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# Nonlinear response of a harmonic diatomic molecule: Algebraic nonperturbative calculation

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Even harmonic molecules display a nonlinear behavior when driven by an inhomogeneous field. We calculate the response of single harmonic molecules to a monochromatic time and space dependent electric field $E(r,t)$ of frequency $\omega$ employing exact algebraic methods. We evaluate the responses at the fundamental frequency $\omega$ and at successive harmonics $2\omega$, $3\omega$, etc., as a function of the intensity and of the frequency of the field and compare the results with those of first and second order perturbation theory.

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## I. INTRODUCTION

Even though the harmonic oscillator is the prototype of a linear system, its response to inhomogeneous time dependent fields contains nonlinear contributions. A first order Taylor expansion of the forcing electric field close to the center of the oscillator, when inserted into the classical equation of motion, yields a time modulation of the restoring force, i.e., of the term linear in the displacement from equilibrium. Thus, the ordinary oscillator becomes a parametric oscillator, an archetypal nonlinear system [1,2]. The study of the optical linear and nonlinear responses of harmonic systems to periodic electromagnetic fields has been done both with classical [3,4] and quantum mechanical treatments [5]. It has been shown that when perturbation theory is applied both methods yield the same response at the fundamental frequency $\omega$ and at its second harmonic $2\omega$. In this work we employ an algebraic approach to study *nonperturbatively* the time evolution of a quantum mechanical harmonic system forced by a time and space dependent electric field in order to learn about the applicability of the perturbative treatment. Although the algebraic method that we use is applicable to fields with an arbitrary time dependence, in this paper we will restrict ourselves to the adiabatically switched monochromatic fields for which the perturbative treatment has been employed.

The structure of the paper is the following: In Sec. II we summarize the classical perturbative approach [3] to the response of an harmonic system in order to understand the origin of its nonlinearity, whose results are known to agree with the quantum mechanical perturbative treatment. In Sec. III we develop an algebraic approach to the problem and we take advantage of its group structure to obtain an exact quantum mechanical solution. In Sec. IV we present results for the time evolution of a system perturbed by fields with different frequencies and field strengths, we analyze the generation of the first few harmonics and compare them with the predictions of perturbation theory. Finally, we devote Sec. V to conclusions.

## II. CLASSICAL APPROACH

We calculate the response of a single polar molecule bound by harmonic forces. In the center of mass system it is enough to consider the motion of a single dynamic charge $q$ with mass $m$ corresponding to the reduced mass of the molecule and displaced a separation $x$ from its equilibrium position $r_0$, to which it is bound by a harmonic force with resonant frequency $\omega_0$ and driven by a classical electric field $E(r,t)$. For simplicity, in this paper we assume that the system is one-dimensional (both $r$ and $E$ point in the same direction) and consequently we neglect the transverse nature of the electromagnetic field and any magnetic effects, although we do expect them to be as large as the nonlinear electric effects in three-dimensional (3D) systems. The interaction potential is then given by

$$V = -qxE(r_0,t) - \frac{q}{2}x^2\partial_r E(r_0,t). \tag{1}$$

The first term is the usual dipolar interaction while the second term is the quadrupolar interaction which is present whenever the field is inhomogeneous, and we disregarded higher multipoles. The resulting classical equation of motion is

$$m\frac{d^2x}{dt^2} = qE(r_0,t) - m\omega_0^2 x + qx\partial_r E(r_0,t), \tag{2}$$

where the electrical forces on the right-hand side (RHS) may be identified with the electric field

$$E(r,t) \approx E(r_0,t) + x\partial_r E(r_0,t), \tag{3}$$

evaluated at the actual position $r=r_0+x$ of the charge instead of its equilibrium position $r_0$. Notice that the restoring force in Eq. (2), i.e., the terms linear in the displacement $x$, depend on the spatial derivative of the electric field, which are given functions of time. Thus, the spatial variations of the field transform the harmonic oscillator, the most linear system we can conceive, into a forced parametric oscillator, a well-known nonlinear system [1,2].

