Automatic Feynman diagram generation for nonlinear optical spectroscopies

Peter A. Rose
Department of Physics, University of Ottawa, Ottawa, ON, K1N 6N5, Canada

Jacob J. Krich
Department of Physics, University of Ottawa, Ottawa, ON, K1N 6N5, Canada and
School of Electrical Engineering and Computer Science,
University of Ottawa, Ottawa, ON, K1N 6N5, Canada

Perturbative nonlinear optical spectroscopies are powerful methods to understand the dynamics of excitonic and other condensed phase systems. Feynman diagrams have long provided the essential tool to understand and interpret experimental spectra and to organize the calculation of spectra for model systems. When optical pulses are strictly time ordered, only a small number of diagrams contribute, but in many experiments pulse-overlap effects are important for interpreting results. When pulses overlap, the number of contributing diagrams can increase rapidly, especially with higher order spectroscopies, and human error is especially likely when attempting to write down all of the diagrams. We present an automated Diagram Generator (DG) that generates all of the Feynman diagrams needed to calculate any \( n \)-th-order spectroscopic signal. We characterize all perturbative nonlinear spectroscopies by their associated phase-discrimination condition as well as the time intervals where pulse amplitudes are nonzero. Although the DG can be used to automate impulsive calculations, its greatest strength lies in automating finite-pulse calculations where pulse overlaps are important. We consider the cases of third-order 2D photon echo spectroscopy and fifth-order exciton-exciton interaction 2D spectroscopy, which are respectively described by 6 or 7 diagrams in the impulsive limit but 16 or 240 diagrams, respectively, when pulses overlap. The DG allows users to automatically include all relevant diagrams at relatively low computational cost, since the extra diagrams are only generated for the inter-pulse delays where they are relevant.

I. INTRODUCTION

Nonlinear optical spectroscopies (NLOS) are powerful tools for elucidating excited state dynamics of a variety of condensed phase systems and have been particularly important for determining the evolution of excitonic systems [1–10]. Interpretation of data-rich NLOS signals is centered on Feynman diagrams, which conveniently graphically summarize time-dependent perturbation theory contributions to the signals [11]. These diagrams give a visual understanding of what types of excited- and ground-state dynamics and/or coherences are probed and can be straightforwardly turned into calculations of contributions to signals. In many cases, diagrams can be determined to give zero contribution without a complicated calculation, making theoretical interpretation easier and calculation less expensive.

When pulse durations are shorter than system dynamics – the impulsive limit – the number of contributing diagrams is often small, especially for third-order spectroscopies. It has been easiest to build intuition about the experimental signatures of particular excitonic processes by considering the impulsive limit [2, 3, 5–7, 12–19]. When pulse durations are similar to the timescale of system evolution, however, the effects of pulse overlaps – where the tail of a nominally earlier pulse arrives after the beginning of a nominally later pulse – become important to accurately model and understand experimental results [20–30]. Considering such processes requires many more contributing diagrams. Higher-order spectroscopies, both in the impulsive and pulse-overlap limits, also involve rapidly increasing numbers of contributing diagrams. Human error and fatigue in determining these diagrams accurately become increasingly likely as their numbers proliferate.

We present here an automated Feynman Diagram Generator (DG), which allows convenient, fast, and accurate determination of the diagrams contributing to a particular spectroscopy. We describe all perturbative nonlinear spectroscopies by their associated phase-discrimination conditions. These conditions allow description of both non-colinear phase-matching and colinear phase-cycling experiments [11, 13, 17, 31]. Users input those conditions and the time intervals in which their pulses are nonzero, and the DG produces a list of contributing diagrams. That list can be passed directly to calculation engines to predict the associated spectroscopic signals or can be drawn in the standard diagrammatic format for review. The DG is part of a set of NLOS tools called the Ultrafast Spectroscopy Suite (UFSS), which also contains methods to generate Hamiltonians or Liouvillians for vibronic systems and to calculate the contributions from each diagram [37–39], but its output diagrams can be used with other computational tools or analytic methods to calculate spectroscopic signals [7, 17, 21, 27, 28, 39–48]. The DG is free and open-source software written in Python, available for download from github.

The DG (and the larger UFSS) is designed to make simple the inclusion of the effects of finite-duration pulses in NLOS. While modeling often considers the impulsive limit, pulse-overlap effects can dominate third-order signals such as two-dimensional photon echo (2DPE) spec-
troscopy, even outside of what is commonly thought of as the pulse-overlap window \[30\]. 2DPE is usually calculated using 6 time-ordered diagrams (3 for the rephasing and 3 for the non-rephasing pathway). When pulses overlap, up to 16 diagrams (shown in Fig. 1) contribute to the signal \[49\]. In higher-order methods, such as fifth-order exciton-exciton interaction 2D spectroscopy (EEI2D), there are 7 Feynman diagrams in the impulsive limit \[15\]. We show that outside of the impulsive limit, EEI2D requires up to 240 Feynman diagrams, a number that requires automation to be sure each one has been calculated correctly. The DG automatically creates all of the diagrams that satisfy a given phase-discrimination condition. For each set of pulse delays, the DG determines whether pulses are overlapping, and thus whether overlap diagrams contribute. This determination provides a significant computational time savings, since it automatically allows us to calculate only the diagrams that are important.

