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Nonlinear response of closed-shell atoms in the density-functional formalism

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The nonlinear response of an arbitrary electronic system to a time-dependent perturbation is treated within the density-functional formalism. Expressions for quadratic and cubic responses for a system of independent electrons are obtained in a form suitable for numerical calculations. The frequency dependence of the linear and cubic electric susceptibilities of rare-gas atoms are computed and compared with experiment.

I. INTRODUCTION

Linear response theory[1,2] within the density-functional (DF) formalism[3] has been successfully applied to atoms,[1,2] molecules,[4] and small metal particles.[5] The appeal of such an approach is that only independent-particle response functions and local, self-consistent potentials are needed in it. In the case of response to a static perturbation the theory is rigorously based on the Hohenberg-Kohn theorem.[6] This is true for response of any order. Further, a partial rationalization of the dynamical response theory has been recently provided by Gross and Kohn.[7] These authors have also shown how to recover the results of Zangwill and Soven[2] by a suitable combination of local density and adiabatic approximation.

The extension of the theory to treat nonlinear response is clearly of interest since nonlinear susceptibilities[8-10] enter in a fundamental way in optical processes such as the Kerr effect, wave mixing, and Raman scattering. Although perturbation-theoretic formulations based on Hartree-Fock[11] and configuration-interaction[12] methods exist, the local-density approximation (LDA) has the advantage of facilitating calculations for large electronic systems. We have already examined[9,10] the ability of LDA to describe the static nonlinear response of closed-shell atoms and ions by means of a perturbative expansion of the Kohn-Sham equations,[13] namely, by a self-consistent Sternheimer procedure. However, for the case of time-dependent perturbations, the response function technique appears to be more suitable.[8] In this paper we report on the frequency dependence of the cubic hyperpolarizabilities (third-harmonic response) of rare-gas atoms calculated by the latter technique.

In Sec. II we derive general expressions for the density-density response functions up to the third order. These are then specialized to a system of independent particles. In Sec. III results for the frequency dependence of the linear and third-harmonic response of rare-gas atoms are presented and compared with experimental results. Section IV contains a summary of our investigation. Some technical details on the angular decomposition of the response functions are given in an Appendix.

II. RESPONSE FUNCTIONS IN LDA

We consider the effect of a time-dependent perturbation $V(t)$ on a system of many interacting particles described, in the absence of the perturbation, by the Hamiltonian H_0. The expectation value of an operator $O(t)$ is given by the standard expression[4]

$$\langle O(t)\rangle_H = \left\langle T\left[\exp\left(i\int_{t_0}^{t} d\tau\, V(\tau)\right)\right] O(t) T \times \left[\exp\left(-i\int_{t_0}^{t} d\tau\, V(\tau)\right)\right]\right\rangle_{H_0} . \tag{2.1}$$

Here T indicates time ordering, all operators and state kets are in the Heisenberg picture relative to the unperturbed Hamiltonian H_0, and t_0 denotes the time at which the perturbation is turned on. To obtain density-density response functions we specialize Eq. (2.1) to the calculation of the density change produced by a perturbation which couples to the density operator $n(\mathbf{r},t)$,

$$V(t)=\int d^3r\, n(\mathbf{r},t)v(\mathbf{r},t) . \tag{2.2}$$

A straightforward expansion of the time-ordered exponentials appearing in Eq. (2.1) and reordering of all terms in increasing powers of v yields, after some algebra,

$$\delta\langle n(\mathbf{r},\omega)\rangle = \lim_{\eta\to 0^+}\sum_{k=1}^{\infty}\int d^3r_1\int\frac{d\omega_1}{2\pi}\cdots\int d^3r_k\int\frac{d\omega_k}{2\pi}\chi^{(k)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_k;\omega_1+i\eta,\omega_2+i\eta,\ldots,\omega_k+i\eta) \times v(\mathbf{r}_1,\omega_1)v(\mathbf{r}_2,\omega_2)\cdots v(\mathbf{r}_k,\omega_k)2\pi\delta(\omega-\omega_1-\omega_2-\cdots-\omega_k) . \tag{2.3}$$

In the above equation the Fourier transform of the density change with respect to time has been taken and the infinitesimal η guarantees the causality of the response. The kth-order response function is explicitly given by

$$\chi^{(k)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_k;z_1,z_2,\ldots,z_k)$$
$$=\frac{1}{k!}\int\frac{d\omega_1}{2\pi}\int\frac{d\omega_2}{2\pi}\cdots\int\frac{d\omega_k}{2\pi}$$
$$\times\left[\frac{\chi^{(k)''}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_k;\omega_1,\omega_2,\ldots,\omega_k)}{(z_1+z_2+\cdots+z_k-\omega_1-\omega_2-\cdots-\omega_k)(z_2+z_3+\cdots+z_k-\omega_2-\omega_3-\cdots-\omega_k)\cdots(z_k-\omega_k)}\right.$$
$$\left.+[\text{all permutations of }(\mathbf{r}_1,z_1;\mathbf{r}_2,z_2;\ldots;\mathbf{r}_k,z_k)]\right]. \tag{2.4}$$