Now assume that the driving field is monochromatic with frequency $\omega$, $E(r,t)=\mathrm{Re}[E_\omega(r)e^{-i\omega t}]$. Using a perturbative treatment [3], we obtain the stationary induced electric dipole moment $p^{(1)}(t)=\mathrm{Re}(p_\omega e^{-i\omega t})$ with

$$p_\omega = qx_\omega = \alpha(\omega)E_\omega(r_0) \tag{4}$$

to first order in the driving field, where the linear polarizability $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{q^2/m}{\omega_0^2 - \omega^2}. \tag{5}$$

The second order equation of motion at $2\omega$ becomes

$$-m(2\omega)^2 x_{2\omega} = -m\omega_0^2 x_{2\omega} + q x_\omega \partial_r E_\omega(r_0), \tag{6}$$

whose solution is

$$x_{2\omega} = \frac{1}{2q^2}\alpha(\omega)\alpha(2\omega)[\partial_r E_\omega^2(r_0)]. \tag{7}$$

The second order dipole moment at $2\omega$ is, therefore,

$$p_{2\omega} = \frac{1}{2q}\alpha(\omega)\alpha(2\omega)[\partial_r E_\omega^2(r_0)]. \tag{8}$$

As mentioned above, the nonlinear response (8) of a harmonic oscillator derived above classically using a perturbative solution, coincides with the corresponding expressions derived from a quantum mechanical perturbative treatment. It is interesting to note that for the harmonic oscillator model, the response at $2\omega$ due to the spatial variation of the field is proportional to the product of the linear responses at $\omega$ and $2\omega$.

Similarly, we also obtain a second order response at zero frequency, given by

$$p_0 = \frac{1}{q}\mathrm{Re}\ \alpha(0)\alpha(\omega)[E_\omega(r_0)\partial_r E_\omega^*(r_0)]. \tag{9}$$

## III. ALGEBRAIC APPROACH

The purpose of this work is to develop an algebraic approach [6] which yields an exact solution to the problem of the forced oscillator and to explore the validity of the perturbative calculation. The system's Hamiltonian is given by

$$H = H_0 + V, \tag{10}$$

where $H_0$ is the unperturbed harmonic oscillator Hamiltonian and $V$ is the interaction (1). In order to obtain the temporal evolution of a given observable $O$ under this Hamiltonian, we write the evolution operator as $U(t) = U_0(t)U_I(t)$, with

$$U_0(t) = e^{-iH_0(t-t_0)/\hbar} \tag{11}$$

the unperturbed Schrödinger evolution and $U_I(t)$ the evolution operator in the interaction picture, obeying

$$i\hbar\partial_t U_I(t) = H_I(t)U_I(t), \tag{12}$$

with

$$H_I(t) = U_0^\dagger(t)V(t)U_0(t) \tag{13}$$

the *interaction Hamiltonian*, and subject to the *initial* condition

$$U_I(t_0) = 1, \tag{14}$$

where we choose $t = t_0$ as a reference time. We assume that the interaction is null or insignificant for times $t < t_0$. Any operator $O$ at time $t$ is then given by

$$O(t) = U_I^\dagger(t)U_0^\dagger(t)OU_0(t)U_I(t), \tag{15}$$

with the convention that the explicit time dependence of an operator $O(t)$ indicates that the operator is evaluated within the Heisenberg picture at time $t$, while an unadorned $O$ denotes the operator at $t \leq t_0$ before the interaction has acted, or equivalently, it denotes the operator in the Schrödinger picture. The time dependent potential $V(t)$ and the electromagnetic field components will be taken as exceptions to this convention. We will use appropriate subscripts to indicate the precise meaning of the different evolution operators.

We consider first a system forced by a homogeneous field, so that only the linear term of Eq. (1) is present. The interaction Hamiltonian is then

$$\begin{aligned} H_I(t) &= -q\sqrt{\hbar/2m\omega_0}\big(ae^{-i\omega_0(t-t_0)} + a^\dagger e^{i\omega_0(t-t_0)}\big)E(r_0,t) \\ &\equiv f_1(t)a + f_2(t)a^\dagger, \end{aligned} \tag{16}$$

where the position operator $x$ has been written in terms of creation and annihilation operators $a^\dagger$, $a$, as

$$x = \sqrt{\hbar/2m\omega_0}(a^\dagger + a). \tag{17}$$

The time evolution operator in the interaction picture may then be written in a product form [7]

$$U_I(t) = e^{-\alpha_+(t)a^\dagger}e^{-\alpha_-(t)a}e^{-\alpha_0(t)} \tag{18}$$

with complex, time dependent functions $\alpha_i(t)$, $i = +, -, 0$. These functions obey first order differential equations which may be determined by substituting Eq. (18) into (12), subject to the initial conditions $\alpha_i(t_0) = 0$ as required by Eq. (14). Assuming an adiabatically switched monochromatic field of the form

