

# Atomic Polarizability by Semi-Local and Non-Local Density-Functional Approximations

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## Abstract

The static dipole polarizability of atoms with up to  $Z = 20$  electrons has been determined by density functional theory using prototypical local, semi-local and non-local approximations for the exchange-correlation energy. These successive generations of approximations provide very similar results for  $\alpha_d$ , suggesting that their success in predicting atomization energies of condensed systems is mainly due to a better description of the atomic core region, while the description of valence sp electrons is largely unchanged.

Density functional (DF) theory together with simple local and semilocal approximations for the exchange correlation energy  $E_{xc}$  provides the basis for most of the computational studies of ground state properties of condensed matter [1]. Semi-local approximations adding gradient corrections to the popular local spin density approximation (LSD) for  $E_{xc}$  predict cohesive energies and ground state geometries in fair agreement with experiments, as extensively documented in the literature [2]. The description of atomization energies, in particular, has improved dramatically in going from LSD to gradient corrected schemes, and there are clear indications of a further systematic (although quantitatively not very big) improvement in going from semi-local to fully non local approximations [3].

Despite the obvious success of these recent DF schemes, it is nevertheless meaningful to investigate whether the progress in atomization energies results from a better description of the highest energy occupied states (those directly involved in bonding), of the lowest energy atomic states, or of both core and valence states.

A quantitative analysis of ground state properties other than atomization energies and geometries is required to answer these questions. We discuss here the static dipole polarizability ( $\alpha_d$ ) of atoms, whose role is particularly important since this property is very sensitive to the energy, shape and symmetry of the electron states close to the Fermi energy, and polarization of the electronic cloud is the first elementary step towards the formation of a chemical bond. The sensitivity of  $\alpha_d$  on the electronic configuration is emphasized by the large variations of this quantity along the periodic table, as shown in Fig. 1. Moreover, the static polarizability is related to optical properties by well known sum rules, and, for finite systems,

it provides a measure of the spatial extension of the electron distribution [4].

We focus our attention on two recent approximations for  $E_{xc}$ : (1) the semi-local Perdew–Burke–Ernzerhof approximation (PBE, see Ref. [2]), that is extensively used for applications, and (2) the meta-GGA approximation of Ref. [3], that introduces an explicit dependence of  $E_{xc}$  on the local kinetic energy density of the occupied Kohn–Sham electrons.

Polarizability is one of the first properties discussed in basic physics courses, and has a clear and intuitive definition. It is therefore surprising that dipole polarizability is not accurately known even for atoms. Most experimental determinations of polarizability rely on optical spectroscopy data. This route is very convenient for closed shell atoms, but far more challenging for open shell systems, resulting in large uncertainties in the experimental estimate of  $\alpha_d$ .

Similar difficulties affect computational schemes: the polarizability of closed shell atoms has been determined many times and by accurate methods, while open shell atoms have been far less investigated. The majority of the computational determinations of atomic polarizability relied on quantum chemistry many-body methods, including Hartree–Fock and post Hartree–Fock methods like configuration interactions, coupled clusters, etc. Hartree–Fock underestimates the polarizability of rare gas atoms, and overestimates it for the other elements. Post Hartree–Fock methods converge fairly rapidly to the (in principle exact) solution in the case of closed shell light atoms, while their accuracy degrades rapidly for open shell atoms or for heavy elements. This same trend is observed also for the computation of atomic polarizabilities.

Systematic determinations of polarizability for closed shell atoms using DF methods have been pioneered by Mahan [5], Stott and Zaremba [6], Zangwill and Soven [7]. Numerical results were obtained mainly for closed shell atoms and ions, showing that LSD overestimates the atomic polarizability of rare gases by  $\sim 10\%$ , and underestimates the polarizability of alkali-earth metals. To the best of our knowledge, no systematic determination of  $\alpha_d$  has been reported for the other elements. A non local recipe (self-interaction corrections to LSD, SIC) was implemented in Ref. [8], providing a systematic improvement in the evaluation of  $\alpha_d$ , but, at the same time, manifesting fundamental and computational problems related to the SIC approximation. The application of

