Theory of nuclear motion in RABBITT spectra

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Reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) is a powerful photoelectron spectroscopy, offering direct access to internal dynamics of the target. It is being increasingly applied to molecular systems, but a general, computationally tractable theory of RABBITT spectra in molecules has so far been lacking. We show that under quite general assumptions, RABBITT spectra in molecules can be expressed as a convolution of the vibronic cross-correlation functions and two-electron photoionization matrix elements. We specialize the general expressions to the commonly-encountered special cases. We expect our theory to enable accurate modeling and interpretation of molecular RABBITT spectra in most medium-sized molecules.

I. INTRODUCTION

Reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) is an ingenious photoelectron spectroscopy, offering direct access to the photoelectron phases, and consequently to the intricate details of the electronic and nuclear dynamics in atoms and molecules. RABBITT spectroscopy is being increasingly applied to molecular systems, with many notable recent theory developments (see e.g. [3–5] and references therein). An essential factor, affecting all molecular spectroscopies, is nuclear motion, which however received only limited attention in the literature so far. This oversight is likely partially due to the enormous cost of the brute-force treatment of the electron-nuclear coupling in photoionization, which so far limited practical calculations to a very few nuclear degrees of freedom. A similar difficulty arises in molecular spectroscopy of bound-to-bound transitions, where it has been recognized that the problem can nonetheless be made numerically tractable, by recasting it in a time-dependent form. The observable effects of the nuclear motion are then compactly summarized by vibronic auto- and cross-correlation functions. The utility of the nuclear auto- and cross-correlation functions has also been recognized in the strong-field and attosecond domain, where they have been used to describe nuclear-motion effects in high-harmonics generation and attosecond electron-hole migration. Very recently, an elegant theory of the molecular electron-streaking spectra has been developed with the single-surface nuclear autocorrelation functions taking the central role.

In this contribution, we extend the approach of Ref. [19] to the theory of molecular RABBITT photoelectron spectra. We derive a compact, general expression for the relevant transition amplitudes in terms of vibronic cross-correlation functions. Our treatment includes, at least in principle, all nuclear motion effects relevant for RABBITT transitions. In particular, it describes the effects of the coherent averaging over the initial vibrational function, including the zero-point effects; the redistribution of the absorbed- photon energy between the photoelectron and internal degrees of freedom; the effects of absorption and emission of additional IR photons by the cationic core; the effects of the finite pulse duration. The treatment naturally includes complex vibronic dynamics in the vicinity of conical intersections as well.

The rest of this manuscript is organized as follows: The following section develops the general theory of RABBITT spectra in molecules. Section considers some relevant special cases, which allow further simplifications of the general expression. Finally, section summarizes the work, and presents an outlook for follow-up investigations and applications.

II. THEORY

We are interested in modeling photoelectron spectra of a molecular system, described by a field-free, time-independent Hamiltonian $\hat{H}_0$, produced as a result of interacting with a three-colour laser field. The individual components of the field, all taken to be linearly-polarized, are given by:

$$F_{IR} (t) = f_{IR} (t) \bar{n}_R \cos (\omega t)$$
$$F_i (t) = f_i (t) \bar{n}_i \cos (\Omega_i t + \Phi_i),$$

where $i = 1, 2$, $\bar{n}$ is field polarization direction, and $f (t)$ is a slowly-varying envelope. The corresponding terms in the total Hamiltonian are given by:

$$\hat{V}_{IR} = \frac{1}{2} \bar{\mu}_{IR} f_{IR} (t) \left[ e^{i \omega t} + e^{-i \omega t} \right]$$
$$\hat{V}_i = \frac{1}{2} \bar{\mu}_i f_i (t) \left[ e^{i \Omega_i t + i \Phi_i} + e^{-i \Omega_i t - i \Phi_i} \right],$$

where the terms in brackets correspond to the emission $(+)$ and absorption $(-)$ of a photon. We assume that the

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field parameters are such that only absorption is possible for the XUV fields ($V_r$), while the IR photons can be both absorbed and emitted. Operators $\hat{\mu}$ incorporate the specific form of the field-interaction Hamiltonian and field polarization properties. Eqs. (3, 4) implicitly assume that the laser field is treated in the length gauge and dipole approximation.

In addition to the field-free Hamiltonian $\hat{H}_0$, we will also consider Hamiltonians $\hat{H}_{IR}$ and $\hat{H}_i$, defined as:

$$\hat{H}_{IR} = \hat{H}_0 + \hat{V}_{IR},$$

$$\hat{H}_i = \hat{H}_0 + \hat{V}_{IR} + \hat{V}_i,$$

(5)

(6)

corresponding to our preferred order of treating the perturbations. For each Hamiltonian $\hat{H}_a$, the corresponding propagator $\hat{U}_a$ is symbolically given by:

$$\hat{U}_a (t', t; E) = e^{-i \int_{t_0}^{t'} dt' \langle \hat{H}_a - E \rangle},$$

(7)

where we have chosen to pull the rapidly-oscillating phase $e^{-i E t}$ out. The “characteristic energy” $E$ is in principle arbitrary; however, we expect that it is selected such as to make $\hat{U}_a$ a slow function of time. We note that a propagator in Eq. (7) satisfies the energy-origin transformation:

$$\hat{U}_a (t', t; E) = e^{i(E-E')(t'-t)} \hat{U}_a (t', t; E').$$

(8)

II.1. Wavefunction response to a two-colour field

Our first task is to calculate the wavefunction response to the combined effects of the IR and one of the XUV fields. We will only consider the contribution bilinear in the two fields, and assume that the contributions due to each field alone can be neglected (e.g. because they are energetically separated).

