

## Application of density-functional perturbation theory to calculate nonlinear polarizabilities of helium-like systems

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MS received 29 April 1997; revised 16 August 1997

**Abstract.** Density-based perturbation theory within the Hohenberg–Kohn (HK) formalism of density functional theory (DFT), developed recently by us, is employed to calculate hyperpolarizabilities of helium-like ions from their ground-state densities obtained from their respective Hylleraas wavefunctions. The only approximation made is that of the local density (LDA) for exchange and correlation. Use of densities – instead of wavefunctions – in density-based perturbation theory together with simple approximate energy functionals makes our calculations much simpler than those based on wavefunctions. They lead, however, to accurate results.

**Keywords.** Static polarizabilities; perturbation theory; density functional theory.

**PACS Nos** 31.15; 32.10

Recently we have developed the density-based perturbation theory (DFPT) [1] within the Hohenberg–Kohn (HK) formalism of density functional theory (DFT). In this theory perturbative calculations are performed in terms of the density. The theory is different from the widely used Kohn–Sham version [2] of density-functional theory where an orbital based approach is used. The two key theorems of DFPT are: (a) the  $(2n+1)$  theorem which states that the density correct to order ' $n$ ' in terms of perturbation parameter is sufficient to give energy up to order  $(2n+1)$ , and (b) as a corollary, if the density is known exactly to order  $(n-1)$ , the even order energy change  $E^{(2n)}$  is variational with respect to the  $n$ th order induced density  $\rho^{(n)}$ . Of these, the  $(2n+1)$  theorem has been mentioned [3] before in the literature. However, it is only now that perturbation theory in terms of density and associated theorems have been fully developed. This paves the way for obtaining both linear as well as non-linear response properties of a system directly from its density. In this paper we apply the  $(2n+1)$  theorem and its even-order corollary in DFPT to calculate variationally the electric dipole polarizabilities  $\alpha$  and hyperpolarizabilities  $\gamma$  for two-electron helium-like ions from their ground-state densities. Thus  $\alpha$  is obtained by minimizing the second-order energy change  $\Delta E^{(2)}$  and using the relationship

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

Similarly  $\gamma$  is obtained by minimizing the fourth-order energy

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

where  $\mathcal{E}$  is the applied uniform static electric field. The above equations are the simplified versions (for spherically symmetric systems considered in this paper) of more general equations in which  $\alpha$  and  $\gamma$  are tensors. Our motivation in carrying out the calculation is to demonstrate that with approximate exchange-correlation energy functionals, density-based DFPT can be applied to calculate linear and non-linear response properties of these systems. We note that the density-based calculation for linear response properties of atoms have been performed earlier [3, 4]. However, it is only after the development of density-based variation-perturbation theory within the Hohenberg–Kohn (HK) formalism of DFT that, the calculation of nonlinear response properties of electronic systems from their ground-state densities has become possible. Further, since the energy changes are calculated from the ground-state densities, rather than the wavefunctions of the atoms, the present method is much simpler and numerically easier than its wavefunctional counterpart.

In the present paper we employ the near exact densities constructed [5] from explicitly correlated two-electron Hylleraas wavefunctions [6]. The approximate forms for the kinetic and exchange-correlation energy functionals employed are described later in the paper.

In the following we briefly describe DFT [2] and its perturbative extension along with the energy functionals chosen for our calculations. We then present our calculations and results and follow them with a discussion.

