

Generalized Ehrenfest+R Dynamics for Semiclassical Simulation of Raman Scattering

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The recent proposed Ehrenfest+R method is generalized to explore Raman scattering within a mixed quantum-classical theory framework. Instead of extrapolating the behavior of quantum subsystem for scattering signals, we explicitly treat quantum subsystems and classical electromagnetic fields governed by coupled Maxwell–Liouville equations. Ehrenfest+R dynamics provide qualitatively significant corrections to standard Ehrenfest dynamics for both resonance and off-resonance cases. For resonance Raman scattering, we also exhibit the quantitative agreement with quantum mechanical descriptions which highlighting the power of Ehrenfest+R approach.

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I. INTRODUCTION

Raman scattering has been expanding horizons as an important research tool for decades. More recently, there has been an explosion of interest in Raman scattering, especially surface- and tip-enhanced Raman scattering¹⁻⁶, as a probe to investigate plasmonic excitations of molecules near a metal surface^{7,8} and chemical reactions at catalytic surfaces.⁹

The existing theory of Raman scattering is based on Kramers-Heisenberg-Dirac (KHD) formalism^{10,11} which can be reduced to Placzek's classical theory of polarizability for off-resonance cases^{12,13} and also derive Albrecht's vibronic theory for resonance cases.¹⁴⁻¹⁶ Despite difficulties of implementing the KHD formalism in practice, many semiclassical calculations for Raman spectroscopy has been developed within excited-state gradient approximation based on short time dynamics.^{13,17-20} Recent advances also incorporate electronic structure theories and semiclassical description of Raman spectroscopy.²¹⁻²⁴

For molecular systems involving strong coupling such as plasmonic excitations, Raman scattering is usually affected by collective behaviors of quantum subsystem.²⁵ To take into account strong couplings through radiation fields in a semiclassical manner, one needs to consider quantum subsystems and classical electromagnetic (EM) fields on an equal footing. However, existing semiclassical approaches usually treat the incoming field as a standalone field and extrapolate the behavior of quantum subsystems for emission lights.^{17,20,26} Our recent developments in mixed quantum-classical approaches provide a possible means to include the feedback of the subsystem on the EM field.^{27,28} We proposed Ehrenfest+R approach for an *ad hoc* algorithm to recover spontaneous emission by adding a complementary correction on top of Ehrenfest dynamics. Ehrenfest+R method and its variants opens up an interesting new avenue for studying light-matter interactions in a mixed quantum-classical theory framework. In this work, we generalize Ehrenfest+R method for an unified treatment to capture both resonance and off-resonance Raman scattering.

The paper is organized as follows. In Sec. II, we review the KHD formalism and obtain the polarizability of a three-level system setup for Raman scattering. In Sec. III, we formulate an Ehrenfest+R approach in the context of the three-level system and compare Raman spectra predicted by Ehrenfest+R dynamics against KHD formalism. In Sec. IV, we conclude.

II. QUANTUM THEORY OF RAMAN SCATTERING

Raman light scattering is an inelastic process that the incident photons interact with a molecule and lead to a small fraction of the scattered photons having a energy shift in emission spectra. This energy shift of scattered photons is characteristic for Raman scattering.

To qualitatively describe Raman scattering, we consider a molecular system involving the interaction between electronic states and nuclear vibration. The incident photons excite the molecular system to an intermediate state (could be a virtual state) which coupled to the ground state as well to other vibronic states. Subsequently, the system will emit two types of photons through spontaneous emission.²⁹ On one hand, the transition back to the ground state yields scattered photons with the same energy with the incident photons (known as Rayleigh scattering). On the other hand, the transition to other vibronic states will generate scattered photons with energy different from the incident photons (known as Raman scattering).

In this section, we review the KHD dispersion formula as a quantum theory for Raman scattering^{10,14,30} and obtain the polarizability and the scattering cross section in the context of a three-level model in a 1D system.

