Coherent Stimulated X-ray Raman Spectroscopy; Attosecond Extension of RIXS

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Spontaneous and stimulated resonant inelastic X-ray Raman scattering signals are calculated using the Keldysh-Schwinger closed-time path loop and expressed as overlaps of Doorway and Window electron-hole wavepackets. These are recast in terms of the one-particle Green’s functions and expansion coefficients of configuration interaction singles for valence excitations, which can be obtained from standard electronic structure codes. Calculation for many-body states of ground and core-excited system is avoided.

Resonant nonlinear spectroscopy in the X-ray regime may become possible by new bright ultra-fast sources\textsuperscript{1, 2, 3, 4, 5}. The theoretical formulation of nonlinear spectroscopy with attosecond X-ray pulses is of considerable interest\textsuperscript{6, 7, 8, 9}. The picosecond optical pump/x-ray probe technique has been used to study photophysical and photochemical molecular processes\textsuperscript{10, 11, 12, 13}. An all-X-ray pump-probe experiment with attosecond X-ray pulses has been proposed in Ref. \textsuperscript{8}. The pump pulse interacts with the system to create a valence excited state wave-packet which evolves for a controlled delay time \( \tau \) when a second probe pulse interacts with it. \( \tau \) is not limited by the core-hole life-time. The dependence of this coherent stimulated X-ray Raman signal (CXRS) on the delay time \( \tau \) carries information about valence excited state dynamics. The pump-probe signal may be recast in the Doorway/Window representation of optical nonlinear spectroscopy\textsuperscript{14}. In Ref. \textsuperscript{8} these were computed within the equivalent core single Slater determinant approximation. Here we express them using the single-body Green’s functions. Thus avoiding the explicit computation of the many electron core excitations.

Green’s functions have been extensively used to study X-ray absorption fine structure (XAFS)\textsuperscript{15, 16, 17, 18, 19, 20}. The formalism is well developed and incorporates intrinsic and extrinsic losses\textsuperscript{19} coming from the many-body interactions (electron-phonon, electron-hole pairs etc.). These provide a high level, yet practical, approach that goes beyond the density-functional theory considered in Ref. \textsuperscript{8}. By invoking the “sudden approximation” whereby a core-hole is created and destroyed instantaneously we express the signal in term of one-particle Green’s functions which depend on the core-hole parametrically\textsuperscript{19}.

We compare CXRS with resonance inelastic X-ray Raman scattering (RIXS) which is a common frequency-domain technique used in the study of core excited states in solids and molecules\textsuperscript{21, 22, 23, 24}. The RIXS signal can be described by the Kramers-Heisenberg expression\textsuperscript{23, 22} as is done for valence excitations in the optical regime\textsuperscript{14}.

\[ S_{RIXS}(\omega_1, \omega_2) = \sum_{ac} |A_{ca}(\omega_1)|^2 \delta(\omega_1 - \omega_2 - \omega_{ca}) \]  

(1)

where the transition amplitude is given by

\[ A_{ca}(\omega_1) = \sum_{e} \frac{B_{ca} B_{ea}}{\omega_1 - \omega_{ca} + i \Gamma_{ca}} \]  

(2)

with the transition amplitudes \( B_{ca} \) and \( B_{ea} \) are matrix elements of dipole operator.

Displaying this signal vs. \( \omega_1 - \omega_2 \) reveals the valence transitions (\( \omega_{ca} \)). The core-hole resonances (\( \omega_{ca} \)) in the transition amplitude (\( \omega_{ca} \)) are typically much broader and less resolved due to the large core-hole lifetime contribution to \( \Gamma_{ca} \approx \sim 0.05 \text{ eV} \)\textsuperscript{23}. CXRS is a closely related technique, performed with a pair of attosecond pulses. We show how that how the signal can be recast in a form resembling Eq.\textsuperscript{14}, making it a natural time-domain extension of RIXS. Varying the envelopes of both pulses and their delay offer a much higher degree of control of the signal. Both signals can be described as a valence electron-hole wavepacket (a doorway state) prepared by the pump beam with high spatial and temporal resolution. This wavepacket is probed by projecting it into a second (window) wavepacket prepared by the probe\textsuperscript{26}. This wavepacket can be visualized in real space when the valence excitations are treated at the configuration-interaction-singles (CIS) level.

