Wavepacket control and simulation protocol for entangled
two-photon-absorption of molecules

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Quantum light spectroscopy, providing novel molecular information non-accessible by classical light, necessitates new computational tools when applied for complex molecular systems. We introduce two computational protocols for the molecular nuclear wave packet dynamics interacting with an entangled photon pair to produce the entangled two-photon absorption signal. The first involves summing over transition pathways in a temporal grid defined by two light-matter interaction times accompanied by the field correlation functions of quantum light. The signal is obtained by averaging over the two-time distribution characteristic of the entangled photon state. The other protocol involves a Schmidt decomposition of the entangled light and requires summing over the Schmidt modes. We demonstrate how photon entanglement can be used to control and manipulate the two-photon excited nuclear wave packets in a displaced harmonic oscillator model.

I. INTRODUCTION

Numerous novel spectroscopic techniques which exploit the variation of photon statistics upon interaction with matter are made possible by quantum light [1, 2]. Such quantum spectroscopy has been demonstrated, both theoretically and experimentally, to be a powerful technique that can reveal molecular information not accessible by classical light [2] and can further enhance the signal-to-noise ratio and resolution beyond the classical limit [3]. The incoming photon statistics can be employed as a novel control knob for the optical response functions of matter [4, 5]. Quantum optical effects such as the Hong-Ou-Mandel two-photon interference [6] can be used to generate signals which have no classical analogs [7–9].
Entangled two-photon absorption (ETPA) has recently attracted considerable attention [10–26]. The extent to which two-photon absorption rate can be enhanced by entangled light is under debate. While several ETPA experiments have been reported [27, 28], a recent theoretical analysis shows that ETPA events is below the detection level for typical molecular systems in realistic experimental setup [10]. In ETPA, a molecule is promoted from the ground state to an excited state by simultaneously absorbing two, degenerate or nondegenerate, photons. This technique drastically differs from classical two-photon absorption. At low photon fluxes, it scales linearly, rather than quadratically with the pump photon intensity [24, 29]. This is because the entangled photon pair generated by e.g. spontaneous parametric downconversion [30–33] is created simultaneously and thus interacts with molecules at the same time. Furthermore, when a narrowband pump is utilized in the twin-photon generation, they exhibit a strong frequency-anticorrelation, i.e., detection of one photon reveals the frequency of its twin within a small uncertainty determined by the pump bandwidth. This energy-time entanglement can be used in spectroscopy to manipulate the quantum interference among transition pathways, which have been shown to induce classically disallowed collective excitations [34], and to probe classically-dark bipolariton states [20]. Since the ETPA signal depends on the entangled photon pair statistics, the biphoton joint spectral amplitude can be used to optimize the two-photon excitation process, leading to quantum control by entangled light [35]. Early applications have focused on controlling the electronically excited-state populations in model systems with frozen nuclear motion [35]. However, nuclear motions are responsible for reactive dynamics initiated by two-photon absorption, especially for molecules passing through conical intersections with strong vibrational-electronic (vibronic) coupling.

To fully describe the coupled electron-vibration-photonic dynamics, we develop a computational framework involving molecular nuclear wave packet quantum dynamics interacting with quantum light. While the response to classical laser pulses can be obtained by solving the time-dependent Schrödinger equation, this is not the case for quantum light.

Our simulation protocol, based on time-dependent perturbation theory for the light-matter interaction, involves summing over all two-photon transition pathways in a two-dimensional temporal grid defined by the two interaction times with the entangled photon pair. Using a displaced harmonic oscillator model widely used to describe vibronic transitions [36], we demonstrate how photon entanglement, a novel control knob not available for classical light, can be utilized to control the nuclear
wave packet in electronically excited states. Three scenarios are examined whereby the intermediate electronic state is resonant, off-resonant, and, far off-resonant with the incoming photons. We find that the two-photon-excited population is largest for the resonant case. A linear dependence of the final-state population on the entanglement time is found for short entanglement times. This observation is rationalized by an analytical analysis based on sum-over-states expression. We further demonstrate that entanglement provides a useful control knob for the two-photon excited wave packets. Modulating the entanglement time has the strongest effect on the shape of created nuclear wave packet in the off-resonant case.