We start by treating $\hat{H}_{IR}$ as the zeroth-order Hamiltonian, and $\hat{V}_i$ as the perturbation. The usual time-dependent perturbation theory then yields[12 20 21]:

$$|\Psi_1^{(1)} (t)\rangle = -i \int_{t_0}^{t} dt' e^{-i E_{I} (t-t')} \hat{U}_I (t, t'; E_I) \hat{V}_i (t') e^{-i E_N (t'-t_0)} \hat{U}_{IR} (t', t_0; E_N) |\Psi^{(0)} (t_0)\rangle$$

$$= -i \int_{t_0}^{t} dt' e^{-i E_I (t'-t')} \hat{U}_I (t, t'; E_I) \frac{1}{2} \hat{\mu}_i f_i (t') e^{-i \Omega (t'-t_0)} e^{-i E_N (t'-t_0)} \hat{U}_{IR} (t', t_0; E_N) |\Psi^{(0)} (t_0)\rangle$$

$$= -\frac{i}{2} e^{-i \Omega t} e^{i E_I t} \int_{t_0}^{t} dt' e^{-i E_I (t'-t)} f_i (t') \hat{U}_I (t, t'; E_I) \hat{\mu}_i \hat{U}_{IR} (t', t_0; E_N) |\Psi^{(0)} (t_0)\rangle$$

$$\approx -\frac{i}{2} e^{-i \Omega t} e^{i E_I t} \int_{t_0}^{t} dt' e^{-i E_I (t'-t)} f_i (t') \hat{U}_{IR} (t, t'; E_I) \hat{\mu}_i \hat{U}_{IR} (t', t_0; E_N) |\Psi^{(0)} (t_0)\rangle$$

(9)

where $E_N$ and $E_I$ are respectively characteristic energies of the system before and after XUV photon absorption, and $t_0$ is chosen before the start of the XUV pulse [i.e. $f_i (t' < t_0) = 0$]. We will also assume that the observation time $t$ is past the end of the laser pulse. The initial wavefunction $|\Psi^{(0)}\rangle$ is a vibronic wavefunction, including both electronic and nuclear degrees of freedom. In the last line, we replaced $\hat{U}_I (t, t'; E_I)$ by $\hat{U}_{IR} (t, t'; E_I)$, thus neglecting the possibility of absorbing additional XUV photons.

So far, we have avoided choosing a specific representation of the vibronic wavefunctions. For the initial wavefunction $\Psi^{(0)}$, we use the standard adiabatic Born-Huang Ansatz:

$$|\Psi^{(0)} (t)\rangle = \sum_a |\psi_a (r; q)\rangle |\chi_a (q, t)\rangle,$$

(10)

where $\psi_a$ are the discrete, time-independent electronic states of the neutral species, which depend on the electronic coordinates $r$ and parametrically on the nuclear coordinates $q$. Time-dependent nuclear wavepackets $\chi_a$ propagate on these electronic surfaces. We take that the electronic states $\psi_a$ and the corresponding surfaces are available to us through some other means. (If desired, e.g. for treating the situation where the initial, neutral wavepacket finds itself in a vicinity of a conical intersection, Eq. (10) can be taken as a diabatic vibronic Ansatz, with minimal changes to the treatment.)

We assume that the set of electronic states $\psi_a$ is complete with respect to the action of the propagator $\hat{U}_{IR}$. Under this assumption, one can define an identity operator $\hat{1}_N$, which can be inserted between operators $\hat{\mu}_i$ and $\hat{U}_{IR} (t', t_0; E_N)$ in Eq. (9):

$$\hat{1}_N = \sum_a |\psi_a (r; q)\rangle \langle \psi_a (r; q)|,$$

(11)

where the brackets are understood to imply integration over electronic coordinates $r$ alone. The result is:
where we have chosen to introduce vibrational propagator \( \hat{u}_{ab} (t', t_0; E_N) \).

The quantity \( |\chi_a (q, t')\rangle \) is to be understood as a vibrational wavepacket on an electronic surface \( a \) at time \( t' \). We assume that efficient means of propagating these wavepackets are available to us. In the most common special case, where \( |\Psi(0) (t_0)\rangle \) is an eigenstate of the field-free Hamiltonian with energy \( E_N \), and the effects of the IR field on the initial neutral wavefunction can be neglected, Eq. \( \ref{eq:psi0} \) reduces simply to:

\[
|\chi_a (q, t')\rangle = \big| \chi_{G.S.} (q, t_0) \bigangle .
\]

Under our assumptions, absorption of an XUV photon brings the molecule into a highly-excited electronic state, with one of the electrons either ionized or in a Rydberg state. If we assume that at most one electron is ionized or excited, while the others remain tightly bound, it is natural to expand the wavefunction after XUV absorption

\[
|\Psi^{(1)}_i (t)\rangle = -\frac{i}{2} e^{-i\Phi_i + iE_N t_0} \sum_a \int_{t_0}^{t} dt' e^{-iE_i t' \Omega_i} f_i (t') \hat{\mu}_i |\psi_a (r; q)\rangle |\chi_a (q, t')\rangle ,
\]

in the form:

\[
|\Psi^{(1)} (t)\rangle = \sum_c \int dk |\psi_{ck} (r; q)\rangle |\chi_c (q, t)\rangle ,
\]

where discrete index \( c \) is understood to run over the asymptotically-populated, tightly-bound states of the residual ion, while the general index \( k \) labels the full electronic state (continuum or discrete) associated to this ion core. As before, functions \( \psi_{ck} \) and the corresponding energy surfaces are assumed to be available to us.

