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Phase averaging for calculations involving two-color intense-field excitation

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A general and computationally efficient method for averaging both the time-dependent and the steady-state atomic or molecular state populations over the phases, δ_1 and δ_2, of two continuous-wave laser fields involved in an excitation process is developed based on the Floquet formalism. Explicit calculations are presented for the coherent one- and three-photon electronic excitation of a two-level model molecule in order to illustrate the importance of phase averaging in situations where the relative phase difference between the two fields is fixed. While the explicit results involve electronic excitation, they are presented in reduced form so that they can be scaled to other regions of the electromagnetic spectrum and to other field strengths. The results have important implications in situations where the relative phase difference between two intense continuous-wave laser fields is used to control the excitation process.

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I. INTRODUCTION

There is a great deal of interest in using laser fields consisting of two phase-related components to control or to modify excitation processes in both atoms and molecules [1–15]. When the use of phase-related fields to control excitation was first proposed for molecules [1], the laser fields considered were weak enough that the process could be examined theoretically using perturbation theory. However, extensions of phase control to intense laser fields have been presented in both atomic and molecular systems [5–13]. In these nonperturbative regimes, the field-matter interaction must be considered using more exact techniques.

In general, phase control arises by setting a constant relative phase difference (δ_d) between the two components of the total field. Often the two components of the field are defined by their carrier frequencies. The frequencies normally considered are the fundamental and one of its higher-order harmonics, usually second or third. In many calculations [6–12,14,15], the phase difference (δ_d) between the two fields is chosen by varying the phase of one laser field (δ_2) while *arbitrarily* setting the phase of the other field to zero. Under these restrictions on frequency and phase, the total field for a combination of two linearly polarized continuous-wave (cw) lasers can be expressed as

$$\varepsilon_{\text{total}}(t)=\hat{\mathbf{e}}_1\varepsilon_1^0\cos(\omega_1 t)+\hat{\mathbf{e}}_2\varepsilon_2^0\cos(n\omega_1 t+\delta_d) \qquad (1)$$

where $n=2$ or 3, ε_i^0 is the electric-field amplitude, $\hat{\mathbf{e}}_i$ is the polarization vector, and ω_1 is the fundamental circular frequency. In its most general form, the total electric field for two cw lasers should be written as

$$\varepsilon_{\text{total}}(t)=\hat{\mathbf{e}}_1\varepsilon_1^0\cos(\omega_1 t+\delta_1)+\hat{\mathbf{e}}_2\varepsilon_2^0\cos(\omega_2 t+\delta_2), \qquad (2)$$

where each component of the field has its own intrinsic absolute phase, δ_1 or δ_2. In this paper, the terms absolute phase and initial phase are used interchangeably. For cw lasers, it is readily apparent that initial phase and initial time are formally equivalent [16]. However, for pulsed laser fields, a clear distinction must be drawn between phase and time; see Ref. [17] for a complete discussion.

The effects of absolute laser phase for the interaction of an atom or molecule with a one-color (single-frequency) cw laser are well documented [16,18–22]. In one-color cw problems, the phase dependence is related to the atom or molecule electromagnetic field (EMF) coupling strength parameter, $b=(\mu_{21}\hat{e}_1\varepsilon_1^0)/E_{21}$. Here μ_{21} and $E_{21}=E_2-E_1$ are the transition dipole moment and the energy-level separation, respectively, for the two-level transition of interest, and ε_1^0 is the electric-field amplitude. For weak system-EMF couplings ($b\ll 1$), the phase dependence of the populations of the atomic or molecular states is negligible. On the other hand, if the field strength is increased so that $b\leqslant 1$ (e.g., $b\approx 0.2$), the populations of the atomic or molecular states become strongly phase dependent. For these situations, it is of utmost importance to take the phase effects into account when performing calculations of the physical observables associated with the interactions of cw lasers with atoms or molecules. In fact, for the interaction of an atom or molecule with a cw laser, generally, the physical observables correspond to the phase-averaged results [16,18–22]. The physical observables that are of interest are the time-dependent and long-time averaged (steady-state) populations of the system states. The time-dependent populations represent the dynamics of the system while the steady-state excited-state populations, as a function of the excitation frequency, represent the absorption spectrum (resonance profile) for the system.

While the one-color problem has been examined in detail, the role of absolute laser phase (initial phase) and, hence, phase averaging for the interaction of an atom or a molecule with two cw lasers has received very little attention [13]. Chen *et al.* [13] have examined the effects of the initial laser phase on the kinetic energy and angular distribution of electrons ejected following the intense field two-color ionization of an atomic system. They then perform the phase averaging necessary for determining the physically meaningful results

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*Present address: Department of Physics and Astronomy, University of Alabama, Box 870324, Tuscaloosa, AL 35487. Email address: abrown@bama.ua.edu by averaging over a random distribution of 10^5 initial phases. However, there have been no studies focusing on the conditions where the initial phase is important in two-color problems, and, more importantly, no techniques have been developed for efficiently determining the properly phase-averaged results. Therefore, the purpose of this paper is twofold: (1) to develop a method for the computationally efficient evaluation of phase-averaged time-dependent and steady-state system state populations for two-color problems and (2) to determine the conditions for which the steady-state and time-dependent atomic or molecular state populations depend upon the choice of the absolute phases, δ_1 and δ_2, used to obtain the particular relative phase difference (δ_d) between the two laser fields.

The paper is organized as follows. In Sec. II A, a transformation from the time variable ''t'' to the variable ''θ_b,'' which is useful for phase averaging, is developed for the two laser (two-color) problem where the lasers have a fixed relative phase difference between them. The Floquet formalism [16,18–26] for determining phase-dependent and phase-averaged results for the time-dependent and long-time averaged (steady-state) populations of the atomic or molecular states from the evolution operator over the first period of the Hamiltonian is briefly reviewed in Sec. II B as applied to the two-color problem. In Sec. III, phase-dependent and phase-averaged results are determined for the simultaneous one- and three-photon excitation of a two-level model molecule. These results are utilized to determine the conditions for which phase averaging is required. Finally, some brief conclusions regarding the importance of phase averaging for two-color phase-control problems are drawn in Sec. IV.

Atomic units are utilized throughout this paper. The units for energy E, the transition dipole moments μ_{jk}, the field frequencies ω_j, and the field strengths ε_j^0 are E_H, ea_0, $E_H\hbar^{-1}$, and $E_H(ea_0)^{-1}$, respectively. E_H is the Hartree of energy, e is the absolute value of the charge of an electron, a_0 is the Bohr radius, and $\hbar$ is the Planck constant. The following conversion factors will be useful in what follows: $ea_0\approx 2.5415D$, $E_H\hbar^{-1}\approx 4.556\times 10^{-6}$ cm^{-1}, and the field intensity corresponding to a cw electric field is $I \approx 3.509\times 10^{16}(\varepsilon^0)^2$ W/cm^2.

