Trion in time-resolved ARPES

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Theory of TR-ARPES

The most generic theory requires Keldysh formalism but let's spare ourselves the burden. . .

Ingredients of our model of ARPES

- Electric dipole interaction only
- Sudden approximation
- *Separation between pump and probe*: system *not* driven when probed; pump prepares an initial state and nothing more
- Fermi's golden rule in probing

Theory of TR-ARPES

Main result Output intensity $I_{\mathbf{k}}(t) \propto \sum_c P^c_{\mathbf{k}}(t)$,

$$P^c_{\mathbf{k}}(t) = \sum_{n,\mathbf{k}'} \rho_n \left| M^{fc}_{\mathbf{k}\mathbf{k}'} \right|^2 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \, \mathrm{e}^{-\mathrm{i}(E_n - \omega)(t_1 - t_2)} \langle \Psi_n(t_0) | c^\dagger_{\mathbf{k}'} U(t_2, t_1) c_{\mathbf{k}'} | \Psi_n(t_0) \rangle s(t_1) s(t_2).$$

1. ρ_n: distribution of the final state of pumping (initial state of probing).
2. Probe field is $\mathbf{E} = s(t) \mathbf{E}_0 \mathrm{e}^{-\mathrm{i}\omega_0 t} + \text{c.c.}$, and the transition matrix is $M^{fc}_{\mathbf{k}\mathbf{k}'} = \langle f \mathbf{k} | -\mathbf{d} \cdot \mathbf{E}_0 | c \mathbf{k}' \rangle$; c is the probed electron, f is the out-going state.
3. The $\mathrm{e}^{-\mathrm{i}(E_n - \omega)(t_1 - t_2)}$ factor gives half of energy conservation condition; ω is driving frequency ω_0 shifted by work function.
4. $\langle \Psi_n | \cdots | \Psi_n \rangle$: electron Green function with excited state background $|\Psi_n\rangle$; it gives the structure of $|\Psi_n\rangle$ in electron basis, and the second half of energy conservation condition (energy after one electron being kicked out);
5. $s(t_1) s(t_2)$: shape of probe pulse; broadening $\delta(E_n - \omega - E_{\text{after}})$

Successful example: exciton

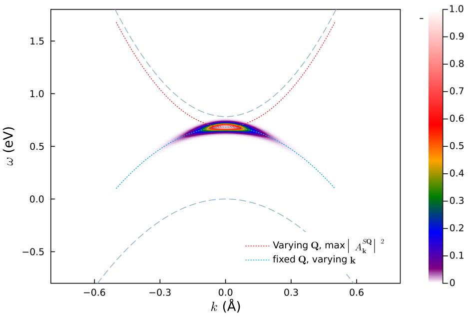
- Below we work with 2D material $\Rightarrow \mathbf{k}_{\parallel}^{\text{out}} = \mathbf{k}'$; we refer to $\mathbf{k}_{\parallel}^{\text{out}}$ as $\mathbf{k}$
- Only consider valence band top and conduction band valley: parabolic bands

ARPES response of an exciton (besides valence band electron)

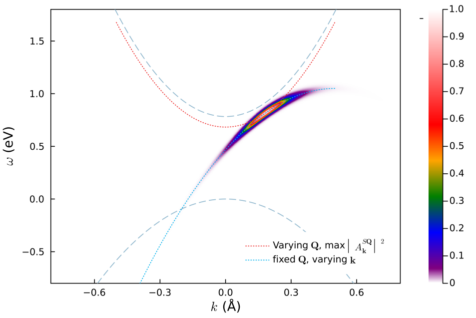
$$P(t) = \sum_{S,\mathbf{Q}} \rho_{S\mathbf{Q}} \left| A_{\mathbf{k}'}^{S\mathbf{Q}} \right|^2 \left| M_{\mathbf{k}\mathbf{k}'}^{fc} \right|^2 \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \, \mathrm{e}^{-\mathrm{i}(E_{S\mathbf{Q}} + \epsilon_{v\mathbf{k}'-\mathbf{Q}} - \omega)(t_1 - t_2)} s(t_1) s(t_2).$$

