Static Dipole Polarizabilities through Density Functional Methods

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Various density functionals have been tested in calculating atomic and molecular dipole polarizabilities. For atoms, it has been found that the results are not competitive with more sophisticated ab initio methods. Exchange and correlation effects have been analyzed separately to show that the main cause of errors lies in the exchange functional models. Strong numerical evidence is given to support the idea that a right asymptotic behavior of the exchange potential is essential to obtain reliable values for the dipole polarizabilities. In this sense, the hybrid method proposed by Becke (*J. Chem. Phys.* **1993**, *98*, 5648) and the phenomenological exchange potential proposed by van Leeuwen and Baerends (*Phys. Rev.* **1994**, *A49*, 2421), performed much better. For molecules, the comparison is more difficult because of the scarcity of reliable experimental values as well as ab initio calculations including correlation effects. The results have however shown that the bonding effects predominate over the asymptotic behavior of the potential.

Introduction

The static electric dipole polarizability is a measure of the distortion of the electronic density under the effect of an external static electric field. Since the majority of atomic interactions occurring in nature are governed by electric forces, it is no surprise that the dipole polarizability is an important quantity in a variety of phenomena,[1,2] especially in studies of intermolecular forces,[2] electron scattering,[3] and finally clusters.[4]

For light atoms the static electric dipole polarizabilities are known with reasonable accuracy,[5] and almost all traditional methods of quantum chemistry and atomic physics have been applied in calculating them. Without being exhaustive, we mention the works of Werner and Meyer,[6] Bishop et al. (see for instance ref 7), Sadlej and collaborators (see for instance ref 8), Maroulis and Thakkar (see for instance ref 9), and the book written by Mahan and Subbaswamy.[10] Those works show, besides good final numbers, that the incorporation of the electronic correlation is an important and difficult task and that the basis set must be very carefully chosen. For molecules the situation is more complicated. Large CI calculations are necessary in order to obtain a well-balanced description of the perturbed and unperturbed system. The comparison with experimental values is complicated because the measurements are not at zero temperature, and therefore, they include vibrational corrections which are by no means negligible.

On the other hand, density functional methods are finally being widely used in many fields of atomic, molecular physics, and quantum chemistry. Therefore, it is important to study and understand its possibilities and weaknesses. Very recently, it has been stated that density functional methods are not competitive in accuracy with more sophisticated methods in calculating molecular polarizabilities.[11] The numerical results are in general too high in comparison with the most accurate known values. This is an important point because failures in calculating dipole polarizabilities imply unreliable results in the study of intermolecular forces, e.g., van der Waals molecules and hydrogen bonds.

The aim of this paper is to study in more detail the behavior of various density functionals in calculating atomic and molecular static electric dipole polarizabilities. We choose to study the first-row atoms Li−Ne because the principal effects in the polarizability are well understood and there are reliable values for comparison. Special mention deserves the already classical work by Werner and Meyer,[6] which represents until today the most complete and accurate calculation of the dipole polarizability for the ground state of the atoms Li through Ne. For molecules, we choose to study three diatomic molecules, N_2, O_2, and F_2, for which the most important effects on the calculated polarizabilities are well understand and there are reliable values for comparison.[12]

In atoms, we study the effects of exchange and correlation separately to show first that the main cause of error lies in the exchange functional and, second, that the errors are largely due to the incorrect long-range asymptotic behavior of the exchange potential. In molecules, the exchange-correlation functionals are tested, confirming that a correct asymptotic behavior of the potential is necessary to obtain reliable values. However, for molecules the binding effects are obviously the most important ones.

In the comparison of density functional calculations with ab initio ones, care must be taken of the different definitions for the exchange and correlation energies. Whereas in the ab initio definition they are only effects of the electron−electron repulsion in density functional theory, they have a kinetic energy contribution. However, the numerical differences are in general negligible in systems where one Hartree−Fock determinant is a good zero-order starting point. In fact, some of the exchange-correlation functionals currently used are numerically fitted to ab initio exchange and correlation energies. Therefore, in this paper, especially in the discussion of the results, no reference will be made to the conceptual differences.

