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A Density-Functional Calculation of Dynamic Dipole Polarizabilities of Noble Gas Atoms

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Using a very simple trial function and unperturbed electron densities calculated by a new procedure, the frequency-dependent dipole polarizability $\alpha(\omega)$ of Ne, Ar, Kr and Xe has been calculated in the range $0 \leq \omega \leq 0.45$ a.u., by a Karplus–Kolker-type variation-perturbation method. Results progressively worsen for larger systems so that, for Xe, $\alpha(0)$ is only 75% of the experimental value. Probable reasons for this are discussed.

Key words: Density-functional theory – Dynamic polarizability – Noble gas atoms – Variation-perturbation method – Direct density calculation.

1. Introduction

Dynamic polarizability of a many-electron system is a measure of its response to an external time-dependent oscillating electric field and is of considerable value in the study of optical properties of matter as well as long-range interactions between molecular systems [1–3]. We have recently proposed [4] a Karplus–Kolker-type [5] variation-perturbation (VP) method and a hydrodynamical method for calculating the dynamic (frequency-dependent) polarizability, based on a time-dependent extension [6] of the Hohenberg–Kohn–Sham (HKS) density-functional theory [7] and its connection [6, 8] with the hydrodynamical analogy to quantum mechanics. Our calculated static (zero-frequency) dipole polarizability for He atom was numerically better than other density-functional

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calculations [9] of the same quantity. We have also proposed [10] a new nonlinear second-order differential equation for the direct calculation of electron density in many-electron systems; this gives results in satisfactory agreement with the Hartree–Fock ground-state energies and radial densities for Ne, Ar, Kr and Xe atoms.

In view of the well-known predictive and interpretive significance of electron density [11], we employ a similar theme in the present work as in our earlier paper [4], but develop the VP method in terms of the net 3-D density rather than the individual (e.g. HKS) orbitals. As an illustration, we calculate the frequency-dependent dipole polarizabilities of the atoms Ne, Ar, Kr and Xe using the densities calculated by ourselves [10].

After a brief review of our density calculation scheme in Section 2, we present the VP method employing this electron density in Section 3. Section 4 outlines the method of calculation while Section 5 discusses the reasons for unsatisfactory results in case of the larger atoms.

2. A Time-Dependent Density Equation

Using the relation between the correlation function [12] and the one- and two-particle density matrices, within the Hartree–Fock approximation, it has been shown [10, 13] that the kinetic-energy functional $T[\rho]$ of the HKS energy functional $E[\rho]=T[\rho]+V_{ne}[\rho]+V_{ee}[\rho]+E_{xc}[\rho]$, can be written[1] as a sum of the full Weizsäcker term and a modified Thomas–Fermi (TF) term involving a variable correction factor $f(\mathbf{r})$, viz.,

$$T[\rho]=\frac{1}{8}\int\frac{\nabla\rho\cdot\nabla\rho}{\rho}\,d\boldsymbol{r}+C_{\mathrm{TF}}\int f(\boldsymbol{r})\rho^{5/3}\,d\boldsymbol{r}, \tag{1}$$

where $C_{\mathrm{TF}}=\frac{3}{10}(3\pi^2)^{2/3}$. Variational minimization of $E[\rho]$ with respect to ρ, subject to the normalization constraint

$$\int\rho(\boldsymbol{r})\,d\boldsymbol{r}=N, \tag{2}$$

N being the number of electrons, leads to the one-particle equation

$$[-\tfrac{1}{2}\nabla^2+v_{\mathrm{eff}}]\phi=\mu\phi, \tag{3}$$

where μ is the chemical potential and

$$v_{\mathrm{eff}}(\boldsymbol{r})=v_N(\boldsymbol{r})+\int\frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\,d\boldsymbol{r}'+v_{xc}(\boldsymbol{r};\rho)+\tfrac{5}{3}C_{\mathrm{TF}}g(\boldsymbol{r})\rho^{2/3} \tag{4}$$

$$\rho(\boldsymbol{r})=|\phi(\boldsymbol{r})|^2. \tag{5}$$

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[1] Atomic units used throughout this paper.

