Limitations of time-dependent mean-field approximations to second-order nonlinear optical phenomena

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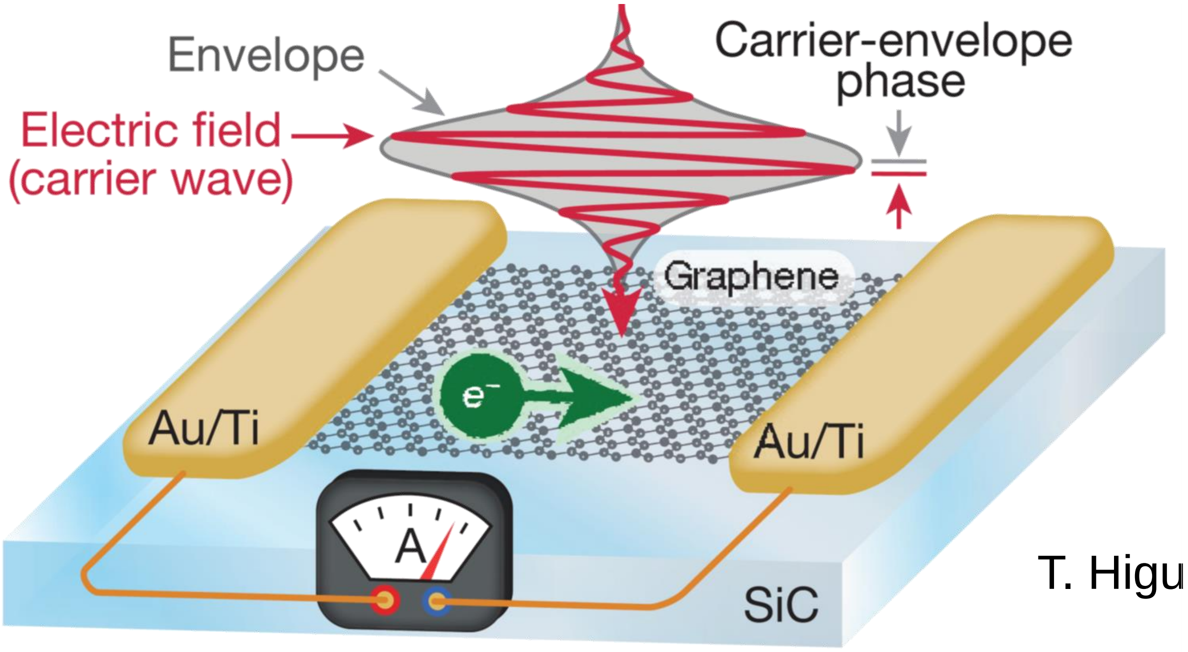
Introduction

Strong field physics (including attosecond physics)

Intense and short laser pulses induce nonlinear ultrafast phenomena in solids.

Opt-electronic device (PetaHertz electronics)



T. Higuchi, *et al*, Nature 550,224 (2017)

Our research aim

- To understand the microscopic mechanism of such strongly-nonlinear ultrafast phenomena in solids.
- For this aim, we employ the first-principles calculation based on time-dependent density functional theory (TDDFT).

Lowest order nonlinear current injection

Second-order nonlinear optical

Second-order nonlinear polarization (time-domain)

$$P^{(2)}(t) = \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' \chi^{(2)}(t-t', t-t'') E(t') E(t''),$$

Second-order nonlinear polarization (frequency domain)

$$\tilde{P}^{(2)}(\omega_\Sigma) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \tilde{\chi}^{(2)}(\omega_\Sigma; \omega', \omega_\Sigma - \omega') \tilde{E}(\omega') \tilde{E}(\omega_\Sigma - \omega'),$$

Second-order susceptibility (Low frequency response limit; $\omega_\Sigma = \omega' + \omega'' \to 0$)

