Symmetry properties of attosecond transient absorption spectroscopy in crystalline dielectrics

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We theoretically investigate a relation between the crystalline symmetry and the transient modulation of optical properties of crystalline dielectrics in pump-probe measurements using intense pump and attosecond probe fields. When the photon energy of the pump field is much below the bandgap energy, the modulation of the optical conductivity is caused by the intraband electronic motion, that is, the dynamical Franz-Keldysh effect. We analytically investigate symmetry properties of the modulated optical conductivity utilizing the Houston function and derive a formula that relates the temporal oscillation in the absorption with the transformation properties of the modulated optical conductivity. To verify the validity of the formula, we perform real-time first-principles calculations based on the time-dependent density functional theory for a pump-probe process taking 4H-SiC crystal as an example.

I. INTRODUCTION

Recent progress in attosecond metrology has made it possible to investigate electron motion in solids in a timescale less than a cycle of an optical pulse [1]. To explore the ultrafast electron motion, the attosecond transient absorption spectroscopy (ATAS) method has been often utilized [2–4]. In the ATAS measurements, a strong pump pulse of visible or infrared frequency and a weak attosecond probe pulse irradiate on a thin film with a certain time delay. The modulation of the optical absorption of the probe pulse is used to explore the ultrafast change of optical properties of the thin film. In a number of measurements in dielectric materials, field-driven oscillations of the absorption change as a function of the pump-probe delay time have been observed [5–10].

Depending on the choices of parameters of applied laser pulses and materials, several mechanisms that contribute to modulations in ATAS have been proposed. Among them, the intraband motion of electrons induced by the strong pump electric field that causes the dynamical Franz-Keldysh effect (DFKE) is considered to be one of the primary mechanisms. The Franz-Keldysh effect (FKE) is a modulation of the absorption properties of dielectrics at around the bandgap energy under a static electric field and has been extensively investigated since it was first discussed more than half a century ago [11–18]. The DFKE is the modulation under an alternating electric field and has also been investigated in a number of literatures [19–25].

In Ref. [26], it has been analytically shown that the frequency of ATAS modulation is twice the pump frequency Ω in an isotropic two-band model. It was also confirmed numerically by the first-principles calculations conducted for a crystalline diamond. There are some cases where oscillations different from 2Ω frequency: an oscillation with frequency Ω was theoretically described in two-dimensional material [27], while an oscillation with 3Ω has been reported in GaN [7]. Although a relation between the crystalline symmetry and

the static FKE has been discussed [17,28,29], such analysis has not been reported for the time-resolved DFKE. We note that, for the high harmonic generation in solids, dynamical symmetries that involve temporal as well as spatial invariances have been extensively studied [30–43].

In the present paper, we first theoretically investigate a relation between symmetry properties of a dielectric crystal and its DFKE response using an analytical framework extending that introduced in Ref. [26]. We will show that the oscillation property of the time-resolved DFKE response is determined from the transformation properties of the pump-modulated conductivity tensor under the point group symmetry operation of the crystal. We next numerically verify this statement by performing first-principles calculations employing the time-dependent density functional theory (TDDFT) [44] for hexagonal silicon carbide (4H-SiC) crystal. We solve the time-dependent Kohn-Sham (TDKS) equation in the time domain and directly simulate ATAS in the crystal. We show that the calculated results under several polarization conditions confirm the validity of our analytical results.

This paper is organized as follows. In Sec. II, a general description of the ATAS is considered introducing a frequency-resolved absorbance function. Section III describes analytical considerations for DFKE and its symmetry dependence. In Sec. IV, we present a formalism and results of real-time first-principles calculations. In Sec. V, a conclusion is presented.

II. TRANSIENT ABSORPTION IN A UNIT CELL OF SOLIDS

We first provide a theoretical description of ATAS extending and clarifying the description presented in Ref. [26]. We introduce a transient conductivity that depends both on the time and frequency. In the derivation, we put emphasis on the relation between the frequency-dependent absorption spectrum of the probe pulse and the transient conductivity under the intense pump field.

A. Frequency-dependent modulation of probe absorption

We consider a unit cell of dielectrics under irradiation of intense pump and weak probe fields. In ATAS, the frequency of the probe pulse is much higher than that of the pump pulse. We assume that there is no overlap between two pulses in the frequency domain. Assuming that both wavelengths of the pump and the probe pulses are sufficiently longer than the size of the unit cell, we employ a dipole approximation treating electric fields of the pump and the probe pulses as spatially uniform fields. This assumption will be justified for attosecond probe fields up to, at least, a few tens of eV.

We express the electric field applied to the unit cell as $\boldsymbol{E}(t)$. It induces electron dynamics and charge current in the unit cell. We express the macroscopic charge-current density as $\boldsymbol{I}(t)$ that is obtained as a spatial average of the microscopic current density in the unit cell. The optical absorption can be evaluated from the work done by the electric field $\boldsymbol{E}(t)$ to electrons in the unit cell. It is expressed as

$$W[\boldsymbol{E}] = \int dt \boldsymbol{I}[\boldsymbol{E}](t) \cdot \boldsymbol{E}(t). \tag{1}$$

In the above expression, we write the work as $W[\boldsymbol{E}]$ and the macroscopic current density as $\boldsymbol{I}[\boldsymbol{E}](t)$ to stress that they are defined for the electric field $\boldsymbol{E}(t)$.

To discuss frequency-resolved signals, we rewrite the work as the integral over frequency,

$$W[\boldsymbol{E}] = \frac{1}{\pi} \int_0^\infty d\omega \frac{d\tilde{W}}{d\omega}, \tag{2}$$

where the frequency-resolved work is defined by

$$\frac{d\tilde{W}}{d\omega} = \mathrm{Re}[\tilde{\boldsymbol{I}}[\boldsymbol{E}](\omega) \cdot \tilde{\boldsymbol{E}}^*(\omega)]. \tag{3}$$

Here we introduce time-frequency Fourier transformations, for example, by

$$\tilde{\boldsymbol{E}}(\omega) = \int_{-\infty}^\infty dt e^{i\omega t} \boldsymbol{E}(t). \tag{4}$$

We consider three cases, pump only, probe only, and pump plus probe. Expressing the pump field as $\boldsymbol{E}^{\mathrm{pump}}(t)$ and the probe field as $\boldsymbol{E}^{\mathrm{probe}}(t)$, we have

$$\frac{dW^{\mathrm{pump}}}{d\omega} = \mathrm{Re}\{\tilde{\boldsymbol{I}}[\boldsymbol{E}^{\mathrm{pump}}](\omega) \cdot \tilde{\boldsymbol{E}}^{\mathrm{pump}*}(\omega)\}, \tag{5}$$

$$\frac{dW^{\mathrm{probe}}}{d\omega} = \mathrm{Re}\{\tilde{\boldsymbol{I}}[\boldsymbol{E}^{\mathrm{probe}}](\omega) \cdot \tilde{\boldsymbol{E}}^{\mathrm{probe}*}(\omega)\}, \tag{6}$$

$$\frac{dW^{\mathrm{pump+probe}}}{d\omega} = \mathrm{Re}\{\tilde{\boldsymbol{I}}[\boldsymbol{E}^{\mathrm{pump+probe}}](\omega) \cdot \tilde{\boldsymbol{E}}^{\mathrm{pump+probe}*}(\omega)\}, \tag{7}$$

where $\tilde{\boldsymbol{E}}^{\mathrm{pump+probe}}(\omega)$ is given by $\tilde{\boldsymbol{E}}^{\mathrm{pump}}(\omega) + \tilde{\boldsymbol{E}}^{\mathrm{probe}}(\omega)$. The modulation in the ATAS is then given as the difference between $dW^{\mathrm{pump+probe}}/d\omega$ and $dW^{\mathrm{probe}}/d\omega$.