The spectral function $\chi^{(k)''}$ is the Fourier transform of the expectation value of a kth-order commutator

$$\chi^{(k)''}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_k;t-t_1,t-t_2,\ldots,t-t_k)=\langle[\cdots[[n(\mathbf{r},t),n(\mathbf{r}_1,t_1)],n(\mathbf{r}_2,t_2)]\cdots,n(\mathbf{r}_k,t_k)]\rangle_{H_0}. \tag{2.5}$$

Equations (2.3)—(2.5) constitute the obvious generalization to arbitrary order of the linear response found in standard texts.[14] They should be compared with the finite temperature results of Wehrum and Hermeking.[15]

For a system of independent particles Eqs. (2.4) and (2.5) yield simple expressions for the response functions in terms of unperturbed one-particle orbitals and energies (or, one-particle Green's functions). In particular, for a system of independent fermions one obtains, up to the third order,

$$\chi^{(1)}(\mathbf{r},\mathbf{r}_1;\omega)=\sum_{\substack{i\\ \text{occ}}}[\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}_1)G^R(\mathbf{r},\mathbf{r}_1;\varepsilon_i+\omega_1)+\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}_1)G^{R*}(\mathbf{r},\mathbf{r}_1;\varepsilon_i-\omega_1)], \tag{2.6}$$

$$\chi^{(2)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2;\omega_1,\omega_2)=\frac{1}{2}\sum_{\substack{i\\ \text{occ}}}\{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}_2)G^R(\mathbf{r},\mathbf{r}_1;\varepsilon_i+\omega_1+\omega_2)G^R(\mathbf{r}_1,\mathbf{r}_2;\varepsilon_i+\omega_2)$$
$$+\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}_2)G^{R*}(\mathbf{r},\mathbf{r}_1;\varepsilon_i-\omega_1-\omega_2)G^{R*}(\mathbf{r}_1,\mathbf{r}_2;\varepsilon_i-\omega_2)$$
$$+\phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2)G^R(\mathbf{r},\mathbf{r}_1;\varepsilon_i+\omega_1)G^{R*}(\mathbf{r},\mathbf{r}_2;\varepsilon_i-\omega_2)+[\text{permutations of }(\mathbf{r}_1,\omega_1;\mathbf{r}_2,\omega_2)]\}, \tag{2.7}$$

$$\chi^{(3)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\omega_1,\omega_2,\omega_3)$$
$$=\frac{1}{3!}\sum_{\substack{i\\ \text{occ}}}\{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}_3)G^R(\mathbf{r},\mathbf{r}_1;\varepsilon_i+\omega_1+\omega_2+\omega_3)G^R(\mathbf{r}_1,\mathbf{r}_2;\varepsilon_i+\omega_2+\omega_3)G^R(\mathbf{r}_2,\mathbf{r}_3;\varepsilon_i+\omega_3)$$
$$+\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}_3)G^{R*}(\mathbf{r},\mathbf{r}_1;\varepsilon_i-\omega_1-\omega_2-\omega_3)G^{R*}(\mathbf{r}_1,\mathbf{r}_2;\varepsilon_i-\omega_2-\omega_3)G^{R*}(\mathbf{r}_2,\mathbf{r}_3;\varepsilon_i-\omega_3)$$
$$+\phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2)G^R(\mathbf{r}_3,\mathbf{r}_2;\varepsilon_i+\omega_2)G^R(\mathbf{r},\mathbf{r}_3;\varepsilon_i+\omega_2+\omega_3)G^{R*}(\mathbf{r},\mathbf{r}_1;\varepsilon_i-\omega_1)$$
$$+\phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2)G^{R*}(\mathbf{r}_3,\mathbf{r}_2;\varepsilon_i-\omega_2)G^{R*}(\mathbf{r},\mathbf{r}_3;\varepsilon_i-\omega_2-\omega_3)G^R(\mathbf{r},\mathbf{r}_1;\varepsilon_i+\omega_1)$$
$$+[\text{all permutations of }(\mathbf{r}_1,\omega_1;\mathbf{r}_2,\omega_2;\mathbf{r}_3,\omega_3)]\}. \tag{2.8}$$

The retarded one-particle Green's function appearing in Eqs. (2.6)—(2.8) is explicitly given by

$$G^R(\mathbf{r},\mathbf{r}';\omega)=\sum_i\frac{\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}')}{\omega-\varepsilon_i+i\eta} \tag{2.9}$$

in terms of the orbitals $\phi_i(r)$ with energies ε_i. We notice that in Eq. (2.9) the sum runs over all the independent values of the one-particle energies, whereas, in Eqs. (2.6)—(2.8) the sum is over occupied orbitals only.

