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Density-functional calculations of electric-dipole polarizabilities for atoms

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Static electric-dipole polarizabilities for closed-shell atoms and positive ions are calculated directly from the ground-state densities of these systems. Calculations are performed using the variational principle for the energy by making an ansatz for the change in the density when the atom is put in an electric field. Since the energies are calculated from the density, the kinetic and the exchange-correlation energies have to be approximated. The exchange-correlation energy is taken within the local-density approximation. To calculate the changes in the ground-state energies accurately, we suggest the use of a kinetic-energy functional of the density which is particularly suited for such situations where the changes in the energy are of importance.

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In this paper we present an alternative approach based on density-functional theory [1] to calculate electric-dipole polarizabilities of atoms and ions. In this approach only the ground-state density of the system of interest is required as an input for calculating this quantity. As such our approach is different, and numerically easier, than the usual single-particle orbital theory methods. Whereas these methods obtain the changes in the ground-state density and energy by first calculating the perturbed orbitals, we calculate the induced density directly using the variational principle for the energy. However, if the density is used for calculating energies, the kinetic energy and the exchange-correlation energies can be treated only approximately. We treat the exchange and correlation within the local-density approximation (LDA) [1]. The kinetic energy, on the other hand, is a major component of the total energy, and therefore one has to be more judicious in choosing which of the many available functionals to use. We will discuss this later in the paper. In the following we begin with a brief review of the perturbation theory approach to calculating the electric-dipole polarizabilities within the single-particle picture of the LDA Kohn-Sham approach [1]. For details the reader is referred to the book by Mahan and Subbaswamy [2]. We then discuss our method and demonstrate its accuracy by applying it to spherically symmetric atoms and positive ions within the LDA [1] for the exchange and correlation. The results obtained compare well with those obtained [2] by the time-dependent local-density-approximation (TDLDA) calculations. We conclude with a discussion of the possible extension of the method to calculating higher-order polarizabilities.

In the Kohn-Sham formalism, a system of N interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$ is replaced by a system of N noninteracting fermions moving in a local effective potential comprising the Hartree potential and the exchange-correlation potential. The single-particle orbitals of these noninteracting particles are obtained by solving the Kohn-Sham equation (atomic units are used throughout the paper)

$$[-\tfrac{1}{2}\nabla^2+V_{\text{ext}}(\mathbf{r})+V_H(\mathbf{r})+V_{\text{xc}}(\mathbf{r})]\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r}) , \tag{1}$$

where $V_H(\mathbf{r})$ is the Hartree potential and $V_{\text{xc}}(\mathbf{r})$ is the exchange-correlation potential. The orbitals $\varphi_i(\mathbf{r})$ themselves have no meaning but lead to the ground-state density $\rho(\mathbf{r})$ of the interacting electronic system via $\rho(\mathbf{r})=\sum_i|\varphi_i(\mathbf{r})|^2$. The Hartree potential is obtained from the density by

$$V_H(\mathbf{r})=\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \tag{2}$$

and the exchange-correlation potential is given as

$$V_{\text{xc}}(\mathbf{r})=\frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r})} , \tag{3}$$

where $E_{\text{xc}}[\rho]$ is the exchange-correlation energy functional. Since the exact expression for this functional is not known, one usually makes the LDA for the exchange and correlation. In this approximation the exchange-correlation energy is calculated by treating each point in the electron gas as homogeneous with the local density. The total ground-state energy is calculated as the sum

$$T_s[\rho]+\int\rho(\mathbf{r})V_{\text{ext}}(\mathbf{r})+E_H[\rho]+E_{\text{xc}}[\rho] , \tag{4}$$

where

$$T_s[\rho]=\sum_i\langle\phi_i|-\tfrac{1}{2}\nabla^2|\phi_i\rangle \tag{5}$$

is the noninteracting kinetic energy and

$$E_H[\rho]=\tfrac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \tag{6}$$

is the Hartree energy. The exchange energy within the local-density approximation is given in terms of the density as

$$E_x^{\text{LDA}}[\rho]=\int\rho(\mathbf{r})\varepsilon_x^{\text{hom}}(\mathbf{r})d\mathbf{r} , \tag{7a}$$

