Calculation of the optical response of $C_{60}$ and $Na_8$ using time-dependent density functional theory and local orbitals

Argyrios Tsolakidis, Daniel Sánchez-Portal*, and Richard M. Martin

Department of Physics and Materials Research Laboratory
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(March 22, 2022)

We report on a general method for the calculation of the frequency-dependent optical response of clusters based upon time-dependent density functional theory (TDDFT). The implementation is done using explicit propagation in the time domain and a self-consistent program that uses a linear combination of atomic orbitals (LCAO). Our actual calculations employ the SIESTA program, which is designed to be fast and accurate for large clusters. We use the adiabatic local density approximation to account for exchange and correlation effects. Results are presented for the imaginary part of the linear polarizability, $\Im \alpha(\omega)$, and the dipole strength function, $S(\omega)$, of $C_{60}$ and $Na_8$, compared to previous calculations and to experiment. We also show how to calculate the integrated frequency-dependent second order non-linear polarizability for the case of a step function electric field, $\tilde{\gamma}_{\text{step}}(\omega)$, and present results for $C_{60}$.  

I. INTRODUCTION

Although density functional theory (DFT) is a very successful theory for the ground state properties, the excited states calculated within the Kohn-Sham scheme often are much less successful in describing the optical response and the excitation spectra. The solution to this problem, in principle, is the extension of DFT to the time-dependent systems. It is interesting to note that the first calculations using TDDFT preceded any formal development and it relied heavily on the analogy with the time-dependent Hartree-Fock method. The first steps towards the formulation of TDDFT were done by Deb and Gosh, who focused on potentials periodic in time, and by Bartolotti, who focused on adiabatic processes. Runge and Gross established the foundations of TDDFT for a generic form of the time-dependent potential. TDDFT was further developed to acquire a structure that is very similar to that of the conventional DFT. A very interesting feature of TDDFT, that does not appear in DFT, is the dependence of the density functional on the initial state. For more information about TDDFT the reader is advised to read the authoritative reviews of Gross, Ulrich, and Gossman and Gross, Dobson, and Petersilka.

The polarizability describes the distortion of the charge cloud caused by the application of an external field. It is one of the most important response functions because it is directly related to electron-electron interactions, and correlations. In addition, it determines the response to charged particles, and optical properties. A quantity of particular interest is the dipole strength function, $S(\omega)$, which is directly related to the frequency-dependent linear polarizability, $\alpha(\omega)$, by

$$\alpha(\omega) = \frac{e^2}{m} \int_0^\infty \frac{S(\omega^\prime)d\omega^\prime}{\omega^2 - \omega^2}. \quad (1)$$

By taking the imaginary part of Eq. $\[1\]$, we obtain

$$S(\omega) = \frac{2m}{\pi e^2 \hbar^2} \Im \alpha(\omega). \quad (2)$$

The dipole strength function, $S(\omega)$, is proportional to the photoabsorption cross section, $\sigma(\omega)$, measured by most experiments and, therefore, allows direct comparison with experiment. In addition, the integration of $S$ over energy gives the number of electrons, $N_e$, ($f$-sum rule) i.e.

$$\int_0^\infty dE S(E) = \sum_i f_i = N_e, \quad (3)$$

where $f_i$ are the oscillator strengths. This sum rule is very important because it provides an internal consistency test for the calculations, indicating the completeness and adequacy of the basis set used for the computation of the optical response.

Optical probes are some of the most successful experimental tools that allow access to the properties of clusters. Consequently, there are many calculations of the optical response of small atomic aggregates. In particular, there exist several theoretical studies of the examples chosen here, $C_{60}$ and $Na_8$. This allows us to calibrate the accuracy of our method in comparison with other computational schemes. One of the first $ab\ initio$ calculations of the dipole response of atomic clusters within TDDFT was performed by Yabana and Bertsch, who studied large sodium and lithium clusters, and the $C_{60}$ molecule using a real time and space approach. For small Na clusters, Vasiliev et al. calculated the absorption cross section using the time-dependent density functional response theory (TD-DFRT) developed by Casida.

The purpose of this work is to propose a method that will have significant advantages for the calculation of the polarizability of large clusters, reducing considerably the computation time while retaining the desired accuracy. This paper is organized as follows: In section $[\[1\]}$, we describe the method of calculation. In section $[\[1\]}$, we give details about the way we solve the time-dependent
Kohn-Sham equation and briefly summarize other methods available. In section II, we present an overview of relevant calculations and the results of our calculation for C$_{60}$ and Na$_8$. We compare our results with other calculations and experiments. In section III, we describe the calculation and present the results for the imaginary part of the integrated frequency-dependent second order non-linear polarizability for the case of a step function electric field, $\tilde{\gamma}_{step}(\omega)$, for C$_{60}$. In section IV, we give the conclusions.

**II. METHOD OF CALCULATION**

**A. Electronic structure calculations**

Our method involves the description of the electronic states using linear combination of atomic orbitals (LCAO). Because the size of the LCAO basis is small, compared with other usual choices like plane waves or real space grids, the TDDFT calculations can be done efficiently using the techniques described below. Our scheme is based on the SIESTA code, which is used to compute the initial wavefunctions and the Hamiltonian matrix for each time step. SIESTA is a general-purpose DFT code which uses a local basis, and has been specially optimized to deal with large systems. As such, it represents an ideal tool for treating large clusters. Core electrons are replaced by norm-conserving pseudopotentials in the fully nonlocal Kleinman-Bylander form, and the basis set is a general and flexible linear combination of numerical atomic orbitals (NAOs), constructed from the eigenstates of the atomic pseudopotentials.