Equation\textsuperscript{11} can be derived in the time domain using the closed-time-path loop (CTPL) diagram shown in Fig. 1. This diagram may then be modified to represent CXRS. In this diagram time runs clockwise and all the interactions are ordered along the loop. In physical time, however, only interactions on the same branch of the loop are time-ordered with respect to each other. Interactions on different branches are not time-ordered\textsuperscript{27}. The correlation- function expression for the RIXS signal is readily obtained from Fig. 1 by assigning each interaction an excitation operator (\( B \) or \( B^\dagger \)) according to the
rules given in Ref. [27]. We then get

\[ S_{\text{RIXS}}(\omega_1, \omega_2, t) = 2 \text{Re} \int_0^\infty ds_2 \int_0^\infty ds_1 \int_0^\infty ds_3 e^{-i\omega_1 s_2} e^{i\omega_2 (s_1 + s_2 + s_3)} E_1(t - s_1 - s_2) E_2^\dagger(t - s_3) \langle B_m(t - s_3) B_m^\dagger(t - s_2) B_n(t - s_1 - s_2) \rangle. \]  

The operator \( B_m \) creates (annihilates) a core-hole/valence-electron pair.

\[ B_m = \sum_i \mu_{im} c_i^\dagger, \quad B_m^\dagger = \sum_i \mu_{mi} c_i \]  

Here \( c_m \) annihilates electron at the \( m \)th core orbital and \( c_i^\dagger \) creates an electron at the \( i \)th valence orbital. These are Fermi operators. \( \omega_1 \) and \( \omega_2 \) are the carrier frequencies of the two pulses and \( \mu_{im} \) is the dipole matrix element between the \( i \)th valence orbital and \( m \)th core orbital. \( E_j(r, t) \), \( j = 1, 2 \) are complex field envelopes

\[ E_j(r, t) = E_j(t) \exp(-i\mathbf{k}_j \cdot \mathbf{r} - \omega_j t) + E_j^* \exp(-i\mathbf{k}_j \cdot \mathbf{r} + \omega_j t) \]  

The time dependence of exciton operators in Eq. \( \text{(3)} \) is given by the free molecular Hamiltonian (no field), \( B_m(t) = e^{iHt} B_m e^{-iHt} \). By inserting the identity operator \( \sum_\nu |\nu\rangle \langle \nu| \), expanded in the many-body states of the molecule, between the exciton operators in the middle of Eq. \( \text{(3)} \) and assuming stationary carrier \( E_j(t) = 1 \), we can carry out the \( s_2 \) integration and we immediately recover the Kramers-Heisenberg (KH) expression \( \text{(4)} \) for the signal.

The single-particle many-body Green’s functions provide a standard tool for computing X-ray absorption near edge spectra (XANES) [19]. Computer codes based on the GW approximation developed for these Green’s functions are broadly applied to molecules and crystals [15, 16, 17, 18]. We next show that the signal can be approximately expressed in terms of these Green’s functions. The correlation function in Eq. \( \text{(3)} \) can be recast as,

\[ \langle B_m(t - s_3) B_m^\dagger(t) B_n(t - s_2) B_n^\dagger(t - s_1 - s_2) \rangle = \langle a | B_m U(-s_3) B_m^\dagger U(s_2) B_n U(s_1) B_n^\dagger | a \rangle \]  

where \( U(s) = e^{iHs} \) is the time evolution operator and \( H \) is free molecular Hamiltonian. We set the ground state energy \( \omega_n = 0 \).

We next define the following projection-operator in the \( N + 1 \)-valence electron/1-core-hole space.

\[ \mathcal{P}_m = \sum_i c^\dagger_i c_i |a\rangle \langle c_m c_i | \]  

where \( |a\rangle \) is the ground many-body state with \( N \)-valence electrons. \( \mathcal{P}_m \) selects a sub-space of the full \( N+1 \)-electron space which includes single valence electron-hole pair excitations. By inserting the projection operator \( \text{(7)} \) twice inside the average on the r.h.s. of Eq. \( \text{(3)} \), we obtain an approximate expression for the correlation function. Using Eqs. \( \text{(4)} \) and \( \text{(7)} \), it factorizes into a product of three correlation functions.

\[ \langle B_m(t - s_3) B_m^\dagger(t) B_n(t - s_2) B_n^\dagger(t - s_1 - s_2) \rangle \approx \langle a | B_m U(-s_3) \mathcal{P}_m B_m^\dagger U(s_2) B_n U(s_1) B_n^\dagger | a \rangle \]

\[ = \sum_{ijkl} \mu_{im} \mu_{mn} \mu_{jl} \langle a | c^\dagger_m c_i U(-s_3) c^\dagger_j c_n | a \rangle \times \langle a | c^\dagger_i c^\dagger_j U(s_2) c_j U(s_1) c_i | a \rangle. \]  

Since the core-holes are highly localized on the parent atom, their dynamics is very slow compared to the valence electrons and may be ignored. We shall ignore this dynamics and treat the core-hole indices as fixed parameters.