where

$$\varepsilon_x^{\text{hom}}=d_0\rho^{1/3}(\mathbf{r}) , \tag{7b}$$

with $d_0 = -\frac{3}{4}(3/\pi)^{1/3}$. For the correlation energy we use the Gunnarsson-Lundquist [3] formula in which the correlation energy is given as [1]

$$E_c^{\mathrm{LDA}}[\rho] = \int \rho(\mathbf{r})\varepsilon_c^{\mathrm{hom}}(\mathbf{r})d\mathbf{r} \ , \tag{8a}$$

where

$$\varepsilon_c^{\mathrm{hom}}(\mathbf{r}) = c\left\{(1+x^3)\ln\left[1+\frac{1}{x}\right]+\frac{x}{2}-x^2-\frac{1}{3}\right\} \tag{8b}$$

with $c=-0.0333$, $x=r_s/A$, $A=11.4$, and where $r_s=[3/4\pi\rho(\mathbf{r})]^{1/3}$ is the local r_s value.

Now if the system is put in a weak external electric field $\mathcal{E}$ in the z direction, the external potential changes to $V_{\mathrm{ext}}(r)+\mathcal{E}r\cos\theta$. This induces a change in the orbitals and therefore in the density. The change in the density also makes $V_H(\mathbf{r})$ and $V_{xc}(\mathbf{r})$ different from the original problem. As such the new Kohn Sham equation is

$$\begin{aligned}&[-\tfrac{1}{2}\nabla^2+V_{\mathrm{ext}}(\mathbf{r})+\mathcal{E}r\cos\theta+V_H(\mathbf{r})+\delta V_H(\mathbf{r})\\ &\quad +V_{\mathrm{xc}}(\mathbf{r})+\delta V_{\mathrm{xc}}(\mathbf{r})](\phi_i+\delta\phi_i)=(\varepsilon_i+\delta\varepsilon_i)(\phi_i+\delta\phi_i) \ ,\end{aligned} \tag{9}$$

where $\delta V_H(\mathbf{r})$ and $\delta V_{\mathrm{xc}}(\mathbf{r})$ are the changes in the Hartree and the exchange-correlation potentials, respectively. This equation is to be solved self-consistently up to the desired order to obtain the new perturbed orbitals $\varphi_i(\mathbf{r})+\delta\varphi_i(\mathbf{r})$, which lead to the new density $\rho'(\mathbf{r})$ and energy E'.

The new ground state energy E' can be written as a power series in $\mathcal{E}$ with the zeroth order being the unperturbed energy. For systems for which the first-order change in the energy vanishes (systems of interest in this paper), it is given to $O(\mathcal{E}^2)$ as

$$E'=E-\tfrac{1}{2}\alpha\mathcal{E}^2 \ , \tag{10}$$

where α is the static electric-dipole polarizability. It is related to the change in the density by

$$\alpha=p_z/\mathcal{E} \ , \tag{11}$$

where

$$p_z=\int z[\rho'(\mathbf{r})-\rho(\mathbf{r})]d\mathbf{r} \tag{12}$$

is the induced dipole moment.

The purpose of present work is to calculate α directly from the density without getting involved with the orbitals. The question then naturally arises whether we can easily calculate or approximately represent the induced density in terms of the known ground-state density when the system is put in an external field. Furthermore, in order for the differences in the total energy to be obtained accurately, we need a kinetic-energy functional of the density which gives the change in the kinetic energy accurately when the density is changed. In the following we first discuss how to obtain the induced density accurately in terms of the ground-state density.