In the following development, we will consider a quantity $A(\omega)$ defined below instead of $dW^{\mathrm{pump+probe}}/d\omega$,

$$A(\omega) = \mathrm{Re}[\delta\tilde{\boldsymbol{I}}(\omega) \cdot \tilde{\boldsymbol{E}}^{\mathrm{probe},*}(\omega)], \tag{8}$$

where we introduce a modulated current density of the probe pulse,

$$\delta\tilde{\boldsymbol{I}}(\omega) = \tilde{\boldsymbol{I}}[E^{\mathrm{pump+probe}}](\omega) - \tilde{\boldsymbol{I}}[E^{\mathrm{pump}}](\omega). \tag{9}$$

We note that $A(\omega)$ accurately describes the absorption in the frequency region of the probe pulse,

$$A(\omega) \simeq \frac{dW^{\mathrm{pump+probe}}}{d\omega} \quad (\omega_1^{\mathrm{probe}} < \omega < \omega_2^{\mathrm{probe}}), \tag{10}$$

where $\omega_{1/2}^{\mathrm{probe}}$ is the lower/upper bound of the frequency spectrum of the probe pulse. To understand it, we note that $\tilde{\boldsymbol{E}}^{\mathrm{pump}}(\omega)$ in $\tilde{\boldsymbol{E}}^{\mathrm{pump+probe}}(\omega)$ of Eq. (7) does not contribute in the probe frequency region, since we assume that there is no overlap between pump and probe fields in the frequency domain. A term containing $\tilde{\boldsymbol{I}}[E^{\mathrm{pump}}](\omega)$ of Eq. (9) in $A(\omega)$ does not contribute in the probe frequency region, since we assume that frequencies of the pump and the probe pulses are well separated. In practice, $\tilde{\boldsymbol{I}}[E^{\mathrm{pump}}](\omega)$ has a small contribution in the spectral region of the probe pulse through nonlinear effects such as high harmonic generation. However, the contribution will be extremely small since it is related with high order nonlinear processes. In the following, we will call $A(\omega)$ the frequency-resolved absorbance. We note that $A(\omega)$ was treated as a central quantity to discuss the modulation of the dielectric property in the literatures [8,26].

B. Conductivity under a strong pump field

We consider the current difference introduced in Eq. (9) in time domain,

$$\delta\boldsymbol{I}(t) = \boldsymbol{I}[E^{\mathrm{pump+probe}}](t) - \boldsymbol{I}[E^{\mathrm{pump}}](t). \tag{11}$$

Since we assume that the probe pulse is a weak perturbation, we may introduce a linear constitutive relation,

$$\delta I_\alpha(t) = \sum_\beta \int dt' \sigma_{\alpha\beta}(t, t') E_\beta^{\mathrm{probe}}(t'), \tag{12}$$

where α and β denote the Cartesian components, $\alpha, \beta = x, y, z$. Here we introduced a conductivity $\sigma_{\alpha\beta}(t, t')$ under the strong pump field, $\boldsymbol{E}^{\mathrm{pump}}(t)$. It depends on t and t' separately, since the pump field breaks the translational invariance in time.

We may express the constitutive relation in the frequency representation as

$$\delta\tilde{I}_\alpha(\omega) = \sum_\beta \int d\omega' \tilde{\sigma}_{\alpha\beta}(\omega, \omega') \tilde{E}_\beta^{\mathrm{probe}}(\omega'), \tag{13}$$

where the frequency-dependent conductivity is defined by

$$\tilde{\sigma}_{\alpha\beta}(\omega, \omega') = \int \frac{dt\,dt'}{2\pi} e^{i\omega t - i\omega' t'} \sigma_{\alpha\beta}(t, t'). \tag{14}$$

This conductivity is related to the ordinary conductivity in the absence of the pump pulse, which we denote as $\tilde{\sigma}_{\alpha\beta}^0(\omega)$, by

$$\tilde{\sigma}_{\alpha\beta}[E^{\mathrm{pump}} = 0](\omega, \omega') = \delta(\omega - \omega')\tilde{\sigma}_{\alpha\beta}^0(\omega). \tag{15}$$

Using the conductivity thus defined, the frequency-resolved absorbance defined by Eq. (8) is expressed as

$$A(\omega) = \text{Re} \sum_{\alpha\beta} \int d\omega' \tilde{E}_\alpha^{\text{probe}*}(\omega) \tilde{\sigma}_{\alpha\beta}(\omega, \omega') \tilde{E}_\beta^{\text{probe}}(\omega'). \quad (16)$$

C. Periodic pump field

We next assume that the pump field is periodic in time with a frequency Ω,

$$\boldsymbol{E}^{\text{pump}}(t + T_\Omega) = \boldsymbol{E}^{\text{pump}}(t), \quad (17)$$

where $T_\Omega = 2\pi/\Omega$ is the period of the pump field. We assume that the conductivity has the same periodicity.

$$\sigma_{\alpha\beta}(t + T_\Omega, t' + T_\Omega) = \sigma_{\alpha\beta}(t, t'). \quad (18)$$

This assumption may be justified for systems without resonant absorption, for example, a wide-gap dielectric under a pump pulse whose photon energy is much below the bandgap energy. Hence, our discussion is restricted to the ATAS signal caused by the DFKE, which is a nonresonant process. We leave an extension to resonant processes where signal grows nonadiabatically in time as a future task.

To proceed, we write the two-time conductivity $\sigma_{\alpha\beta}(t, t')$ as $\sigma_{\alpha\beta}(t + s, t)$, and recognize it as a function of t and s. Then, it is a periodic function of t with the period T_Ω, and we may introduce a Fourier decomposition,

$$\sigma_{\alpha\beta}(t + s, t) = \sum_{n=-\infty}^{\infty} e^{in\Omega t} \sigma_{\alpha\beta}^{(n)}(s), \quad (19)$$

$$\sigma_{\alpha\beta}^{(n)}(s) = \frac{1}{T_\Omega} \int_0^{T_\Omega} dt\, e^{-in\Omega t} \sigma_{\alpha\beta}(t + s, t). \quad (20)$$

Using this property, we may express $\tilde{\sigma}_{\alpha\beta}(\omega, \omega')$ defined by Eq. (14) as

$$\tilde{\sigma}_{\alpha\beta}(\omega, \omega') = \sum_n \delta(\omega - \omega' + n\Omega) \tilde{\sigma}_{\alpha\beta}^{(n)}(\omega), \quad (21)$$

$$\tilde{\sigma}_{\alpha\beta}^{(n)}(\omega) = \int ds\, e^{i\omega s} \sigma_{\alpha\beta}^{(n)}(s). \quad (22)$$

Therefore the conductivity $\tilde{\sigma}_{\alpha\beta}(\omega, \omega')$ contributes only when $\omega - \omega'$ is equal to integer multiples of the pump frequency Ω. The frequency-resolved absorbance now becomes

$$A(\omega) = \text{Re} \sum_{\alpha\beta n} \tilde{E}_\alpha^{\text{probe}*}(\omega) \tilde{E}_\beta^{\text{probe}}(\omega + n\Omega) \tilde{\sigma}_{\alpha\beta}^{(n)}(\omega). \quad (23)$$

D. Transient absorption using impulsive probe pulse

To proceed, we next specify the pulse shape of the probe pulse. We first consider an impulsive field as an extreme case,

$$E_\alpha^{\text{I}}(t) = F_\alpha \delta(t - T), \quad (24)$$

where T specifies the time when the impulsive field is applied and F_α is a parameter that specifies the strength of the field in α direction. For this impulsive field, the induced current is given by

$$\delta I_\alpha^{\text{I}}(t) = \sum_\beta \sigma_{\alpha\beta}(t, T) F_\beta. \quad (25)$$

Taking Fourier transformation of the both sides, we have

$$\delta \tilde{I}_\alpha^{\text{I}}(\omega) = \sum_\beta \tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega) \tilde{E}_\beta^{\text{I}}(\omega), \quad (26)$$

where the conductivity $\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega)$ that depends on both time T and frequency ω is introduced as

$$\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega) = \int dt\, e^{i\omega(t-T)} \sigma_{\alpha\beta}(t, T)$$

$$= \sum_n e^{in\Omega T} \tilde{\sigma}_{\alpha\beta}^{(n)}(\omega). \quad (27)$$

Using this conductivity, the frequency-resolved absorbance of Eq. (8) is expressed as

$$A(\omega) = \text{Re} \sum_{\alpha\beta} F_\alpha F_\beta \tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega). \quad (28)$$

In this way, we can introduce the conductivity $\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega)$ with mixed indices, the time T that specifies when the impulsive field is applied and the frequency ω that specifies the frequency of the absorption of the probe pulse.