The basic variable in DFT is the ground-state density  $\rho(\mathbf{r})$  and all the properties of the system are expressed as functionals of it. In particular, the ground-state energy of a system is also written as the functional

$$E[\rho] = F[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \quad (3)$$

where  $F[\rho]$  is a universal functional of  $\rho(\mathbf{r})$  and comprises the kinetic and the interaction energy of the electrons, and  $v_{\text{ext}}(\mathbf{r})$  is the external potential including  $v^{(1)}(\mathbf{r}) = \mathcal{E}r \cos \theta$  due to the applied field  $\mathcal{E}$ . The functional  $F[\rho]$  is generally split as

$$F[\rho] = T_s[\rho] + E_H[\rho] + E_{\text{xc}}[\rho], \quad (4)$$

where  $T_s[\rho]$  is the kinetic energy of the non-interacting electrons of the same density as the interacting ones,

$$E_H[\rho] = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5)$$

is the Hartree energy, and  $E_{\text{xc}}[\rho]$  is the exchange-correlation energy. The difference between the true kinetic energy of the electrons and  $T_s[\rho]$  is absorbed into the exchange-correlation energy  $E_{\text{xc}}[\rho]$ . Employing the variational principle for the energy, both the ground-state density and energy are obtained by minimizing the energy functional with respect to the density. This leads to the following Euler equation for the density

$$\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} - \mu = 0, \quad (6)$$

*Density-functional perturbation theory*

where  $\mu$  is the Lagrange multiplier to ensure that the number of electrons is conserved. When the system is subjected to an external applied field, both the ground-state density and energy change from unperturbed  $\rho_0$  and  $E_0$  to  $\rho_0 + \Delta\rho$  and  $E_0 + \Delta E$  respectively. In DFPT these changes are expanded in perturbation series as

$$\Delta\rho = \sum_i \lambda^i \rho^{(i)}, \quad (7)$$

with

$$\int \rho^{(i)}(\mathbf{r}) \, d\mathbf{r} = 0 \quad (8)$$

for each order, and

$$\Delta E = \sum_i \lambda^i E^{(i)}, \quad (9)$$

where  $\lambda$  is the perturbation parameter. The energy changes to different orders are calculated in terms of  $\rho^{(i)}$ . By the  $(2n + 1)$  theorem of DFPT, energy up to  $E^{(2n+1)}$  requires knowledge of  $\rho$  only to order  $n$ . As such [1]

$$E^{(2)} = \int v^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r})\,d\mathbf{r} + \frac{1}{2} \int \frac{\delta^{(2)}F[\rho_0]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)\,d\mathbf{r}_1 \, d\mathbf{r}_2, \quad (10)$$

involves density up to  $\rho^{(1)}$ , and

$$\begin{aligned} E^{(4)} = & \frac{1}{2} \int \frac{\delta^{(2)}F[\rho_0]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)} \rho^{(2)}(\mathbf{r}_1)\rho^{(2)}(\mathbf{r}_2)\,d\mathbf{r}_1 \, d\mathbf{r}_2 \\ & + \frac{1}{2} \int \frac{\delta^{(3)}F[\rho_0]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)} \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)\rho^{(2)}(\mathbf{r}_3)\,d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 \\ & + \frac{1}{24} \int \frac{\delta^{(4)}F[\rho_0]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)\delta\rho(\mathbf{r}_3)\delta\rho(\mathbf{r}_4)} \\ & \times \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)\rho^{(1)}(\mathbf{r}_3)\rho^{(1)}(\mathbf{r}_4) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 \, d\mathbf{r}_4 \end{aligned} \quad (11)$$

is given by density up to order 2. (For the present problem all the odd orders of energy vanish due to spherical symmetry). All the functional derivatives in the expressions above have been taken at the ground-state density  $\rho_0$ . Furthermore, by the even-order corollary of the theorem,  $E^{(2)}$  is variational with respect to  $\rho^{(1)}$  and, with known  $\rho^{(1)}$ ,  $E^{(4)}$  is variational with respect to  $\rho^{(2)}$ . This results in the equations for the induced densities  $\rho^{(1)}$  and  $\rho^{(2)}$  which can be solved to obtain these quantities. The induced densities and the energies can also be determined by applying the variational procedure sequentially [7] in two steps. First  $\rho^{(1)}$  is determined by minimizing  $E^{(2)}$ . Then  $\rho^{(1)}$  is kept fixed and  $E^{(4)}$  is minimized to determine  $\rho^{(2)}$ . It is this variational approach that we take in this paper. Notice that the expression for  $E^{(4)}$  does not involve explicitly the applied external field. Thus the information about the field is carried to  $E^{(4)}$  by the induced density  $\rho^{(1)}$ .

