

# Theory and simulations of the interactions of intense radiation with atoms, molecules, and solids

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## Abstract

We report time-dependent simulations of the evolution of atoms, molecules, and solids in the presence of intense electromagnetic radiation using the density functional theory. In the case of the ionic degrees of freedom we find that selective breaking of strong bonds may be possible at off-resonant infrared frequencies by a novel “concerted kick” mechanism. In the case of the electron response we find the following: free atoms and ions under intense infrared light respond with high harmonics in the X-ray regime; for a free molecule ( $\text{Si}_2$ ), we predict an unusual third harmonic response to a UV pulse centered at a frequency equal to the primary electronic excitation of the molecule; for a semiconductor (Si), we find several odd harmonics in response to a continuous wave of subgap infrared radiation. Prospects for future calculations are discussed.

## 1. INTRODUCTION

Density functional theory, formulated by Kohn and coworkers in the 1960's (Hohenberg & Kohn 1964; Kohn & Sham 1965), has proved to be a very powerful method to treat ground-state properties of many electron systems, especially molecules and solids. In this theory the properties of the system are determined entirely by the ground-state electron density, which is expressed in terms of one-electron wave functions that are eigensolutions of an effective one-electron Hamiltonian. In 1985, Car and Parrinello (1985) introduced a ground breaking innovation that allows dynamical simulations of the evolution of polyatomic systems. In these simulations, there are no time-dependent external forces so that the conditions of validity of the original density functional theory are satisfied. At each time step, the electrons are maintained in their instantaneous ground state and forces on the ions are calculated using the Hellmann–Feynman theorem (Payne *et al.*, 1992).

The presence of an external time-dependent potential, such as electromagnetic radiation, calls for the time-dependent density functional theory. A version of such theory was developed and used in the 1980's to describe the *linear* response of the electron system, assuming stationary nuclei (Stott & Zaremba, 1980; Zangwill & Soven, 1980; Levine & Soven, 1984). A generalization of the original density-

functional theory to describe the full *nonlinear* response of the electron system was developed by Runge and Gross (1984). In this theory, the properties of the system are again determined by the electron density, which evolves with time. The density is expressed in terms of one-electron wave functions that satisfy a time-dependent one-electron Schrödinger equation. If the system is started in its ground state and the radiation is turned on either in continuous wave or pulse form, the one-electron wave functions evolve gradually.

The Runge–Gross density functional theory for electrons can be extended to include the response of the ions to the external time-dependent electromagnetic field. This is in effect Car–Parrinello dynamics combined with electron dynamics in the presence of external time-dependent fields, fully nonlinear. The only missing ingredient for such a formulation is a Hellmann–Feynman theorem that allows the definition of forces in the presence of time-dependent external potential. Such a theorem was recently developed by Di Ventura and Pantelides (2000).

It is important to note that, unlike other formulations of the many-electron problem, density functional theory does not have “excited” one-electron states. The only meaningful one-electron wave functions are those describing the electrons, in terms of which one constructs the electron density. Electron excitations manifest themselves through the evolution of the occupied one-electron wave functions. For example, at any time step, one can project the instantaneous wave functions onto the corresponding ground state wave functions and thus determine what fraction of the total elec-

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tron density is in “excited states.” One can also project the instantaneous wave functions on the complete one-electron spectrum of the ground-state effective Hamiltonian.

There have been very few applications of the nonlinear time-dependent density functional theory to free atoms (Gross *et al.*, 1996). Most other nonlinear theoretical calculations of light interacting with atoms and molecules use the time-dependent Hartree–Fock formulation or semiempirical schemes (Kulander, 1991; Bandrauk, 1994; Giusti-Suzor *et al.*, 1995). We have launched a systematic development of computer codes to implement nonlinear time-dependent density functional theory to atoms, molecules, and solids and study their response in the presence of intense electromagnetic radiation. In this paper we report initial representative results.

In the very first application (Ferconi *et al.*, 1999), we studied the effect of intense infrared light on a molecule (HCN) with a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) so that electronic excitations would require a high-order multiphoton process. We could then use an adiabatic approximation whereby we could maintain the electrons in their instantaneous ground state. In this approximation, time-dependent density functional theory reduces to the conventional ground-state density functional theory except for the fact that the external potential is time-dependent. We will give a brief account of these results in Section 2.