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Methods

Most of the density functional calculations based on the Kohn–Sham equations differ basically in the exchange and correlation functionals they used. Besides the Kohn–Sham equations, one can choose the Hartree–Fock ones as the starting point and add only the correlation energy as a functional of the density. This type of calculation is called the mixed method. One of the possibilities is to perform a Hartree-Fock (HF) calculation and then with the HF density to compute the correlation energy using some correlation functional. In this way, one has for sure the exact HF exchange, but the obtained density has no corrections for the correlation effects. Since for the polarizabilities the density distortions are of vital importance, we proceed in another way. The correlation potential is taken into the self-consistent equations. Hence, the density is corrected for the correlation effects. However, the exchange now is calculated with a set of orbitals which are not exactly the HF orbitals. In this work the orbitals (Kohn–Sham orbitals) have been calculated using the exchange functional of Becke,[13] B88. It consists in a phenomenological gradient correction to the homogeneous electron gas exchange functional and contains one empirical parameter fitted to the Hartree–Fock exchange energy of He atom. The difference between the exact exchange calculated using the HF orbitals and the one calculated using the Kohn–Sham orbitals should be negligible. In fact, for the total energy of the neon atom we did not find any difference in the first 10 digits.

The correlation energy has been calculated using two different functionals. The one proposed by Lee, Yang, and Parr[14] in the version given by Miehlich, Savin, Stoll, and Preuss[15] which is the density functional variant of the Colle–Salvetti[16] correlation energy model. It will be denoted LYP. The other one is the correlation energy functional proposed by Perdew and Wang,[17] PW91. This is the only one with no empirical parameter.

The three mentioned functionals have proven to be very successful in a broad range of applications, and the literature on its successes is wide (see ref 18 for applications). On the contrary, well-documented weaknesses are until now rather scarce (see refs 11 and 19).

In this work we have used the exchange and correlation functionals separately in order to get insight whether the possible errors are in the exchange or correlation part, and also in combination, in order to cover both exchange and correlation effects. All functional combinations are possible. To be precise, we have done the following type of calculations: HF means no density functional and B88 only an exchange functional without taking care of the correlation effects. Hence, the results should be nearly identical to the HF ones. LYP means the exact exchange calculated with the Kohn–Sham orbitals plus the LYP functional for correlation and PW91 the same but with the Perdew and Wang correlation energy functional. BLYP and BPW91 represent both exchange and correlation energy functionals with an obvious meaning of the notation. We have also used the new hybrid method proposed by Becke, B3PW91.[20] The method has some parameters that were chosen as the best fit of a great sample of properties of molecular and atomic systems. In an attempt to study the effect of the parameters in the calculation of the polarizabilities, we tried to fit the set of parameters of the method B3PW91 in order to obtain an exact result for the polarizability of the Ne atom. The results are quoted as BαPW91. The motivation for the fit will be clear in the discussion of the results. Some test calculations were also done with the variant B3LYP as proposed by Stephens et al.[21] However, the results do not defer in any significant amount with the values obtained by B3PW91. Hence, those results will not be discussed further.

As a rather different approach and in order to test our hypothesis on the role of the right asymptotic behavior, the exchange-correlation potential proposed by van Leeuwen and Baerends[22] has also been tested. Starting with the known fact that the Becke's exchange functional, as all other known functionals, does not yield an exchange potential with the right asymptotic behavior, they directly proposed a phenomenological potential with the right asymptotic behavior as r goes to infinity. The potential has a free parameter which was fitted in order to reproduce as closely as possible the exact potential of the Be atom. The calculations will be denoted by LB94. To make the comparison with BαPW91 more transparent, we also fitted the parameter in the van Leeuwen and Baerends potential to get the polarizability of the Ne atom. The calculations will be denoted LBα94. Very recently, van Gisbergen et al.[23] implemented the LB94 potential to calculate dynamic and static polarizabilities for closed-shell atoms and molecules.

For all the calculations, except for the LB94 and LBα94 approaches, the dipole polarizabilities have been calculated by the finite field method with analytical derivatives with respect to the electric field as it is programmed in the GAUSSIAN94 package of programs.[24] Because for many it could be an unexpected result, it is worth mentioning that the density functional calculations are slower than the corresponding HF ones by a factor of 4. It seems that the analytical derivatives with respect to the field are much more laborious and time-consuming. The calculations using the van Leeuwen and Baerends potential have been done with a modified version of the DFT program written by St. Amant.[25] The program uses auxiliary charge density and exchange-correlation density basis sets. From the compilation of Godbout,[26] the ones recommended for a triple-zeta basis set quality have been used. The dipole polarizabilities have been calculated using the finite field method numerically. Point charges have been introduced to produce an electric field which was varied in order to get the limit of zero electric field. Care must be taken in order to have a sufficiently small field to assure the correctness of the limit and sufficiently large to avoid numerical errors. The fields were typically of the order of magnitude of 10^{-3} au. The dipole polarizabilities have been calculated through the variation of the induced dipole moment.