Let us consider a distribution of electrons described by the density $\rho(\mathbf{r})$. When subjected to an electric field, this distribution changes to a new one given by $\rho'(\mathbf{r})$. The simplest possible change in this density is that the electronic distribution shifts rigidly in the direction opposite to that of the field so that

$$\rho'(\mathbf{r})=\rho(\mathbf{r})+a\mathcal{E}\cdot\nabla\rho \tag{13}$$

to the first order in $\mathcal{E}$. Here a is a constant which gives the amount by which the density shifts. Thus we see that in this case the induced density is proportional to the gradient of the density. As such we may expect that in the general case too, the induced density would have a factor proportional to the gradient of the density. The question is whether it can be represented by a simple form such as that of Eq. (13). As we discuss below, the induced density can indeed be assumed, at least for spherical systems, to be a simple function involving the gradient of the density. This is indicated by the calculation for the hydrogen atom [4]. To the first order in $\mathcal{E}$, the induced density in the hydrogen atom is given as

$$\begin{aligned}\rho^{\mathrm{ind}}(\mathbf{r})&=\rho'(\mathbf{r})-\rho(\mathbf{r})\\ &=-(2r+r^2)\mathcal{E}\rho(\mathbf{r})\cos\theta \ .\end{aligned} \tag{14}$$

However, for the hydrogen atom, $\rho(\mathbf{r})$ is proportional to $|\nabla\rho(r)|$ so that (14) can be rewritten

$$\rho'(\mathbf{r})=\rho(\mathbf{r})+(ar+br^2)\mathcal{E}\cdot\nabla\rho(\mathbf{r}) \ , \tag{15}$$

where a and b are two constants. Now Eq. (15) has an interpretation similar to that of Eq. (13). It represents a distortion in the density as if locally the density contours are being shifted in the direction of the field by $(ar+br^2)$. On these physical grounds, we now assume that for any spherical system in general the new density can be written as Eq. (15) with $(ar+br^2)$ replaced by a more general distortion function $\Delta(\mathbf{r})$ so that

$$\rho'(\mathbf{r})=\rho(\mathbf{r})+\Delta(\mathbf{r})\mathcal{E}\cdot\nabla\rho(\mathbf{r}) \ . \tag{16}$$

The function $\Delta(\mathbf{r})$ is to be so chosen that the integral of the induced density vanishes. For spherically symmetric systems considered in the paper, this is guaranteed with a function that depends only on r. We also assume that the next-order correction to the density is negligible.

Now the procedure is to calculate the change in the total energy in terms of $\Delta(\mathbf{r})$ and minimize this change with respect to variations in it. The difference in the two ground-state energies thus obtained leads to α via Eq. (10). This brings us to the question of obtaining the energy changes accurately which we now discuss.

Changes in the external energy, Hartree energy, and the exchange-correlation energies (within LDA) can be calculated directly from their expressions above in terms of the density. For kinetic energy, however, there exist many functionals [1] which give the total kinetic energy in terms of the ground-state densities quite accurately. The question arises as to which of these functionals be used to give the *change* in the kinetic energy accurately. For this purpose we use the functional [5]

$$T_s[\rho]=T_W[\rho]+f(N)T_{\mathrm{TF}}[\rho] \ , \tag{17}$$

where

$$T_W[\rho]=\frac{1}{8}\int\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}d\mathbf{r} \tag{18}$$

is the von-Weizäcker functional and

$$T_{\mathrm{TF}}[\rho]=c_0\int\rho^{5/3}(\mathbf{r})d\mathbf{r} \tag{19}$$

with $c_0=\frac{3}{10}(3\pi^2)^{2/3}$ is the Thomas-Fermi kinetic energy. In this functional the von-Weizsäcker term is used as the zeroth-order term, and thus it is different from the gradient expansion [6] based functionals for the kinetic energy. The factor [7]

$$f(N)=\left[1-\frac{2}{N}\right]\left[1-\frac{A_1}{N^{1/3}}+\frac{A_2}{N^{2/3}}\right] \tag{20}$$

is used with the optimized parameters $A_1=1.314$ and $A_2=0.0021$ [8]. This kinetic-energy functional is used because T_W (T_{TF}) represent accurately the changes in the kinetic energy of a homogeneous electron gas in the limit of it being put in a rapidly (slowly) varying perturbing field [9,10]. Thus an optimized combination of the two can be expected to give accurately the change in kinetic energy of a system when it is subjected to a perturbing field. Furthermore the functional is exact in the limit of one- (in spin-polarized form) and two-electron systems.