A. Kramers-Heisenberg-Dirac Formalism

For a quantitative description of Raman scattering, KHD formula is a conventional, frequency domain expression for the scattering cross section¹³

$$\sigma_{fi}^{3D}(\omega_S, \omega_I) = \frac{8\pi\omega_I\omega_S^3}{9c^4} \sum_{\rho, \lambda} \left| [\alpha_{fi}(\omega_I)]^{\nu\nu'} \right|^2, \quad (1)$$

where the polarizability is given by

$$[\alpha_{fi}(\omega_I)]^{\nu\nu'} = - \sum_{k,n} \left(\frac{\langle \psi_f | \hat{\mathcal{P}}^\nu | \psi_{k,n} \rangle \langle \psi_{k,n} | \hat{\mathcal{P}}^{\nu'} | \psi_i \rangle}{\varepsilon_i + \hbar\omega_I - \varepsilon_{kn} + i\hbar\gamma} + \frac{\langle \psi_f | \hat{\mathcal{P}}^{\nu'} | \psi_{k,n} \rangle \langle \psi_n | \hat{\mathcal{P}}^\nu | \psi_i \rangle}{\varepsilon_f - \hbar\omega_I - \varepsilon_{kn} + i\hbar\gamma} \right), \quad (2)$$

All the EM fields take the form of photons: ω_I for incident photons and ω_S for scattered photons, and satisfy energy conservation $\hbar\omega_S = \varepsilon_i + \hbar\omega_I - \varepsilon_f$.

The KHD formula is also known as the “sum-over-states” formula since the polarizability expression requires a summation over all possible intermediate states $\psi_{k,n}$ where the index k labels electronic states and the index n labels vibrational states within a electronic state. Here $\widehat{\mathcal{P}}^\nu$ denotes the transition dipole moment operator for $\nu, \nu' = \{x, y, z\}$. The linewidth γ is corresponding the averaged lifetime of the intermediate state.

According to the scattering cross section given by Eq. (1), Raman spectroscopy is considered a two-photon spectroscopy. One usually fixes ω_I and observes the emission spectrum as a function of ω_S . A peak at frequency $\omega_S = \omega_I$ corresponds to the contribution of Rayleigh scattering, and other emission peaks are attributed to Raman scattering. Note that the KHD formula can be derived based on second order perturbation theory of the subsystem in the presence of the incident photon¹³— the scattering cross section is extrapolated from the change of electronic population.

B. Three-level System

To address Raman scattering, we consider a model system with three vibronic states: two lower energy states for an electronic ground state with different vibrational modes: $|gn_1\rangle \equiv |0\rangle$ and $|gn'_1\rangle \equiv |1\rangle$ and one for an excited state $|en_2\rangle \equiv |2\rangle$. We assume the energies of the vibronic states are $\varepsilon_0 \leq \varepsilon_1 < \varepsilon_2$ and the electric dipole interactions couple the ground and excited states only. In this case, the electronic Hamiltonian is given by

$$\widehat{H}^{\text{el}} = \begin{pmatrix} \varepsilon_0 & 0 & \mathcal{V}_{02} \\ 0 & \varepsilon_1 & \mathcal{V}_{12} \\ \mathcal{V}_{02}^* & \mathcal{V}_{12}^* & \varepsilon_2 \end{pmatrix} \quad (3)$$

where the electric dipole coupling is

$$\mathcal{V}_{ij} = - \int dx \mathbf{E}(x, t) \cdot \mathbf{P}_{ij}(x). \quad (4)$$

in a 1D space.

For frequency domain measurement, consider the incident field as a single-mode continuous wave (CW) electromagnetic field with frequency ω_I ,

$$\mathbf{E}_I(x, t) = \frac{A_I}{\sqrt{\epsilon_0}} \cos(k_I x - \omega_I t) \hat{\mathbf{z}} \quad (5)$$

$$\mathbf{B}_I(x, t) = -\sqrt{\mu_0} A_I \sin(k_I x - \omega_I t) \hat{\mathbf{y}} \quad (6)$$

where $\omega_I = ck_I$ and A_I is the amplitude of the incoming field. We assume the spatial size of the polarization is small in space, i.e. $\mathcal{P}_{ij}(x) \approx \mu_{ij}\delta(x)\hat{\mathbf{z}}$, so that the electric dipole interactions are approximated as $\int d\mathbf{x}\mathbf{E}(x,t) \cdot \mathcal{P}_{ij}(x) \approx \mu_{ij}\frac{A_I}{\sqrt{\epsilon_0}}\cos(\omega_I t)$.