II. THEORY AND COMPUTATION

A. The entangled two-photon absorption signal

We consider a molecule-photon system described by the Hamiltonian ($\hbar = e = 4\pi\epsilon_0 = 1$)

$$H = H_M + H_R + H_{RM}. \quad (1)$$

The molecular Hamiltonian $H_M = T_n + H_{BO}(R)$ represents the vibronic dynamics where $T_n$ is the nuclear kinetic energy operator, $H_{BO}(R) = \sum_\alpha V_\alpha(R) |\psi_\alpha(R)\rangle \langle \psi_\alpha(R)|$ the adiabatic (Born-Oppenheimer) electronic Hamiltonian with $V_\alpha(R)$ being the $\alpha$th potential energy surface (PES). The radiation Hamiltonian

$$H_R = \sum_{j=s,i} \int_0^\infty d\omega \hbar \omega \left( a_j^\dagger(\omega_j) a_j(\omega_j) + \frac{1}{2} \right) \quad (2)$$

represents two continua of photon modes, signal and idler, generated by a SPDC process, $H_{RM} = \sum_j -\mu \cdot E_j(r)$ is the light-matter interaction in the electric dipole approximation, where $E_j(r) = E_j^{(+)}(r) + E_j^{(-)}(r)$ and

$$E_j^{(+)}(r) = i \int_0^\infty d\omega \mathcal{E}(\omega) e_j a_j(\omega) e^{-i\mathbf{k} \cdot r} \quad (3)$$

the electric field operator of the $j$th photon beam with polarization $e_j$ at molecular location $r$, and $\mathcal{E}(\omega) \equiv \sqrt{\frac{2\omega}{c\pi A}}$ with the beam transversal area $A$, the refractive index $n$, and the speed of light.
c. The joint electron-nuclei-photonic space is given by the tensor product of the electron-nuclear Hilbert space and the photon modes Fock space. The joint light-matter state is

$$|\Psi(t)\rangle = \sum_{\alpha,n} |\psi_\alpha(R)\rangle |\chi_{\alpha,n}(t)\rangle |n(\omega)\cdots\rangle$$  \hspace{1cm} (4)$$

where $|\psi_\alpha(R)\rangle$ is the adiabatic electronic state, $\chi_{\alpha,n}(R,t)$ the nuclear wavefunction at the $\alpha$th electronic state and the photon state is described in the occupation number representation $|n(\omega)\rangle \equiv |n(\omega)n(\omega')\cdots\rangle$. The initial state of the joint light-matter system is $|\psi_0(R)\rangle |\chi_0\rangle |\Phi_0\rangle$ where $|\Phi_0\rangle$ describes the quantum light. The probability to arrive at the final electronic state $|\psi_f\rangle$ at time $t$ is given by

$$P(t) = \int dR \langle \tilde{\Psi}(t) | \psi_f(R), R \rangle \langle \psi_f(R), R | \otimes |0\rangle \langle 0| |\Psi(t)\rangle = \int dR |\chi_f(R,t)|^2$$  \hspace{1cm} (5)$$

where

$$\chi_f(R,t) = \langle \psi_f(R), R | \otimes \langle 0| |\Psi(t)\rangle$$  \hspace{1cm} (6)$$

is the nuclear wavefunction for the final electronic state created by the two-photon excitation process where the photon modes are in the vacuum state $|0\rangle$. This is obtained by projecting the total state onto the final electronic state and the photon vacuum after the pump pulse $t > t_p$. The joint light-matter state at time $t$ is obtained using time-dependent perturbation theory in the light-matter interaction in the interaction picture of $H_0 = H_M + H_R$. To second-order, we have

$$|\tilde{\Psi}(t)\rangle = -\sum_{i,j} \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 \mu(t_2) \cdot e_j (\mu(t_1) \cdot e_i |\psi_0\rangle |\chi_0\rangle E_j^{(+)}(t_2)E_i^{(+)}(t_1) |\Phi_0\rangle$$  \hspace{1cm} (7)$$