$$E(r_0,t) = E_\omega(r_0)\cos(\omega t)e^{\eta t}, \tag{19}$$

we obtain

$$\begin{aligned} \alpha_\pm(t) = \frac{iqE_\omega}{2\hbar}\sqrt{\frac{\hbar}{2m\omega_0}}e^{\pm i\omega_0(t-t_0)}\bigg(&\frac{e^{i\omega t}}{i(\omega+\omega_0)+\eta} \\ &- \frac{e^{-i\omega t}}{i(\omega-\omega_0)-\eta}\bigg)e^{\eta t}, \end{aligned} \tag{20}$$

where $\eta$ is a small switching rate and we have chosen an initial time $t_0$ far enough into the past so that $e^{\eta t_0} \approx 0$.

The temporal evolution of any observable can be obtained from that of the creation and annihilation operators,

$$a(t) = e^{-i\omega_0(t-t_0)}[a - \alpha_+(t)], \quad a^\dagger(t) = e^{i\omega_0(t-t_0)}[a^\dagger + \alpha_-(t)]. \tag{21}$$

Thus, the average value of the position operator $\langle x(t)\rangle = \langle n|x(t)|n\rangle$ is

$$\langle x(t)\rangle = \sqrt{\hbar/2m\omega_0}[\alpha_-(t)e^{i\omega_0(t-t_0)} - \alpha_+(t)e^{-i\omega_0(t-t_0)}]. \tag{22}$$

Substitution of the above results yields the average value of the dipole moment $p(t) = q\langle x(t)\rangle$,

$$p(t) = \frac{q^2/m}{2\omega_0}\left(\frac{\omega+\omega_0}{\eta^2+(\omega+\omega_0)^2} - \frac{\omega-\omega_0}{\eta^2+(\omega-\omega_0)^2}\right)E_\omega e^{\eta t}\cos(\omega t) + \frac{q^2/m}{2\omega_0}\eta\left(\frac{1}{\eta^2+(\omega-\omega_0)^2} - \frac{1}{\eta^2+(\omega+\omega_0)^2}\right)E_\omega e^{\eta t}\sin(\omega t), \tag{23}$$

consistent in the limit $\eta \to 0$ with the linear polarizability

$$\alpha(\omega > 0) = \frac{q^2/m}{\omega_0^2-\omega^2} + i\pi\frac{q^2}{m\omega_0}\delta(\omega-\omega_0), \tag{24}$$

showing that the response of an harmonic system to a homogeneous field is exactly given by the linear perturbative result. This result has been confirmed recently employing Floquet's theory [8].

Now consider the full interaction potential (1) including the dipolar and the quadrupolar couplings to the field. Besides the terms considered above, it will contain terms of the form $-qx^2\partial_r E/2$, so that we now have both linear and quadratic terms. We assume an adiabatically switched monochromatic field as in Eq. (19), so that we write

$$V(x,t) = -q\left[xE_\omega(r_0)\cos\omega t + \tfrac{1}{2}x^2\partial_r E_\omega(r_0)\cos(\omega t-\theta_0)\right]e^{\eta t}. \tag{25}$$

The phase difference $\theta_0$ between the dipolar and quadrupolar contributions, i.e., between the field and its gradient, is expected to have the values $\pm\pi/2$ for running waves. However, the gradient of the field for a free running wave is usually very small due to the long wavelength of light. On the other hand, the interaction among neighboring molecules or between an adsorbed molecule and its image on its supporting substrate might produce a local field with a large gradient [4,9,10]. In these cases, the choice $\theta_0=0$ would be appropriate. For definitiveness, we make this choice of phase, although the results do not differ essentially from those following other choices.

We can write Eq. (25) in terms of creation and annihilation operators as a linear combination of operators from the set $\{X_n\}$, where

$$X_1 \equiv a^\dagger a, \quad X_2 \equiv (a^\dagger)^2, \quad X_3 \equiv a^\dagger,$$
$$X_4 \equiv a, \quad X_5 \equiv a^2, \quad X_6 \equiv 1. \tag{26}$$

