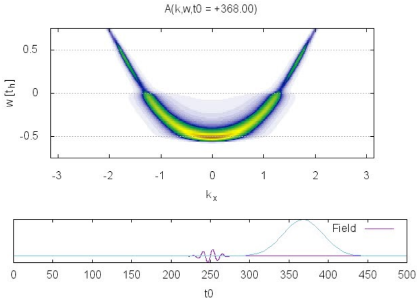

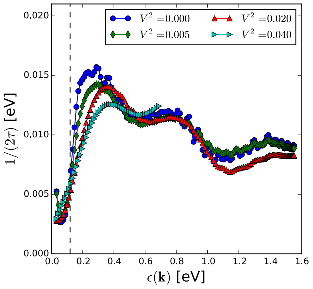

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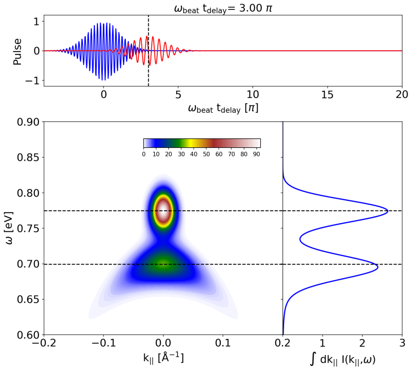
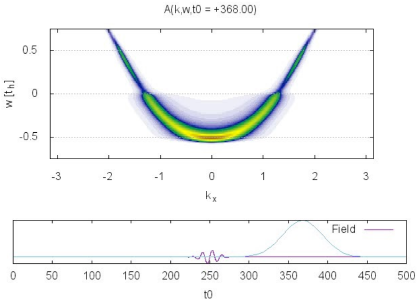


Phys. Rev. B 97, 235310 (2018)
Phys. Rev. B 99, 125303 (2019)
arXiv:2005.08978



PRX 10.1103/PhysRevX.8.041009
J. Elec. Spec. Rel. Phenom. 251, 147104 (2021)