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Assessment of adiabatic local-density approximation for nonlinear optical properties

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Abstract. Employing a near exact Hylleraas wavefunction we calculate various third-order nonlinear optical properties for the helium atom within the time-dependent Kohn-Sham theory. In our calculations we employ the adiabatic local-density approximation (ALDA) for the exchange and correlation kernels f_{xc} and g_{xc}, and compare the numbers obtained by us with the available accurate theoretical as well as experimental results. Our results demonstrate the accuracy of ALDA for the calculation of nonlinear optical properties of many electron systems.

PACS. 31.15.Ew Density-functional theory – 31.15.Md Perturbation theory – 32.10.Dk Electric and magnetic moments, polarizability

1 Introduction

Time-dependent density functional theory (TDDFT) [1] is being used extensively to obtain frequency dependent response properties [2–7] of atoms and molecules, and recently it has also been applied to determine excitation energies [8] of atoms. The theory had first been applied without any rigorous justification for its existence by Zangwill and Soven [2] and Stott and Zaremba [3] to calculate frequency dependent polarizabilities and photoabsorption cross-section of atoms and molecules. Theoretical foundations of TDDFT were laid later in the works of Deb and Ghosh [9], Bartolotti [10] and Runge and Gross [11]. Like its static counterpart the theory is exact in principle but its implementation requires approximating the exchange-correlation energy functional. In most of the applications the adiabatic local-density approximation (ALDA) is used. The results of these calculations unequivocally show that both the polarizability at zero frequency (static polarizability) and its frequency dependence are overestimated. The error in the calculation of higher order polarizabilities and quadrupole polarizabilities is even more pronounced. The overestimation is evidently due to the wrong asymptotic behaviour of the density obtained with the local-density approximation (LDA). Furthermore, the LDA also predicts a smaller difference between the occupied and unoccupied eigenvalues which leads to an overestimate of the frequency dependence. In addition to these errors arising from the unperturbed potential, response properties are also affected by ALDA. This is because of two reasons: further change in the potential itself is being calculated approximately, and secondly it is valid only in the limit of zero frequency. There have been some attempts to rectify these errors by improving the nature of LDA potentials, particularly their asymptotic behaviour. Senatore and Subbaswamy [6] applied a self-interaction correction (SIC) method to improve the effective potential. Later, Zong *et al.* [12] employed a scissors operator technique, and Gisbergen *et al.* [7] devised a model potential with desired asymptotic behaviour to improve the results for polarizabilities. Recently, Gisbergen *et al.* [13] extended the study of reference [7] by using an accurate exchange-correlation potential for He, Be and Ne. All these studies show that by improving the asymptotic nature of the potential both static and frequency dependence of the polarizability can be improved significantly. The general conclusion of these studies is that if the unperturbed exchange-correlation potential is improved the kernels obtained by using ALDA are reasonably accurate enough to give linear polarizabilities comparable to their *ab initio* and experimental counterparts.

Against this background, the question which then arises is whether with the nearly exact exchange-correlation potential (which essentially gives exact Kohn-Sham (KS) orbitals), the ALDA for exchange-correlation kernels f_{xc} and g_{xc} reproduces sufficiently accurate results for nonlinear polarizabilities – both its magnitude as well as the frequency dependence. This is particularly so because higher order response properties are more sensitive to the approximation employed. In this paper we address this question by studying the frequency dependent hyperpolarizabilities of the helium atom. We consider the helium atom because for it very accurate theoretical and experimental results corresponding to both linear and nonlinear polarizabilities are available in the

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literature [14–19]. These results then provide a benchmark for testing the accuracy of ALDA. We calculate the frequency dependent hyper-polarizabilities corresponding to four different nonlinear (third order) optical processes. These are $\gamma(\omega;\omega,-\omega,\omega)$, $\gamma(\omega;\omega,0,0)$, $\gamma(2\omega;\omega,\omega,0)$ and $\gamma(3\omega;\omega,\omega,\omega)$ responsible for degenerate four wave mixing (DFWM), Kerr effect, electric field-induced second harmonic generation (EFISH) and third harmonic generation (THG), respectively [20].

There are several methods available to calculate frequency dependent response properties within TDDFT [6,7]. We employ the variation-perturbation method [21] in time-dependent KS (TDKS) formalism of TDDFT. We choose this particular method because of its ease of implementation. This method requires as input ground-state single particle orbitals and the density of the system. Since our aim is to study the accuracy of ALDA we work with a nearly exact Kohn-Sham orbital for the helium atom obtained from its 206-parameter Hylleraas wave function [22].

The paper is organized as follows. In Section 2 we discuss the variation-perturbation approach in TDKS formalism and the way various frequency dependent hyper-polarizabilities are computed variationally. In Section 3 we present results of our calculations and discuss these. The paper is concluded in Section 4.