II. THEORY

Within the semiclassical dipole approximation, the time-dependent wave equation for an N-level system interacting with an electric field (laser or lasers) is given in matrix form by

$$i\frac{\partial \mathbf{a}(t)}{\partial t}=\mathbf{H}(t)\mathbf{a}(t)=[E-\mu\cdot\varepsilon_{\text{total}}(t)]\mathbf{a}(t). \tag{3}$$

Here $\mathbf{a}(t)$ is the column vector defined by $[a(t)]_j=a_j(t)$, the square energy and dipole moment matrices are defined by $(E)_{jk}=E_j\delta_{jk}$ and $(\mu)_{jk}=\langle\phi_j|\mu|\phi_k\rangle$, where μ is the dipole moment operator for the system, ϕ_j are the orthonormalized time-independent wave functions for the stationary states having energy E_j, and $\varepsilon_{\text{total}}(t)$ is the total time-dependent electric field. The ''system'' referred to can be either an atom or a molecule; throughout this paper, we shall refer to all systems as ''molecules'' although ''atom or molecule'' is implied.

A. Defining θ_b for two-color phase averaging

The general goal in an efficient cw calculation is to exploit the periodicity of the Hamiltonian. By determining the evolution operator over only the first period of the Hamiltonian, the time-dependent, or steady-state, populations of the molecular states for any laser phase (δ_1) for one-color calculations, or any laser phases (δ_1,δ_2) for two-color calculations, and the phase-averaged behavior can be determined. For problems involving the interaction of a molecule with a single cw electric field, it has been shown [16,18–21,23,26] that efficient calculations of both phase-dependent and phase-averaged results can be carried out by defining a new variable $\theta_1=\omega_1 t+\delta_1$. In this section, the definition of an analogous variable θ_b for the efficient calculation of results for problems involving the interaction of a molecule with two cw electric fields is outlined.

For the interaction of a molecule with two cw lasers, where the total electric field is given by Eq. (2), the Hamiltonian is periodic in the beat period T_b, which represents the (minimum) time containing an integer multiple of each of the field periods $2\pi/\omega_1$ and $2\pi/\omega_2$ [24,25,27–29]. From this relationship, the beat frequency ω_b can be defined as

$$\omega_b=\frac{\omega_1}{m_1}=\frac{\omega_2}{m_2}, \tag{4}$$

where m_1 and m_2 are the lowest possible integers giving the ratio ω_1/ω_2 and the beat period $T_b=2\pi/\omega_b$.

Using the definition of the beat frequency, the total electric field for two cw lasers, Eq. (2), can be rewritten as

$$\varepsilon_{\text{total}}(t)=\hat{\mathbf{e}}_1\varepsilon_1^0\cos\left[m_1\left(\omega_b t+\frac{\delta_1}{m_1}\right)\right] +\hat{\mathbf{e}}_2\varepsilon_2^0\cos\left[m_2\left(\omega_b t+\frac{\delta_2}{m_2}\right)\right]. \tag{5}$$

Since phase-control problems involve maintaining a relative phase difference between the two components of the total electric field, a general phase difference can be defined as

$$\delta_d=m_2\delta_1-m_1\delta_2, \tag{6}$$

where m_1 and m_2 are the integers that define the beat frequency. It should be noted that a phase difference defined in this manner recovers the familiar forms [1–3,14,15] for one- versus two-photon excitation, i.e., $\delta_d=\delta_1-2\delta_2$, and one versus three-photon excitation, i.e., $\delta_d=\delta_1-3\delta_2$, where the subscript ''1'' refers to the one-photon field and the subscript ''2'' refers to the multiphoton field.

Similar to the one-color problem, where the phase that is averaged over is the phase (δ_1) of the laser field, for the two-color problem, a beat phase (δ_b), which is related to the beat frequency, can be defined. From Eq. (5), a single beat phase can be associated with one of the laser fields, here field 1 is chosen, and is given by

$$\delta_b = \frac{\delta_1}{m_1}. \tag{7}$$

Upon substituting Eq. (7) into Eq. (6), the phase of the second laser field can be written in terms of the beat phase and the relative phase difference between the laser fields

$$\delta_2 = m_2 \delta_b - \frac{\delta_d}{m_1}. \tag{8}$$

Using the definitions of the two laser phases, δ_1 and δ_2, written in terms of the beat phase and the relative phase difference between the laser fields, the total electric field can be rewritten in the desired form as

$$\varepsilon_{\text{total}}(t) = \hat{\mathbf{e}}_1 \varepsilon_1^0 \cos[m_1 \theta_b] + \hat{\mathbf{e}}_2 \varepsilon_2^0 \cos\left[m_2 \theta_b t - \frac{\delta_d}{m_1}\right], \tag{9}$$

where we have defined a new variable $\theta_b = \omega_b t + \delta_b$.

Analogous to the one-color cw Hamiltonian [16,18–21,23,26], by changing from the variable t to the variable θ_b, the Hamiltonian changes from passing through one period for $0 \leqslant t \leqslant 2\pi/\omega_b$ to a period over $0 \leqslant \theta_b \leqslant 2\pi$. Note that over the Hamiltonian's period in θ_b, the two fields are driven through m_1 and m_2 field periods, respectively. The phase-dependent and phase-averaged results, for a fixed relative phase difference (δ_d), can be determined by solving for the evolution operator over only the first θ_b period of the Hamiltonian. From a particular choice of one field's phase (δ_1), the beat phase can be determined using Eq. (7). From the chosen relative phase difference (δ_d), the other laser phase (δ_2) required to maintain this phase difference can be determined from Eq. (8). The phase-dependent results can be calculated since the beat phase determined simply changes the initial time (phase) of interaction. The phase-averaged results can be determined by averaging the beat phase over $0 \leqslant \delta_b \leqslant 2\pi$, which corresponds to averaging over the first θ_b period of the Hamiltonian. Although the focus of this paper is on phase averaging for problems where the phase difference between the two fields is fixed, the above formalism provides an efficient route for determining the fully phase-averaged results, which corresponds to averaging over both the initial phase and the relative phase difference $0 \leqslant \delta_d \leqslant 2\pi$.

B. The Floquet formalism

If the Hamiltonian is periodic and self adjoint, the Floquet formalism [16,18,20,21,24,25] can be utilized to determine the time-dependent populations of the system states to long times from the determination of the evolution operator over the first θ_b period of the Hamiltonian. Furthermore, the long time-averaged and phase-averaged populations of the system states can be efficiently calculated using the Floquet formalism [16,18,20,21,24,25]. Once the variable θ_b has been defined, the two-color Floquet treatment is exactly analogous to that for the one-color problem [16,18,20,21,24,25]. Therefore, only the basic equations needed for implementing the Floquet formalism for the calculation of long time-averaged (steady-state) results are presented here. For a more detailed discussion, including a discussion of calculating time-dependent results, the reader is referred to Refs. [18,19] and [23].

