Non Linear Response of a Harmonic Diatomic Molecule: an Exact Algebraic Approach

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Abstract. Even harmonic molecules display a nonlinear behavior when driven by an inhomogeneous field. Here we present the response of a single harmonic molecule 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 of the field and compare the results with those of the first and second order perturbation theory.

1. Introduction

Even though the harmonic oscillator is the prototype of a linear system, its response to inhomogeneous time dependent fields contains nonlinear contributions. The study of the optical linear and nonlinear responses of harmonic systems to periodic electromagnetic fields has been done both with classical [2–4] 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 and at its second harmonic $2\omega$. Here we present an algebraic treatment to study nonperturbatively the time evolution of a quantum mechanical harmonic system forced by a time and space dependent electric field.

Consider a dynamic charge $q$ with mass $m$ displaced a distance $x$ from its equilibrium position $r_0$, to which it is bound by a harmonic force with resonant frequency $\omega_0$ driven by a classical electric field $E(r,t)$. For simplicity, we assume that the system is one-dimensional. The interaction potential is then, up to second order in the displacement $x$:

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

(1)

the first term is the usual dipolar interaction while the second term is the quadrupolar interaction. The classical equation of motion is:

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

(2)

where the field

$$E(r,t) \simeq E(r_0,t) + x\partial_r E(r_0,t)$$

Most of the information presented in this contribution has already been published in Ref. [1].
is evaluated at the position of the charge \( r = r_0 + x \). Notice that the terms linear in the displacement are time dependent, thus the spatial dependence of the field transforms the harmonic oscillator into a forced parametric oscillator. Notice also that the sign of the contribution arising from the inhomogeneity of the field has a sign opposite to that of the harmonic oscillator contribution, then there will be a competition between the confining term and the quadrupolar term. Now assume a monochromatic field

\[
E(r, t) = Re[E_\omega(r)e^{-i\omega t}]
\]

Using Ref. [2] we see that the induced dipole moment is given by

\[
p^{(1)}(t) = Re(p_\omega e^{i\omega t})
\]

with

\[
p_\omega = qx_\omega = \alpha(\omega)E_\omega(r_0)
\]

to first order in the driving field, and the linear polarizability is:

\[
\alpha(\omega) = \frac{q^2/m}{\omega_0^2 - \omega^2}.
\]

The equation of motion at \( 2\omega \) is:

\[
-m(2\omega)^2 x_{2\omega} = -m\omega_0^2 x_{2\omega} + qx_\omega \partial_t E_\omega(r_0)
\]

whose solution is:

\[
x_{2\omega} = \frac{1}{2q^2} \alpha(\omega) \alpha(2\omega) [\partial_t E_\omega^2(r_0)].
\]

and the second order dipole moment at \( 2\omega \) is, therefore,

\[
p_{2\omega} = \frac{1}{2q} \alpha(\omega) \alpha(2\omega) [\partial_t E_\omega^2(r_0)].
\]

As mentioned before, the nonlinear response derived above classically using a perturbative solution, coincides with the quantum mechanical expressions obtained with perturbation theory.

2. Algebraic approach: harmonic oscillator

Here we present a Lie algebraic approach that yields the exact solution to the problem [6–8]. First we write the system’s Hamiltonian as:

\[
H = H_0 + V,
\]

where \( H_0 \) is the unperturbed harmonic oscillator Hamiltonian and \( V \) is the interaction given in Eq. 1. We go into the interaction picture where the time evolution operator satisfies the equation:

\[
i\hbar \partial_t U_I(t, t_0) = H_I(t)U_I(t, t_0), \quad U_I(t_0, t_0) = 1
\]

with the interaction picture Hamiltonian given as:

\[
H_I(t) = U_0^\dagger(t, t_0) V U_0(t, t_0),
\]

and where \( U_0(t, t_0) \) is the free time evolution operator. We have chosen \( t = t_0 \) as our reference time and assumed that the interaction is negligible for times \( t < t_0 \).