E. Transient absorption using general probe pulse

We next consider a more general case with a finite duration of the probe pulse. For a probe pulse applied at time $t = T$, we express the time profile of the probe pulse by

$$E_\alpha^{\text{probe}}(t) = f_\alpha(t - T), \quad (29)$$

where the function $f_\alpha(t)$ has a maximum at $t = 0$. The Fourier transform of the probe pulse is given by

$$\tilde{E}_\alpha^{\text{probe}}(\omega) = e^{i\omega T} \tilde{f}_\alpha(\omega). \quad (30)$$

The phase of the function $\tilde{f}_\alpha(\omega)$ may not depend much on the frequency. For example, if $f_\alpha(t)$ is an even function of t, $\tilde{f}_\alpha(\omega)$ is a real function. If $f_\alpha(t)$ is an odd function of t, $\tilde{f}_\alpha(\omega)$ is a pure imaginary function. In both cases, the phase part of $\tilde{f}_\alpha(\omega)$ shows no frequency dependence.

The frequency-resolved absorbance of Eq. (8) is calculated as

$$A(\omega) = \text{Re} \sum_{\alpha\beta n} \tilde{f}_\alpha^*(\omega) \tilde{f}_\beta(\omega + n\Omega) e^{in\Omega T} \tilde{\sigma}_{\alpha\beta}^{(n)}(\omega). \quad (31)$$

This result indicates again that the modulation in the absorption depends on the time T through the frequency Ω and its multiples.

In the ATAS, an extremely short attosecond pulse is used for the probe pulse. For such pulses, we may approximate $\tilde{f}_\beta(\omega + n\Omega) \simeq \tilde{f}_\beta(\omega)$, then Eq. (31) can be expressed as,

$$A(\omega) \simeq \text{Re} \sum_{\alpha\beta} \tilde{f}_\alpha^*(\omega) \tilde{f}_\beta(\omega) \tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega). \quad (32)$$

We thus find that the frequency-resolved modulation in the absorption of the probe pulse can be described using the impulsive time-resolved conductivity, $\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega)$, if the probe pulse is sufficiently short. In the next section, we focus on the symmetry properties of this conductivity.

III. ANALYTIC CONSIDERATION

A. Conductivity using Houston function

To investigate symmetry properties of the conductivity in the presence of a strong pump field, we utilize a model description in which the electronic system in a unit cell of the crystal is described by a single-electron Bloch equation. We first consider a static problem,

$$H_k u_{nk}(\boldsymbol{r}) \equiv \left[\tfrac{1}{2}(\boldsymbol{p} + \boldsymbol{k})^2 + V(\boldsymbol{r})\right] u_{nk}(\boldsymbol{r}) = \varepsilon_{nk} u_{nk}(\boldsymbol{r}), \quad (33)$$

where H_k and u_{nk} are the effective single-electron Hamiltonian and the Bloch orbital in the ground state, respectively. We next consider electron dynamics under a spatially uniform electric field which is described by the vector potential $\boldsymbol{A}(t)$. The Bloch orbital that describes electron dynamics under the electric field, $v_{nk}(\boldsymbol{r}, t)$, follows the time-dependent Schrödinger equation,

$$i \frac{\partial}{\partial t} v_{nk}(\boldsymbol{r}, t) = H_{k + \frac{1}{c} A(t)} v_{nk}(\boldsymbol{r}, t). \quad (34)$$

Here we assume that the same periodic potential $V(\boldsymbol{r})$ is used in Eqs. (33) and (34). The electric current density averaged over the unit cell is given by

$$\boldsymbol{I}(t) = -\frac{1}{V} \sum_{nk} f_{nk} \int_{\text{cell}} d\boldsymbol{r}\, v_{nk}^*(\boldsymbol{r}, t)$$
$$\times \left(\boldsymbol{p} + \boldsymbol{k} + \frac{\boldsymbol{A}(t)}{c} \right) v_{nk}(\boldsymbol{r}, t), \quad (35)$$

where V and f_{nk} are the volume of the unit cell and the occupation rate, respectively.

We will derive an explicit expression for the conductivity $\sigma_{\alpha\beta}(t, t')$ defined by Eq. (12) in this model. We express the vector potential for the pump pulse as $\boldsymbol{A}^{\text{pump}}(t)$ and for the probe pulse as $\boldsymbol{A}^{\text{probe}}(t)$. They are related to the electric field by $\boldsymbol{E}^{\text{pump,probe}}(t) = -(1/c)(d/dt)\boldsymbol{A}^{\text{pump,probe}}(t)$. The Hamiltonian with both pump and probe fields is given by

$$H_k^{\text{pump+probe}}(t)$$
$$= \frac{1}{2}\left[\boldsymbol{p} + \boldsymbol{k} + \frac{1}{c}\left\{ \boldsymbol{A}^{\text{pump}}(t) + \boldsymbol{A}^{\text{probe}}(t) \right\} \right]^2 + V(\boldsymbol{r})$$
$$= H_{K(t)} + \Delta V(t) + O((A^{\text{probe}})^2), \quad (36)$$

where we have defined $\boldsymbol{K}(t) = \boldsymbol{k} + \boldsymbol{A}^{\text{pump}}(t)/c$ and the perturbation potential $\Delta V(t) = \frac{1}{c}(\boldsymbol{p} + \boldsymbol{K}(t)) \cdot \boldsymbol{A}^{\text{probe}}(t)$. We express the current density defined by Eq. (35) as $\boldsymbol{I}^{\text{pump+probe}}(t) = \boldsymbol{I}^{\text{pump}}(t) + \delta \boldsymbol{I}(t)$, where $\delta \boldsymbol{I}(t)$ is the current density defined by Eq. (11). Using the standard procedure of the time-dependent perturbation theory, we obtain a formula for the conductivity defined by Eq. (12) as

$$\sigma_{\alpha\beta}(t, t') = n_e \delta_{\alpha\beta} \theta(t - t') + \frac{2}{V} \theta(t - t') \,\text{Im} \int_{t'}^{t} dt''$$
$$\times \sum_{k} \sum_{n \neq n'} f_{nk} \left[\boldsymbol{P}_{nn'}^k(t) \right]_\alpha \left[\boldsymbol{P}_{n'n}^k(t'') \right]_\beta, \quad (37)$$

where we have introduced the averaged electron number density, $n_e = \sum_{nk} f_{nk}/V$, and the matrix element of the

momentum operator,

$$\boldsymbol{P}_{nn'}^k(t) = \int_{\text{cell}} d\boldsymbol{r}\, w_{nk}^*(\boldsymbol{r}, t)\, \boldsymbol{p}\, w_{n'k}(\boldsymbol{r}, t). \quad (38)$$

Here, $w_{nk}(\boldsymbol{r}, t)$ is the Bloch orbital in the presence of the pump field only, which satisfies

$$i\frac{\partial}{\partial t} w_{nk}(\boldsymbol{r}, t) = H_{K(t)} w_{nk}(\boldsymbol{r}, t). \quad (39)$$