In Floquet form, the exact state amplitudes can be written as

$$\begin{aligned} a(t) &= Z(\omega_b t + \delta_b) e^{i\Delta(\omega_b t + \delta_b)} b_0(\delta_d, \delta_1, \delta_2) \\ &= Z(\theta_b) e^{i\Delta(\theta_b)} b_0(\delta_d, \delta_1, \delta_2), \end{aligned} \tag{10}$$

where Z is a periodic matrix, Δ is the real diagonal characteristic exponent matrix, and $b_0(\delta_d, \delta_1, \delta_2)$ is a column vector, which contains the initial condition information. Note that the initial conditions for the two-color problem depend on the phases of both fields and the relative phase difference between the two fields. In Sec. II A, we have shown how this phase dependence can be expressed in terms of two phases—the relative phase difference δ_d, and the beat phase δ_b. In order to relate to the phase-dependent work of others [6–12,14,15,27,28] and to discuss the role of phase averaging, we define the phase-dependent steady-state molecular state population for state j (steady-state induced transition probability)

$$\begin{aligned} \overline{P}_j(\delta_d, \delta_1, \delta_2) = \frac{\omega_b}{2\pi} \int_0^{2\pi/\omega_b} \sum_{k=1}^{2} |Z_{jk}(\omega_b t + \delta_b)|^2 \\ \times dt |b_k(\delta_d, \delta_1, \delta_2)|^2 \end{aligned} \tag{11}$$

and the phase-averaged steady-state induced transition probability as

$$\overline{\overline{P}}_j(\delta_d) = \frac{1}{2\pi} \int_0^{2\pi} \overline{P}_j(\delta_d, \delta_1, \delta_2) d\delta_b. \tag{12}$$

For phase control problems, where the relative phase difference between the two fields is fixed, these are the only results that need to be considered. However, for the case where the phase difference between the fields fluctuates, fully phase-averaged results can be defined

$$\overline{\overline{\overline{P}}}_j = \frac{1}{2\pi} \int_0^{2\pi} \overline{\overline{P}}_j(\delta_d) d\delta_d. \tag{13}$$

Note that the limits of integration $0 \leqslant \delta_d \leqslant 2\pi$ are for the most general two field case. In certain instances [6,14,15], these limits of integration can be reduced due to symmetry considerations. For example, in the one-versus two-photon case, these limits can be reduced to $0 \leqslant \delta_d \leqslant \pi/2$, while in the one-versus three-photon case, they can be reduced to $0 \leqslant \delta_d \leqslant \pi$. While the formalism that has been introduced leads to convenient expressions for the fully phase-averaged results, the primary motivation is to illustrate the importance of phase-averaging in problems where the relative phase difference between the field is fixed, i.e., phase control problems. Hence, fully phase-averaged results are not considered explicitly in this paper.

For the evaluation of the steady-state populations, the Riemann product integral method [20,26,30–32] was used to calculate the evolution operator over the first θ_b period of the Hamiltonian. The number of Riemann intervals used is $180m_g$, where m_g is the larger of m_1 and m_2. For the simultaneous one- and three-photon excitation considered in Sec. III, the total number of Riemann intervals was 540. Using this method of subdivision ensures that the shorter period of the two fields is divided into 180 subintervals. The long time and phase averages of the populations are determined by evaluating the relevant integrals over $0 \leqslant \theta_b \leqslant 2\pi$ using Simpson's rule, with the number of integration points being one sixth the number of Riemann points.

III. RESULTS AND DISCUSSION

The explicit examples considered in this section involve the harmonic two-color simultaneous one- and three-photon transitions between two energy levels with the molecular parameters given by $E_{21}=0.1$ and $\mu_{21}=3.0$. These parameters are representative of a two-level configuration in substituted aromatic molecules [33] and have been used in previous theoretical calculations [14,15,27,34–37]. The previous calculations were concerned with the effects of permanent dipole moments on the excitation process, and, therefore, the system considered has a nonzero difference in permanent dipole moments, $d=\mu_{22}-\mu_{11}=6.5$. In order to clearly separate phase effects from the effects of the permanent dipole moments, a ''pseudomolecule'' with $d=0$ is considered, as was done previously [15]. In addition, all results presented in this paper are given in reduced form in terms of the molecule-EMF coupling strength parameters, $b_i=(\mu_{21}\cdot\hat{e}_i\varepsilon_i^0)/E_{21}$. The results as presented are independent of the choice of model (assuming the effects of the permanent dipole moments are negligible) and can be scaled to different regions of the electromagnetic spectrum and to different field strengths.

In order to optimize control, the field strengths should be chosen such that the molecule-EMF couplings for the one- and three-photon transition are equivalent [14]. However, in order to illustrate the importance of phase averaging, we first consider the case where the field strengths (intensities) of the fundamental and its third harmonic are chosen to be equal, i.e., $\varepsilon_1^0=\varepsilon_2^0$, as has been done in previous fixed phase calculations [6–9]. The electric fields are taken to be parallel to each other and to the transition dipole moment $\hat{e}_1 || \hat{e}_2 || \mu_{21}$. Throughout this paper, the subscript ''1'' will refer to the third harmonic ($\omega_1=E_{21}$) corresponding to the one-photon transition while the subscript ''2'' will refer to the fundamental laser frequency ($\omega_2=E_{21}/3$) corresponding to the three-photon transition: $\omega_b=\omega_2$.

In order to determine the relative contributions of the one- and three-photon transitions to the overall transition strength, it is useful to consider the perturbative molecule-EMF couplings. The perturbative overall molecule-EMF coupling is given by [14]

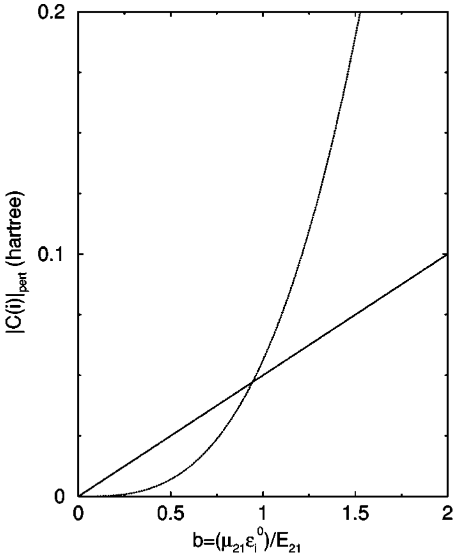

FIG. 1. The one-photon (solid line) and the three-photon (dotted line) perturbative molecule-EMF coupling strength parameters as a function of the (dimensionless) variable $b=(\mu_{21}\varepsilon_1^0)/E_{21}$.

$$|\zeta(\delta_d,\delta_1,\delta_2)|=[[C(1)]_{pert}^2+[C(3)]_{pert}^2 + 2[C(1)]_{pert}[C(3)]_{pert}\cos(\delta_d)]^{1/2}, \tag{14}$$

where $\delta_d=\delta_1-3\delta_2$. The one-photon molecule-EMF coupling $[C(1)]_{pert}$ is given by

$$[C(1)]_{pert}=\frac{(\mu_{21}\cdot\hat{e}_1\varepsilon_1^0)}{2}, \tag{15}$$

and the three-photon molecule-EMF coupling is

$$[C(3)]_{pert}=\frac{(\mu_{21}\cdot\hat{e}_2\varepsilon_2^0)^3}{16\omega_2^2}. \tag{16}$$