The NAOs are confined, being strictly zero beyond a certain radius. In addition, the electron wavefunctions and density are projected onto a real space grid in order to calculate the Hartree and exchange-correlation potentials and their matrix elements.

The use of confined NAOs is very important for the efficiency of the SIESTA code. With them, by exploiting the explicit sparseness of the Hamiltonian and density matrices, the computational cost for the construction and storage of the Hamiltonian and the electronic density can be made to scale linearly with the number of atoms, in the limit of large systems. Therefore, a considerable effort has been devoted to obtain orbital bases that would meet the standards of precision of conventional first-principles calculations, while keeping their range as small as possible. A simple scheme for the generation of transferable bases that satisfy both requirements was presented in Refs. 17 and 22. These bases, which we utilize in this work, have been successfully applied to study the ground state properties of very different systems, ranging from insulators to metals, and from bulk to surfaces and nanostructures. It is not obvious however that these confined basis sets will be also adequate for the TDDFT calculation of the optical response. In this paper we show that, at least for the two systems considered, the optical absorption can be accurately calculated using basis of NAOs with reasonable confinement radii, and a moderate number of orbitals per atom. Our results are in good agreement with other TDDFT calculations using computationally more demanding basis sets.

Our approach is to carry out the calculations in the time domain, explicitly evolving the wavefunctions. We consider a bounded system in a finite electric field, i.e. the Hamiltonian includes a perturbation $\Delta H = -E \cdot x$. For the linear response calculations in this paper we have set the value of this field to 0.01 eV/Å. The system is solved for the ground state using standard time independent density functional theory. Then we switch off the electric field at time $t = 0$, and for every subsequent time step we propagate the occupied Kohn-Sham eigenstates by solving the time-dependent Kohn-Sham equation ($\hbar = 1$)

$$\frac{i}{\hbar} \frac{\partial \Psi}{\partial t} = H \Psi,$$

where H is the time-dependent Hamiltonian given by

$$H = -\frac{1}{2} \nabla^2 + V_{ext}(r, t) + \int \frac{\rho(r', t)}{|r - r'|} dr' + V_{xc}[\rho(r, t)].$$

The calculation of the exchange-correlation potential is done using the adiabatic local density approximation (ALDA) where $V_{xc}$ takes the form

$$V_{xc}[\rho(r, t), \rho(t)] \approx \frac{\delta E^{LDA}_{xc}[\rho]}{\delta \rho(r)} = V^{LDA}_{xc}[\rho](r).$$

$E^{LDA}_{xc}[\rho]$ is the exchange-correlation energy of the homogeneous electron gas. It is important to notice that the $V_{xc}$ in ALDA is local both in time and space. For every time step we solve Eq. (6), and from the new wavefunctions we construct the new density matrix

$$\rho^{\mu\nu}(t) = \sum_{i \in occ} c^\mu_i(t) c^\nu_i(t),$$

where $c_i^\mu(t)$ are the coefficients of the occupied wavefunctions which correspond to the basis orbitals $\phi_\mu(r)$. $\rho^{\mu\nu}(t)$ has to be calculated and stored for overlapping orbitals only. The electron density is then obtained by

$$\rho(r, t) = \sum_{\mu, \nu} \rho^{\mu\nu}(t) \phi_\mu(r) \phi_\nu(r),$$

and used for the calculation of the Hamiltonian in the new cycle.

**B. Calculation of the polarizabilities**

For every time step we calculate the dipole moment $D(t)$ of the electrons in the cluster. This defines the
response to all orders and the frequency dependent response is found by the Fourier transform

$$D(\omega) \equiv \int dt e^{i\omega t - \delta t} D(t).$$

In our case we Fourier transform the dipole moment only for t > 0. It is necessary to include a damping factor \(\delta\) in order to perform the Fourier transform. This damping factor gives the minimum width of the peaks of the imaginary part of the response. Physically, it can be regarded as an approximate way to account for broadening. To linear order the polarizability is given by \(D(\omega) = \alpha(\omega)E(\omega)\), so that

$$\Re \alpha(\omega) = \omega \frac{R D(\omega)}{E},$$

where the field is given by \(E(t) = E \theta(-t)\). After Fourier transforming the dipole moment we obtain the elements of the frequency-dependent polarizability tensor \(\alpha_{ij}(\omega)\). We repeat the calculation with the electric field along different axis unless the symmetry is high enough that this is not needed. The average linear polarizability is given by

$$< \alpha(\omega) >= \frac{1}{3} \text{Tr}\{\alpha_{ij}(\omega)\}.$$  \(\text{(11)}\)

The choice of the coordinate system does not affect the average polarizability because of the rotational invariance of the trace.

C. Solution of the time-dependent Kohn-Sham equation

Efficient solution of the time-dependent Kohn-Sham equation (Eq. 4) is of particular interest because together with the calculation of the Hamiltonian, they are the most time consuming parts of the calculation. In this section we describe our approach of solving Eq. (4), as well as other existing methods used for the same purpose.