We next introduce the following set of many-body states

\[ |\chi(i, j)\rangle = c_i c_j^\dagger |a\rangle. \]
These represent one electron-hole pair excitation state of the valence $N$-electron system with one electron-hole pair.

We define the one-electron Green’s function computed in the presence of a core-hole at $m$.

$$G_{ij}^{(m)}(t, t') = -i(Tc_i(t)e_j^\dagger(t'))_m$$

where $T$ is the time-ordering operator which rearranges a product of operators in increasing order in time from the right to the left and $(\cdot)_m$ represents a trace over $N$-electron ground state of the valence in presence of Coulomb potential due to a core-hole at $m$.

We also define the one-sided Fourier transform

$$G_{j'i'}^{R(n)}(\omega_1) = \int_0^{\infty} dt \ e^{-i\omega_1 t} G_{j'i'}^{(n)}(t)$$

where $G^R$ is the retarded Green’s function.

Using Eqs. (9) and (10), the correlation-function (8) can be recast as

$$\langle B_m(t-s_3)B_n(t-s_2)B_n^\dagger(t-s_1-s_2) \rangle = \sum_{ijkl} \sum_{ij'} \sum_{jj'} \mu_{lmn}\mu_{km}\mu_{jn}\mu_{nl} \theta(s_1)\theta(s_3) \ G_{ij'}^{(m)}(s_3) G_{jl}^{(n)}(s_1) \langle \chi(i', j') \rangle e^{-iH_{2e}^s |\chi(j, j')|}. \ (12)$$

The many-body eigenstates $|\psi\rangle$ (with energy $\epsilon_{c, \omega_{2c}}$) of the molecular Hamiltonian $H$ at the configuration interaction single (CIS) level are given by the linear combinations of single electron-hole pair states.

$$|\psi\rangle = \sum_{ij} f_{cij} |\chi(i, j)\rangle \ (13)$$

where $f_{cij}$ are expansion coefficients. $|\psi\rangle$ constitute an orthonormal single electron-hole pair basis set,

$$\sum_c |\psi\rangle\langle\psi| = \sum_{ij} |\chi(i, j)\rangle\langle\chi(i, j)| = 1. \ (14)$$

Inserting this identity into the last term in Eq. (12), and substituting it in Eq. (8) gives

$$S_{RIXS}(\omega_1, \omega_2) = -\sum_{ijkl} \sum_{jj'} \sum_{nn'} f_{ji} f_{ij'}^* \mu_{imn}\mu_{kmn} \ G_{ij'}^{(m)}(s_3) e^{i\omega_{2e}^s (s_1+s_3)}$$

$$\int_0^{\infty} ds_1 \int_0^{\infty} ds_3 \theta(s_1)\theta(s_3) e^{i\omega_1 s_1} \ G_{ij'}^{(m)}(s_3)$$

$$\int_{-\infty}^{\infty} ds_2 e^{i(\omega_1-\omega_2-\omega_{2e})s_2} E_1(t-s_1-s_2) E_1^\dagger(t-s_3)$$

$$G_{ij}^{(m)}(s_3) G_{jl}^{(n)}(s_1) \ (15)$$

where $\omega_{2c} = \omega_{2c} - \omega_c$. Equation (15) corresponds to the RIXS signal obtained earlier using the Keldysh Green’s functions approach [Eq. 47 in Ref. (30)]. However unlike in Ref. (30), the RIXS signal derived here takes in to account of the shape of incoming pulse which provides a better control on the signal.

Assuming stationary field envelopes, the $s_2$ integral in Eq. (15) reduces to a Dirac-delta function and Eq. (15) takes the KH form (16) with the transition amplitude

$$A_{c\alpha}(\omega_1) = \sum_{nij'} f_{cij} G_{j'i'}^{R(n)}(\omega_1) \mu_{jn}\mu_{nl} \ (16)$$

Equation (16) may be interpreted as follows: The $N$-electron ground state $|\psi\rangle$ is excited by the incoming X-ray beam, creating a core excited state with $(N + 1)$ valence electrons. This state evolves during the short time window permitted by the core-hole lifetime. This evolution in the presence of a core-hole is described by the frequency-dependent Green’s function. Finally this excited state is transformed by a dipole transition to a singly excited valence ground state $|\psi\rangle$.