2 Theoretical methods

2.1 Variation-perturbation methods in TDKS

The KS equation for a time-dependent potential is given by [1]

$$[-\frac{1}{2}\nabla^2+v_s(\mathbf{r},t)-i\frac{\partial}{\partial t}]u_i(\mathbf{r},t)=0 \tag{1}$$

such that

$$\rho(\mathbf{r},t)=\sum_i|u_i(\mathbf{r},t)|^2, \tag{2}$$

and the effective potential

$$v_s(\mathbf{r},t)=v_{ext}(\mathbf{r},t)+\frac{\delta E_H[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r},t)}+\frac{\delta E_{xc}[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r},t)} \tag{3}$$

where $u_i(\mathbf{r},t)$ are the time-dependent KS orbitals, E_H is the Hartree energy and E_{xc} is the exchange-correlation energy. The external potential has two components

$$v_{ext}(\mathbf{r},t)=v_o(\mathbf{r})+v^{(1)}_{app}(\mathbf{r},t) \tag{4}$$

here $v_o(\mathbf{r})$ is the time-independent nuclear potential and the applied potential

$$v^{(1)}_{app}(\mathbf{r},t)=v^{(1)}_{stat}(\mathbf{r})+v^{(1)}_{dyn}(\mathbf{r},t) \tag{5}$$

has both a static ($v^{(1)}_{stat}(\mathbf{r})$) as well as a time-dependent ($v^{(1)}_{dyn}(\mathbf{r},t)$) part. Here we take the time-dependent part to be periodic in time with time period ω, that is

$$v^{(1)}_{dyn}(\mathbf{r},t)=\frac{1}{2}v^{(1)}_{dyn}(\mathbf{r})(e^{\imath\omega t}+e^{-\imath\omega t}) \tag{6}$$

so that the total applied field is also periodic with the same frequency.

Response to the applied field to various orders is calculated using the time-dependent perturbation theory. For this $u_i(\mathbf{r},t)$ are expanded in perturbation series and the resulting equations for each order is solved. As is well-known [23–25], to avoid difficulties arising from secular terms, it is better to separate out the overall phase factor from the orbitals $u_i(\mathbf{r},t)$ and work instead with transformed orbitals $\chi_i(\mathbf{r},t)$. This separation of the phase part makes the structure of resulting perturbation equations similar to that of the static case and also ensures the correct zero-frequency behaviour of perturbed orbitals. The perturbative equation for nth order orbital $\chi^{(n)}$ is

$$(H^{(o)}-\epsilon_o-i\frac{\partial}{\partial t})\chi^{(n)}+\sum_{i=1}^{n}(H^{(i)}-\epsilon^{(i)})\chi^{(n-i)}=0 \tag{7}$$

and the normalization condition

$$\langle\chi^{(o)}|\chi^{(n)}\rangle=\langle\chi^{(n)}|\chi^{(o)}\rangle=-\frac{1}{2}\sum_{i=1}^{n-1}\langle\chi^{(i)}|\chi^{(n-i)}\rangle. \tag{8}$$

Here, $H^{(o)}$ is the unperturbed Hamiltonian and $H^{(i)}$ is the ith order correction to the Hamiltonian arising due to self-consistent screening:

$$H^{(i)}=v^{(1)}_{app}\delta_{i1}+\sum_{n=1}^{\infty}\frac{1}{n!}\int\frac{\delta^{(n+1)}E_{Hxc}}{\delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}_1,t)\cdots\delta\rho(\mathbf{r}_n,t)} \times \Delta\rho(\mathbf{r}_1,t)\cdots\Delta\rho(\mathbf{r}_n,t)d\mathbf{r}_1\cdots d\mathbf{r}_n \tag{9}$$

with

$$\Delta\rho(\mathbf{r},t)=\sum_i\rho^{(i)}(\mathbf{r},t) \tag{10}$$

and $\epsilon^{(i)}$ denotes ith order change in the time-dependent KS eigenvalue. Furthermore, following expressions are obtained for the time-average energies which are related to dynamic polarizabilities of the system to different orders

$$E^{(1)}=\left\{\int v^{(1)}(\mathbf{r},t)\rho^{(o)}(\mathbf{r})d\mathbf{r}\right\}_{average}$$

$$E^{(2)}=\left\{\langle\chi^{(1)}|\mathcal{H}_o-\epsilon_o|\chi^{(1)}\rangle +\langle\chi^{(1)}|v^{(1)}|\chi^{(o)}\rangle+\langle\chi^{(o)}|v^{(1)}|\chi^{(1)}\rangle+\frac{1}{2} \times\int\frac{\delta^2E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}\rho^{(1)}(\mathbf{r}_1,t)\rho^{(1)}(\mathbf{r}_2,t)d\mathbf{r}_1d\mathbf{r}_2\right\}_{average}$$