We begin with an overview of perturbative spectroscopy calculations in Sec. [II] in order to establish the construction of Feynman diagrams. We describe the algorithm of the DG in Sec. [III] including optional methods to reduce the number of diagrams, depending on the system under study. We demonstrate the utility of the DG by exploring EEI2D spectroscopy in Sec. [IV]. We consider the same model system as in Ref. \[50\] and show that when optical pulses have slightly longer durations than considered in that work, neither the impulsive limit nor the time-ordered diagrams with pulse-shape effects included accurately predict spectra. The calculation with all 240 diagrams requires less than twice the time as using only the 7 time-ordered diagrams despite considering 34 times as many diagrams. These results underscore the importance of including all of the additional 233 overlap diagrams, as well as the utility of the DG in not only generating these diagrams, but also automatically determining in which conditions they contribute.

II. NONLINEAR SPECTROSCOPY AND FEYNMAN DIAGRAMS

We begin by establishing the standard perturbative framework of nonlinear optical spectroscopy, from which Feynman diagrams are defined [11]. Consider a system with density matrix \(\rho\), which evolves in the absence of perturbation according to

\[
\rho(t) = \mathcal{T}_0(t, t')\rho(t'),
\]

where \(\mathcal{T}_0\) is a time evolution operator. We restrict the following discussion to the case of Hamiltonian systems or Markovian open systems, in which \(\mathcal{T}_0(t, t') = \mathcal{T}_0(t - t')\), which must be known or approximated in order to complete calculations, but the resulting diagrams are broadly applicable to non-Markovian situations, as well. For the purposes of diagram generation, however, we simply need to assume \(\mathcal{T}_0\) exists. We also define the differential time evolution operator \(\mathcal{L}_0\) so

\[
\frac{d\rho(t)}{dt} = \mathcal{L}_0\rho(t).
\]

The perturbative optical fields are described as classical electric fields \(\mathbf{E}(t)\), which interact with the system in the electric-dipole approximation through the perturbation Hamiltonian

\[
H'(t) = -\mu \cdot \mathbf{E}(t),
\]

where \(\mu\) is the electric dipole operator. Then the time evolution of the system is

\[
\frac{d\rho(t)}{dt} = \mathcal{L}_0\rho(t) - \frac{i}{\hbar}[H'(t), \rho(t)].
\]

This form is the basis for diagrammatic perturbation theory in \(\mathbf{E}(t)\).

We describe \(\mathbf{E}(t)\) as a sum over \(L\) pulses, where each pulse is denoted by a lowercase letter starting from \(a\). A typical \(3^L\)-order signal is calculated using up to 4 pulses. We write the electric field as

\[
\mathbf{E}(t) = \sum_{j=a, b, \ldots, L} \mathbf{e}_j \varepsilon_j(t) + \mathbf{e}_j^* \varepsilon_j^*(t)
\]

where \(\mathbf{e}_j\) is the possibly complex polarization vector, and the amplitude \(\varepsilon_j\) of each pulse is defined with envelope \(A_j\), central frequency \(\omega_j\), wavevector \(\mathbf{k}_j\), and phase \(\phi_j\) as

\[
\varepsilon_j(t) = A_j (t - t_j) e^{-i(\omega_j(t-t_j) - \mathbf{k}_j \cdot \mathbf{r} - \phi_j)},
\]

where \(t_j\) is the arrival time of each pulse. We make the physical assumption that each pulse is nonzero in the finite interval \([t_{j,\text{min}}, t_{j,\text{max}}]\). The DG uses this range to determine when pulses overlap; the form of \(A_j(t)\) is unimportant for diagram generation. The light-matter interaction is a sum over the rotating (\(\varepsilon_j\)) and counter-rotating (\(\varepsilon_j^*\)) terms. In the rotating wave approximation (RWA), the rotating terms excite the ket-side and de-excite the bra-side of the density matrix, respectively, and the counter-rotating terms excite the bra-side and de-excite the ket side, respectively [11].