The one- and three-photon perturbative molecule-EMF coupling strength parameters are illustrated as a function of the scaled molecule-EMF coupling parameter b in Fig. 1. For the chosen field strength relationship, i.e., $\varepsilon_1^0=\varepsilon_2^0$, there are clearly three distinct regions that can be identified. For $b<0.25$, the overall excitation is dominated by the one-photon transition. The relative contribution of the three-photon transition increases for $0.25 \leqslant b \leqslant 1.0$ and the one- and three-photon contributions are equal for $b=0.94$. Finally, beyond $b=1.0$, the three-photon transition rapidly begins to dominate the overall excitation process. The perturbative couplings should not be considered accurate for the intense field processes that are examined in this paper. For example, the perturbative expression for the overall molecule-EMF coupling, Eq. (14), depends only on the relative phase difference (δ_d) between the two laser fields while the results discussed below exhibit a dependence on both the relative phase difference and the choice of absolute phases δ_1 and δ_2. However, the perturbative molecule-EMF couplings do provide a qualitative comparison for the relative one- and three-photon

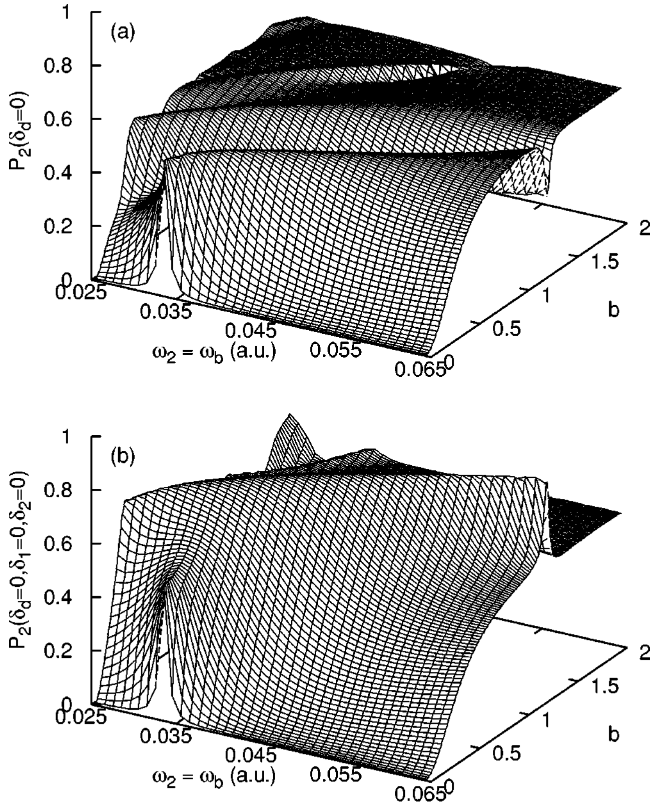

FIG. 2. The steady-state induced transition probability, for a phase difference $\delta_d = 0$, as a function of both the (dimensionless) molecule-EMF coupling strength parameter, $b = (\mu_{21}\varepsilon_1^0)/E_{21}$, with $\varepsilon_1^0 = \varepsilon_2^0$, and of the fundamental frequency ω_2 where $\omega_1 = 3\omega_2$. (a) The phase-averaged results, $\overline{P}_2(\delta_d=0)$ and (b) the fixed phase results $\overline{P}_2(\delta_d=0,\delta_1=0,\delta_2=0)$.

contributions to the overall transition strength that will prove useful in discussing the following results.

Figure 2 illustrates the steady-state induced transition probability as a function of both the molecule-EMF coupling strength parameter (the field strength) and the frequency of the three-photon exciting field; the frequency of the one-photon field is given by $\omega_1 = 3\omega_2$ and $\varepsilon_1^0 = \varepsilon_2^0$. The phase-averaged results, see Eq. (12), for a relative phase difference of zero ($\delta_d = 0$) are presented in Fig. 2(a) while Fig. 2(b) illustrates the phase-dependent results, see Eq. (11), for the fixed phases ($\delta_d = 0, \delta_1 = 0, \delta_2 = 0$). The phase-averaged and fixed phase results are clearly different with the discrepancy increasing (in general) as the field strength increases. We will begin with a discussion of the phase-averaged results and then discuss and contrast the fixed phase results.

For low molecule-EMF coupling strength parameters ($b \ll 1$), the resonance frequency, i.e., the frequency where $\overline{P}_2(\delta_d=0)$ is a maximum, is given by the expected weak-field frequencies, $\omega_1 = E_{21}$ and $\omega_2 = E_{21}/3 = 0.033$. However, as the field strengths are increased, the resonance profile exhibits a shift to higher frequency. In one-color problems, the shift of the exact resonance frequency away from the weak-field resonance frequency as the field strength increases is referred to as the Bloch-Siegert shift [22,36–39]. When $d = 0$, the one-color Bloch-Siegert shifts only occur to frequencies higher than the weak-field resonance frequency, while for $d \neq 0$, the shifts can be to higher or lower frequencies [36,37,39]. Analogous shifts in the resonance frequencies for two-color excitations and their importance in phase control calculations have been noted previously [14,15,27]. It is assumed that the two-color shifts for $d = 0$ and $d \neq 0$ will behave similarly to their one-color counterparts, but, while analytic expressions exist for predicting the one-color Bloch-Siegert shifts [22,36–39], analogous two-color expressions have yet to be derived.

The phase-averaged steady-state transition probability at the resonance frequency, as a function of b, is given by exactly 0.5. In fact, the phase-averaged steady-state transition probability does not exceed 0.5 for any combinations of frequency and field strength. On the other hand, for large molecule-EMF coupling parameters, the fixed phase results, see Fig. 2(b), exceed 0.5 for a variety of frequency and field strength combinations. For example, when the frequencies are at their weak-field resonance values ($\omega_1 = E_{21}$ and $\omega_2 = E_{21}/3$), the maximum steady-state induced transition probability is given by $P_2(\delta_d=0,\delta_1=0,\delta_2=0) = 0.765$ at $b = 0.525$ ($\varepsilon_1^0 = \varepsilon_2^0 = 0.0175$ a.u. $= 1.1 \times 10^{13}$ W/cm^2). In fact, for the fixed phases illustrated ($\delta_d = 0, \delta_1 = 0, \delta_2 = 0$), the induced transition probability loses the shape of a traditional absorption profile [$\approx$Lorentzian, see Fig. 2(b) as a function of ω_2 for $b \approx 0$] for increasing field strength, and, therefore, it is difficult to identify a ''resonance'' frequency as can readily be done for the phase-averaged results. For frequency and field strength combinations where the phase-averaged results equal 0.5, the fixed phase steady-state induced transition probability equals 0.5 as well. Hence, there is a seam of intersection along the phase-averaged resonance frequency path. The intersection between the phase-averaged and the phase-dependent results can be readily seen if we consider ''cuts'' at fixed frequencies (see the following).