Analogously to Eq. \( \ref{eq:psi0} \), we introduce identity-resolution operator \( \hat{I}_C \) in the ion space:

\[
\hat{I}_C = \sum_c \int dk |\psi_{ck} (r; q)\rangle \langle \psi_{ck} (r; q)| .
\]

Inserting \( \hat{I}_C \) into Eq. \( \ref{eq:psi1} \) between \( \hat{U}_{IR} \) and \( \hat{\mu}_i \) and rearranging the terms, we obtain:

\[
\hat{\mu}_{ck,a} (q) = \langle \psi_{ck} (r; q) | \hat{\mu}_i | \psi_a (r; q) \rangle ,
\]

where operator \( \hat{\mu}_{ck,a} \) is the transition dipole for ionization (or excitation) of an electronic state \( |\psi_a (r; q)\rangle \), forming state \( |\psi_{ck} (r; q)\rangle \). This operator depends parametrically on the nuclear coordinates \( q \).

We can now introduce yet another identity-resolution operator \( \hat{I}_{C'} \), in the form:

\[
\hat{I}_{C'} = \sum_d \int dp |\psi_{dp} (r; q)\rangle \langle \psi_{dp} (r; q)| ,
\]

where the (discrete) index \( d \) and general parameter \( p \) are understood as the labels of the final state of the photoion and photoelectron, respectively. Inserting \( \hat{I}_{C'} \) to the left of the operator \( \hat{U}_{IR} \) in Eq. \( \ref{eq:psi1} \) and rearranging, we obtain:

\[
|\Psi^{(1)}_i (t)\rangle = -\frac{i}{2} e^{-i\Phi_i + iE_N t_0} \sum_d \int dp e^{-iE_i t} |\psi_{dp} (r; q)\rangle |\chi_{dpi} (q, t)\rangle ,
\]

\[
|\chi_{dpi} (q, t)\rangle = \sum_{a,c} \int dk \int_{t_0}^{t} dt' e^{i(E_i-E_N-\Omega_i)t'} f_i (t') \hat{u}_{dp,ck} (t, t'; E_I) \hat{\mu}_{ck,a} |\chi_a (q, t')\rangle ,
\]
In Eq. (21), \( \chi_{dp} (q, t) \) is the final amplitude of the ion state \( d \) and photoelectron state \( p \), at nuclear coordinates \( q \) and time \( t \), generated by the XUV field \( F_I \). Propagator \( \hat{U}_{IR} \) describes evolution of the initially-prepared ionized (or excited) state under the influence of the IR field. We note that the meaning of the phase factor \( e^{-iE_I t} \) is subtly different between Eqs. (17) and (20). In Eq. (17), it is a global overall phase, while in Eq. (20) \( E_I \) is permitted to be \( p \)-dependent. This change amounts to a gauge transformation of \( |\chi_{dp} (q, t)\rangle \), which is compensated by the counteracting transformation of the \( \hat{u}_{dp,ck} \) propagator in Eq. (21).

We would now like to examine the propagator \( \hat{u}_{dp,ck} (t, t'; E_I) \) of Eq. (22) a bit more closely. Without any formal justification, we will now introduce the crucial approximation of our treatment. We will assume that:

\[
\hat{u}_{dp,ck} (t, t'; E_I) \approx \hat{u}_{p,k} (t, t'; E_I - E_C) \hat{u}_{d,c} (t, t'; E_C),
\]

\[
\hat{u}_{d,c} (t, t'; E_C) = \langle \psi_d (r; q) | \hat{U}_{IR} (t, t'; E_C) | \psi_c (r; q) \rangle,
\]

\[
\hat{u}_{p,k} (t, t'; E_I - E_C) = \langle \psi_p (r; q) | \hat{U}_{IR} (t, t'; E_I - E_C) | \psi_k (r; q) \rangle,
\]

\[
[\hat{u}_{d,c}, \hat{u}_{p,k}] = 0.
\]

In Eq. (24), \( E_C \) is the characteristic energy of the cationic manifold, while \( |\psi_c (r; q)\rangle \) are Born-Oppenheimer electronic wavefunctions of the cation. Similar to Eq. (14), we assume that efficient means of evaluating Eq. (24) are available to us. Propagator \( \hat{u}_{dp,ck} \), could have been formally (and tautologically) defined as:

\[
\hat{u}_{dp,ck} (t, t'; E_I) \equiv \hat{u}_{p,k} (t, t'; E_I - E_C) \hat{u}_{d,c} (t, t'; E_C).
\]

(Note however that the putative definition (27) does not satisfy the commutator relation (26), except for the trivial case of a single-state cationic manifold.)

From Eq. (27), it is clear that in adopting Eq. (23), we neglect the possibility of a transition in the \((c, d)\) manifold inducing a transition in the \((k, p)\) manifold and vice versa. Examples of such transitions are collisionally-induced transitions in the ion core, as well as shake-off and shake-up transitions. By our initial assumptions, the two manifolds (the compact ion core and the extended photoelectron/Rydberg orbital) are energetically and spatially separated, so that such transitions are expected to have low relative cross-sections. If necessary, they could be treated as higher-order perturbations.

We should also emphasize that partitioning of the Hamiltonian implied by the Eq. (23) does not introduce the single-particle approximation. This can be clearly seen in the special case where the cationic manifold consists of an isolated, non-degenerate ground state. Then, the propagator \( \hat{u}_{d,c} \) amounts to a \( q \)-dependent phase change, and Eq. (23) is exact, rather than an approximation. Indices \( k, p \) then enumerate all electronic states in the system — both excited and ionized. The energies of these states must however be taken relative to the energy of the target state, \( E_C \).