- Detection of $\left|A_{\mathbf{k}}^{S\mathbf{Q}}\right|^2$
- $\mathbf{Q} = 0 \Rightarrow$ dispersion relation $\omega = \epsilon_{v\mathbf{k}}$ (energy conservation)
- $\mathbf{Q}$ obeys $\mathrm{e}^{-\beta E_{\mathbf{Q}}}$ distribution: dispersion relation is $\omega = E_{\mathrm{g}} + E_{\mathrm{B}} + \frac{\mathbf{k}^2}{2m_{\mathrm{e}}}$ (energy conservation; $\left|A_{\mathbf{k}}^{S\mathbf{Q}}\right|^2$ reaches peak when $\mathbf{v}_{\mathrm{e}} = \mathbf{v}_{\mathrm{h}}$)

Successful example: exciton



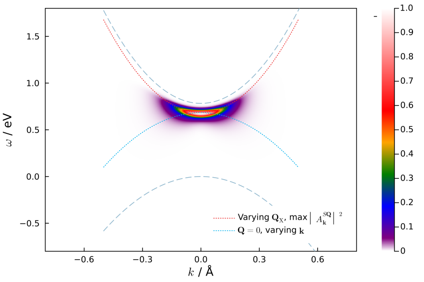
Single exciton, $\mathbf{Q} = 0.0\,\text{Å}^{-1}$



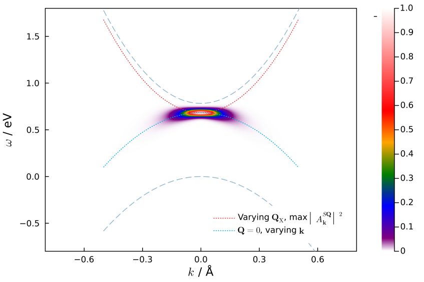
Single exciton, $\mathbf{Q} = 0.5\,\text{Å}^{-1}$

- The center of the signature is on a replica of the conduction band
- The shape of the signature is a replica of the valence band

Successful example: exciton



Thermalized exciton, $\beta = 10\,\text{eV}$



Thermalized exciton, $\beta = 100\,\text{eV}$

- The center of the signature is on a replica of the conduction band
- The shape of the signature is a replica of the valence band
- When excitons are hot, the dispersion relation is the conduction band; when they are cold, the dispersion relation is the valence band

Trion in two-band model

Configuration of trion structure

- Two holes, one electron (what likely happens in ARPES)
- *Two holes on one band* – to simplify analysis
- *No hole scattering after the electron is kicked out* – realistic or not?

$$H = \frac{(\mathbf{k}_\mathrm{e} - \mathbf{w})^2}{2m_\mathrm{e}} + E_\mathrm{g} + \frac{\mathbf{k}_\mathrm{h1}^2}{2m_\mathrm{h}} + \frac{\mathbf{k}_\mathrm{h2}^2}{2m_\mathrm{h}} + V(\mathbf{r}_\mathrm{h1} - \mathbf{r}_\mathrm{h2}) - V(\mathbf{r}_\mathrm{e} - \mathbf{r}_\mathrm{h1}) - V(\mathbf{r}_\mathrm{e} - \mathbf{r}_\mathrm{h2}). \quad (1)$$

Trion in two-band model

Redefining coordinates What we want: $\mathbf{k}_{\mathrm{e,h1,h2}} \to \mathbf{P}, \mathbf{k}_1, \mathbf{k}_2$, following these constraints:

$$\mathbf{k}_{1,2} = -\mathrm{i}\,\hbar\partial_{\mathbf{r}_{1,2}} = \text{const}, \quad \mathbf{r}_{1,2} = \mathbf{r}_{\mathrm{h}1,2} - \mathbf{r}_{\mathrm{e}}, \quad \mathbf{R} = \mathrm{i}\,\partial_{\mathbf{P}} = \frac{m_{\mathrm{h}}\mathbf{r}_{\mathrm{h}1} + m_{\mathrm{h}}\mathbf{r}_{\mathrm{h}2} + m_{\mathrm{e}}\mathbf{r}_{\mathrm{e}}}{2m_{\mathrm{h}} + m_{\mathrm{e}}}.$$