For light scattering in a 1D space, the scattering cross section is defined as the ratio between the number of the scattered photon per time over the number of the incident photon per time. With this definition, the KHD formula for 1D system can be obtained as (see Appendix A)

$$\sigma_{fi}^{1D}(\omega_S, \omega_I) = \frac{\omega_I \omega_S}{2\hbar^2 c^2} |\alpha_{fi}^{1D}(\omega_I)|^2 \quad (7)$$

For such a system, the KHD expression for the polarizability can be simplified as

$$\alpha_{fi}^{1D}(\omega_I) = - \left(\frac{\mu_{02}\mu_{12}}{\epsilon_i + \hbar\omega_I - \epsilon_2 + i\hbar\gamma} + \frac{\mu_{02}\mu_{12}}{\epsilon_f - \hbar\omega_I - \epsilon_2 + i\hbar\gamma} \right). \quad (8)$$

Here the linewidth γ is the average lifetime for the electronic transitions of the excited state:

$$\frac{1}{\gamma} = \frac{1}{2} \left(\frac{1}{\kappa_{02}} + \frac{1}{\kappa_{12}} \right), \quad (9)$$

where the corresponding Fermi's golden rule (FGR) rates are given by

$$\kappa_{fi} = \frac{\epsilon_i - \epsilon_f}{\hbar^2 \epsilon_0 c} \mu_{fi}^2. \quad (10)$$

In the case of resonance Raman scattering (the incident photon line up with the excited state, i.e. $\epsilon_i + \hbar\omega_I = \epsilon_2$), the first term of Eq. (8) dominate. Resonance Raman scattering includes two possibilities. When $\hbar\omega_I = \epsilon_2 - \epsilon_0$ and the scattered photon energy is $\hbar\omega_S = \epsilon_2 - \epsilon_1$, the polarizability with $i = 0$ and $f = 1$ ($\alpha_{10}^{1D}(\omega_I)$) leads to a Stokes Raman peak (i.e. $\omega_S < \omega_I$) for resonance Raman spectrum. On the contrary, when $\hbar\omega_I = \epsilon_2 - \epsilon_1$ the scattered photon energy is $\hbar\omega_S = \epsilon_2 - \epsilon_0$, the polarizability with $i = 1$ and $f = 0$ ($\alpha_{01}^{1D}(\omega_I)$) leads to an anti-Stokes Raman peak (i.e. $\omega_S > \omega_I$).

In the case that the incident photon does not line up with any excited state, the excitation is detuned far off resonance (known as off-resonance Raman scattering). In this case, the intermediate state of the light scattering process is a virtual state, i.e. $\epsilon_k = \epsilon_i + \hbar\omega_I$. For a weak field, scattered photons must be dominated by Rayleigh scattering (i.e. $\omega_S = \omega_I$).

III. EHRENFEST+R APPROACH FOR RAMAN SCATTERING

Given that Raman scattering is based on spontaneous emission,²⁹ Ehrenfest+R dynamics should provide a proper tool for a mixed quantum-classical simulation since it is designed

to recover spontaneous emission. A straightforward prescription for generalizing of Ehrenfest+R method to more than two level system can be obtained as follow: we will add distinct +R corrections for electronic transition of each individual pair of vibronic states, i.e. $2 \rightarrow 0$ and $2 \rightarrow 1$. In addition, to reach a steady state, we will allow a phenomenological, non-radiative dissipation between $|0\rangle$ and $|1\rangle$. In this section, we start with formulating a generalized Ehrenfest+R approach in the context of the three-level system, then we compare Ehrenfest+R results against the KHD formula.

A. Generalized Ehrenfest+R Method

According to Hamiltonian Eq. (3), there are two electronic transitions through electric dipole couplings: \mathcal{V}_{02} and \mathcal{V}_{12} corresponding to spontaneous emission rates κ_{02} and κ_{12} given by Eq. (10), respectively. Here, based on Ref. 28, we add pairwise +R corrections on top of Ehrenfest dynamics to recover each individual spontaneous emission rate (κ_{fi}) from $|i\rangle$ to $|f\rangle$ while other states remain fixed.

