Effective Raman Hamiltonian revisited

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In this paper, the effective Raman Hamiltonian is revisited. A common way to obtain the effective Raman Hamiltonian is by using the time-dependent perturbation method (TDPT) along with Fermi's golden rule to keep the total energy and probability constant. However, for a non-resonant Raman process the obtained effective Hamiltonian is not convenient because it is not Hermitian. Hence, we present the Magnus expansion method for obtaining the effective Raman Hamiltonian, which has the advantages of being Hermitian and featuring effects absent in the TDPT effective Hamiltonian. To our knowledge, this is the first time that the Magnus expansion is utilized as an alternative method. We compare the our obtained effective Hamiltonian to that obtained from canonical transformation method. We determine the extra piece in second-order time-dependent perturbation theory which causes loss or gain of total probability.

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I. INTRODUCTION

The effective Hamiltonian is one of the most widely used methods in physics and computational chemistry. In the effective Hamiltonian formalism, instead of treating the whole Hamiltonian completely, a more compact effective Hamiltonian in a lower-dimensional subspace is studied. There are several ways to obtain an effective Hamiltonian for the Raman scattering process, and as we show, each provides a somewhat different result. For instance, some methods give a non-Hermitian effective Hamiltonian. The most common method for obtaining an effective Hamiltonian is the time-dependent perturbation method [1, 2], where a two-photon resonant effective Raman Hamiltonian can be obtained under the assumption of adiabatic elimination. The adiabatic elimination is only valid when one photon detunings are sufficiently larger than the corresponding coupling constant, which implies almost no population in any intermediate level during the Raman scattering. This allows one to focus on the two lowest-lying states.

More detailed semiclassical derivations can be found in the papers by Chelkowski *et al.* [3] and Kien *et al.* [4]. Moreover, a graphical technique is also developed and applied for the Stark-induced adiabatic Raman passage [5, 6]. These two methods give the same effective Raman Hamiltonian and their only drawback is that the obtained effective Raman Hamiltonian is non-Hermitian if the system is out of two-photon resonance. Besides, several authors have already considered the adiabatic elimination in the Heisenberg picture [7–9].

On the other hand, an elegant and clever way of attaining an effective Raman Hamiltonian is the canonical transformation method developed by Alexanian and Bose [10]. They claim that one can obtain an effective Raman Hamiltonian using a properly-chosen canonical transformation in the operator form, and using successive perturbations up to second order, they obtain a similar effective Raman Hamiltonian for large one-photon detuning. Later, Wu showed that it is possible to find exact transformed effective Raman Hamiltonian valid for any magnitude of the one-photon detunings via canonical transformation method without any perturbations [11].

We show three distinct methods to obtain the effective Raman Hamiltonian. These methods are the time-dependent perturbation method, the canonical transformation method, and the Magnus expansion method which we propose as an alternative method. In the last method, the solution of the Schrödinger equation in terms of a Magnus expansion is truncated up to second order and compared with the solution truncated up to first order. The obtained effective Raman Hamiltonian exactly matches the result of the canonical transformation method. Note that the validity of the obtained Hamiltonian is in the range of large one-photon detuning compared with the corresponding coupling constant.

The structure of this paper is as follows. In Sec. II, we introduce the model of the Raman system and consider three methods, namely, the time-dependent perturbation method, the Magnus expansion method, and the canonical transformation method. In Sec. III, we compare the resulting effective Raman Hamiltonians and present our conclusions.

Our main result, the effective Raman Hamiltonian obtained via Magnus expansion could be found in Eq. (36) (to be completed by Eq. (12) and (14)), and the extra piece in second-order time-dependent perturbation theory is written in Eq. (28).

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II. EFFECTIVE RAMAN HAMILTONIAN IN THREE DIFFERENT WAYS

In this section, we show how to obtain an effective Raman Hamiltonian by three different methods, using the time-dependent perturbation theory, the Magnus expansion method, and the canonical transformation method. In order to model the Raman system, we introduce a Λ-type scheme for the molecule interacting with pump and Stokes laser fields denoted by indexes p and s respectively. The Hamiltonian of the model in the Schrödinger picture is given by [12]

$$\hat{H} = \hat{H}_0 + \hat{V}_0, \tag{1}$$

where

$$\begin{aligned}\hat{H}_0 =& \hbar\omega_b|b\rangle\langle b| + \hbar\omega_c|c\rangle\langle c| \\ &+ \sum_{a_i}\hbar\omega_i|a_i\rangle\langle a_i| + \sum_{\ell=\mathrm{p,s}}\hbar\nu_\ell\hat{a}_\ell^\dagger\hat{a}_\ell\end{aligned} \tag{2}$$

and

$$\hat{V}_0 = \hbar\sum_j\sum_{j'}\sum_{\ell=\mathrm{p,s}} g_{j,j'}|j\rangle\langle j'|(\hat{a}_\ell^\dagger + \hat{a}_\ell). \tag{3}$$

Here, j and j' stand for the molecular vibrational levels b, c, and the set of vibrational levels a_i (see Fig. 1). The annihilation and creation operators for the pump and Stokes fields are denoted by $\hat{a}_\ell$ and $\hat{a}_\ell^\dagger$, $\ell = \mathrm{p,s}$ respectively. Because of the Λ configuration, coupling constants $g_{j',j}$ which govern the amplitude of transition from level j to level j' due to the ℓth electric field is non-zero only if it couples level b or c to the levels a_i. The molecular and field frequencies are ω_b, ω_c, ω_i, and ν_ℓ, respectively. In the interaction picture, the Hamiltonian has the form

$$\hat{V}(t) = \\ \hbar\sum_j\sum_{j'}\sum_{\ell=\mathrm{p,s}} g_{j,j',l}|j\rangle\langle j'|\mathrm{e}^{i(\omega_j-\omega_j')t}\left(\hat{a}_\ell^\dagger\mathrm{e}^{i\nu_\ell t} + \hat{a}_\ell\mathrm{e}^{-\nu_\ell t}\right). \tag{4}$$

Here, our goal is to eliminate the intermediate levels a_i and get the effective Hamiltonian in the two dimensional subspace with two orthonormal bases b and c.