J. E. Sipe et al., PRB 61, 5337 (2000)

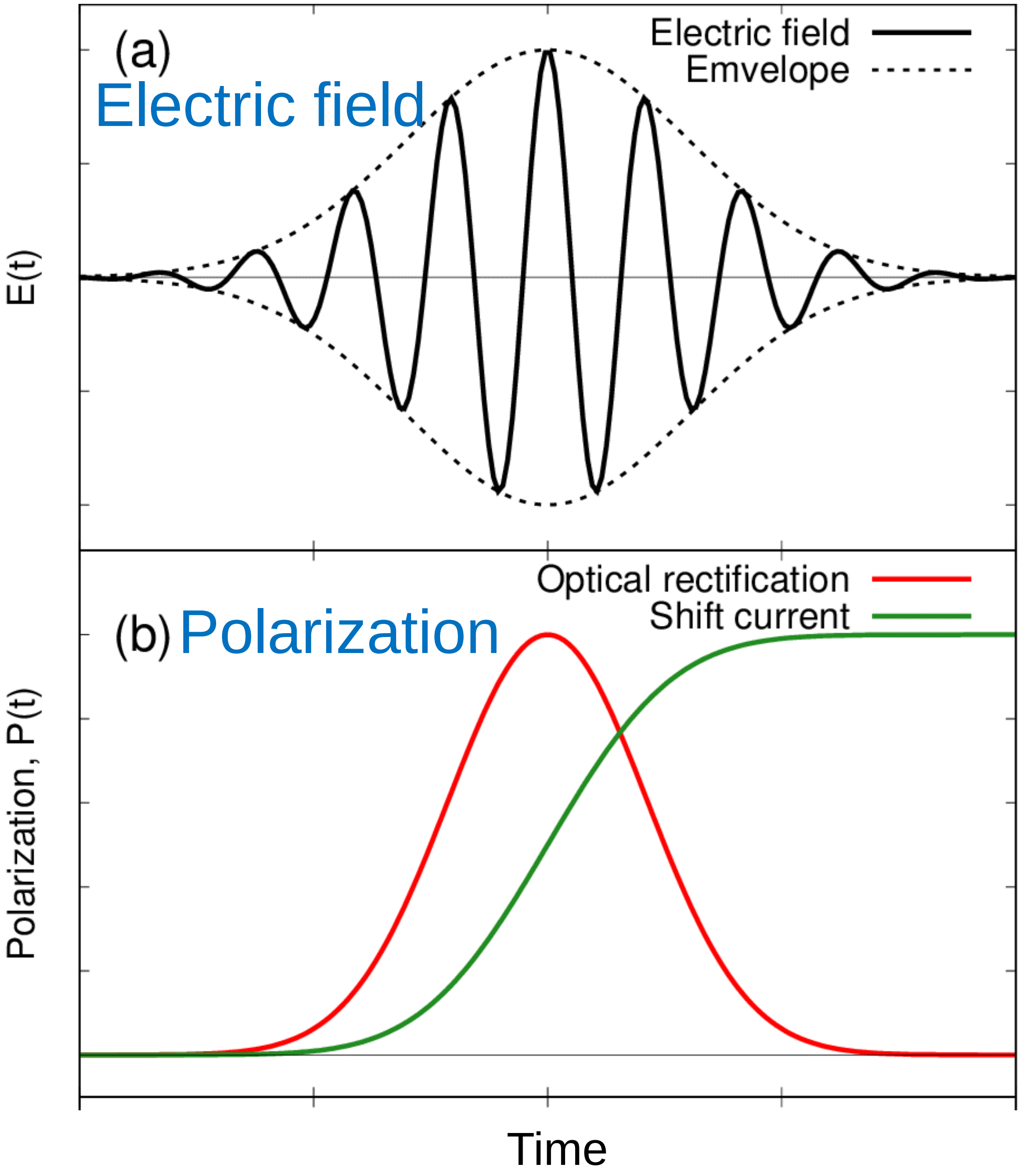
$$\tilde{\chi}(\omega_\Sigma, \omega', \omega'') = \tilde{\chi}^{(2)}_{\mathrm{rec}}(\omega', \omega'') + \frac{\tilde{\sigma}^{(2)}_{\mathrm{sft}}(\omega', \omega'')}{-i\omega_\Sigma} + \frac{\tilde{\eta}^{(2)}_{\mathrm{inj}}(\omega', \omega'')}{(-i\omega_\Sigma)^2},$$