where $A(t) = U_0^\dagger(t)AU_0(t)$ is the operator $A$ in the interaction picture, $i, j$ are the beam indices, and $|\tilde{\Psi}(t)\rangle = U_0^\dagger(t) |\Psi(t)\rangle$. We consider two incoming beams and neglect the zero- (no interaction) and first-order (one-photon) processes in Eq. (7) as they do not contribute to the two-photon absorption. The dipole operator acts in the joint electron-nuclear space

$$\mu = \sum_{\alpha \neq \beta} \int dR \langle \psi_\beta(R) | \mu | \psi_\alpha(R) \rangle_R |\psi_\beta(R), R \rangle \langle \psi_\alpha(R), R |$$  \hspace{1cm} (8)$$

where $\alpha, \beta$ labels the electronic states and $\langle \cdots \rangle_R$ refers to integrating over electronic degrees of freedom. We further assume that the molecule has no permanent dipole moments so that $\alpha \neq \beta$. Inserting Eq. (7) into Eq. (6) yields

$$\tilde{\chi}_f(R,t) = -\sum_{i,j} \sum_e \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 V_{je}^{(j)}(R,t_2) V_{eg}^{(i)}(R,t_1) \chi_0(R) \Phi_{j,i}(t_2,t_1)$$  \hspace{1cm} (9)$$
where \( V^{(j)}_{\alpha \beta}(R) = \langle \psi_\beta(R) | \mu \cdot e_j | \psi_\alpha(R) \rangle \) is the transition dipole moment projected on the polarization of \( j \)th photon beam, \( e \) runs over all intermediate electronic surfaces, and

\[
\Phi_{ji}(t_2, t_1) = \langle 0 | E^{(+)}_j(t_2) E^{(+)}_i(t_1) | \Phi_0 \rangle
\]  
(10)

is the entangled two-photon transition amplitude. Transforming back to the Schrödinger picture we obtain

\[
\chi_f(R, t) = -\sum_{i,j} \sum_{e} \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \xi(t_2, t_1)
\]

\[
\xi(t_2, t_1) \equiv U_f(t, t_2) V^{(j)}_{fe}(R) U_e(t_2, t_1) V^{(i)}_{eg}(R) U_g(t_1, t_0) \chi_0(R) \Phi_{ji}(t_2, t_1)
\]  
(11)

where \( U_M(t, t') = e^{-iH_M(t-t')} \) is the molecular free propagator. The wave packet \( \xi(t_2, t_1) \) represents a single two-photon-absorption event with two light-matter interactions occurring at \( t_1 \) and \( t_2 \). This reduces to the \( |g\rangle \rightarrow |f\rangle \) transition amplitude if the nuclear motion is frozen.

Using the Feynman diagram Fig. 1, Eq. (11) can be interpreted as follows: The final nuclear wave packet at time \( t \) on the \( f \)th PES is given by a sum over of all possible transition pathways. Each pathway contains two dipole interaction times \( t_1 \) and \( t_2 \), where the molecule undergoes a transition between electronic states. Between \( t_0 \) and \( t_1 \), the molecule remains at the ground state. At \( t_1 \), the molecule makes a transition to the \( e \)th electronic state, launching a nuclear wave packet dynamics until it interacts with the second photon at \( t_2 \), which brings it to the final \( f \)-PES. Nuclear dynamics then takes place between \( t_2 \) and the final time \( t \) on this PES. Each two-photon transition pathway depends on the two-photon transition amplitude \( \Phi_{ji}(t_2, t_1) \), whose modulus squared gives the probability of detecting the \( i \)-photon at time \( t_1 \) and \( j \)-photon at \( t_2 \). The molecule thus serves as a photodetector [37]. The dependence of the ETPA signal on the photon statistics allows to control the two-photon excited nuclear wave packet on the excited-state PES by shaping the two-photon wave function.

B. Energy-Time entangled light

The two-photon wavefunction is described by the joint spectral amplitude (JSA) of the entangled photon pair. Here we employ the twin-photon, signal and idler, state, generated by a type-II SPDC
FIG. 1. Feynman diagram representing Eq. (11). $|g⟩$, $|e⟩$, $|f⟩$ represent the ground, intermediate, and final electronic states. The $U_α(t,t′) = e^{i(T_α + V_α(R))(t−t′)}$ is the free-molecule propagator on the $α$th PES. Between $t_0$ and $t_1$, the molecule remains in the ground state. The first photon, either signal and idler, brings the molecule to the intermediate state, launching nuclear dynamics on the associated PES.