In the LCAO formalism Eq. (4) takes the form

$$i \frac{\partial c}{\partial t} = S^{-1} H c,$$

where \(S\) is the overlap matrix between the orbitals and \(c\) is the column of the coefficients of the local orbitals. The overlap matrix is fixed for a given atomic configuration, hence we have to calculate and invert it only once.

The formal solution of Eq. (12) is

$$c(t) = U(t,0)c(0) = T\exp \left(-i \int_0^t S^{-1} H(t')dt' \right) c(0),$$

where \(T\) is the time ordering operator. The most elementary solution is obtained by breaking the total evolution operator into evolution operators of small time durations

$$U(t,0) \simeq \prod_{n=0}^{N-1} U((n+1)\Delta t, n\Delta t),$$

where \(\Delta t = \frac{T_{\text{tot}}}{N}\) and

$$U(t + \Delta t, t) = \exp \left(-i S^{-1} H(t)\Delta t \right).$$

\(T_{\text{tot}}\) is the total time that we allow the system to evolve. The differences among propagation schemes arise from the way the exponential in Eq. (13) is approximated. In our approach, we approximate the exponential in Eq. (13) with the Crank-Nicholson operator. The coefficients between the steps \(n+1\) and \(n\) are related by the equation

$$c^{n+1} = \frac{1 - i S^{-1} H(t_n) \Delta t}{1 + i S^{-1} H(t_n) \Delta t} c^n.$$  \(\text{(16)}\)

This method is unitary, strictly preserving the orthonormality of the states for an arbitrary time evolution. For time independent Hamiltonians it is also explicitly time reversal invariant, and exactly conserves energy. In practice, with a suitable choice of \(\Delta t\), the energy is satisfactorily conserved even when the Hamiltonian changes with time. For example, in the calculations described below, the drift of the total energy at the end of the simulation (~130 fs in both cases) was only \(\Delta E_{\text{tot}}/E_{\text{tot}} \sim 3 \times 10^{-7}\) for \(\text{C}_{60}\) and, ~ \(8 \times 10^{-6}\) for \(\text{Na}_8\), after \(\text{Na}_{60}\) ~ 6100 and \(\text{Na}_{64}\) ~ 2800 time steps, respectively. The larger energy drift in the case of \(\text{Na}_8\) is attributed to the use of larger time step. The method is stable when \(\Delta t \Delta E_{\text{max}} < 1\), where \(\Delta E_{\text{max}}\) is the range of the eigenstates of \(S^{-1} H\).

We can increase the stability of the solution if we include more terms of the expansion in the numerator and denominator of the Crank-Nicholson operator, i.e.

$$c^{n+1} = \frac{1 - i S^{-1} H \frac{\Delta t}{2} - \frac{1}{2}(S^{-1} H \frac{\Delta t}{2})^2 + i \frac{1}{6}(S^{-1} H \frac{\Delta t}{2})^3}{1 + i S^{-1} H \frac{\Delta t}{2} - \frac{1}{2}(S^{-1} H \frac{\Delta t}{2})^2 - i \frac{1}{6}(S^{-1} H \frac{\Delta t}{2})^3} c^n.$$  \(\text{(17)}\)

By including more terms in the expansion it is possible either to increase the time step preserving the accuracy, or to increase the accuracy of the dynamics and the energy conservation for a given time step. The main advantage of using a bigger time step is the saving of time because we have to calculate the Hamiltonian fewer times. The energy resolution will not be affected since it depends on the total time that we allow the system to evolve.

The method presented in this work has many similarities with that described by Yabana and Bertsch for the main difference being the use of an LCAO basis set in the present case. However, this is a key difference because the size of the matrices used in the calculations is considerably smaller compared to other basis choices. In addition, our method has other advantages associated with the real time formalism of TDDFT. Only occupied states are used in the calculation, in contrast to the
perturbative approach where there is a sum over the excited states of the system. The implementation is relatively simple, since we use essentially the same operations as already used to find the ground state properties. It is also advantageous that nonlinear effects can be included in a straightforward way. One disadvantage of the real time approach is the calculation of the Hamiltonian for every time step. Although this is not an attractive feature there is no other way to calculate the time evolution of the system.

There are many other ways to approach the solution of the equations. For completeness, we discuss in the Appendix several methods that could be of potential relevance for our calculations. One of the main goals of these methods is to enable longer time steps. This would be a great advantage in our work; however, the fact that the self-consistent Hamiltonian changes as a function of time, limits their use.

III. DISCUSSION OF RESULTS

A. Small metal clusters: Na$_8$

The first calculation we performed is the optical response of Na$_8$. The main purpose of this calculation was to investigate the accuracy of our method in the case of a small cluster, where the effects related to the confinement of the orbitals should be more noticeable and where the size of our basis is much smaller than in previous calculations using real space grids. Na$_8$ is the smallest closed shell Na cluster that its optical response exhibits the presence of a plasmon which is experimentally observed at 2.53 eV$^{14,27,28}$. The width of the plasmon is due to Landau damping.