Correspondingly, the interaction Hamiltonia is

$$H_I(t) = \sum_{n=1}^{6} f_n(t)X_n, \tag{27}$$

where the functions $f_n(t)$ are given by

$$f_1(t) = -q\left(\frac{\hbar}{2m\omega_0}\right)\partial_x E_\omega\cos(\omega t)e^{\eta t}, \tag{28}$$

$$f_2(t) = -q\left(\frac{\hbar}{2m\omega_0}\right)e^{2i\omega_0 t}\partial_x E_\omega\cos(\omega t)e^{\eta t}/2, \tag{29}$$

$$f_3(t) = -q\sqrt{\frac{\hbar}{2m\omega_0}}e^{i\omega_0 t}E_\omega\cos(\omega t)e^{\eta t}, \tag{30}$$

$$f_4(t) = -q\sqrt{\frac{\hbar}{2m\omega_0}}e^{-i\omega_0 t}E_\omega\cos(\omega t)e^{\eta t}, \tag{31}$$

$$f_5(t) = -q\left(\frac{\hbar}{2m\omega_0}\right)e^{-2i\omega_0 t}\partial_x E_\omega\cos(\omega t)e^{\eta t}/2, \tag{32}$$

$$f_6(t) = -q\left(\frac{\hbar}{2m\omega_0}\right)\partial_x E_\omega\cos(\omega t)e^{\eta t}/2. \tag{33}$$

The set $\{X_n\}$ forms a *finite Lie algebra* and thus the time evolution operator can be written *exactly* in a product form [11,12]

$$U_I(t) = e^{-\alpha_1(t)a^\dagger a}e^{-\alpha_2(t)a^{\dagger 2}}e^{-\alpha_3(t)a^\dagger}e^{-\alpha_4(t)a}e^{-\alpha_5(t)a^2}e^{-\alpha_6(t)}, \tag{34}$$

where the $\alpha_n(t)$ are complex functions to be determined. Transforming the position operator with the time evolution operator (34) yields

$$x(t) = d_1(t)a^\dagger + d_2(t)a + d_3(t), \tag{35}$$

where

$$d_1(t) = \sqrt{\frac{\hbar}{2m\omega_0}}\left[e^{\alpha_1(t)+i\omega_0(t-t_0)} - 2\alpha_2(t)e^{-\alpha_1(t)-i\omega_0(t-t_0)}\right], \tag{36}$$

$$d_2(t) = \sqrt{\frac{\hbar}{2m\omega_0}}\{2\alpha_5(t)e^{\alpha_1(t)+i\omega_0(t-t_0)} + [1-4\alpha_2(t)\alpha_5(t)]e^{-\alpha_1(t)-i\omega_0(t-t_0)}\}, \tag{37}$$

$$d_3(t) = \sqrt{\frac{\hbar}{2m\omega_0}}\{\alpha_4(t)e^{\alpha_1(t)+i\omega_0(t-t_0)} - [\alpha_3(t)+2\alpha_2(t)\alpha_4(t)]e^{-\alpha_1(t)-i\omega_0(t-t_0)}\}, \tag{38}$$

so that its average value taken between number states is

$$\langle n|x(t)|n\rangle = d_3(t). \tag{39}$$

Substitution of the ansatz given by Eq. (34) into Eq. (12) yields a set of coupled, first order, nonlinear differential equations for the complex functions $\alpha_n(t)$,

$$\partial_t\alpha_1 = \frac{i}{\hbar}(f_1 - 4f_5\alpha_2 e^{-2\alpha_1}), \tag{40}$$

$$\partial_t\alpha_2 = \frac{i}{\hbar}(f_2 e^{2\alpha_1} - 4\alpha_2^2 f_5 e^{-2\alpha_1}), \tag{41}$$

$$\partial_t\alpha_3 = \frac{i}{\hbar}(f_3 e^{\alpha_1} - 2\alpha_2 f_4 e^{-\alpha_1}), \tag{42}$$

$$\partial_t\alpha_4 = \frac{i}{\hbar}(f_4 e^{-\alpha_1} - 2\alpha_3 f_5 e^{-2\alpha_1}), \tag{43}$$