To proceed further, we approximate the time-dependent Bloch orbital $w_{nk}(\boldsymbol{r}, t)$ using the Houston function [19,45],

$$u_{nk}^{\text{H}}(\boldsymbol{r}, t) = u_{nK(t)}(\boldsymbol{r}) \exp\left[-i \int_{-\infty}^{t} d\tau\, \varepsilon_{nK(\tau)} \right]. \quad (40)$$

Then, Eq. (38) is given by

$$\boldsymbol{P}_{nn'}^k(t) \simeq (\boldsymbol{p})_{nn'}^{K(t)} \exp\left[i \int_{-\infty}^{t} d\tau\, \omega_{nn'}^{K(\tau)} \right], \quad (41)$$

where we have defined $(\boldsymbol{p})_{nn'}^k = \int_{\text{cell}} d\boldsymbol{r}\, u_{nk}^*\, \boldsymbol{p}\, u_{n'k}$ and $\omega_{nn'}^k = \varepsilon_{nk} - \varepsilon_{n'k}$. Using this matrix element, we have [26]

$$\sigma_{\alpha\beta}(t, t')$$
$$= n_e \delta_{\alpha\beta} \theta(t - t') + \frac{2}{V} \theta(t - t') \int_{t'}^{t} dt'' \sum_{k} \sum_{n \neq n'} f_{nk}$$
$$\times \text{Im}\left[(p_\alpha)_{nn'}^{K(t)} (p_\beta)_{n'n}^{K(t'')} \exp\left(i \int_{t''}^{t} d\tau\, \omega_{nn'}^{K(\tau)} \right) \right]. \quad (42)$$

Substituting Eq. (42) into Eq. (27), we have the following expression for the impulsive time-resolved conductivity:

$$\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega) = \frac{i n_e}{\omega} \delta_{\alpha\beta} + \frac{2}{V} \sum_{k} \sum_{n \neq n'} f_{nk} \int_{0}^{\infty} ds\, e^{i\omega s} \int_{0}^{s} dt''\, \text{Im}$$
$$\times (p_\alpha)_{nn'}^{K(T+s)} (p_\beta)_{n'n}^{K(T+t'')} \exp\left(i \int_{t''}^{s} d\tau\, \omega_{nn'}^{K(T+\tau)} \right). \quad (43)$$

Below, we will investigate the symmetry properties of the transient conductivity using this expression. For this purpose, we introduce a quantity $F_{\alpha\beta}^\omega[\boldsymbol{K}(t)]$ that is regarded as a functional of $\boldsymbol{K}(t) = \boldsymbol{k} + \boldsymbol{A}^{\text{pump}}(t)/c$,

$$F_{\alpha\beta}^\omega[\boldsymbol{K}(t)] = \sum_{n \neq n'} f_{nk} \int_{0}^{\infty} ds\, e^{i\omega s} \int_{0}^{s} dt''$$
$$\times (p_\alpha)_{nn'}^{K(s)} (p_\beta)_{n'n}^{K(t'')} \exp\left[i \int_{t''}^{s} d\tau\, \omega_{nn'}^{K(\tau)} \right]. \quad (44)$$

Using this quantity, we can rewrite the impulsive time-resolved conductivity as

$$\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega) = \frac{i n_e}{\omega} \delta_{\alpha\beta} - \frac{i}{V} \sum_{k} \left(F_{\alpha\beta}^\omega \left[\boldsymbol{k} + \boldsymbol{A}_T^{\text{pump}}(t)/c \right] \right.$$
$$\left. - F_{\alpha\beta}^{-\omega} \left[\boldsymbol{k} + \boldsymbol{A}_T^{\text{pump}}(t)/c \right]^* \right), \quad (45)$$

where we have introduced a time-shifted vector potential, $\boldsymbol{A}_T^{\text{pump}}(t) \equiv \boldsymbol{A}^{\text{pump}}(T + t)$. Hereafter, we will often use a notation $\tilde{\sigma}_{\alpha\beta}^\omega[\boldsymbol{A}_T^{\text{pump}}(t)]$ instead of $\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega)$ to stress that this conductivity is the functional of $\boldsymbol{A}_T^{\text{pump}}(t)$.

B. Symmetry properties of the time-resolved conductivity

Let us consider a point group symmetry operation of the crystal. We consider a 3×3 orthogonal matrix corresponding to the symmetry operation, $S = (S_{\alpha\beta})$, such that the crystalline potential satisfies $V(S\boldsymbol{r}) = V(\boldsymbol{r})$. For this symmetry operation, we have

$$(p_\alpha)_{nn'}^{S\boldsymbol{k}} = \sum_\beta S_{\alpha\beta}(p_\beta)_{nn'}^{\boldsymbol{k}}, \tag{46}$$

$$\varepsilon_{n,S\boldsymbol{k}} = \varepsilon_{n\boldsymbol{k}}, \tag{47}$$

where we have used the well-known relation for Bloch orbital, $u_{n,S\boldsymbol{k}}(\boldsymbol{r}) = u_{n\boldsymbol{k}}(S^{-1}\boldsymbol{r})[]$. Therefore the functional $F^\omega = (F_{\alpha\beta}^\omega)$ satisfies the following relation:

$$F^\omega[S\boldsymbol{K}] = SF^\omega[\boldsymbol{K}]S^T, \tag{48}$$

where we have used the matrix notation for tensors of rank 2. Summing up this relation over the Brillouin zone, we get

$$\sum_{\boldsymbol{k}} SF^\omega[\boldsymbol{k} + \boldsymbol{A}_T^{\text{pump}}/c]S^T = \sum_{\boldsymbol{k}} F^\omega[S(\boldsymbol{k} + \boldsymbol{A}_T^{\text{pump}}/c)]$$

$$= \sum_{\boldsymbol{k}} F^\omega[\boldsymbol{k} + S\boldsymbol{A}_T^{\text{pump}}/c], \tag{49}$$

where we have used the symmetry of the Brillouin zone: $\sum_{\boldsymbol{k}}(\cdots)_{S\boldsymbol{k}} = \sum_{S^{-1}\boldsymbol{k}}(\cdots)_{\boldsymbol{k}} = \sum_{\boldsymbol{k}}(\cdots)_{\boldsymbol{k}}$. Finally, we obtain the symmetry relation of the time-resolved conductivity as follows:

$$S\tilde{\sigma}^\omega[\boldsymbol{A}_T^{\text{pump}}]S^T = \tilde{\sigma}^\omega[S\boldsymbol{A}_T^{\text{pump}}]. \tag{50}$$

This is the central result of this paper. Let us consider a periodic pump field which satisfies the following relation for certain sets of symmetry operation S and period T_S,

$$\boldsymbol{A}^{\text{pump}}(t + T_S) = S\boldsymbol{A}^{\text{pump}}(t). \tag{51}$$

Combining it with Eq. (50), we obtain dynamical symmetry properties of the time-resolved conductivity,

$$S\tilde{\sigma}^{\text{I}}(T, \omega)S^T = \tilde{\sigma}^{\text{I}}(T + T_S, \omega). \tag{52}$$

This relation is a direct consequence of the dynamical symmetry of the Hamiltonian,

$$H_{\boldsymbol{k} + \frac{1}{c}\boldsymbol{A}^{\text{pump}}(t+T_S)} = U_S H_{S^T \boldsymbol{k} + \frac{1}{c}\boldsymbol{A}^{\text{pump}}(t)} U_S^\dagger, \tag{53}$$

where U_S is the unitary operator representing S. With this operator, the position and the momentum operators satisfy $U_S^\dagger \boldsymbol{r} U_S = S\boldsymbol{r}$ and $U_S^\dagger \boldsymbol{p} U_S = S\boldsymbol{p}$, respectively.