$$\begin{aligned}
p_i &= p_i^0 + \alpha_{ij}(0)\mathcal{E}_j(0)\\
&\quad +\alpha_{ij}(-\omega;\omega)\mathcal{E}_j(\omega)\cos\omega t + \frac{1}{2}\beta_{ijk}(0;0,0)\mathcal{E}_j(0)\mathcal{E}_k(0) + \frac{1}{4}\beta_{ijk}(0;\omega,-\omega)\mathcal{E}_j(\omega)\mathcal{E}_k(\omega) + \beta_{ijk}(0;\omega,-\omega)\mathcal{E}_j(\omega)\mathcal{E}_k(\omega)\cos\omega t\\
&\quad +\frac{1}{4}\beta_{ijk}(2\omega;\omega,\omega)\mathcal{E}_j(\omega)\mathcal{E}_k(\omega)\cos 2\omega t + \frac{1}{6}\gamma_{ijkl}(0;0,0,0)\mathcal{E}_j(0)\mathcal{E}_k(0)\mathcal{E}_l(0) + \frac{1}{4}\gamma_{ijkl}(0;\omega,-\omega,0)\mathcal{E}_j(\omega)\mathcal{E}_k(\omega)\mathcal{E}_l(0)\\
&\quad +\frac{1}{2}\gamma_{ijkl}(\omega;\omega,0,0)\mathcal{E}_j(\omega)\mathcal{E}_k(0)\mathcal{E}_l(0)\cos\omega t + \frac{1}{8}\gamma_{ijkl}(\omega;\omega,-\omega,\omega)\mathcal{E}_j(\omega)\mathcal{E}_k(\omega)\mathcal{E}_l(\omega)\cos\omega t\\
&\quad +\frac{1}{4}\gamma_{ijkl}(2\omega;\omega,\omega,0)\mathcal{E}_j(\omega)\mathcal{E}_k(\omega)\mathcal{E}_l(0)\cos 2\omega t + \frac{1}{24}\gamma_{ijkl}(3\omega;\omega,\omega,\omega)\mathcal{E}_j(\omega)\mathcal{E}_k(\omega)\mathcal{E}_l(\omega)\cos 3\omega t + \cdots
\end{aligned}\tag{17}$$

$$\begin{aligned}
E^{(3)} = \Big\{ &\langle\chi^{(1)}|H^{(1)} - \epsilon^{(1)}|\chi^{(1)}\rangle\\
&+\frac{1}{6}\int \frac{\delta^3 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)}\rho^{(1)}(\mathbf{r}_1,t)\\
&\times\rho^{(1)}(\mathbf{r}_2,t)\rho^{(1)}(\mathbf{r}_3,t)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\Big\}_{average}\\
E^{(4)} = \Big\{ &\langle\chi^{(2)}|\mathcal{H}_o - \epsilon_o|\chi^{(2)}\rangle\\
&+\langle\chi^{(2)}|H^{(1)} - \epsilon^{(1)}|\chi^{(1)}\rangle + \langle\chi^{(1)}|H^{(1)} - \epsilon^{(1)}|\chi^{(2)}\rangle\\
&+\frac{1}{2}\int \frac{\delta^2 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}\rho^{(2)}(\mathbf{r}_1,t)\rho^{(2)}(\mathbf{r}_2,t)d\mathbf{r}_1 d\mathbf{r}_2\\
&+\frac{1}{2}\int \frac{\delta^3 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)}\rho^{(1)}(\mathbf{r}_1,t)\\
&\times\rho^{(1)}(\mathbf{r}_2,t)\rho^{(2)}(\mathbf{r}_3,t)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\\
&+\frac{1}{24}\int \frac{\delta^4 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)\delta\rho(\mathbf{r}_4)}\rho^{(1)}(\mathbf{r}_1,t)\rho^{(1)}(\mathbf{r}_2,t)\\
&\times\rho^{(1)}(\mathbf{r}_3,t)\rho^{(1)}(\mathbf{r}_4,t)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4\Big\}_{average}.
\end{aligned}\tag{11}$$

In equation (11), $\mathcal{H}_o = H^{(0)} - i\partial/\partial t$, sum over occupied orbital is implicit, and curly bracket denotes the time average over a period of the applied perturbation. The average energy expressions above follow from the $(2n+1)$ theorem. Thus only $\chi^{(1)}$ is required to obtain energy up to order 3. The even-order energy changes $E^{(2)}$ and $E^{(4)}$ are stationary [21] (minimum for $\omega < \epsilon_o$ and $\omega < \epsilon_o/2$ corresponding to $E^{(2)}$ and $E^{(4)}$, respectively) with respect to $\chi^{(1)}$ and $\chi^{(2)}$, respectively. It is this variational nature of energies that we make use of to calculate the dynamic hyper-polarizabilities of the helium atom. The relationship between different hyper-polarizabilities, even-order energies and orbitals $\chi^{(1)}$ and $\chi^{(2)}$ is discussed below in Section 2.2 of the present section.