In order to more clearly understand the roles of absolute phase versus relative phase difference, several absolute phase combinations are considered for the relative phase differences $\delta_d = 0$, $\delta_d = \pi/2$, and $\delta_d = \pi$. According to the expression for the overall perturbative molecule-EMF coupling, see Eq. (14), changing the relative phase difference will modify the contribution of the interference term to the overall coupling, i.e., positive, zero, and negative for $\delta_d = 0, \pi/2$, and π, respectively. First, we consider the steady-state transition probabilities as a function of the molecule-EMF coupling parameter (the field strengths) with $\varepsilon_1^0 = \varepsilon_2^0$, where the frequencies are kept at their weak-field values of $\omega_1 = E_{21}$ and $\omega_2 = E_{21}/3$, see Figs. 3(a)–3(c) for the relative phase differences $\delta_d = 0$, $\delta_d = \pi/2$, and $\delta_d = \pi$, respectively. For the relative phase difference $\delta_d = 0$, the steady-state induced transition probability is illustrated for the fixed phases ($\delta_1 = 0, \delta_2 = 0$), ($\delta_1 = \pi/2, \delta_2 = \pi/6$), and ($\delta_1 = \pi, \delta_2 = \pi/3$); for $\delta_d = \pi/2$, ($\delta_1 = \pi/2, \delta_2 = 0$), ($\delta_1 = \pi, \delta_2 = \pi/6$), and ($\delta_1 = 3\pi/2, \delta_2 = \pi/3$); and for $\delta_d = \pi$, ($\delta_1 = \pi, \delta_2 = 0$), ($\delta_1 = 3\pi/2, \delta_2 = \pi/6$), and ($\delta_1 = 2\pi, \delta_2 = \pi/3$). The chosen fixed phases, δ_1 and δ_2, for a relative phase difference δ_d, fulfill Eq. (8). Clearly, while there are

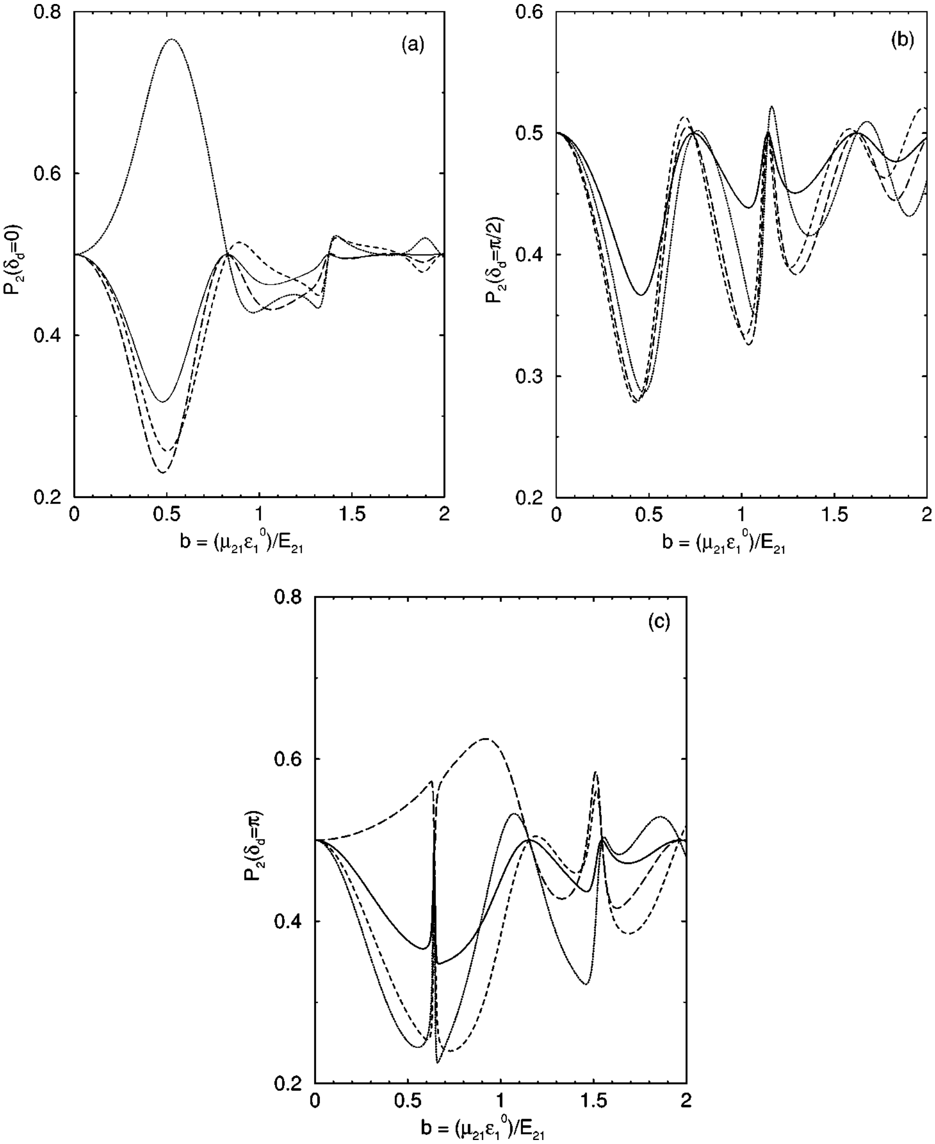

FIG. 3. Phase-averaged steady-state induced transition probability, $\overline{P_2}(\delta_d)$ (solid line), and the fixed phase steady-state induced transition probabilities, $\overline{P_2}(\delta_d,\delta_1,\delta_2=0)$ (dotted line), $\overline{P_2}(\delta_d,\delta_1,\delta_2=\pi/6)$ (short-dashed line), and $\overline{P_2}(\delta_d,\delta_1,\delta_2=\pi/3)$ (long-dashed line), as a function of the (dimensionless) molecule-EMF coupling strength parameter $b=(\mu_{21}\varepsilon_1^0)/E_{21}$, with $\varepsilon_1^0=\varepsilon_2^0$, and with the frequencies set to their weak-field resonance values, i.e., $\omega_1=E_{21}$ and $\omega_2=E_{21}/3$. The values of δ_1 are such that they fulfill Eq. (8) for the chosen δ_2 and relative phase difference values (a) $\delta_d=0$, (b) $\delta_d=\pi/2$, and (c) $\delta_d=\pi$ (see the text for details).

differences for each of the relative phase differences, there are some features that are common to all three plots.