In the case of density-functional theory ϕ_i and ε_i are, respectively, the Kohn-Sham orbitals and energies.[3] Also, the infinite sum in Eq. (2.9) is easily circumvented by determining $G^R(r,r';\omega)$ through a direct integration of the differential equation

$$[-\nabla^2+V_{\text{eff}}(\mathbf{r})-\omega]G^R(\mathbf{r},\mathbf{r}';\omega)=\delta(\mathbf{r}-\mathbf{r}'). \tag{2.10}$$

In the above equation $V_{\text{eff}}(\mathbf{r})$ is the local, one-body potential entering the Kohn-Sham equations. Also, the units of energy and length have been taken to be rydbergs, and bohrs, respectively.

In the density-functional formalism the potential $v(\mathbf{r},\omega)$ in Eq. (2.3) is a combination of the external potential and of exchange and correlation contributions arising from the distortion of the particle density caused by the perturbation. This will be explicitly shown in the applications considered in Sec. III.

One advantage of using response functions over the use of the self-consistent Sternheimer procedure[9,10,13] is the absence of the problem of the correct normalization of the perturbed orbitals.[9,10] In fact, it is readily seen that

$$\int d^3r\langle\delta n(\mathbf{r},\omega)\rangle=0 \tag{2.11}$$

to any order. This follows immediately from Eqs. (2.3)–(2.5) when one observes that

$$\int d^3r[n(\mathbf{r},t),n(\mathbf{r}_1,t)]=0 \tag{2.12}$$

implies

$$\int d^3r\,\chi^{(k)\prime\prime}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_k;\omega_1,\omega_2,\ldots,\omega_k)=0 \tag{2.13}$$

for each k. In fact, one can go further. The explicit construction of the spectral functions $\chi^{(k)\prime\prime}$ appearing in Eqs. (2.4), (2.5), and (2.13) in the case of independent particles shows that they are naturally decomposed into contributions $\chi_i^{(k)\prime\prime}$ arising from each occupied orbital i. The same is true for the density change. We have found that at least up to $k=3$, each orbital contribution to $\chi^{(k)\prime\prime}$ satisfies a condition like the one in Eq. (2.13). Thus for $k=1,2,3$ each contribution to the density change satisfies

$$\int d^3r\langle\delta n_i^{(k)}(\mathbf{r},\omega)\rangle=0\ . \tag{2.14}$$

In the static limit the response function formalism developed above is completely equivalent to the self-consistent Sternheimer method.[10] However, some care must be exercised in taking the limit $\omega\rightarrow 0$ for the response functions in Eqs. (2.6)–(2.8). While divergences can occur in individual terms, they cancel out when the various terms are grouped together. This point will be illustrated in the numerical applications below.

III. APPLICATION TO THE SUSCEPTIBILITIES OF RARE-GAS ATOMS

A. Frequency dependence of the linear polarizability

Here we consider the LDA linear response of a closed-shell atom to a harmonic dipole potential

$$V_{\text{ext}}(\mathbf{r},t)=r\cos\theta\cos(\omega t)\ . \tag{3.1}$$

Following Zangwill and Soven,[2] in the spirit of perturbation theory, we assume that the local effective potential is changed by an amount

$$V_{\text{eff}}^{(1)}(\mathbf{r},t)=2\int d^3r'\frac{n^{(1)}(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}+n^{(1)}(\mathbf{r},t)V'_{\text{XC}}[n^{(0)}(\mathbf{r})]\ . \tag{3.2}$$

Here $n^{(1)}(\mathbf{r},t)$ is the density change induced by the perturbing potential, $n^{(0)}(\mathbf{r})$ is the unperturbed LDA ground-state density, and V'_{XC} denotes the first derivative of the exchange and correlation energy of the homogeneous electron gas. The so-called time-dependent LDA (TDLDA) is obtained by assuming that the response to the total first-order potential

$$v^{(1)}(\mathbf{r},t)=V_{\text{ext}}(\mathbf{r},t)+V_{\text{eff}}^{(1)}(\mathbf{r},t) \tag{3.3}$$

is described by the independent-particle response function of Eq. (2.6).

