Frequency dependent hyperpolarizabilities of atoms; calculations using density-functional theory

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Abstract

Using the orbitals generated by the van Leeuwen-Baerends potential [Phys. Rev. A 49, 2421 (1994)], we calculate frequency-dependent response properties of the noble gas atoms of helium, neon and argon and the alkaline earth atoms of beryllium and magnesium, with particular emphasis on their nonlinear polarizabilities. For this, we employ the time-dependent Kohn-Sham formalism with the adiabatic local-density approximation (ALDA) for the exchange and correlation. We show that the results thus obtained for frequency-dependent polarizabilities (both linear and nonlinear) of the inert gas atoms are highly accurate. On the other hand, polarizabilities of the alkaline earths are not given with the same degree of accuracy. In light of this, we make an assessment of ALDA for obtaining linear and nonlinear response properties by employing time-dependent density-functional theory.
I. INTRODUCTION

Over the past decade, the time dependent density-functional theory (TDDFT) [1,4] is being used increasingly to study frequency dependent response properties [3–14] and excitation energies [2,11,15] of many-electron systems. The theory found its first application in the calculation of frequency dependent polarizabilities of atoms and photo-absorption cross section of atoms and molecules [3,4]. However, the existence of TDDFT was not formally proved at that time. It was some years later that Deb and Ghosh [16], Bartolotti [17] and Runge and Gross [18] laid rigorous foundations of TDDFT. Analogous to its stationary counterpart TDDFT is exact in principle but its practical implementation requires approximating the exchange-correlation (XC) energy functional. In most of the applications the adiabatic local density approximation (ALDA) [1] is used. In this approximation the nonlocal time-dependence of the functional is ignored and the spatial dependence is also treated locally. As such the functional has the same form as the local-density approximation (LDA) of the stationary-state theory [19,20]. Results for the response properties using the LDA for the unperturbed system and ALDA for perturbation calculations show that with these approximations the polarizability at zero frequency (static polarizability) as well as its frequency dependence are overestimated. Use of LDA+ALDA for the response property calculations introduces errors at two different levels. First, the use of the LDA for calculation of the unperturbed orbitals gives potentials and densities which are asymptotically not correct. In particular the tail of the LDA potential is exponential rather than its correct $-\frac{1}{r}$ behaviour [21]. Thus the physical properties that depend on the asymptotic nature of the ground-state orbitals and densities, for example the response properties, are not determined accurately by the LDA orbitals. Secondly, errors in the response property calculations arise because: (i) further change in the potential itself is being calculated approximately, and (ii) ALDA is valid only in the limit of zero frequency. There have been attempts to rectify the problem at the first level by employing methods which reproduce the asymptotic behaviour of the potential correctly. Thus Senatore and Subbaswamy [7] applied the self-interaction correction
method to obtain accurate orbitals with proper asymptotic decay. Later Zong et. al \cite{8} devised a scissors operator technique and Gisbergen et al. \cite{9} employed a model potential with the desired asymptotic behaviour to improve the polarizabilities. Gisbergen et al. \cite{11} also studied frequency dependent polarizabilities of He, Be and Ne by employing exact XC potential for the ground-state of these atoms coupled with ALDA for the XC kernels. Nearly exact ground-state wavefunction along with the ALDA for XC kernels were employed by us \cite{13} to calculate nonlinear optical coefficients of helium, and to investigate the accuracy of ALDA in predicting the frequency dependence of nonlinear polarizabilities.

All these studies show that the inaccuracy in the response properties arise mainly from the use of the LDA to obtain the unperturbed densities; For perturbative calculations, on the other hand, ALDA appears to be a reasonably accurate approximation, particularly at frequencies in the optical range. One may therefore conclude that if the asymptotic nature of the potential is corrected, the response properties at optical frequencies will come out to be comparable to the ab-initio or experimental values even with the use of ALDA. However, the conclusions above cannot said to be general since most of the studies have been confined to investigating the linear polarizabilities.