I. X-RAY PUMP-PROBE SIMULATED RAMAN SIGNAL

We assume high probe intensity so that stimulated emission is dominant and spontaneous emission can be neglected. The signal is given by the difference between the transmitted intensities of the probe ($k_2$) with and without the pump ($k_1$). Four CTPL diagrams contribute to the signal for our two-band model (Fig. 2). When the pump and probe pulse envelopes are well sepa-

![FIG. 3: Two CTPL diagrams that contribute to the pump-probe signal for a two valence level scheme sketched in Fig. 2.](image)
Doorway/Window form $[6, 8, 14]$.

$$S_{CXRS}(\tau) = \sum_{ac} |D_{ac}W_{ca}e^{-i\omega_{ca}\tau} + c.c.\rangle. \quad (17)$$

The pump prepares a Doorway wavepacket (A6)

$$|D\rangle = \sum_c D_{ac}|c\rangle \quad (18)$$

and the probe creates a Window wavepacket (A7)

$$|W\rangle = \sum_c W_{ac}|c\rangle. \quad (19)$$

The signal is given by the overlap of these two wavepackets. Note that the signal in (17) is given for $\tau > 0$ and the signal in (17) is given for $\tau < 0$, we define the CXRS signal to be the same as in Eq. (17).

Fourier transform of Eq. (17) gives

$$S_{CXRS}(\omega) = \sum_{ac} D_{ac}W_{ca}\delta(\omega - \omega_{ca}) + \sum_{ac} [D_{ac}W_{ca}]^*\delta(\omega + \omega_{ca}). \quad (20)$$

As was done in Eq. (16) for RIXS, we can express the Doorway and the Window in terms of the Green’s functions and the CIS coefficients. Details are given in the Appendix. We then obtain

$$D_{ac} := P(a) \sum_{ijk} \mu_{im}\mu_{mj}f_{ijk}^{*} \int \frac{d\omega}{2\pi} G_{kj}^{R(m)}(\omega - \omega_{ca}) \times E_{i}^{*}(\omega)E_{1}(\omega - \omega_{ca}) \quad (21)$$

$$W_{ca} := 2\sum_{ijk} \mu_{kn}\mu_{nj}f_{cji} \int \frac{d\omega}{2\pi} \text{Im} G_{ki}^{R(n)}(\omega - \omega_{ca}) \times E_{2}(\omega)E_{2}^{*}(\omega - \omega_{ca}). \quad (22)$$

Note that the exact expression for the pump-probe signal, Eq. (15) with (A6) and (A7), requires the computation of many-body states for the $N$ and the $N + 1$ valence electron system. In contrast, the Green’s function expressions, Eq. (21) and (22), only require the one-particle Green’s functions and valence excited states at the CIS level. These may be obtained using standard electronic structure computer codes. In Appendix we show that Eqs. (A6)-(A7) reduce to (21)-(22) within the CIS approximation.

The physical picture offered by the Doorway and the Window in Eq. (21) and (22) is shown schematically in Fig. 4. The system interacts twice with the pump creating a valence excited state electronic wave packet [Eq. (18) together with (21)]. This wave-packet evolves freely for a time $\tau$, which is not limited by the core-hole lifetime. The two dipole matrix elements $\mu_{im}$ and $\mu_{mj}$ represent the two interactions with the X-ray pulse which create and annihilate the core-hole at $m$. The Green’s function $G_{kj}(\omega)$ together with coefficients $f^{*}c; ik$ represents the relevant dynamics. The Window, Eq. (19) with (22), is similarly created by the probe X-ray pulse and the signal is given by the overlap of these two wavepackets.