Since the Raman process is a two-photon process, the square of the Hamiltonian $\hat{V}\hat{V}$ plays a key role yielding 256 terms (because $\hat{V}$ has 16 terms overall). Fortunately, we can eliminate most of the 256 terms. The terms related to the transition paths illustrated in the Fig. 1 are considered in the current paper.

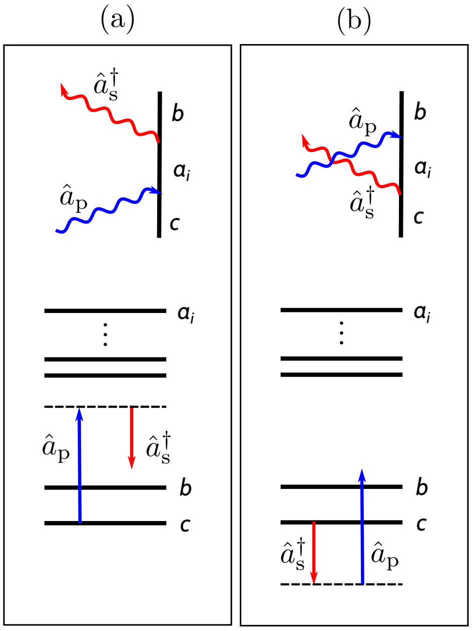

Figure 1: The transition paths involved in the Raman process and their corresponding Feynman diagrams. The doubly-co-rotating transition path, where absorption is followed by emission is drawn in (a); and the doubly-counter-rotating transition path, where emission *precedes* absorption is drawn in (b). Levels c and b are the molecular vibrational ground and excited energy levels, respectively, and a_i stands for the (multiple) vibrational levels belonging to the excited electronic state. The annihilation (creation) operators of the pump and Stokes pulses are $\hat{a}_\mathrm{p}$ ($\hat{a}_\mathrm{p}^\dagger$) and $\hat{a}_\mathrm{s}$ ($\hat{a}_\mathrm{s}^\dagger$) respectively. Time goes from bottom to top in the Feynman diagrams.

A. Time-dependent perturbation method

In time-dependent perturbation theory, the time evolution operator of the system $\hat{U}(t)$ at time t can be written as [13]

$$\begin{aligned}\hat{U}(t) =& \hat{1} + \frac{1}{i\hbar}\int_0^t \hat{V}(t')dt' \\ &+ \frac{1}{(i\hbar)^2}\int_0^t dt'\int_0^{t'} dt''\hat{V}(t')\hat{V}(t'') + \cdots .\end{aligned} \tag{5}$$

The matrix elements of this evolution operator in the two dimensional subspace with orthonormal bases $|b\rangle$, $|c\rangle$ are

$$\begin{aligned}&\langle i|\hat{U}(t)|i'\rangle \cong \langle i|i'\rangle \\ &+ \frac{1}{i\hbar}\int_0^t dt'\left(\frac{1}{i\hbar}\int_0^{t'} dt''\langle i|\hat{V}(t')\hat{V}(t'')|i'\rangle\right),\end{aligned} \tag{6}$$

where $|i\rangle$ and $|i'\rangle$ are any of $\{|b\rangle, |c\rangle\}$. By comparing Eq. (6) with the effective time evolution operator, $\hat{U}_\mathrm{eff}(t)$, truncated up to the first order

$$\langle i|\hat{U}_\mathrm{eff}(t)|i'\rangle \cong \langle i|i'\rangle + \frac{1}{i\hbar}\int_0^t dt'\langle i|\hat{H}_\mathrm{eff}(t')|i'\rangle, \tag{7}$$

where $\hat{H}_\mathrm{eff}$ is an effective two-level Hamiltonian in the interaction picture. We can obtain the matrix elements of the effective Raman Hamiltonian

$$\langle i|\hat{H}_{\text{eff}}(t')|i'\rangle = \frac{1}{i\hbar}\int_0^{t'} dt''\langle i|\hat{V}(t')\hat{V}(t'')|i'\rangle. \tag{8}$$

This equation gives the connection between the full and effective Hamiltonians. Note that since we use the second-order perturbation method, Eq. (8) is obtained under the assumption that the one-photon detunings must be much larger than the coupling constants $g_{i,c}$ and $g_{i,b}$, i.e. the perturbing field strength should be weak enough for safe use of the second-order perturbation expansion. This assumption is called adiabatic elimination, and it implies a negligibly small population in the excited intermediate levels $\{a_i\}$ at any time during system evolution.

We emphasize that Eq. (8) requires only a single integral and not two. Indeed, two integrals are needed in order to calculate the probability amplitude of the process, since we use the second order perturbation theory. However, the equation (8) provides us with a shortcut since we are not interested in the probability amplitude, but rather in the effective Hamiltonian H_{eff}. The probability amplitude can then be obtained from H_{eff} by first-order time-dependent perturbation theory.