By exploiting the spherical symmetry of closed-shell atoms one can show that[2]

$$\chi^{(1)}(\mathbf{r},\mathbf{r}_1;\omega_1)=\sum_{l,m}\chi_l^{(1)}(r,r_1;\omega_1)Y_l^m(\hat{\mathbf{r}})Y_l^{m*}(\hat{\mathbf{r}}_1)\ . \tag{3.4}$$

It then follows that

$$n^{(1)}(\mathbf{r},t)=n_1^{(1)}(r,\omega)\cos\theta\cos(\omega t)\ , \tag{3.5}$$

with

$$n_1^{(1)}(r,\omega)=\int_0^\infty dr_1 r_1^2\chi_1^{(1)}(r,r_1;\omega_1)v_1^{(1)}(r_1,\omega) \tag{3.6}$$

and

$$v_1^{(1)}(r,\omega)=r+\frac{8\pi}{3}\int_0^\infty dr'\,r'^2 n_1^{(1)}(r',\omega)\frac{r_<}{r_>^2}+n_1^{(1)}(r,\omega)V'_{\text{XC}}(n^{(0)}(r))\ . \tag{3.7}$$

In writing Eq. (3.6) use has been made of the fact that for a closed-shell system and away from resonances $\chi_1^{(1)}(r,r',\omega)$ is real if one restricts to values of ω below the one-particle ionization threshold. The self-consistent solution of Eqs. (3.6) and (3.7) yields the TDLDA density change $n_1^{(1)}(r,\omega)$ and hence the dynamical polarizability $\alpha(\omega)$. In our units we have

$$\alpha(\omega)=-\frac{4\pi}{3}\int_0^\infty dr\,r^3 n_1^{(1)}(r,\omega)\ . \tag{3.8}$$

We have numerically solved Eqs. (3.6) and (3.7) for rare-gas atoms by using the explicit expression for $\chi_1^{(1)}$ in terms of orbital wave functions and Green's functions given in the Appendix. The Green's functions were calculated by straightforward Numerov integration of the differential equation, Eq. (2.10). In particular, one has

$$G^R(\mathbf{r},\mathbf{r}';\omega)=\sum_{l,m}G_l^R(r,r';\omega)Y_l^m(\hat{\mathbf{r}})Y_l^{m*}(\hat{\mathbf{r}}')\ , \tag{3.9}$$

with

$$G_l^R(r,r';\omega)=\frac{u_l^{(1)}(r_<)u_l^{(2)}(r_>)}{rr'W[u_l^{(1)},u_l^{(2)}]}\ . \tag{3.10}$$

Here $u_l^{(1)}$ and $u_l^{(2)}$ are solutions of

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+V_{\text{eff}}(r)-\omega\right]u_l^{(i)}(r)=0 \tag{3.11}$$

which are regular at the origin and at infinity, respectively. $W[u^{(1)},u^{(2)}]$ denotes the Wronskian of these two functions. Self-consistent solutions of Eqs. (3.6) and (3.7) were readily obtained with a few iterations (of the order of 10) to an accuracy of one part in 10^4 for $\alpha(\omega)$. The

Ceperly-Alder results[16] for the exchange and correlation energy of the uniform electron gas, as parametrized by Perdew and Zunger[17] were employed.

As a preliminary check of the numerical procedure we have calculated the static polarizability of hydrogen by setting $V_{\mathrm{XC}}=0$. Our result differs from the exact result by only four parts in 10^6. It should be noted that in their calculations, Stott and Zaremba[1] quote a result which is worse by 3 orders of magnitude for the same check. We have also repeated the calculations for the static polarizability of rare-gas atoms. We find agreement with our previous results using the Sternheimer procedure to within a few parts in 10^5 or better. Then we performed calculations of $\alpha(\omega)$ at optical frequencies. In this frequency region both our theoretical results and experimental results[18] are accurately described by the simple formula

$$\alpha(\omega)=\alpha_0(1+C_2\omega^2)\ . \tag{3.12}$$

In Table I we report our results for α_0 and C_2 for rare-gas atoms, together with the experimental values for these quantities. Note that our values for α_0, using the Ceperly-Alder exchange correlation results, are slightly higher than those reported previously[1,2,13] using the Gunnarsson-Lundquist parametrization[19] of V_{XC}. The overall agreement with experimental data is satisfactory, although the LDA systematically overestimates the deformability of the electronic cloud.[10] The limits of LDA are even more evident in the coefficient C_2 which describes the dispersion of the dipole polarizability. The agreement with experiment improves in going to the heavier atoms as is to be expected.

We note that while the LDA makes the atoms too "soft," any modification to introduce self-interaction corrections (SIC)[10,20] would appear to destroy the simplicity of the response function formalism. Indeed, it is not obvious how to calculate the Green's functions for a Hamiltonian which is state dependent. As to the discrepancies between calculated and measured values of C_2, we argue that these should be ascribed to the LDA ground state rather than to the "adiabatic approximation" needed to obtain the time-dependent LDA. Gross and Kohn[7] have, in fact, shown that the adiabatic approximation is not a severe one.