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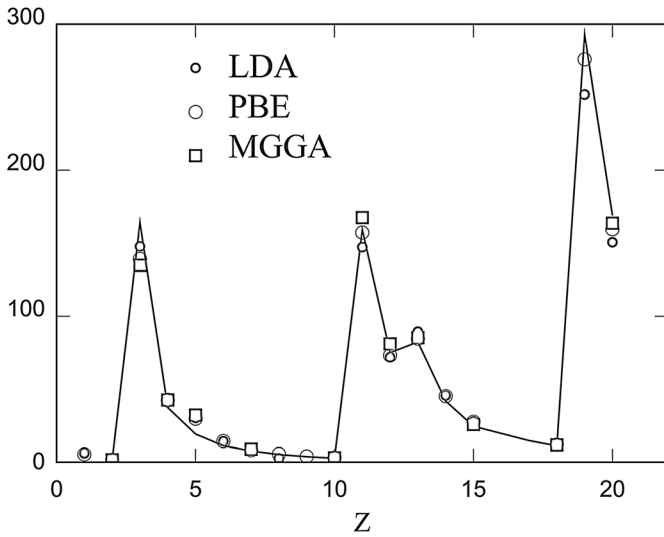


Fig. 1. Comparison of experimental and computed values of the static dipole polarizability for atoms with up to  $Z = 20$ .

more recent exchange-correlation approximations to the investigation of atomic polarizability has been very limited. Two representative studies are reported in Ref. [9] and Ref. [10], both based on the exchange-correlation potential of Ref. [11]. The lack of explicit computations is probably partly due to the difficulty of implementing efficient computational schemes suitable for the most promising but also most complex approximations, sometimes relying on implicit exchange-correlation functionals, or on orbital dependent potentials.

The most accurate determinations of atomic polarizability by density functional methods have been performed using the Sternheimer approach [12], representing Kohn–Sham (KS) orbitals and their derivatives with respect to the external field on a radial logarithmic mesh centered on the atomic nucleus [5–6]. The resulting equations and their computational implementation are simple and elegant for closed shell spherical atoms. However, they become cumbersome for open shell atoms, and the representation of orbitals as radial functions times a single spherical harmonic implies that the unperturbed density is spherically symmetric. The method can be extended to non-spherical atoms, but its simplicity and computational efficiency are, to a large extent, lost.

An additional difficulty is represented by the fact that the Sternheimer approach requires the analytic determination of the second functional derivative of the exchange-correlation energy. This task is trivial for LDA, but it becomes increasingly difficult by including corrections of increasing sophistication. This problem becomes even more relevant in applying the Sternheimer approach to higher order response functions. The difficulty is not limited to the algebraic determination of the functional derivatives, but often includes numerical problems due to singularities in the exchange-correlation potential and of its functional derivatives.

To overcome these difficulties, we implemented a program for the numerical minimization of the Kohn–Sham functional not relying on the analytic computation of any functional derivative of the exchange-correlation energy with respect to the density. The static dipole polarizability is computed from the dipole moment

developed upon applying an external field of the appropriate symmetry to the atom. The method is easily generalized to deal with perturbation of different symmetry (quadrupole, octupole, etc.) or to perturbations coupled to the spin density instead than to the electron density. Moreover, the computation of non-linear response coefficients could be performed by repeated computations of the induced moment as a function of the applied field.

The method relies on the direct minimization of the Kohn–Sham functional for KS orbitals represented on a logarithmic grid for the radial coordinate, and on a discrete mesh for the  $(\theta, \varphi)$  angular variables. The selection of the angular grid is performed in order to optimize the integration over the angular coordinates, as discussed in Ref. [13]. The computations presented below have been performed for grids of 2001 points for the radial coordinate, and 32 directions in the  $[0 \leq \theta \leq \pi] \times [0 \leq \varphi \leq 2\pi]$  domain. The angular mesh, together with appropriate weights, allows the exact numerical integration of all spherical harmonics  $Y_{lm}$  with up to  $l = 9$  (see Ref. [14]). The combination of radial and of an angular grid allows to describe non spherical density distributions, either due to the perturbation or to a broken symmetry ground state.