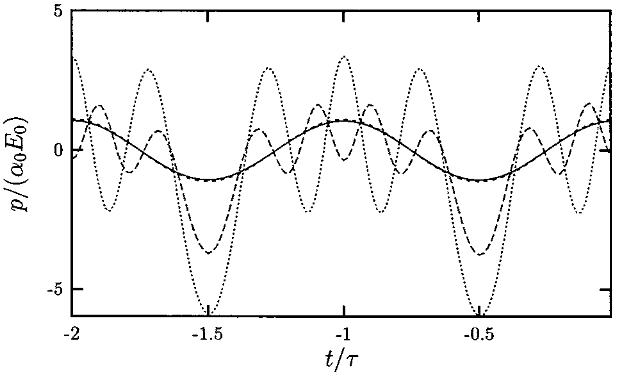

FIG. 1. Dipole moment $p(t)$ induced in a harmonic molecule by a inhomogeneous field ($\beta{=}0.05/\ell$) as a function of time $t$ for different values of the fundamental frequency $\omega$ and for different amplitudes $E_\omega$ of the driving field, $\omega{=}0.24\omega_0$ and $E_\omega{=}0.1\mathcal{E}$ (full line), $\omega{=}0.24\omega_0$ and $E_\omega{=}10\mathcal{E}$ (dashed line), $\omega{=}0.32\omega_0$ and $E_\omega{=}0.1\mathcal{E}$ (small dashed line), and $\omega{=}0.32\omega_0$ and $E_\omega{=}10\mathcal{E}$ (dotted line). The dipole moment is normalized to $\alpha_0 E_\omega$ where $\alpha_0$ is the static polarizability of the oscillator and the time is normalized by the fundamental period $\tau{=}2\pi/\omega$.

$$\partial_t \alpha_5 = \frac{i}{\hbar} f_5 e^{-2\alpha_1}, \tag{44}$$

$$\partial_t \alpha_6 = \frac{i}{\hbar}[f_6 - \alpha_3 f_4 e^{-\alpha_1} + (\alpha_3^2 - 2\alpha_2) f_5 e^{-2\alpha_1}], \tag{45}$$

with the initial conditions

$$\alpha_1(t_0) = \alpha_2(t_0) = \alpha_3(t_0) = \alpha_4(t_0) = \alpha_5(t_0) = \alpha_6(t_0) = 0. \tag{46}$$

Thus, using our algebraic approach, we have reduced the problem of calculating the quantum mechanical response of an oscillator nonlinearly driven by a time and space dependent field, to the solution of a small set of coupled nonlinear differential equations. Although we wrote Eqs. (28)–(33) for monochromatic fields, it is trivial to modify them for any time dependence, so that solving Eqs. (40)–(45) we could calculate the response to finite pulses of arbitrary shape. As expected, in the absence of a field's gradient, there are no nonlinear terms in the interaction, $f_1{=}f_2{=}f_5{=}f_6{=}0$, and the average value of the position given by Eqs. (38) and (39) coincides with the expression obtained previously [Eq. (22)].

## IV. RESULTS

In Fig. 1 we show the time-dependent dipole moment induced in a harmonic molecule by an inhomogeneous field. The inhomogeneity is characterized through the parameter $\beta \equiv \partial_r E_\omega(r_0)/E_\omega(r_0)$ to which we gave the value $\beta{=}0.05/\ell$, where $\ell = \sqrt{\hbar/m\omega_0}$ is a convenient length scale, of the order of the amplitude of the molecular vibrations in the ground state. To produce Fig. 1 we choose a small switching rate $\eta{=}2\times10^{-4}$ and an initial time $|t_0| \gg 1/\eta$ such that $e^{\eta t_0} < 10^{-5}$. We notice that for a relatively small electric field, such as $E_\omega{=}0.1\mathcal{E}$, the response of the system is dominated by its linear contribution, which we have verified agrees with Eq. (5) as expected. Here we introduced the convenient field scale $\mathcal{E}{=}\hbar\omega_0/q\ell$ which is the field that would produce an appreciable energy change, of the order of the vibration energy quantum $\hbar\omega_0$ when a charge $q$ is displaced a distance of the order of a typical vibration amplitude $\ell$. Nevertheless, due to the nonlinear character of the set of differential equations (40)–(45), the evolution contains contributions from several harmonics which become clearly discernible in Fig. 1 for large fields $E_\omega > \mathcal{E}$. For example, $p(t)$ has a large contribution from the fourth harmonic for $\omega{=}0.24\omega_0$, as $4\omega$ is nearly resonant with the natural frequency $\omega_0$. Similarly, $p(t)$ has a large contribution from the third harmonic for $\omega = 0.32$, as it is $3\omega$ which resonates with the natural frequency of the oscillator in this case.