We have since developed a fully time-dependent code and have studied the response of the electron systems in free atoms, molecules, and solids. We describe the initial results in Section 3. We summarize and discuss future prospects in Section 4.

## 2. SELECTIVE BOND BREAKING

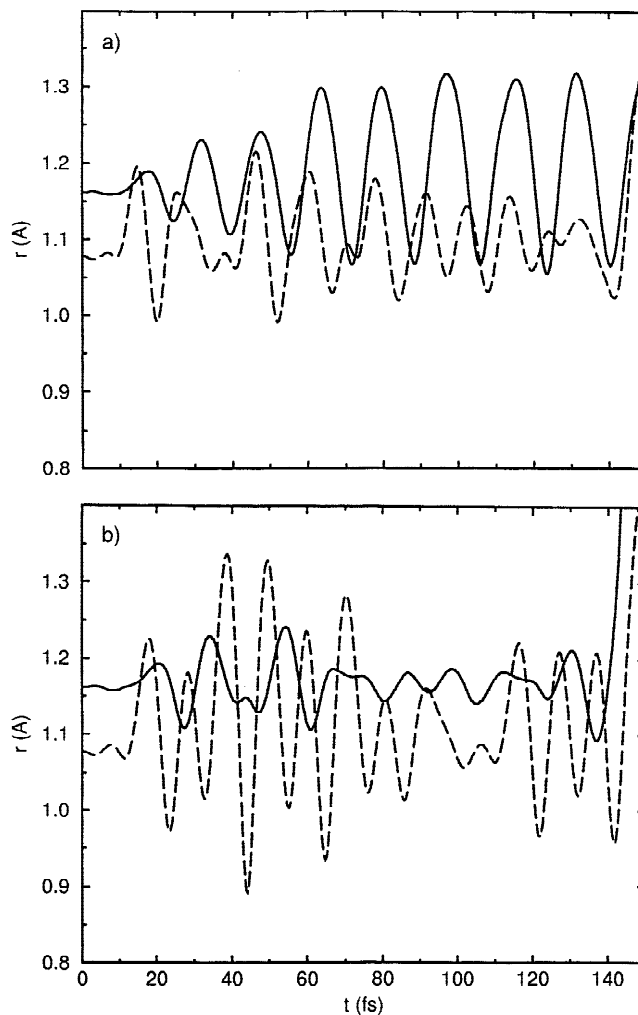
Infrared light couples with the vibrational modes of a molecule. It is reasonable to expect, therefore, that intense infrared light at a frequency that is resonant with the vibrational stretch mode of a particular bond might selectively break that bond. Such an effect would have important implications for selective, nonthermal processing. Unfortunately, experiments aiming to demonstrate selective bond-breaking over the years have failed to demonstrate selectivity. It seems that the weaker bonds break first, even if one targets the stretch modes of the strong bonds. The phenomenon has been attributed to rapid distribution of the absorbed energy to the entire molecule as if it had been supplied by thermal means.

Earlier theoretical work on the dynamics of molecules has been based mostly on potential energy surfaces of either the ground or excited configurations and on empirical models of how the electrical dipole of the molecule depends on interatomic distances in the absence of radiation (Heather & Metiu, 1984; Kulander, 1991; Bandrauk 1994; Botina *et al.*, 1995; Giusti-Suzor *et al.*, 1995). Such assumptions are expected to be valid for weak or moderate field intensities, but should break down for higher intensities when the electron

density and bonding potentials are altered significantly by the time-dependent radiation field.

Our calculations employed a supercell, placing a molecule in a box with periodic boundary conditions. The external field is effectively constant over the supercell so that the corresponding potential is linear in  $x$ . We used a periodic saw-tooth potential with the correct linear behavior in the region of the molecule. The effect of the extraneous “teeth” at the box boundaries was carefully monitored and controlled. We used Vanderbilt’s ultrasoft pseudopotentials, a plane-wave basis set with an energy cutoff of 25 Ry and conjugate gradients for the determination of the instantaneous ground-state electron density (Car & Parrinello, 1985; Payne *et al.*, 1992).