The interaction picture Hamiltonian is then:

\[
H_I(t) = -q E(r_0, t) \sqrt{\frac{\hbar}{2m\omega_0}} (\hat{a} e^{-i\omega_0(t-t_0)} + \hat{a}^\dagger e^{i\omega_0(t-t_0)})
\]

\[
+ \frac{q}{2} \partial_t E(r_0, t) \left( \frac{\hbar}{2m\omega_0} \right) (\hat{a}^2 e^{-2i\omega_0(t-t_0)} + 2\hat{a}^\dagger \hat{a} + 1 + \hat{a}^\dagger \hat{a}^\dagger e^{2i\omega_0(t-t_0)})
\]
which can be written as:

\[ H_I(t) = \sum_{n=1}^{6} F_n(t) \hat{X}_n \]

with known, time dependent functions \( F_n(t) \) and where the operators \( \hat{X}_n \) are given in the Schrödinger picture. Since the set of operators in \( H_I(t) \) is closed under commutation, we can use the Wei-Norman Theorem \([6]\) and write the exact time evolution operator as:

\[ U_I(t) = \prod_{n=1}^{6} e^{\alpha_n(t) \hat{X}_n} \]

For simplicity, we choose normal ordering in the product of exponentials, that is: \( \hat{X}_1 = \hat{n}, \hat{X}_2 = \hat{a}^{\dagger 2}, \hat{X}_3 = \hat{a}^{\dagger}, \hat{X}_4 = \hat{a}, \hat{X}_5 = \hat{a}^2 \) and \( \hat{X}_6 = 1 \). After substitution of Eq. 10 into Eq. 7 we get the following set of first order, coupled, nonlinear differential equations for the complex functions \( \alpha_n(t) \) which is generally solved by numerical means:

\[ \partial_t \alpha_1 = \frac{i}{\hbar} (F_1 - 4F_5 \alpha_2 e^{-2\alpha_1}) \]

\[ \partial_t \alpha_2 = \frac{i}{\hbar} (F_2 e^{2\alpha_1} - 4F_5 \alpha_2 e^{-2\alpha_1}) \]

\[ \partial_t \alpha_3 = \frac{i}{\hbar} (F_3 e^{\alpha_1} - 2F_5 \alpha_3 e^{-\alpha_1}) \]

\[ \partial_t \alpha_4 = \frac{i}{\hbar} (F_4 e^{-\alpha_1} - 2F_5 \alpha_3 e^{-2\alpha_1}) \]

\[ \partial_t \alpha_5 = \frac{i}{\hbar} F_5 e^{-2\alpha_1} \]

\[ \partial_t \alpha_6 = \frac{i}{\hbar} (F_6 - F_4 \alpha_3 e^{-\alpha_1} + (\alpha_3^2 - 2\alpha_2) F_5 e^{-2\alpha_1}) \]

with initial conditions \( \alpha_i(t_0) = 0, i = 1, \ldots, 6 \).

The temporal evolution of any observable can be obtained from the creation, annihilation operators in the Heisenberg picture, these are given by:

\[ \hat{a}(t) = U_I(t)^\dagger U_0(t)^\dagger \hat{a} U_0(t) U_I(t) = t_{11}(t) \hat{a} + t_{12}(t) \hat{a}^\dagger + t_{13}(t) \]

\[ \hat{a}^\dagger(t) = U_I(t)^\dagger U_0(t)^\dagger \hat{a}^\dagger U_0(t) U_I(t) = t_{21}(t) \hat{a} + t_{22}(t) \hat{a}^\dagger + t_{23}(t) \]

where the functions \( t_{ij}(t) \) are known functions of the \( \alpha_n(t) \). The transformation amounts to a rotation due to the presence of the quadratic operators and a displacement due to the linear operators in \( H_I(t) \).