II. CONCLUSIONS

We have presented a many-body Green’s function theory of stimulated attosecond Raman X-ray scattering. The Green’s function expression avoids the explicit computation of the ground and the core-hole excited states of the system. The single particle Green’s functions can be obtained by the self-consistent solution of Hedin’s equations [31, 32, 33] which is implemented in standard computer codes [19]. We have assumed that the core-hole is localized and only enters as a parameter. This allows to express the signal using single-particle Green’s functions. The “shakeup” and “shakeoff” excitations [19] in which more than one electron is excited due to creation of a core-hole is included within the CIS approximation. Equation (12) expresses the correlation function of exciton operators in terms of the single-electron Green’s functions and the particle-hole propagator for valence orbitals. The propagator is subsequently expressed in terms of the CIS expansion coefficients for the valence excited states. This approximation can be relaxed by calculating this propagator using the time-dependent Hartree Fock (TDHF). Since TDHF is often insufficient, higher-order corrections can be derived systematically using the many-body expansion for the particle-hole propagator [34]. The present formulation can be extended to incorporate core-hole and nuclear dynamics through the corresponding Green’s functions using equation of motion technique [35] as was done in Ref. [31].

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APPENDIX A: DERIVATION OF EQ. [17]

The correlation function expression corresponding to the diagrams shown in Figs. 3a and 3b is given by

\[ S_{\text{CXRS}}(\tau) = 2\text{Re} \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt_3 \times \left[ \int_{-\infty}^{t_2} dt_1 \langle B(t_3)B^\dagger(t_1)B(t_2)B^\dagger(t_1) \rangle + \int_{-\infty}^{t_1} dt_1 \int_{-\infty}^{t} dt_2 \langle B(t_2)B^\dagger(t_1)B_3(t_3)B^\dagger(t) \rangle E_1^*(t_2-\tau)E_1(t_1-\tau)E_2(t)E_2^*(t_3) \right]. \]  

(A1)

Since the pulses are temporally-well-separated and are short compared to the time delay \( \tau \), the upper limits of \( t_2 \) and \( t_3 \) integrals in the first and second terms may be safely extended to infinity. Interchanging the integration variables \( t_1 \) and \( t_2 \) in the first term we obtain

\[ S_{\text{CXRS}}(\tau) = 2\text{Re} \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt_3 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 E_2(t)E_2^*(t_3) \times \left[ \langle B(t_3)B^\dagger(t)B(t_1)B^\dagger(t_2) \rangle E_1^*(t_2-\tau)E_1(t_1-\tau) + \langle B(t_2)B^\dagger(t_1)B(t_3)B^\dagger(t) \rangle E_1^*(t_2-\tau)E_1(t_1-\tau) \right]. \]  

(A2)

The correlation functions in Eq. (A2) can be expanded in terms of the many-body states of the system. By inserting the identity operator \( I = \sum_\nu |\nu\rangle \langle \nu| \), where \( \nu = c, e \), we obtain

\[ \langle B(t_3)B^\dagger(t)B(t_1)B^\dagger(t_2) \rangle = \sum_{ac\nu} P(a) B_{ac} B^\dagger_{ac} B^\dagger_{ce} B^\dagger_{ea} e^{i\omega_{\nu_1} t_1} e^{-i\omega_{\nu_2} t_3} e^{i\omega_{\nu_3} t_2} e^{-i\omega_{\nu_4} t} \]  

(A3)

where \( B_{ac} = \langle a|B|c\rangle \), etc. and \( P(a) \) is the equilibrium probability of the system to be in state \( |a\rangle \). A similar expansion can be obtained for the other correlation function. Substituting these results in Eq. (A2) and defining the Fourier transform of the pulse envelope as

\[ E(t) = \int \frac{d\omega}{2\pi} e^{i\omega t} E(\omega), \]  

(A4)

the signal can be expressed in the Doorway/Window representation as

\[ S_{\text{CXRS}}(\tau) = \sum_{ac} [D_{ac} W_{ca} e^{-i\omega_{ac} \tau} + \text{c.c.}] \]  

(A5)

where the Doorway wavepacket is given by Eq. (15) with

\[ D_{ac} = \sum_e P(a) B_{ac} B^\dagger_{ce} \int \frac{d\omega}{2\pi} E_1^*(\omega) e^{i(\omega - \omega_{ac}) \tau} \]  

(A6)

The Window wavepacket is similarly given by Eq. (19) with

\[ W_{ca} = \sum_e B^\dagger_{ce} B^\dagger_{ea} \int \frac{d\omega}{2\pi} \frac{1}{\omega + \omega_{ee} + i\eta} - \frac{1}{\omega + \omega_{cc} - i\eta} E_2^*(\omega) E_2(\omega + \omega_{ac}). \]  

(A7)

Since in the limit \( \eta \to 0 \)

\[ \frac{1}{\omega + \omega_{ee} \pm i\eta} = \text{PP} \frac{1}{\omega + \omega_{ee}} \mp i\pi \delta(\omega + \omega_{cc}), \]  