For moderate electric fields, the molecule vibrates in linear response, following the field. For intense fields, however, the response is highly nonlinear. It is shown in Figure 1 at two different frequencies: (a) resonant with the stretch mode of the strong C–N bond and (b) an off-resonant fre-



**Fig. 1.** Variation of the C–N bond length (solid) and the C–H bond length (dashed) in an HCN molecule in the presence of high-intensity infrared light a) at the frequency of the C–N bond, b) at an off-resonance frequency.

quency. We note that the phases of the C–H and C–N vibrations are not correlated. At the resonant frequency, the C–N amplitude rises quickly to a large value and remains fairly constant, following a nearly harmonic pattern. A break of the C–N bond does not, therefore, appear likely. At the same time, the C–H motion is not harmonic and has a relatively small amplitude. Overall, the system is not absorbing energy monotonically as it does in the weak-field case. Examination of the electron density of the molecule revealed that it changes significantly so that the effective “spring constant” varies with time. The ground-state normal modes are no longer relevant at intense radiation fields.

The response of the molecule at the nonresonant frequency (56.76 THz) reveals no harmonic behavior for either the C–H or the C–N motions. Again energy is not absorbed monotonically. A break occurs after about 140 fs. The break is shown in an expanded scale in Figure 2. Careful examination of the relative motions just before the break reveals that the N atom is rebounding from its closest proximity to the C atom while the H atom is rebounding from its farthest distance from the C atom. We called the process a “concerted kick”: as the N atom is moving away from the C atom, the H atom is giving it a kick from the back side. Unfortunately the length of the computations does not allow systematic studies of the effect to extract a rate. We therefore present this result as a possible mechanism for selective bond breaking.

We were able to address the validity of the adiabatic approximation by using fully time-dependent codes which we will describe in more detail in the next section. In Figure 3 we show the response of the electron system of HCN at the equilibrium bond length at two different intensities: corresponding to a field amplitude of 2 V/Å and 4 V/Å. The latter is the intensity at which the C–N bond break occurred. We see that at the lower intensity some structure develops at

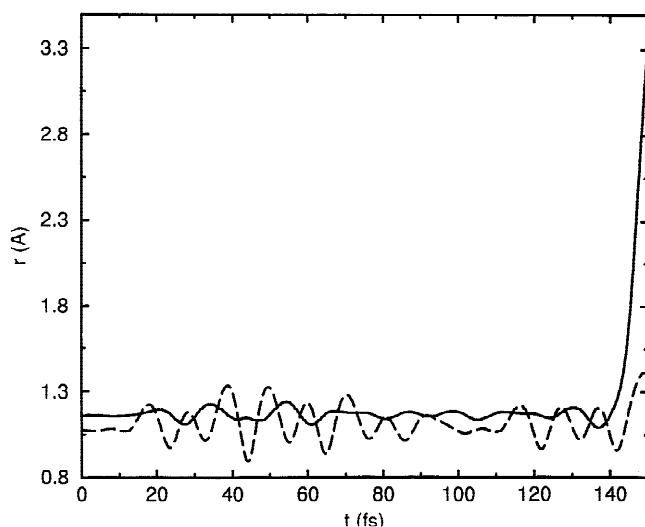


Fig. 2. Expanded version of Fig. 1b showing the break of the C–N bond that occurs at about 140 fs.