1. System propagator

To implement the pairwise treatment for Ehenfest+R dynamics, the Liouville equation together with additional relaxations can be written as

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}^{\text{el}}, \hat{\rho}] + \sum_{\substack{fi= \\ \{02,12\}}} \mathcal{L}_R^{fi} \hat{\rho}, \quad (11)$$

where the +R relaxation rate for $i \rightarrow f$ is given by

$$k_R^{fi} \equiv 2\kappa_{fi} (1 - \rho_{ff}) \text{Im} \left[\frac{\rho_{fi}}{|\rho_{fi}|} e^{i\phi} \right]^2. \quad (12)$$

Here $\phi \in (0, 2\pi)$ is a phase chosen randomly for each Ehrenfest+R trajectory. In practice, we use a pure state representation for the density matrix: $\hat{\rho} = |\psi\rangle \langle \psi|$ with wavefunction $|\psi(t)\rangle = c_0(t)|0\rangle + c_1(t)|1\rangle + c_2(t)|2\rangle$. The additional relaxation is defined by a transition

operator:

$$\mathcal{T} [k_R^{fi}] : \begin{pmatrix} \vdots \\ c_i \\ \vdots \\ c_f \\ \vdots \end{pmatrix} \rightarrow \begin{pmatrix} \vdots \\ \frac{c_i}{|c_i|} \sqrt{|c_i|^2 - k_R^{fi} |c_i|^2} dt \\ \vdots \\ \frac{c_f}{|c_f|} \sqrt{|c_f|^2 + k_R^{fi} |c_f|^2} dt \\ \vdots \end{pmatrix}. \quad (13)$$

Finally, the time evolution of subsystem wavefunction can be carried out by

$$|\psi(t + dt)\rangle = \mathcal{T} [k_R^{12}] \mathcal{T} [k_R^{02}] e^{-i\hat{H}^{\text{el}} dt/\hbar} |\psi(t)\rangle. \quad (14)$$

where $e^{-i\hat{H}^{\text{el}} dt/\hbar}$ is responsible for propagating according to the first term of Eq. (11). Note that $\mathcal{T} [k_R^{12}]$ and $\mathcal{T} [k_R^{02}]$ commute as long as dt is sufficiently small.

2. EM field propagator

We write the total EM field in the form of $\mathbf{E} = \mathbf{E}_I + \mathbf{E}_S$ and $\mathbf{B} = \mathbf{B}_I + \mathbf{B}_S$ where \mathbf{E}_S and \mathbf{B}_S are the scattered EM fields. For a CW field given by Eq. (5) and Eq. (6), \mathbf{E}_I and \mathbf{B}_I satisfy source-less Maxwell's equations, so we can treat the CW field as a standalone external field. Therefore, for underlying Ehrenfest dynamics, the scattered fields \mathbf{E}_S and \mathbf{B}_S satisfy Maxwell's equations:

$$\frac{\partial}{\partial t} \mathbf{B}_S = -\nabla \times \mathbf{E}_S, \quad (15)$$

$$\frac{\partial}{\partial t} \mathbf{E}_S = c^2 \nabla \times \mathbf{B}_S - \frac{1}{\epsilon_0} \mathbf{J}, \quad (16)$$

with the average current is

$$\mathbf{J} = \sum_{\substack{fi= \\ \{02,12\}}} 2(\epsilon_f - \epsilon_i) \text{Im} [\rho_{fi}(t)] \mathcal{P}_{fi}(x). \quad (17)$$

Given the pairwise transitions of the subsystem, the classical EM field should be rescaled accordingly. Let us denote the rescaling operator for the EM fields by:

$$\mathcal{R} [\delta U_R^{fi}] : \begin{pmatrix} \mathbf{E}_S \\ \mathbf{B}_S \end{pmatrix} \rightarrow \begin{pmatrix} \mathbf{E}_S + \alpha^{fi} \delta \mathbf{E}_R^{fi} \\ \mathbf{B}_S + \beta^{fi} \delta \mathbf{B}_R^{fi} \end{pmatrix}. \quad (18)$$

where the rescaling coefficients are chosen to be

$$\alpha^{fi} = \sqrt{\frac{cdt}{\Lambda^{fi}} \frac{\delta U_R^{fi}}{\epsilon_0 \int dv |\delta \mathbf{E}_R^{fi}|^2}} \times \text{sgn}(\text{Im}[\rho_{fi} e^{i\phi}]) \quad (19)$$

$$\beta^{fi} = \sqrt{\frac{cdt}{\Lambda^{fi}} \frac{\mu_0 \delta U_R^{fi}}{\int dv |\delta \mathbf{B}_R^{fi}|^2}} \times \text{sgn}(\text{Im}[\rho_{fi} e^{i\phi}]) \quad (20)$$

and Λ^{fi} is self-interference length (see Ref. 28). Here the energy change of each pairwise relaxation $i \rightarrow f$ is

$$\delta U_R^{fi} = (\varepsilon_i - \varepsilon_f) k_R^{fi} \rho_{ii} dt. \quad (21)$$