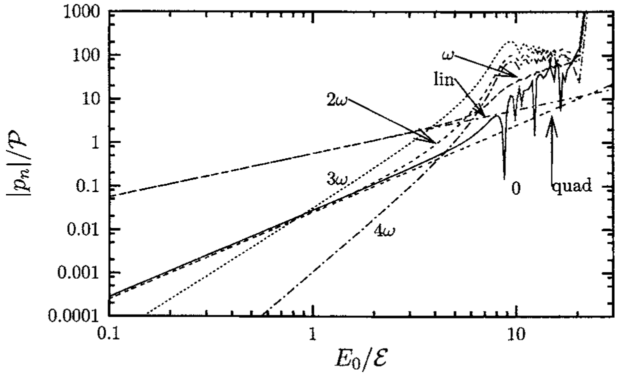

FIG. 2. First Fourier coefficients $|p_{n\omega}|$ of the dipole moment $p(t)$ induced by an adiabatically switched monochromatic field of frequency $\omega{=}0.33\omega_0$ on a harmonic molecule with resonance frequency $\omega_0$ as a function of the field amplitude $E_\omega{=}E_0$. The inhomogeneity parameter is $\beta{=}0.05/\ell$. We show results for $n{=}0$, 1, 2, 3, and 4, as well as the predictions of linear response theory [Eq. (4), labeled lin] and of the second order perturbative calculation of second harmonic generation [Eq. (8), labeled quad].

In order to analyze the contributions from different harmonics as a function of the intensity of the field, in Fig. 2 we show the magnitude $|p_{n\omega}|$ of the $n$th harmonic of the induced polarization as a function of the strength $E_\omega$ of the field, obtained through a Fourier transform of the time responses $p(t)$ such as those illustrated by Fig. 1. To calculate the Fourier coefficients we did a fast Fourier transform on the last period $t \in (-2\pi/\omega, 0)$, multiplying it by $e^{-\eta t}$ to minimize the small discontinuity due to the periodic repetition of the adiabatically switched signal. The dipole moment was normalized to $\mathcal{P}{=}\alpha_0\mathcal{E}$ and the field was normalized to $\mathcal{E}$. We notice that for small fields the $n$th harmonic is proportional to the $n$th power of the perturbing field, except for the dc signal which is proportional to $E_\omega^2$ and which describes the static distortion of the molecule due to the nonlinearity. As expected, in this case the response is dominated by the linear contribution at the fundamental frequency. Furthermore, the linear and quadratic responses are well described by the perturbative results (4) and (8). However, as the field increases, the third harmonic and afterwards the second harmonic acquire more weight and become larger than the response at the fundamental frequency. In this case, the third harmonic dominates as its frequency is relatively close to the natural

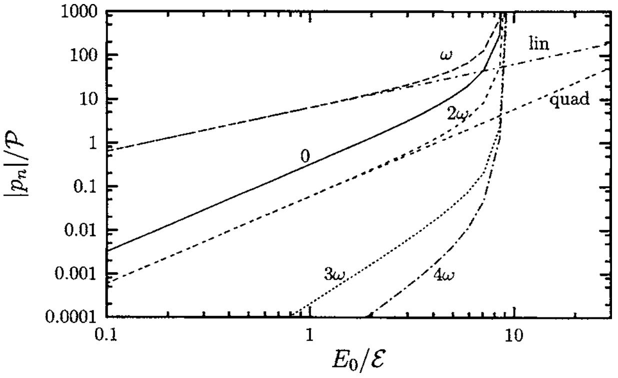

FIG. 3. First Fourier coefficients $|p_{n\omega}|$ of the dipole moment $p(t)$ induced by an adiabatically switched monochromatic field, as in Fig. 2, but for a fundamental frequency $\omega=0.96\omega_0$.

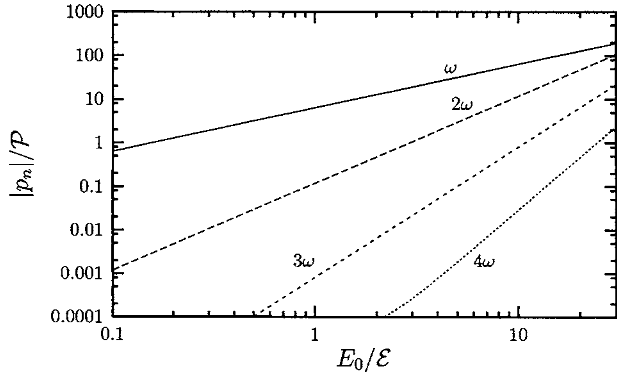

FIG. 4. First Fourier coefficients $|p_{n\omega}|$ of the dipole moment $p(t)$ induced by an adiabatically switched monochromatic field, as in Fig. 2, but for a fundamental frequency $\omega=0.96\omega_0$ and for a driving field $E\propto e^{-i\omega t}$ instead of $E\propto\cos\omega t$.