Here we mention a few special cases. If the pump field does not exist, Eq. (50) is equal to the usual transformation law for rank 2 tensors. If we set the pump field as a static electric field, $\boldsymbol{A}^{\text{pump}}(t) = -c\boldsymbol{E}t + (\text{const.})$, we get

$$S\tilde{\sigma}[\boldsymbol{E}](\omega)S^T = \tilde{\sigma}[S\boldsymbol{E}](\omega), \tag{54}$$

where we express the conductivity in the presence of a static electric field $\boldsymbol{E}$ as $\tilde{\sigma}_{\alpha\beta}[\boldsymbol{E}](\omega)$. This is a transformation law for the static FKE.

We note that the use of the Houston function [Eq. (41)] is not the only route to derive Eq. (50). In the Appendix, we discuss the perturbation expansion of the time-resolved conductivity with respect to the pump field to reach Eq. (50) without the Houston function approximation.

In the following, we investigate the dynamical symmetries of the time-resolved conductivity for each case of crystalline symmetry.

1. Dielectrics with inversion symmetry

We first consider dielectrics with inversion symmetry,

$$S = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{55}$$

exposed to a periodic electric field $\boldsymbol{A}^{\text{pump}}(t) = \text{Re}\,\boldsymbol{A}_0\,e^{-i\Omega t}$. From Eq. (50), the time-resolved conductivity satisfies the following relation,

$$\tilde{\sigma}_{\alpha\beta}^\omega[\boldsymbol{A}_T^{\text{pump}}] = \tilde{\sigma}_{\alpha\beta}^\omega[-\boldsymbol{A}_T^{\text{pump}}]. \tag{56}$$

Namely, we get

$$\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega) = \tilde{\sigma}_{\alpha\beta}^{\text{I}}\left(T + \frac{T_\Omega}{2}, \omega\right). \tag{57}$$

Therefore the transient conductivity $\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega)$ shows an oscillatory behavior with an even multiple of the frequency of the field (2Ω oscillation). This is consistent with previous works reporting the 2Ω oscillation in the transient optical response for inversion symmetric dielectrics [8,26].

2. Dielectrics with reflection symmetry under a linearly polarized field

We next consider dielectrics with reflection symmetry. We consider a system that has reflection symmetry with respect to the xy plane,

$$S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{58}$$

and a linearly polarized periodic field along the z direction:

$$\boldsymbol{A}^{\text{pump}}(t) = (0, 0, A_0 \cos\Omega t). \tag{59}$$

Similarly to Eq. (57), for α, $\beta = x$, y or $\alpha = \beta = z$ components, we obtain

$$\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega) = \tilde{\sigma}_{\alpha\beta}^{\text{I}}\left(T + \frac{T_\Omega}{2}, \omega\right), \tag{60}$$

and therefore these components have a feature of the 2Ω oscillation.

For $\alpha = x$, y and $\beta = z$ (or $\alpha = z$ and $\beta = x$, y), we obtain

$$\tilde{\sigma}_{\alpha\beta}^{\text{I}}(T, \omega) = -\tilde{\sigma}_{\alpha\beta}^{\text{I}}\left(T + \frac{T_\Omega}{2}, \omega\right). \tag{61}$$

These components show oscillation with a period of Ω. Namely, the transient absorption shows no more symmetry than that of the applied field.

In Ref. [27], it has been reported that there appears 2Ω oscillation originating from the reflection symmetry and Ω oscillation for a system without any symmetry.

3. Dielectrics with N-fold proper/improper rotational symmetry under a circularly polarized field

We consider dielectrics with N-fold rotational symmetry around the z axis and a circularly polarized periodic field,

$$A^{\text{pump}}(t) = (A_0 \cos \Omega t, A_0 \sin \Omega t, 0). \qquad (62)$$

In this case, it is convenient to use a complex-valued function in the xy plane,

$$k_c + A_T(t)/c, \quad A_T(t) = A_0 \, e^{i\Omega(T+t)}, \qquad (63)$$

where k_c is given by $k_c = k_x + i k_y$. Using the N-fold rotation operation around the z axis,

$$S : k_c \longrightarrow k_c \, e^{2\pi i/N}, \qquad (64)$$

and Eq. (50), we obtain

$$\tilde{\sigma}_{zz}^{\omega}[A_T] = \tilde{\sigma}_{zz}^{\omega}\big[A_T \, e^{2\pi i/N}\big] = \tilde{\sigma}_{zz}^{\omega}\big[A_{T+\frac{1}{N}T_{\Omega}}\big]. \qquad (65)$$

Namely, we obtain

$$\tilde{\sigma}_{zz}^{\text{I}}(T, \omega) = \tilde{\sigma}_{zz}^{\text{I}}\left(T + \frac{T_{\Omega}}{N}, \omega\right), \qquad (66)$$

and therefore this component has the $N\Omega$ oscillation.

For the case of dielectrics with an improper rotational symmetry, we may consider a product of Eqs. (58) and (64). Since the reflection Eq. (58) does not change Eq. (62), the same discussion as given above holds. Therefore we get Eq. (66) again.

IV. FIRST-PRINCIPLES PUMP-PROBE CALCULATIONS

A. Formalism

In order to verify the symmetry properties of the transient absorption spectroscopy, we perform real-time TDDFT calculations. Since we have made several assumptions and approximations in developing the analytical consideration, numerical calculations will be useful to confirm their validity.

The details of the computational methods have already been reported elsewhere [26,46–48]. We solve TDKS equation for the pump-probe process,

$$i\frac{\partial}{\partial t} v_{nk}^{\text{KS}}(\mathbf{r}, t) = \left[\frac{1}{2}\left[\mathbf{p} + \mathbf{k} + \frac{1}{c}\{A^{\text{pump}}(t) + A^{\text{probe}}(t)\}\right]^2 \right.$$
$$\left. + V_{\text{H}}(\mathbf{r}, t) + V_{\text{xc}}(\mathbf{r}, t) + V_{\text{ion}}(\mathbf{r})\right] v_{nk}^{\text{KS}}(\mathbf{r}, t), \quad (67)$$

where $V_{\text{H}}(\mathbf{r}, t)$, $V_{\text{xc}}(\mathbf{r}, t)$, and $V_{\text{ion}}(\mathbf{r})$ are the electron-electron Hartree, the exchange-correlation, and the electron-ion potential, respectively. If we ignore the time dependence of $V_{\text{H}}(\mathbf{r}, t)$ and $V_{\text{xc}}(\mathbf{r}, t)$, the Hamiltonian of Eq. (67) coincides with Eq. (36). In most dielectric materials, differences of the Hartree and the exchange-correlation potentials from those in the ground state are small and are not significant [8,49]. We employ the norm-conserving pseudopotential [50] for $V_{\text{ion}}(\mathbf{r})$ and the adiabatic local-density approximation [51] for $V_{\text{xc}}(\mathbf{r}, t)$. For simplicity of implementation, we ignore the exchange-correlation term of the vector potential, $A_{\text{xc}}(t)$, which should be included for a rigorous treatment of the exchange-correlation effects of infinite periodic systems [52].

Because of the pseudopotential approximation, our calculations do not take into account core electron dynamics. However, we note that our symmetry consideration is valid even when core electrons are involved as long as the process is nonresonant.