An interesting feature of the Hamiltonian in Eq. (8) is that it is non-Hermitian [1], in general. Indeed, this can be seen from the following consideration

$$\begin{aligned}\left(\langle i|\hat{H}_{\text{eff}}(t')|i'\rangle\right)^{\dagger} &= -\frac{1}{i\hbar}\int_0^{t'} dt''\langle i'|\hat{V}(t'')\hat{V}(t')|i\rangle \\ &\neq \langle i'|\hat{H}_{\text{eff}}(t')|i\rangle. \end{aligned}\tag{9}$$

This non-Hermitian property of the effective Hamiltonian is closely related to loss of probability due to the elimination of the probability in the excited intermediate levels $\{a_i\}$ [1].

The explicit expression for the effective Raman Hamiltonian is obtained from Eq. (8). The off-diagonal element is

$$\langle b|\hat{H}_{\text{eff}}(t')|c\rangle = \frac{1}{i\hbar}\int_0^{t'} dt''\sum_{a_i}\langle b|\hat{V}(t')|a_i\rangle\langle a_i|\hat{V}(t'')|c\rangle. \tag{10}$$

Note that only times t'' which are earlier than t' are involved in the integration. Consequently, we can make two observations about the matrix element $\langle b|\hat{H}_{\text{eff}}(t')|c\rangle$ in Eq. (10). First, only the frequencies of the levels c and a_i appear in the denominator because the integration time t'' appears only in the expression for $\langle i|\hat{V}(t'')|c\rangle$ in Eq. (10). Secondly, for the transition in Fig. 1(a), only the $\hat{a}_{\text{p}}$ operator contribute to the integration because it comes from the Hamiltonian $\hat{V}(t'')$ at time t''. Similarly, only $\hat{a}_{\text{s}}^{\dagger}$ contribute to the transition term in Fig. 1(b). Thus, Eq. (10) becomes

$$\begin{aligned}\langle b|\hat{H}_{\text{eff}}(t')|c\rangle =& -\hbar e^{-i(\nu_{\text{p}}-\nu_{\text{s}})t'}e^{i(\omega_b-\omega_c)t'}\cdot\sum_{a_i} g_{b,i}g_{i,c} \\ &\times\left(\frac{\hat{a}_{\text{s}}^{\dagger}\hat{a}_{\text{p}}}{(\omega_i-\omega_c)-\nu_{\text{p}}}+\frac{\hat{a}_{\text{p}}\hat{a}_{\text{s}}^{\dagger}}{(\omega_i-\omega_c)+\nu_{\text{s}}}\right).\end{aligned}\tag{11}$$

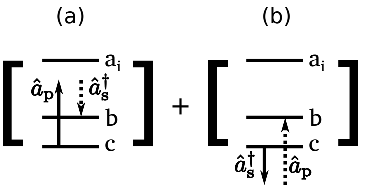

Figure 2: A graphical representation of the effective coupling constant, $\hat{G}_{b,c}$, obtained via second order perturbation theory, Eq. (13) The two terms enclosed within square brackets in Eq. (13) correspond to the two transitions in the brackets in the figure. We use the notation (a) and (b) to refer to the same transition paths depicted in Fig. 1. In transition (a), only annihilation of a pump photon $\hat{a}_{\text{p}}$ is involved in the integration over t'', despite Raman being a two-photon process, i.e., $\hat{a}_{\text{s}}^{\dagger}\hat{a}_{\text{p}}$. On the other hand, for (b), the integration involves an $\hat{a}_{\text{s}}^{\dagger}$ term, but not an $\hat{a}_{\text{p}}$.

The last expression corresponds to Fig. 2. The first term represents the transition in Fig. 2(a), whereas second term represents the transition Fig. 2(b). As a result, the effective Raman Hamiltonian is found to be

$$\begin{aligned}\hat{H}_{\text{eff}} =& \hbar(\delta_{c,\text{p}}\hat{a}_{\text{p}}^{\dagger}\hat{a}_{\text{p}}+\delta_{c,\text{s}}\hat{a}_{\text{s}}^{\dagger}\hat{a}_{\text{s}})|c\rangle\langle c| \\ &+\hbar(\delta_{b,\text{p}}\hat{a}_{\text{p}}^{\dagger}\hat{a}_{\text{p}}+\delta_{b,\text{s}}\hat{a}_{\text{s}}^{\dagger}\hat{a}_{\text{s}})|b\rangle\langle b| \\ &+\hbar G_{b,c}e^{i[(\omega_b-\omega_c)-(\nu_p-\nu_s)]t'}\hat{a}_{\text{s}}^{\dagger}\hat{a}_{\text{p}}|b\rangle\langle c| \\ &+\hbar G_{c,b}e^{-i[(\omega_b-\omega_c)-(\nu_p-\nu_s)]t'}\hat{a}_{\text{p}}^{\dagger}\hat{a}_{\text{s}}|c\rangle\langle b|,\end{aligned}\tag{12}$$

where the effective coupling constants are

$$\begin{aligned}G_{b,c} =& -\sum_{a_i} \\ &\times\left(\left[\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)-\nu_{\text{p}}}\right]+\left[\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)+\nu_{\text{s}}}\right]\right),\end{aligned}\tag{13}$$

and $G_{c,b}$ is obtained by replacing the labels $c \leftrightarrow b$ and p $\leftrightarrow$ s. The $\delta_{b,\text{p}}$ term in the effective Hamiltonian is

$$\delta_{b,\text{p}} = -\sum_{a_i}\left[\frac{|g_{b,i}|^2}{(\omega_i-\omega_b)-\nu_{\text{p}}}+\frac{|g_{b,i}|^2}{(\omega_i-\omega_b)+\nu_{\text{p}}}\right]. \tag{14}$$

The terms $\delta_{b,\text{s}}$, $\delta_{c,\text{p}}$, and $\delta_{c,\text{s}}$ can be found by replacing the labels $c \leftrightarrow b$ and p $\leftrightarrow$ s in Eq. (14). These terms are interpreted as dynamic Stark shifts or Rayleigh scattering terms [14].