(A8)

where \( \text{PP}(1/x) \) denotes the principal part of \( 1/x \), the frequency integration in Eq. (A7) can be performed, resulting in

\[ W_{ca} = 2\pi \sum_e B^\dagger_{ce} E_2(\omega_{ee}) E_2^*(\omega_{ac}). \]  

(A9)

APPENDIX B: GREEN’S FUNCTION EXPRESSION FOR THE PUMP-PROBE SIGNAL

We start with Eq. (A1) and allow for the creation of a core-hole at \( m \) and \( n \). The interaction with \( E_1^* \) \( E_2 \) creates (destroys) a core-hole at \( m \) \( n \). We then have

\[ S_{\text{CXRS}}(\tau) = 2\text{Re} \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt_3 \times \left\{ \int_{-\infty}^{t_2} dt_1 \langle B_n(t_3)B^\dagger_n(t)B_m(t_2)B^\dagger_m(t_1) \rangle + \int_{-\infty}^{t_1} dt_1 \int_{-\infty}^{t} dt_2 \langle B_m(t_2)B^\dagger_m(t_1)B_n(t_3)B^\dagger_n(t) \rangle \right\} \times E_1^*(t_2-\tau)E_1(t_1-\tau)E_2(t)E_2^*(t_3). \]  

(B1)

Inserting the projection operators twice in Eq. (A1), the correlation function in the first term can be expressed as

\[ \langle B_n(t_3)B^\dagger_n(t)B_m(t_2)B^\dagger_m(t_1) \rangle \approx \sum_a P(a) \langle a|B_n(t_3)P_n B^\dagger_n(t)B_m(t_2)P_m B^\dagger_m(t_1) |a \rangle \]

\[ = \sum_a P(a) \sum_{ijkl} \mu_{im} \mu_{kj} \mu_{ik} \mu_{jl} e^{i\omega_a (t_3-t_1)} \times \langle a|c_k c_j^\dagger U(t_3-t)P_n c_n c_i^\dagger U(t_2-t) c_j c_j^\dagger P_m U(t_2-t_1) c_m c_i^\dagger |a \rangle \]  

(B2)

Substituting this back in Eq. (B1), and changing variables \( t_2 - t_1 = s' \) and \( t - t_3 = s \), the first term can be
expressed as
\[ I_1 = 2\text{Re} \sum_{a} P(a) \sum_{ijkl} \mu_{im} \mu_{mj} \mu_{kn} \mu_{nl} \int_{-\infty}^{\infty} dt \int_{0}^{\infty} ds \times \int_{-\infty}^{\infty} dt_2 \int_{0}^{\infty} ds' e^{i\omega_s(t-t_2)} G_{kj'}^{(s')}(s) G_{j'i}^{(s)}(s') \times \langle \chi(i', t)|U(t-t_2)|\chi(i, j') \rangle \times E_2(t) E_2^*(t-s) E_1^*(t_2-t_\tau) E_1(t_2-t-s_\tau) \] (B3)

where the \( |\chi(i, j') \rangle \) basis is defined in Eq. (19) and
\[ \theta(s)|a|c_m c_i U(s)c_j c_m |a \rangle = i\theta(s)e^{-i\omega_s} G_{ij}^{(s)}(s) \]
\[ \theta(s)|a|c_m c_i U(-s)c_j c_m |a \rangle = -i\theta(s)e^{i\omega_s} G_{ij}^{(s)}(s) \] (B4)

Inserting the identity operator in terms of the CIS states in (Eq. (19)), Eq. (B3) finally becomes
\[ I_1 = 2\text{Re} \sum_{ac} P(a) \sum_{ijkl} \mu_{im} \mu_{mj} \mu_{kn} \mu_{nl} f_{c_i c_i'} f_{c_j c_j'}^* \times \int_{-\infty}^{\infty} dt \int_{0}^{\infty} ds e^{-i\omega_s t} G_{kj'}^{(s)}(s) E_2(t) E_2^*(t-s) \times \int_{-\infty}^{\infty} dt_2 \int_{0}^{\infty} ds' e^{i\omega_{s'} t_2} G_{j'i}^{(s')} E_1^*(t_2-t_\tau) E_1(t_2-t-s_\tau) \] (B5)

Performing Fourier transform [Eq. (A4)], Eq. (B3) can also be expressed as
\[ I_1 = 2\text{Re} \sum_{ac} P(a) \sum_{ijkl} \mu_{im} \mu_{mj} \mu_{kn} \mu_{nl} f_{c_i c_i'} f_{c_j c_j'}^* \times \int \frac{d\omega}{2\pi} G_{kj'}^{R(n)}(\omega-\omega_{ca}) E_2(\omega) E_2^*(\omega-\omega_{ca}) e^{i\omega_{ca} \tau} \times \int \frac{d\omega'}{2\pi} G_{j'i}^{R(n)}(\omega-\omega_{ca}) E_1^*(\omega) E_1(\omega-\omega_{ca}) \] (B6)

where \( G_{ij}^{R(n)}(\omega) \) is defined in Eq. (11).