frequency $\omega_0$ of the oscillator. For fields $E_\omega\approx\mathcal{E}$ the second harmonic response starts to deviate noticeably from the simple quadratic response, and for slightly larger fields, $E_\omega\approx 4\mathcal{E}$, all of the harmonics deviate from their simple power law dependences $p_{n\omega}\propto E_\omega^n$. At $E_\omega\approx 10\mathcal{E}$, all of the harmonics display strong oscillations as a function of the field amplitude, most notably, the dc distortion. For $E_\omega\approx 20\mathcal{E}$ the amplitude of the oscillations *explodes* and the molecule essentially breaks up. The reason for this latter behavior is that the quadrupolar contribution to the Hamiltonian (1) becomes larger than the unperturbed Hamiltonian when $|\beta\ell^2 qE_\omega|>\hbar\omega_0$, being both of them quadratic in the coordinate $x$. This condition can be rewritten as $E_\omega/\mathcal{E}>1/\beta\ell$. For Fig. 2 this threshold lies at $1/\beta\ell=20$. Notice that $|p_{n\omega}/\mathcal{P}|=|x_{n\omega}/\ell|$ where $x_{n\omega}$ is the Fourier amplitude of the displacement $\langle x(t)\rangle$ corresponding to frequency $n\omega$ and that $\ell$ is of order $10^{-2}$ -$10^{-1}$ of an atomic distance, so that it is unlikely that a real molecule could still be considered harmonic for distortions larger than $\sim 10\ell$, in which case, other nonlinearities may be expected to become important, as well as higher order multipolar contributions to the interaction energy (1).

Besides calculating the dipolar response of the system, the algebraic method allows a calculation of the occupancy of the oscillator states for different field strengths. Curiously, the population is already strongly redistributed for fields that are still so small that the lowest order perturbative results for $p_{n\omega}$ hold. We believe this is a peculiarity of the harmonic oscillator, with its infinite number of evenly spaced energy levels. For anharmonic systems with a finite number of unevenly spaced levels, we expect that a strong population redistribution would necessarily be accompanied by strong corrections to the perturbative response. Thus, we expect a lower threshold for nonperturbative behavior in anharmonic systems [13].

We have obtained a similar behavior for other frequencies which are close to subharmonics of the resonance frequency $\omega_0$. In Fig. 3 we present the results corresponding to the case when the fundamental frequency of the perturbing field is close to resonance. In this case, the response at the fundamental frequency is stronger than in the previous case and is stronger than the response at the different harmonics. However, for fields $E_\omega\approx\mathcal{E}$ the response starts deviating from the perturbative power law prediction $p_{n\omega}\propto E_\omega^n$ and all of the coefficients $|p_{n\omega}|$ approach one another. In this case their apparent divergence starts earlier, at $E_\omega\approx 10\mathcal{E}$.

The reason for the power law dependence for small fields may be understood from perturbation theory, as the lowest order process which can yield an oscillation at frequency $n\omega$ is the (virtual) absorption of $n$ photons of frequency $\omega$. Within the semiclassical approach we employed, in which the field was treated as a classical entity, we can restate this observation noting that $E^n\propto E_\omega^n\cos^n\omega t$ is the lowest order term which contains the frequency $n\omega$. However, terms of the form $E^{n+2m}$, where $m$ is any positive integer, also contain the frequency $n\omega$. They correspond to absorption of $n+m$ photons intermingled with the stimulated emission of $m$ photons all of frequency $\omega$, leaving the system oscillating with an energy $[(n+m)-m]\hbar\omega=n\hbar\omega$ which could be emitted as a single photon of frequency $n\omega$. Thus, there are higher order corrections to $p_{n\omega}\propto E_\omega^{n+2m}$ which become important for large enough fields. Their calculation would require higher order terms within a perturbative approach. Our exact calculation includes them automatically.

To verify that the deviation from $p_{n\omega}\propto E_\omega^n$ in our calculations above is not an artifact due to lack of numerical accuracy, in Fig. 4 we present the results calculated for a complex external field $E\propto e^{-i\omega t}$ instead of a field $E\propto\cos\omega t$ as in Eq. (25). In this case, the field has only a positive frequency $\omega$ instead of having both positive and negative frequencies $\pm\omega$. Thus, each power of the field $E^n$ contains only the frequency $n\omega$ and we expect there is a one to one mapping between the $n$th harmonic and a power dependence $E_\omega^n$. This is confirmed by our calculations.