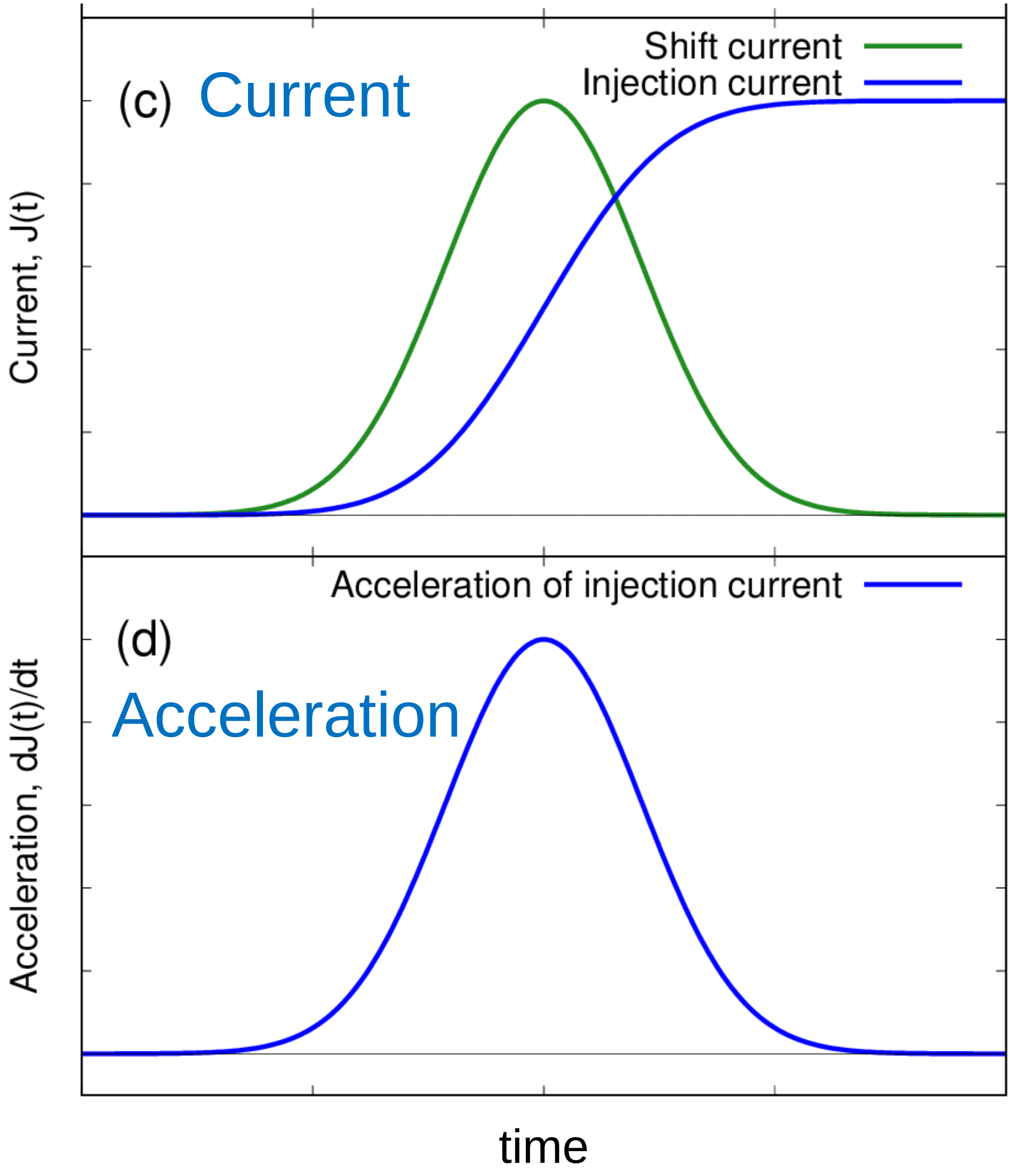
Optical rectification (光整流効果)

Shift current(シフト電流)

