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Polarizability of closed shell atoms and ions in LDA

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Abstract. — The dipole polarizability of rare gas atoms, positive alkali ions and negative halogen ions has been calculated in the local density approximation (LDA) to the density functional theory, corrected for the self-interaction error. The results for the rare gas atoms and the alkali ions are within a few percent of the values obtained by ab initio configuration interaction or many-body perturbation theory (CI) and by experiment. For the negative ions the agreement with coupled Hartree-Fock calculations is also within a few percent but the correlation reduces the LDA values by about 5 % while the CI values exceed the CHF values by 40-60 % for F⁻ and by 12-18 % for Cl⁻.

1. Introduction.

The local density approximation (LDA) to the density functional theory was first used for the calculation of the electronic polarizability of free atoms and ions by Stott and Zaremba [1]. They calculated within the linear response theory the electron density perturbed by an external electric field and used their results to compute the polarizability of rare gas atoms and positive alkali ions. Similar calculations were done at about the same time by Zangwill and Soven [2] for the rare gas atoms.

A different approach was followed by Mahan [3], who solved numerically a self-consistent equation for the first order perturbed wave function in an external electric field, that he called « modified Sternheimer equation ». Mahan applied his method to many positive ions and extended it also to negative ions, adding in the last case a correction for the self-interaction error in LDA [4]. In fact, it is well known that LDA does not give stable solutions for some negative ions, like F⁻, Cl⁻, O⁻ etc. This is due to the fact that the local approximation to the exchange and correlation energy compensates only partially the self-interaction present in the form used for the Coulomb interaction between the electrons, contrary to what happens in the Hartree-Fock approximation.

In this paper we present the results for the electronic polarizability of rare gas atoms, positive alkali and negative halogen ions, treated systematically in the LDA corrected for the self-interaction error in the form proposed in a preceding paper [5] and in the form proposed by Perdew and Zunger [6]. Following Mahan we solve a « modified Sternheimer equation » as will be illustrated in the second section of the paper.

In the third section of the paper we will compare the results obtained using only the exchange part of the exchange and correlation potential with the polarizabilities calculated in the coupled Hartree-Fock approximation (CHF) [7].

Finally in the fourth section we will discuss the effect due to correlation. The results will be compared with those obtained by configuration interaction or by many body perturbation techniques (CI) and with the experimental values.
2. — The Kohn-Sham equation for an atom of atomic number \(Z\) and with \(N\) electrons, in an external uniform electric field \(E\) in the \(z\) direction is (in atomic units)

\[
\left[ -\frac{1}{2} \nabla^2 - \frac{Z}{r} + V_c + V_{xc} \right] \psi_{i\sigma}(r) = \epsilon_i \psi_{i\sigma}(r) = \epsilon_i \psi_{i\sigma}(r) \quad (2.1)
\]

where \(i\) stands for all the quantum numbers and \(\sigma\) is the spin index. \(V_c\) is the Coulomb potential \(\int \frac{n(r')}{|r-r'|} \, dr'\), and \(V_{xc}\) is the exchange and correlation potential derived from the exchange and correlation term \(E_{xc}[n]\) in the energy functional by means of a functional derivative which in LDA reduces to the simple derivative

\[
V_{xc} = \frac{\partial E_{xc}}{\partial n_{\sigma}}. \quad (2.2)
\]

The electron density \(n(r)\) is defined in terms of \(\psi_{i\sigma}\) by

\[
n(r) = \sum_{\sigma} n_{\sigma}(r) = \sum_{i\sigma} |\psi_{i\sigma}(r)|^2 \quad (2.3)
\]

where the last sum is extended over the first \(N\) levels of the atom.

Starting from the solution \(\psi_{i\sigma}^0\) for an external field \(E\) equal to zero, one can write

\[
\psi_{i\sigma}(r) = \psi_{i\sigma}^0(r) + E\eta_{i\sigma}(r)
\]

with

\[
(\psi_{i\sigma}^0, \eta_{i\sigma}) = 0. \quad (2.4)
\]