For the calculation of optical response properties, $v^{(1)}_{stat}(\mathbf{r})$ and $v^{(1)}_{dyn}(\mathbf{r})$ are of the form (in dipole approximation)

$$v^{(1)}_{stat}(\mathbf{r}) = v^{(1)}_{dyn}(\mathbf{r}) = \mathcal{E} r\cos\theta \tag{12}$$

where $\mathcal{E}$ is the field strength in the z-direction. As the overall phase part has been removed from the orbitals, the time dependence of χ has the following form [24,25] for applied perturbation given by equation (5)

$$\begin{aligned}
\chi^{(1)}(\mathbf{r},t) &= \chi^{(1)}_{+1}(\mathbf{r})e^{i\omega t} + \chi^{(1)}_{-1}(\mathbf{r})e^{-i\omega t} + \chi^{(1)}_{0}(\mathbf{r})\\
\chi^{(2)}(\mathbf{r},t) &= \chi^{(2)}_{+2}(\mathbf{r})e^{2i\omega t} + \chi^{(2)}_{-2}(\mathbf{r})e^{-2i\omega t}\\
&\quad + \chi^{(2)}_{+1}(\mathbf{r})e^{i\omega t} + \chi^{(2)}_{-1}(\mathbf{r})e^{-i\omega t} + \chi^{(2)}_{0}(\mathbf{r})
\end{aligned}\tag{13}$$

where $\chi^{(i)}_{\pm,0}$ depend only on the spatial co-ordinate. These are the functions which are determined variationally. The variational forms we choose are

$$\begin{aligned}
\chi^{(1)}_{\pm1,0} &= \varDelta^{1}_{\pm1,0}(r)\chi^{(o)}(r)\cos\theta\\
\chi^{(2)}_{\pm2} &= [\varDelta^{2}_{\pm2}(r) + \varDelta^{3}_{\pm2}(r)\cos^2\theta]\chi^{(o)}(r) + \lambda_{\pm2}\chi^{(o)}(r)\\
\chi^{(2)}_{\pm1} &= [\varDelta^{2}_{\pm1}(r) + \varDelta^{3}_{\pm1}(r)\cos^2\theta]\chi^{(o)}(r) + \lambda_{\pm1}\chi^{(o)}(r)\\
\chi^{(2)}_{0} &= [\varDelta^{2}_{0}(r) + \varDelta^{3}_{0}(r)\cos^2\theta]\chi^{(o)}(r) + \lambda_{0}\chi^{(o)}(r)
\end{aligned}\tag{14}$$

where

$$\varDelta^{i}(r) = a_i r + b_i r^2 + c_i r^3 + \cdots \tag{15}$$

is a polynomial with $a_i, b_i, c_i, \ldots$ being the variational parameters, and $\lambda_{\pm2,\pm1,0}$ are chosen such that normalization condition (Eq. (8)) is satisfied for the second-order orbitals. In the present calculations we have chosen seven parameters for each of the $\varDelta_i$. We have found that with seven parameters results for hyper-polarizabilities converge up to second decimal place. These results are obtained by employing Gunnarson-Lundquist parametrization [26] of correlation energy.

2.2 Calculation of response properties

The response properties are described in terms of polarizabilities by expanding the dipole moment in terms of applied field corresponding to the potential of equations (5, 6).

$$\mathcal{E} = \mathcal{E}(0) + \frac{1}{2}\mathcal{E}(\omega)(e^{\imath\omega t} + e^{-\imath\omega t}) \tag{16}$$

as

see equation (17) *above.*

For an atom in the s-state (spherically symmetric), the static dipole p_i^0 and the first order hyper-polarizabilities β are zero. Moreover, for this system γ_{ijkl} has two independent components namely, γ_{zzzz} and γ_{zzxx} [20]. In this paper we only calculate the component γ_{zzzz}.

$$\begin{aligned}\gamma(3\omega;\omega,\omega,\omega) = 96\Big\{&\langle\chi^{(1)}_{+3}|H^{(2)}_{+2} - \epsilon^{(2)}_{+2}|\chi^{(1)}_{+1}\rangle + \langle\chi^{(1)}_{-1}|H^{(2)}_{-2} - \epsilon^{(2)}_{-2}|\chi^{(1)}_{-3}\rangle + \langle\chi^{(1)}_{+3}|H^{(1)}_{+1} - \epsilon^{(1)}_{+1}|\chi^{(2)}_{+2}\rangle + \langle\chi^{(2)}_{-2}|H^{(1)}_{-1} - \epsilon^{(1)}_{-1}|\chi^{(1)}_{-3}\rangle \\ &+\langle\chi^{(2)}_{-2}|H^{(1)}_{-3} - \epsilon^{(1)}_{-3}|\chi^{(1)}_{+1}\rangle + \langle\chi^{(1)}_{-1}|H^{(1)}_{-3} - \epsilon^{(1)}_{-3}|\chi^{(2)}_{+2}\rangle + \int \frac{\delta^3 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)}\rho^{(1)}_{+1}(\mathbf{r}_1)\rho^{(1)}_{-3}(\mathbf{r}_2)\rho^{(2)}_{+2}(\mathbf{r}_3)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\ &+\frac{1}{6}\int \frac{\delta^4 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)\delta\rho(\mathbf{r}_4)}\rho^{(1)}_{+1}(\mathbf{r}_1)\rho^{(1)}_{+1}(\mathbf{r}_2)\rho^{(1)}_{+1}(\mathbf{r}_3)\rho^{(1)}_{-3}(\mathbf{r}_4)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4\Big\} \qquad (20)\end{aligned}$$