It is well-known that the calculation of the dipole polarizabilities is very sensitive to the quality of the basis set. It is necessary to include diffuse functions in order to describe the distortion of the density produced by the electric field. It is, however, important to point out that the basis set requirement for a CI calculation of the dipole polarizabilities should be stronger than the ones for a density functional method. The former needs more orbitals of higher angular momentum to describe excitations to high virtual orbitals, while for the density functional methods a good basis set for a HF calculation of α should suffice. Very recently, Dickson and Becke[27] have done numerical density functional calculations of the dipole polarizability of some first-row compounds in the local spin-density approximation (LDA). They confirmed the conclusions of Guan et al.,[28] namely, that a good-quality double-zeta basis set augmented with field-induced polarization functions gives well-converged polarizabilities. In this work, for atoms, the basis set have been constructed starting from the triple-zeta quality (TZP) basis set informed by Schaefer et al.[29] We have added two more diffuse s and p orbital and four d orbital functions. The exponents were chosen to maximize the polarizability at the HF level of calculation. The final basis set for each atom

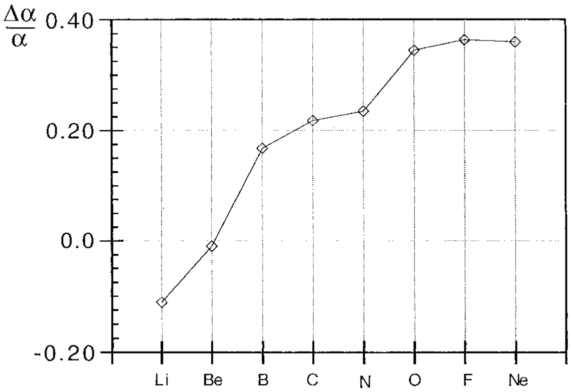

Figure 1. Dipole polarizability relative deviation of B88 results with respect to the HF values.

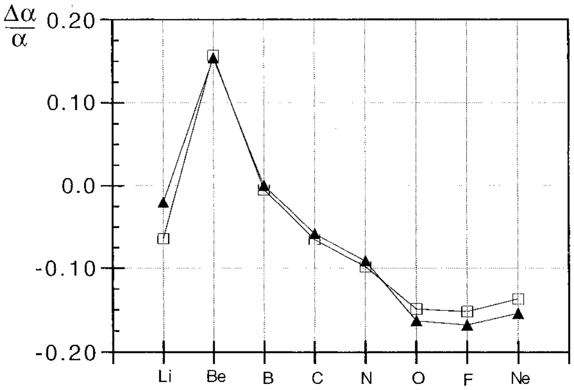

Figure 2. Dipole polarizability relative deviation of PW91 (▲) and LYP (□) results with respect to the CEPA values.

is of the type 12s6p1d/[8s6p1d] for Li atom, 12s7p1d/[8s7p1d] for Be atom, 12s8p4d/[8s6p4d] for B and C atoms, and 13s9p4d/[8s6p4d] for N, O, F, and Ne atoms. The exponents cover essentially the same range as the basis set used by Werner and Meyer.[6] For molecules, the compact basis sets due to Sadlej[30] are used. They were especially designed to obtain reliable electrical properties. They are of the type 8s8p4d/[4s4p2d] with diffuse s and p functions. The exponents and contraction coefficients of the d functions were chosen to give a good representation of the first-order density matrix.

Results and Discussion

Atoms. The calculated atomic average dipole polarizabilities are presented in Table 1 along with the HF and CEPA (coupled electron pairs approximation) results reported by Werner and Meyer.[6] The first point to be mentioned is the coincidence of our HF calculations with the ones described in ref 6. This gives confidence in the basis set used in this paper. The other results obtained in this paper will be analyzed and discussed in comparison with the CEPA values which have a commonly accepted accuracy of around 2%.