The core of the minimization algorithm is an efficient determination of the KS functional for any given set of  $N$  occupied orbitals

$$\begin{aligned}
 E[\{\Psi_i\}, i = 1, N] \\
 = \sum_{i=1}^N \int \Psi_i^*(\mathbf{r}) \left\{ -\frac{1}{2} \nabla^2 - \frac{Z}{r} + \frac{1}{2} V_H(\mathbf{r}) \right\} \Psi_i(\mathbf{r}) d\mathbf{r} \\
 + E_{xc}[\rho]
 \end{aligned} \quad (1)$$

(atomic units are used throughout the paper). In the equation above,  $Z$  is the nuclear charge of the atom,  $E_{xc}[\rho]$  is the exchange correlation energy, and  $V_H(\mathbf{r})$  is the Hartree potential

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

The Hartree potential and the associated energy are computed by projecting  $\rho(\mathbf{r})$  on spherical harmonics, and computing the separate  $(l, m)$  components of  $V_H$  by radial integration. Also the Laplacian is computed by projecting the orbitals on their spherical harmonics components, and combining numerical derivatives with respect to the radial coordinate with analytic derivatives with respect to angular coordinates. Integrals are evaluated using standard algorithms for the radial coordinate, and a two-dimensional Gauss formula for the angular coordinates.

The starting point for the numerical minimization of the KS functional is provided by the unperturbed orbitals for the occupied electron states obtained from a standard program for spherical atoms. These orbitals are iteratively refined by the repeated minimization of the energy on a subspace spanned by a small number of occupied orbitals and of Slater functions  $\{s_i(\mathbf{r}), i = 1, k\}$

$$s_i(\mathbf{r}) = A r^n \exp(-\zeta r) Y_{lm}(\theta, \varphi) \quad (3)$$

Table I. Comparison of measured and computed linear dipole polarizability of atoms (in  $a_0^3$ ). Reference values are from Ref. [16]. The error in percent is given in parentheses.

El.	$\alpha_{\text{ref}}$	$\alpha_{\text{LDA}}$	$\alpha_{\text{PBE}}$	$\alpha_{\text{MGGA}}$	El.	$\alpha_{\text{ref}}$	$\alpha_{\text{LDA}}$	$\alpha_{\text{PBE}}$	$\alpha_{\text{MGGA}}$	El.	$\alpha_{\text{ref}}$	$\alpha_{\text{LDA}}$	$\alpha_{\text{PBE}}$	$\alpha_{\text{MGGA}}$
H	4.5	6.01 (33.6)	5.38 (19.6)	4.89 (8.7)	N	7.63	8.17 (7.1)	8.11 (6.4)	8.74 (14.5)	Al	82.32	96.9 (17.7)	84.6 (2.7)	91.8 (11.5)
He	1.384	1.661 (20.0)	1.583 (14.4)	1.610 (16.3)	O	5.2	5.45 (4.9)	5.52 (6.3)		P	24.52	27.9 (13.9)	27.6 (12.5)	27.5 (12.0)
Li	164.0	147.7 (-9.9)	139.1 (-15.2)	134.8 (-17.8)	Ne	2.663	3.04 (14.1)	3.05 (14.4)	3.03 (13.6)	Ar	11.08	12.0 (8.6)	11.91 (7.6)	11.74 (5.9)
Be	37.298	43.8 (17.6)	42.2 (13.0)	42.5 (14.0)	Na	159.2	147.2 (-7.6)	157.3 (-1.2)	171.0 (7.4)	K	292.8	251.8 (-14.0)	275.9 (-5.8)	308.9 (5.4)
B	26.84	30.1 (12.2)	29.7 (10.7)	34.2 (27.3)	Mg	75.0	71.9 (-4.1)	73.1 (-2.58)	81.0 (8.0)	Ca	169.0	150.6 (-10.9)	159.4 (-5.7)	163.5 (-3.2)