In the effective Hamiltonian, we neglected the terms which will give a probability amplitude for the Raman process which goes as the inverse of the single photon detuning squared,

$$\frac{1}{(\omega_i-\omega_c)-\nu_p}\frac{1}{(\omega_i-\omega_b)+\nu_s}. \tag{15}$$

The neglected term also goes as the probability of populating the excited molecular states. This term was neglected because we are assuming a regime where it is much smaller than the two-photon detuning term, $1/\Delta$, which we would also get

$$\Delta=(\omega_b-\omega_c)-(\nu_p-\nu_s), \tag{16}$$

for the probability amplitude of the Raman process.

As we mentioned above, the effective Hamiltonian in Eqs. (12)–(14), obtained by way of second-order TDPT, is not Hermitian in this case; it can be seen that $(G_{b,c})^*\neq G_{c,b}$. However, the Hamiltonian becomes Hermitian when the system is on two-photon resonance, i.e., if $\omega_b-\omega_c=\nu_\mathrm{p}-\nu_\mathrm{s}$. In the long time limit, the issue of probability conservation is resolved. This is because, in this limit, two-photon resonance is enforced, as we shown below.

In order to conserve the total probability, consider the transition probability $P_{C\to B}$ between the states $|C\rangle=|c,n_\mathrm{p},n_\mathrm{s}\rangle$ and $|B\rangle=|b,n_\mathrm{p}-1,n_\mathrm{s}+1\rangle$ of the molecule–field system

$$\begin{aligned}P_{C\to B}&=|\langle B|\hat U(t)|C\rangle|^2\\&\cong\left|\sum_{a_i}\left(\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)-\nu_\mathrm{p}}+\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)+\nu_\mathrm{s}}\right)\right.\\&\quad\left.\times\frac{\mathrm{e}^{i(\omega_b-\omega_c)t-i(\nu_\mathrm{p}-\nu_\mathrm{s})t}-1}{(\omega_b-\omega_c)-(\nu_\mathrm{p}-\nu_\mathrm{s})}\sqrt{n_\mathrm{p}(n_\mathrm{s}+1)}\right|^2,\end{aligned} \tag{17}$$

and we can rewrite it in the form

$$\begin{aligned}P_{C\to B}\cong&\left|\sum_{a_i}\left(\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)-\nu_\mathrm{p}}+\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)+\nu_\mathrm{s}}\right)\right.\\&\left.\times\frac{\sin(i\Delta t/2)}{\Delta/2}\right|^2 n_\mathrm{p}(n_\mathrm{s}+1),\end{aligned} \tag{18}$$

where $\Delta=(\omega_b-\omega_c)-(\nu_\mathrm{p}-\nu_\mathrm{s})$ is the two-photon detuning. If we notice that the function

$$\frac{t}{2\pi}\frac{\sin^2(\Delta t/2)}{(\Delta t/2)^2} \tag{19}$$

becomes a Dirac delta function $\delta(\Delta)$ in the limit of sufficiently large time, $t\to\infty$, then the transition rate $W(t)=P_{C\to B}(t)/t$ is given by

$$\begin{aligned}W(t)=2\pi&\left|\sum_{a_i}\left(\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)-\nu_\mathrm{p}}+\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)+\nu_\mathrm{s}}\right)\right|^2\\&\times\delta(\Delta)n_\mathrm{p}(n_\mathrm{s}+1).\end{aligned} \tag{20}$$

Comparing the transition rate Eq. (20) with that obtained from Fermi's golden rule,

$$W_\mathrm{eff}(t)=2\pi|\langle B|\hat H_\mathrm{eff}|C\rangle|^2\delta(\Delta), \tag{21}$$

we obtain the magnitude of the effective coupling constant $G_{b,c}$ as

$$|G_{b,c}|=\left|\sum_{a_i}\left(\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)-\nu_\mathrm{p}}+\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)+\nu_\mathrm{s}}\right)\right|. \tag{22}$$

Because of the Dirac delta function $\delta(\Delta)$ in the derivation, Expression (22) as well as (13) are valid only when the system is on two-photon resonance, i.e., it conserves energy as well as total probability.

B. Magnus expansion method

One of our main results is that the approximate time evolution operator, as obtained by way of the Magnus expansion, leads to a similar, yet Hermitian effective Raman Hamiltonian to Eq. (12). This Hermitian effective Hamiltonian is much more convenient especially when considering the dynamics of the Raman adiabatic passage where a non-resonant two-photon Raman process is concerned with taking dynamic Stark shift into account. Using the Magnus expansion, we are also able to find the extra part in second-order perturbation theory, which we present in Eq. (30)

The Magnus expansion, formulated by Wilhelm Magnus is an exponential type of solution for a set of first-order, homogeneous, linear differential equations [15–17]. The Magnus expression for time evolution operator is

$$\hat U(t)=\exp\left(\sum_{n=1}^{\infty}\frac{1}{(i\hbar)^n}\hat S_n\right) \tag{23}$$

where the first two Magnus terms $\hat S_1$ and $\hat S_2$ are given by

$$\begin{aligned}\hat S_1&=\int_0^t dt'\hat V(t'),\\\hat S_2&=\frac{1}{2}\int_0^t dt'\int_0^{t_1}dt''[\hat V(t'),\hat V(t'')].\end{aligned} \tag{24}$$

Here, we emphasize that the Magnus expansion solution possesses a crucial property that it conserves symmetries of the linear differential equation. In our case, the unitarity of the time evolution operator is guaranteed to any order of truncation of the Magnus expansion. Thus, the time evolution operator Eq. (23) always keeps the total probability to be 1 no matter to which order in n it is truncated.