According to Eq. (14), we need to perform two rescaling operators ($\mathcal{R}[\delta U_R^{12}]$ and $\mathcal{R}[\delta U_R^{02}]$) in correspondence with two additional relaxation operators.

For simplicity, we assume that the transition dipole moments are the same for both $2 \rightarrow 1$ and $2 \rightarrow 0$ transitions, i.e. $\mathcal{P}_{02} = \mathcal{P}_{12} = \mathcal{P}$, so that the rescaling fields can be chosen to be $\delta \mathbf{E}_R^{fi} = \delta \mathbf{E}_R$ and $\delta \mathbf{B}_R^{fi} = \delta \mathbf{B}_R$. For a 1D system, the rescaling fields take the form of

$$\delta \mathbf{E}_R = \nabla \times \nabla \times \mathcal{P} - g \mathcal{P}, \quad (22)$$

$$\delta \mathbf{B}_R = -\nabla \times \mathcal{P} - h (\nabla \times)^3 \mathcal{P}, \quad (23)$$

where g and h will be determined later according to Ref. 28. With this assumption, we can combine the two rescaling operators as $\mathcal{R}[\delta U_R^{12} + \delta U_R^{02}]$.

In the end, each Ehrenfest+R trajectory for classical EM fields can be propagated by

$$\begin{pmatrix} \mathbf{E}_S(t+dt) \\ \mathbf{B}_S(t+dt) \end{pmatrix} = \mathcal{R}[\delta U_R^{12} + \delta U_R^{02}] \mathcal{M}[dt] \begin{pmatrix} \mathbf{E}_S(t) \\ \mathbf{B}_S(t) \end{pmatrix}. \quad (24)$$

Here $\mathcal{M}[dt]$ denotes the linear propagator of Maxwell's equations (Eq. (15) and (16)) for time step dt .

3. Non-radiative dissipation

However, without any dissipation involved, the three-level system in the presence of the CW field will end up in an asymptotic state, $|\psi(t \rightarrow \infty)\rangle = |1\rangle$, by construction. To reach

a steady state, we need to take into account vibrational dissipation of vibronic states. Thus, we introduce a non-radiative relaxation from $|1\rangle$ to $|0\rangle$ by a transition operator:

$$|\psi(t+dt)\rangle \rightarrow \mathcal{T}[k_{\text{vib}}^{01}] |\psi(t+dt)\rangle \quad (25)$$

to impose a phenomenological dissipation. The classical EM field does not rescale accordingly for this non-radiative transition. Here the vibrational decay rate k_{vib}^{01} is an empirical parameter to be specified later. The decay rate is related to nuclear reorganization, which determine how fast the vibrational modes of the molecule reach equilibrium. Note that we exclude the thermal transition from $|0\rangle$ to $|1\rangle$ since we assume the system is at zero temperature.

B. Ehrenfest+R results

As far as simulating Raman scattering by Ehrenfest+R approach, we consider a three-level system with $\varepsilon_0 = 0$, $\varepsilon_1 = 0.25\hbar\Omega = 4.115$ eV, and $\varepsilon_2 = \hbar\Omega = 16.46$ eV. We assume the initial state of the system is on the ground state, $|\psi(t=0)\rangle = |0\rangle$ and turn on the incident CW field at $t = 0$. The transition dipole moment takes the form of a Gaussian distribution:

$$\mathcal{P}_{02}(x) = \mathcal{P}_{12}(x) = \mu \sqrt{\frac{a}{\pi}} e^{-ax^2} \hat{\mathbf{z}}, \quad (26)$$

where $\mu = 11282$ C/nm/mol and $a = 1/2\sigma^2$ with $\sigma = 3.0$ nm. With this polarization, we employ the rescaling fields from Ref. 28:

$$\delta\mathbf{E}_R(x) = -\mu \sqrt{\frac{a}{\pi}} 4a^2 x^2 e^{-ax^2} \hat{\mathbf{z}}, \quad (27)$$

$$\delta\mathbf{B}_R(x) = \mu \sqrt{\frac{a}{\pi}} \frac{4}{3} a^2 x^3 e^{-ax^2} \hat{\mathbf{y}}. \quad (28)$$

For the non-radiative dissipation, we choose a vibrational decay rate $k_{\text{vib}}^{01} = 0.1$ [1/fs]. In the following calculation, we run Ehrenfest+R dynamics to 500 fs to reach a steady state and average over $N_{\text{traj}} = 50$ trajectories.