Injection current

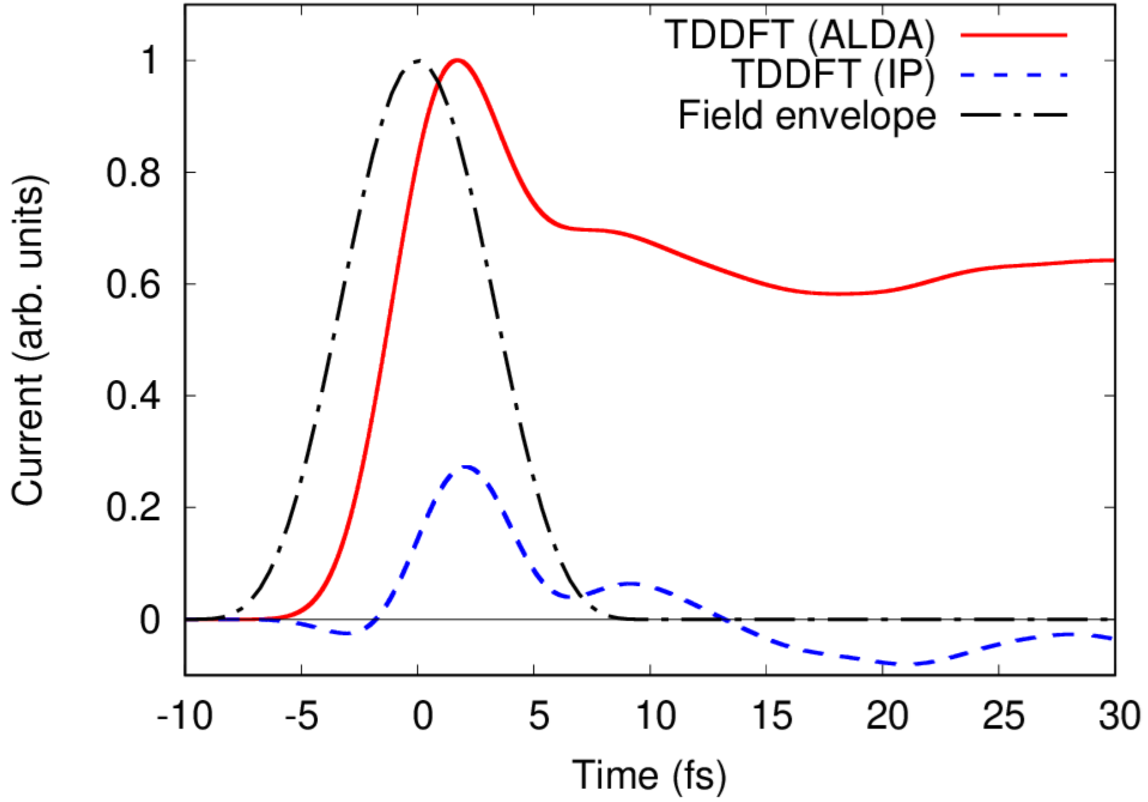
Second-order nonlinear optical response in time domain

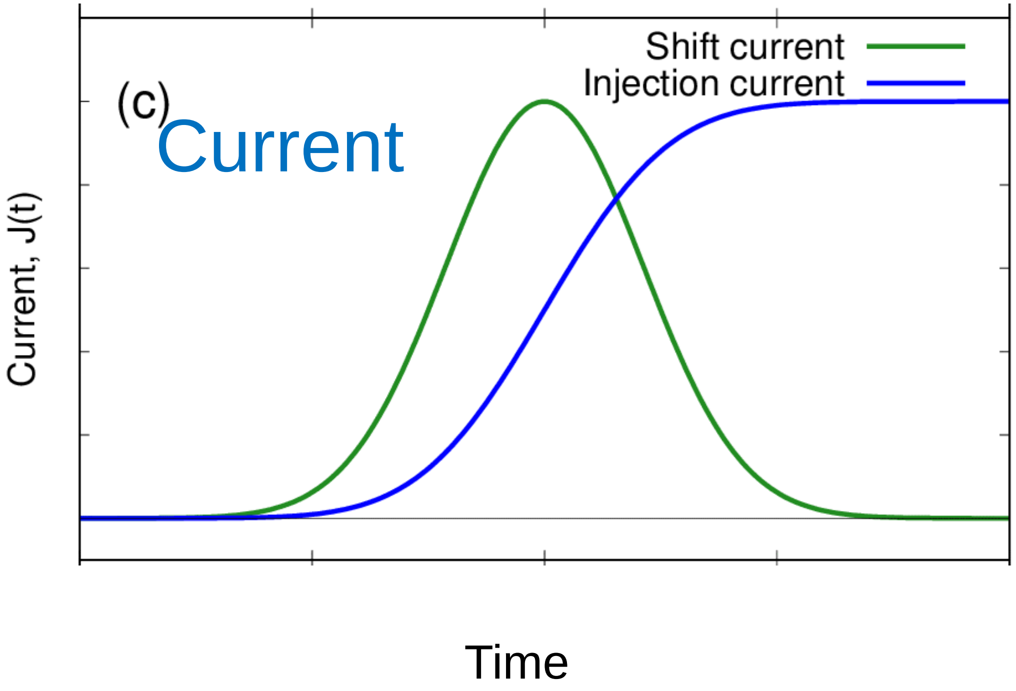




Mean-field artifact?

Photo-induced current in BaTiO3 under linearly polarized light pulse





- TDDFT (mean-field) calculations shows the residual current even after the irradiation of linearly polarized light.
- The residual DC current is classified as the injection current, and it is usually observed under circular/elliptically polarized light
- The residual DC current indicates a breakdown of the time-reversal symmetry. Artifact?

Perturbation analysis (Exact many-body Schrödinger eq.)

Many-body Schrödinger eq.