Here $v_N(\boldsymbol{r})$ is the potential due to the nuclei, v_{xc} $(\equiv \delta E_{xc}/\delta\rho)$ is the exchange-correlation potential and the function $g(\boldsymbol{r})$ is related to $f(\boldsymbol{r})$. Also, the N-representability conditions [14] for $\rho(\boldsymbol{r})$ are automatically satisfied.

For the four closed-shell atoms[2], Ne, Ar, Kr and Xe, the *forms* of $f(r)$ and $g(r)$ have been obtained through Hartree–Fock wave functions [15] and then fitted by gaussian sums as

$$f(r)=\sum_{i=1}^{n} a_i \exp\left[-b_i(r-r_i)^2\right] \tag{6}$$

$$g(r)=\sum_{i=1}^{n} a_i \exp\left[-c_i(r-r_i)^2\right]. \tag{7}$$

The peak heights $\{a_i\}$ and the peak positions $\{r_i\}$ have been expressed as functions of the atomic number Z and the number n of electronic shells. The exponents $\{b_i\}$ and $\{c_i\}$ are adjusted to obtain satisfactory results for energy and density. With a suitable $g(r)$, Eq. (3) has been numerically solved for each atom by a finite difference method after linearization.

The calculations are easy to perform and the ground-state energies as well as radial densities agree quite nicely with the corresponding Hartree–Fock results. The function $\phi(\boldsymbol{r})$ in Eq. (3) may be interpreted as a 3-D wave function for a many-electron system.

Now, in presence of an oscillating external time-dependent potential,

$$v_{\text{ext}}(\boldsymbol{r},t)=v_{ex}(\boldsymbol{r})[e^{i\omega t}+e^{-i\omega t}], \tag{8}$$

the time-dependent version of Eq. (3) can be written as [6]

$$\left[-\tfrac{1}{2}\nabla^2+v_{\text{ext}}+v_{\text{eff}}\right]\psi=i\frac{\partial\psi}{\partial t}, \tag{9}$$

where v_{eff} is now time-dependent through $\rho(\boldsymbol{r},t)=|\psi(\boldsymbol{r},t)|^2$. Eq. (9) serves as the basis for the VP method developed in the following section.

In the absence of an external time-dependent potential, Eq. (9) becomes

$$\left[-\tfrac{1}{2}\nabla^2+v_{\text{eff}}^0\right]\psi^0=i\frac{\partial\psi^0}{\partial t}, \tag{10}$$

where the unperturbed function, $\psi^0(\boldsymbol{r},t)=\phi^0(\boldsymbol{r})\,e^{-i\varepsilon_0 t}$, is assumed to be known, even if approximately.

3. Karplus–Kolker-Type Variation-Perturbation Method for Dynamic Dipole Polarizability

In presence of a uniform oscillating electric field, F_0 $(e^{i\omega t}+e^{-i\omega t})$, v_{ext} is written as

$$v_{\text{ext}}(\boldsymbol{r},t)=\boldsymbol{r}\cdot\boldsymbol{F}_0(e^{i\omega t}+e^{-i\omega t}). \tag{11}$$

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[2] For a closed-shell atom, the problem can be treated as a 1-D case.

Taking the field direction as the z-axis,

$$v_{\text{ext}}(\boldsymbol{r}, t) = \bar{V}_0 F_0, \tag{12}$$

where

$$\bar{V}_0(\boldsymbol{r}, t) = V_0(\boldsymbol{r})\,[e^{i\omega t} + e^{-i\omega t}] \tag{13}$$

$$V_0(\boldsymbol{r}) = r\cos\theta. \tag{14}$$

Now, the time-dependent Eq. (9) is simply

$$h\psi = i\frac{\partial\psi}{\partial t}, \tag{15}$$

where

$$h = h_0 + \Delta v_{\text{eff}}(\boldsymbol{r}, t) + v_{\text{ext}}(\boldsymbol{r}, t) \tag{16}$$

$$\Delta v_{\text{eff}}(\boldsymbol{r}, t) = v_{\text{eff}}(\boldsymbol{r}, t) - v^0_{\text{eff}}(\boldsymbol{r}). \tag{17}$$

For a small perturbation, the perturbed wave function may be taken as

$$\psi(\boldsymbol{r}, t) = \psi_0(\boldsymbol{r}, t) + \psi_1(\boldsymbol{r}, t)F_0. \tag{18}$$