Before utilizing the Magnus expansion, we discuss some issues of unitarity and the difference between the Magnus and time-dependent perturbation theory methods in this regard. This detour will also further introduce the details of the Magnus expansion on a deeper level. Using the power series representation of exponentials to express the time evolution operator in Eq. (23),

$$\hat{U}(t) \simeq \hat{1} + \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n}\hat{S}_n + \frac{1}{2}\left(\sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n}\hat{S}_n\right)^2 + \cdots . \tag{25}$$

If we truncate this series for the time evolution operator up to second-order in $1/\hbar$, we would have

$$\hat{U}(t) \simeq \hat{1} + \frac{1}{i\hbar}\hat{S}_1 + \frac{1}{(i\hbar)^2}\hat{S}_2 + \frac{1}{2}\frac{1}{(i\hbar)^2}\hat{S}_1^2, \tag{26}$$

which is no longer unitary. We can see that the time evolution operator in Eq. (26) is exactly the same as that which is obtained by second-order perturbation theory, since

$$\hat{S}_2 + \frac{1}{2}\hat{S}_1^2 = \int_0^t dt' \int_0^{t'} dt'' \hat{V}(t')\hat{V}(t''). \tag{27}$$

This implies that truncating Eq. (25) up to second order in $1/\hbar$ is identical to the second-order time-dependent perturbation method. This observation allows us to isolate the issue of non-unitarity in the time-dependent perturbation method. Since Eq. (26) includes[1] only the

$$\frac{1}{2}\left(\frac{\hat{S}_1}{i\hbar}\right)^2 \qquad \text{(extra term in } 2^{nd}\text{-order TDPT)} \tag{28}$$

from the third term of Eq. (25), rather than keeping the entire third term $\frac{1}{2}\left(\frac{\hat{S}_1}{i\hbar} + \frac{\hat{S}_2}{(i\hbar)^2}\right)^2$, the approximate time evolution operator in Eq. (26) cannot be expressed as a truncated power series representation of the exponential function of $\hat{S}_1 + \hat{S}_2$. By this, we mean that the unitary operator expression should be constructed in such a way that it be a truncated series representation of the exponential function of some argument $\hat{F}(\hat{S}_1 + \hat{S}_2 + \cdots + \hat{S}_N)$, where N is integer number. According to this statement, the time evolution operator must have the form

$$\hat{U}(t) \simeq \hat{1} + \hat{F} + \frac{\hat{F}^2}{2!} + \cdots . \tag{29}$$

To make the evolution unitary (conserving total probability), we should either neglect the extra term, Eq. (28), in $\hat{U}(t)$ as obtained via time-dependent perturbation method Eq. (26) which is

$$\frac{1}{2}\frac{1}{(i\hbar)^2}\hat{S}_1^2 = \frac{1}{2}\frac{1}{(i\hbar)^2}\int_0^t dt' \int_0^{t'} dt'' \left(\hat{V}(t')\hat{V}(t'') + \hat{V}(t'')\hat{V}(t')\right), \tag{30}$$

or, add the missing

$$\frac{1}{2}\left\{2\frac{\hat{S}_1\hat{S}_2}{(i\hbar)^3} + \frac{(\hat{S}_2)^2}{(i\hbar)^4}\right\} \tag{31}$$

term. Therefore, for simplicity, we take only first two terms in Eq. (29) and write the time evolution operator as

$$\hat{U}(t) \simeq \hat{1} + \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n}\hat{S}_n \simeq \hat{1} + \frac{1}{i\hbar}\hat{S}_1 + \frac{1}{(i\hbar)^2}\hat{S}_2 \tag{32}$$

where we choose $\hat{F} = \frac{1}{i\hbar}\hat{S}_1 + \frac{1}{(i\hbar)^2}\hat{S}_2$. This time evolution operator, as we desired, is a truncated power series representation of the exponential of $\hat{F}$. Moreover, the second-order time evolution operator obtained by the Magnus expansion is

$$\hat{U}(t) \simeq \hat{1} + \frac{1}{i\hbar}\hat{S}_1 + \frac{1}{(i\hbar)^2}\hat{S}_2 = \hat{1} + \frac{1}{i\hbar}\int_0^t dt'\hat{V}(t') + \frac{1}{2}\frac{1}{(i\hbar)^2}\int_0^t dt' \int_0^{t'} dt''[\hat{V}(t'), \hat{V}(t'')]. \tag{33}$$

The only difference between this time-evolution operator and that of Eq. (5) – obtained via time-dependent perturbation theory – is the commutator $[\hat{V}(t'), \hat{V}(t'')]$ and the factor of 1/2. Consequently, the derivation of the effective Hamiltonian follows the same procedure as in the previous subsection. The matrix elements of the effective Hamiltonian as

$$\langle i|\hat{H}_{\text{eff}}(t')|i'\rangle = \frac{1}{2}\frac{1}{i\hbar}\int_0^{t'} dt''\langle i|[\hat{V}(t'), \hat{V}(t'')]|i'\rangle, \tag{34}$$

which is the Magnus expansion analog of Eq. (8). We must remark here that the Hamiltonian in Eq. (34) is obtained under the adiabatic elimination condition $g_{i,c} \ll (\omega_i - \omega_c) - \nu_{\text{p}}$ and $g_{i,b} \ll (\omega_i - \omega_b) - \nu_{\text{s}}$, just as in the perturbation method. Moreover, the Hamiltonian we obtain is Hermitian. This can be seen from

$$\left(\langle i|\hat{H}_{\text{eff}}(t')|i'\rangle\right)^{\dagger} = -\frac{1}{2}\frac{1}{i\hbar}\int_0^{t'} dt''\langle i'|[\hat{V}(t''), \hat{V}(t')]|i\rangle = \langle i'|\hat{H}_{\text{eff}}(t')|i\rangle. \tag{35}$$

In the following, we derive an explicit form of the effective Raman Hamiltonian. Plugging the explicit form of the interaction Hamiltonian, Eq. (4), into

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[1] Alternatively, we can think of second-order TDPT as lacking the $\frac{1}{2}\left\{2\frac{\hat{S}_1\hat{S}_2}{(i\hbar)^3} + \frac{(\hat{S}_2)^2}{(i\hbar)^4}\right\}$-term.