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = \hat{H}(t)\left|\Psi(t)\right\rangle,$$

$$\hat{H}(t) = \sum_i \left[\frac{1}{2m_e}\left(\boldsymbol{p}_i + e\boldsymbol{A}(t)\right)^2 + v(\boldsymbol{r}_i)\right] + \frac{1}{2}\sum_{ij} w(\boldsymbol{r}_i - \boldsymbol{r}_j)$$

Perturbative expansion & eigen function expansion

$$|\tilde{\Psi}(t)\rangle = \exp\left[-\frac{i}{\hbar}E_0 t - \frac{i}{\hbar}\int^t dt' E^{(1)}(t') - \frac{i}{\hbar}\int^t dt' E^{(2)}(t')\right]\left[|\Phi_0\rangle + |\delta\Psi^{(1)}(t)\rangle + |\delta\Psi^{(2)}(t)\rangle\right]$$

$$|\delta\Psi^{(1)}(t)\rangle = \sum_{a\neq 0} C_a^{(1)}(t) e^{-i\Omega_a t}|\Phi_a\rangle,$$

$$|\delta\Psi^{(2)}(t)\rangle = \sum_{a\neq 0} C_a^{(2)}(t) e^{-i\Omega_a t}|\Phi_a\rangle,$$

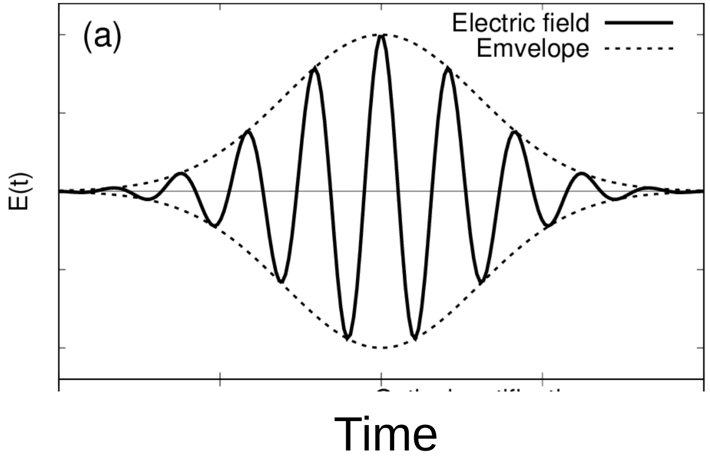
DC current after the pulse ends (with exact many-body TDSE)

We assume the laser-fields vanish after the time, t_f: $\boldsymbol{A}(t) = 0$ for $t > t_f$

$$\boldsymbol{J}^{(2)}_{\mathrm{dc}} = \lim_{T\to\infty} \frac{1}{T} \int_{t_f}^{t_f+T} dt \boldsymbol{J}^{(2)}(t)$$

$$= -\frac{e}{m_e} \sum_a |C_a^{(1)}(t_f)|^2 \langle \Phi_a | \boldsymbol{P} | \Phi_a \rangle$$

$$= -\frac{e}{m_e} \sum_a \left| \frac{e}{m_e} \frac{1}{i\hbar} \tilde{\boldsymbol{A}}(\Omega_a) \cdot \langle \Phi_a | \boldsymbol{P} | \Phi_0 \rangle \right|^2 \langle \Phi_a | \boldsymbol{P} | \Phi_a \rangle.$$