For the time profile of the pump and the probe pulses, we employ the following form:

$$A^{\text{pump}}(t) = -\frac{cE_0^{\text{pump}}}{\Omega} \cos^2 \frac{\pi t}{T_{\text{pump}}} \sin \Omega t,$$
$$(-T_{\text{pump}}/2 < t < T_{\text{pump}}/2), \qquad (68)$$

$$A^{\text{probe}}(t) = -\frac{cE_0^{\text{probe}}}{\omega_{\text{probe}}} \cos^2 \frac{\pi (t - T)}{T_{\text{probe}}} \sin[\omega_{\text{probe}}(t - T)],$$
$$(-T_{\text{probe}}/2 < t - T < T_{\text{probe}}/2), \qquad (69)$$

where T_{pump} and T_{probe} are the full duration of the pump and probe pulses, respectively. Here, ω_{probe} stands for the average frequency of the probe pulse. Again, T is the central time of the probe pulse and now corresponds to the delay time between the pump and probe pulses. In the calculations below, we will use a sufficiently large value for T_{pump} so that the pump field $A^{\text{pump}}(t)$ can be regarded as periodic as given in Eq. (17).

Using the TDKS orbital $v_{nk}^{\text{KS}}(\mathbf{r}, t)$ instead of $v_{nk}(\mathbf{r}, t)$ in Eq. (35), we can obtain the spatially averaged current density corresponding to the pump-probe process. We include a term originating from the nonlocality of the pseudopotential as well [47]. We calculate the energy transfer, or work, from the probe pulse to electron in the unit cell of dielectrics,

$$\delta W = \int dt \, \delta \mathbf{I}(t) \cdot \mathbf{E}^{\text{probe}}(t), \qquad (70)$$

where $\delta \mathbf{I}(t)$ is defined by Eq. (11). If we make a frequency-resolved analysis, we obtain $A(\omega)$ defined in Eq. (8). To confirm the symmetry property, however, it is sufficient to examine without frequency resolution.

B. Results

We present results for 4H-SiC crystal, which has C_{6v} point group symmetry. We employ the pump pulse of $\hbar\Omega = 1.55$ eV and the probe pulse of $\hbar\omega_{\text{probe}} = 40$ eV. We set T_{pump} and T_{probe} to 20 fs and 1 fs, respectively. The field strength of the pump and probe pulses are set to $E_0^{\text{pump}} = 6.1 \times 10^{-1}$ V/Å and $E_0^{\text{probe}} = 2.7 \times 10^{-2}$ V/Å, respectively, where the latter value is small enough to justify the perturbative treatment for the probe process.

We performed the calculations by using the open-source software SALMON (Scalable Ab-initio Light-Matter simulator for Optics and Nanoscience) [53] which has been developed in our group and is available from the website, Ref. [54]. The code solves Eq. (67) in the time domain with the real-space finite-difference method in the 3D Cartesian coordinate. We employ a real-space grid of $20 \times 32 \times 64$ for the rectangular unit cell of 16 atoms and a k-space grid of $20 \times 12 \times 6$ for the Brillouin zone sampling. The Taylor expansion method is used for the time evolution with a time step of $dt = 0.02$ in atomic units. The number of time steps is typically 42 000.

Figure 1 shows the energy transfer as a function of the delay time T using the pump and probe pulses of the linear
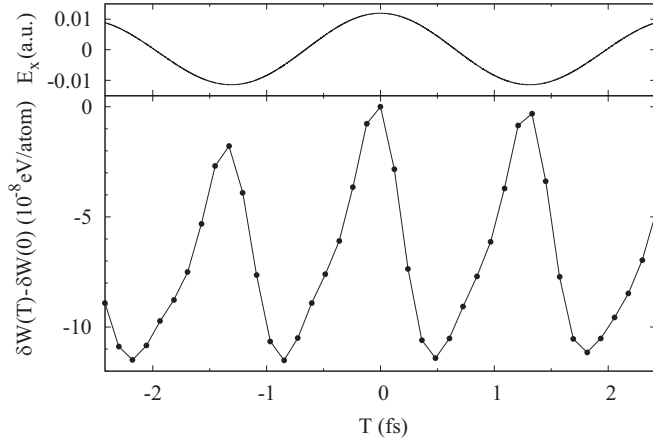
FIG. 1. Energy transfer [Eq. (70)] as a function of the delay time T with the pump and the probe pulses of the x polarization (bottom). (Top) Time profile of pump electric field for comparison.

polarization along the x axis. The energy transfer shows an oscillation with the frequency of twice the pump frequency Ω. This 2Ω oscillation is due to the reflection symmetry of the hexagonal structure with respect to the x axis [see Eq. (60)].

Figure 2 shows the energy transfer for the pump and probe pulses with the z polarization. Since the hexagonal crystal structure has no symmetry along the z axis, the energy transfer indicates the Ω oscillation.

Figure 3 shows the energy transfer for the circularly polarized pump field in the xy plane and the linearly polarized probe field in the z direction. The energy transfer shows the 6Ω oscillation. This is expected from Eq. (66) and the sixfold rotational symmetry of the crystal structure.

We thus find that the oscillatory structures of the energy transfer seen in our calculations are all consistent with our analytical investigation for three cases of different symmetry properties. The difference in the magnitude of the modulation seen in Figs. 1–3 can be understood from perturbation orders with respect to the pump field (see Appendix). Equation (A7) suggests that the $n\Omega$ oscillation of the time-resolved conductivity starts to appear in the $(n + 1)$th order nonlinear response. Therefore the magnitude of the 6Ω oscillation (Fig. 3)
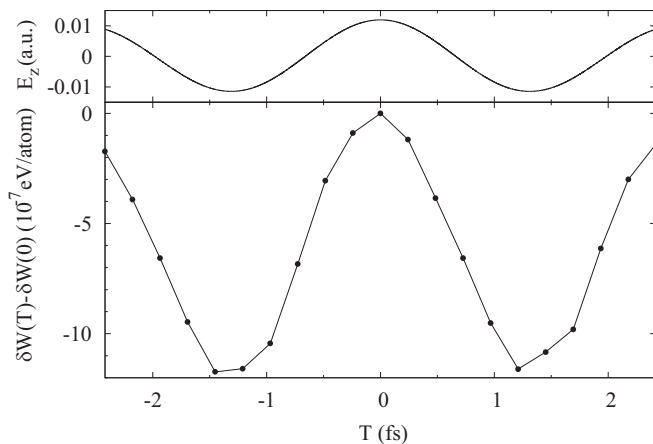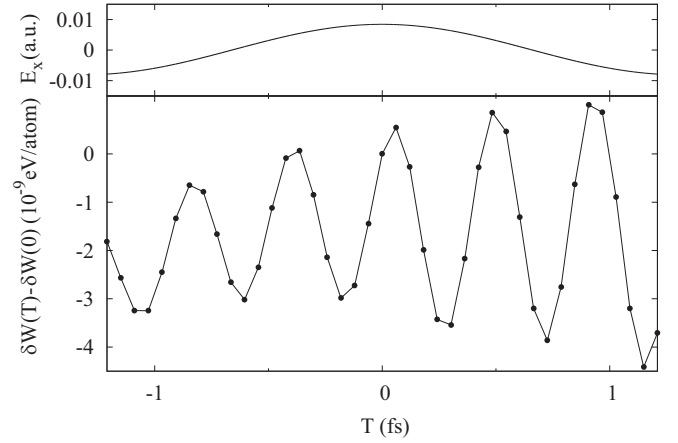

FIG. 2. The same as in Fig. 1, but for the z polarization.

is five orders smaller than that of the Ω oscillation (Fig. 2), and so on.

In Ref. [55], it was reported that an oscillation of the DFKE response in diamond crystal almost disappears for circularly polarized light from TDDFT calculation. It could be understood from the order of the perturbation: 4Ω oscillation signal is expected from the fourfold rotational symmetry of the diamond structure. However, the magnitude is two orders smaller than the 2Ω oscillation signal seen in the linearly polarized probe field. Because of the difference of two orders in the perturbation, the signal in the circularly polarized pulse looks extremely small.

