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Nonlinear polarizabilities of atoms from their ground-state densities

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Abstract. Using density based perturbation theory [M.K. Harbola, A. Banerjee, Phys. Lett. A **222**, 315 (1996)], we calculate the static hyperpolarizabilty γ for spherical atoms and ions from their ground-state densities. Since densities are being employed, calculations are performed using approximate functionals for the kinetic and the exchange-correlation energies. Use of densities - instead of the wavefunctions or Kohn-Sham orbitals - reduces the computational effort substantially. The results obtained are within 5%−15% of those calculated from the corresponding orbital-based calculations.

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

Application of a strong electric field $\mathcal{E}$ to an atom or an ion induces in it a dipole moment $\mathbf{p}$ with

$$p_i = \alpha_{ij}\mathcal{E}_j + \frac{1}{2!}\beta_{ijk}\mathcal{E}_j\mathcal{E}_k + \frac{1}{3!}\gamma_{ijkl}\mathcal{E}_j\mathcal{E}_k\mathcal{E}_l + \cdots \quad (1)$$

where α is the dipole polarizability and the nonlinear coefficiants β and γ are called the first and second hyperpolarizabilities of the system. The nonlinear response of the system gives rise to interesting effects [1] such as second-and third-harmonic generation, intensity dependent refractive index etc. Induced moment is accompanied by a corresponding shift

$$\Delta E = -\frac{1}{2!}\alpha_{ij}\mathcal{E}_i\mathcal{E}_j - \frac{1}{3!}\beta_{ijk}\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k - \frac{1}{4!}\gamma_{ijkl}\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k\mathcal{E}_l - \cdots \quad (2)$$

in the energy of the system. For the spherical atoms and ions considered in this paper $\beta = 0$, and there is only one independent component [2] of α and γ so that equations (1) and (2) can be written simply as

$$p = \alpha\mathcal{E} + \frac{1}{3!}\gamma\mathcal{E}^3 \quad (3)$$

and

$$\Delta E = -\frac{1}{2}\alpha\mathcal{E}^2 - \frac{1}{24}\gamma\mathcal{E}^4. \quad (4)$$

From now on we are going to concentrate on spherical systems only. The induced dipole moment is a measure of the distortion caused by the applied field. It can be calculated from the electronic density as

$$p = \int z\Delta\rho(\mathbf{r})\mathrm{d}\mathbf{r} \quad (5)$$

where $\Delta\rho(\mathbf{r})$ is the change in the density when the atom is in a field in z direction. $\Delta\rho(\mathbf{r})$ in turn is calculated from the induced wavefunctions to appropriate orders by employing perturbation theory [3]. This leads to α and γ *via* equation (3). Alternatively, perturbation theory also gives the energy change ΔE, and α and γ can be obtained from this quantity by equation (4). The latter scheme is easier because of the variational principle for the energy and the $(2n+1)$ theorem [4] of perturbation theory. According to the $(2n+1)$ theorem, the energy to order $(2n+1)$ is given by wavefunctions correct up to order n only. Thus if equation (4) is used to calculate α or γ, wavefunction only up to order 2 is required. On the other hand, wavefunction up to order 3 is needed if equation (3) is to be used.

We have recently developed [5] density based perturbation theory within the framework of Hohenberg-Kohn density-functional theory (DFT) [6,7] for many-electron systems. In this theory the induced densities and change in the energy to any order are calculated from the unperturbed ground-state density. Since exact form of the total energy functional is not known, density-based perturbation calculations can be performed only approximately. The purpose of this paper is to demonstrate - against the background of well studied atomic systems - that, with appropriately chosen functionals, reasonable estimates for non-linear response properties of a system can be obtained from its ground-state density. Thus the theory would be particularly useful for calculating approximately the

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response properties of systems for which orbital-based calculations may not be easy to perform. We note that density-based calculations for linear response have been performed [8] earlier. However, going beyond it to non-linear regime has become possible only now after the development of density based variation-perturbation theory [5].

In density based perturbation theory, energy to order $(2n+1)$ is determined by the perturbation expansion of the density correct to order n only. Further, the even-order energy correction $E^{(2n+2)}$ is minimum for the exact induced density $\rho^{(n+1)}$, if expansion up to order n is known exactly. For details of the theory, we refer the reader to reference [5]. It is sufficient to note here that α and γ are calculated from the second-order energy $\Delta E^{(2)}$ and the fourth-order energy $\Delta E^{(4)}$ by employing equation (4). These energy changes are in turn obtained variationally by minimising