We treat the effect of the optical fields using standard time-dependent perturbation theory and assume that at time \(t_0\) the system is in a stationary state of \(\mathcal{L}_0\), which is \(\rho(0)\). Then

\[
\rho(t) = \rho^{(0)} + \rho^{(1)}(t) + \rho^{(2)}(t) + \ldots
\]

where [11]

\[
\rho^{(n+1)}(t) = \int_0^\infty dt' \mathcal{T}_0(t') \left[ -\frac{i}{\hbar} \mu \cdot \mathbf{E}(t-t'), \rho^{(n)}(t-t') \right].
\]
Using Eq. 3 we define $\rho^{(n+1)}(t)$ as a sum over four types of terms,
\[ \rho^{(n+1)}(t) = \sum_j (K_j + K_j^* + B_j + B_j^*) \rho^{(n)}(t), \] (6)
where $K_j$ and $B_j$ are superoperators representing ket- and bra-side actions, respectively, of the rotating terms of pulse $j$ on $\rho$, while $K_j^*$ and $B_j^*$ give the equivalent counter-rotating terms. By inspection of Eq. 3 all four types of terms in Eq. 6 can be compactly defined as
\[ O_{j()} = \frac{\eta}{\hbar} \int_0^\infty \! dt' \mathcal{T}_0(t') \left( \mu^O \cdot \epsilon_j(t - t') \right), \] (7)
where $O = K, B$, $\eta_K = 1$ and $\eta_B = -1$, and we define dipole superoperators $\mu^B \rho \equiv \mu \rho$ and $\mu^B \rho \equiv \rho \mu$. The operators \{\(O_{j()})\} are the building blocks for all perturbative spectroscopies. The full $\rho^{(n)}$ is constructed from the unperturbed state $\rho^{(0)}$ as
\[ \rho^{(n)}(t) = \left[ \sum_{j=a,b,\ldots,L} (K_j + K_j^* + B_j + B_j^*) \right]^{n} \rho^{(0)}(t), \] (8)
which involves $(4L)^n$ terms when the exponent and sum are fully expanded. Each of these terms is a sequence of $n$ applications of $O_{j()}$, and can be represented as a Feynman diagram. Most of these diagrams are unimportant for any given spectroscopy, and the subset of diagrams that contributes to a particular experiment is determined by the set of optical pulses and a phase-discrimination condition.

Regardless of the computational details used to calculate the \{\(O_{j()})\}, all perturbative calculations can be represented and organized using the same Feynman diagrams, and thus the DG is useful for any perturbative spectroscopy algorithm. For example, UFSS contains two methods for calculating the action of the $O_{j()}$ operators, which are derived for closed systems in Ref. 37 and for open systems in Ref. 38. The integral form of the $O_{j()}$ in Eq. 2 is convenient for UF$^2$ and is the open-systems analogue of similar expressions derived for wavefunctions.

The two widely used phase-discrimination conditions are phase matching and phase cycling. Phase-matching conditions are achieved by using pulses that travel along different directions denoted by wavevectors $\mathbf{k}_j$, converging to interact with a sample that is assumed to be uniform over a volume large compared to the wavelength of the pulses. The pulses induce a polarization field in the sample $\mathbf{P}(t) = \langle \mu \rho(t) \rangle$, which produces radiation in all directions. A detector placed in a direction that satisfies the phase-matching condition $\mathbf{k}_d = \sum_j n_j \mathbf{k}_j$, where $n_j$ are integers, is sensitive to a polarization field that is described by only a subset of diagrams. Often one is interested in the lowest-order signal in perturbation theory that contributes to the given phase-discrimination condition. Heterodyne detection with a local oscillator (LO) allows full determination of amplitude and phase of the emitted radiation.

For example 2D photon echo (2DPE) signals involve three pulses, $a, b, c$, that interact with the sample and a fourth LO pulse $d$. The 2DPE rephasing and non-rephasing signals are measured with detectors placed in the $\mathbf{k}_d = -\mathbf{k}_a + \mathbf{k}_b + \mathbf{k}_c$ (see Fig. 1) and $\mathbf{k}_d = \mathbf{k}_a - \mathbf{k}_b + \mathbf{k}_c$ directions, respectively. These signals are calculated using
\[ \mathbf{P}^{(3)}_{k_d}(t) = \langle \mu \rho^{(3)}_{k_d}(t) \rangle \]
\[ \mathbf{P}^{(3)}_{k_d} (\omega) = \int_{-\infty}^\infty \! dt e^{i\omega t} \mathbf{P}^{(3)}_{k_d}(t) \]
\[ \mathbf{S}^{(3)}_{k_d}(\omega) = \text{Im} \left[ \mathbf{P}^{(3)}_{k_d} (\omega) \right] \]
where $\mathbf{S}^{(3)}_{k_d}(\omega)$ are the signals and $\rho^{(3)}_{k_d}(t)$ is the portion of $\rho^{(3)}(t)$ that produces radiation in the $\mathbf{k}_d$ direction; the primary purpose of diagrammatic perturbation theory is to organize the efficient calculation of $\rho^{(3)}_{k_d}(t)$ without needing to calculate all contributions to $\rho^{(3)}(t)$.

An alternative phase discrimination method uses phase cycling over the relative phases of collinear pulses. This method generally detects a signal proportional to an excited state population, such as fluorescence or photocurrent. A fourth-order signal $\mathbf{S}^{(4)}_{d}(t)$ in such a setup is calculated as
\[ \mathbf{S}^{(4)}_{d}(t) = \langle Q \rho^{(4)}_{d}(t) \rangle, \]
where $Q$ is a projection operator onto the relevant excited electronic states and $\rho^{(4)}_{d}(t)$ includes only those contributions to $\rho^{(4)}(t)$ that contribute to the chosen phase-cycling condition.