V. CONCLUSION

We have discussed the relation between crystalline symmetry and the signal of attosecond transient absorption spectroscopy caused by the dynamical Franz-Keldysh effect. We found that an oscillation property of a transient conductivity in a laser-exposed crystal is determined by a transformation low of the transient conductivity tensor under a crystalline symmetry operation. We obtained selection rules for the frequency of the laser-driven oscillation of the probe response in the pump-probe time domain. First-principles calculations based on the time-dependent density functional theory confirmed validity of these selection rules for several crystalline symmetries. This work paves the way for understanding the physics of attosecond transient absorption spectroscopy in crystalline solids.

FIG. 3. The same as in Fig. 1, but for the circular polarized pump field in the xy plane and the z polarized probe field.

APPENDIX: PERTURBATION EXPANSION

In this Appendix, we develop a perturbation theory for the modulation of the conductivity in which the perturbation expansion is carried out with respect to the pump field of the form, $\mathbf{A}^{\text{pump}}(t) = \sum_p \tilde{\mathbf{A}}(\Omega_p)e^{-i\Omega_p t}$. The Hamiltonian of Eq. (34) can be rewritten as

$$H_{\mathbf{K}(t)} = H_{\mathbf{k}} + \Delta V_{\text{pump}}(t) + c_{\mathbf{k}}(t), \tag{A1}$$

where $\Delta V_{\text{pump}}(t) = \mathbf{p} \cdot \mathbf{A}^{\text{pump}}(t)/c$ and $c_{\mathbf{k}}(t)$ are the perturbation potential and the remaining c-number term, respectively. The time-dependent Bloch orbital $w_{n\mathbf{k}}(\mathbf{r}, t)$ is expanded as

$$|w_{n\mathbf{k}}(t)\rangle = \sum_{N=0}^{\infty} |w_{n\mathbf{k}}^{(N)}(t)\rangle, \tag{A2}$$

where the subscript "(N)" stands for the Nth perturbation order. Nth-order orbital is expressed as

$$\begin{aligned}
|w_{n\mathbf{k}}^{(N)}(t)\rangle = e^{-i\varepsilon_{n\mathbf{k}}t} \sum_m |u_{m\mathbf{k}}\rangle \sum_{p_1 \cdots p_N} \\
\times \tilde{C}_{mn\mathbf{k}}^{(N)}(\Omega_{p_1}, \cdots, \Omega_{p_N}) e^{-i \sum_{i=1}^N \Omega_{p_i}t}.
\end{aligned} \tag{A3}$$

Here the coefficient $\tilde{C}_{mn\mathbf{k}}^{(N)}$ is determined from $\tilde{C}_{mn\mathbf{k}}^{(0)} = \delta_{mn}$ and a recursion formula,

$$\begin{aligned}
\tilde{C}_{mn\mathbf{k}}^{(N)}(\Omega_{p_1}, \cdots, \Omega_{p_N}) = \frac{1}{c} \sum_l \frac{(\mathbf{p})_{ml}^{\mathbf{k}} \cdot \tilde{\mathbf{A}}(\Omega_{p_N})}{\sum_{i=1}^N \Omega_{p_i} - \omega_{mn}^{\mathbf{k}}} \\
\times \tilde{C}_{ln\mathbf{k}}^{(N-1)}(\Omega_{p_1}, \cdots, \Omega_{p_{N-1}}).
\end{aligned} \tag{A4}$$

Up to here the procedure is mostly the same as that of the ordinary time-dependent perturbation theory for nonlinear optical susceptibility [56].

Hereafter we will deal with monochromatic light: $\mathbf{A}^{\text{pump}}(t) = \text{Re}\, \mathbf{A}_0 e^{-i\Omega t}$. Namely, we set the frequency as $\Omega_p = p\Omega$, $(p = \pm)$ and the coefficients as $\tilde{\mathbf{A}}(\Omega_+) = \mathbf{A}_0/2$, $\tilde{\mathbf{A}}(\Omega_-) = \mathbf{A}_0^*/2$. Then we rewrite the matrix element

of Eq. (38) as

$$\mathbf{P}_{nn'}^{\mathbf{k}}(t) = e^{i\omega_{nn'}^{\mathbf{k}}t} \sum_{\nu=-\infty}^{\infty} e^{-i\nu\Omega t} \tilde{\mathbf{P}}_{nn'}^{\mathbf{k}}(\nu), \tag{A5}$$

where

$$\begin{aligned}
\tilde{\mathbf{P}}_{nn'}^{\mathbf{k}}(\nu) = \sum_{N,N'=0}^{\infty} \sum_{p_1 \cdots p_N} \sum_{q_1 \cdots q_{N'}} \delta_{\nu, -\sum p_i + \sum q_i} \\
\times \sum_{mm'} \tilde{C}_{mn\mathbf{k}}^{(N)*}(\Omega_{p_1}, \cdots, \Omega_{p_N}) \\
\times (\mathbf{p})_{mm'}^{\mathbf{k}} \tilde{C}_{m'n'\mathbf{k}}^{(N')}(\Omega_{q_1}, \cdots, \Omega_{q_{N'}}).
\end{aligned} \tag{A6}$$

Using Eqs. (37) and (27), we get

$$\begin{aligned}
\tilde{\sigma}_{\alpha\beta}^{\text{I}}(t, \omega) = \frac{in_e}{\omega}\delta_{\alpha\beta} + \frac{i}{V} \sum_{\mathbf{k}} \sum_{n\neq n'} f_{n\mathbf{k}} \sum_{\nu\nu'} \\
\times \frac{[\tilde{\mathbf{P}}_{nn'}^{\mathbf{k}}(\nu)]_{\alpha}[\tilde{\mathbf{P}}_{n'n}^{\mathbf{k}}(\nu')]_{\beta} e^{-i(\nu+\nu')\Omega t}}{\{\omega^+ - (\nu+\nu')\Omega\}(\omega^+ - \nu\Omega + \omega_{nn'}^{\mathbf{k}})} \\
+ (\omega \to -\omega)^*,
\end{aligned} \tag{A7}$$

where $\omega^+ = \omega + i0$.

From Eqs. (A3) and (A4), the t dependence of Eq. (A7) can be absorbed in the vector potential of the pump field by redefinition, $\mathbf{A}_0 \to \mathbf{A}_{t,0} \equiv \mathbf{A}_0 e^{-i\Omega t}$. Here, $\mathbf{A}_{t,0}$ is equal to the coefficient of the time-shifted vector potential $\mathbf{A}_t^{\text{pump}}(x) = \mathbf{A}^{\text{pump}}(t + x)$. Furthermore, Eq. (50) is valid in this situation because the coefficient $\tilde{C}_{mn\mathbf{k}}^{(N)}$ is unchanged under a transformation $S : \mathbf{k} \to S\mathbf{k}$, $\mathbf{A}_t^{\text{pump}} \to S\mathbf{A}_t^{\text{pump}}$. Therefore we can repeat the argument described below Eq. (50). We note that for the case of $\mathbf{A}^{\text{pump}}(t) = 0$, Eq. (A7) agrees with the well-known Kubo-Greenwood formula of the conductivity since $\nu = \nu' = 0$ and $\tilde{\mathbf{P}}_{nn'}^{\mathbf{k}}(\nu) = (\mathbf{p})_{nn'}^{\mathbf{k}}$.

[1] E. Goulielmakis, V. S. Yakovlev, A. L. Cavalieri, M. Uiberacker, V. Pervak, A. Apolonski, R. Kienberger, U. Kleineberg, and F. Krausz, Science **317**, 769 (2007).

[2] E. Goulielmakis, Z.-H. Loh, A. Wirth, R. Santra, N. Rohringer, V. S. Yakovlev, S. Zherebtsov, T. Pfeifer, A. M. Azzeer, M. F. Kling, S. R. Leone, and F. Krausz, Nature (London) **466**, 739 (2010).