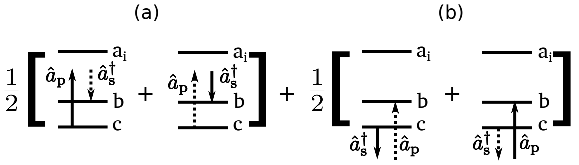

Figure 3: Graphical representation of the coupling constant $\hat{G}_{b,c}$ obtained by the Magnus expansion method, Eq. (36). The first term represents the transition from level c to level a_i followed by one-photon absorption at frequency ν_p. This has a factor of $1/(\omega_i - \omega_c - \nu_\mathrm{p})$. Next, term $1/(\omega_b - \omega_i + \nu_\mathrm{s})$ can be read as transition from level a_i to level b, followed by emission at the frequency ν_s. These first two terms are depicted in the plot (a) and also these correspond to transition (a) in Fig. 1. The explanation of the last two terms follows by the same procedure we used for the first two terms.
The utility of this diagrams is in that, used correctly, they give the answer without calculation. One graphically 'enumerates' all processes, which correspond to terms in the effective coupling constant $G_{b,c}$. Upward and downward arrows correspond to absorption and emission, respectively. The denominator of a process corresponds to the energy difference between the actual atomic level to which the atom is transitioning and the 'virtual' level (energy) at which the arrows terminate.

Eq. (34), we obtain the explicit form of the effective coupling constants $G_{b,c}$ and $G_{c,b}$ as

$$G_{b,c} = -\frac{1}{2}\sum_{a_i}\left(\left[\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)-\nu_\mathrm{p}} + \frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_b)-\nu_\mathrm{s}}\right] + \left[\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)+\nu_\mathrm{s}} + \frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_b)+\nu_\mathrm{p}}\right]\right), \tag{36}$$

and

$$G_{c,b} = (G_{b,c})^*, \tag{37}$$

where

$$\begin{aligned}\hat{H}_\mathrm{eff} &= \hbar(\delta_{c,\mathrm{p}}\hat{a}_\mathrm{p}^\dagger\hat{a}_\mathrm{p} + \delta_{c,\mathrm{s}}\hat{a}_\mathrm{s}^\dagger\hat{a}_\mathrm{s})|c\rangle\langle c| \\ &+ \hbar(\delta_{b,\mathrm{p}}\hat{a}_\mathrm{p}^\dagger\hat{a}_\mathrm{p} + \delta_{b,\mathrm{s}}\hat{a}_\mathrm{s}^\dagger\hat{a}_\mathrm{s})|b\rangle\langle b| \\ &+ \hbar G_{b,c}e^{i[(\omega_b-\omega_c)-(\nu_p-\nu_s)]t'}\hat{a}_\mathrm{s}^\dagger\hat{a}_\mathrm{p}|b\rangle\langle c| \\ &+ \hbar G_{c,b}e^{-i[(\omega_b-\omega_c)-(\nu_p-\nu_s)]t'}\hat{a}_\mathrm{p}^\dagger\hat{a}_\mathrm{s}|c\rangle\langle b|,\end{aligned} \tag{38}$$

and the dynamic Stark shifts are the same as those in Eq. (14)

$$\delta_{b,\mathrm{p}} = -\sum_{a_i}\left[\frac{|g_{b,i}|^2}{(\omega_i-\omega_b)-\nu_\mathrm{p}} + \frac{|g_{b,i}|^2}{(\omega_i-\omega_b)+\nu_\mathrm{p}}\right]. \tag{39}$$

The terms in the first square brackets in Eq. (36) are associated with the transition path in Fig. 1a, while the second term with the transition path in Fig. 1b. Again, each term in Eq. (36) corresponds to a graphical representation, illustrated in Fig. 3.

Here too, as in the TDPT case (and along the same reasoning), we neglect the terms which lead to a probability amplitude of the Raman process that goes as the inverse of the single-photon detuning, squared.

We can obtain the probability amplitude of the Raman process by using the first-order Magnus expansion with $\hat{F} = \hat{S}_1/i\hbar$, where now $\hat{S}_1$ makes use of the effective Hamiltonian rather than $\hat{V}$ in Eq. (24). We then get the critical overall two-photon resonance term $[(\omega_b - \omega_c) - (\nu_p - \nu_s)]^{-1}$ for the probability amplitude at large times. The same two-photon resonance term is obtained from the effective Hamiltonian in the second-order time-dependent perturbation theory case. There, the effective Hamiltonian is employed in a first-order time-dependent perturbation theory calculation of the transition amplitude, where there too, the effective Hamiltonian is utilized in place of $\hat{V}$. Interestingly, first-order time-dependent perturbation theory is identical to the first-order Magnus expansion with $\hat{F} = \hat{S}_1/i\hbar$.