For example, the 2DPE rephasing signal is composed of the 16 diagrams in Fig. 1 which were automatically generated and drawn using the DG. If, however, $\tau_{a,\min} > \tau_{b,\max}$ and $\tau_{c,\min} > \tau_{b,\max}$ (that is, the pulses are time ordered), then only three diagrams contribute, shown in the black box.

The operators \{\(O_{j()})\} as an abstract concept have previously been introduced in various forms. To our knowledge, they have not been used for the purposes of automated calculations before. In Sec. III we describe how users inputs the pulse intervals and phase discrimination conditions and present the algorithm that produces the relevant diagrams. In Sec. IV we demonstrate the DG by using up to 240 diagrams and show the importance of including the full set of diagrams when performing simulations with finite pulse durations.

III. DIAGRAM GENERATOR

The user of the DG inputs the desired phase discrimination condition and pulse intervals, and the DG automatically generates all Feynman diagrams, including...
In order to determine which diagrams are causally allowed, spectroscopy is given by
\[ \sum \phi \]
with phase matching and detection of signals in phase. The number of diagrams that must be considered when dealing with finite pulses expands dramatically as one considers higher-order signals, such as exciton-exciton interaction 2D spectra (the 3-pulse 5th-order signal measured in the \( k_d = -2k_1 + 2k_2 + k_3 \) direction, see Sec. IV), where the number of time-ordered diagrams is \( 7 \). However, when all pulses overlap, there are 240 diagrams. In a fully automated calculation, the computational cost of evaluating the diagrams greatly exceeds the cost of the DG, so it is easy to rerun the DG for each set of considered pulse delays.

We outline the steps for determining all diagrams that contribute to the signal for a given pulse configuration in Fig. 2, which includes the general scheme and two examples.

1. Starting from \( [(n_j^a, n_j^b)]_{i=a,b,\ldots,L} \), we begin with a canonical list of interactions, where we list the pulses in order of pulse number starting from \( a \), with rotating terms coming before counter-rotating terms (see Fig. 2 for examples). The length of the resulting list is \( n_{total} \).

2. For each pulse there are \( n_j^a \) repetitions of \( "j" \) with the rotating term and \( n_j^b \) repetitions of \( "j"^* \) with the counter-rotating term, as shown in Fig. 2. We then generate all unique permutations of this canonical list of interactions. The number of unique permutations is
\[ \frac{n_{total}!}{n_j^a!n_j^b!n_i^c!} \]

3. Using the list of pulse durations \( \{[t_{j,\min}, t_{j,\max}]\}_{j=a,b,\ldots,L} \), non-causal orderings are removed. For each permutation of the time-ordered list, we check whether \( t_{min} \) of each pulse occurs before \( t_{max} \) of each following pulse in the list and remove the permutation if not.

4. For each permutation from step 2, we generate all of the allowed diagrams that satisfy the phase-discrimination conditions. Each interaction can occur either on the ket-side (\( K_{j\curvearrowright} \)) or the bra-side (\( B_{j\leftarrow} \)), giving \( 2^{n_{total}} \) diagrams associated with each permutation from step 2. For example, the interaction \( a^* \) can act as \( K_{a^*} \) or as \( B_{a^*} \), while the interaction \( b \) can act as either \( K_b \) or \( B_b \).

At this point we have the maximum number of diagrams that could contribute to the calculation, given the phase-discrimination condition. However, many of these diagrams do not contribute under common assumptions. Using some minimal information about the material system that is being modeled, many of these diagrams can be removed in the optional step 4.

(a) Keep only diagrams that remain in accessible states. For instance, consider optical spectroscopy of a system that has three optically separated manifolds, each separated by an energy gap \( E_g \). If the temperature is much less than \( E_g \), we can approximate that the initial thermal state is entirely in the ground-state manifold. Any diagram that includes excitation above the highest manifold or de-excitation from the lowest manifold is removed. We
track the number of optical excitations by assigning manifold indices for both the ket and bra sides of a density matrix. We say that the initial density matrix $\rho^{(0)}$ is entirely composed of ground-state populations, and therefore it has manifold indices $[0, 0]$. We then assign the following rules describing the action of the $O_{j(i)}$ operators:

\begin{align*}
K_j &: [+1, 0] \\
K_{j'} &: [-1, 0] \\
B_j &: [0, -1] \\
B_{j'} &: [0, +1]
\end{align*}

We apply these rules in succession for a diagram and track the indices $[i, l]$ after each interaction. If either $i$ or $l$ drop below 0 or rise above the maximum allowed manifold, the diagram is removed. When the manifolds are coupled by relaxation processes, we no longer remove diagrams that rise above the allowed maximum manifold, since population can decay to a lower manifold and then be excited up again by a subsequent interaction. We do still remove diagrams where $i$ or $l$ drop below zero.