Previous work can be grouped into two types: earlier work on jellium spheres$^{27,29}–31$ that reproduces the qualitative features but not the quantitative energies of the peaks, and more recent work$^{14,32}$ that takes into account the detailed atomic structure and is in general in very good agreement with experiments$^{27,28}$. In the first category are the calculations of Selby$^{27,30}$ et al., who calculated the photoabsorption cross section using the modified Mie theory, which is a classical theory. The plasmon was found to be at $\sim 2.76$ eV. By using the self-consistent jellium model in the time dependent local density approximation (TDLDA), first introduced by Ekardt$^{29}$ and Yannouleas$^{31}$ et al., calculated the photoabsorption cross section using the modified Mie theory, which is a classical theory. The plasmon was predicted at $\sim 2.55$ eV. Vasiliev$^{14}$ et al.$^{15}$ calculated the photoabsorption cross section using TD-DFRT$^{33}$. Their calculations made use of norm-conserving pseudopotentials and a real-space mesh as a basis set. The position of the plasmon agreed with the photoabsorption experiments of Selby$^{27}$ et al.$^{27}$ and Wang$^{28}$ et al.$^{28}$ within 0.1-0.2 eV.

In our calculation we let the system evolve for the total time of $T=31.42$ eV$^{-1}$. The energy resolution, determined by $\Delta \omega = \frac{\pi}{T}$, is, in consequence, equal to 0.1 eV. The time step is $11.025 \times 10^{-3}$ eV$^{-1}$, and the damping factor used in the Fourier transform is 0.095 eV. Troullier-Martins pseudopotentials$^{19}$ including non-linear partial core corrections$^{33}$ for the exchange-correlation interaction between valence and core electrons, and an auxiliary real-space grid$^{16}$ equivalent to a plane-wave cutoff of 70 Ry are also used in this calculation. The basis set includes 13 NAOs per
atom: two radial shapes to represent the 3s states plus a polarization $p$ shell with confinement radii $r_s=r_p^{pol}=12.2$ a.u., and two additional 3$p$ and 3$d$ shells with radii $r_p=r_d=10.0$ a.u.

Fig. 1 and Fig. 2 present, respectively, our results for the dipole strength function and the imaginary part of the linear polarizability of Na$_8$ for energies up to 4 eV. The shape of these curves is in excellent agreement with both, the calculations of Vasiliev et al.

However, the results appear to be shifted to higher energies. In fact, the maximum of the plasmon peak is obtained at 2.86 eV, which is 0.33 eV higher than the experimentally observed value. This shift to higher energies seems to be related to the extension of the LCAO basis: using more confined orbitals we get a larger shift. The integrated dipole strength is equal to 6.97 out of 8, thus fulfilling 87.13 % of the sum rule. The partial fulfillment of the sum rule signifies the incompleteness of our basis set. The static linear polarizability $\alpha(0)$ can be obtained from standard (static) calculations of the induced dipole as a function of the applied field. Using this approach we obtain a value of 13.2 Å$^3$/atom. An alternative way to calculate $\alpha(0)$ is provided by the formula

$$\alpha(0) = \frac{e^2 \hbar}{m} \int_0^\infty \frac{S(\omega)d\omega}{\omega^2} = \frac{2}{\pi} \int_0^\infty \frac{3\alpha(\omega)}{\omega} d\omega,$$

from which we obtain a value of 12.5 Å$^3$/atom. (This result can also be derived from the fact that for the step perturbation $D(t=0) = \alpha(0)E$.) The discrepancy between both estimations is probably related with the lack of energy resolution of the calculated $\alpha(\omega)$ to perform the integral in Eq. (18) with the required accuracy. Both results are in reasonable agreement with the values of 14.6 Å$^3$/atom and 14.7 Å$^3$/atom, computed by Vasiliev et al.

B. Large molecules: C$_{60}$

The best known Buckyball C$_{60}$ is a very interesting system with strong electron-electron interactions due to the confinement. There are quite a few calculations concerning the optical properties of C$_{60}$ and in particular its optical response. The main feature of the optical response of C$_{60}$ is the presence of two collective excitations (plasmons). The low energy plasmon can be associated with the $\pi$ electrons while the high energy plasmon with both the $\sigma$ and $\pi$ electrons, in analogy with the plasmons in graphite. The plasmons have been observed by a plethora of experiments.

The earliest theoretical work on C$_{60}$ involved simplifying approximations for the electron states (tight-binding or spherical averaging) and for the electron interaction (neglect or RPA-like treatments). We will compare our results with those of Westin et al. and Yabana and Bertsch, who used large basis sets and realistic carbon potentials. Westin et al. used single particle wavefunctions, determined from a local density approximation (LDA) calculation, to evaluate the dipole matrix elements which combined with a sum over states approach yielded the unscreened frequency-dependent linear polarizability. Screening was included in a RPA-like fashion by introducing an effective screening parameter. The polarizability calculated in the static limit was used to evaluate this parameter for the calculation of the dynamic response. The optical response and the sum rule for the low energy part were in reasonable agreement with the experiment of Leach et al. However, the results appear to be shifted to higher energies. Their calculation also gives agreement with the experimental data of Leach et al. for the sum rule of the low energy part although it misses many details of the structure. This calculation is very similar in quality to ours.