Before we present our results, it is worth pointing out the difference between the density-based perturbation theory used in this paper and the Kohn–Sham perturbation theory. In the density-based approach the correction from  $E^{(3)}$  onwards are given by the

universal functional  $F[\rho]$  alone. On the other hand the Kohn–Sham approach employs the full Hamiltonian (including the applied perturbation) for the energy changes to all orders. In principle both should lead to the same result. However, from the application point of view the two theories differ because of their treatment of the kinetic energy. In Kohn–Sham theory the non-interacting component of the kinetic energy is treated *exactly* whereas in the density-based approach it has to be approximated for systems with number of electrons greater than two. Although many approximate functionals for the kinetic energy exists [2], it is not clear which one should lead to accurate response properties for a many-electron system; the application of Kohn–Sham approach [7, 8] has no such limitation.

To perform variational calculations, the question arises how to choose the functional form for the induced densities  $\rho^{(1)}$  and  $\rho^{(2)}$ . For this purpose, we take a cue from the hydrogen atom problem which can be solved exactly [9, 10] and employ similar form for the variational densities. They are taken to be

$$\rho^{(1)}(\mathbf{r}) = \Delta_1(r) \cos \theta \rho_0(r) \quad (12)$$

and

$$\rho^{(2)}(\mathbf{r}) = [\Delta_2(r) + \Delta_3(r) \cos^2 \theta] \rho_0(r) + \lambda \rho_0(\mathbf{r}), \quad (13)$$

where

$$\Delta_i(r) = a_i r + b_i r^2 + c_i r^3 + d_i r^4 + e_i r^5 + \dots; \quad i = 1, 2, 3 \quad (14)$$

with  $a_i, b_i, \dots, e_i$  being the variational parameters which are optimized to obtain the minimum of energy. Notice that with these choices for the induced densities, eq. (8) is automatically satisfied for  $\rho^{(1)}$ ; to satisfy it for  $\rho^{(2)}$ ,  $\lambda$  is appropriately chosen for each set of parameters.

As stated in the beginning, density-based calculations for an  $N$ -electron system perforce employ approximate energy functionals, since the exact ones are not known. For the exchange and correlation energy we make the local-density approximation (LDA). Thus

$$E_{xc}^{\text{LDA}}[\rho] = E_x^{\text{LDA}}[\rho] + E_c^{\text{LDA}}[\rho], \quad (15)$$

where the exchange energy

$$E_x^{\text{LDA}}[\rho] = -\frac{3}{4}(3/\pi)^{1/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad (16)$$

and the correlation energy [11]

$$E_c^{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) c \left[ \left(1 + x^3\right) \ln \left(1 + \frac{1}{x}\right) + \frac{x}{2} - x^2 - \frac{1}{3} \right] d\mathbf{r} \quad (17)$$

with  $c = -0.0333$ ,  $x = r_s/A$ ,  $A = 11.4$ , where  $r_s = [3/4\pi\rho(\mathbf{r})]^{1/3}$ . On the other hand, for two-electron systems the non-interacting kinetic energy is given exactly by the von-Weizsacker energy functional [12]

$$T_w = \frac{1}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}. \quad (18)$$

**Table 1.** Electric dipole polarizabilities  $\alpha$  in atomic units for various helium-like ions obtained from their Hylleraas densities. Theoretical values from the other *ab-initio* schemes, and the experimental numbers are also given.