(b) The integer logic of part 4(a) is also helpful in determining which diagrams contribute to the final signal. For spectroscopies that measure the emitted polarization field, we are interested in the object $\text{Tr} [\mu T]$. Typically in optical spectroscopy, $\mu$ connects only adjacent manifolds (either because this is an accurate model for the dipole operator or because the measurement bandwidth only supports 1-manifold transitions). The components of $\rho$ that contribute are then coherences between adjacent optical manifolds. Therefore, we filter out all diagrams except those that end in a state $[i + 1, i]$ (Note that the diagrams that end in $[i, i + 1]$ are physically valid; however, we do not calculate them, as they are the Hermitian conjugate pairs of the calculated diagrams $[11]$). Note that we again cannot apply this filter when $T$ includes inter-manifold relaxation.

(c) If the final observable is instead linked to excited-state populations, as in the case of fluorescence or photo-current detection, we look only for diagrams that end in a population $[i, i]$ where $i > 0$. Again, we cannot apply this filter when $T$ includes inter-manifold relaxation.

Each of the diagram reductions from step 4 can be turned off with a flag or modified to suit an accurate model for the system in question. For example, in vibrational spectroscopy, rule 4a) does not apply, but rules 4b) or 4c) (or modifications of them) may still apply. Thus far we have described how the DG creates the double-sided Feynman diagrams associated with density-matrix-based calculations. The DG can also create the one-sided Feynman diagrams used for wavefunction-based calculations $[11]$. This procedure begins by creating all relevant double-sided diagrams. Each double-sided diagram is converted to a pair of one-sided diagrams associated with the bra and ket wavefunctions. Since wavefunction-based calculations do not impose time-ordering between the bra and ket sides $[11]$, several of the double-sided diagrams map onto the same pair of single-sided diagrams. After creating all of the pairs of single-sided diagrams, we eliminate duplicates to avoid over-counting some pathways.
Figure 3. (a)-(c) Real part of the EEI2D spectrum at a delay time of $T = 60$ fs for a dimer of three-level systems with a relaxation rate of 0.015 fs$^{-1}$, as described in the text, using different electric field shapes. (d) Impulsive calculation, which requires only time-ordered diagrams, (b) 15 fs FWHM Gaussian pulses using only time-ordered diagrams, (c) 15 fs FWHM Gaussian pulses including all 240 diagrams. (a)-(c) are normalized independently so that the largest peak has magnitude 1. (d) Maximum of the absolute value of the signal contained within the black boxes in (a)-(c) as a function of delay time $T$. Dashed vertical line shows $T$ used in (a-c). The impulsive and time-ordered calculations both quantitatively and qualitatively deviate from the full calculation.

The DG both produces a full set of contributing diagrams to be calculated and updates that list as the pulse timings change. In the example 3-pulse 5$^{th}$-order spectroscopy considered in Sec. IV, the pulse delays vary to produce frequency-domain signals. Only a small number of pulse configurations have all three pulses overlapping. In those cases, 240 diagrams must be calculated, but as the pulse delays change, calculations can be reduced to 54, 21, or 7 diagrams, which all occur automatically. Including overlap diagrams increases the number of required diagrams by a factor of about 34, but since diagrams are only included when pulse delays require, calculations of frequency-domain spectra are only 1.5-5 times longer than those including only the 7 time-ordered diagrams, depending upon which pulse delays are calculated.

IV. IMPORTANCE OF OVERLAP DIAGRAMS

Spectra are often calculated assuming impulsive pulses. Even when finite pulse shapes are considered, the overlap diagrams are often neglected. In some cases these approximations are warranted, but sometimes the overlap diagrams are important to understand signals both quantitatively and qualitatively. Here, we demonstrate an example where neglecting overlap diagrams leads to significant artifacts in predicted spectra.

We consider a model system used in Ref. 50 to study exciton-exciton annihilation, using three-pulse exciton-exciton interaction 2D (EEI2D) spectroscopy. The model consists of a dimer of two coupled three-level systems (3LS). The Hamiltonian takes the form

$$H_0 = E_{gg} \langle gg | gg \rangle + E_{eg} \langle eg | eg \rangle + |ge \rangle \langle ge | + h.c. + E_{ee} \langle ee | ee \rangle + E_{fg} \langle fg | fg \rangle + |gf \rangle \langle gf | + h.c. + E_{ef} \langle fe | fe \rangle + |ef \rangle \langle ef | + L \langle ef \rangle \langle ef | + h.c. + E_{ff} \langle ff \rangle \langle ff |$$