To first order in \(E\), putting

\[
n(r) = \sum_{i\sigma} |\psi_{i\sigma}^0|^2 + E\eta_{i\sigma}^2
\]

\[
= \sum_{i\sigma} |\psi_{i\sigma}^0|^2 + 2E \text{Re} \sum_{i\sigma} \psi_{i\sigma}^0 \eta_{i\sigma}^* = n^0(r) + E n^1(r) \quad (2.5)
\]

one has to solve for \(\eta_{i\sigma}\) the following equation

\[
\left[ -\frac{1}{2} \Delta^2 - \frac{Z}{r} + V_c^0 + V_{xc}^0 - \epsilon_i^0 \right] \eta_{i\sigma}(r) = \left( -\cos \theta - V_{SCF}^0 + \epsilon_i^0 \right) \psi_{i\sigma}^0(r) \quad (2.6)
\]

where \(\psi_{i\sigma}^0\) is a solution of

\[
\left[ -\frac{1}{2} \Delta^2 - \frac{Z}{r} + V_c^0 + V_{xc}^0 - \epsilon_i^0 \right] \psi_{i\sigma}^0(r) = 0 \quad (2.7)
\]

and

\[
V_{SCF}^\sigma = \int \frac{n^1(r')}{|r-r'|} \, dr' + \frac{\partial V_{xc}^\sigma}{\partial n^0} n^1(r). \quad (2.8)
\]

Equations (2.6) and (2.7) are a set of equations which must be solved self-consistently and represent the analogue for the Kohn-Sham equation of the coupled Hartree-Fock approximation of Dalgarno [7]. The dipole polarizability is then given by

\[
\alpha = \int n^1(r) \, r \cos \theta \, dr. \quad (2.9)
\]

In LDA the exchange part of the exchange and correlation potential is assumed to be

\[
V_{xc}^\sigma = -\left[ \frac{6}{\pi^2} n_\sigma(r) \right]^{1/3} \quad (2.10)
\]

as for a uniform gas of electrons of spin \(\sigma\) with density \(n_\sigma\). As we said in the introduction, this approximation introduces in the Kohn-Sham equation a self-interaction error that we try to correct using two procedures. In the first, due to Böbel and Cortona [5], we eliminate the self-interaction writing the difference \(n(r) - \left| \psi_{i\sigma}(r) \right|^2\) in place of \(n(r)\) in the Coulomb potential and multiplying the exchange part by a factor depending on the number \(N_\sigma\) of electrons with spin \(\sigma\) in the system. Reference [5] considered a factor \(\gamma(N_\sigma)\) as well as a factor \(\delta(N_\sigma)\). The factor \(\gamma(N_\sigma)\) is zero for \(N_\sigma = 1\) and reaches the value one for \(N_\sigma\) very large, while \(\delta(N_\sigma)\) tends to one for \(N_\sigma\) very large, but for \(N_\sigma = 1\) has the value \(\delta(1) = 0.0833\), indicating an overestimate of the exchange in systems with few electrons. In the second procedure, introduced in LDA by Perdew and Zunger [6], the exchange term is corrected by subtracting the contribution due to the orbital considered:

\[
V_{xc}^\sigma = -\left( \frac{6}{\pi^2} \right)^{1/3} \left[ n_{\sigma}^{1/3}(r) - \left| \psi_{i\sigma}(r) \right|^{2/3} \right]. \quad (2.11)
\]

The polarizabilities calculated with these corrections to the Coulomb and to the exchange potentials, without any contribution from the correlation potential, are compared in the next section with the results obtained by the coupled Hartree-Fock approximation.

3. — The system of equations (2.6) and (2.7) can be reduced to a radial form by developing the angular dependence of the various terms in spherical harmonics [3, 7].

Putting

\[
\psi_{i\sigma}(r) = \psi_{i\sigma}^0(r) = \frac{P_0(r; n, l)}{r} Y_{lm}(\theta, \varphi) \quad (3.1)
\]

with \(P_0(r; n, l)\) real, from equation (2.7) one obtains

\[
\frac{1}{2} \frac{d^2}{dr^2} P_0(r; n, l) - \left[ \frac{l(l+1)}{2r^2} - \frac{Z}{r} + V_c^0 + V_{xc}^0 - \epsilon_i^0 \right] \times P_0(r; n, l) = 0. \quad (3.2)
\]

The density becomes

\[
n^0(r) = \frac{1}{4 \pi r^2} \sum_m 2(2l+1) P_0^2(r; n, l) \quad (3.3)
\]
and

\[ V^0_c = V^0_c (r; n, l) = \int \frac{n^0 (r') - |\psi^0_{nlm}|^2}{|r - r'|} \, dr' \]  \hspace{1cm} (3.4)

\[ = \int \frac{n^0 (r') \frac{1}{4 \pi r'^2} P^2 \frac{P_1^0 (r'; n, l)}{|r - r'|} \, dr'} {dr'} \]

where we have eliminated the angular dependence by approximating \(|\psi^0_{nlm}|^2\) by its mean value

\[ \left| \psi^0_{nlm} \right|^2 = \frac{1}{2l + 1} \sum_m \left| \psi^0_{nlm} \right|^2. \]  \hspace{1cm} (3.5)