$$E^{(2)} = \int v^{(1)}(\mathbf{r_1})\rho^{(1)}(\mathbf{r_1})\mathrm{d}\mathbf{r_1} + \frac{1}{2}\int \frac{\delta^2 F[\rho_0]}{\delta\rho(\mathbf{r_1})\delta\rho(\mathbf{r_2})}\rho^{(1)}(\mathbf{r_1})\rho^{(1)}(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2} \quad (6)$$

with respect to $\rho^{(1)}$, and

$$\begin{aligned}E^{(4)} = {}& \frac{1}{2}\int \frac{\delta^2 F[\rho_0]}{\delta\rho(\mathbf{r_1})\delta\rho(\mathbf{r_2})}\rho^{(2)}(\mathbf{r_1})\rho^{(2)}(\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2} \\ & + \frac{1}{2}\int \frac{\delta^3 F[\rho_0]}{\delta\rho(\mathbf{r_1})\delta\rho(\mathbf{r_2})\delta\rho(\mathbf{r_3})} \\ & \times\rho^{(1)}(\mathbf{r_1})\rho^{(1)}(\mathbf{r_2})\rho^{(2)}(\mathbf{r_3})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}\mathrm{d}\mathbf{r_3} \\ & + \frac{1}{24}\int \frac{\delta^4 F[\rho_0]}{\delta\rho(\mathbf{r_1})\delta\rho(\mathbf{r_2})\delta\rho(\mathbf{r_3})\delta\rho(\mathbf{r_4})} \\ & \times\rho^{(1)}(\mathbf{r_1})\rho^{(1)}(\mathbf{r_2})\rho^{(1)}(\mathbf{r_3})\rho^{(1)}(\mathbf{r_4})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2}\mathrm{d}\mathbf{r_3}\mathrm{d}\mathbf{r_4}\end{aligned} \quad (7)$$

with respect to $\rho^{(2)}$. Here $v^{(1)}(\mathbf{r})$ is the applied (external) perturbation. $F[\rho]$ is the sum of the kinetic, Hartree and the exchange-correlation energy (Eqs. (10), (11) and (12) below) of the electrons; It is a universal functional of the density. All the functional derivative in the equations above are evaluated at the ground state density ρ_0. The variational ansatz for $\rho^{(1)}$ and $\rho^{(2)}$ is

$$\begin{aligned}\rho^{(1)}(\mathbf{r}) &= \Delta_1(r)\cos\theta\rho_0(r), \\ \rho^{(2)}(\mathbf{r}) &= [\Delta_2(r) + \Delta_3(r)\cos^2\theta]\rho_0(r) + \lambda\rho_0(r)\end{aligned} \quad (8)$$

where

$$\Delta_i(r) = a_i r + b_i r^2 + c_i r^3 + d_i r^4 + e_i r^5 + \cdots, i = 1\cdots 3 \quad (9)$$

with $a_i \cdots e_i \cdots$ being the variational parameters. λ is fixed for each set of parameters by the normalization condition that $\int \rho^{(2)}(\mathbf{r})\mathrm{d}\mathbf{r} = 0$. We have used 5 parameters for Δ_1 and 7 each for Δ_2 and Δ_3. Adding more parameters does not affect the results significantly indicating their covergence. This form of the variational densities is motivated by the exactly known solutions [9] for the hydrogen atom in a static electric field. Besides its simplicity, the ansatz above has an additional advantage that the expressions for various energy terms become quite simple. Further, as the changes $E^{(2)}$ and $E^{(4)}$ in the energy are being minimized individually, there is no need to apply static finite field explicitly. This makes calculations numerically accurate.

Since densities are being employed for calculations, functional derivatives (Eqs. (6) and (7)) corresponding to the kinetic and the exchange and correlation energies have to be approximated; Only that corresponding to the Hartree energy can be calculated exactly. For evaluating the functional derivatives of the the exchange and correlation energies, we use the local-density approximation (LDA). Thus the exchange energy is given as

$$E_x^{\mathrm{LDA}}[\rho] = d_0 \int \rho^{\frac{4}{3}}(\mathbf{r})\mathrm{d}\mathbf{r} \quad (10)$$

where $d_0 = -\frac{3}{4}(3/\pi)^{\frac{1}{3}}$. For the correlation energy we use the Gunnarsson-Lundquist parametrization [10] in which

$$E_{\mathrm{c}}^{\mathrm{LDA}}[\rho] = c\int \rho(\mathbf{r})[(1+x^3)\ln(1+1/x) + x/2 - x^2 - 1/3]\mathrm{d}\mathbf{r} \quad (11)$$

with $c = -0.0333, x = r_s/A$, $A = 11.4$, where $r_s = [3/4\pi\rho(\mathbf{r})]^{\frac{1}{3}}$ is the local r_s value. On the other hand, one has to be more judicious in the choice of the kinetic energy functional for it is a major component of the total energy change. Functional derivatives of Thomas-Fermi or the gradient expansion approximation (GEA) functional cannot be employed [8] as these functionals are derived for slowly varying densities. In contrast, the induced densities are concentrated mainly on the outer regions of the atom and tend to be rapidly varying. A kinetic energy functional which is accurate in the outer regions of the atoms - in fact it becomes exact asymptotically far from the nucleus - is the von-Weizsacker functional [11]

$$T_{\mathrm{W}}[\rho] = \frac{1}{8}\int \frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}\mathrm{d}\mathbf{r}. \quad (12)$$