Against this background it then becomes necessary to investigate how does ALDA perform in the calculation of frequency dependent nonlinear optical coefficients of heavier atoms when asymptotically accurate ground-state orbitals are used for this purpose. For the helium atom we could perform such a study with a near exact ground-state orbital \cite{23} obtained from its Hylleraas wavefunction. However, this is not possible for systems with larger number of electrons. For such systems we generate the ground-state orbitals and potentials by using the model potential introduced by van Leeuwen and Baerdens (LB) \cite{24} as a correction to the LDA XC potential. Recently we have employed this potential to calculate the static nonlinear response properties of several atoms and ions \cite{25}. We found that the orbitals given by this model potential, when used with the LDA for the higher derivatives of XC potential, give reasonably accurate static hyperpolarizabilities for the inert gas atoms. Thus to assess the accuracy of ALDA in predicting the frequency dependence of nonlinear
polarizabilities, in this paper we first study dynamic hyperpolarizabilities of these atoms calculated by employing the orbitals generated by the LB potential. In our study \[13\] of the static properties, we also found that the hyperpolarizabilities for the alkaline earths show some improvement with the inclusion of the LB correction although their linear polarizabilities remain unaffected. In this paper we study the frequency-dependent polarizabilities of the alkaline earth atoms of Be and Mg also and show that the dynamic polarizabilities of these systems follow the same trend as their static counterparts. In the following, we first briefly describe the LB potential. We follow that with a short description of the variation-perturbation method of calculating the dynamic response properties. We then present our results and conclude the paper with a discussion.

van Leeuwen and Baerends \[24\] proposed a correction to the LDA potential primarily to correct its asymptotic behaviour. For this they first noted that the Becke’s correction \[26\] to the LDA functional gives the correct exchange-energy density but fails to give the potential correctly. Thus they suggested that a Becke-like correction be added to the potential directly, and found that such a correction brings the approximate potential very close to the exact one. Thus the highest occupied orbital eigenenergy as obtained from this potential is close to the ionization energy of a many-electron system. More recently, it has been shown that the corresponding total energy is also quite accurate \[25\]. The effective potential proposed by LB has the form

$$v_{xc}(\mathbf{r}) = v_{xc}^{LDA}(\mathbf{r}) + v^{LB}(\mathbf{r})$$

(1)

with

$$v^{LB}(\mathbf{r}) = -\beta \frac{\rho^{\frac{1}{3}}x^2}{1 + 3\beta x \sinh^{-1}(x)},$$

(2)

where $x = \frac{\mathbf{\nabla} \rho}{\rho^{\frac{1}{3}}}$ and $\beta = 0.05$. Note that the extra term $v^{LB}(\mathbf{r})$ added to the LDA potential is like the Becke term. It therefore represents the correction to only the exchange component of the potential. Using the potential given by Eq.\((1)\) and \((2)\) we generate the ground-state orbitals and potentials for the above mentioned atoms and then employ these orbitals for the calculation of frequency dependent linear and nonlinear polarizabilities.
We perform calculations of the optical response properties by employing the variation-perturbation method \[10\] within the time dependent Kohn-Sham (TDKS) formalism of TDDFT. This method has been used in the past to calculate \[13\] polarizabilities corresponding to several nonlinear optical phenomena. The method and expressions for various hyperpolarizabilities have been discussed \[10,13\] in our earlier works. Thus we do not describe these in detail here. It is sufficient to mention that the linear polarizability and the coefficient corresponding to the degenerate-four-wave-mixing (DFWM) are obtained directly by minimizing the second-order and fourth-order changes in the quasi-energy with respect to the first and second-order orbitals, respectively. The other nonlinear coefficients are not related directly with the fourth-order energy change. However, expressions for these coefficients in terms of second-order orbitals have been derived \[13,27\] within TDKS theory and it is these expressions which we employ here. To perform our calculations, we represent the radial part of the induced orbitals by a linear combination of the Slater type orbitals (STO). Thus it is given as

\[ f(r) = \sum_i C_i r^{n_i} e^{-\eta_i r}, \]  

(3)

where \( n_i \) and \( \eta_i \) are the parameters of STO which are fixed and \( C_i \) are the linear variational parameters. Parameters \( n_i \) and \( \eta_i \) are chosen in such a way that the functions correctly represent the excited states. We have optimized these parameters by calculating the static polarizabilities and hyperpolarizabilities from the LDA ground-state orbitals, and matching the results with the numbers obtained by Stott and Zaremba \[4\]. For the exchange-correlation energy we have used the Gunnarsson-Lundquist parametrization \[28\], which is the same as used by Stott and Zaremba. Thus our results for hyperpolarizabilities are around 10% less than those of Senatore and Subbaswamy \[7\] who use the Perdew-Zunger \[22\] parametrization.