In Figure 1 we plotted the deviation of the B88 values with respect to the HF ones, that is, without any contamination coming from the correlation part which is absent in both calculations. One can see that there are severe deviations making the DFT results higher by as much as 30%. It is also interesting to note a marked shell structure in the deviations. They are almost constant for configurations p^1-p^3 and then again for configurations p^4-p^6. On the other hand, errors due to the correlation functional are lower as can be seen in Figure 2, where we have plotted the deviations of PW91 and LYP calculations with respect to the CEPA values. Here the Hartree–Fock exchange has been used. The electron correlation contribution to the polarizability may have both signs. It is negative for atoms Li to C and positive for N to Ne. This change in sign is not reproduced by any density functional calculation. The functionals are unable to reproduce the increase in the polarizability due to the electron correlation from the atoms N to Ne and which, unfortunately, is the dominant effect in all molecules. Roughly speaking, electron correlation augments the mean electron–electron distance, making the electron density more diffuse and, therefore, easier to polarize. This effect is not well reproduced by neither the PW91 nor the LYP functional. As it is known, this dynamics functionals do not remove the delocalization error of Hartree–Fock. However, because the errors have a different sign with respect to the deviations in the exchange part, one can expect some sort of compensation when both functionals are used together. This is in fact what occurs as can be observed from Figure 3, where the deviations of the BLYP, BPW91, and B3PW91 calculations with respect to the CEPA values are plotted. The errors are clearly smaller than those produced by the exchange functional, and except for the Li atom, they show the already-described[11] overestimation of the dipole polarizabilities. Li atom presents various peculiarities on its polarizability. It is markedly bigger than the α of the other atoms in the row and almost equal to the α of the next alkali metal atom. It has a very polarizable electron density because of the strong nuclear shielding effect and the low-lying empty p orbitals. Furthermore, almost all the important correlation contribution to α comes from the core–valence interaction in a region of space where the gradient of the density is high and, therefore, the right functional very nonlocal.

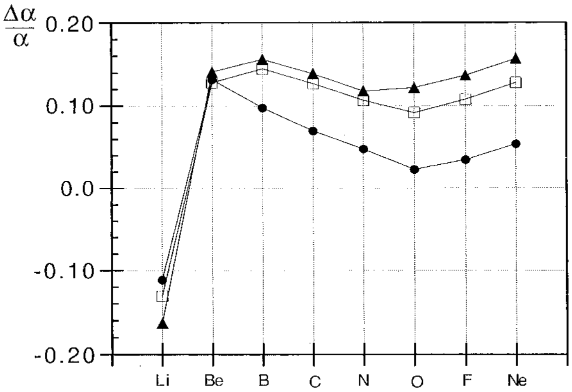

Figure 3. Dipole polarizability relative deviation of BLYP (▲), BPW91 (□), and B3PW91 (●) results with respect to the CEPA values.

The deviations of the BLYP and BPW91 methods are very similar and bigger than the deviations obtained by the hybrid method B3PW91. Confirming the suggestion of McDowell, Amos, and Handy,[11] the mixing of Hartree–Fock exchange into the functional improves the results. A further improvement can be obtained when the degree of Hartree–Fock and DFT exchange mixing is determined as reproducing as closely as possible the dipole polarizability of the Ne atom. The results termed BαPW91 are shown in Table 1 and in Figure 4. Except for Be atom, the errors are less than 10% and overall are the best ones obtained in this work.

The improvement obtained with the hybrid method strongly supports the idea that a right asymptotic behavior in the exchange potential is mandatory to obtaining reliable polarizabilities. This is further supported by the results obtained using the van Leeuwen and Baerends exchange potential which shows the correct asymptotic behavior. The results can be seen in Table 1 and Figure 4. They present in general slightly larger deviations than the B3PW91 method but of opposite sign. They tend to be smaller than the CEPA values. In Figure 4 we plotted

TABLE 1: Atomic Dipole Polarizabilities; Mean Values (in au)

	Li	Be	B	C	N	O	F	Ne
HF	168.0	45.54	22.02	11.89	7.140	4.797	3.288	2.367
B88	149.4	45.13	25.72	14.49	8.821	6.454	4.488	3.221
PW91	163.1	43.69	20.48	11.15	6.750	4.529	3.129	2.265
LYP	154.0	43.80	20.37	11.07	6.701	4.601	3.188	2.309
BPW91	142.9	42.68	23.43	13.35	8.224	5.912	4.165	3.018
BLYP	137.7	43.18	23.67	13.49	8.308	6.070	4.275	3.095
B3PW91	146.3	42.85	22.47	12.67	7.790	5.536	3.889	2.820
BαPW91	149.5	42.96	21.94	12.28	7.529	5.276	3.696	2.681
LB94	156.0	37.73	21.88	10.32	6.967	4.678	3.278	2.554
LBα94	156.0	38.85	23.69	10.69	7.317	4.883	3.416	2.673
HF[a]	170.3	45.63	22.16	12.07	7.365	4.772	3.291	2.368
PNO-CEPA[a]	164.5	37.84	20.47	11.84	7.430	5.412	3.759	2.676

[a] Values from ref 6.