where $E_{ii} = E_i + E_j$, all of the constants are defined in Table 1, and $\rho$ is the ground, singly excited, and doubly excited states, respectively, of each 3LS, and $|ur\rangle = |u\rangle_1 \otimes |v\rangle_2$. Following Ref. 50 we consider relaxation processes at zero temperature for each isolated monomer unit from $|f_i\rangle$ to $|e_i\rangle$ at rate $k_M$ and neglect relaxation from $|e_i\rangle$ to $|g_i\rangle$, since it is not important for exciton-exciton interactions. Reference 50 included relaxation using the stochastic Schrodinger equation, while we include relaxation using the Lindblad formalism with

$$\dot{\rho} = -\frac{i}{\hbar} [H_0, \rho] - \sum_{n \neq m} k_{nm} L [ |m\rangle \langle n | ] \rho$$

where $|m\rangle$ and $|n\rangle$ are eigenstates of $H_0$ and the Lindblad superoperator $L[O]$ is defined by

$$L[O]\rho = 2O\rho O^\dagger - O^\dagger O\rho - \rho O^\dagger O.$$

We follow Ref. 50 by projecting the monomer relaxation rates into the eigenstates $|n\rangle$ with energy $E_n$. New relaxation rates coupling the eigenstates of $H_0$ are defined as

$$k_{nm} = \left( \frac{\langle n | f_g \rangle}{\langle e_n | m \rangle} \right)^2 \frac{\langle eg | m \rangle}{\langle ge | m \rangle} + \frac{\langle n | gf \rangle}{\langle e_n | m \rangle} \frac{\langle ef | m \rangle}{\langle ee | m \rangle} + \frac{\langle n | ef \rangle}{\langle e_n | m \rangle} \frac{\langle ee | m \rangle}{\langle ee | m \rangle} \right) k_M.$$

EEI2D is designed to probe the dynamics of the doubly excited states. Diagonalizing $H_0$ shows that the two optically bright doubly excited states are separated by 0.35 eV, corresponding to an oscillation period of $T_o = 12$ fs, which is the fastest important oscillation in
Table I. Values used in the Hamiltonian $H_0$ and bath coupling rates for the model dimer system studied using EEI2D, adapted from Ref. 50.

| $E_d$ | $E_e$ | $E_f$ | $J$ | $K$ | $L$ | $k_M$ | Rate (fs$^{-1}$) |
|------|------|------|-----|-----|-----|-------|----------------|
| 0.0  | 1.0  | 2.2  |
| 0.2  | 0.1  | 0.05 |

where $t$ is the time measured after the arrival of pulse $c$. The 2D frequency-frequency correlation spectrum is calculated as

$$\tilde{P}^{(5)}_{kd}(\omega_\tau, T, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega_\tau} \int_{-\infty}^{\infty} dt e^{i\omega t} P^{(5)}_{kd}(\tau, T, t),$$

which is approximated using the discrete Fourier transform. We use $\tilde{P}^{(5)}_{kd}(\omega_\tau, T, t)$ as a proxy for the signal field, which would in practice be detected using heterodyne detection with a local oscillator.

We compare calculations of EEI2D spectra using three approximations: impulsive pulses, finite pulses with only time-ordered diagrams, and finite-pulses including all diagrams. Figure 3(a) shows the impulsive limit with a delay time of $T = 60$ fs. In keeping with Ref. 50, we perform all calculations with $\tau$ and $t$ each ranging from 0 to 823 fs and $T$ ranging from 0 to 350 fs, and multiply the $\tau$ and $t$ axes with a Gaussian window function of $\sigma = 200$ fs to avoid ringing effects from the discrete Fourier transform. We calculate spectra for 275 values of $\tau$ and $t$ as well as 467 values of $T$, which are more than sufficient to produce well-resolved frequency-frequency spectra. Reference 50 performs calculations in the impulsive limit and states that calculations using time-ordered diagrams with 5 fs FWHM pulses are visually nearly identical to the impulsive limit, which we also find. Finite-pulse effects are, unsurprisingly, unimportant when the pulse durations are shorter than $T_o$, the fastest timescale in the system. We use this model system to illustrate the differences that occur with only modestly longer pulses.

We consider Gaussian pulses with FWHM of 15 fs, similar to $T_o$. Figure 3(b) shows calculations using finite pulses but only the 7 time-ordered diagrams, showing clear differences from the impulsive limit in 3(a). Figure 3(c) shows results using the same finite pulses but including all of the 233 additional pulse overlap diagrams at delay times when they are required. The visual difference between Fig. 3(b) and (c) demonstrates the importance of including pulse-overlap diagrams in addition to finite-pulse effects in time-ordered diagrams. Simply adding finite pulse effects to the time-ordered diagrams is not sufficient for making good spectroscopic predictions.

Figure 3(d) shows the magnitude of the cross peak contained in the solid box in panels (a)-(c), and the oscillation period $T_o$ is clearly visible. That peak corresponds to absorption into one and emission from another doubly excited eigenstate of $H_0$. This peak is clearly visible in the impulsive limit in Fig. 3(a), but is dominated by significant horizontal streaks in Fig. 3(b), which bleed over from the stronger peak at $\hbar \omega_\tau = 2.3$ eV. This significant extension of the peaks in the $\omega_\tau$ direction is an artifact of neglecting the overlap diagrams, demonstrated by its removal in Fig. 3(c). Figure 3(d) shows that both the visibility of the oscillation and the overall evolution of the envelope are qualitatively different in the three studied approximations. Neither impulsive nor time-ordered calculations with finite pulses accurately predict this EEI2D spectrum despite using an ultrafast optical pulse.