The functional is also exact in the limit of one- and two-electron systems. In addition, it has the desirable property that it represents exactly [12] the second order change in the kinetic energy of a homogeneous electron gas subjected to a rapidly varying perturbation. Keeping all these points in mind, it is the functional derivative of the von-Weizsacker functional which we employ for the kinetic energy (KE). We discover that it is also a good zeroth-order approximation to the changes up to the fourth order in the kinetic energy when calculating the response properties. We wish to point out that the KE functional employed for perturbative calculations is different from that used for the calculation of unperturbed density. Although

Table 1. Polarizability α and Hyperpolarizability γ of the noble gas atoms calculated from the Hartree-Fock densities. Atomic units are used.

Atom	α		γ	
	Present	Wavefunctional[a]	Present	Wavefunctional[a]
He	1.34	1.32	36.86	36.2
Ne	3.1	2.34	74.05	71.9
Ar	12.52	10.73	1393	967
Kr	18.74	16.47	1964	2260
Xe	30.71	27.08	5792	5870

[a] Reference [14].

Table 2. Polarizability α and hyperpolarizability γ of the noble gas atoms calculated from the Kohn-Sham LDA densities. Atomic units are used.

Atom	α		γ	
	Present	Kohn-Sham[a*]	Present	Kohn-Sham[a*]
He	1.63	1.66	82.48	88.15
Ne	3.68	3.05	164.95	210.84
Ar	13.31	12.02	1471	1858
Kr	19.50	18.04	3229	3955
Xe	30.99	28.78	7104	9160

[a] Reference [15].

[*] Employs Perdew-Zunger parameterization [18] of Ceperly-Alder exchange-correlation energy.

Table 3. Experimental polarizabilities α and γ of noble gas atoms. The static value for γ quoted are extrapolations from finite frequency measurements. Numbers are in atomic units.

Atom	α[a]	γ
He	1.39	35.7[b]; 41.7[c]; 42.6[d]; 52.4[e]
Ne	2.67	70.3[c]; 95.3[e]
Ar	11.08	858[c]; 1084[e]; 1096[d]; 1251[b]
Kr	16.75	2073[c]; 2239[d]; 2406[e]; 2728[b]
Xe	27.29	4800[c]; 4812[d]; 5825[e]

[a] Reference [19]; [b] Reference [20];

[c] Reference [21]; [d] Reference [22];

[e] Reference [23].

for consistency it is desirable that the two functionals be the same - it is not possible with the current knowledge of KE functionals. Nonetheless, our results indicate that this does not cause any problem.

In the following we present the results for α and γ obtained by using the approximations described above. Although our main focus is the non-linear polarizabilities of atoms, we nonetheless include in our discussion the numbers obtained for linear polarizabilities also in order to provide a complete picture.

First we calculate the response properties of the noble gas atoms. The standard values for α and γ of these atoms are well established. Thus the accuracy of the approximation employed can be judged well by performing calculations for these atoms. Given in Table 1 are the numbers for the atoms He–Xe using densities obtained from their Hartree-Fock (HF) wavefunctions [13]. Since the HF densities are obtained by neglecting Coulomb correlations, our calculations are also performed within the exchange-only LDA. The values obtained by us are thus compared with the standard Hartree-Fock values [14]. As is evident, the functionals employed are decent zeroth-order approximation for the calculation of response properties to the third order. The values for α are relatively closer to the exact numbers than those for γ. This shows the sensitivity of γ towards the approximate form for the energy functionals. The value for γ is most accurate for helium since the von-Weizsacker functional is exact for two-electron systems. For the rest of the atoms except Argon, values of γ are off by about 5%−15%.

In Table 2, we present the results for α and γ of noble gas atoms obtained from Kohn-Sham LDA (KSLDA) densities. Again for helium the values of α and γ are accurate in comparison with the values obtained from the Kohn-Sham perturbation theory [15]. For the other atoms our values are lower by about 20% The actual difference would be slightly less because the reported LDA numbers [15–17] have been obtained by Perdew-Zunger parametrization [18] of the exchange correlation energy which gives [15] slightly larger numbers than the Gunnarsson-Lundquist parametrization [10] used by us. Nonetheless, the comparison again shows that the von-Weizsacker functional employed by us is a reasonably good zeroth-order approximation up to the fourth order changes in kinetic energy of perturbed atoms. As noted, GEA would not lead to accurate results for the reasons given above. For example with HF densities, GEA up to the second order gives highly inaccurate results of $\alpha = 4.42$ a.u., $\gamma = 10800$ a.u. for He and $\alpha = 7.82$ a.u., $\gamma = 102000$ a.u. for Ne. Similar trends are observed for the other atoms too.