The total simulation time in our calculation of the polarizability and dipole strength of the C$_{60}$ molecule is again 31.416 eV$^{-1}$, and the corresponding maximum energy resolution of 0.1 eV. The time step however, which is set equal to 5.145 × 10$^{-3}$ eV$^{-1}$, is smaller than the one used for Na$_8$. This is because of the higher frequency range of the response of C$_{60}$. The damping factor used in the Fourier transform is equal to 0.34 eV in this case. Troullier-Martins pseudopotentials, a double-$\zeta$ polarized basis set, and a real-space grid cutoff of 70 Ry were used in this calculation. There are 13 NAOs per C atom: two different radial shapes for the description of the 2$s$ states, another two for the 2$p$, plus an additional shell of $d$ orbitals. The radii of confinement used are $r_s=5.12$ a.u. and $r_p=r_d^{pol}=6.25$ a.u. (corresponding to an energy shift of 50 meV). For C$_{60}$, the calculated spectra show small dependence in these radii, at least as far as they are not selected to be very stringent. In Fig. 3, the dipole moment is shown as a function of the time step number. The dipole strength function obtained from the time evolution of the dipole moment is shown in Fig. 4 for energies up to 60 eV. Its main features are the low energy transitions that come from the $\pi$ electrons and the $\sigma$ and $\pi$ electron transitions in the region of 14-27 eV. In the low energy part of dipole strength function we have peaks at 3.46, 4.35, 5.36, and 5.84 eV, which agree very well with the ones obtained by the calculations of Westin et al. By integrating the dipole strength function over energy we get the sum rule strength. The total sum rule strength is 223.78 out of 240. Therefore, we satisfy the sum rule up to 93.24 %. This reflects the incompleteness of our basis set, which fails to reproduce some of the excitations in the high energy part of the spectrum. The $\sigma$ plasmon is broadened, but this is a common feature of all the TDDFT calculations done for C$_{60}$. In Fig. 5, the imaginary part of the polarizability is given as function of energy. By using Eq. (18), the static linear polarizability $\alpha(0)$ is found to be 91.1 Å$^3$, while
our finite field calculations produce a value of 87.3 Å³. Results for \( \alpha(0) \), from very accurate finite-field calculations using fifteen values of the field, are given in section IV. Both values are higher than the lower limit estimation of 62.5 Å³ from quantum-mechanical calculations, and in good agreement with the value of 85 Å³ obtained by Yabana and Bertsch. They also agree well with the experimental values of 79.3 Å³ from UV absorption, and 85.2 Å³ from EELS spectra.

IV. NON-LINEAR POLARIZABILITIES

Because of the non-perturbative nature of our method we are able, for large values of the applied field, to obtain non-linear polarizabilities. In this section, we present the calculation of the imaginary part of the integrated frequency-dependent second order non-linear polarizability, \( \Im \tilde{\gamma}_{\text{step}}(\omega) \), which is related to the response to a step function, for \( C_{60} \). Because \( C_{60} \) is centrosymmetric the first order non-linear polarizability, \( \beta(\omega) \), and all other polarizabilities involving an even number of fields, vanish by symmetry.

The advantage of the explicit time method is that exactly the same methods can be used to calculate the non-linear response of the system. The disadvantage is that (unlike the linear case where each Fourier component is independent) the non-linear response depends upon the detailed spectrum of the applied field. Here we derive the non-linear response of an electric field coupled to a \( C_{60} \) for the case where the field is the step function used before. A different calculation would have to be done to find the non-linear response to a field with a different time dependence.

First we give the relation of our calculation to the general definition of second order non-linear response, as a function of time, which is

\[
D^{(3)}(t) = \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t} dt_3 \gamma(t; t_1, t_2, t_3)E(t_1)E(t_2)E(t_3).
\]

For the case of a step function perturbation i.e. \( E(t) = E \theta(-t) \), it takes the form

\[
D^{(3)}(t) = iE^3 \lim_{\delta \rightarrow 0^+} \int \frac{d\omega_1 d\omega_2 d\omega_3}{(2\pi)^3} e^{-i(\omega_1 + \omega_2 + \omega_3)} \gamma(-\omega_1 - \omega_2 - \omega_3; \omega_1, \omega_2, \omega_3) \frac{1}{(\omega_1 - i\delta_1)(\omega_2 - i\delta_2)(\omega_3 - i\delta_3)}.
\]

We Fourier transform Eq. (20) and obtain the second order non-linear response as a function of frequency

\[
D^{(3)}(\omega) = iE^3 \lim_{\delta \rightarrow 0^+} \int \frac{d\omega_2 d\omega_3}{(2\pi)^2} \frac{\gamma(-\omega; \omega - \omega_2 - \omega_3; \omega_1, \omega_2, \omega_3)}{(\omega - \omega_2 - \omega_3 - i\delta_1)(\omega_2 - i\delta_2)(\omega_3 - i\delta_3)}.
\]
The quantity we calculate is the real part of the second order non-linear response, $\Re D^{(3)}(\omega)$, from which we can extract the imaginary part of the integrated second order non-linear polarizability, $\Im \tilde{\gamma}_{\text{step}}(\omega)$. Explicit details are given below and in analogy to Eq. (10) $\Im \tilde{\gamma}_{\text{step}}(\omega)$ is given by

$$\Im \tilde{\gamma}_{\text{step}}(\omega) = -\omega \lim_{\delta \to 0^+} \int \frac{d\omega_2 d\omega_3}{(2\pi)^2} \frac{\Re D^{(3)}(\omega)}{E^3}.$$  \hspace{1cm} (22)