$\Phi⟩ = ∫∫_{0}^{∞} dω_s dω_i J(ω_s, ω_i)a_s^\dagger(ω_s)a_i^\dagger(ω_i)|0⟩$ \hspace{1cm} (12)

where the JSA $J(ω_s, ω_i)$ is the amplitude of detecting the signal photon with frequency $ω_s$ and idler photon with frequency $ω_i$, and $a_j(ω)$ ($a_j^\dagger(ω)$) annihilates (creates) a $j$-photon with frequency $ω$ satisfying the boson commutation relation $[a_j(ω), a_j^\dagger(ω′)] = δ_{jj′}\delta(ω−ω′)$. We focus on the frequency anti-correlation of the entangled photons, and suppress the spatial degrees of freedom \cite{32, 38}. For a Gaussian pump with central frequency $\bar{ω}_p$ and bandwidth $σ_p$, the JSA reads

$J(ω_1, ω_2) = \mathcal{N} \exp \left(-\frac{(ω_1 + ω_2 − \bar{ω}_p)^2}{4σ_p^2}\right)\text{sinc} \left(\frac{ΔkL}{2}\right)$ \hspace{1cm} (13)

where $L$ is the crystal length, $Δk = k_s(ω_s) + k_i(ω_i) − k_p(ω_s + ω_i)$ is the wavenumber mismatch and $k_j = n_j(ω_j)ω_j/c$. $\mathcal{N}$ is the normalization factor ensuring $∫∫ dω_s dω_i |J(ω_s, ω_i)|^2 = 1$, and $\text{sinc} (x) = \frac{\sin(x)}{x}$. We focus on the degenerate state where the central frequencies for the signal and idler photons
are identical $\bar{\omega}_s = \bar{\omega}_i = \frac{1}{2}\bar{\omega}_p$. Taylor expansion of the wave number gives $k_j(\omega_j) \approx k_j(\bar{\omega}_j) + \Delta_j/v_j$ where $\Delta_j = \omega_j - \bar{\omega}_j$ and $v_j \equiv \frac{d\omega_j}{d\bar{\omega}_j}$ is the group velocity of $j$th beam. Under the phase matching condition $k_s(\bar{\omega}_s) + k_i(\bar{\omega}_i) - k_p(\bar{\omega}_p) = 0$, the JSA becomes

$$J(\Delta_s, \Delta_i) = N \exp \left( -\frac{(\Delta_s + \Delta_i)^2}{4\sigma_p^2} \right) \text{sinc} \left( \frac{1}{2} \bar{T} (\Delta_s + \Delta_i) + \frac{1}{2} (\Delta_s - \Delta_i) T_e \right)$$  (14)

where $T_e = \frac{1}{2} \left( \frac{T_s}{v_s} - \frac{T_i}{v_i} \right)$ is the entanglement time characterizing the difference between the arrival times of the photon pair and $\bar{T} = \frac{1}{2} \left( \frac{T_s}{v_s} + \frac{T_i}{v_i} \right) - \frac{T_p}{v_p}$ is the travel time difference between the biphoton and the pump inside the nonlinear crystal. The twin-photon JSA for different entanglement times are shown in Fig. 2. Each photon bandwidth is controlled by the entanglement time with shorter $T_e$ leading to broader bandwidth, whereas the sum frequency of the signal and idler beams are narrowly distributed independent of the bandwidth of individual photon.