We now present the results of our calculation. Although our main focus in this paper is on the frequency dependent hyperpolarizabilities, for completeness we first discuss the results for frequency dependent polarizabilities.
In Figs. 1-3 we show the ratio $\frac{\alpha(\omega)}{\alpha(0)}$ for the inert gas atoms He, Ne and Ar as a function of frequency $\omega$ and for comparison also display the corresponding ab-initio results. For helium we compare our results with the results of Bishop and Lam [29] and for neon and argon the comparison is made with the MP2 results of Rice [30]. Since $\alpha(0)$ is already reproduced quite accurately with the LB orbitals, it is clear from these figures that $\alpha(\omega)$ is also accurate and matches quite well with the ab-initio results. For helium the ab-initio results are essentially reproduced by our calculations for frequencies up to 0.5 a.u. (wavelength of about 914 Å). For neon the match with the MP2 results is good till about 0.1 a.u. and for argon good match is obtained up to $\omega = 0.07$ a.u.. For comparison we also show the corresponding LDA results. It is quite clear that the LDA results are highly inflated in comparison to both the LB corrected and the ab-initio numbers.

In Figs. 4 and 5, we present the results of $\frac{\alpha(\omega)}{\alpha(0)}$ for the Be and Mg atoms. The results for these atoms are quite different from those of the inert gas atoms discussed above. Here the LDA and the LB corrected results are essentially the same. This is intriguing since the energies and the highest occupied eigenvalues obtained from the two schemes differ significantly. A possible reason for this could be that since the outer electrons in these systems are less tightly bound, the exchange and correlation effects play a relatively more important role in determining the polarizabilities, and ALDA is not sufficient to represent their effects accurately. Thus although the unperturbed orbitals are improved by inclusion of the LB correction, this alone is not sufficient to get over the inaccuracy of ALDA for these systems.

Having discussed linear polarizabilities, we now proceed on to present the results for the nonlinear coefficients corresponding to third harmonic generation (THG) and DFWM of these atoms. As is the case with polarizabilities, these results are also obtained from the orbitals generated by the LB potential with the use of ALDA for perturbative calculations.

First, we discuss the results for helium. Exact results corresponding to the above mentioned nonlinear optical effects for helium are available over a range of frequencies. In Figs.
6 and 7 we display our results in comparison with the ab-initio results \[31\]. Plotted in Fig. 6 is the DFWM coefficient $\gamma(\omega)\gamma(0)$, and in Fig. 7 we plot the THG coefficient $\gamma(3\omega)\gamma(0)$ as a function of $\omega$. It is evident from the figures that the results for hyperpolarizabilities obtained from the LB orbitals are also highly accurate. The LDA, on the other hand, overestimates the frequency dependence of these quantities by a large amount. A comparative study like this is not possible at all frequencies for neon and argon because of the lack of available data. However, some experimental results are available \[32,33\] at few discrete frequencies for all three atoms. We now compare our results with these experimental numbers.

In Table I we present our results for the THG coefficients of the atoms considered in this paper at two distinct wavelengths, namely, $\lambda = 10550\text{Å}$ ($\omega \approx 0.0433$ a.u.) and $\lambda = 6943\text{Å}$ ($\omega \approx 0.0658$ a.u.). We do so because experimental results for THG by helium, neon and argon exist at these wavelengths. For a complete picture, we give the results obtained from both the LDA and the LB orbitals. It is again clear that although the LDA orbitals give a large error in the estimates of these quantities for the noble gas atoms, the LB corrections to the LDA eliminates almost all of this error. Further, the numbers obtained from the LB orbitals lie within the experimental error bounds. For the other two atoms also the LB corrected results for the THG coefficients are less than the LDA numbers. However, there are no experimental numbers available for these systems. Nonetheless, on the basis of their zero frequency results, we expect the LB numbers to be closer to experiments than the LDA numbers. In Table II we present the results of DFWM coefficients at the same frequencies, although no experimental data exists for this effect. However, we expect these results to be quite accurate for the noble gas atoms, and moderately accurate for the alkaline earths. This is because the maximum deviation from the ab-initio or the experimental results is observed for THG coefficients which have already been shown to be accurate.