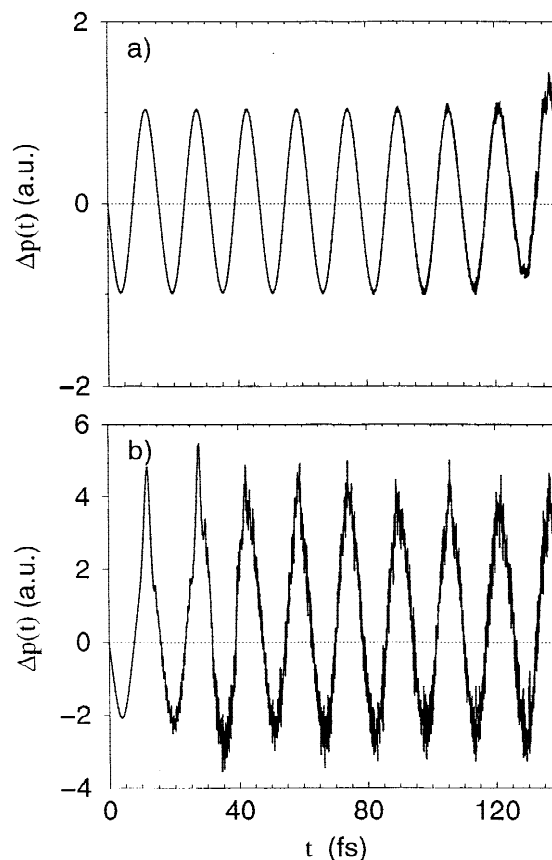


Fig. 3. Variation of the electrical dipole of HCN in the presence of intense infrared light with the nuclei held frozen at the equilibrium positions a) at 4 V/Å and b) 8 V/Å. The high-frequency structure is high-harmonic response.

about 120 fs. At the higher intensity the superposed structure develops much earlier. Careful analysis of the structure and convergence tests reveal that it corresponds to high harmonics. It constitutes a small effect on the overall response of the molecule suggesting that the adiabatic approximation is in fact valid. We will discuss the high-harmonic response further in the next section.

### 3. NONLINEAR ELECTRON RESPONSE

We have implemented time-dependent density functional theory (Runge & Gross, 1984) in a general code that is capable of handling the effect of an external time-dependent potential (e.g. electromagnetic radiation) for an atom, molecule, or solid. The core of the program is the time-dependent Schrödinger equation

$$i \frac{\partial \Phi_\alpha(\mathbf{x}, t)}{\partial t} = H(t) \Phi_\alpha(\mathbf{x}, t) \quad (1)$$

where we use atomic units and  $H(t) = H_0(t) + H_I(t)$ . Here,  $H_0(t)$  is the standard effective one-electron Hamiltonian of density functional theory except that the electron density  $\rho(r, t)$  is now time-dependent. By using the local-density

approximation for the exchange-correlation potential with a time-dependent density we are adopting an adiabatic approximation. The  $H_I(t)$  is the interaction term which, in the dipole approximation for electromagnetic radiation, is normally given by the Lorentz gauge, namely,

$$V(\mathbf{x}, t) = -\mathbf{x} \cdot \mathbf{E}_0 \sin \omega t. \quad (2)$$

This form can be used for atoms and molecules in a large supercell with periodic conditions. It produces a saw-tooth function but the atom or molecule is in the linear region. This approach was used successfully in the calculations discussed in the previous sections and in calculations of electron response in atoms and molecules to be discussed below. For solids, this form cannot be used. We, therefore, adopted an alternative gauge where the scalar potential is zero and the electric field is given in terms of the vector potential (Coulomb gauge), namely

$$\mathbf{E}(\mathbf{x}) = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}. \quad (3)$$

As is standard in density functional theory, the electron density is given by

$$\rho(\mathbf{x}, t) = \sum_{\alpha=occ.} |\Phi_{\alpha}(\mathbf{x}, t)|^2 \quad (4)$$

where *occ.* stands for ‘‘occupied wave functions.’’ It should be emphasized that this theory has only occupied one-electron wave functions and that ‘‘excitations’’ occur as the occupied wave functions evolve.

The time-stepping of Eq. (1) is done by applying the evolution operator  $U(t, t + \delta t)$  to the one-electron wave functions:

$$\begin{aligned} \Phi_{\alpha}(t + \delta t) &= U(t, t + \delta t) \Phi_{\alpha}(t) \\ &= T_t \exp \left[ -i \int_t^{t+\delta t} dt' H(t') \right] \Phi_{\alpha}(t) \end{aligned} \quad (5)$$

where  $T_t$  is the time-order operator and  $\delta t$  is the time step. For numerical calculations, we express the evolution operator in terms of a power series expansion, namely,

$$U(t, t + \delta t) = \sum_{n=0}^N \frac{(-i)^n}{n!} H^n(t) \delta t^n. \quad (6)$$

The time step  $\delta t$  and the cutoff  $N$  are chosen to ensure convergence. We found typical values of  $N$  to be  $\sim 12$  and  $\delta t \sim 5 \cdot 10^{-4}$  fs. Convergence is monitored through the norm of the wave function.