![FIG. 2. The joint spectral amplitude $|J(\Delta_s, \Delta_i)|$ of the quantum light [Eq. (14)] for different entanglement times $T_e$. Here $\sigma_p = 0.2 \text{eV}, \bar{T} = 0$.](image)

The two-photon detection amplitude is given by

$$\Phi_{is}(t_2, t_1) = \int \int d\omega_s d\omega_i \mathcal{E}(\omega_i) \mathcal{E}(\omega_s) e^{-i\omega_1 t_2 - i\omega_s t_1} f(\omega_s, \omega_i)$$  (15)
Invoking the narrowband limit $\mathcal{E}(\omega_j) \approx \mathcal{E}(\bar{\omega}_j)$, changing the variables to $\Delta_j$ and extending the integration range to $(-\infty, \infty)$, yields

$$\Phi_{is}(t_2, t_1) = (2\pi)^2 \mathcal{E}(\bar{\omega}_i) \mathcal{E}(\bar{\omega}_s) \exp(-i\bar{\omega}_it_2 - i\bar{\omega}_st_1) J(t_1, t_2)$$

where $J(t_1, t_2) = \int_{-\infty}^{\infty} \frac{d\Delta_i d\Delta_s}{(2\pi)^2} \mathcal{J}(\Delta_s, \Delta_i) e^{-i\Delta_it_2 - i\Delta_st_1}$ is the joint temporal amplitude of the twin-photons. For $\bar{T} = 0$,

$$J(t_1, t_2) = \sqrt{\frac{\sigma_p}{T_\epsilon}} (2\pi)^{-5/4} e^{-\sigma_p^2(t_1 + t_2)^2/4} \Pi \left( \frac{t_1 - t_2}{2T_\epsilon} \right)$$

where $\Pi(x) = 1$ for $|x| < \frac{1}{2}$ and 0 otherwise.

C. Simulation Protocol Based on a Time Grid

Equation (11) suggests the following simulation protocol: we first sample $(t_2, t_1)$ on a two-dimensional triangular grid with $t_2$ ranging from $t_0$ to the final time $t$, and $t_1$ samples $t_0$ to $t_2$; for each $(t_1, t_2)$, we compute the nuclear wave packet $\xi(t_2, t_1)$ by a wave packet dynamics solver. The final wave packet can then be obtained by a sum over all $\xi(t_2, t_1)$.

The final nuclear wave packet Eq. (11) is simulated as follows (for brevity, we assume a single intermediate electronic state $e$):

1. Set the initial wave packet to $\chi_e(R) = \mu_{eg}(R) \chi_0(R)$

2. Propagate the wave packet on the $e$th PES for time interval $\tau$ leading to $\chi_e(R, \tau) = U_M(\tau) \mu_{eg}(R) \chi_0(R)$.

3. Using Eq. (15), perform the following integration to obtain an auxiliary wavepacket $\zeta(R, \tau)$,

$$\zeta(R, \tau_2) = \int_0^{\tau_2} d\tau \Phi(\tau_2 + t_0, \tau_2 - \tau + t_0) \chi_e(R, \tau)$$

4. For each $\tau_2 = t - t_0 - t_2$, apply the dipole operator to $\zeta(R, \tau_2)$ that brings the molecule to the final electronic state, $\mu_{fe}(R) \zeta(R, \tau_2)$, and propagate the wave packet for $t - t_0 - \tau_2$ on the final PES. Summing up all possible $\tau_2$ leads to

$$\chi_f(R, T = t - t_0) = \int_0^T d\tau_2 U_M(t - t_0 - \tau_2) \mu_{fe}(R) \zeta(R, \tau_2)$$
The molecular propagator is computed using a wave packet dynamics on a single PES [39]. The second-order split-operator method is employed for adiabatic wave packet dynamics on a single PES $V_\alpha(R)$. A Trotter decomposition of the propagator is employed

$$U_\alpha(\delta t) = e^{-iV_\alpha \delta t/2} e^{-iT_\alpha \delta t} e^{-iV_\alpha \delta t/2} + \mathcal{O}(\delta t^3)$$

for a short time interval $\delta t$ and fast Fourier transform switching the wavefunction between the coordinate and momentum space.

III. RESULTS AND DISCUSSION

Simulations were carried out for a three-state displaced harmonic oscillator model with a single nuclear coordinate $x$ and corresponding momentum $p$. The PESs depicted in Fig. 3 are given by

$$V_\alpha(x) = \frac{p^2}{2} + \frac{\omega^2}{2} (x - d_\alpha)^2 + E_\alpha$$

where $\alpha = \{g, e, f\}$ referring to the ground, intermediate, and final electronic states, respectively, and $d_\alpha$ is the displacement, and $E_\alpha$ is the zero-phonon line. By tuning the energy $E_e$, we cover three scenarios whereby the intermediate PES is resonant, off-resonant and far off-resonant with respect to the incoming photons. Other parameters are $E_g = 0, E_f = 2 \text{eV}, d_g = 0, d_e = -d_f = -10a_0$.