To conclude, our study above indicates that when accurate orbitals are employed to calculate response properties, ALDA reproduces the frequency dependence of linear as well as nonlinear response properties of the noble gas atoms quite accurately. On the other hand, for the alkaline earths its behaviour with respect to the linear and nonlinear polarizabilities
is quite different. Thus it appears that for systems, such as Be and Mg, where the electrons are loosely bound, ALDA is not a good approximation to calculate the effects of exchange and correlation. In a recent study, it has been shown that ALDA is a major component of the exchange-correlation functional for time-dependent hamiltonians. This has been done by considering two electrons moving in a time-dependent potential. However, our study indicates that this is true only if the electrons are tightly bound.
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A. Table Captions

**Table I:** THG coefficients with and without the LB correction to the LDA along with their experimental values (in atomic units).

**Table II:** DFWM coefficients with and without the LB correction to the LDA (in atomic units).
### Table I

| Atom | $\lambda = 6943\text{Å}$ | $\lambda = 10550\text{Å}$ |
|------|----------------|------------------|
|      | LDA   | LDA+LB | Expt. [33] | LDA   | LDA+LB | Expt. [32] |
| He   | 98.46 | 48.35  | 53.6±7     | 89.12 | 45.11  | 44.07±4.8  |
|      |       |        | 53.6±2.4   |       |        |           |
| Ne   | 230.30| 103.68 | 119±13     | 202.67| 95.50  | 78.27±8.3  |
|      |       |        | 96.5±4.8   |       |        |           |
| Ar   | 2532.8| 1560.3 | 1691±167   | 1925  | 1275.1 | 1021.3±107 |
|      |       |        | 786±48     |       |        |           |
| Be   | $6.42 \times 10^8$ | $1.45 \times 10^8$ | - | $1.41 \times 10^5$ | $1.07 \times 10^5$ | - |
| Mg   | no minimum | no minimum | - | $1.88 \times 10^{11}$ | $3.17 \times 10^9$ | - |

### Table II

| Atom | $\lambda = 6943\text{Å}$ | $\lambda = 10550\text{Å}$ |
|------|----------------|------------------|
|      | LDA   | LDA+LB | LDA   | LDA+LB |
| He   | 87.62 | 44.57  | 84.86 | 43.58  |
| Ne   | 198.16| 94.06  | 190.45| 91.65  |
| Ar   | 1863.0| 1226.1 | 1725.5| 1154.8 |
| Be   | $9.83 \times 10^4$ | $7.33 \times 10^4$ | $6.17 \times 10^4$ | $4.83 \times 10^4$ |
| Mg   | $4.46 \times 10^5$ | $1.98 \times 10^5$ | $2.08 \times 10^5$ | $1.14 \times 10^5$ |
**Figure Captions**

**Fig. 1**: Plot of $\frac{\alpha(\omega)}{\alpha(0)}$ as a function of frequency $\omega$ for helium. The squares, open circles and filled circles represent the LDA, the LDA+LB and ab-initio results [29], respectively.

**Fig. 2**: Plot of $\frac{\alpha(\omega)}{\alpha(0)}$ as a function of frequency $\omega$ for neon. The squares, open circles and filled circles represent the LDA, the LDA+LB and ab-initio results [30], respectively.

**Fig. 3**: Plot of $\frac{\alpha(\omega)}{\alpha(0)}$ as a function of frequency $\omega$ for argon. The squares, open circles and filled circles represent the LDA, the LDA+LB and ab-initio results [30], respectively.

**Fig. 4**: Plot of $\frac{\alpha(\omega)}{\alpha(0)}$ as a function of frequency $\omega$ for Be. The squares and filled circles represent the LDA and the LDA+LB results, respectively.

**Fig. 5**: Plot of $\frac{\alpha(\omega)}{\alpha(0)}$ as a function of frequency $\omega$ for Mg. The squares and filled circles represent the LDA and the LDA+LB results, respectively.

**Fig. 6**: Plot of $\frac{\gamma(3\omega)}{\gamma(0)}$ (THG) as a function of frequency $\omega$ for helium. The squares, open circles and filled circles represent the LDA, the LDA+LB and ab-initio results [31], respectively.

**Fig. 7**: Plot of $\frac{\gamma(\omega)}{\gamma(0)}$ (DFWM) as a function of frequency $\omega$ for helium. The squares, open circles and filled circles represent the LDA, the LDA+LB and ab-initio results [31], respectively.
$\alpha(\omega)/\alpha(0)$
$\frac{\alpha(\omega)}{\alpha(0)}$ vs $\omega$
\[ \frac{\gamma(\omega; \omega, -\omega, \omega)}{\gamma(0)} \]
$\gamma(3\omega; \omega, \omega, \omega) / \gamma(0)$