$$\begin{aligned}\gamma(2\omega;\omega,\omega,0) = 16\Big\{&\langle\chi^{(1)}_{+2}|H^{(2)}_{+1} - \epsilon^{(2)}_{+1}|\chi^{(1)}_{+1}\rangle + \langle\chi^{(1)}_{-1}|H^{(2)}_{-1} - \epsilon^{(2)}_{-1}|\chi^{(1)}_{-2}\rangle + \langle\chi^{(1)}_{+2}|H^{(2)}_{+2} - \epsilon^{(2)}_{+2}|\chi^{(1)}_{0}\rangle + \langle\chi^{(1)}_{0}|H^{(2)}_{-2} - \epsilon^{(2)}_{-2}|\chi^{(1)}_{-2}\rangle \\ &+\langle\chi^{(1)}_{+2}|H^{(1)}_{+1} - \epsilon^{(1)}_{+1}|\chi^{(2)}_{+1}\rangle + \langle\chi^{(2)}_{-1}|H^{(1)}_{-1} - \epsilon^{(1)}_{-1}|\chi^{(1)}_{-2}\rangle + \langle\chi^{(1)}_{+2}|H^{(1)}_{0} - \epsilon^{(1)}_{0}|\chi^{(2)}_{+2}\rangle + \langle\chi^{(2)}_{-2}|H^{(1)}_{0} - \epsilon^{(1)}_{0}|\chi^{(1)}_{-2}\rangle \\ &+\langle\chi^{(1)}_{-1}|H^{(1)}_{-2} - \epsilon^{(1)}_{-2}|\chi^{(2)}_{+1}\rangle + \langle\chi^{(2)}_{-1}|H^{(1)}_{-2} - \epsilon^{(1)}_{-2}|\chi^{(1)}_{+1}\rangle + \langle\chi^{(1)}_{0}|H^{(1)}_{-2} - \epsilon^{(1)}_{-2}|\chi^{(2)}_{+2}\rangle + \langle\chi^{(2)}_{-2}|H^{(1)}_{-2} - \epsilon^{(1)}_{-2}|\chi^{(1)}_{0}\rangle \\ &+\int \frac{\delta^3 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)}(\rho^{(1)}_{+1}(\mathbf{r}_1)\rho^{(1)}_{-2}(\mathbf{r}_2)\rho^{(2)}_{+1}(\mathbf{r}_3) + \rho^{(1)}_{0}(\mathbf{r}_1)\rho^{(1)}_{-2}(\mathbf{r}_2)\rho^{(2)}_{+2}(\mathbf{r}_3))d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\ &+\frac{1}{6}\int \frac{\delta^4 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)\delta\rho(\mathbf{r}_4)}(\rho^{(1)}_{+1}(\mathbf{r}_1)\rho^{(1)}_{+1}(\mathbf{r}_2)\rho^{(1)}_{0}(\mathbf{r}_3)\rho^{(1)}_{-2}(\mathbf{r}_4) + \rho^{(1)}_{+1}(\mathbf{r}_1)\rho^{(1)}_{0}(\mathbf{r}_2)\rho^{(1)}_{+1}(\mathbf{r}_3)\rho^{(1)}_{-2}(\mathbf{r}_4) \\ &+\rho^{(1)}_{0}(\mathbf{r}_1)\rho^{(1)}_{+1}(\mathbf{r}_2)\rho^{(1)}_{+1}(\mathbf{r}_3)\rho^{(1)}_{-2}(\mathbf{r}_4))d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4\Big\} \qquad (21)\end{aligned}$$

As pointed out earlier [21], it is possible to determine directly from $E^{(4)}$ polarizabilities which are associated with dipole moment oscillating at frequency ω (see Eq. (17)). More specifically, when only a time-dependent field at frequency ω is applied to the system, the fourth-order energy change $E^{(4)}$ can be written as

$$\frac{E^{(4)}}{\mathcal{E}^4} = \frac{3}{192}\gamma(\omega;\omega,-\omega,\omega). \qquad (18)$$

Furthermore, when a static field (field with $\omega = 0$) is added with the time dependent field (Eq. (18)) modifies to

$$\frac{E^{(4)}}{\mathcal{E}^4} = \left[\frac{1}{64}\gamma(\omega;\omega,-\omega,\omega) + \frac{1}{8}\gamma(\omega;\omega,0,0) + \frac{1}{24}\gamma(0;0,0,0)\right]. \qquad (19)$$

Thus, by using equation (18) we directly obtain $\gamma(\omega;\omega,-\omega,\omega)$ by minimizing the fourth-order change in the energy when only a time-dependent field is applied. Similarly, equation (19) gives us $\gamma(\omega;\omega,0,0)$ directly from $E^{(4)}$ with both static and dynamic fields applied. On the other hand, to determine hyper-polarizabilities which are not associated with dipole moments oscillating at frequency ω we make use of the $2n+1$ rule for time dependent perturbation theory [27,28]. According to this rule it is possible to determine third-order hyper-polarizabilities using wavefunctions up to second-order. Application of this rule gives the following expression for $\gamma(3\omega;\omega,\omega,\omega)$ in terms $\chi^{(1)}$ and $\chi^{(2)}$

see equation (20) above.