B. Third-order nonlinear susceptibility of rare-gas atoms

Recent experimental results for the cubic hyperpolarizability[21] for rare-gas atoms have been reported. They were obtained both with electric-field-induced second-harmonic generation (EFSG)[22] and third-harmonic generation (THG).[23]

TABLE I. Linear polarizabilities of rare-gas atoms in LDA. Frequency dependence is expressed as $\alpha(\omega)=\alpha_0(1+C_2\omega^2)$, where ω is in wave numbers.

	α_0 (10^{-24} cm^3)		C_2 (10^{-10} cm^2)	
	Theory	Expt.[a]	Theory	Expt.[a]
He	0.246	0.205	0.31	0.24
Ne	0.452	0.395	0.31	0.23
Ar	1.78	1.64	0.65	0.54
Kr	2.67	2.48	0.85	0.75
Xe	4.26	4.04	1.14	1.05

[a] From Ref. 18.

Here we consider the TDLDA calculation of $\gamma(3\omega)$, which is the quantity measured in the THG experiments. To this purpose one has to examine the third-order response to the harmonic field of Eq. (3.5). This, however, requires the knowledge of the first- and second-order response. The first order was explicitly considered in the previous section. We therefore start by examining the second-order response to a harmonic field. We are only interested in that part of the second-order induced density which oscillates with frequency 2ω. We use below the fact that the second-order response function can be written as (see the Appendix)

$$\begin{aligned}\chi^{(2)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2;\omega_1,\omega_2) &= \sum_{\substack{l,l_1,l_2\\ m,m_1,m_2}} \chi^{(2)}_{\substack{l\,l_1\,l_2\\ m\,m_1\,m_2}}(r,r_1,r_2;\omega_1,\omega_2)\\ &\quad\times Y_l^m(\hat{\mathbf{r}})Y_{l_1}^{m_1^*}(\hat{\mathbf{r}}_1)Y_{l_2}^{m_2^*}(\hat{\mathbf{r}}_2)\ .\end{aligned} \tag{3.13}$$

By expanding the local effective potential up to the third order in the density change, in a way similar to that employed for the first-order calculation, we find that the second-order density change contains the term

$$\begin{aligned}n^{(2)}(\mathbf{r},t)&=[n_0^{(2)}(r,2\omega)+n_2^{(2)}(r,2\omega)P_2(\cos\theta)]\\ &\quad\times\cos(2\omega t)\ ,\end{aligned} \tag{3.14}$$

where

$$n_l^{(2)}(r,2\omega)=\frac{\sqrt{\pi(2l+1)}}{3}\int_0^\infty dr_1\int_0^\infty dr_2 r_1^2 r_2^2 \chi^{(2)}_{\substack{l\,1\,1\\ 0\,0\,0}}(r,r_1,r_2;\omega,\omega)v_1^{(1)}(r_1,\omega)v_1^{(1)}(r_2,\omega)+\int_0^\infty dr_1\chi_l^{(1)}(r,r_1;2\omega)v_l^{(2)}(r_1,2\omega) \tag{3.15}$$

for $l=0,2$. In the above equation

$$v_l^{(2)}(r_1,2\omega)=\frac{8\pi}{2l+1}\int_0^\infty dr' r'^2 n_l^{(2)}(r',2\omega)\frac{r_<^l}{r_>^{l+1}}+n_l^{(2)}(r_1,2\omega)V'_{\mathrm{XC}}(n^{(0)}(r))+\frac{l+2}{24}[n_1^{(1)}(r_1,\omega)]^2V''_{\mathrm{XC}}(n^{(0)}(r))\ , \tag{3.16}$$

and V''_{XC} denotes the second derivative of the exchange and correlation potential. Similarly, by using the fact that (see the Appendix)

$$\chi^{(3)}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\omega_1,\omega_2,\omega_3)=\sum_{\substack{l,l_1,l_2,l_3\\ m,m_1,m_2,m_3}}\chi^{(3)}_{\substack{l\,l_1\,l_2\,l_3\\ m\,m_1\,m_2\,m_3}}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\omega_1,\omega_2,\omega_3)Y_l^m(\hat{\mathbf{r}})Y_{l_1}^{m_1^*}(\hat{\mathbf{r}}_1)Y_{l_2}^{m_2^*}(\hat{\mathbf{r}}_2)Y_{l_3}^{m_3^*}(\hat{\mathbf{r}}_3)\ , \tag{3.17}$$

we find that the third-order density change contains the term

$$n^{(3)}(\mathbf{r},t)=n_1^{(3)}(r,3\omega)\cos\theta\cos(3\omega t)\ , \tag{3.18}$$