A. Sum-over-states expansion of the molecular response

We explore the variation of the electronic populations and wave packets with the entanglement time by employing the sum-over-states expression for the molecular response in the vibronic eigenstates of the molecular Hamiltonian $H_M$. Let $|\alpha \nu\rangle$ denote the vibronic states associated with $\alpha$th electronic state with eigenenergies $\omega_{\alpha \nu}$, the molecular propagator and the interaction picture dipole operator is

$$U_M(t) = \sum_\alpha \sum_\nu e^{-i\omega_{\alpha \nu} t} |\alpha \nu\rangle \langle \alpha \nu|$$

and

$$V^{(j)}(t) = \sum_{\beta \nu', \alpha \nu} V^{(j)}_{\beta \nu', \alpha \nu} e^{i\omega_{\beta \nu', \alpha \nu} t} \langle \beta \nu' | \alpha \nu \rangle$$

with $\omega_{\beta \nu', \alpha \nu} = \omega_{\beta \nu'} - \omega_{\alpha \nu}$. Inserting these into Eq. (11) yields

$$|\chi_f(t)\rangle = \sum_\nu A_{\nu \nu' \alpha \nu}(t) |\nu \nu' \rangle$$

where

$$T_{\nu \nu' \alpha \nu}(t) = (2\pi)^2 \mathcal{E}(\overline{\omega}_g) \mathcal{E}(\overline{\omega}_s) \sum_{e, \nu''} \mu^{(s)}_{e, \nu'' \nu' \nu''} \int_{t_0}^t dt_2 e^{i(\omega_{e, \nu'' \nu' - \overline{\omega}_g})t_2} \int_{t_0}^{t_2} dt_1 e^{i(\omega_{e, \nu'' \nu' - \overline{\omega}_s})t_1} J(t_1, t_2)$$

(22)
FIG. 3. Potential energy surfaces of the displaced harmonic oscillator model corresponding to three different cases where the intermediate electronic state is resonant, off-resonant, and far off-resonant with the incoming photons. Correspondingly, $E_e = 1, 2, 3, 8 \text{eV}$.

is the transition amplitude from the ground vibrational state in the ground electronic state PES $|g0\rangle$ to the vibronic state $|f\nu\rangle$. Using Eq. (17) and taking $t \to \infty, t_0 \to -\infty$ yields

$$A_{f\nu,g0} = (2\pi)^{3/4} \sqrt{\pi \sigma_p T_e} \mathcal{E} (\tilde{\omega}_i) \mathcal{E} (\tilde{\omega}_s) \exp \left( -\frac{(\omega_{f\nu,g0} - \tilde{\omega}_p)^2}{4\sigma_p^2} \right) \sum_{\nu'} \frac{i \Delta\nu T_e - 1}{i \Delta\nu'} + (s \leftrightarrow i)$$

(23)

where $\nu'$ runs over the vibrational eigenstates in e-th PES, $\Delta\nu = \frac{1}{2}(\omega_{f\nu,g0} - \omega_{e\nu',g0})$ and $\mu_{\beta\nu',\alpha\nu} = \langle \beta\nu' | \mu | \alpha\nu \rangle$ is the transition dipole moment between vibronic states.