Initial calculations of nonlinear response of electrons to electromagnetic radiation were carried out for atoms, molecules, and solids without allowing the nuclei to move. The results of these calculations follow.

### 3.1. Atoms

We studied rare-gas atoms in pulsed intense infrared light. In Figure 4 we show the electrical dipole of an Ar atom in a pulse of two different intensities, corresponding to  $E_0=4$  and  $8 \text{ eV/\AA}$ . In the weaker intensity, the dipole follows the electric field halfway through the pulse (linear regime) and then starts exhibiting higher harmonics. In the higher intensity, the higher harmonics appear earlier. In Figure 5, we show the Fourier transform of the electrical dipole (power spectrum) showing the frequencies contained in the response. We see a sequence of odd harmonics with diminishing contribution. The calculation does not include spontaneous emission, but classical electrodynamics tells us that oscillating charges will emit electromagnetic radiation at the frequency of oscillation. The calculations, therefore, show that the atom will emit light in a large number of odd harmonics, as observed experimentally (Schnürer *et al.*, 1997). In Figure 6, we show the actual power output relative to the input power, showing that the emission intensity drops quite slowly as a function of frequency. The rate of intensity drop-off is a function of the intensity of the pulse. These results are consistent with experimental observations of X-ray emission.

In the simulations we did not record any ionization events. We have not pursued investigations of ionization because of limitations of density functional theory. We investigated the accuracy of the numerical calculations for the harmonic response and have shown that the calculations can be extremely accurate if the time step and convergence are tight enough. In Figure 7 we show the response of a  $\text{Be}^{++}$  ion (equivalent to a He atom) to a continuous-wave infrared light. The odd harmonics are seen to be extremely well defined and sharp. The even harmonics are zero. In the pulsed light of Figures 4–6, the harmonics are broadened by the fact that there is a spectrum of frequencies that are present in the pulse and in the response.

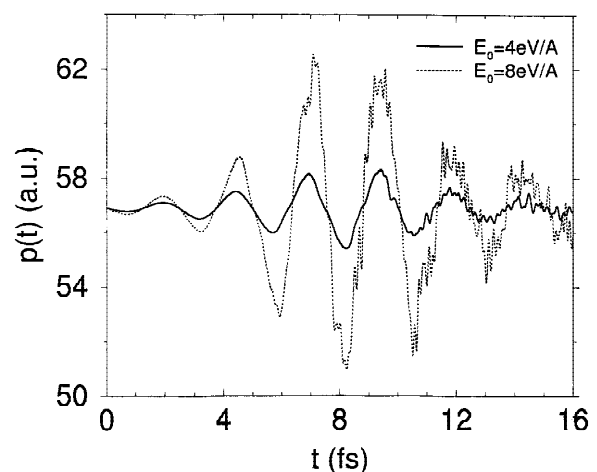


Fig. 4. Response of the electron system in an Ar atom under a pulse of infrared light at two different intensities.

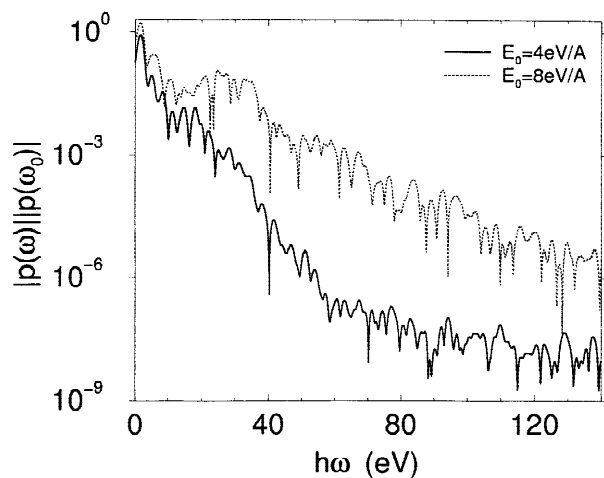


Fig. 5. Power spectra corresponding to Fig. 4.