where

$$\begin{aligned}n_1^{(3)}(r,3\omega)={}&\frac{\pi}{3}\int_0^\infty dr_1\int_0^\infty dr_2\int_0^\infty dr_3 r_1^2r_2^2r_3^2\chi^{(3)}_{\substack{1111\\0000}}(r,r_1,r_2,r_3;\omega,\omega,\omega)v_1^{(1)}(r_1,\omega)v_1^{(1)}(r_2,\omega)v_1^{(1)}(r_3,\omega)\\&+\sum_{l=0,2}\left[\frac{\pi}{2l+1}\right]^{1/2}\int_0^\infty dr_1\int_0^\infty dr_2 r_1^2r_2^2\Big[\chi^{(2)}_{\substack{11l\\000}}(r,r_1,r_2;\omega,2\omega)v_1^{(1)}(r_1,\omega)v_l^{(2)}(r_2,2\omega)\\&\qquad+\chi^{(2)}_{\substack{1l1\\000}}(r,r_1,r_2;2\omega,\omega)v_1^{(1)}(r_2,\omega)v_l^{(2)}(r_1,2\omega)\Big]\\&+\int_0^\infty dr_1r_1^2\chi_1^{(1)}(r,r_1;3\omega)v_1^{(3)}(r_1,3\omega)\ .\end{aligned} \tag{3.19}$$

In the above,

$$\begin{aligned}v_1^{(3)}(r,3\omega)={}&\frac{8\pi}{3}\int_0^\infty dr'r'^2n_1^{(3)}(r',3\omega)\frac{r_<}{r_>^2}+n_1^{(3)}(r,3\omega)V'_{\mathrm{XC}}(n^{(0)}(r))\\&+\tfrac{1}{2}n_1^{(1)}(r,\omega)[n_0^{(2)}(r,2\omega)+\tfrac{2}{5}n_2^{(2)}(r,2\omega)]V''_{\mathrm{XC}}(n^{(0)}(r))+\tfrac{1}{40}[n_1^{(1)}(r,\omega)]^3V'''_{\mathrm{XC}}(n^{(0)}(r))\ ,\end{aligned} \tag{3.20}$$

and V'''_{XC} denotes the third derivative of V_{XC}. Also, we have restricted ourselves to the case in which 3ω lies below the one-particle ionization threshold. In order to obtain $n_1^{(3)}(r,3\omega)$ one has first to solve the self-consistent Eqs. (3.15) and (3.16) for the second-order density change and then Eqs. (3.19) and (3.20). Once $n_1^{(3)}(r,3\omega)$ is known, the cubic dipole polarizability $\gamma(3\omega)$ is readily obtained as

$$\tfrac{1}{6}\gamma(3\omega)=-\frac{4\pi}{3}\int_0^\infty dr\, r^3n_1^{(3)}(r,3\omega)\ . \tag{3.21}$$

We have performed calculations of $\gamma(3\omega)$, as outlined above, for all the rare-gas atoms at a few frequencies, up to that corresponding to $\lambda=10\,550$ Å. This was the wavelength of the laser light utilized in the THG experiment.[23] As is customary we define[24]

$$\chi^{(3)}(3\omega)=4\frac{\gamma(3\omega)}{6} \tag{3.22}$$

so that in the limit $\omega\to 0$, $\chi^{(3)}(3\omega)$ tends to

$$\chi^{(3)}_{\mathrm{static}}=\gamma_{\mathrm{static}}/6\ . \tag{3.23}$$

We have checked that in the limit $\omega\to 0$, $\chi^{(3)}(3\omega)$ reproduces the values of $\chi^{(3)}_{\mathrm{static}}$ obtained within the Sternheimer method,[10] within two parts in 10^3 or better. In Table II we report the TDLDA predictions for $\chi^{(3)}(3\omega)$ together with the experimental results of Lehemeier *et al.*[23] The static results[10] are also listed. As we previously found for the static case,[10] the TDLDA grossly overestimates the deformability of the electronic clouds in a way which increases in going to higher-order processes. This, we argue, happens because of the major importance of the outer part of the electronic distribution which is not well treated in LDA. Nevertheless, we find again the same trend as that encountered in the linear process, in that the situation is worst for lighter atoms and tends to improve somewhat for heavier ones. Qualitatively TDLDA predicts an increase in $\chi^{(3)}$ with frequency, in agreement with experiments.

IV. SUMMARY

We have extended the LDA linear-response theory[1,2] to treat nonlinear processes. Expressions for the quadratic and cubic response of a system of independent electrons

TABLE II. Hyperpolarizability $\chi^{(3)}$ of rare-gas atoms in LDA. Both static values and values for third-harmonic generation with $\lambda=10\,550$ Å are given.