Just as in Eq. (10) for the linear term, $\Im \tilde{\gamma}_{\text{step}}(\omega)$ can be related to the static second order non-linear polarizability by the expression

$$\frac{2}{\pi} \int_0^\infty \frac{d\omega}{\omega} \Im \tilde{\gamma}_{\text{step}}(\omega) = \gamma(0; 0, 0, 0).$$  \hspace{1cm} (23)

Eq. (23) can be trivially derived by realizing that $D^{(3)}(t = 0) = \gamma(0; 0, 0, 0) E^3$ when a step function perturbation is applied. Alternatively, we can derive Eq. (23) directly from Eq. (22) by applying the Kramers-Kroning relations for $\gamma(-\omega_1 - \omega_2 - \omega_3; \omega_1, \omega_2, \omega_3)$. In fact, with the help of the Kramers-Kroning relations we can derive another interesting equality for the first moment of our integrated response,

$$\frac{1}{3} \int d\omega \Im \tilde{\gamma}_{\text{step}}(\omega) = \int d\omega \Im \gamma(-\omega; 0, 0, 0).$$  \hspace{1cm} (24)

For the calculation of $\tilde{\gamma}_{\text{step}}(\omega)$ we calculate the response of the system under two different step function perturbations. In the first calculation the field used is equal to $E_1 = 0.10$ V/Å, and we assume that the response $D_1(\omega)$ is linear with respect to the field. This assumption is true since for $\omega = 0$ the non-linear terms contribute to the response only $4.82 \times 10^{-3}\%$. The contribution is of the same order of magnitude for $\omega \neq 0$. In the second calculation the field is equal to $E_2 = 1.00$ V/Å, and we assume that the response $D_2(\omega)$ consists of the linear response and the second order non-linear response $D^{(3)}_2(\omega)$. The values of the field are in the same range as those used by Westin et al.\cite{Westin} for the determination of the static second order non-linear polarizability. Using Eq. (10), we have that

$$D_1(\omega) = \alpha(\omega) E_1(\omega) = \alpha(\omega) \frac{E_1}{i\omega}$$  \hspace{1cm} (25)

and

$$D_2(\omega) - \alpha(\omega) E_2(\omega) = D^{(3)}_2(\omega).$$  \hspace{1cm} (26)

From Eq. (24) it follows that

$$D^{(3)}_2(\omega) = \frac{\tilde{\gamma}_{\text{step}}(\omega)}{i\omega} E_2^3,$$  \hspace{1cm} (27)

and from Eqs. (23), (26), and (27) we obtain

$$\tilde{\gamma}_{\text{step}}(\omega) = i\omega \left( \frac{D_2(\omega) - E_2 D_1(\omega)}{E_1} \right).$$  \hspace{1cm} (28)

Our calculation for $\tilde{\gamma}_{\text{step}}(\omega)$ is quite straightforward in contrast to the perturbative method where it becomes computationally very demanding.

In Fig. 6, we present the results, up to 60 eV, for $\Im \tilde{\gamma}_{\text{step}}(\omega)$, where $\Im \tilde{\gamma}_{\text{step}}(\omega)$ is given by Eq. (23). As expected, $\Im \tilde{\gamma}_{\text{step}}(\omega)$ has both positive and negative values. The reason why $\Im \tilde{\gamma}_{\text{step}}(\omega)$ does not vanish below some finite frequency (as does the linear response) is because the second-order non-linear term represents many processes of both absorption and emission of photons and the C$_{60}$ molecule can couple to a continuum of modes that extends to zero frequency. This can also be seen in the integral expression Eq. (23).

Similarly to the case of the linear polarizability, we can obtain an estimation of the magnitude of $\gamma(0; 0, 0, 0)$ from static self-consistent calculations performed with finite fields. This value can be contrasted to similar calculations in the literature, providing an estimation of the uncertainty of our calculations of the non-linear terms, and an internal consistency test for our calculation of the integrated frequency-dependent second order non-linear polarizability. We have followed here a procedure similar to that used in Ref. 32, performing LDA calculations of the total energy and electric dipole of the C$_{60}$ molecule for fifteen different values of an external static electric field, this value can be contrasted to similar calculations in the literature, providing an estimation of the uncertainty of our calculations of the non-linear terms, and an internal consistency test for our calculation of the integrated frequency-dependent second order non-linear polarizability.

In Ref. 32, we have used a procedure similar to that used in Ref. 32, performing LDA calculations of the total energy and electric dipole of the C$_{60}$ molecule for fifteen different values of an external static electric field, this value can be contrasted to similar calculations in the literature, providing an estimation of the uncertainty of our calculations of the non-linear terms, and an internal consistency test for our calculation of the integrated frequency-dependent second order non-linear polarizability.
experiments of Geng and Wright. Also, our results for γ(0;0,0,0) are in reasonably good agreement with other LDA calculations in the literature. Quong et al.\textsuperscript{53} reported values of 82.7 Å\textsuperscript{3} and 7.0×10\textsuperscript{-36} esu, for α and γ, respectively, using an all-electron method with a Gaussian expansion as a basis set. Van Gisbergen et al.\textsuperscript{54} reported very similar values, 82.5 Å\textsuperscript{3} and 7.3×10\textsuperscript{-36} esu, using a computational scheme based on a frozen-core approximation, and a basis set of Slater functions. It is interesting to note that these results are much smaller than those obtained using simplified tight-binding models within an independent electron picture, where the effects of screening are neglected. In such calculations the values of γ(0;0,0,0) obtained are of the order of 200×10\textsuperscript{-36} esu.\textsuperscript{55}