The plots illustrate that the steady-state transition probability depends intimately on the choice of the absolute phases used to produce a particular relative phase difference. The fixed phase results rapidly diverge from the phase-averaged results as the molecule-EMF coupling increases. However, there are certain molecule-EMF coupling parameters for which the fixed phase and the phase-averaged converge on a value of 0.5. For one-color excitation, the points at which all $\overline{P_2}$'s equal 0.5, as a function of the molecule-EMF coupling strength parameter b, correspond to successive n-photon resonance peaks crossing the line $\omega_1=E_{21}$ in the frequency domain [16]. For a two-level model system with $d=0$, only odd-photon transitions are allowed. However, for the case of two-color excitation where two simultaneous transitions corresponding to the absorption of different numbers of photons can occur, this interpretation is not quite so transparent. For example, for one-color excitation, the point at $b\rightarrow 0$ corresponds to $n=1$ (the one-photon transition) but for the two-color excitation considered here, the point $b\rightarrow 0$ corresponds to a simultaneous one- and three-photon excitation. The molecule-EMF coupling strength parameter beyond $b\rightarrow 0$ at which the fixed phase and the phase-averaged results first coincide at $\overline{P_2}=0.5$, changes as a function of the relative phase difference between the two fields, i.e., $b=0.828$ for $\delta_d=0$, $b=0.738$ for $\delta_d=\pi/2$, and $b=0.642$ for $\delta_d=\pi$. Based on one-color plots analogous to Fig. 3 for the one- and three-photon transition frequencies (not illustrated), this first intersection point corresponds to simultaneous three- and five-photon excitation. The subsequent intersection points correspond to increases in the number of photons contained in both of the two transitions involved (see discussion below).

It is interesting to note that the steady-state induced transition probability for the relative phase difference of zero ($\delta_d=0$), see Fig. 3(a), has a very similar behavior to the one-photon one-color results for low values of $b(b\leqslant 0.5)$, see Fig. 1, Ref. [16]. However, in light of the fact that for low values of the molecule-EMF coupling parameter the overall two-color transition strength is dominated by the one-

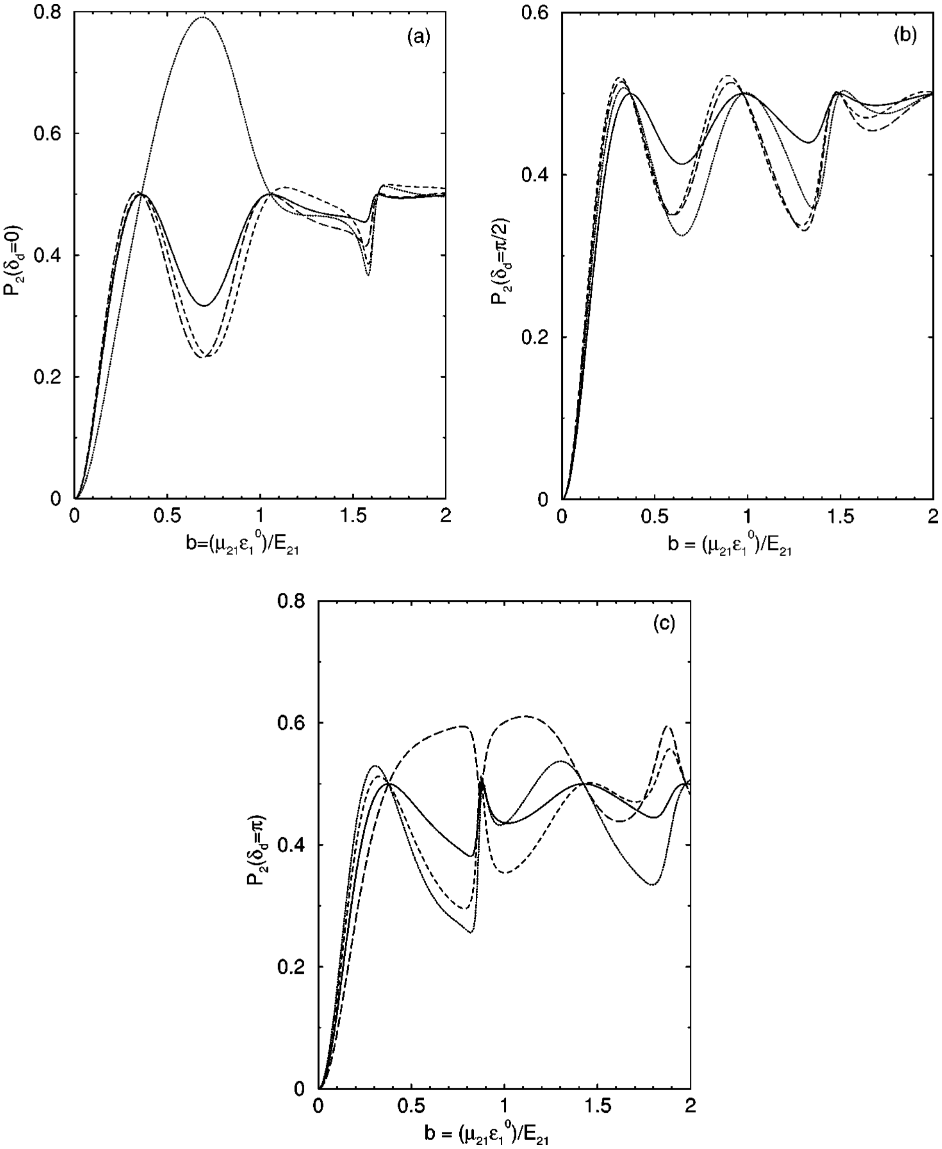

FIG. 4. Same as Fig. 3 but with the frequencies changed such that $\omega_1=1.2E_{21}$ and $\omega_2=0.4E_{21}$. Note that this fundamental frequency corresponds to the Bloch-Siegert shifted resonance frequency, i.e., the first values of the electric fields where all of the steady-state induced transition probabilities equal to 0.5, for (a) $\varepsilon_1^0=\varepsilon_2^0=0.0120$ a.u. $=5.05\times10^{12}$ W/cm^2, (b) $\varepsilon_1^0=\varepsilon_2^0=0.0123$ a.u. $=5.31\times10^{12}$ W/cm^2, and (c) $\varepsilon_1^0=\varepsilon_2^0=0.0126$ a.u. $=5.57\times10^{12}$ W/cm^2.

photon process, see Fig. 1, this behavior is not at all surprising.

For the two-level model under consideration, the resonance frequency is Bloch-Siegert shifted to higher frequency as the field strengths are increased, see Fig. 2(a) for example. Therefore, it is useful to consider plots similar to those of Fig. 3 for frequencies greater than the weak-field resonance frequencies of $\omega_1=E_{21}$ and $\omega_2=E_{21}/3$. The steady-state transition probabilities as a function of the molecule-EMF coupling parameter (the field strengths) with $\varepsilon_1^0=\varepsilon_2^0$, where the frequencies are given by $\omega_2=0.4E_{21}$ and $\omega_1=3\omega_2=1.2E_{21}$, have been determined; see Figs. 4(a)–4(c) for the relative phase differences $\delta_d=0$, $\delta_d=\pi/2$, and $\delta_d=\pi$, respectively. The fixed phase combinations used to obtain these relative phase differences are identical to those for Fig. 2. The Bloch-Siegert shifted resonance frequency is determined by considering the molecule-EMF coupling strength parameter, where the fixed phase and the phase-averaged results first coincide at $\overline{P}_2(\delta_d)=0.5$. Since the chosen frequencies are greater than their weak-field counterparts, this first intersection corresponds to a simultaneous one- and three-photon excitation. From Fig. 4, the choice of frequencies corresponds to the Bloch-Siegert resonance frequency for $b=0.360$ ($\varepsilon_1^0=\varepsilon_2^0=5.05\times10^{12}$ W/cm^2), $b=0.369$ ($\varepsilon_1^0=\varepsilon_2^0=5.31\times10^{12}$ W/cm^2), and $b=0.378$ ($\varepsilon_1^0=\varepsilon_2^0=5.57\times10^{12}$ W/cm^2), for the relative phase differences $\delta_d=0$, $\delta_d=\pi/2$, and $\delta_d=\pi$, respectively. The steady-state induced transition probabilities clearly depend intimately on the choice of absolute phases used to produce a particular relative phase difference as was seen for the frequencies set to their weak-field values, $\omega_1=E_{21}$ and $\omega_2=E_{21}/3$, see Fig. 3.