1. Resonance and off-resonance scatterings

We first focus on frequency-domain spectrum of Raman scattering. In Fig. 1, we plot the Fourier transform of the scattered electric field (\mathbf{E}_S) at steady state as a function of ω_S

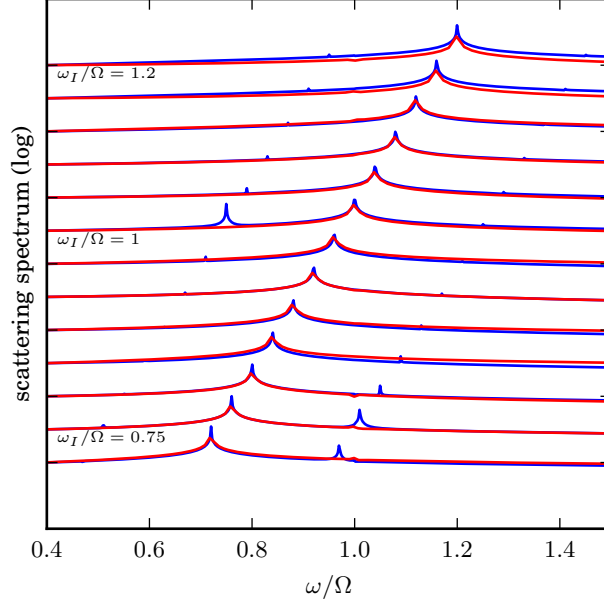


Figure 1. Raman spectra as a function of ω_S/Ω with varying incident CW field frequency ω_I/Ω obtained by standard Ehrenfest dynamics (red) and Ehrenfest+R dynamics (blue). For visualization purpose, the spectrum is plotted in log-scale. The incoming field amplitude is $A_I/\sqrt{\hbar\Omega} = 10^{-2}$. For all CW frequencies, Rayleigh scattering peaks are observed at $\omega_S = \omega_I$ (central peak). The Stokes resonance Raman scattering occurs at $\omega_S/\Omega = 0.75$ when $\omega_I/\Omega = 1$; the anti-Stokes resonance Raman scattering occurs at $\omega_S/\Omega = 1$ when $\omega_S/\Omega = 0.75$. Note that Ehrenfest+R dynamics can recover both resonance Raman scattering peaks while standard Ehrenfest dynamics does not predict any Raman scattering.

for various incident frequencies ω_I . When the incident field is far from resonance, we find that the scattered EM field is dominated by Rayleigh scattering ($\omega_S = \omega_I$), as we expected from the KHD formula. Qualitatively, both standard Ehrenfest dynamics and Ehrenfest+R dynamics predict Rayleigh scattering peaks at correct frequencies and show a linear shift with respect to the incident frequencies.

When the incident photon is at resonance i.e. the incident frequency line up with electronic excitation, Ehrenfest+R dynamics can capture Raman scattering peaks qualitatively. At steady state, we observe two resonance scattering outcomes: Stokes Raman scattering peak at $(\omega_I, \omega_S) = (\Omega, \frac{3}{4}\Omega)$ and anti-Stokes Raman scattering peak at $(\omega_I, \omega_S) = (\frac{3}{4}\Omega, \Omega)$. The Stokes Raman scattering occurs when the incident frequency is $\omega_I = \varepsilon_2 - \varepsilon_0$ and the anti-Stokes Raman scattering occurs when $\omega_I = \varepsilon_2 - \varepsilon_1$. Note that, since the initial state

is on the ground state exclusively, the anti-Stokes Raman scattering will not be observed initially. As the system approaches a steady state, an anti-Stokes Raman peak emerges when the population on state $|1\rangle$ becomes non-zero.