Substituting Eq. (18) into Eq. (15), the zero- and first-order expressions can be gathered as:

$$\left(h_0 - i\frac{\partial}{\partial t}\right)\psi_0 = 0 \tag{19}$$

$$\left(h_0 - i\frac{\partial}{\partial t}\right)\psi_1 + [\Delta v^1_{\text{eff}}(\boldsymbol{r}, t) + \bar{V}_0(\boldsymbol{r}, t)]\psi_0 = 0, \tag{20}$$

where

$$\Delta v_{\text{eff}}(\boldsymbol{r}, t) = \Delta v^1_{\text{eff}}(\boldsymbol{r}, t)F_0, \tag{21}$$

retaining terms only up to first order, as done in Eq. (18). The explicit form of $\Delta v^1_{\text{eff}}(\boldsymbol{r}, t)$, within the local density approximation, is given by Eq. (28).

The perturbed density, up to first order, is

$$\rho(\boldsymbol{r}, t) = \rho_0(\boldsymbol{r}) + \delta\rho(\boldsymbol{r}, t)F_0, \tag{22}$$

where

$$\delta\rho = 2\,\text{Re}\,\{\psi_0\psi_1\}. \tag{23}$$

Since ψ_1 is arbitrary to the extent of any added multiple of ψ_0, without loss of generality one can employ the intermediate normalization

$$\langle\psi(\boldsymbol{r}, t)|\psi_0(\boldsymbol{r}, t)\rangle = 1 \tag{24}$$

i.e.

$$\langle\psi_1(\boldsymbol{r}, t)|\psi_0(\boldsymbol{r}, t)\rangle = 0. \tag{25}$$

Because of the use of a harmonic perturbation, Eq. (12), the time-dependent Eq. (20) can now be transformed into a time-independent equation involving frequency. Writing Eq. (20) in the form

$$\left(h_0 - i\frac{\partial}{\partial t}\right)\psi_1 + [\Delta v^1_{\text{eff}}(\boldsymbol{r}, t) + V_0(\boldsymbol{r})\{e^{i\omega t} + e^{-i\omega t}\}]e^{-i\omega_0 t}\phi_0 = 0, \tag{26}$$

where $\omega_0 = \varepsilon_0/\hbar = \varepsilon_0$ (in a.u.), it becomes clear [5, 16] that the essential part of $\psi_1(\boldsymbol{r}, t)$ has a time-dependence of the form

$$\psi_1(\boldsymbol{r}, t) = x_1(\boldsymbol{r}, \omega)\, e^{i(\omega-\omega_0)t} + x_1(\boldsymbol{r}, -\omega)\, e^{-i(\omega+\omega_0)t} \tag{27}$$

while $\Delta v^1_{\text{eff}}(\boldsymbol{r}, t)$ has the following time-dependence [4]:

$$\Delta v^1_{\text{eff}}(\boldsymbol{r}, t) = \Delta\bar{v}^1_{\text{eff}}(\boldsymbol{r}, \omega)\, e^{i\omega t} + \Delta\bar{v}^1_{\text{eff}}(\boldsymbol{r}, -\omega)\, e^{-i\omega t}. \tag{28}$$

Substitution of Eqs. (27) and (28) into Eq. (26) yields the pair of time-independent coupled equations

$$(h_0 - \varepsilon_0 + \omega)x_1(\boldsymbol{r}, \omega) + [\Delta\bar{v}^1_{\text{eff}}(\boldsymbol{r}, \omega) + V_0(\boldsymbol{r})]\phi_0 = 0 \tag{29}$$

$$(h_0 - \varepsilon_0 - \omega)x_1(\boldsymbol{r}, -\omega) + [\Delta\bar{v}^1_{\text{eff}}(\boldsymbol{r}, -\omega) + V_0(\boldsymbol{r})]\phi_0 = 0, \tag{30}$$

Using the solutions $x_1(\boldsymbol{r}, \pm\omega)$ of Eqs. (29) and (30), the frequency-dependent (dynamic) dipole polarizability can be calculated as [5]

$$\alpha(\omega) = \text{Re}\,\{\langle x_1(\boldsymbol{r}, \omega)|V_0|\phi_0\rangle + \langle x_1(\boldsymbol{r}, -\omega)|V_0|\phi_0\rangle\}. \tag{31}$$