There are similarities between the fixed phase and phase-averaged behavior for a particular relative phase difference for the two frequencies considered, compare Fig. 3(a) to Fig. 4(a), Fig. 3(b) to Fig. 4(b), and Fig. 3(c) to Fig. 4(c). For example, the fixed phase induced transition probability $P_2(\delta_d=0,\delta_1=0,\delta_2=0)$ peaks at a very high value (≈ 0.8) for both frequency combinations considered. Also, both the fixed phase and phase-averaged results show a very narrow

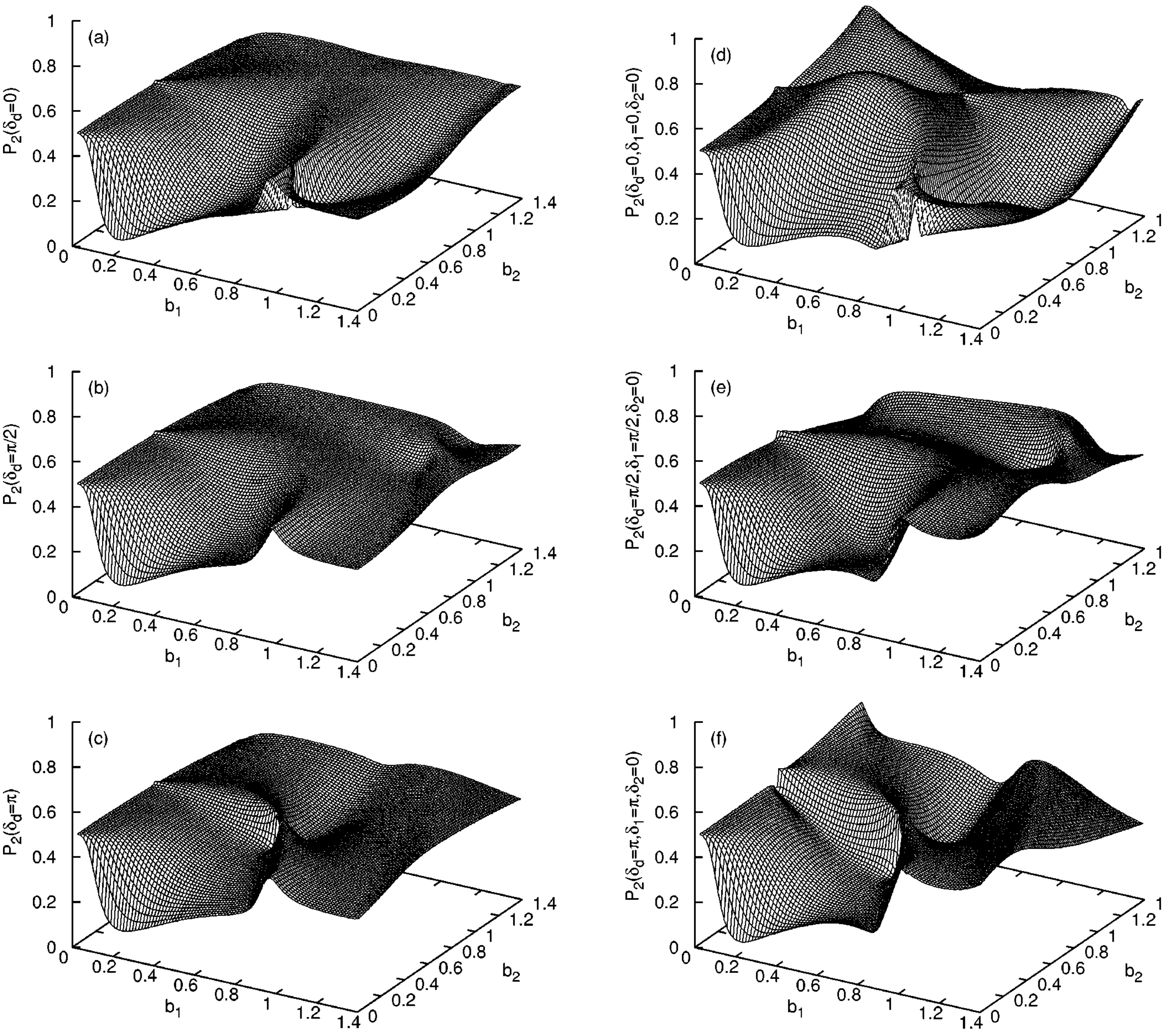

FIG. 5. The steady-state induced transition probability, for the phase difference $\delta_d=0$, $\pi/2$, and π, as a function of both the (dimensionless) one-photon molecule-EMF coupling strength parameter, $b_1=(\mu_{21}\varepsilon_1^0)/E_{21}$ and the (dimensionless) three-photon molecule-EMF coupling strength parameter, $b_2=(\mu_{21}\varepsilon_2^0)/E_{21}$. The frequencies are set to their weak-field resonance values, i.e., $\omega_1=E_{21}$ and $\omega_2=E_{21}/3$. The phase-averaged results (a) $\overline{P}_2(\delta_d=0)$, (b) $\overline{P}_2(\delta_d=\pi/2)$, and (c) $\overline{P}_2(\delta_d=\pi)$, and the fixed phase results (d) $\overline{P}_2(\delta_d=0,\delta_1=0,\delta_2=0)$, (e) $\overline{P}_2(\delta_d=\pi/2,\delta_1=\pi/2,\delta_2=0)$, and (f) $\overline{P}_2(\delta_d=\pi,\delta_1=\pi,\delta_2=0)$.

first ''resonance'' at $b\approx 1.0$ for the relative phase difference $\delta_d=\pi$. While these behaviors are interesting to note, the most important result is that the fixed phase and the phase-averaged steady-state molecular state populations are different for $b\geqslant 0.1$ independent of the choice of excitation frequency.

As mentioned previously, in order to optimize control, the one- and three-photon field strengths should be chosen such that the molecule-EMF couplings for the two individual transitions are equivalent. However, optimization based on the one- and three-photon perturbative couplings, Eqs. (15) and (16), is only valid in the weak-field regime. As the field strength of either or both fields is increased, the ''resonances'' correspond to absorption of increasing numbers of photons. Although the frequencies may be set to $\omega_1=E_{21}$ and $\omega_2=E_{21}/3$, the absorptions can no longer be considered as one- or three- photon. For these reasons, in the strong-field regime, it is difficult to determine the ''best'' choice of field strengths to optimize control *a priori*. Therefore, while considering optimized field strengths would be best and examining equal field strengths is interesting, it is useful to consider the importance of phase averaging, and the underlying physics, in situations where the two field strengths are not equivalent and are varied independently.