Atom/Ion	Present results	<i>Ab-initio</i>	Expt. <sup>c</sup>
H <sup>-</sup>	231.23	206.39 <sup>a</sup>	—
He	1.3891	1.3834 <sup>a</sup>	1.3838
Li <sup>+</sup>	0.1928	0.1925 <sup>a</sup>	0.1911
Be <sup>2+</sup>	0.0523	0.0519 <sup>b</sup>	—
B <sup>3+</sup>	0.0197	0.0196 <sup>c</sup>	—

<sup>a</sup> Ref. [15], <sup>b</sup> Ref. [16] and <sup>c</sup> Ref. [17].

**Table 2.** Electric dipole hyperpolarizabilities in atomic units for various helium-like ions obtained from their Hylleraas densities. Theoretical values from the *ab-initio* schemes, and the experimental numbers are also given. Experimental values differ from each other because of the different methods used to determine them.

Atom/Ion	Present results	<i>Ab-initio</i>	Expt.
H <sup>-</sup>	$1.12 \times 10^8$	$0.803 \times 10^{8a}$	—
He	47.16	43.6 <sup>b</sup>	35.7 <sup>e</sup> 41.7 <sup>f</sup> 42.6 <sup>g</sup> 52.4 <sup>h</sup>
Li <sup>+</sup>	0.2471	0.2427 <sup>c</sup>	—
Be <sup>2+</sup>	0.0087	0.0085 <sup>d</sup>	—
B <sup>3+</sup>	0.0007	0.0007 <sup>d</sup>	—

<sup>a</sup> Ref. [18], <sup>b</sup> Ref. [19], <sup>c</sup> Ref. [14] and [17], <sup>d</sup> Ref. [17], <sup>e</sup> Ref. [24], <sup>f</sup> Ref. [25], <sup>g</sup> Ref. [26] and [27], <sup>h</sup> Ref. [20].

In tables 1 and 2 we show the polarizabilities and hyperpolarizabilities, respectively, for two-electron systems H<sup>-</sup>, He, Li<sup>+</sup>, Be<sup>2+</sup> and B<sup>3+</sup> obtained by us. Although this paper is devoted to the calculation of nonlinear response properties of two-electron systems, we nonetheless include the numbers obtained for linear polarizabilities also in order to provide a complete picture. Also shown are the theoretical results obtained by other *ab-initio* methods [13–19] along with available experimental results [20–27]. The ground-state density employed by us corresponds to 204-term Hylleraas type wavefunctions [5].

It is evident from the results that they are highly accurate in comparison to the numbers available by other methods. We also note that the numbers for polarizability are also consistent with those obtained previously from a similar calculation [4] but with a different form for the induced density  $\rho^{(1)}$ . The maximum deviation for both  $\alpha$  and  $\gamma$  occurs for H<sup>-</sup> for which the effect of Coulomb correlations is the largest and therefore the LDA is relatively less accurate. We wish to point out that we have performed our calculations with six parameters for  $\alpha$  and fourteen parameters for  $\gamma$ . On the other hand, if calculations were to be performed using the wavefunctions directly, one would require 612 parameters for  $\alpha$  and 1224 for  $\gamma - 3N$  [13] and  $6N$  [14] parameters are needed for  $\alpha$  and  $\gamma$  respectively, if an  $N$  term Hylleraas-type wavefunction is employed. We have also checked our results by increasing the number of parameters in  $\Delta_i(r)$ . They do not change appreciably which indicates their proper convergence.

As pointed out before, the calculations reported here differ from the widely used Kohn–Sham approach of density functional theory and its perturbative extensions [8,28,29]. The Kohn–Sham approach is an orbital based scheme, and as such its perturbation theory methodology [7,29,30] is similar to that of coupled Hartree–Fock theory [31]. On the other hand present calculations are performed entirely in terms of the density.

To conclude, we have shown that DFPT can be employed with approximate functionals for the exchange–correlation energies (LDA) to obtain reasonably accurate results for both linear as well as non-linear response properties of helium-like systems.

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