The average value of the displacement coordinate taken between number states is:

\[ \langle n|\hat{x}(t)|n\rangle = \sqrt{\frac{\hbar}{2m\omega_0}} (t_{13}(t) + t_{23}(t)) \]

Using an algebraic approach we have reduced the problem of calculating the quantum mechanical response of a nonlinearly driven harmonic diatomic molecule forced by a time and space dependent field, to the solution of a small set of coupled nonlinear ordinary differential equations.
3. Numerical results

In order to be specific we now consider an adiabatically switched monochromatic field of the form

$$E(r_0, t) = E_\omega(r_0) \cos(\omega t) e^{\eta t}$$  \hspace{1cm} (20)

where $\eta$ is a small switching rate and the initial time is such that $e^{\eta t_0} \ll 1$. In Fig. 1 we show the time-dependent dipole moment induced by an inhomogeneous field. The inhomogeneity is characterized by the parameter $\beta \equiv \partial_r E_\omega(r_0)/E_\omega(r_0)$ which we set as $\beta = 0.05/l$ where $l = \sqrt{\hbar/m\omega_0}$ is a length scale, of the order of the amplitude of a molecular vibration in the ground state. We also introduce a field scale $\mathcal{E} = \hbar\omega_0/ql$ which is the field that would produce an appreciable energy change, of the order of a vibrational quantum when a charge $q$ is displaced a distance of the order of $l$. To produce Fig. 1 we have chosen $\eta = 2 \times 10^{-4}$ and an initial time $|t_0| \gg 1/\eta$ such that $e^{\eta t_0} \leq 10^{-5}$. In this figure we have also set $\omega = 0.24\omega_0$ so that the fourth harmonic is nearly resonant with the natural frequency ($4\omega \simeq \omega_0$) and we consider several values for the field intensity. For a small value of the field intensity $E_\omega = 0.1\mathcal{E}$ the response of the system is dominated by the linear contribution (line with points), response that coincides with that of first order perturbation theory. When we increase the field intensity to $E_\omega = 5\mathcal{E}$ the nonlinear contributions start to play a role as can be seen from the figure (points). Finally, when the intensity of the field is large $E_\omega = 10\mathcal{E}$ the response is dominated by the fourth harmonic (full line). This conduct cannot be obtained from a perturbative treatment.

In Fig. 2 we have chosen $\omega = 0.325\omega_0$ so that the third harmonic is nearly resonant with the natural frequency ($3\omega \simeq \omega_0$) and we consider several values for the field intensity. For a small
value of the field intensity $E_{\omega} = 0.1\mathcal{E}$ the response of the system is again dominated by the linear contribution (line with cruces). When we increase the field intensity to $E_{\omega} = 5\mathcal{E}$ the nonlinear effects are evident and we can see the appearance of structure at $\omega/3$ (line with points) and at even larger values of the field intensity $E_{\omega} = 8\mathcal{E}$ the structure is much more evident with a much larger amplitude.

4. Discussion

Here we have presented an algebraic approach which allows the calculation of the dipole moment nonlinearity induced by a time and space dependent electric field acting upon a harmonic diatomic molecule. The nonlinearity is due to the quadrupolar coupling between the system and the field transforming the problem of a forced harmonic diatomic into that of a forced parametric one. The method used here does not depend on the specific form of the temporal dependence of the field, however, we specified its functional form as adiabatically switched monochromatic in order to analyze the Fourier components of the polarization. We found that, for small field amplitudes $E_{\omega} \ll \mathcal{E}$ the $n'th$ order polarization $p_{n\omega} \propto \alpha E_{\omega}^n$ as expected from perturbation theory. At high enough fields this power law is no longer valid. When the field’s frequency is close to a subharmonic of the resonance frequency ($\omega \simeq \omega_0/n$) the response is dominated by its $n'th$ harmonic component. Since the quadrupolar contribution has an opposite sign to the harmonic one, for large enough fields the nonlinear coupling may overwhelm the restoring force causing the braking of the molecule.

We introduced a length unit $l$ of the order of a fraction of an atomic unit and the gradient of
the field was characterized by the parameter $\beta$; for an $H_2$ molecule $l \approx 2\text{Å}$. For a free wave interacting with an isolated molecule we would expect the nonlinearity contribution of the order of $\beta l$, thus, a very small quantity. However, for a molecule adsorbed on a surface or interacting with nearby neighbors, the local field that 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 used in this work for $\beta l = 0.05$ might be attainable. There are other nonperturbative approaches to analyze the response of a molecular system to an applied field; the most common being Floquet theory [9], which allows calculations for time-periodic fields.

References

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