Figure 5 illustrates the steady-state induced transition probability as a function of both the one- and three-photon molecule-EMF coupling strength parameters, b_1 and b_2, respectively. The frequencies are set to their weak-field resonance values, i.e., $\omega_1 = E_{21}$ and $\omega_2 = E_{21}/3$. The phase-averaged results, see Eq. (12), for the relative phase differences of zero, $\pi/2$, and π, are illustrated in Figs. 5(a)–5(c), respectively. Figures 5(d)–5(f) illustrate the corresponding fixed phase results for the commonly considered case, see Eq. (1), where the three-photon field's phase is set to zero, i.e., $\delta_2 = 0$ with δ_1 chosen to achieve the desired phase difference. The phase-averaged and the fixed phase results are clearly different with the discrepancy increasing as either (or both) field strength(s) increases, as has been seen in Figs. 2–4 for equivalent field strengths. The phase-averaged and fixed phase ($\delta_2 = 0$) plots of Fig. 3 correspond to ''cuts'' along the $b_1 = b_2$ diagonals of Fig. 5. It should be noted that the minimum values of b_1 and b_2 are not equal to zero in the graphs but rather the minimum is shown for $b_i = 0.015$, i.e., a field strength of $\varepsilon_i^0 = 5 \times 10^{-4}$ a.u. $\approx 8.8 \times 10^9$ W/cm^2. Hence, the values for $b_2 \rightarrow 0$ do not correspond to Moloney and Meath's [16] one-color results. We will begin with a discussion of the phase-averaged results, where, as before, ''resonances'' can be clearly identified, and then discuss and contrast the fixed phase results.

In order to discuss the number of photons absorbed as a function of increasing field strength, the limits $b_1 = b_2 \rightarrow 0$, $b_1 = 0$, and $b_2 = 0$ should be examined. Note that while the $b_i = 0$ limits have not been plotted, the following discussion extrapolates to these limits. The peak in the transition probability at $b_1 = b_2 \approx 0$ corresponds to simultaneous one- and three-photon excitation. If the steady-state transition probability is followed as a function of increasing one-photon field strength b_1, with the three-photon field turned off ($b_2 = 0$), the next peak corresponds to three-photon excitation at the frequency $\omega_1 = E_{21}$. Since only odd-photon transitions are allowed for a two-level system with $d = 0$, there is no two-photon absorption. On the other hand, if the steady-state transition probability is followed as a function of increasing three-photon field strength b_2, with the one-photon field turned off ($b_1 = 0$), the next peak corresponds to five-photon excitation at the frequency $\omega_2 = E_{21}/3$. Clearly, the second resonance positions, i.e., the b_1 and b_2 combinations connecting these limits where $\overline{P}_2(\delta_d) = 0.5$, correspond to an increase in the number of photons absorbed in both transitions. On the plots illustrated here, and as was discussed in Fig. 3, the second resonance corresponds to simultaneous three- and five-photon excitation. The numbers of photons absorbed in both transitions will continue to increase as either field strength is increased. For example, for the relative phase difference of $\pi/2$, see Fig. 5(b), the simultaneous five- and seven-photon resonance can be seen at $b_1 \approx b_2 \approx 1.2$.

The phase-averaged results of Figs. 5(a)–5(c), demonstrate that the steady-state transition probability, as expected, depends upon the choice of relative phase difference. The two most obvious differences are that the width of the three- plus five-photon resonance decreases and its position moves to smaller values of b_i as the relative phase changes from 0 to π (seen more clearly along the cut $b_1 = b_2$, see Fig. 3). While the shift to smaller b_i for increasing relative phase is seen clearly for the three- plus five-photon resonance, the next higher-order resonance, i.e., five- plus seven photon, is only seen for the relative phase difference $\pi/2$. For the relative phase differences of 0 and π, the field strengths must be increased further in order for the five- plus seven-photon resonance to occur.

As has been seen for the equivalent field strengths in Figs. 2–4, the phase-averaged steady-state transition probability does not exceed 0.5 for any combination of field strengths. This behavior allows the ''resonances'' to be easily identified. We can conclude quite confidently from these results, and from the results for equivalent field strengths, that the phase-averaged steady-state transition probability will not exceed 0.5 for any combinations of field strengths and frequencies. On the other hand, the fixed phase results exceed 0.5 in several regions of (b_1, b_2) space, see Figs. 5(d)–5(f); although, the fixed phase results coincide with the phase-averaged results at all field strength combinations where $\overline{P}_2(\delta_d) = 0.5$. Clearly, except for fortuitous combinations of frequencies and field strengths, by arbitrarily setting one of the field's phases to zero rather than properly phase averaging, one would erroneously predict the steady-state populations, and hence, the time-dependent populations (dynamics) which underlie the absorption, when two intense ($b_i \geqslant 0.1$) cw lasers interact with a molecule.

IV. CONCLUSIONS

In this paper, a computationally efficient method for calculating the phase-averaged steady-state and time-dependent atomic or molecular state populations for a system interacting with a two-color laser field has been developed. The method has been applied to a model two-level system interacting with a laser field comprised of the fundamental frequency and its third harmonic. Except for fortuitous combinations of field strengths and frequencies corresponding to higher-order multiphoton transitions, where both the phase-dependent and the phase-averaged steady-state molecular state populations equal 0.5, there can be large differences between these results. The steady-state transition probabilities depend intimately on the absolute phases (initial phase) of the two laser fields, δ_1 and δ_2, for a fixed relative phase difference δ_d, between them when the molecule-EMF coupling strength parameter exceeds $b \approx 0.1$, most clearly seen in Figs. 3 and 4. By examining the cases for equal field strengths $\varepsilon_1^0 = \varepsilon_2^0$, and for independently varied ε_1^0 and ε_2^0, the two-color results presented, combined with the known one-color results [16,18–22], provide a good general criterion ($b \geqslant 0.1$) to apply to any of the fields involved in a one- or two-color transition for estimating when the molecular state populations will depend upon the initial laser phase. We have seen that increasing one (or both) field strength(s) leads to an increase in the number of photons absorbed at both frequencies. Thus, the process changes from one of competing one- and three-photon excitation, to one of three- and five-photon excitation, and so on. The position of the higher-order resonance was seen to change as a function of the relative phase difference. For the atomic ($d = 0$) two-level system, only odd photon transitions are allowed and the

Bloch-Siegert shift is always to higher frequency. It will be interesting to examine the two-color process as a function of frequency and of increasing field strengths for the molecular $(d\neq 0)$ case where both even- and odd-photon transitions can occur and the Bloch-Siegert shifts can be to lower as well as higher frequencies. Most importantly, we have demonstrated that when examining the interaction of an atom or molecule with two intense cw laser fields, the calculated physical observables must be determined by properly averaging over the absolute phases (initial phase) of the two laser fields and we have provided an efficient method for accomplishing this goal.

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