with  $n \geq l$ , and  $k$  usually taken up to 10. The integer  $n$  and the inverse length  $\zeta$  are chosen at random within the range:  $l \leq n \leq 5$ ,  $0.1 \leq \zeta \leq 2Z$ . The subset of occupied orbitals to be optimized at each step is selected on the basis of symmetry considerations. In other words, assuming for simplicity that we refine occupied orbitals one at a time, the updated orbital  $\Psi_i^{\text{new}}(\mathbf{r})$  is expressed as a linear combination

$$\Psi_i^{\text{new}}(\mathbf{r}) = A\Psi_i^{\text{old}}(\mathbf{r}) + \sum_{j=1}^k B_j s_j(\mathbf{r}) \quad (4)$$

The coefficients  $A$  and  $\{B_j\}$  are selected in order to minimize the KS functional, and the search for the minimum is guided by approximate first and second derivatives of the energy with respect to these linear coefficients computed by finite differences. The scheme

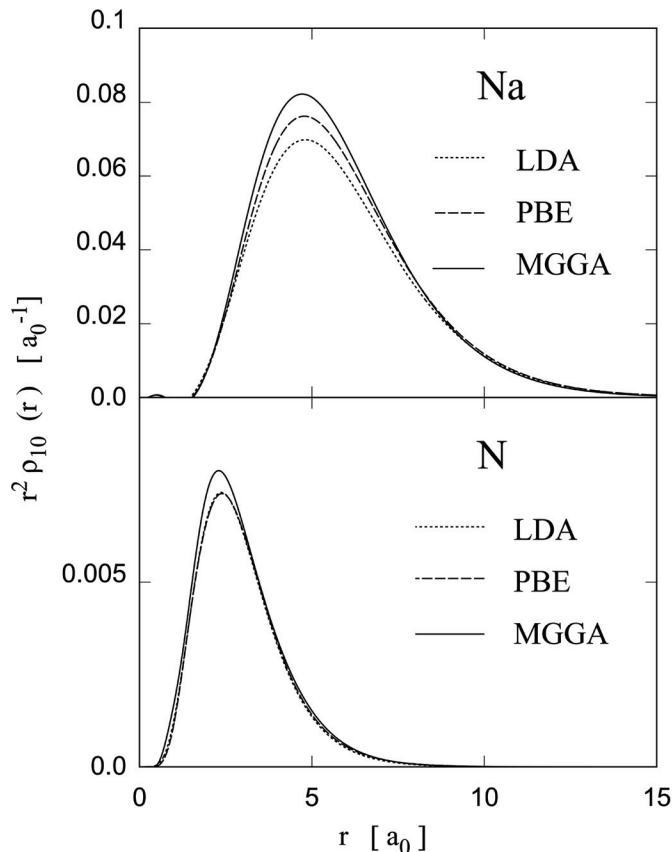


Fig. 2. Radial dependence of the induced dipole electron density for two open shell spherical atoms.

does not require the computation of any functional derivative of the exchange correlation energy. Since the computation of the energy is relatively inexpensive even with complex exchange correlation approximations, the required derivatives are evaluated at a modest computational cost.

The basic optimization sequence described above is repeated many times with different random choices of  $n$  and  $\zeta$ . This procedure provides quickly a fairly accurate estimate of polarizability. Moreover, the implementation effort is very limited even for complex exchange-correlation approximations, since only the energy has to be evaluated. Achieving high accuracy, however, sometimes requires a sizable effort. This might not be a major problem, because the accuracy of the experimental data is often limited to a few percent, and this level of accuracy is reached by the computation within a fairly short iteration time.

In many respects, our algorithm is a simplified version of the method described in Ref. [15].