We can now evaluate the propagator of Eq. (25), treating the IR field as a perturbation to the zeroth-order Hamiltonian:

\[
\hat{U}_{IR} (t, t'; E_k) |\psi_k (r; q)\rangle = \hat{U}_0 (t, t'; E_k) |\psi_k (r; q)\rangle - i \int_{t'}^t dt'' \hat{U}_{IR} (t, t''; E_k) \hat{V}_{IR} \hat{U}_0 (t'', t'; E_k) |\psi_k (r; q)\rangle,
\]

where \( E_k = E_I - E_C \) is the “excess” characteristic energy of the state \( |\psi_k\rangle \) relative to \( E_C \) — the characteristic energy of the cation. The first term on the right-hand side of Eq. (28) preserves \( k \), leading to the \( \delta_{p-k} \) contribution upon substitution into Eq. (25). Because we are interested in the RABBITT sidebands, rather than in the main harmonic line, we can ignore this contribution from now on. Then, substituting \( \hat{V}_{IR} \) from Eq. (13), we obtain, separately for emission \((+\) \) and absorption \((-\) or an IR photon:
where in the second line, we have neglected the possibility of absorbing the second IR photon. In the third line, we shifted the energy origin of the left-most propagator and rearranged the terms. In the fourth line, we have used the assumption that $|\psi_k\rangle$ are eigenfunctions of the field-free Hamiltonian with energy $E_k$, so that:

$$\hat{U}_0 (t_2, t_1; E_k) |\psi_k (r; q)\rangle = |\psi_k (r; q)\rangle,$$

and moved the IR-dipole matrix element outside of the integral.

To progress further, we now evaluate the $dt''$ integral in Eq. (29) by parts, using adiabatic turn-on procedure (see §42 of Ref. 22):

$$\int_{t'}^t dt'' f_{IR} (t'') e^{\lambda t''} e^{i(E_p - E_k \pm \omega) t''} = \int_{t'}^t dt'' f_{IR} (t'') \frac{d}{dt''} \left( -\frac{e^{\lambda t''} + i(E_p - E_k \pm \omega) t''}{(E_p - E_k \pm \omega) - i\lambda} \right)$$

$$= -i f_{IR} (t'') \frac{e^{\lambda t''} + i(E_p - E_k \pm \omega) t''}{(E_p - E_k \pm \omega) - i\lambda} \bigg|_{t'}^t + i \int_{t'}^t dt'' \frac{df_{IR} (t'')}{dt''} e^{\lambda t''} + i(E_p - E_k \pm \omega) t''$$

$$\lambda \rightarrow +0 i f_{IR} (t') \frac{e^{\lambda t'} + i(E_p - E_k \pm \omega) t'}{(E_p - E_k \pm \omega) - i0^+},$$

where we have used the slowly-varying envelope approximation to neglect the time derivative of the envelope $f_{IR}$, and assumed that the observation time $t$ is past the end of the IR pulse.

Inserting Eq. (31) into Eq. (29), we then obtain our final expression for $\hat{u}_{p,k,\pm}$:

$$\hat{u}_{p,k,\pm} (t, t'; E_k) = \frac{1}{2} e^{-i(E_p - E_k)t} f_{IR} (t') \langle \psi_p (r; q) | \hat{U}_{IR} (t, t''; E_k) \hat{u}_{IR} \hat{U}_0 (t', t'; E_k) | \psi_k (r; q) \rangle e^{i(E_p - E_k \pm \omega) t'} (E_p - E_k \pm \omega) - i0^+.$$

Substituting Eqs. (32) and (29) into Eqs. (29, 31), we then obtain for the second-order wavefunction response $\Psi^{(2)}_{\pm}$, where we have chosen to separate contributions due to emission and absorption of the IR photons:

$$\Psi^{(2)}_{\pm},$$
\[ |\Psi_{i\pm}^{(2)}(t)\rangle = \frac{1}{2} e^{-i\Phi_{i} + iE_{N}t_{0}} \sum_{d} \int dp \ e^{-i(E_{C} + E_{p})t} |\psi_{dp}(r; q)\rangle e^{i(E_{p} - E_{k})t} |\chi_{dp\pm}(q, t)\rangle, \]

\[ = \frac{1}{2} e^{-i\Phi_{i} - E_{C}t + iE_{N}t_{0}} \sum_{d} \int dp \ e^{-iE_{p}t} |\psi_{dp}(r; q)\rangle |\tilde{\chi}_{dp\pm}(q, t)\rangle, \quad (33) \]

\[ |\tilde{\chi}_{dp\pm}(q, t)\rangle = e^{i(E_{p} - E_{k})t} \sum_{a, c} \int dk \ \int_{t_{0}}^{t} dt' e^{i(E_{p} + E_{k} - E_{N} - \Omega_{1})t'} f_{i}(t') \frac{1}{2} e^{-i(E_{p} - E_{k})t} f_{IR}(t') \langle \psi_{p}(r; q) | \hat{\mu}_{IR} | \psi_{k}(r; q)\rangle \]

\[ \times \left( E_{p} - E_{k} + \omega \right)^{t'} \tilde{\mu}_{d,c}(t, t'; E_{C}) \tilde{\mu}_{c,k,a} |\chi_{a}(q, t')\rangle \]

\[ = \frac{1}{2} \sum_{a, c} \int_{t_{0}}^{t} dt' e^{i(E_{p} + E_{C} - E_{N} - \Omega_{\pm})t'} f_{i}(t') \frac{1}{2} e^{-i(E_{p} - E_{k})t} f_{IR}(t') \tilde{\mu}_{d,c}(t, t'; E_{C}) \int dk \ \hat{\mu}_{p,c,k,a} |\chi_{a}(q, t')\rangle, \quad (34) \]