In the above expression, superscripts denote order of perturbation and subscripts correspond to the components of oscillating frequency.

Thus, to evaluate $\gamma(3\omega;\omega,\omega,\omega)$ one needs first-order orbital $\chi^{(1)}$ oscillating at frequency ω and 3ω and $\chi^{(2)}$ at 2ω. Orbitals $\chi^{(1)}_{\pm 1}(\mathbf{r})$ and $\chi^{(1)}_{\pm 3}(\mathbf{r})$ are obtained by minimizing $E^{(2)}$ given by equation (11) with respect to $\chi^{(1)}$ at frequency ω and 3ω, respectively. Then minimization of $E^{(4)}$ with respect to $\chi^{(2)}$ gives $\chi^{(2)}_{\pm 2}(\mathbf{r})$. By substituting these orbitals in equation (20) we determine $\gamma(3\omega;\omega,\omega,\omega)$. Similarly, $\gamma(2\omega;\omega,\omega,0)$ can be also expressed in terms of $\chi^{(1)}$ and $\chi^{(2)}$ as

see equation (21) above.

Using a similar procedure as described for $\gamma(3\omega;\omega,\omega,\omega)$, we evaluate $\gamma(2\omega;\omega,\omega,0)$ from equation (21). Results of these calculations are discussed in the next section.

Table 1. Dynamic hyperpolarizabilities of helium atom in atomic units (a.u.).

ω (a.u.)	Kerr	DFWM	EFISH	THG
0.0	46.66	46.66	46.66	46.66
0.02	46.75	46.85	46.90	47.17
0.04	47.04	47.42	47.74	48.90
0.06	47.53	48.42	49.22	52.07
0.08	48.23	49.86	51.44	57.12
0.10	49.16	51.84	54.55	64.89
0.12	50.33	54.44	58.81	77.02
0.14	51.77	57.81	64.60	97.02
0.16	53.51	64.88	77.66	165.5
0.18	55.60	67.96	83.77	311.8
0.20	58.09	75.70	100.3	538.7

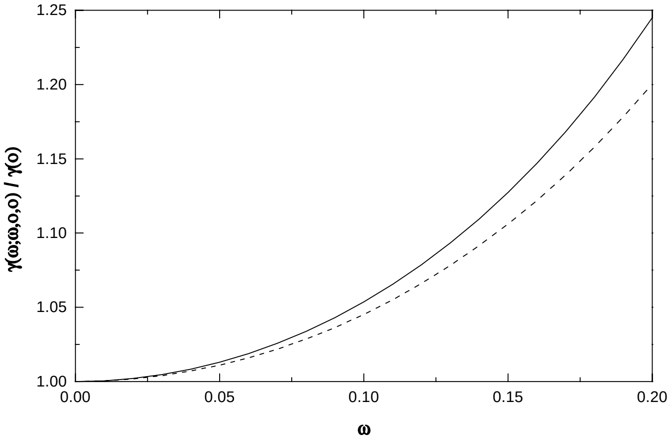

Fig. 1. Plot of $\gamma(\omega;\omega,0,0)/\gamma(0;0,0,0)$ (Kerr effect) as a function of ω for the helium atom; solid line: our result and dashed line: reference [14].

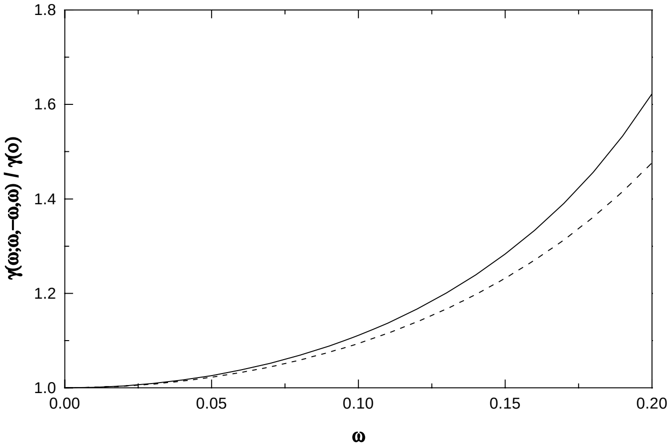

Fig. 2. Plot of $\gamma(\omega;\omega,-\omega,\omega)/\gamma(0;0,0,0)$ (DFWM) as a function of ω for the helium atom; solid line: our result and dashed line: reference [14].