	$\chi^{(3)}$(static) (10^{-39} esu)		$\chi^{(3)}(3\omega)$ (10^{-39} esu)	
	LDA[a]	Expt.[b]	TLDA	Expt.[c]
He	7.40	3.5±0.4	7.96	3.7±0.4
Ne	17.7	5.9±0.6	19.5	6.6±0.7
Ar	156	72 ±7	187	86 ±9
Kr	332	174 ±17	420	234 ±23
Xe	769	403 ±40	1048	688 ±69

[a] From Ref. 10.

[b] Extrapolated from finite frequency measurements of Ref. 23.

[c] From Ref. 23.

have been obtained in a form suitable for numerical calculations. As applications we have computed the frequency dependence of the linear and third-harmonic electric susceptibilities of rare-gas atoms. The discrepancies in the results are of the same order as those found for the static response. The discrepancies are worse for the lighter atoms than for the heavier ones. We attribute the discrepancies primarily to the rather unsatisfactory treatment of the electronic tails in the LDA. Conceptual difficulties are encountered in including self-interaction corrections within the response function scheme.

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APPENDIX: ANGULAR COMPONENTS OF RESPONSE FUNCTIONS UP TO THIRD ORDER

Here we give explicit expressions for the angular components of the response functions up to third order, appearing in Secs. II and III. We start by writing the occupied LDA ground-state orbitals as

$$\phi_{nlm}(\mathbf{r})=R_{nl}(r)Y_l^m(\mathbf{r}) \ . \tag{A1}$$

The spin projection quantum number σ has been dropped here. Factors of 2, to account for the sum over σ, will be explicitly included where needed.

When Eqs. (3.9) and (A1) are used in Eqs. (2.6)–(2.8), after some algebra and use of $3j,6j,9j$ technology,[25] we find the following.

(1) First order:

$$\chi_l^{(1)}(r,r_1;\omega)=2\sum_{n,l'}R_{nl'}(r)R_{nl'}(r_1)\sum_{k=0}^{\min\{l,l'\}}C_{l',l}^{l'+l-2k}[G^R_{l'+l-2k}(r,r_1;\varepsilon_{nl'}+\omega_1)+G^{R*}_{l'+l-2k}(r,r_1;\varepsilon_{nl'}-\omega_1)] \tag{A2}$$

with

$$C_{l',l}^{l'+l-2k}=\frac{2l'+1}{4\pi}\,\frac{a_{l-k}a_k a_{l'-k}}{a_{l'+l-k}}\,\frac{2(l'+l)-4k+1}{2(l'+l)-2k+1} \ . \tag{A3}$$

and $a_k=(2k)!/[2^k(k!)^2]$. Formulas (A2) and (A3) were already given by Ekardt.[26]

(2) Second order:

$$\begin{aligned}
&\chi^{(2)}_{\substack{l\;l_1\;l_2\\ m\,m_1 m_2}}(r,r_1,r_2;\omega_1,\omega_2)\\
&\quad=\sum_{n,l'}\Bigg[\sum_{l'_1,l'_2}\{R_{nl'}(r)R_{nl'}(r_2)[C^{l'\,l'_1\,l'_2}_{\substack{l\;l_1\;l_2\\ m\,m_1 m_2}}G^R_{l'_1}(r,r_1;\varepsilon_{nl'}+\omega_1+\omega_2)G^R_{l'_2}(r_1,r_2;\varepsilon_{nl'}+\omega_2)\\
&\qquad\qquad+C^{l'\;\;l'_1\;\;l'_2}_{\substack{l\;\;l_1\;\;l_2\\ -m-m_1-m_2}}G^{R*}_{l'_1}(r,r_1;\varepsilon_{n_l'}-\omega_1-\omega_2)G^{R*}_{l'_2}(r_1,r_2;\varepsilon_{nl'}-\omega_2)]\\
&\qquad+R_{nl'}(r_1)R_{nl'}(r_2)C^{l'_1\,l'_2\,l'}_{\substack{l\;l_1\;l_2\\ m\,m_1 m_2}}G^{R*}_{l'_1}(r,r_2;\varepsilon_{nl'}-\omega_2)G^R_{l_2}(r,r_1;\varepsilon_{nl'}+\omega_1)\}\\
&\qquad+\text{all permutations of }(r_1,\omega_1,l_1,m_1;r_2,\omega_2,l_2,m_2)\Bigg] \ .
\end{aligned} \tag{A4}$$

In the above,

$$\begin{aligned}
C^{l'\,l'_1\,l'_2}_{\substack{l\;l_1\;l_2\\ m\,m_1 m_2}}&=\frac{(-1)^{l'+l'_1+l'_2}}{(4\pi)^{3/2}}[(2l+1)(2l_1+1)(2l_2+1)]^{1/2}(2l'+1)(2l'_1+1)(2l'_2+1)\\
&\quad\times\begin{bmatrix}l' & l'_1 & l\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}l'_1 & l'_2 & l_1\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}l'_2 & l' & l_2\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}l & l_1 & l_2\\ m & m_1 & m_2\end{bmatrix}\begin{Bmatrix}l & l_1 & l_2\\ l'_2 & l' & l'_1\end{Bmatrix} ,
\end{aligned} \tag{A5}$$

where $3j$ and $6j$ symbols[25] are used.