Now, Eqs. (29) and (30) may be solved variationally [5, 17] by replacing them with the Euler equations

$$\delta L(+\omega) = 0 \tag{32}$$

$$\delta L(-\omega) = 0, \tag{33}$$

where the functionals $L(\pm\omega)$ are given by

$$\begin{aligned} L(\pm\omega) = {} & \langle\chi_1(\boldsymbol{r}, \pm\omega)|h_0 - \varepsilon_0 \pm \omega|\chi_1(\boldsymbol{r}, \pm\omega)\rangle \\ & + 2\,\text{Re}\,\{\langle\chi_1(\boldsymbol{r}, \pm\omega)|\Delta\bar{v}^1_{\text{eff}}(\boldsymbol{r}, \pm\omega) + V_0(\boldsymbol{r})|\phi_0\rangle\}. \end{aligned} \tag{34}$$

The extremum of $L(+\omega)$ is an absolute minimum for all positive ω and that of $L(-\omega)$ is an absolute minimum for $\omega < (\varepsilon_1 - \varepsilon_0)$, the first excitation frequency [5]. The functions $\chi_1(\boldsymbol{r}, \pm\omega)$ can be determined by extremizing the functionals $L(\pm\omega)$ with respect to trial functions $\tilde{\chi}_1(\boldsymbol{r}, \pm\omega)$, subject to the orthogonality requirements [2]

$$\text{Re}\,\{\langle\phi_0|\tilde{\chi}_1(\boldsymbol{r}, \pm\omega)\rangle\} = 0. \tag{35}$$

4. Method of Calculation

In order to minimize the functional $L(\pm\omega)$ the trial functions $\tilde{\chi}_1(\boldsymbol{r}, \pm\omega)$ are chosen as

$$\tilde{\chi}_1(\boldsymbol{r}, \pm\omega) = f_\pm\phi_0, \tag{36}$$

where the new trial functions $f_\pm \equiv f(\boldsymbol{r}, \pm\omega)$ can be taken as real since the perturbation is real Hermitian. Using Eq. (36), Eq. (34) becomes

$$\begin{aligned} L(\pm\omega) = {} & \langle\phi_0|\tfrac{1}{2}\nabla f_\pm \cdot \nabla f_\pm \pm \omega (f_\pm)^2|\phi_0\rangle \\ & + 2\,\mathrm{Re}\,\{\langle f_\pm \phi_0|\Delta\bar{v}^1_{\mathrm{eff}\pm} + V_0|\phi_0\rangle\}. \end{aligned} \tag{37}$$

$L(\pm\omega)$ can now be minimized with respect to $f_\pm$ or, more specifically, to certain adjustable parameters embedded in $f_\pm$.

Consider a 1-D situation, e.g. closed-shell atoms. The trial functions may be chosen as

$$f_\pm = r \cos\theta \sum_{K=1}^{M} C_{K\pm} r^{K-1}, \tag{38}$$

where $C_{K\pm} \equiv C_K(\pm\omega)$. Minimizing the functional in Eq. (37) with respect to $\{C_{K\pm}\}$ leads to the set of linear equations

$$\sum_{l=1}^{M} A_{Kl\pm} C_{l\pm} = B_K; \qquad K = 1, \ldots, M, \tag{39}$$

where $A_{Kl\pm}$ and B_K are combinations of certain matrix elements in terms of ϕ_0. The solutions of (39) yields the coefficients $\{C_{K\pm}\}$. The dipole polarizability is now given by

$$\begin{aligned} \alpha(\omega) &= \mathrm{Re}\,\{\langle\phi_0|f_+ V_0|\phi_0\rangle + \langle\phi_0|f_- V_0|\phi_0\rangle\} \\ &= \tfrac{1}{3} \sum_{K=1}^{M} \langle r^{K+1}\rangle (C_{K+} + C_{K-}), \end{aligned} \tag{40}$$

where

$$\langle r^n\rangle = 4\pi \int \rho(r) r^n r^2 \,\mathrm{d}r. \tag{41}$$

The value of M depends on the required convergence. In the present work, $M = 6$ for all the four atoms studied. This ensures convergence of $\alpha(\omega)$ up to the second decimal place.