Proceeding along the same steps that lead from Eq. (B2) to (B6), and taking the complex conjugate (this is allowed since we are looking for the real part), the second term in Equation (B1) can be recast as
\[ I_2 = -2\text{Re} \sum_{ac} P(a) \sum_{ijkl} \mu_{im} \mu_{mj} \mu_{kn} \mu_{nl} f_{c_i c_i'} f_{c_j c_j'}^* \times \int \frac{d\omega}{2\pi} G_{kj'}^{R(n)}(\omega-\omega_{ca}) E_2(\omega) E_2^*(\omega-\omega_{ca}) e^{i\omega_{ca} \tau} \times \int \frac{d\omega'}{2\pi} G_{j'i}^{R(n)}(\omega-\omega_{ca}) E_1^*(\omega) E_1(\omega-\omega_{ca}) \] (B7)

The signal is finally given by
\[ S_{CXR}(\tau) = I_1 + I_2 \] (B8)

which results in Eqs. (21) and (22).

**APPENDIX C: EQUIVALENCE OF EQUATIONS (A6)–(A7) AND (21)–(22) WITHIN THE CIS APPROXIMATION**

The pump-probe signal is given by Eq. (15) where the Doorway and the Window are given in terms of the many-body states by Eqs. (A5) and (A7). Green’s function expressions are given by Eqs. (21) and (22).

We first expand the GF in the many-body states. Using Eqs. (11) and (B3), we can write
\[ G_{ij}^{R(n)}(\omega+\omega_{ac}) = -i \int_{0}^{\infty} dt e^{-i(\omega-\omega_{ec})t} (|a|c_m c_i U(t)c_j c_m |a \rangle \times \int \frac{d\omega}{2\pi} \omega + \omega_{ac} - \frac{1}{\omega + \omega_{ac} - \eta} \right] \] (C1)

By inserting the identity operator, \[ \sum_v |e\rangle \langle e| \], before and after the evolution operator and performing the integration over time, Eq. (C1) reduces to
\[ G_{ij}^{R(n)}(\omega+\omega_{ac}) = -\sum_{v} \frac{\langle v|c_m c_i |e\rangle \langle e|c_m c_j |v \rangle}{\omega + \omega_{ec} - \eta} \] (C2)

Substituting this in Eqs. (21) and (22), we obtain
\[ D_{ac} := -\sum_{ijke} P(a) \mu_{im} \mu_{mj} f_{c_i c_k}^* (|a|c_m c_i |v \rangle \times \int \frac{d\omega}{2\pi} \omega + \omega_{ac} - \frac{1}{\omega + \omega_{ac} - \eta} \right] \] (C3)

We next consider the expressions for the Doorway and Window in terms of the many-body states. Using Eq. (4), Eqs. (A5) and (A7) can be expressed as,
\[ D_{ac} = \sum_{ijke} P(a) \mu_{im} \mu_{mj} (|a|c_m c_i |v \rangle \times \int \frac{d\omega}{2\pi} \omega + \omega_{ac} - \frac{1}{\omega + \omega_{ac} - \eta} \right] \] (C5)

and
\[ W_{ca} := \sum_{ijke} \mu_{kn} \mu_{nj} (|c_k c_i |v \rangle \times \int \frac{d\omega}{2\pi} \omega + \omega_{ac} + \frac{1}{\omega + \omega_{ac} - \eta} \right] \] (C6)

Using the CIS expansion for the excited states \( |e \rangle \), Eq. (13), we can write
\[ \langle e|c_m c_j |v \rangle = \sum_{i,j'} f_{c_i c_j'} \langle e|c_m c_i c_j' |v \rangle \] (C7)
where in going to the second line the sum over \( i' \) can be done since state \( |e\rangle \) corresponds to single excited \( N+1 \)-valence electrons. Substituting (C7) in (C6) we get

\[
D_{ac} = \sum_{i,j,k} P(a)\mu_{im}\mu_{jm} f_{eijk} \langle e|c_m^\dagger|e\rangle \langle e|c_{m'}^\dagger|a\rangle 
\]

\[
\int \frac{d\omega}{2\pi} \frac{E_1(\omega)E_1^*(\omega + \omega_{ac})}{\omega + \omega_{ec} + i\eta}
\]

(C8)

Taking the complex conjugate and interchanging dummy indices \( i \) and \( j \), Eq. (C8) becomes same as (C3). Similarly one can show that Eq. (C6) is same as (C4) within CIS approximation.