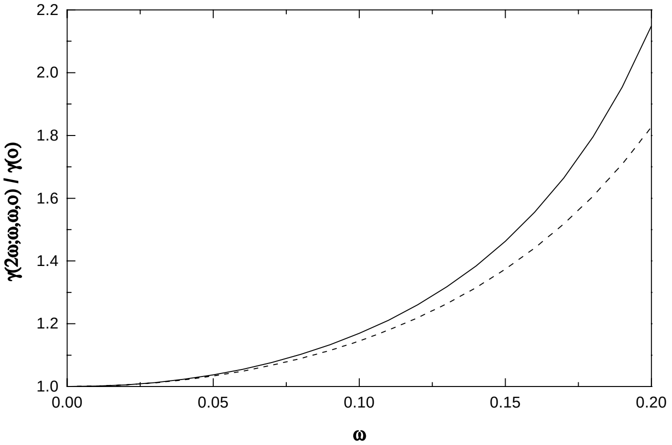

Fig. 3. Plot of $\gamma(2\omega;\omega,\omega,0)/\gamma(0;0,0,0)$ (EFISH) as a function of ω for the helium atom; solid line: our result and dashed line: reference [14].

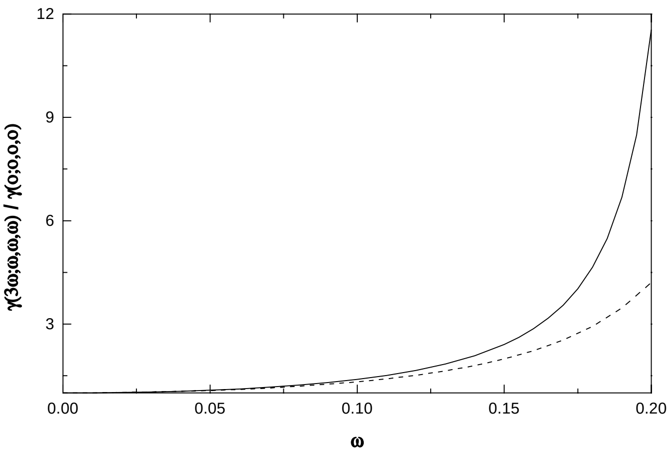

Fig. 4. Plot of $\gamma(3\omega;\omega,\omega,\omega)/\gamma(0;0,0,0)$ (THG) as a function of ω for the helium atom; solid line: our result and dashed line: reference [14].

3 Results and discussions

In order to provide a proper understanding of our results for nonlinear optical properties, we start with a brief discussion of linear polarizability $\alpha(\omega)$ of the helium atom as obtained in our calculations. The static value of linear polarizability $\alpha(0)$ obtained by us is 1.390, which is quite close to both the *ab initio* result 1.383 [14] and the experimental value 1.38 [15]. To examine the frequency dependence of α we fit the frequency dependent polarizability with the formula [15]

$$\alpha(\omega) = \alpha(0)\left(1 + C_2\omega^2\right). \tag{22}$$

This relation is valid for small values of ω, the coefficient C_2 is a measure of frequency dependence and is independent of the static value. The result obtained by us for C_2 is 1.18. Again, it compares well with the *ab initio* result 1.16 [14] and the experimental value $C_2 = 1.16$ [15].

Next we present results for frequency dependent hyper-polarizabilities in Table 1 for values of ω from 0 to 0.2 a.u. (which is well below the resonance frequency for these processes). The static value of hyper-polarizability $\gamma(0;0,0,0)$ is 46.66; it differs by only 8% from the *ab initio* result of Bishop and Pipin [14]. It is important to note that, when the ground-state density obtained with the LDA exchange-correlation is used for calculating the value of $\gamma(0;0,0,0)$ it is 83.35 [29] which is off by about 45%. This then clearly shows that by using accurate ground-state orbitals and density along with ALDA for exchange-correlation kernels one can obtain static nonlinear response properties which are reasonably accurate in comparison to the *ab initio* results. To examine the effect of ALDA on frequency dependence of hyper-polarizabilities we plot $\gamma(\omega)/\gamma(0)$ as a function of frequency in Figures 1–4. For comparison we also display *ab initio* results [14] (shown by dashed lines) in Figures 1–4. It is clear from these figures that for low frequencies ALDA does reproduce the frequency dependence quite accurately as compared to the *ab initio* results. In particular, for $\omega \leq 0.05$ the agreement between our results and that of reference [14] is excellent. For, $\omega = 0.05$ to 0.1 the match is moderate for all hyper-polarizabilities. We note that this frequency band is quite important from an experimental point of view. Going beyond this frequency range, that is for $\omega > 0.1$, the frequency dependence of all the hyper-polarizabilities are substantially different from *ab initio* results. For the coefficients of DFWM, Kerr effect and EFISH, the frequency dependence is almost the same. On the other hand, deviation of THG coefficients for large frequencies is much greater as evident from Figure 4. The results presented here also match quite well with experimental values. For example, the experimental value for $\gamma_{Kerr} = (3/2)(\gamma_{zzzz}(\omega;\omega,0,0) - \gamma_{xxzz}(\omega;\omega,0,0))$ is 47.2 ± 3 at 5145 Å ($\omega \approx 0.089$ a.u.) [16]. Our theoretical value (determined by assuming Kleinman symmetry [30]) is 48.86 and it lies within the experimental bound. Two more experimental results for Kerr effect at 6328 Å ($\omega \approx 0.07$ a.u.) are $\gamma_{Kerr} = 54 \pm 4$ [17] and 52 ± 8 a.u. [18]. Our value at this frequency is 47.67 which lies within experimental bound of the second result.