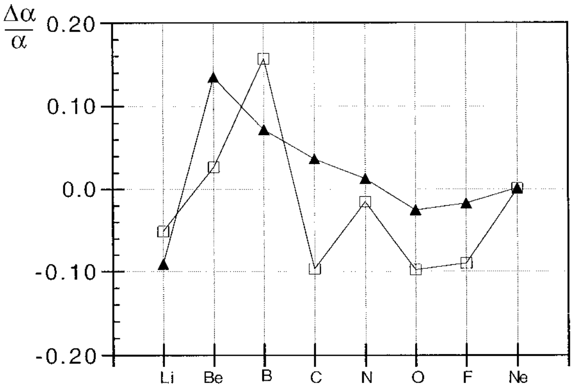

Figure 4. Dipole polarizability relative deviation of BαPW91 (▲) and LBα94 (□) results with respect to the CEPA values.

TABLE 2: N_2 Dipole Polarizability (in au)

	$\alpha_{\|}$	$\alpha_{\perp}$	$\langle\alpha\rangle$	$\Delta\alpha$
HF	15.00	9.586	11.39	5.41
BPW91	15.31	10.24	11.93	5.07
BLYP	15.57	10.49	12.18	5.08
B3PW91	15.07	9.983	11.68	5.09
BαPW91	14.90	9.777	11.48	5.12
LB94	14.79	9.86	11.50	4.93
LBα94	14.89	9.95	11.60	4.94
HF[a]	15.05	9.84	11.58	5.21
CEPA[a]	14.40	10.14	11.56	4.26
MR-CI[a]	15.05	10.18	11.80	4.87
exp[a]	14.82	10.20	11.74	4.62

[a] Frequency-corrected values taken from ref 12.

TABLE 3: O_2 Dipole Polarizability (in au)

	$\alpha_{\|}$	$\alpha_{\perp}$	$\langle\alpha\rangle$	$\Delta\alpha$
HF	18.04	7.789	11.21	10.3
BPW91	15.43	8.485	10.80	6.95
BLYP	15.64	8.638	10.97	7.00
B3PW91	15.41	8.175	10.59	7.24
BαPW91	15.53	7.971	10.49	7.56
LB94	14.26	7.87	10.0	6.39
LBα94	14.61	7.89	10.1	6.72
HF[a]	21.09	7.51	12.04	13.58
MR-CI[a]	15.08	7.87	10.27	7.21
exp[a]	15.37−15.45	8.16−8.22	10.59	7.15−7.29

[a] Frequency-corrected values taken from ref 12.

TABLE 4: F_2 Dipole Polarizability (in au)

	$\alpha_{\|}$	$\alpha_{\perp}$	$\langle\alpha\rangle$	$\Delta\alpha$
HF	14.80	5.594	8.663	9.21
BPW91	12.68	6.910	8.833	5.77
BLYP	12.93	7.007	8.981	5.92
B3PW91	12.83	6.511	8.617	6.32
BαPW91	13.00	6.236	8.491	6.76
LB94	11.95	5.70	7.78	6.25
LBα94	12.21	5.95	8.04	6.26
HF[a]	14.87	5.58	8.68	9.29
MR-CI[a]	12.75	5.96	8.22	6.79
exp[a]			8.38	

[a] Frequency-corrected values taken from ref 12.

the deviations with respect to the CEPA values of the calculations using the hybrid method of Becke and the exchange potential of van Leeuwen and Baerends, both of them with one free parameter adjusted in order to reproduce the polarizability of the Ne atom. In both cases the errors are substantially smaller than the obtained with the other functionals. In fact, the deviations are smaller than the produced by the correlation part alone. Hence, some sort of error compensation is already there. Very recently, van Gisbergen et al.[23] have calculated the dipole polarizability of the Ne atom using the LB potential. Their result (2.55 au) agrees very nicely with ours. It is worth mentioning that the exact asymptotic behavior of the correlation potential is not known, and therefore nothing can be said about its influence on the calculated polarizabilities.