This proves the equivalence of Eqs. (A6)-(A7) and Eqs. (21)-(22).

[1] M. Drescher, M. Hentschel, R. Kienbereger, G. Tempea, C. Spielman, G. A. Reider, P. B. Corkum and F. Krausz, Science 291, 1923 (2001).
[2] R. F. Service, Science 298, 1356 (2002).
[3] Attosecond Spectroscopy: Special Issue of Science 317, August (2007).
[4] I. Thomann, E. Gregonis, X. Liu, R. Trebino, A. S. Oulianov, I. V. Tomov, A. S. Dvornikov and P. M. L. X. Chen, X. Zhang, E. C. Wasinger, K. Attenkofer, R. Santra, C. Buth, E. R. Peterson, R. W. Dunford, E. P. J. J. Rehr and R. C. Albers, Rev. Mod. Phys. 80, 011806 (2008).
[5] J. A. Soininen, A. L. Ankudinov, J. J. Rehr, and E. L. Shirley, Phys. Rev. B 77, 165202 (2008).
[6] T. Privalov, F. Gel’mukhanov and H. Ågren, Phys. Rep. 312, 87 (1999).
[7] M. Magnuson, L.-C. Duda, S. M. Butorin, P. Kuiper and J. Nordgren, Phys. Rev. B 74, 172409 (2006); C. Sathe, F. F. Guimarães, J.-E. Rubensson, J. Nordgren, A. Agui, J. Guo, U. Ekstrom, P. Norman, F. Gel’mukhanov, and H. Ågren, Phys. Rev. A 74, 062512 (2006).
[8] F. de Groot and A. Kotani, "Core Level Spectroscopy of Solids", CRC Press (Taylor & Francis Group), New York (2008). A. Kotani and S. Shin, Rev. Mod. Phys. 73, 203 (2001).
[9] H. Sternemann, J. A. Soininen, C. Sternemann, K. Hamalainen and M. Tolan, Phys. Rev. B 75, 075118 (2007); S. Galambosi, M. Knaapila, J. A. Soininen, K. Ngyard, S. Huotari, F. Galbrecht, U. Scherf, A. P. Monkman and K. Hamalainen, Macromolecules 39, 9261 (2006).
[10] Y. Hikosaka, Y. Velkov, E. Shigemasa, T. Kaneyasu, Y. Tanemori, J. Liu and F. Gel’mukhanov, Phys. Rev. Lett. 101, 073001 (2008).
[11] C. Bressler and M. Chergui, Chem. Rev. 104, 1781 (2004).
[12] D. A. Oulianov, I. V. Tomov, A. S. Dvornikov and P. M. Rentzepis, PNAS, 99, 12556 (2002).
[13] L. X. Chen, X. Zhang, E. C. Wasinger, K. Attenkofer, G. Jennings, A. Z. Muresan and J. S. Lindsey, J. Am. Chem. Soc. 129, 9616 (2007); L. X. Chen, Ann. Rev. Phys. Chem. 56, 221 (2005).
[14] R. Santan, C. Buth, E. R. Peterson, R. W. Dunford, E. P. Kaunter, H. Southworth, L. Young, Journal of Physics: Conference Series 88, 012052 (2007).
[15] S. Mukamel, Principles of Nonlinear Optical Spectroscopy, Oxford University Press, New York (1995).
[16] A. C. Ashley and S. Doniach, Phys. Rev. B 11, 1279 (1975).
[17] J. J. Rehr and A. L. Ankudinov, Coordination Chem. Rev. 249, 131 (2005).
[18] J. A. Soininen, A. L. Ankudinov and J. J. Rehr, Phys. Rev. B 72, 045136 (2005).
[19] A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, Phys. Rev. B 58, 7565 (1998).
[20] J.J. Rehr and R. C. Albers, Rev. Mod. Phys. 72, 621 (2000).