Note that the differences between the full calculation and the ones using only the time-ordered diagrams persist even with delay times $T$ much greater than the pulse durations. In constructing $\tilde{P}^{(5)}_{kd}(\omega_\tau, T, t)$, contributions with $\tau$, $t$ smaller than the pulse duration are always included, making pulse-overlap effects apparent even at long $T$.

Since the DG only produces the extra diagrams for time delays that merit their evaluation, the full calculation is not much more expensive than the case with 7 time-ordered diagrams. For example, the calculation of the green curve in Fig. 3(d) took 33 minutes on a 2017 MacBook Pro, while the orange curve in Fig. 3(d) took 17 minutes on the same computer (note that these calculations involve over 120,000 combinations of $\tau$ and $T$). Even though the full calculation includes contributions from up to about 34 times more diagrams, it required less than twice the time to run than the time-ordered calculation.

V. CONCLUSION

We have presented the Diagram Generator, a tool for automatically generating the Feynman diagrams that contribute to perturbative nonlinear optical spectroscopies. The DG automatically determines when pulses
overlap and only generates extra overlap diagrams when required. This automated process allows users to get the full advantage of including all causally allowed diagrams with a low computational cost.

We have shown that including these overlap diagrams can be important to correctly predicting or interpreting spectra when pulses are not in the impulsive limit. Using EE12D as an example, we have shown significant errors when using only the time-ordered diagrams with pulses whose duration is similar to the dynamics of the system.

The DG is one module of the larger Ultrafast Spectroscopy Suite. The other tools in UFSS are described in Refs. [37, 38]. Taken together, UFSS is a tool for automatically calculating arbitrary-order spectroscopic signals while accounting for effects of finite pulse shapes, which can be of arbitrary form. The diagrams produced by the DG can also be used in other analytical or numerical tools. The DG can be used for determining all of the diagrams that contribute to any order spectra, whether in the impulsive limit or with finite pulses. The DG may open the door to more easily calculating higher-order corrections to commonly used 3rd-order spectroscopies and may lend itself to developing intuition for higher-order spectroscopic techniques.

ACKNOWLEDGMENTS

We acknowledge support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Ontario Trillium Scholarship.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