It can be verified that with

$$\mathbf{P} = \mathbf{k}_{\mathrm{e}} + \mathbf{k}_{\mathrm{h}1} + \mathbf{k}_{\mathrm{h}2}, \quad \mathbf{k}_{1,2} = -\mathrm{i}\,\hbar\partial_{\mathbf{r}_{1,2}} + \frac{m_{\mathrm{h}}}{2m_{\mathrm{h}} + m_{\mathrm{e}}}\mathbf{w}, \tag{2}$$

$$M = 2m_{\mathrm{h}} + m_{\mathrm{e}}, \quad \mu = \frac{m_{\mathrm{e}}m_{\mathrm{h}}}{m_{\mathrm{e}} + m_{\mathrm{h}}}, \quad H_{\mathrm{X}} = -\frac{\nabla^2}{2\mu} + V(\mathbf{r}), \tag{3}$$

$$H = \underbrace{H_{\mathrm{X}}(\mathbf{r}_1) + H_{\mathrm{X}}(\mathbf{r}_2) - \frac{\hbar^2\nabla^2}{2m_{\mathrm{e}}} + V(\mathbf{r}_1 - \mathbf{r}_2)}_{\text{causing } E_{\mathrm{B}}} + \frac{\mathbf{P}^2}{2m_{\mathrm{T}}} + E_{\mathrm{g}} \tag{4}$$

That's to say: a trion, when the two holes of it are of the same species, can be seen as the bound state of two excitons.

Trion wave function Thus in this specific case:

$$\phi_{\mathrm{T}}(\mathbf{r}_{\mathrm{e}}, \mathbf{r}_{\mathrm{h1}}, \mathbf{r}_{\mathrm{h2}}) = \sum_{S_1, S_2} \phi_{\mathrm{X}}^{S}(\mathbf{r}_1) \phi_{\mathrm{X}}^{S}(\mathbf{r}_2) \, \mathrm{e}^{\mathrm{i} \, \mathbf{P} \cdot \mathbf{R}}, \tag{5}$$

where $\mathbf{r}_{1,2}$ are defined above.

The below ansatz is frequently used:

$$\phi_{\mathrm{T}}(\mathbf{r}_1, \mathbf{r}_2) \propto \phi_{1\mathrm{s}}(\mathbf{r}_1; a) \phi_{1\mathrm{s}}(\mathbf{r}_2; b) + \phi_{1\mathrm{s}}(\mathbf{r}_1; b) \phi_{1\mathrm{s}}(\mathbf{r}_2; a) \tag{6}$$

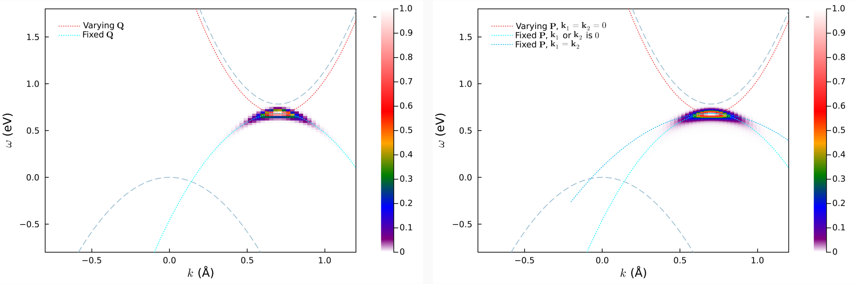
where a, b are exciton radii.