(3) Third order:

$$\begin{aligned}
&\chi^{(3)}_{\substack{l\;l_1\;l_2\;l_3\\ m\,m_1 m_2 m_3}}(r,r_1,r_2,r_3;\omega_1,\omega_2,\omega_3)\\
&=\frac{1}{3}\sum_{n,l'}\Bigg[\sum_{l'_1,l'_2,l'_3}\{R_{nl'}(r)R_{nl'}(r_3)[\,C^{l'\,l'_1\,l'_2\,l'_3}_{\substack{l\;l_1\;l_2\;l_3\\ m\,m_1 m_2 m_3}}G^{R}_{l'_1}(r,r_1;\varepsilon_{nl'}+\omega_1+\omega_2+\omega_3)\\
&\qquad\times G^{R}_{l'_2}(r_1,r_2;\varepsilon_{nl'}+\omega_2+\omega_3)G^{R}_{l'_3}(r_2,r_3;\varepsilon_{nl'}+\omega_3)\\
&\qquad+C^{l'\;\;l'_1\;\;l'_2\;\;l'_3}_{\substack{l\;\;l_1\;\;l_2\;\;l_3\\ -m\,-m_1-m_2-m_3}}G^{R\,*}_{l'_1}(r,r_1;\varepsilon_{nl'}-\omega_1-\omega_2-\omega_3)\\
&\qquad\times G^{R\,*}_{l'_2}(r_1,r_2;\varepsilon_{nl'}-\omega_2-\omega_3)G^{*}_{l'_3}(r_2,r_3;\varepsilon_{nl'}-\omega_3)]\\
&\quad+R_{nl'}(r_1)R_{nl'}(r_2)[\,C^{l'_2\,l'_3\,l'\,l'_1}_{\substack{l\;l_1\;l_2\;l_3\\ m\,m_1\,m_2\,m_3}}G^{R\,*}_{l'_1}(r_3,r_2;\varepsilon_{nl'}-\omega_2)\\
&\qquad\times G^{R\,*}_{l'_2}(r,r_3;\varepsilon_{nl'}-\omega_2-\omega_3)G^{R}_{l'_3}(r,r_1;\varepsilon_{nl'}+\omega_1)\\
&\qquad+C^{l'_2\;\;l'_3\;\;l'\;\;l'_1}_{\substack{l\;\;l_1\;\;l_2\;\;l_3\\ -m\,-m_1-m_2-m_3}}G^{R}_{l'_1}(r_3,r_2;\varepsilon_{nl'}+\omega_2)\\
&\qquad\times G^{R}_{l'_2}(r,r_3;\varepsilon_{nl'}+\omega_2+\omega_3)G^{R\,*}_{l'_3}(r,r_1;\varepsilon_{nl'}-\omega_1)]\}\\
&\quad+\text{all permutations of }[(r_1,\omega_1,l_1,m_1),(r_2,\omega_2,l_2,m_2),(r_3,\omega_3,l_3,m_3)]\Bigg]\,.
\end{aligned}\tag{A6}$$

In the above equation,

$$\begin{aligned}
C^{l'\,l'_1\,l'_2\,l'_3}_{\substack{l\;l_1\;l_2\;l_3\\ m\,m_1 m_2 m_3}}&=\frac{(-1)^m}{(4\pi)^2}[(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)]^{1/2}\\
&\quad\times(2l'+1)(2l'_1+1)(2l'_2+1)(2l'_3+1)\begin{bmatrix} l & l'_1 & l' \\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l_2 & l'_2 & l'_3 \\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l'_1 & l'_2 & l_1 \\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l' & l'_3 & l_3 \\ 0 & 0 & 0\end{bmatrix}\\
&\quad\times\sum_{\mu,k}(2k+1)\begin{bmatrix} l & l_2 & k \\ -m & m_2 & \mu\end{bmatrix}\begin{bmatrix} k & l_1 & l_3 \\ \mu & m_1 & m_3\end{bmatrix}\begin{Bmatrix} l & l_2 & k \\ l'_1 & l'_2 & l_1 \\ l' & l'_3 & l_3\end{Bmatrix}\,,
\end{aligned}\tag{A7}$$

where use has been made also of $9j$ symbols.[25]

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