[1] W. M. Zhang, T. Meier, V. Chernvay, and S. Mukamel, The Journal of Chemical Physics 108, 7763 (1998).
[2] T. Brixner, J. Stenger, H. M. Vaswani, M. Cho, R. E. Blankenship, and G. R. Fleming, Nature 434, 625 (2005).
[3] M. Cho, H. M. Vaszware, T. Brixner, J. Stenger, and G. R. Fleming, The Journal of Physical Chemistry B 109, 10542 (2005).
[4] D. Abramavicus, B. Paliarnier, D. V. Voronine, F. Sanda, and S. Mukamel, Chemical Reviews 109, 2350 (2009).
[5] G. Panitchayangkoon, D. V. Voronine, D. Abramavicus, J. R. Caram, N. H. C. Lewis, S. Mukamel, and G. S. Engel, Proceedings of the National Academy of Sciences 108, 20908 (2011).
[6] N. Christensson, H. F. Kauffmann, T. Pullerits, and T. Mančal, J. Phys. Chem. B 116, 7449 (2012).
[7] J. H. Fetherolf and T. C. Bertelbach, The Journal of Chemical Physics 147, 244109 (2017).
[8] S. J. Jang and B. Mennucci, Rev. Mod. Phys. 90, 035003 (2018).
[9] C. D. Cruz, J. Yuan, C. Clement, N. T. Ticer, P. R. Christensen, E. L. Chronister, D. Casanova, M. O. Wolf, and C. J. Bardeen, Chem. Sci. 10, 7561 (2019).
[10] A. J. Kiessling and J. A. Cina, The Journal of Chemical Physics 152, 244311 (2020).
[11] S. Mukamel, Principles of Nonlinear Optical Spectroscopy (Oxford University Press, 1999).
[12] L. Yang, I. V. Schweigert, S. T. Cundiff, and S. Mukamel, Phys. Rev. B 75, 125302 (2007).
[13] P. Huo and D. F. Coker, J. Phys. Chem. Lett. 2, 825 (2011).
[14] A. Perdomo-Ortiz, J. R. Widom, G. A. Lott, A. Aspuru-Guzik, and A. H. Marcus, J. Phys. Chem. B 116, 10757 (2012).
[15] J. Dostal, T. Mančal, R.-n. Augulis, F. Vácha, J. Pšenčík, and D. Zigmantas, J. Am. Chem. Soc. 134, 11611 (2012).
[16] K. J. Karki, J. R. Widom, J. Selbt, I. Moody, M. C. Lonergan, T. Pullerits, and A. H. Marcus, Nature Communications 5, 5869 (2014).
[17] J. Provazza, F. Segatta, M. Garavelli, and D. F. Coker, Journal of Chemical Theory and Computation 14, 856 (2018) pMID: 29244497.
[18] J. Dostál, F. Fennel, F. Koch, S. Herbst, F. Würthner, and T. Brixner, Nature Communications 9, 2466 (2018).
[19] P. Malý and T. Mančal, J. Phys. Chem. Lett. 9, 5654 (2018).
[20] S. M. Gallagher Faeder and D. M. Jonas, The Journal of Physical Chemistry A 103, 10489 (1999).
[21] N. Belabas and D. M. Jonas, Opt. Lett. 29, 1811 (2004).
[22] M. K. Yetzbacher, N. Belabas, K. A. Kitney, and D. M. Jonas, The Journal of Chemical Physics 126, 044511 (2007).
[23] P. F. Tekavec, J. A. Myers, K. L. M. Lewis, F. D. Fuller, and J. P. Ogilvie, Opt. Express 18, 11015 (2010).
[24] J. Yuen-Zhou, J. J. Krich, and A. Aspuru-Guzik, The Journal of Chemical Physics 136, 234501 (2012).
[25] V. Tiwari, W. K. Peters, and D. M. Jonas, Proceedings of the National Academy of Sciences 110, 1203 (2013).
[26] H. Li, A. P. Spencer, A. Kortyna, G. Moody, D. M. Jonas, and S. T. Cundiff, J. Phys. Chem. A 117, 6279 (2013).
[27] V. Perlik, J. Hauer, and F. Sanda, J. Opt. Soc. Am. B 34, 430 (2017).
[28] C. L. Smallwood, T. M. Autry, and S. T. Cundiff, J. Opt. Soc. Am. B 34, 419 (2017).
[29] T. N. Do, M. F. Gelin, and H.-S. Tan, The Journal of Chemical Physics 147, 144103 (2017).
[30] D. Paleček, P. Edlund, E. Gustavsson, S. Westenhoff, and D. Zigmantas, The Journal of Chemical Physics 151, 024201 (2019).
[31] P. F. Tekavec, G. A. Lott, and A. H. Marcus, J. Chem. Phys. 127, 214307 (2007).
[32] M. Cho, Two-Dimensional Optical Spectroscopy (CRC Press, 2009).
[33] M. Z. Peter Hamm, Concepts and Methods of 2D Infrared Spectroscopy (Cambridge University Press, 2011).
[34] G. Nardin, T. M. Autry, K. L. Silverman, and S. T. Cundiff, Opt. Express 21, 28617 (2013).
[35] A. A. Bakulin, C. Silva, and E. Vella, The Journal of Physical Chemistry Letters 7, 250 (2016).
[36] V. Tiwari and D. M. Jonas, The Journal of Chemical Physics 148, 084308 (2018).
[37] P. A. Rose and J. J. Krich, The Journal of Chemical Physics 150, 214105 (2019).
[38] P. A. Rose and J. J. Krich, “Efficient numerical method for predicting nonlinear optical spectroscopies of open systems,” Submitted to J Chem Phys.
[39] V. Engel, Computer Physics Communications 63, 228 (1991).
[40] M. Beck, A. Jackle, G. Worth, and H.-D. Meyer, Physics Reports 324, 1 (2000).
[41] K. Renziehausen, P. Marquetand, and V. Engel, Journal of Physics B: Atomic, Molecular and Optical Physics 42, 195402 (2009).
[42] Y. Tanimura, The Journal of Chemical Physics 137, 22A550 (2012).
[43] J. Johansson, P. Nation, and F. Nori, Computer Physics Communications 183, 1760 (2012).
[44] J. Yuen-Zhou, J. J. Krich, I. Kassal, A. S. Johnson, and A. Aspuru-Guzik, *Ultrafast Spectroscopy* (IOP Publishing, 2014).
[45] J. Albert, M. Falge, M. Keß, J. G. Wehner, P.-P. Zhang, A. Eisfeld, and V. Engel, The Journal of Chemical Physics 142, 212440 (2015).
[46] Y.-a. Yan, Chinese Journal of Chemical Physics 30, 277 (2017).
[47] Y. Ke and Y. Zhao, The Journal of Chemical Physics 149, 014104 (2018).
[48] T. Mančal, “Quantarhei: Molecular open quantum systems package,” [http://github.com/tmancal74/quantarhei](http://github.com/tmancal74/quantarhei) (2020).
[49] D. M. Jonas, Annual Review of Physical Chemistry 54, 425 (2003).
[50] J. Süß, J. Wehner, J. Dostál, T. Brixner, and V. Engel, The Journal of Chemical Physics 150, 104304 (2019).