In contrast to Ehrenfest+R dynamics, we also show the spectra obtained by standard Ehrenfest calculations. Since there is only one frequency involved in the classical EM field, it is not surprising that Ehrenfest dynamics can capture Rayleigh scattering peaks only, but not Raman scattering peaks. To see this, we recall that Ehrenfest decay rate for spontaneous emission depends linearly on the lower state population.²⁸ For the initial state $c_0 = 1$ and $c_1 = c_2 = 0$, the system will excite to state $|2\rangle$ by the incident field, but it will not populate $|1\rangle$. Therefore, we always have $c_1 = 0$ within Ehrenfest dynamics and the spontaneous emission via electronic transition $2 \rightarrow 1$ will never happen.

2. *Resonance Raman scattering*

We now turn our attention to a near-resonance regime, i.e. $\omega_I \approx \Omega$ for a discussion of Stokes Raman scattering in more detail. To compare against the KHD formula, we extract the scattering cross section from Ehrenfest+R dynamics by

$$\sigma_{10}^{1D}(\omega_S, \omega_I) = \frac{|\mathbf{E}_S(\omega_S)|^2 / \omega_S}{A_I^2 / \omega_I}, \quad (29)$$

according to the definition of 1D scattering cross section and Einstein relation (see Eq. A3). Here we denote the intensity of Raman scattering signal at frequency ω_S as $|\mathbf{E}_S(\omega_S)|^2$ where $\mathbf{E}_S(\omega_S)$ is the amplitude of the scattered field satisfying $\mathbf{E}_S(x, t) = \sum_{\omega_S} \mathbf{E}_S(\omega_S) \cos(k_S x - \omega_S t)$.

In comparison with the KHD formula (Eq. (7)), we find that Ehrenfest+R approach can quantitatively recover the enhancement of the Raman scattering cross section near resonance regime (see Fig. 2(a)), while the standard Ehrenfest dynamics does not predict any enhancement. Furthermore, the linewidth obtained by Ehrenfest+R approach also agree with the average lifetime for the KHD formula (Eq. (9)). In Fig. 2(b), the difference between standard Ehrenfest and Ehrenfest+R results are manifested in logarithmic scale. The +R correction is qualitatively significant for semiclassical simulation to recover resonance Raman scattering.

Now we focus on the intensity of resonance Raman scattering (i.e. $\omega_I = \Omega$) in response to various incident field amplitudes. From the KHD formula, the resonance Raman signal

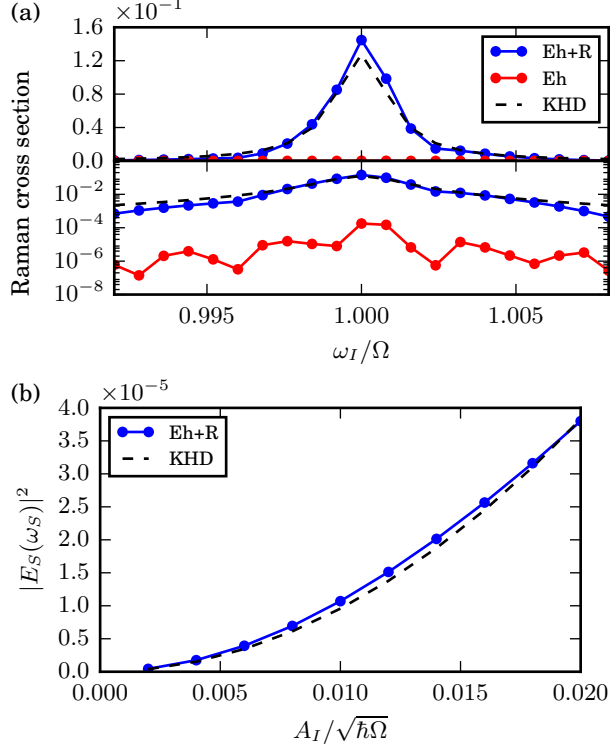


Figure 2. (a) Raman scattering cross section as a function of incident frequency near resonance ($\omega_I/\Omega \approx 1$) obtained by standard Ehrenfest dynamics (red) and Ehrenfest+R dynamics (blue). The incoming field amplitude is $A_I/\sqrt{\hbar\Omega} = 10^{-2}$. The KHD formula is plotted in dashed line. Note that Ehrenfest+R dynamics shows a qualitative correction to standard Ehrenfest dynamics. (b) Resonance Raman scattering signal intensity as a function of incident CW amplitude A_I . The incident and scattered frequencies are $\omega_S = 0.75\Omega$, $\omega_I = \Omega$. The black dashed line is the intensity given by the KHD formula (Eq. (30)).