[3] H. Wang, M. Chini, S. Chen, C.-H. Zhang, F. He, Y. Cheng, Y. Wu, U. Thumm, and Z. Chang, Phys. Rev. Lett. **105**, 143002 (2010).

[4] M. Holler, F. Schapper, L. Gallmann, and U. Keller, Phys. Rev. Lett. **106**, 123601 (2011).

[5] M. Schultze, E. M. Bothschafter, A. Sommer, S. Holzner, W. Schweinberger, M. Fiess, M. Hofstetter, R. Kienberger, V. Apalkov, V. S. Yakovlev, M. I. Stockman, and F. Krausz, Nature (London) **493**, 75 (2013).

[6] M. Schultze, K. Ramasesha, C. D. Pemmaraju, S. A. Sato, D. Whitmore, A. Gandman, J. S. Prell, L. J. Borja, D. Prendergast, K. Yabana, D. M. Neumark, and S. R. Leone, Science **346**, 1348 (2014).

[7] H. Mashiko, K. Oguri, T. Yamaguchi, A. Suda, and H. Gotoh, Nat. Phys. **12**, 741 (2016).

[8] M. Lucchini, S. A. Sato, A. Ludwig, J. Herrmann, M. Volkov, L. Kasmi, Y. Shinohara, K. Yabana, L. Gallmann, and U. Keller, Science **353**, 916 (2016).

[9] A. Moulet, J. B. Bertrand, T. Klostermann, A. Guggenmos, N. Karpowicz, and E. Goulielmakis, Science **357**, 1134 (2017).

[10] F. Schlaepfer, M. Lucchini, S. A. Sato, M. Volkov, L. Kasmi, N. Hartmann, A. Rubio, L. Gallmann, and U. Keller, Nat. Phys. **14**, 560 (2018).

[11] W. Franz, Z. Naturforsch. **13a**, 484 (1958).

[12] L. V. Keldysh, Sov. Phys. JETP **6**, 763 (1958).

[13] K. Tharmalingam, Phys. Rev. **130**, 2204 (1963).

[14] B. O. Seraphin and R. B. Hess, Phys. Rev. Lett. **14**, 138 (1965).

[15] R. E. Nahory and J. L. Shay, Phys. Rev. Lett. **21**, 1569 (1968).

[16] H. Shen and M. Dutta, J. Appl. Phys. **78**, 2151 (1995).

[17] J. K. Wahlstrand and J. E. Sipe, Phys. Rev. B **82**, 075206 (2010).

[18] F. Duque-Gomez and J. Sipe, J. Phys. Chem. Solids **76**, 138 (2015).

[19] Y. Yacoby, Phys. Rev. **169**, 610 (1968).

[20] A. P. Jauho and K. Johnsen, Phys. Rev. Lett. **76**, 4576 (1996).

[21] K. B. Nordstrom, K. Johnsen, S. J. Allen, A.-P. Jauho, B. Birnir, J. Kono, T. Noda, H. Akiyama, and H. Sakaki, Phys. Rev. Lett. **81**, 457 (1998).

[22] A. Srivastava, R. Srivastava, J. Wang, and J. Kono, Phys. Rev. Lett. **93**, 157401 (2004).

[23] Y. Mizumoto, Y. Kayanuma, A. Srivastava, J. Kono, and A. H. Chin, Phys. Rev. B **74**, 045216 (2006).

[24] S. Ghimire, A. D. DiChiara, E. Sistrunk, U. B. Szafruga, P. Agostini, L. F. DiMauro, and D. A. Reis, Phys. Rev. Lett. **107**, 167407 (2011).

[25] A. H. Chin, J. M. Bakker, and J. Kono, Phys. Rev. Lett. **85**, 3293 (2000).

[26] T. Otobe, Y. Shinohara, S. A. Sato, and K. Yabana, Phys. Rev. B **93**, 045124 (2016).

[27] S. A. Sato, H. Hübener, U. De Giovannini, and A. Rubio, Appl. Sci. **8**, 1777 (2018).

[28] J. K. Wahlstrand, H. Zhang, S. B. Choi, S. Kannan, D. S. Dessau, J. E. Sipe, and S. T. Cundiff, Phys. Rev. Lett. **106**, 247404 (2011).

[29] J. K. Wahlstrand, S. T. Cundiff, and J. E. Sipe, Phys. Rev. B **83**, 233201 (2011).

[30] C. L. Tang and H. Rabin, Phys. Rev. B **3**, 4025 (1971).

[31] O. E. Alon, V. Averbukh, and N. Moiseyev, Phys. Rev. Lett. **80**, 3743 (1998).

[32] V. Averbukh, O. E. Alon, and N. Moiseyev, Phys. Rev. A **60**, 2585 (1999).

[33] H. J. Simon and N. Bloembergen, Phys. Rev. **171**, 1104 (1968).

[34] K. Konishi, T. Higuchi, J. Li, J. Larsson, S. Ishii, and M. Kuwata-Gonokami, Phys. Rev. Lett. **112**, 135502 (2014).

[35] S. Chen, G. Li, F. Zeuner, W. H. Wong, E. Y. B. Pun, T. Zentgraf, K. W. Cheah, and S. Zhang, Phys. Rev. Lett. **113**, 033901 (2014).

[36] A. McPherson, G. Gibson, H. Jara, U. Johann, T. S. Luk, I. A. McIntyre, K. Boyer, and C. K. Rhodes, J. Opt. Soc. Am. B **4**, 595 (1987).

[37] F. Krausz and M. Ivanov, Rev. Mod. Phys. **81**, 163 (2009).

[38] F. Ceccherini, D. Bauer, and F. Cornolti, J. Phys. B At. Mol. Opt. Phys. **34**, 5017 (2001).

[39] V. Averbukh, O. E. Alon, and N. Moiseyev, Phys. Rev. A **64**, 033411 (2001).

[40] O. E. Alon, Phys. Rev. A **66**, 013414 (2002).

[41] X. Liu, X. Zhu, L. Li, Y. Li, Q. Zhang, P. Lan, and P. Lu, Phys. Rev. A **94**, 033410 (2016).

[42] N. Saito, P. Xia, F. Lu, T. Kanai, J. Itatani, and N. Ishii, Optica **4**, 1333 (2017).

[43] O. Neufeld, D. Podolsky, and O. Cohen, Nat. Commun. **10**, 405 (2019).

[44] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[45] W. V. Houston, Phys. Rev. **57**, 184 (1940).

[46] K. Yabana and G. F. Bertsch, Phys. Rev. B **54**, 4484 (1996).

[47] G. F. Bertsch, J.-I. Iwata, A. Rubio, and K. Yabana, Phys. Rev. B **62**, 7998 (2000).

[48] T. Otobe, M. Yamagiwa, J.-I. Iwata, K. Yabana, T. Nakatsukasa, and G. F. Bertsch, Phys. Rev. B **77**, 165104 (2008).

[49] N. Tancogne-Dejean, O. D. Mücke, F. X. Kärtner, and A. Rubio, Phys. Rev. Lett. **118**, 087403 (2017).

[50] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[51] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[52] G. Vignale and W. Kohn, Phys. Rev. Lett. **77**, 2037 (1996).

[53] M. Noda, S. A. Sato, Y. Hirokawa, M. Uemoto, T. Takeuchi, S. Yamada, A. Yamada, Y. Shinohara, M. Yamaguchi, K. Iida, I. Floss, T. Otobe, K.-M. Lee, K. Ishimura, T. Boku, G. F. Bertsch, K. Nobusada, and K. Yabana, Comput. Phys. Commun. **235**, 356 (2019).

[54] SALMON official website, http://salmon-tddft.jp.

[55] T. Otobe, Phys. Rev. B **94**, 165152 (2016).

[56] R. W. Boyd, *Nonlinear Optics*, 3rd ed. (Academic, Burlington, MA, 2008).