V. CONCLUSION

We presented a method for the calculation of the optical response of atoms and clusters. The main features of the method are the description of the wavefunctions in terms of an efficient local orbital (LCAO) basis and the explicit evolution of the system in time. This approach is designed for large clusters and in fact it gives excellent results for C\textsubscript{60}. It is also shown to work remarkably well even for systems for which the LCAO basis is very small, such as Na\textsubscript{3}. Our approach has the desirable features that only occupied states are needed and that all the most computationally intensive operations are essentially the same as those used to calculate the ground state properties. In addition, non-linear effects can be included in a straightforward way, and we have shown how to calculate the second order non-linear response for C\textsubscript{60}.

ACKNOWLEDGMENTS

We would like to thank Prof. L. Cooper for the useful discussions, and Dr. I. Vasiliev for reading the manuscript. This material is based upon work supported by the U.S. Department of Energy, Division of Materials Sciences under Award No. DEFG02-ER9645439, through the Frederick Seitz Materials Research Laboratory.

APPENDIX: ALTERNATIVE APPROACHES FOR THE SOLUTION OF THE TIME-DEPENDENT KOHN-SHAM EQUATION

Other ways to approximate the exponential in Eq. (14) include the expansion of the exponential in a series of Chebyshev polynomials.\textsuperscript{56,57} exp(−i\textsuperscript{-1}S\textsuperscript{-1}H\textsuperscript{1}\textsuperscript{2}t) \simeq exp(−i(ΔE/2 + E\textsubscript{min})\textsuperscript{1}\textsuperscript{2}t) × (A1)

\[ \sum_{n=0}^{N} a_n \left( \frac{ΔE t}{2} \right)^n φ_n(H_{\text{norm}}) \]

where φ\textsubscript{n} are the Chebyshev polynomials, and the expansion coefficients a\textsubscript{n}(x) can be shown to be analogous to Bessel functions of the first kind of order n. H\textsubscript{norm} is a normalized Hamiltonian 2(S\textsuperscript{-1}H - E\textsubscript{av})/ΔE, where E\textsubscript{av}=(E\textsubscript{max} + E\textsubscript{min})/2, ΔE=E\textsubscript{max} - E\textsubscript{min}. E\textsubscript{max} and E\textsubscript{min} are, respectively, the maximum and minimum eigenvalues of S\textsuperscript{-1}H. The Chebyshev polynomials are chosen because their error decreases exponentially when N is large enough, due to the uniform character of the Chebyshev expansion.\textsuperscript{58} Time reversal is built into the expansion coefficients, but the method does not effectively conserve norm or energy. While it works remarkably well for time-independent Hamiltonians,\textsuperscript{59} for time-dependent Hamiltonians the method becomes inefficient as the Chebyshev polynomials of the Hamiltonian have to be recalculated for each time step.

Another approximation for the exponential in Eq. (14) is performed by using the split-operator method introduced by Feit et al.\textsuperscript{60} According to this method, the exponential which contains the Hamiltonian operator can be split as

\[ \exp[-i(T + V)\textsuperscript{1}\textsuperscript{2}t] \simeq \exp(-i\frac{1}{2}T\textsuperscript{1}\textsuperscript{2}t) \exp(-iV\textsuperscript{1}\textsuperscript{2}t) \exp(-i\frac{1}{2}T\textsuperscript{1}\textsuperscript{2}t). \]

This method was later generalized by Suzuki\textsuperscript{61} for an arbitrary number of operators, providing higher order expansions (formula (A2) corresponds to second order in Δt), and a rigorous extension of the method to time-dependent Hamiltonians.\textsuperscript{62} The split operator method takes advantage of the fact that it is very convenient to treat operators in their diagonal representations. For example, it is trivial to apply the kinetic energy operator to a wave-function in Fourier space, while the effect of a local potential is more easily calculated in real space. This method is, in principle, unconditionally stable and norm conserving. On the other hand, it does not conserve energy and it can only be used to Hamiltonian operators which can be split into two non-commuting parts with a simple transformation between them. Therefore, the method is very well suited for plane wave or real space methods, where efficient fast Fourier transform algorithms provide an exact transformation between finite plane-wave expansions and real space grids. In other words, they span exactly the same subspace of functions, and it is possible to switch between representations where the kinetic energy and the potential are diagonal within a given subspace. For an LCAO basis this is not possible. If we take an arbitrary wavefunction expanded in an orbital basis ψ(r) = \[ \sum_{ν} c_ν ψ_ν(r) \], the result of applying the operator \[ \exp(-iVt) \] using a grid of points in real-space \[ f(r_i) = \exp(-iV(r_i)t)ψ(r_i) \] will be, in general, not
representable using the same local basis, i.e. some of the resulting function has been spilled from the subspace spanned by the local basis.