### 3.2. Molecules

In the case of infrared light in atoms and molecules presented in the previous sections (Figs. 3–7), we found that both pulses and continuous waves produced high harmonic response. In the case of UV light on molecules, continuous waves produced a rather undramatic response. Fascinating behavior was observed, however, in the case of a short Gaussian pulse (40 fs) on a  $\text{Si}_2$  molecule at the frequency of the lowest electronic excitation ( $0.5859 \times 10^{15}$  Hz). Figure 8a shows the input pulse and Fig. 8b shows the response. It is clear that in the first half of the pulse the electrons follow the external field. Shortly after the half-way point of the pulse is reached, the electrons burst into a highly nonlinear mode oscillating at the third harmonic. We are not aware of experiments along these lines, but clearly such systems show enormous promise for nonlinear optical studies and possible applications.

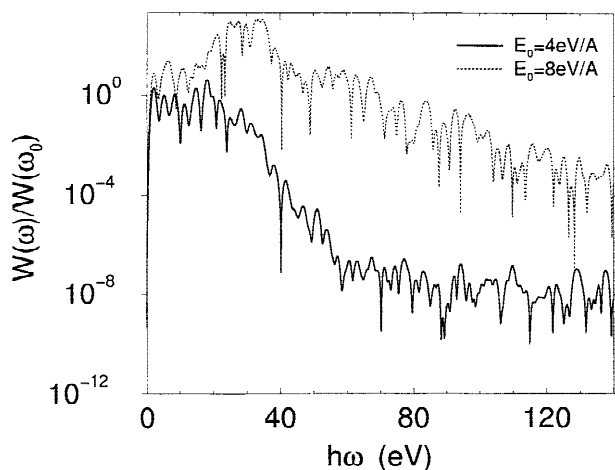


Fig. 6. Power output relative to power input for the Ar case of Figs. 4 and 5.

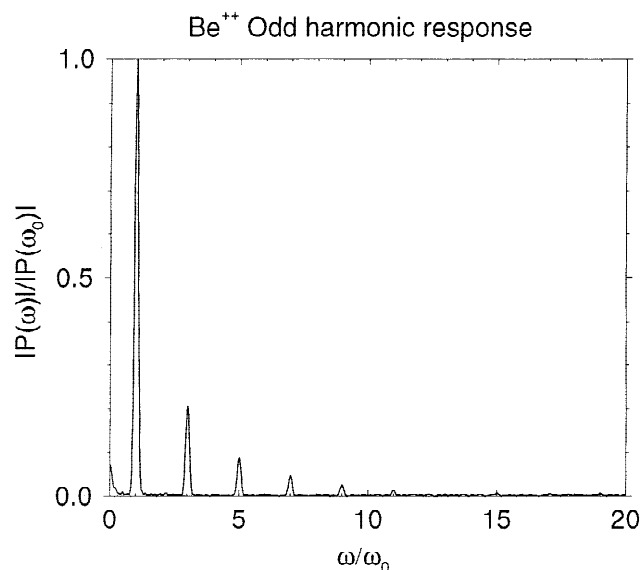


Fig. 7. Power spectrum of the response of a  $\text{Be}^{++}$  ion to an intense infrared light showing the odd high harmonics.