\[ \epsilon_{cp, a, \pm} = (\Omega_{1} \mp \omega) - (E_{p} + E_{C} - E_{N}), \quad (35) \]

\[ \hat{D}_{cp,a,\pm}(q) = \int dk \ \frac{\hat{\mu}_{p,c,k,a}}{(E_{p} - E_{k} \pm \omega)^{t'}}, \quad (36) \]

\[ \tilde{\mu}_{p, c, k, a}(q) = \langle \psi_{p}(r; q) | \hat{\mu}_{IR} | \psi_{k}(r; q)\rangle, \quad (37) \]

where we used \( E_{1} = E_{k} + E_{C} \), and moved the phase contribution in \( |\chi_{dp\pm}\rangle \) dependent solely on \( t \) into the definition of \( \Psi_{i\pm}^{(2)} \).

The individual terms in Eqs. (33-37) have a transparent physical interpretation. The quantity \( (E_{p} + E_{C}) \) is the total electronic energy of the final state of the system. The non-trivial dynamics in the system is described by nuclear wavepacket(s) \( |\chi_{dp\pm}\rangle \), which propagate on ionic surface \( d \) and are entangled with final photoelectron momentum \( p \). The operator \( \hat{D}_{cp,a,\pm} \) is the standard electronic matrix element for 2-photon absorption. The quantity \( \epsilon_{cp, a, \pm} \) is the amount of energy deposited into the nuclear degrees of freedom of the system. Finally, Eq. (37) describes time evolution of the nuclear wavepacket on the (generally coupled) ionic energy surfaces. The Fourier transform in Eq. (34) picks out the relevant spectral component of the nuclear wavepacket.

### II.2. RABBITT signal: General case

Using Eqs. (34-37), we are ready to describe the RABBITT sidebands. Sideband \( M \) due to interference between two-photon transitions involving two neighboring harmonics:

\[ \Omega_{1} = (M - 1)\omega, \quad \Omega_{2} = (M + 1)\omega, \quad (38, 39) \]

The signal at final photoelectron momentum \( p \) is given by a sum of four contributions:

\[ I(p) = I_{1-1-}(p) + I_{2+2+}(p) + I_{1-2+}(p) + I_{2+1-}(p). \quad (40) \]

The first contribution is the photoelectron signal due to the simultaneous absorption of an \( \Omega_{1} \) and \( \omega \) photons. The second term describes absorption of an \( \Omega_{2} \) and emission of an \( \omega \) photons. The two remaining terms, which form a complex-conjugate pair, is the delay-dependent interference term.

From Eq. (33), the individual contributions are given by:

\[ I_{l,r}(p) = \langle \Psi_{i}^{(2)}(t) | p' \rangle \langle p | \Psi_{r}^{(2)}(t) \rangle \bigg|_{p' \rightarrow p} \]

\[ = \left( -\frac{i}{2} e^{-i\Phi_{i} - E_{C}t + iE_{N}t_{0}} \sum_{c} e^{-iE_{p}t} |\psi_{cp'}(r; q)\rangle |\tilde{\chi}_{cp}(q, t)\rangle \right)^{l} \]
\[
\times \left( -\frac{\text{i}}{2} e^{-\text{i}\Phi_r - \text{i}E_{\text{r}}t + \text{i}E_{\text{N}}t_0} \sum_d e^{-\text{i}E_{\text{r}}t} \langle \psi_{dp} (r; q) | \hat{\chi}_{dpr} (q, t) \rangle \right) \bigg|_{p' \rightarrow p} \\
= \frac{1}{4} e^{\text{i}(\Phi_l - \Phi_r)} \sum_{cd} \langle \hat{\chi}_{cp'} (q, t) | \langle \psi_{cp'} (r; q) | e^{(E_{p'} - E_{p})t} | \psi_{dp} (r; q) \rangle | \hat{\chi}_{dpr} (q, t) \rangle \bigg|_{p' \rightarrow p} \\
= \frac{1}{4} e^{\text{i}(\Phi_l - \Phi_r)} \sum_{cd} \langle \hat{\chi}_{cp'} (q, t) | E \delta \left( \frac{\vec{p}' - \vec{p}}{2\pi} \right) \hat{\chi}_{dpr} (q, t) \rangle \bigg|_{p' \rightarrow p} \\
= \frac{1}{4} \delta \left( \frac{\vec{p}' - \vec{p}}{2\pi} \right) e^{\text{i}(\Phi_l - \Phi_r)} \sum_d \langle \hat{\chi}_{dpt} (q, t) | \hat{\chi}_{dpr} (q, t) \rangle ,
\]

where \( l, r = 1-, 2+, \) and we assumed that the continuum functions are normalized to \( \delta \left( \frac{\vec{p}' - \vec{p}}{2\pi} \right) \). Any other normalization choice will lead to an equivalent expression, provided that a consistent choice is make in Eq. (36). We will therefore omit the continuum normalization factor from now on. Substituting \( |\hat{\chi}_{dpt\pm}\rangle \) from eq. (34), we get:

\[
I_{l,r} (p) = \frac{1}{4} e^{\text{i}(\Phi_l - \Phi_r)} \sum_d \left( \frac{1}{4} \sum_{b,e} \int_{t_0}^{t} \! dt' e^{-\text{i}\varepsilon_{ep,bl}t'f_l(t')} f_{IR}(t') \hat{u}_{d,e} (t, t'; E_C) \hat{D}_{ep,bl} (q) |\chi_b (q, t')\rangle \right) \\
\times \left( \frac{1}{2} \sum_{a,c} \int_{t_0}^{t} \! dt' e^{-\text{i}\varepsilon_{cp,ar}t'f_r(t')} f_{IR}(t') \hat{u}_{d,e} (t, t'; E_C) \hat{D}_{ep,ar} (q) |\chi_a (q, t')\rangle \right) \\
= \frac{1}{16} e^{\text{i}(\Phi_l - \Phi_r)} \sum_{b,e,a,c} \int_{t_0}^{t} \! dt' e^{-\text{i}\varepsilon_{ep,bl}t'f_l(t')} f_{IR}(t') f_r(t') f_{IR}(t') \\
\times \langle \chi_b (q, t') | \hat{D}_{ep,bl}^\dagger (q) \left( \sum_d \hat{u}_{e,d} (t', t; E_C) \hat{u}_{d,e} (t, t'; E_C) \right) \hat{D}_{ep,ar} (q) |\chi_a (q, t')\rangle \\
\tag{41}
\]

where we used \( \varepsilon_{ep,bl} = \varepsilon_{ep,ar} = \varepsilon_p \), which holds due to our choice of \( \Omega_1 \) and \( \Omega_2 \), and \( \hat{u}_{d,e} (t, t'; E_C)^\dagger = \hat{u}_{e,d} (t', t; E_C) \). We further use the ion-state completeness assumption to replace:

\[
\sum_d \hat{u}_{e,d} (t', t; E_C) \hat{u}_{d,e} (t, t'; E_C) = \hat{u}_{e,c} (t', t; E_C) \\
\tag{42}
\]

giving:

\[
I_{l,r} (p) = e^{\text{i}(\Phi_l - \Phi_r)} \tilde{I}_{l,r} (p) , \\
\tag{43}
\]

\[
\tilde{I}_{l,r} (p) = \frac{1}{16} \int_{t_0}^{t} \! dt' \int_{t_0}^{t} \! dt' e^{\text{i}\varepsilon_{ep,bl}t'f_l(t')} f_{IR}(t') f_r(t') f_{IR}(t') \\
\times \sum_{a,b,e} \langle \chi_b (q, t') | \hat{D}_{ep,bl}^\dagger (q) \hat{u}_{e,c} (t', t; E_C) \hat{D}_{ep,ar} (q) |\chi_a (q, t')\rangle. \\
\tag{44}
\]

The quantity \( \tilde{I}_{l,r} \) is the “intrinsic” part of the RABBITT matrix element, which does not depend on the relative
delay of the XUV and the IR fields. The entire delay dependence is encapsulated by the phase prefactor $e^{i(\Phi_l - \Phi_r)}$ in Eq. (43). As expected on physical grounds, the initial and observation times ($t_0$ and $t$) drop out of the final expression, provided that the envelopes of all pulses are zero outside of the $|t_0 : t|$ interval. These integration limits can therefore be replaced by $[-\infty : +\infty]$ if desired. Equations (43), (44), and (45) are our general-case result for the RABBITT spectrum. Below, we consider some of the relevant special cases.

III. RABBITT SIGNAL: SPECIAL CASES

Although the result of Eq. (44) is compact and physically transparent, it is invokes a rather complex object: a weighted two-time nuclear cross-correlation function $\langle |\chi(\tau)|\chi_0(q)\rangle$. We would like to consider possible simplifications to Eq. (44). For weak IR fields and short pulses, it is reasonable to neglect vibrational excitation by the IR field can be neglected, both in the neutral and in the cationic manifolds. Then, the propagator $\hat{u}_{e,c}$ can be replaced by the field-free propagator $\hat{u}_{e,c}^0$, which is invariant with respect to shift of the time origin:

$$\hat{u}_{e,c}(t', t'; E_C) \approx \hat{u}_{e,c}^0(t' - t'; E_C) \quad (45)$$

$$\hat{u}_{e,c}^0(\tau; E_C) = \langle \psi_e (\tau; q) | \hat{U}_0 (\tau, 0; E_C) | \psi_e (\tau; q) \rangle. \quad (46)$$

Furthermore, the initial, neutral vibronic wavefunction in many stable molecules is well-represented by a single-surface Born-Oppenheimer product, so that the $a, b$ sums in Eq. (44) collapse to a single, time-independent term:

$$|\chi_0 (q, t)\rangle \approx |\chi_0 (q)\rangle. \quad (47)$$

Additionally, the characteristic decay time scale for the cationic autocorrelation functions is often small, on the order of a few femtoseconds or tens of femtoseconds [12, 13]. On these time scales, the difference between pulse envelopes at $t'$ and $t''$ can be neglected (CW approximation). Furthermore, in the diabatic representation, the cationic cross-correlation functions remain small on the timescale of the IR and XUV pulse duration, and only the diabatic autocorrelations need to be considered:

$$\hat{u}_{e,c}^0 (\tau; E_C) \approx \delta_{cc} \hat{u}_{e,c}^0 (\tau; E_C) \equiv \hat{u}_{0,c}^0 (\tau; E_C). \quad (48)$$