The reduction of equation (2.6) is a little bit more elaborate, but limiting oneself to the calculation of the dipolar polarizability it is necessary to know only the \(Y^1_0\) component of \(n^1 (r)\). Putting

\[ n^1 (r) = \sum_{\lambda} n^1 (r; \lambda) \ Y^0_{\lambda} (\theta, \varphi) \]  \hspace{1cm} (3.6)

and

\[ \delta Y^0_{\lambda} = \int \frac{n^1 (r') - \frac{1}{r} \nabla \cdot \nabla \psi^0_{nlm}}{|r - r'|} \, dr' \]

where only the \(m = 0\) components enter owing to the axial symmetry, one obtains for \(n^1 (r; 1)\) the following expression

\[ n^1 (r; 1) = \frac{1}{\pi r^2} \sum_{\lambda} \left[ (l + 1) P^0_0 (r; n, l) P_1 (r; n, l + 1) + \frac{1}{l} P^0_0 (r; n, l) P_1 (r; n, l - 1) \right] \]  \hspace{1cm} (3.8)

where \(P_1 (r; n, j)\) is a solution of the radial equation

\[ \frac{1}{2} \frac{d^2}{dr^2} P_1 (r; n, j) = \left[ \frac{\lambda (j + 1)}{2 r^2} - Z + V^0_c + V^0_{sc} - \epsilon^0_{nl} \right] P_1 (r; n, j) = \]

\[ = \left[ \frac{4 \pi}{3} r + V^0_{SCF} (r; 1) \right] P_0 (r; n, l) \]  \hspace{1cm} (3.9)

\[ j = l \pm 1. \]

For the polarizability one obtains the following formula

\[ \alpha = \sqrt{\frac{4 \pi}{3}} \int_0^\infty n^1 (r; 1) \ r^3 \, dr. \]  \hspace{1cm} (3.10)

The system of equations (3.2)-(3.10) has been solved numerically adapting a program due to J. P. Desclaux [8].

In table I the results obtained with the exchange potential only are compared with the results obtained in the coupled Hartree-Fock approximation (CHF).

In [5] it was already noted that in systems with several electrons \(^{(1)}\) the \(\delta\) factor gives results in better agreement with Hartree-Fock than the \(\gamma\) factor, and this is confirmed here. In table I we report only the values calculated with the \(\delta\) factor.

The table also includes the values of Stott and Zaremba, calculated with exchange only but without self interaction correction. It is evident that the introduction of this correction reduces the discrepancy with the CHF results. The values calculated with the Böbel-Cortona correction with the \(\delta\) factor are in good agreement with the CHF values: the negative sign of the deviation from the CHF value for Ne and Na\(^+\) is due to the overestimate of the exchange contribution. For the results obtained with the Perdew and Zunger correction, the discrepancy is particularly strong for the negative ions (of the order of 20\%), while it is smaller (within 10\%) for the positive ions and the neutral atoms, all the values being greater than the CHF ones.

4. — In LDA when the correlation is added, the exchange and correlation potential \(V^0_{sc}\) becomes more attractive and the polarizabilities decrease. As already noted by Stott and Zaremba [1] this effect is contrary to what one obtains in CI calculations. In fact one can schematically consider two types of effects due to correlation in an atomic system: an angular effect in which electrons tend to stay on opposite sides with respect to the nucleus, and an in-out effect in which electrons tend to occupy orbitals with different mean radius. In the first case the polarizability is lowered (this effect is prevalent in open shell systems) while in

\(^{(1)}\) For He, Li\(^+\) and H\(^-\) the values of \(\alpha\) calculated in LDA with the self-interaction correction coincide with the CHF values.
Table I. — *Electronic polarizabilities in LDA (without correlation) and in CHF (in A$^3$).*

<table>
<thead>
<tr>
<th></th>
<th>BC (*)</th>
<th>PZ (+)</th>
<th>SZ (*)</th>
<th>CHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.342</td>
<td>0.368</td>
<td>0.483</td>
<td>0.351</td>
</tr>
<tr>
<td>Ar</td>
<td>1.64</td>
<td>1.72</td>
<td>1.90</td>
<td>1.59</td>
</tr>
<tr>
<td>Kr</td>
<td>2.47</td>
<td>2.65</td>
<td>2.84</td>
<td>2.44</td>
</tr>
<tr>
<td>Xe</td>
<td>3.99</td>
<td>4.33</td>
<td>4.55</td>
<td>4.01</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.134</td>
<td>0.143</td>
<td>(+ 2%)</td>
<td>0.140</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.822</td>
<td>0.844</td>
<td>(+ 5%)</td>
<td>0.800</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>1.37</td>
<td>1.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>2.38</td>
<td>2.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>1.63</td>
<td>1.84</td>
<td>(+ 16%)</td>
<td>1.58</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>4.90</td>
<td>5.62</td>
<td>(+ 21%)</td>
<td>4.66</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>6.25</td>
<td>7.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$^-$</td>
<td>8.88</td>
<td>11.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*(In parenthesis we report the deviations from the CHF values.)*

| (*) | Bobel-Cortona correction with factor $\delta$.
| (+) | Perdew-Zunger correction.