in the weak field regime is

$$\left| \mathbf{E}_S \left(\omega_S = \frac{3}{4}\Omega \right) \right|^2 = A_I^2 \frac{\omega_S^2}{2\hbar^2 c^2} \frac{\mu^4}{\gamma^2}. \quad (30)$$

In Fig 2(c), we show that, Raman scattering intensity obtained by Ehrenfest+R dynamics is quadratic with respect to A_I , and quantitatively agree with the KHD formula.

IV. CONCLUSIONS

In this work, we have generalized Ehrenfest+R approach to treat a multi-level (more than two) system for a semiclassical simulation of Raman scattering. In the context of a three-

level system model, the proposed prescription of +R corrections can overcome qualitative deficiencies of Ehrenfest dynamics and recover both (Stokes and anti-Stokes) resonance and off-resonance Raman scattering. In addition, a comparison with quantum mechanical KHD formalism shows that Ehrenfest+R dynamics quantitatively agree with resonance Raman scattering cross sections.

Given the promising results in this work, there are many further questions need to be addressed. First, the proposed prescription is based on pairwise +R transitions without relative phases for rescaling fields. Does the relative phases introduce more quantum fluctuation? Second, the data in this work was generated for a three level system in one dimension only, while also assuming that the polarization density has a simple Gaussian profile. Does this prescription work for a system with nuclear motion in three dimensions with arbitrary polarization density? Finally, the current setup includes one quantum subsystem only. How can we to treat the collective behavior of a set of molecular subsystems with strong electronic coupling? These questions will be investigated in future work.

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Appendix A: Scattering Cross section in a 1D space

Here we derive the scattering cross section for a 1D system within the KHD formalism.

Following second order perturbation theory,¹³ we can write down the time derivative of second order correction to the wavefunction:

$$\frac{d}{dt} \|\psi^{(2)}(t)\|^2 = \frac{2\pi E_S^2 E_I^2}{16\hbar^4} \sum_f |\alpha_{fi}(\omega_I)|^2 \delta(\omega - \omega_f) \quad (\text{A1})$$

where $|\psi^{(2)}(t)\rangle = \int dt_1 \int dt_2 \mathbf{V}(t_2) \mathbf{V}g(t_1) |\psi(0)\rangle$ and E_I , E_S are the amplitudes for incident and scattered electric fields. The change of the second order wavefunction can be extrapolated to be the number of photon scattered per unit time.

Now we impose the density of state for photons in 1D system $\rho(\omega_f) = 2\frac{L}{2\pi c}$ to write

$$\frac{d}{dt} \|\psi^{(2)}(t)\|^2 = \frac{L}{8\hbar^4 c} E_S^2 E_I^2 |\alpha_{fi}(\omega_I)|^2. \quad (\text{A2})$$

By Einstein relation of photon, the total EM field energy is related to the photon frequency ω and photon number N by

$$U = L \frac{E^2}{2} = N\hbar\omega. \quad (\text{A3})$$

For spontaneous emission, we have $N_S = 1$ such that

$$E_S^2 = \frac{2\hbar\omega_S}{L}, \quad (\text{A4})$$

$$E_I^2 = N_I \frac{2\hbar\omega_I}{L}. \quad (\text{A5})$$

Thus, in terms of photon frequencies and numbers, we can write

$$\frac{d}{dt} \|\psi^{(2)}(t)\|^2 = \frac{1}{2\hbar^2 c} \frac{N_I \omega_I \omega_S}{L} |\alpha_{fi}(\omega_I)|^2 \quad (\text{A6})$$

and the number of incident photon per unit time is $\frac{N_I c}{L}$.

In the end, the 1D light scattering photon scattering can be written as

$$\sigma_{fi}^{1D}(\omega_S, \omega_I) = \frac{\omega_I \omega_S}{2\hbar^2 c^2} |\alpha_{fi}(\omega_I)|^2. \quad (\text{A7})$$

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