In the tentative plots below We ignore spin and choose $S_1 = S_2 = 1\text{s}$. The ARPES response (here ϵ_v are *negative*):

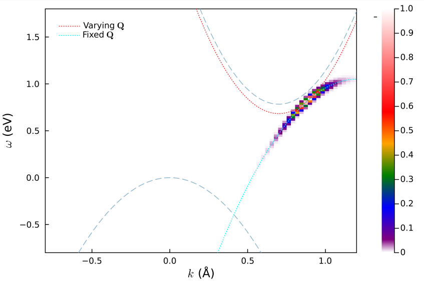
$$
\begin{aligned}
P_{\mathbf{k}}(t) = \sum_{\mathbf{P}} \rho_{\mathbf{P}} \sum_{\mathbf{k}_{\mathrm{h}1}, \mathbf{k}_{\mathrm{h}2}} \sum_{S_1, S_2} \left| M^{fc}_{\mathbf{k}\mathbf{k}_{\mathrm{e}}} \right|^2 \left| A_{S_1 S_2} \right|^2 \left| \phi_{S_1}(\mathbf{k}_1) \right|^2 \left| \phi_{S_2}(\mathbf{k}_2) \right|^2 \\
\times \int_{t_0}^{t} \mathrm{d}t_1 \int_{t_0}^{t} \mathrm{d}t_2 \, \mathrm{e}^{-\mathrm{i}(E_{S\mathbf{P}} + \epsilon_{v\mathbf{k}_{\mathrm{h}1}} + \epsilon_{v\mathbf{k}_{\mathrm{h}2}} - \omega)(t_1 - t_2)} s(t_1) s(t_2)
\end{aligned}
\tag{7}
$$

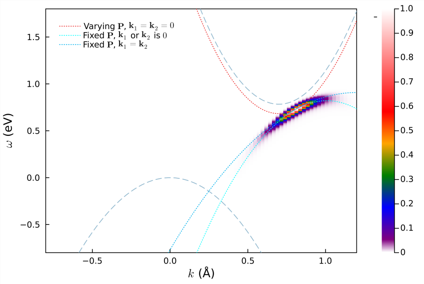
Signature maximum: $\mathbf{k}_1 = 0$ or $\mathbf{k}_2 = 0$, or $\mathbf{k}_1 = \mathbf{k}_2$?

Trion and exciton: $\mathbf{Q} = \mathbf{w}$



Main difference: curvature. In trion the signature partially has the shape of $2\epsilon_{\mathrm{v},\mathbf{k}/2}$

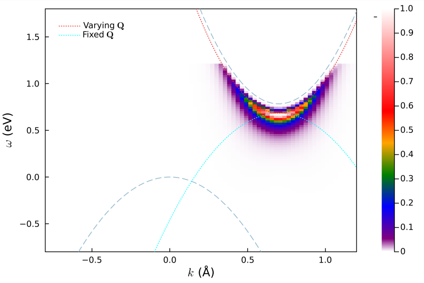


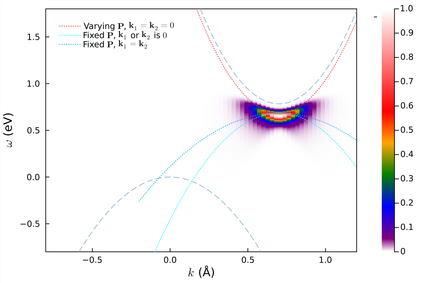


- The signature curvature difference is more obvious.
- The positions of the signatures are different!

$$\mathbf{k}_{\text{exciton, max}} = \frac{m_\mathrm{e}\mathbf{Q} + m_\mathrm{h}\mathbf{w}}{m_\mathrm{e} + m_\mathrm{h}}, \quad \mathbf{k}_{\text{trion, max}} = \frac{m_\mathrm{e}}{2m_\mathrm{h} + m_\mathrm{e}}\mathbf{P} + \frac{2m_\mathrm{h}}{2m_\mathrm{h} + m_\mathrm{e}}\mathbf{w}.$$

Exciton and trion: thermalized, $\beta = 10$





The trion calculation is not well-conserved: the sampling grid of $\mathbf{P}$ is too small; I don't expect to see any large difference because the shape of the two signatures should both follow ϵ_{c}.

Conclusion

- Trion signature on ARPES spectrum looks similar to that of exciton
- The finite-T induced "upper" dispersion of the two is the same
- The trion and exciton binding energies are different
- With finite momenta, exciton and trion signatures are different in shape and position.