Before going to the application of the method discussed above, we wish to note that, in the past, similar variational procedures, although in terms of the orbitals, have been applied [11] to calculate the dipole and quadrupole polarizabilities of atoms and ions. Although these calculations are quite easy for one- and two-electron atoms and ions, they become rather complicated as the number of electrons increases. Not only does the number of variational parameters increase with the orbitals, inclusion of self-consistency also becomes quite difficult [12]. On the other hand, if the density is used instead of orbitals, the number of parameters remains the same irrespective of the number of orbitals needed to describe the system.

We now apply the method above to spherically symmetric atoms and positive ions. For the choice of $\Delta(r)$, we have again taken the cue from the hydrogen-atom problem and chosen it to be a polynomial of the form $ar+br^2+\cdots$. The change in the energy in presence of an external field is minimized with respect to the parameters $a,b\ldots$. If the variational procedure outlined above is to be meaningful, the value of the dipole polarizability must converge as the number of parameters is increased. This is indeed seen to be the case.

In Table I the values of α obtained by employing two, three, and four parameters in the function $\Delta(r)$ for various atoms and ions are shown. The unperturbed ground-state density employed is that obtained by solving the Kohn-Sham equation with the Gunnarsson-Lundquist exchange-correlation energy functional. Also shown are the values obtained with the perturbation theory approach of TDLDA and the experimental polarizabilities. As is clearly shown, the values of α obtained converge to a particular value as the number of parameters is increased. Thus a three-parameter calculation is sufficient for the calculations as the inclusion of the fourth parameter does not change α much. The values thus obtained for α are quite accurate in comparison to the TDLDA values. Furthermore the large variation of polarizabilities from one atom to the other is correctly reproduced. For the helium atom, for which the kinetic-energy functional is exact, the polarizability is most accurate. For most of the other atoms, the estimate is within 10% of the TDLDA values. This points to the correct-

TABLE I. Values of static dipole polarizabilities (in atomic units) as calculated with different number of parameters. Values obtained within time-dependent local-density approximation (TDLDA) and experimental polarizabilities are also given.

	$\Delta(r)$				
Atom or ion	$ar+br^2$	$ar+br^2+cr^3$	$ar+br^2+cr^3+dr^4$	TDLDA[a]	Expt.
He	1.63	1.63	1.63	1.66	1.35[a]
Ne	2.91	3.28	3.29	2.99	2.66[a]
Na^+	1.26	1.30	1.31	1.07	1.00[a]
Mg^{2+}	0.66	0.66	0.66	0.51	0.49[a]
Ar	8.45	11.27	11.44	11.80	11.08[a]
K^+	4.56	5.44	5.60	5.70	5.47[a]
Ca^{2+}	2.77	3.13	3.25	3.34	3.26[a]
Cu^+	2.56	5.17	5.17	7.68	
Zn^{2+}	1.49	2.28	2.29	2.85	
Kr	7.43	16.17	16.35	17.70	16.75[a]
Rb^+	4.67	8.58	8.83	9.41	9.25[b]
Sr^{2+}	3.23	5.34	5.58	5.95	5.67[c]
Ag^+	3.67	7.48	7.50	9.93	
Cd^{2+}	2.54	4.36	4.36	5.30	
Xe	9.27	25.26	25.28	28.77	27.29[a]

[a] Reference [2].

[b] Reference [12].

[c] Reference [13].

ness of the ansatz for the form of induced density and the accuracy of the kinetic-energy functional used. There is a possibility that the factor $f(N)$ in Eq. (19) may be different [1] for the positive ions. This is indicated by the deviation of α calculated with the present method from the TDLDA numbers for the positive ions.

We conclude that a physical picture which represents the induced density in the presence of an external field as a local shift of the density leads to accurate estimates of the electric-dipole polarizabilities of atoms. This approach is also intuitively appealing. Numerically, the present method is comparatively easier to apply. Thus it may prove useful for quick and accurate estimates of polarizabilities. Of course, to get the exact results within the LDA, one must solve the TDLDA equation.

For the future work, we wish to investigate the possibility of extending the present approach to calculate higher-order polarizabilities of simple systems. This should be possible by expanding the density further to include higher-order corrections to the density. Also we would like to investigate if this approach can be applied easily to more complex systems which are not spherically symmetric.

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