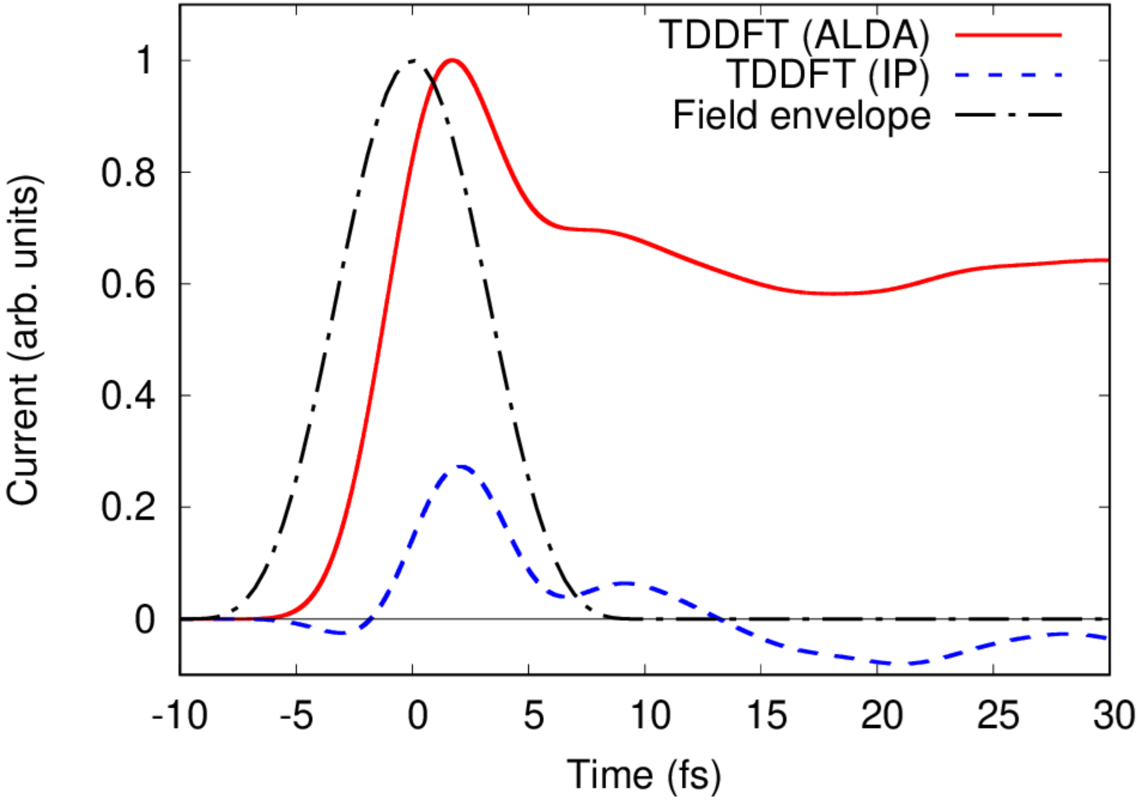


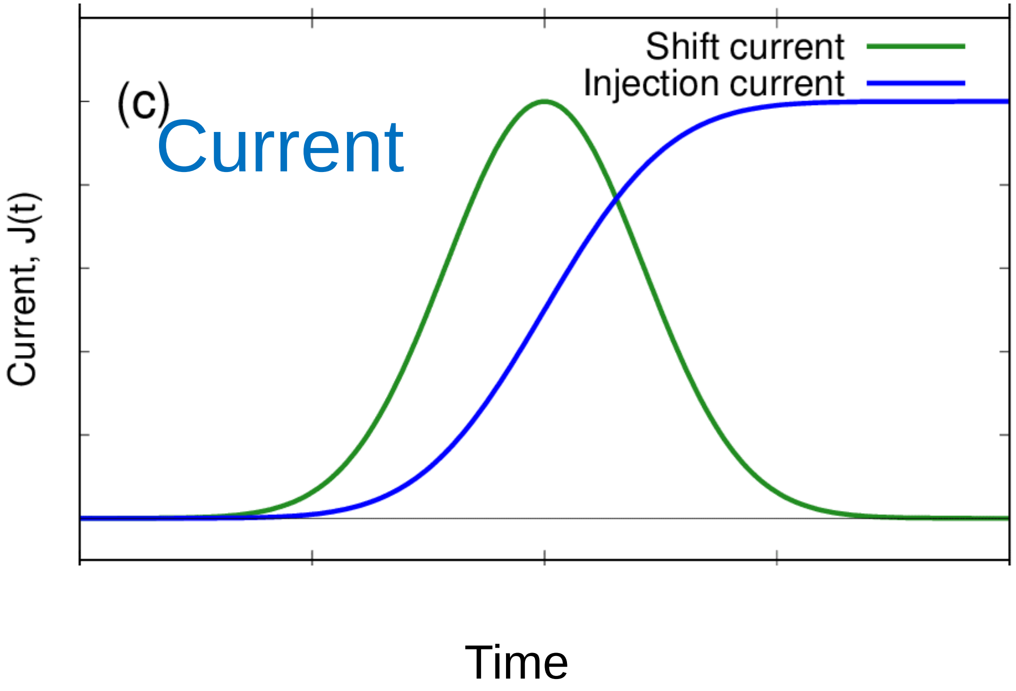
Assuming the Hermiteness of the problem, we can analytically prove that the residual current is ZERO under linearly polarized light.
=> Exact many-body Schrodinger equation forbids the injection current under linearly polarized light.