4 Conclusion

In this paper we have assessed the accuracy of ALDA in the calculation of nonlinear optical properties of the helium atom. Our study clearly shows that with accurate ground-state Kohn-Sham orbitals and densities, it is possible to determine both static value and the frequency dependence of hyper-polarizabilities up to $\omega = 0.1$ a.u. employing the adiabatic local-density approximation for exchange-correlation kernel. The values thus obtained compare well with the *ab initio* results. Moreover, our results in this frequency range fall well within the bounds of experimental values. Encouraged by these results we are now applying ALDA for calculating nonlinear optical properties of heavier atoms within TDDFT.

References

1. E.K.U. Gross, J.F. Dobson, M. Petersilka, in *Density Functional Theory, Topics in Current Chemistry*, edited by R.F. Nalewajski (Springer, Berlin, 1996), Vol. 181.
2. A. Zangwill, P. Soven, Phys. Rev. A **21**, 4274 (1980).
3. M.J. Stott, E. Zaremba, Phys. Rev. A **21**, 12 (1980); Phys. Rev. A **22**, 2293 (1980).
4. S.K. Ghosh, B.M. Deb, Chem. Phys. **71**, 295 (1982); J. Mol. Stru. (Theochem) **103**, 163 (1983).
5. L.J. Bartolotti, J. Chem. Phys. **80**, 5187 (1984); J. Phys. Chem. **90**, 5518 (1986).
6. G. Senatore, K.R. Subbaswamy, Phys. Rev. A **35**, 2440 (1987).
7. S.J.A. Gisbergen, V.P. Osinga, O.V. Gritsenko, R. van Leeuwen, J.G. Snijders, E.J. Baerands, J. Chem. Phys. **105**, 3142 (1996).
8. M. Petersilka, U.J. Grossmann, E.K.U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).
9. B.M. Deb, S.K. Ghosh, J. Chem. Phys. **77**, 342 (1982).
10. L.J. Bartolloti, Phys. Rev. A **24**, 1661 (1981); Phys. Rev. A **26**, 2243 (1982).
11. E. Runge, E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1994).
12. H. Zong, Z. Levine, J.W. Wilkins, Phys. Rev. A **43**, 4629 (1991).
13. S.J.A. Gisbergen, F. Kootstra, P.R.T. Schipper, O.V. Gritsenko, J.G. Snijders, E.J. Baerends, Phys. Rev. A **57**, 2259 (1998).
14. D.M. Bishop, J. Pipin, J. Chem. Phys. **91**, 3549 (1989).
15. J. Leonard, At. Data Nucl. Data Tab. **14**, 21 (1974).
16. S. Carusotto, E. Iacopini, F. Scuri, G. Stefanini, E. Zavatini, Nuovo Cimento D **5**, 328 (1985).
17. A.D. Buckingham, D.A. Dunmur, Trans. Faraday Soc. **64**, 1776 (1968).
18. L.L. Boyle, A.D. Bukingham, R.L. Disch, D.A. Dunmur, J. Chem. Phys. **45**, 1318 (1966).
19. V. Mizrahi, D.P. Shelton, Phys. Rev. A **31**, 3145 (1985).
20. Y.R. Shen, in *The Principles of Nonlinear Optics* (John Wiley, New York, 1984).
21. A. Banerjee, M.K. Harbola, Phys. Lett. A **236**, 525 (1997).
22. T. Koga, Y. Kasai, A.J. Thakkar, Int. J. Quantum Chem. **46**, 689 (1993).
23. K.T. Chung, Phys. Rev. **163**, 1343 (1967).
24. H. Sambe, Phys. Rev. A **7**, 2203 (1973).
25. P.W. Langhoff, S.T. Epstein, M. Karplus, Rev. Mod. Phys. **44**, 602 (1972).
26. O. Gunnarson, B.I. Lundquist, Phys. Rev. B **13**, 4274 (1979).
27. R. Kleingbell, V.G. Kaveeshwar, R.P. Hurst, Phys. Rev. A **4**, 1760 (1971).
28. S.P. Karna, J. Chem. Phys. **104**, 6590 (1996).
29. M.K. Harbola, A. Banerjee, Phys. Rev. A **54**, 283 (1996); Phys. Rev. A **56**, 3307 (1997).
30. D.A. Kleinman, Phys. Rev. A **126**, 1977 (1962).