There is a crucial point that must be emphasized here. There is a striking difference between the effective Hamiltonians obtained via the Magnus method and the time-dependent perturbation theory method. As long as two fields, namely, pump and Stokes, are involved in the Raman process, one-photon resonance of either the pump or Stokes fields should be included in the effective coupling constants. Furthermore, transition path 1(a) has two resonance conditions – one for the pump and another for the Stokes field. But in Eq. (13), obtained via time-dependent perturbation theory, the term which corresponds the transition path 1(a) has only the pump field resonance condition $\omega_i - \omega_c = \nu_\mathrm{p}$. This means that Eq. (13) cannot predict any effect due to one photon Stokes field resonance $\omega_i - \omega_b = \nu_\mathrm{s}$. In stark contrast to this, Eq. (36) which we obtained via the Magnus method, captures both single-photon resonance conditions, $\omega_i - \omega_c = \nu_\mathrm{p}$ and $\omega_i - \omega_b = \nu_\mathrm{s}$ (corresponding to pump and Stokes, respectively), in transition path 1(a) We will see that the canonical transform method also predicts an effect due to the a single Stokes photon in path 1(a). It is also important that on two-photon resonance, that is, when $(\omega_b - \omega_c) = (\nu_p - \nu_s)$, second order perturbation theory gives the same effective Hamiltonian as the Magnus expansion method. This happens automatically at the long-time limit, because at that limit, two-photon resonance is enforced.

Comparing Eqs. (13) and (36) for the effective coupling constant $G_{b,c}$, we notice that the number of terms is doubled in the case of the Magnus expansion, but also scaled by a factor of 1/2. Consequently, the total magnitude of the effective coupling constants are approximately equal for the different methods.

C. Canonical transformation method

Next we show how an effective Raman Hamiltonian can be obtained by the canonical transformation method. Defining the operator[2] $\hat{S}$ we transform $\hat{H}$ into the Hamiltonian $\hat{H}_{\text{eff}}$ as follows

$$\begin{aligned}\hat{H}_{\text{eff}} &= e^{\hat{S}}\hat{H}e^{-\hat{S}} \\ &= \hat{H}_0 + \hat{V}_0 + [\hat{S}, \hat{H}_0] + [\hat{S}, \hat{V}_0] + \frac{1}{2}[\hat{S}, [\hat{S}, \hat{H}_0]] + \cdots . \end{aligned} \tag{40}$$

We choose the operator $\hat{S}$ so that the second and third terms in Eq. (40) cancel each other, i.e.

$$[\hat{S}, \hat{H}_0] = -\hat{V}_0. \tag{41}$$

Since $\hat{H}_0$ and $\hat{V}_0$ are of order zero and one in coupling constant, respectively, we find that $\hat{S}$, as defined in[3] Eq. (41), is also first-order in the coupling constant. Thus, the effective Hamiltonian truncated up to second order in coupling constant is

$$\begin{aligned}\hat{H}_{\text{eff}} &\simeq \hat{H}_0 + [\hat{S}, \hat{V}_0] + \frac{1}{2}[\hat{S}, [\hat{S}, \hat{H}_0]] \\ &= \hat{H}_0 + \frac{1}{2}[\hat{S}, \hat{V}_0]. \end{aligned} \tag{42}$$

Remarkably, the effective Hamiltonian in Eq. (42) is Hermitian, provided that the operator $\hat{S}$ is anti-Hermitian, $\hat{S}^\dagger = -\hat{S}$.

	(a)	(b)
	$\hat{a}_{\text{s}}^\dagger \hat{a}_{\text{p}} \lvert b\rangle\langle c\rvert$	$\hat{a}_{\text{p}} \hat{a}_{\text{s}}^\dagger \lvert b\rangle\langle c\rvert$
$\lvert C\rangle$	$\lvert c, n_{\text{p}}, n_{\text{s}}\rangle$	$\lvert c, n_{\text{p}}, n_2\rangle$
$\lvert I\rangle$	$\lvert a_i, n_{\text{p}} - 1, n_{\text{s}}\rangle$	$\lvert a_i, n_{\text{p}}, n_{\text{s}} + 1\rangle$
$\lvert B\rangle$	$\lvert b, n_{\text{p}} - 1, n_{\text{s}} + 1\rangle$	$\lvert b, n_{\text{p}} - 1, n_{\text{s}} + 1\rangle$

Table I: The explicit form of the states B, C, and I for the two transition paths of the Raman process. We use these for calculating the amplitude $\langle B|H_{\text{eff}}|C\rangle$, see Eq. (45). Transition path (a), as shown diagrammatically in Fig. 1, involves two successive transitions, particularly, the transition from level c to level a_i coupled by pump photons, and the transition from level a_i to level b coupled by Stokes photons. For transition path (b), the two successive transitions are the transition from level c to level a_i coupled by Stokes photons, and the transition from level a_i to level b coupled by pump photons. See Fig. 1.

One can show that in the original $\hat{H}_0$ basis the matrix elements of the effective Hamiltonian are

$$\begin{aligned}&\langle B|\hat{H}_{\text{eff}}|C\rangle = \langle B|\hat{H}_0|C\rangle \\ &+ \frac{1}{2}\sum_I \left(\langle B|\hat{S}|I\rangle\langle I|\hat{V}_0|C\rangle - \langle B|\hat{V}_0|I\rangle\langle I|\hat{S}|C\rangle\right), \end{aligned} \tag{43}$$

where states $|B\rangle$, $|C\rangle$, and $|I\rangle$ are states of the whole system (molecule plus fields), as illustrated in Tab. I. Using Eq.(41), the matrix elements of $\hat{S}$ are

$$\langle B|\hat{S}|I\rangle = \frac{\langle B|\hat{V}_0|I\rangle}{(E_B - E_I)}, \quad \langle I|\hat{S}|C\rangle = -\frac{\langle I|\hat{V}_0|C\rangle}{(E_C - E_I)}, \tag{44}$$

where E_B, E_C, and E_I are the energy of states B, C, and I, respectively. Ultimately, plugging Eq. (44) into Eq. (43), we obtain the matrix elements of the effective Hamiltonian,

$$\begin{aligned}&\langle B|\hat{H}_{\text{eff}}|C\rangle = \langle B|\hat{H}_0|C\rangle \\ &+ \frac{1}{2}\sum_I \left(\frac{\langle B|\hat{V}_0|I\rangle\langle I|\hat{V}_0|C\rangle}{E_B - E_I} + \frac{\langle B|\hat{V}_0|I\rangle\langle I|\hat{V}_0|C\rangle}{E_C - E_I}\right). \end{aligned} \tag{45}$$