## V. CONCLUSIONS

In this work we have developed an algebraic approach which permits the calculation of the dipole moment nonlinearly induced by a space and time dependent field acting on a harmonic molecule. The origin of the nonlinearity is the quadrupolar coupling between the system and the field, which involves the space derivatives of the field and which converts the problem of a forced harmonic oscillator into the problem of a forced parametric oscillator. The algebraic structure of the perturbed Hamiltonian corresponds to a finite Lie algebra which yields an *exact* solution in terms of a set of functions which may be obtained by solving numerically a small system of coupled nonlinear differential equations. We obtained the polarization $p(t)$ induced by an adiabatically switched monochromatic field and analyzed its Fourier components $p_{n\omega}$. We verified that for a small enough field amplitude $E_\omega \ll \mathcal{E}$, $p_0 \propto E_\omega^2$, and $p_{n\omega} \propto E_\omega^n$, $(n=1,2,\ldots)$ as expected from perturbation theory. We also verified that the responses at the fundamental and the second harmonic frequencies agree with the linear polarizability and the quadratical hyperpolarizability previously reported [3,5]. However, at high enough fields, of the order of $\mathcal{E}$, noticeable deviations from these power laws are observed. Whenever the driving frequency is close to a subharmonic of the resonance frequency $(\omega=\omega_0/n)$, then the high field signal is dominated by its $n$th harmonic component. At very high fields $E_\omega \approx \mathcal{E}/\beta\ell$ the nonlinear coupling to the field may overwhelm the harmonic restoring force of the molecules which therefore is broken up.

In this calculation we introduced a length scale $\ell$ which is typically of the order of a fraction of an atomic unit. For an $H_2$ molecule, $\ell \approx 0.2$ Å and decreases as the inverse square root of the reduced mass. We characterized the gradient of the field by the quantity $\beta \equiv \partial_r E_\omega(r_\omega)/E_0(r_0)$. Thus, for a free wave interacting with an isolated molecule we might expect $\beta\ell$, and thus, the nonlinearity, to be a very small quantity. However, for a molecule adsorbed on a surface or a molecule interacting with nearby neighbors, the *local field* that actually polarizes the molecule might have a longitudinal character and may be a few orders of magnitude larger than that for a free wave. Thus, the values $\beta \approx 0.05/\ell$ that we employed in our calculations and even larger values may be attainable. We also introduced a field scale, namely, $\mathcal{E}=\hbar\omega_0/q\ell$. Typical values for this field are between one and two orders of magnitude smaller than the atomic field scale $e/a_B^2$, with $e$ the electronic charge and $a_B$ Bohr's radius. Thus, fields of order $\mathcal{E}$ are also attainable with currently available light sources.

There are other nonperturbative approaches for the calculation of the response of molecular systems to applied fields. The most common is Floquet theory [14], which allows calculations for time-periodic fields and to pulses with relatively slowly varying amplitudes and frequencies [15]. Floquet theory has been employed to calculate transition probabilities for strong fields of different frequencies [14], to optimize pulses in order to perform efficient population transfer [15], to study Berry phases [16], field-free orientation of molecules [17], conservation of molecular alignment for cyclic rotational wave packets in periodic pulse trains [18], etc. Unfortunately, the mathematical basis of Floquet theory is most appropriate for the study of systems with a finite number of states [19]. There has been some progress in applying Floquet theory to systems with infinite Hilbert spaces [20], but only a few to the harmonic oscillator [8,21]. It would be interesting to interpret our results above in terms of the behavior of the Floquet dressed states, to follow the Floquet dressed energies as the frequency, the field intensity, and the field gradient vary, to identify their avoided crossing and to ascertain under which conditions is the adiabatic approximation useful. In principle, a Floquet calculation requires solving a Schrödinger-type equation in an infinitely extended Hilbert space of time-periodic wave functions. At this time there are no calculations within the Floquet scheme for a harmonic system forced both dipolarly by an external field and quadrupolarly by its gradient [8]. On the other hand, our algebraic calculation requires only the solution of a small set of differential equations.

We performed calculations for monochromatic fields in order to compare our results with previously developed perturbative calculations [3,5]. However, our formalism, summarized by Eqs. (36)–(45) is even better suited for pulsed fields, as the inhomogeneous part of Eqs. (40)–(45) would then have a finite support. In the present work we focused our attention in harmonic molecules. Our results display nonperturbative behavior at fields so large that the harmonic approximation for describing the oscillation of a molecule may be questionable. Thus, it will be important to extend our calculations to anharmonic oscillators. To that end, our formalism may be generalized [13] to other potentials which have proved amenable to an algebraic treatment [22–25].

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