Polarizability is determined by the computed induced dipole moment. An alternative route is provided by the field dependence of the total energy. Both routes have advantages and disadvantages: the total energy is a variational quantity, whose determination is in principle more accurate than that of the dipole moment. However, at low applied field the energy change is only a very low fraction of the total energy, whose precise determination is hampered by numerical round-off. On the other hand, the dipole moment of the unperturbed ground state is zero for the atoms considered here, and the determination of the induced dipole is not affected by any uncertainty on the zero field value. In our experience, the estimate based on the induced dipole converges more quickly to the final value.

The results obtained by LSD, PBE and MGGA approximations for atoms with  $Z \leq 20$  are shown in Table I. In the case of non-spherical atoms, the static dipole response is characterized by two distinct values, corresponding to the  $m = 0$  and  $m = \pm 1$  configurations. In Table I we report the largest of these two values, corresponding to the absolute minimum of the atomic energy in the presence of a dipole external field of non-vanishing amplitude. The computed values are compared to experimental values when available, and to high level quantum chemistry computations for the other atoms.

Our LSD results for rare gas atoms and for alkali-earth metals agree well with the data from previous computa-

tions of comparable accuracy [8]. In the case of open shell atoms (for which no systematic investigation has been published) we observe that our LSD estimate for  $\alpha_d$  underestimates the experimental values in the case of alkali metals, and overestimates the values predicted by high level correlated quantum chemistry computations for the other elements.

For PBE and MGGA, our results provide the first systematic analysis of atomic polarizability. It is apparent from the data reported in Table I that semi-local (PBE) and non-local (MGGA) approximations provide  $\alpha_d$  values very close to those given by LSD. Besides being quantitatively small, the variations observed in going from LSD to the more recent recipes do not represent a systematic improvement in comparison with the reference data reported in Table I. This disappointing observation is confirmed by the analysis of the induced charge density (see Fig. 2) showing that the static dipole response of atoms computed by PBE and MGGA is everywhere very close to that given by LSD.

In conclusion, we have implemented a simple scheme to estimate the static dipole polarizability of atoms using only repeated evaluations of the Kohn–Sham functional. The scheme is particularly convenient for semi-local and non-local DF approximations relying on complex or implicit definition of  $E_{xc}$  as a function of the electron density and KS orbitals.

The static polarizability is computed from the dipole moment induced by an external electric field of the appropriate symmetry. Kohn–Sham orbitals are represented on a logarithmic mesh for the radial coordinate, and on a discrete mesh in the  $(\theta, \varphi)$  variables, corresponding to 32 distinct directions originating from the atomic nucleus. The scheme allows the atom to acquire a non-spherical density distribution, either because of the perturbing field and/or because of a broken symmetry ground state.

The computational scheme has been tested by comparison of our LSD data for rare gases and alkali-earth metals with the results of previous computations.

Comparison of the computational results with reference data provided by experiments or by correlated quantum chemistry computations shows that, in most cases, LSD over-estimates the atomic polarizability, but errors of the opposite sign are observed for alkali and alkali-earth metals.

Prototypical semi-local and non-local approximations provide values of  $\alpha_d$  very similar to those of LSD. The analysis of the radial dependence of the induced charge confirms that neither PBE nor MGGA represent a

significant or systematic improvement on LSD for what concerns the response of valence electrons of sp symmetry.

These observations suggest that (as already pointed out in the literature) the significant improvement in the atomization energies achieved by PBE and MGGA is due mainly to a better estimation of atomic energies, that depends crucially on the description of core states. The description of sp valence electrons, instead, is largely unchanged. Although LSD approximates fairly well the exchange correlation energy of these states, errors are obviously still present, and manifest themselves in the observed deviations of  $\alpha_d$ .

Besides these disappointing results, there is also a positive side. The systematic trends displayed by the deviation of the DF results from reference data might provide a sensitive diagnostic tool to identify specific problems of old and new approximations in describing different atomic configurations. A fully quantitative assessment of the quality of  $E_{xc}$  approximations is unfortunately hampered by the fact that the available experimental data are few, scattered and not always very accurate. Our study provides a motivation for a systematic experimental investigation of atomic polarizabilities.

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