Molecules. The results for the molecules N_2, O_2, and F_2 are presented in Tables 2−4 together with the theoretical and experimental values reported in ref 12. In that work the experimental dipole polarizabilities were frequency corrected in order to compare with the calculations. All the calculations were done at the experimental equilibrium distances. Since it is known that the polarizabilities are sensitive to small changes in the geometrical parameters, it is necessary to give explicitly the bond distances. They are, 1.098, 1.208, and 1.418 Å for N_2, O_2, and F_2, respectively. In general, for diatomic molecules the observables are the average polarizability $\langle\alpha\rangle = (2\alpha_{\perp} + \alpha_{\|})/3$ and the anisotropy $\Delta\alpha = (\alpha_{\|} - \alpha_{\perp})$. For these quantities one cannot expect that the asymptotic behavior of the potential could be as important as in atoms. For molecules, there are other important bonding and geometrical effects. Further, for the anisotropy one can expect a compensation of the long-range contribution from both components.

In Table 2 the results for N_2 are displayed. Our HF parallel polarizability compares very well with the results of Spelsberg and Meyer;[12] however, the perpendicular component is lower. This implies that our basis set has some room for improvement. For the parallel component the various functionals perform differently. Whereas the most known functionals, BPW91, BLYP, and B3PW91, augment the values in comparison with the HF ones, the functionals BαPW91 together with the implementations of the LB potential yield a lower number in better agreement with the best theoretical and experimental values. For the perpendicular and average polarizability the trend is very similar with the functionals BPW91, BLYP, and B3PW91 overestimating the effects. The anisotropy is a very sensitive quantity as demonstrated for the difference between the MR-CI and the CEPA values. Nevertheless, it seems that the functionals with correct asymptotic potential perform better. The results informed by van Gisbergen et al.[23] using the LB potential ($\langle\alpha\rangle = 11.46$ and $\Delta\alpha = 4.67$ au) agree nicely with our values. Other result is the SDQ-MPPT(4) calculation of Maroulis and Thakkar,[31] who informed $\langle\alpha\rangle = 11.51$ au and $\Delta\alpha = 4.64$ au, in perfect agreement with the LB values. Jamorski et al.[32] have implemented a density functional response function for the calculation of the polarizabilities. For N_2, they informed $\langle\alpha\rangle = 11.95$ au using a local functional.

In Table 3 the results for O_2 are displayed. The ground state of O_2 is an open-shell triplet state. Therefore, there are very few theoretical calculations of its electrical properties. In our DFT implementation there are no great differences between closed- and open-shell systems, and the calculations have the same reliability. At the HF level there is a noticeable difference between our values and the calculations performed by Spelsberg and Meyer.[12] To investigate this point, we repeat the calculations with an expanded basis set. Two diffuse s and p functions were added, and the two more diffuse d functions were uncontracted. However, the differences were less than 0.1 au. A very small difference in the bond distance was also corrected without any appreciable change in the calculated polarizability. Since our basis set seems saturated in the s, p, and d space, the only possibility would be a strong influence of the f functions. Unfortunately, at the moment this is not implemented in our computational codes. We recall that our calculations are done using the unrestricted Hartree–Fock scheme with analytical derivatives to calculate the polarizability as it is implemented in the GAUSSIAN94 package of programs. For the perpendicular component of α the functionals BPW91 and BLYP clearly overestimated the correlation effects, whereas the functionals with corrected asymptotic behavior yield right numbers in comparison with the MR-CI results. For the parallel component the LB94 functional yields a too low value. However, for this component no functional can reproduce the MR-CI value.

In Table 4 the results for F_2 are displayed. Here, our HF values using the Sadlej basis set are in very good agreement with the results of Spelsberg and Meyer.[12] For the parallel component all the functionals perform satisfactorily with the LB potential yielding, like in the other molecules, values somewhat low. However, for the perpendicular component the LB potential yields the best results. No functional performs clearly better than the others. For this molecule, van Gisbergen et al.[23] reported an average polarizability of 8.02 au and an anisotropy of 5.94 au.

The presented molecular results show that for molecules the long-range behavior of the potential is not as important as in atoms, and the gradient-corrected functionals perform relatively better for molecules than they do in atoms. This observation was also done by van Gisbergen et al.[23] and explained in terms of the long-range contribution to the energy gap. It is also confirmed that the anisotropy is a very sensitive quantity. The correlation effects clearly diminish its value. This trend is well reproduced for all the functionals. However, the dispersion in the calculated values is big.

Concluding, we believe to have presented enough evidence in support of the idea that a correct asymptotic behavior of the exchange potential is essential to obtaining reliable values for dipole polarizabilities. This implies, as stated in the Introduction, that one must be very cautious in analyzing density functional results involving intermolecular forces.

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