Table II. — *Electronic polarizabilities in LDA (with correlation) and in CI vs. experimental values (in A$^3$).*

<table>
<thead>
<tr>
<th></th>
<th>BC (*)</th>
<th>PZ (+)</th>
<th>SZ (*)</th>
<th>CI</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.339</td>
<td>0.364</td>
<td>0.444</td>
<td>0.396</td>
<td>0.395</td>
</tr>
<tr>
<td>Ar</td>
<td>1.62</td>
<td>1.69</td>
<td>1.75</td>
<td>1.64</td>
<td>1.64</td>
</tr>
<tr>
<td>Kr</td>
<td>2.43</td>
<td>2.60</td>
<td>2.62</td>
<td>2.48</td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>3.91</td>
<td>4.24</td>
<td>4.19</td>
<td>4.04</td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.134</td>
<td>0.143</td>
<td>(+ 3%)</td>
<td>0.159</td>
<td>0.149</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.817</td>
<td>0.839</td>
<td>0.845</td>
<td>0.796</td>
<td></td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>1.36</td>
<td>1.41</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>2.36</td>
<td>2.46</td>
<td>2.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>1.56</td>
<td>1.75</td>
<td>2.24</td>
<td>2.51</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>4.69</td>
<td>5.33</td>
<td>5.22</td>
<td>5.48</td>
<td></td>
</tr>
<tr>
<td>Br$^-$</td>
<td>5.98</td>
<td>7.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$^-$</td>
<td>8.49</td>
<td>10.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*(In parenthesis we report the deviations from the experimental values.)*

| (*) | Bobel-Cortona correction with factor $\delta$.
| (+) | Perdew-Zunger correction.

the second case the polarizability is increased (as in the case of closed shell systems) [9].

In this calculation we have simply used the interpolation formula of Gunnarson and Lundqvist [10] with the contribution of one orbital subtracted to keep account of the self-interaction error in the correlation energy. The LDA results are reported in table II together with those of CI calculations and with the experimental values. The values calculated by Stott and Zaremba are also reported. By a comparison with the LDA results of table I one sees that the effect of correlation, in the form we used, is to reduce by 1±2 % the values for the rare gas atoms, while the values for the positive alkali ions remain practically unchanged. On the contrary, the CI values are greater than the CHF values by 13 % for Ne, by 3 % for Ar and by 6 % for Na+, while for K+ the value tends to decrease [11].

For the negative halogen ions the effect of correlation is significantly greater. The LDA values decrease by about 5 % while the CI values for F− and Cl− are greater than the corresponding CHF values by about 50 % and by up to 20 %, respectively.

In spite of this, a comparison with the experimental values for the rare gas atoms shows an overall improvement of the self-interaction corrected LDA values with respect to the results of Stott and Zaremba, and for Ar, Kr and Xe the agreement with experiment is actually within a few percent. The larger discrepancy for the BC values for Ne (and Na+) is due to the use of the δ factor that overestimates the exchange contribution for atoms with a small number of electrons (as already noted in § 3), and to the relatively large positive contribution of the correlation, as is apparent from the CI calculations.

5. Conclusions.

For the rare gas atoms and the positive alkali ions (excluding Ne and Na+), LDA calculations with the BC correction give good results for the dipole polarizabilities (within a few percent from experiment and CI calculations which give practically identical results). The agreement is not much affected by the inclusion of correlation, although this reduces the LDA polarizabilities, contrary to the results of CI calculations for these systems.

For the negative halogen ions the results for the polarizability are also good when one compares BC-corrected LDA values without correlation with CHF values. However, the correlation reduces the LDA values more than for the previous atomic systems, while in CI calculations its effect is to sizeably increase the values, in one case (F−) by as much as 50 % with respect to the CHF result.

Acknowledgments.

It is a pleasure to acknowledge useful discussions with Prof. J. Friedel and Dr. P. Cortona.

References

[4] MAHAN, G. D., J. Chem. Phys. 76 (1982) 493. The author does not report his results for the negative halogen ions because the values he found were « too large ». His best values without the self-interaction correction for Ne, Ar, Kr and for Na+, K+, Rb+ practically coincide with the values by Stott and Zaremba [1].
[8] We are indebted to Dr. C. S. Sommers of the University of Paris-Sud for giving us a copy of this program.