Shunsuke A. Sato, Angel Rubio, arXiv:2310.08875 [cond-mat.mtrl-sci]

Mean-field artifact

Photo-induced current in BaTiO3

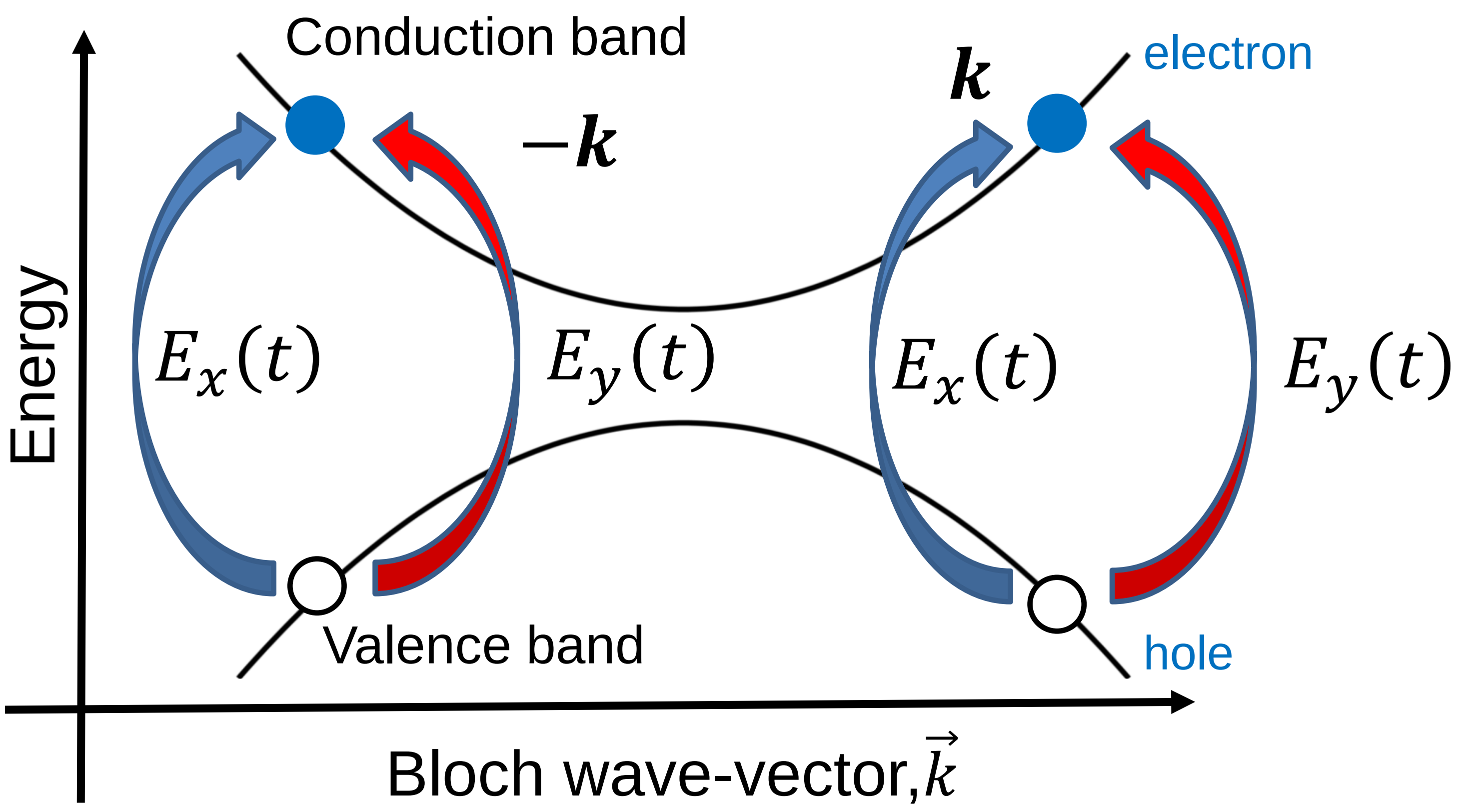




Injection current under circularly polarized light

Circularly polarized light

$$\boldsymbol{E}(t) = \boldsymbol{e}_x E_x(t) + \boldsymbol{e}_y E_y(t)$$



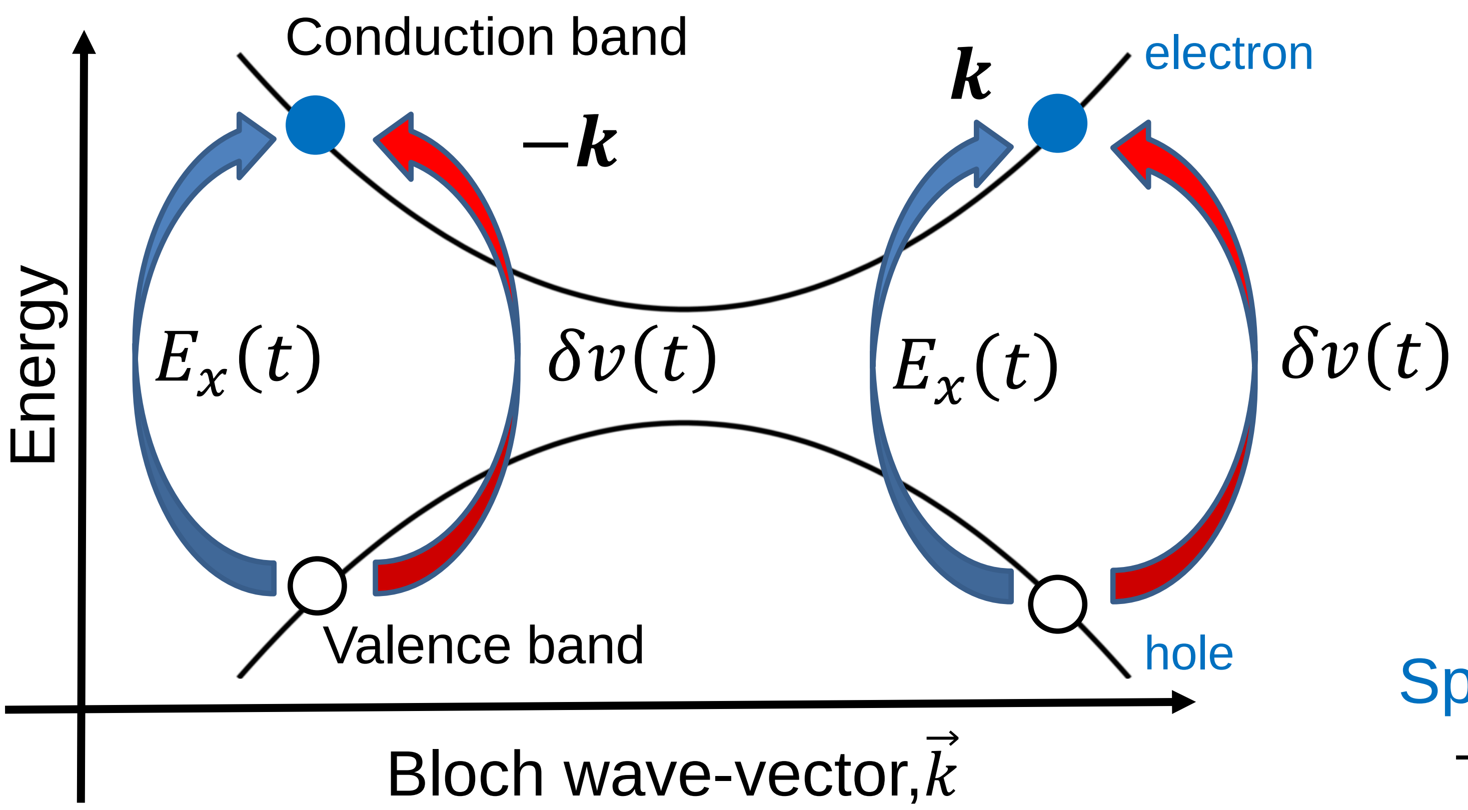
Mechanism of injection current

1. Circularly polarized light causes the quantum interference between two excitation paths.
2. Due to the interference, different photo-carrier population can be created at $\boldsymbol{k}$ and $-\boldsymbol{k}$ points.
3. The population imbalance causes the residual current.

Injection current in the mean-field approximation

Linearly polarized light

$$\boldsymbol{E}(t) = \boldsymbol{e}_x E_x(t)$$



Mechanism of injection current

1. An excitation path caused by the electric field is interfered with a self-excitation path via the induced field.
2. Due to the interference, different photo-carrier population can be created at $\boldsymbol{k}$ and $-\boldsymbol{k}$ points.
3. The population imbalance causes the residual current.

Spontaneous symmetry breaking?

The mean field spontaneously breaks the time-reversal symmetry of the system via the self-excitation path.

Conclusion

- We analyzed the shift-current (second-order nonlinear optical effect) for $BaTiO_3$ from the TDDFT calculation, and we found the injection current induced by linearly polarized light.
- We analyzed the exact many-body Schrodinger equation with perturbation theory, and we found that the generation of the injection current by linearly polarized light is forbidden. Hence, the above findings are mean-field artifacts.
- Further analysis clarified that the unphysical injection current in the mean-field theories are generated by the quantum interference opened via the self-excitation path through the time-dependent mean-field.