Applying the approximations above to the general Eq. (44), we obtain:

$$I_{l,r} (p) = e^{i(\Phi_l - \Phi_r)} P_{l,r} \sum_c M_{c,l,r} (p), \quad (49)$$

$$P_{l,r} = \frac{\pi}{8} \int d\tau f_l (\tau) f_r (\tau) f_{lR} (\tau), \quad (50)$$

$$M_{c,l,r} (p) = \frac{1}{2\pi} \int d\tau e^{i\epsilon_p \tau} \langle \chi_0 (q)|\hat{D}_{c,p,0l}^\dagger (q) \hat{u}_{0,c}^0 (\tau; E_C) \hat{D}_{c,p,0r} (q) |\chi_0 (q)\rangle, \quad (51)$$

where time integrals are over all times, and we have chosen to apply normalization factor $\frac{1}{2\pi}$ to the definition of the matrix element $M_c (p)$, for reasons which will become clear in the following section. In Eq. (49), the pulse-envelope parameters ($P_{l,r}$) are cleanly separated from the molecular factors ($M_{c,l,r}$), while the entire time-delay dependence is encapsulated by the phase prefactor $e^{i(\Phi_l - \Phi_r)}$, similar to the familiar atomic case [1]. While at the first glance, the conditions under which the approximate Eq. (49) is obtained do appear very restrictive, a closer examination shows that they are expected to be satisfied for a large fraction of small, rigid molecules.

It is instructive to examine some limiting cases of Eq. (51).

III.1. No nuclear motion: The “atomic” case

We first consider the case of nuclear motion being entirely absent in the centre-of-mass coordinate system, so that the molecule has well-defined coordinates $q_0$, which are unchanged by the action of the propagator $\hat{u}_{e,c}^0$. Then:

$$M_{c,l,r} (p) = \frac{\delta}{2\pi} \int d\tau e^{i\epsilon_p \tau} \langle \chi_0 (q_0) | \hat{D}_{c,p,0l}^\dagger(q_0) \hat{D}_{c,p,0r} (q_0) \delta (\epsilon_p) \rangle. \quad (52)$$

This result coincides with the familiar atomic case. The RABBITT sidebands appear at the photoelectron energy of $M\omega - IP$, where $IP$ is the ionization potential. Their width is determined by the combined bandwidth of the XUV and IR pulses. Obviously, no isotope dependence is possible in this approximation.
III.2. Nuclear motion: Condon approximation

The next natural approximation to consider is to treat the electronic part of the matrix element as \( q \)-independent: the Condon approximation. Then:

\[
M_{c,t,r} (p) = \frac{1}{2\pi} \int d\tau e^{i p \tau} \langle \chi_0 (\tau) | \hat{u}_c (\tau; E_C) | \chi_0 (\tau) \rangle,
\]

(53)

\[
N_c (\epsilon_p) = \frac{1}{2\pi} \int d\tau e^{i \epsilon_p \tau} A_c (\tau; E_C),
\]

(54)

\[
A_c (\tau; E_C) = \langle \chi_0 (q) | \hat{u}_c (\tau; E_C) | \chi_0 (q) \rangle,
\]

(55)

where \( N_c \) is the Fourier transform of nuclear autocorrelation function on (diabatic) cationic surface \( c \). The field-free autocorrelation function is Hermitian with respect to time reversal \( [12] \):

\[
A_c (-\tau) = A_c (\tau)^\dagger,
\]

so that \( N_c \) is guaranteed to be real. As long as the time integration domain in Eq. (54) is not truncated, \( N_c \) is also guaranteed to be positive semi-definite \( [12] \):

\[
N_c (\epsilon_p) \geq 0.
\]

(57)

An important consequence of Eq. (57) is that vibrational dynamics in the Condon approximation does not introduce additional time delays in the RABBITT spectrum. Time delays remain an exclusively electronic property in this approximation, similar to the atomic case. Nuclear motion however imposes a finite, intrinsic photoelectron energy profile onto the RABBITT spectrum. In the Condon approximation, this profile coincides with the vibrational profile in 1-photon photoionization spectrum at the same photoelectron energy.

Isotopic dependence can arise in two ways in this approximation. First, the initial wavepacket \( |\chi_0\rangle \) and the propagator \( \hat{u}_c \) depend on the nuclear masses, so that the factor \( N_c \) is isotope-dependent. This contribution affects the photoelectron-energy profile, but not the time delays or the contrast of the signal oscillations with time. Additional isotope dependence could arise if the characteristic geometries \( q_0 \), where the electronic matrix elements are determined, are not the same for the isotopomers involved.

III.3. Nuclear motion: Zero-point effects

In the Condon approximation \( [\text{Eq. (53)}] \), the electronic part of the matrix element \( M_{c,t,r} \) is evaluated at a single, characteristic geometry \( q_0 \). A natural refinement is to consider the consequences of the finite spatial extent of the wavepacket, by averaging the electronic matrix element over the initial wavepacket. All nuclear wavepackets will have non-zero spatial extent due to the effects of the zero-point motion. Vibrational excitation will also affect the extent of the wavepacket. If the overall shape of the wavepacket, apart from the central position, is unaffected by nuclear motion, we obtain:

\[
M_{c,t,r} (p) \equiv \langle \chi_0 (q) | \hat{D}_{cp,0z} (q_0) | \chi_0 (q) \rangle,
\]

(58)

\[
G_{c,t,r} (p) = \langle \chi_0 (q) | \hat{D}_{cp,0z} (q_0) | \chi_0 (q) \rangle,
\]

(59)

where \( N_c (\epsilon_p) \) is given by Eq. (53) above. For the most important special case, where \( |\chi_0\rangle \) is the ground-state vibrational wavefunction of a multi-dimensional harmonic oscillator, the integral \( [53] \) can be readily evaluated.