An alternative way to solve Eq. (12) is by using the second-order differencing (SOD) method introduced by Askar and Cakmak. In SOD the symmetric relation is used

\[ c(t + \Delta t) - c(t - \Delta t) = (e^{-iS^{-1}H\Delta t})c(t) - (e^{iS^{-1}H\Delta t})c(t) \]

(A3)

and by expanding the exponential in Taylor series, the second-order propagation scheme is obtained

\[ c(t + \Delta t) \approx c(t - \Delta t) - 2i\Delta tS^{-1}H(t)c(t) \]  \hspace{0.5cm} (A4)

By construction SOD obeys the time-reversal symmetry. SOD is stable, and norm and energy are approximately conserved, only if the Hamiltonian is Hermitian. In spite of its simplicity, an important drawback of this method for its application to large systems is that it is necessary to store the wavefunctions at two different time steps, which may require a large amount of memory.

Finally, another method for solving Eq. (12) is the short iterative Lanczos method. It is very convenient for calculations that involve very big Hamiltonians, especially when they are time independent. The Hamiltonian is projected to a subspace of smaller dimensionality and takes a tridiagonal form that makes easy to perform calculations. The Lanczos recurrence creates a set of orthogonal polynomials which constitute a finite polynomial approximation of the operator. An interesting feature of the method is its dependence on both the operator and the initial vector. The Lanczos recurrence relation is

\[ (S^{-1}H)_{ij} = \beta_{j-1}q_{j-1} + \alpha_j q_j + \beta_j q_{j+1}. \]  \hspace{0.5cm} (A5)

The coefficients are \( \alpha_j = (q_j, (S^{-1}H) q_j) \) and \( \beta_{j-1} = (q_{j-1}, (S^{-1}H) q_j) \), where \( (a, b) = a^\dagger S b \) is the usual complex inner product, and \( (q_i, q_j) = \delta_{ij} \). Matrices \( H \) and \( S \) have \( N_b \times N_b \) dimension and the vectors \( q_i \) have \( N_b \) components, \( N_b \) the total number of basis functions. For very large \( N_b \), where the method is particularly useful, the inverse \( S^{-1} \) is not directly calculated but an iterative method is used instead. The recurrence relation is initiated by setting

\[ q_0 = c(0) \]  \hspace{0.5cm} (A6)

and

\[ (S^{-1}H) q_0 = \alpha_0 q_0 + \beta_0 q_1. \]  \hspace{0.5cm} (A7)

After \( P \) iterations, the projected operator \( (S^{-1}H)_P = (q_P, (S^{-1}H) q_P) \) is a \( P \times P \) matrix with a tridiagonal form that can be very easily diagonalized. The solution of Eq. (2) becomes

\[ c(\Delta t) = Z^\dagger e^{-iD\Delta t} Z c(0), \]  \hspace{0.5cm} (A8)

where \( Z \) is the \( N_b \times P \) transformation matrix that diagonalizes \( (S^{-1}H)_P \) and \( D_P \) is the diagonalized matrix. For an arbitrary initial condition, the accuracy of the time evolution achieved with Eq. (A8) is equivalent to a \( P \) order expansion of the evolution operator

\[ e(\Delta t) = \sum_{k=0}^{P-1} \frac{-i\Delta t^k}{k!} (S^{-1}H)^k c(0), \]  \hspace{0.5cm} (A9)

and, consequently, the energy is only approximately conserved. However, the propagator in Eq. (A8) is unitary, and the normalization condition is strictly preserved. For time independent Hamiltonians, Eq. (A8) can be used to evolve the wavefunction for a time interval \( \tau \) that depends on \( P \). For times larger than \( \tau \), the time evolution predicted by a \( P \) order expansion becomes inaccurate, and it is necessary to recalculate propagator using \( c(\tau) \) as the starting point for the recurrence procedure. The method is, therefore, very well suited to follow the evolution of wavefunctions described by a large basis set during short periods of time (\( \tau < \tau \)).

For the purpose of the calculation of response functions, we believe that the method adopted in this paper, based on the Crank-Nicholson operator, is superior to the short iterative Lanczos, at least for moderate basis sizes. There are several reasons for this: \( i) \) We need to evolve the wavefunctions for long times. \( ii) \) The Hamiltonian is time dependent. This implies that the recurrence cycle for the calculation of the approximated time evolution operator has to be repeated for each time step. \( iii) \) In our case, we have to evolve all the occupied states. The propagator in Eq. (A8), however, depends on the initial state. Therefore, it is necessary to develop some generalization of the scheme presented. For example, it might be also possible to construct an approximate time evolution operator starting from some weighted linear combination of the occupied states, and projecting it into a subspace of dimension \( P > N_{occ} \), where \( N_{occ} \) is the number of occupied wavefunctions.

* Present address: Departamento de Física de Materiales and DIPC, Facultad de Química, UPV/EHU, Apdo. 1072, 50001 E-20080 San Sebastián, Spain.
1. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
2. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
3. A. Zangwill and P. Soven, Phys. Rev. A 21, 1561 (1980).
4. B. M. Deb and S. K. Ghosh, J. Chem. Phys. 77, 342 (1982).
5. S. K. Ghosh and B. M. Deb, Chem. Phys. 71, 295 (1982).
6. L. J. Bartolotti, Phys. Rev. A 24, 1661 (1981).
7. L. J. Bartolotti, Phys. Rev. A 26, 2243 (1982).
8. E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).
9. E. K. U. Gross and W. Kohn, Phys. Rev. Lett. 55, 2850 (1985).

(1978).

64 T. J. Park and J. C. Light, J. Chem. Phys. 85, 5870 (1986).