For comparison, we also give in Table 3 the experimental numbers [19–23] for the polarizabilities and hyperpolarizabilities of these atoms. As is evident, HF values for γ are close to the experimental values than the KSLDA values. The latter are large by almost a factor of two. Differences between the HF and KSLDA values arise mainly because of different asymptotic nature of the respective densities. In this connection, we note that the asymptotic structure of the effective potential affects the value of polarizability significantly, as discussed [24] recently for the case of linear polarizabilities; for non-linear polarizabilities the difference is even more because these are highly sensitive to the quality of the wavefunction.

Table 4. Hyperpolarizability of some cations using Hartree-Fock (HF) and Kohn-Shan LDA (KSLDA) ground state densities. Atomic units are used.

Ion	γ	
	HF	KSLDA
Na^+	4.39	6.90
Mg^{2+}	0.6	0.82
K^+	85.63	116.23
Ca^{2+}	17.94	19.81
Rb^+	268.2	370.3
Sr^{2+}	-	87.37

Table 5. Hyperpolarizability for H^- and halogen anions using Hartree-Fock (HF) densities. Values of these quantities obtained in coupled Hartree-Fock theory are given in brackets. Experimental numbers/accurate theoretical numbers, where available, are also given. Atomic units are used.

ION	γ	
	HF	Expt./Ab in.
H^-	7.8×10^6 (5.98×10^6) [a]	76.0×10^6 [c]
F^-	6691 (9000) [b]	58000
Cl^-	2.95×10^4	
Br^-	4.86×10^4	
I^-	1.44×10^5	

[a] Reference [27]; [b] Reference [26]; [c] Reference [25].

Having demonstrated the application of density based perturbation theory with the aforementioned approximations, we now apply the formulation to estimate the non-linear polarizabilities of some positive and negative ions.

Given in Table 4 are the non-linear polarizabilities for alkali metals and alkaline earth ions employing their HF and KSLDA densities. As in the case of noble gas atoms, the hyperpolarizability numbers obtained from the two densities differ - the KS densities lead consistently to higher values than the HF densities. However, as noted above, the HF numbers should be close to experimental polarizabilities for these ions. To the best of our knowledge, experimental numbers for hyperpolarizabilities of these ions do not exist.

In Table 5 we give the numbers for the negative ions of Hydrogen and Halogens using HF density. Since the Coulomb correlation effects are relatively more important in negative ions, the Hartree-Fock values for these cannot be expected to be as close to the experimental values as for neutral or positive systems. This is clear from the numbers [25,26] for H^- and F^-. However it may be expected that for anions with large Z, the numbers obtained by us will be less off than for H^- and F^-.

All the results presented above are for atoms and ions with electronic configurations similar to the noble gas atoms. Do the approximations and variational forms of the induced density employed also lead to similar accuracy for the other atoms? Our preliminary study in this direction indicates that for atoms like Be, Mg, Ca the von-Weiszacker functional is less accurate, giving only about 70% of the standard results.

To conclude, we have demonstrated in this paper that densities, instead of the wavefunctions, in conjunction with approximate energy functionals can be employed directly in perturbation theory to calculate response properties of inhomogeneous electron gas systems. This has two advantages: (i) visualizing the density is easy and therefore our calculations are physically transparent, and (ii) calculations in terms of density are numerically much easier to perform than their wavefunctional counterparts. Further, we have shown that for kinetic energy, the von-Weizsacker functional is a reasonably good zeroth-order approximation for perturbation theory calculations up to the fourth order. On the other hand, for two-electron systems the functional is exact and therefore leads to results [28] which are comparable to their wavefunctional counterparts. For the exchange-correlation energies, LDA appears to be accurate enough. This is also revealed by our exchange-only LDA calculations. To make calculations more accurate would require going beyond the von-Weizsacker functional for the kinetic energy as the first step. An example of such an extension is the functional [29] used in previous calculations [8] by one of the present authors. Use of this functional, however, makes the polarizability values accurate but does the opposite for the hyperpolarizability values. We are doing investigations in the direction of finding more accurate kinetic energy functionals. With the applicability of the theory demonstrated we are also implementing the present formulation to calculate response properties of molecules. Results of these studies will be reported in the future.

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