Indeed, for a 1-dimensional harmonic oscillator of unit effective mass and force constant \( \omega_i^2 \):

\[
\left( -\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \omega_i^2 q_i^2 - \frac{1}{2} \omega_i \right) \chi_{0,i} (q_i) = 0,
\]

(60)

\[
\chi_{0,i} (q_i) = \left( \frac{\omega_i}{\pi} \right)^{\frac{1}{4}} e^{-\frac{q_i^2}{2\omega_i}},
\]

(61)

\[
|\chi_0 (q)\rangle = \prod_i \chi_{0,i} (q_i),
\]

(62)

where \( q_i \) is the displacement from the equilibrium position \( q_{0,i} \) and \( \omega_i \) is the vibrational quantum. The multi-dimensional vibrational ground state is a product of \( \chi_{0,i} \) for all modes. The first few non-zero moments of \( \chi_{0,i} \), which are required below, are given by:

\[
\int dq_i \chi_{0,i}^2 (q_i) = 1,
\]

(63)

\[
\int dq_i q_i^2 \chi_{0,i}^2 (q_i) = \frac{1}{2\omega_i},
\]

(64)

\[
\int dq_i q_i^4 \chi_{0,i}^2 (q_i) = \frac{3}{4\omega_i^2}.
\]

(65)

The classical turning points of the ground-state vibrational wavefunction of mode \( i \) are found at \( q_i = \pm \omega_i^{-\frac{1}{2}} \).

As long as matrix elements \( \hat{D} \) are sufficiently smooth, they can be expanded in Taylor series:

\[
\hat{D}_{cp,0z} \approx D^{(0)}_z + \sum_i D^{(i)}_z q_i + \frac{1}{2} \sum_{ij} D^{(ij)}_z q_i q_j,
\]

(66)

\[
D^{(0)}_z = \hat{D}_{cp,0z} (q_0),
\]

(67)

\[
D^{(i)}_z = \frac{\partial}{\partial q_i} \hat{D}_{cp,0z} (q_0),
\]

(68)

\[
D^{(ij)}_z = \frac{\partial^2}{\partial q_i \partial q_j} \hat{D}_{cp,0z} (q_0),
\]

(69)

Inserting Eqs. (62) and (66) in Eq. (59), we obtain:
contribution to Eq. \((73)\), which is expensive to evaluate, can be safely omitted.

If analytical derivatives of the matrix elements in Eq. \((70)\) are not available, they can be obtained using the standard finite-difference formulae. It is particularly convenient to use the turning points of the normal modes. Then:

\[
D^{(k)}_x \approx \frac{\sqrt{\omega_k}}{2} (D_{x} (\sqrt{\omega_k}) - D_{x} (-\sqrt{\omega_k})) , \\
D^{(k,k)}_{x} \approx \omega_k (D_{x} (\sqrt{\omega_k}) + D_{x} (-\sqrt{\omega_k}) - 2D_{x} (q_0)) ,
\]

where \(x = l, r\). Substituting into Eq. \((70)\), we then obtain the final working expression:

\[
G_{c,l,r} (p) \overset{Z.P.E.FD}{=} \int \int \int \int \int \int \sum_k D^{(k)}_l W_{l,k} + \sum_k W^{(k)}_l D_{r,k} + \sum_k V^{(k)}_l V_{r,k} + 3 \sum_k W^{(k)}_l W_{r,k} + \sum_{k \neq m} W^{(k)}_l W_{r,m} ,
\]

\[
D_x = \dot{D}_{c_p,0x} (q_c) ,
\]

\[
V_{x,k} = \frac{1}{\sqrt{8}} \left[ \dot{D}_{c_p,0x}^{+} (q_0 + \sqrt{\omega_k}) - \dot{D}_{c_p,0x}^{+} (q_0 - \sqrt{\omega_k}) \right] ,
\]

\[
W_{x,k} = \frac{1}{4} \left[ D_{c_p,0x} (q_0 + \sqrt{\omega_k}) + \dot{D}_{c_p,0x} (q_0 - \sqrt{\omega_k}) - 2\dot{D}_{c_p,0x} (q_0) \right] .
\]
IV. SUMMARY AND OUTLOOK

In this work, we develop the formal theory of RABBITT photoionization spectra in molecular systems. Our most general result is given by Eqs. [10], [13], [14], [15], and [21]. It includes the effects of the nuclear motion in the initial (neutral) and final (cation) state (including vibrational heating by the IR field and IR-induced electronic transitions); coordinate dependence of the two-electron photoionization matrix elements; and effects of the finite pulse duration. It neglects the possibility of collisional excitation of the final ion, as well as of the shake-off and shake-up processes. The possibility of multiphoton transitions due to the XUV, or absorption/emission of multiple IR photons by the ionized electron are also neglected. The vibronic dynamics, including dynamics at conical intersections is treated fully, both in the initial and the final molecular states.

We further analyze important special cases. We demonstrate that in the lowest-order, Condon approximation, nuclear motion does not introduce additional time delays in the RABBITT spectra. The photoelectron energy profile in this approximation coincides with the vibrational profile in 1-photon ionization spectra. In contrast, the zero-point motion leads to non-vanishing phase contributions, and therefore time delays. We develop numerically tractable expressions for the ZPE contributions, both for the case where analytical derivatives of the electronic matrix elements are available, and for the finite-difference evaluation.

The expressions we have developed can be readily evaluated by combining the existing molecular photoionization codes, utilizing fixed-nuclei approximation, \textit{ab initio} potential energy surfaces, and molecular vibronic-dynamics simulations. We envision routine applications of our theory to molecules with tens and potentially hundreds vibrational degrees of freedom, which are entirely out of reach for brute-force, coupled electron-nuclear simulations. Work in this direction is currently underway, and will be reported elsewhere.

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