5. Results and Discussion

We have calculated $\alpha(\omega)$ for the range $0 \le \omega \le 0.45$ a.u. for Ne, Ar, Kr and Xe in Table 1. Table 2 compares our results for $\alpha(0)$ with those of other workers. While $\alpha(0)$ for Ne and Ar is overestimated, those for the other two atoms are progressively underestimated in our calculations.

Apart from the approximate forms of the various functionals used, there are several likely reasons for these trends. First, the overestimation of $\alpha(0)$ for relatively smaller systems like He and Ne is a feature of local density approximations and is less serious for larger systems. The underestimation of $\alpha(\omega)$ is essentially due to the variational calculation with a trial function chosen on the

Table 1. Calculated values of dynamic (frequency-dependent) dipole polarizabilities of Ne, Ar, Kr and Xe; all values are in atomic units (1 a.u. of polarizability $= 4\pi\varepsilon_0 a_0^3 = 0.164878 \times 10^{-40}\ \mathrm{C}^2\,\mathrm{m}^2\,\mathrm{J}^{-1}$; 1 a.u. of frequency $= \hbar/m_e a_0^2 = 4.1341 \times 10^{16}\ \mathrm{rad\ sec}^{-1}$)

	Ne				Ar		Kr		Xe	
Frequency (ω)	Present work	Ref. [18][a]	Ref. [20]	Ref. [21]	Present work	Ref. [18][a]	Present work	Ref. [18][a]	Present work	Ref. [18][a]
0.00	4.12		2.37	2.67	12.71		14.40		20.66	
0.05	4.15		2.37		12.79		14.48		20.78	
0.10	4.20		2.39	2.69	13.06		14.74		21.21	
0.15	4.30		2.42		13.54		15.21		21.99	
0.20	4.46	2.80	2.46	2.77	14.36	12.51	16.00	19.68	23.33	35.15
0.25	4.69	2.88	2.51		15.76	13.50	17.31	21.87	25.70	44.20
0.30	5.05	2.99	2.58	2.91	18.58	15.22	19.75	27.20	30.77	95.52
0.35	5.64	3.14	2.68		28.10	18.40	26.23		54.82	
0.40	6.77		2.81	3.14						
0.45	10.69		2.98							

[a] Quoted in Ref. [19].

Table 2. Static dipole polarizabilities (a.u.) of Ne, Ar, Kr and Xe (see also Table 1)

	Ne	Ar	Kr	Xe	Ref.[a]
	4.12	12.71	14.40	20.66	Present work
	8.2	14.0	21.1	25.5	22
	13.3	19.4	27.4	31.2	23
	14.5	19.3	24.8	27.7	24
	—	10.53	23.01	24.49	25
	8.17	13.50	21.26	25.51	26
	2.43	9.45	13.49	20.24	27
	2.97	11.67	17.41	28.0	9a
	3.00	11.8	17.7	28.3	9b
	2.90	11.74	17.54	27.8	9c
Expt.	2.70	11.1	16.7	27.4	28a
	2.66	11.1	16.75	27.32	28b

[a] Refs. [22–27] are statistical model calculations

basis of Eqs (36) and (38). Since our calculated ϕ_0 is close to the Hartree–Fock result and does not have a node, this by itself is not a major reason for this underestimation. Because a limited variational calculation will give a lower value for $\alpha(\omega)$, we feel that the main reasons are the following:

(a) *Considerable loss in variational flexibility* in our trial function, due to the use of only one, i.e. an average, $f_\pm(r)$ for the entire atom. Several Hartree–Fock procedures [2, 17] have used separate $f_\pm$ for separate orbitals of the same atom. Here, we solve only 2 instead of $2N$ equations.

(b) *Neglect of continuum contribution.* The trial function chosen by us, viz. Eq. (38), poorly describes the contribution from continuum states, which becomes very significant for larger noble gas atoms, even at zero frequency (see, e.g. Ref. [29]).

It may be argued that one should resort to a numerical solution of Eqs. (29) and (30), instead of a variational one. However, since this involves a separate solution at each frequency, this would be quite tiresome for relatively larger systems. In this regard, we feel that a variational approach holds greater promise. However, here the crux of the problem lies in our ability to make a rather delicate choice of trial functions which will include the right amount of flexibility and the requisite continuum character. We are at present trying to devise such a trial function.

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