The effective Hamiltonian itself in the Schrödinger picture is

$$\begin{aligned}\hat{H}_{\text{eff}} = \hat{H}_0 &+ \hbar(\delta_{c,\text{p}}\hat{a}_{\text{p}}^\dagger\hat{a}_{\text{p}} + \delta_{c,\text{s}}\hat{a}_{\text{s}}^\dagger\hat{a}_{\text{s}})|c\rangle\langle c| \\ &+ \hbar(\delta_{b,\text{p}}\hat{a}_{\text{p}}^\dagger\hat{a}_{\text{p}} + \delta_{b,\text{s}}\hat{a}_{\text{s}}^\dagger\hat{a}_{\text{s}})|b\rangle\langle b| \\ &+ \hbar G_{b,c}\hat{a}_{\text{s}}^\dagger\hat{a}_{\text{p}}|b\rangle\langle c| \\ &+ \hbar G_{c,b}\hat{a}_{\text{p}}^\dagger\hat{a}_{\text{s}}|c\rangle\langle b|, \end{aligned} \tag{46}$$

where we ignore the matrix elements for excited states a_i in the free Hamiltonian $\hat{H}_0$, i.e.

$$\hat{H}_0 = \hbar\omega_b|b\rangle\langle b| + \hbar\omega_c|c\rangle\langle c| + \sum_{\ell=\text{p,s}} \hbar\nu_\ell \hat{a}_\ell^\dagger \hat{a}_\ell. \tag{47}$$

When we transform the Hamiltonian (46) from the Schrödinger picture into the interaction picture, we obtain exactly the same *form* of the effective Hamiltonian as in Eq. (12), except that $G_{b,c}$ and $G_{c,b}$ are different from the time-dependent perturbation theory case.

In this framework, along with the Hamiltonian, the state vectors must also be transformed $|\psi\rangle \longrightarrow e^{\hat{S}}|\psi\rangle$. That is, the operator $\hat{H}_{\text{eff}}$ is only a Hamiltonian in the sense that

$$\hat{H}_{\text{eff}} e^{\hat{S}}|\psi\rangle = i\hbar\frac{\partial}{\partial t}e^{\hat{S}}|\psi\rangle. \tag{48}$$

However, for large single-photon detunings, the state $|C\rangle$ transforms approximately to itself

$$|C\rangle \longrightarrow e^{\hat{S}}|C\rangle \simeq |C\rangle, \tag{49}$$

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[2] This operator is not to be confused with the Magnus expansion terms $\hat{S}_n$

[3] We also choose $\hat{S}$ to be zero on the diagonals.

and similarly for the state $|B\rangle$. Thus, in the case of large single-photon detunings, we see that all three methods considered in this and in previous subsections give similar effective Hamiltonians.

For the transition paths (a) and (b) in Tab. I, we are able to calculate the explicit form of the effective coupling constant for the Raman process.

$$G_{b,c} = -\frac{1}{2}\sum_{a_i}\left\{\left[\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)-\nu_{\mathrm{p}}} + \frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_b)-\nu_{\mathrm{s}}}\right] + \left[\frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_c)+\nu_{\mathrm{s}}} + \frac{g_{b,i}g_{i,c}}{(\omega_i-\omega_b)+\nu_{\mathrm{p}}}\right]\right\}, \quad (50)$$

and

$$G_{c,b} = (G_{b,c})^*. \quad (51)$$

Again, the dynamic Stark shifts are the same as in Eq. (14). It is worth mentioning that in the last expression, the effective coupling constant exactly matches that of Eq. (36), which we obtained using the Magnus expansion method.

III. CONCLUSIONS

In the previous section we calculated the effective Raman Hamiltonian using three distinct method. Two of them, namely, the Magnus expansion method, and the canonical transformation method yield the same effective Hamiltonian, whereas time-dependent perturbation method gives a different effective Hamiltonian. However, the difference is only in the effective coupling constant $\hat{G}_{b,c}$ and there is no difference in the dynamic Stark shifts.

We would like to make here several remarks. First, the Hermiticity of the effective Hamiltonian is a major concern because it is deeply connected to the conservation of total probability. For the time-dependent perturbation method, in general, we have shown that the effective Hamiltonian is not Hermitian. Fortunately, the effective Hamiltonian arising from the Magnus expansion and canonical transformation methods is Hermitian.

Second, the effective Hamiltonian obtained via the Magnus expansion method features the one-photon resonance terms that one might expect from physical considerations, whereas that obtained via second order perturbation theory can only describe pump single-photon resonance effects.

Third, the observation tells us that the number of terms is doubled in the case of the Magnus expansion and the canonical transformation methods, scaled by a factor of 1/2. Consequently, the total magnitude of the effective coupling constants are approximately equal for the three different methods.

Fourth, on two-photon resonance (assuming $\nu_p \neq \nu_s$), both the Magnus expansion and second order perturbation theory give the same effective Hamiltonian for the Raman process.

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