Fig. 4 depicts the two-photon-excited population as a function of the entanglement time. The largest excited population occurs for the resonant case (upper panel), as reflected in the detuning factor $1/\Delta\nu$ in Eq. (23). Interestingly, the population grows, roughly linearly, with $T_e$ at short entanglement times. To rationalize this observation, we isolate the $T_e$-dependent factor in Eq. (23)

$$g(T_e) = \frac{1}{\sqrt{T_e}} e^{i \Delta T_e - 1}$$

and we use $e^x \approx 1 + x$

$$P \propto |g(T_e)|^2 \approx T_e.$$  

(24)

Thus, for resonant intermediate states and short entanglement times, the two-photon-excited population grows linearly with $T_e$. After the first photon interacts with the molecules, transient population is built in the intermediate state. This population grows for a short period of time until
FIG. 4. Dependence of the entangled two-photon-excited population on the entanglement time. The parameters read $A = 1\mu m^2$, $n = 1$, $\omega_p = 2.4\text{ eV}$, $\sigma_p = 0.2\text{ eV}$.

the second photon arrives. The time window is bounded by the entanglement time of the quantum light, whereas for classical light there is no such restriction. This linear increase only exists at very short entanglement times below $T_e = 10\text{ fs}$.

For off-resonant and far off-resonant intermediate states (middle and lower panels of Fig. 4), the two-photon-excited population shows a nonlinear dependence on the entanglement time. In both cases the largest population occurs at short entanglement times with the population for the off-resonant case larger than the far off-resonant case, as expected.

Apart from controlling the electronic populations, the JSA may also be used to manipulate the nuclear wave packet. Figs. 5, 6, and 7 show the phase-space Wigner representation of the nuclear
FIG. 5. Phase space representation of entangled two-photon-excited wavepackets for the displaced harmonic oscillator model with a resonant intermediate electronic state for various entanglement times as indicated.

FIG. 6. Same as Fig. 5 but for off-resonant intermediate electronic state.

wave packets prepared by entangled light with various entanglement times at $t = 20\,\text{fs}$ for the resonant, off-resonant, and far off-resonant cases, respectively. The Wigner spectrogram transforms the wavepacket in coordinate space as $\chi_W(x,p,t) = \int_{-\infty}^{\infty} dy \chi_f(x + \frac{y}{2}) \chi_f^*(x - \frac{y}{2}) e^{ipy}$. We see that the nuclear wavepacket is most sensitive to the entanglement time in the off-resonant case with minor variations otherwise. The nuclear wave packet depends on both the amplitude and phase of
the transition amplitude to a vibronic state in the \( f \)th electronic state \( A_{f\nu} \). For the resonant case, Eq. (24) implies that for short entanglement times, the relative phase between vibrational states in the \( f \)-PES does not depend on \( T_e \). For the off-resonant case, the \( g(T_e) \) will show an oscillatory behavior with \( T_e \) and the relation between \( A_{f\nu} \) and the vibrational state \( \nu \) will strongly depend on \( T_e \) thus leading to a considerable change in the wavepacket.

**B. Simulation Protocol Based on the Schmidt decomposition**

Sampling the wavepackets on the two-dimensional time grid is numerically expensive. We now present an alternative simulation protocol for the ETPA, which employs the Schmidt decomposition of the entangled light \([40]\) and replaces the time grid sampling by a summation over Schmidt modes. The entangled light can be expanded in Schmidt modes. Each pair of modes leads to a transition amplitude, and summing over all contributing Schmidt modes leads to the final signal. The photon-pair entanglement is then reflected in the quantum interference among Schmidt modes.
1. Schmidt decomposition of quantum light

With the Schmidt decomposition for the JSA \[40, 41\],
\[
J(\omega_s, \omega_i) = \sum_n \sqrt{\lambda_n} \varphi_n(\omega_s) \varphi_n(\omega_i),
\]
the two-photon wavefunction can then be expressed by
\[
\Phi_{in}(t_2, t_1) = (2\pi)^2 \mathcal{E}(\omega_i) \mathcal{E}(\omega_s) \sum_n \sqrt{\lambda_n} \varphi_n(t_1) \varphi_n(t_2)
\]  \hspace{1cm} (25)

where \( \varphi_n(t) = \int_{t_0}^{t} \frac{d\omega}{2\pi} \phi_n(\omega) e^{i\omega t} \) and \( \varphi_n(t) \) are the temporal modes, i.e., Schmidt modes Fourier transformed to the time domain, \( \phi_n(\omega_s) \) and \( \phi_n(\omega_i) \) are Schmidt modes, that are, respectively, the eigenstates of the reduced density matrices of the signal and idler photons with \( \lambda_n \) the corresponding eigenvalues.