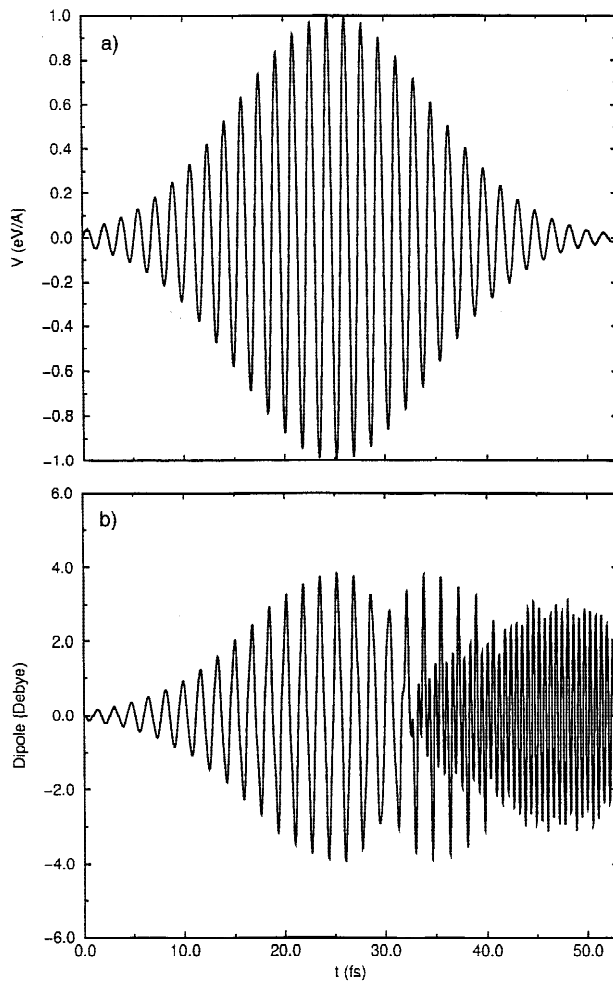
### 3.3. Solids

So far we have applied the method to test the nonlinear response of a pure Si crystal. We found that the intensity of the pulse must be kept low to get numerically stable results. We only have an initial calculation shown in Figure 9 demonstrating the appearance of several odd harmonics at an input intensity of  $0.01 \text{ eV/\AA}$ . Only the odd harmonics ought to be present because the perfect crystal is centrosymmetric. The weak second harmonic appearing in the spectrum is a measure of numerical accuracy that needs to be eliminated by decreasing the time step and increasing other convergence cutoffs. It is clear that the technique is powerful and can produce second-harmonic response from interfaces that break the symmetry. Second harmonic generation is a powerful experimental probe of buried interfaces (Wang *et al.*, 1998), but theory so far has relied on model calculations. Calculations using the present method are very promising but also computationally extremely demanding for large supercells needed to study interfaces.

### 4. FUTURE PROSPECTS

We have presented initial results of a long-term project to compute the nonlinear response of atoms, molecules, and solids using the time-dependent density functional theory. So far we have studied ionic response in molecules in the adiabatic approximation (no electronic excitations) and the nonlinear response of the electron systems in atoms, molecules, and solids while keeping the ions in the ground state positions. The codes have since been extended to include simultaneous ionic motions and electronic response. There is a wide range of problems that can be studied, for example, the nonlinear response of electronic systems, light-induced





**Fig. 8.** a) The electric field of a gaussian pulse of light at  $\nu = 0.5859E15$  Hz. b) The response of the electron system of a  $Si_2$  molecule to the above pulse.

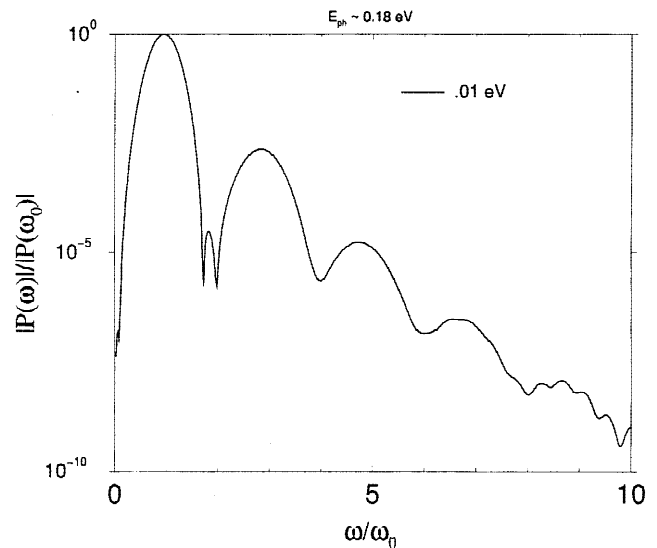
bond breaking in molecules and crystal surfaces with adatoms, and ablation. These are phenomena that have been studied extensively experimentally but theoretical work so far has been limited to semiempirical models.

### ACKNOWLEDGMENTS

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**Fig. 9.** The power spectrum of the response of a Si crystal to infrared light of electrical field amplitude of 0.01 eV/Å. Only odd harmonics should appear. The small second harmonic peak is numerical error.

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