Inserting Eq. (25) into Eq. (11) leads to
\[
\chi_f(R, t) = (2\pi)^2 \mathcal{E}(\omega_i) \mathcal{E}(\omega_s) \sum_n \sqrt{\lambda_n} \kappa_n(R, t)
\]
\[
\kappa_n(R, t) \equiv \sum_e \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 U_{fe}(R) U_{e}(t_2, t_1) V_{eg}^\dagger(R) \chi_0(R) \phi_n(t_1) \varphi_n(t_2)
\]  \hspace{1cm} (26)

\( \kappa_n(R, t) \) is the two-photon-excited nuclear wavepacket with the \( n \)th pair of Schmidt modes. An important observation is that the \( \kappa_n \) can be simply simulated by solving time-dependent Schrödinger equation in the presence of two classical pulses with electric field \( \mathcal{E}_s(t) = \phi_n(t), \mathcal{E}_i(t) = \varphi_n(t) \).

Therefore, instead of using a temporal grid one can simply solve the time-dependent Schrödinger equation to compute the ETPA signal.

However, in classical two-photon absorption, there are additional second-order transition pathways corresponding to absorbing two photons from a single beam, which does not exist in quantum light. This becomes clear in the classical TPA expression
\[
\chi_f(R, t) \propto \int_{t_0}^{t} dt_2 \int_{t_0}^{t} dt_1 V_{fe}(t_2) V_{eg}(t_1) \chi_0(R) (\mathcal{E}_s(t_2) \mathcal{E}_a(t_1) + \mathcal{E}_i(t_2) \mathcal{E}_a(t_1) + \mathcal{E}_s(t_2) \mathcal{E}_i(t_1) + \mathcal{E}_i(t_2) \mathcal{E}_i(t_1))
\]  \hspace{1cm} (27)

where the additional terms are associated with \( \mathcal{E}_i(t_2) \mathcal{E}_i(t_1) \) and \( \mathcal{E}_s(t_2) \mathcal{E}_a(t_1) \). These have the same order as the desired ones absorbing signal and idler photons together, and thus cannot be eliminated by weakening the field.
To remove the undesired transition pathways, we can employ a phase cycling protocol [42, 43]. Phase cycling selectively extracts pathways by applying phases to the pulses,

\[ \mathcal{E}_j(t) \to e^{i\theta_j} \mathcal{E}_j(t) \]  

for \( j = s, i \). It exploits the fact that different pathways respond differently to the phase change.

| \( \theta_s \) | \( \theta_i \) | ss | ii | si | is |
|---|---|---|---|---|---|
| I | 0 | \( \frac{\pi}{2} \) | 1 | -1 | i | i |
| II | \( \frac{\pi}{2} \) | 0 | -1 | 1 | i | i |

TABLE I. Phase cycling protocol to remove additional pathways. The final signal \( S = \frac{1}{2!} (S_I + S_{II}) \). The four pathways are labeled by the signal (s) and idler (i) photons interacting with the molecule in the given order.

A phase cycling protocol that eliminates the two-photon transition pathways ss and ii is shown in Table I.

This protocol with Schmidt modes can be very efficient if the entangled light can be described by a limited number of Schmidt modes [44].

IV. CONCLUSIONS

We have presented a computational protocol for the entangled two-photon absorption signal in molecules which takes the nuclear quantum dynamics into account. It involves summing over all transition pathways determined by two light-matter interaction times. Using a displaced harmonic oscillator model, we have demonstrated how entangled light can be used to manipulate the two-photon-excitation process. Both electronic populations and nuclear wave packets strongly depend on the entanglement time. This protocol applies to any joint spectral amplitude of the entangled light, and thus can be applied for various sources of quantum light from e.g. cascaded emission as well. We have also outlined an alternative protocol based on the Schmidt decomposition of the
entangled light, which can be very efficient if the entangled light can be described by a limited number of Schmidt modes (weak entanglement). Our protocols allows the simulation of quantum light spectroscopy of complex molecular systems fully accounting for the coupled electronic-nuclear-photonic motion. Advances in pulse shaping techniques may allow a complete control of the JSA by varying the parameters other than entanglement time [35].

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