Improved density functional theory results for frequency-dependent polarizabilities, by the use of an exchange-correlation potential with correct asymptotic behavior

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The exchange-correlation potentials v_{xc} which are currently fashionable in density functional theory (DFT), such as those obtained from the local density approximation (LDA) or generalized gradient approximations (GGAs), all suffer from incorrect asymptotic behavior. In atomic calculations, this leads to substantial overestimations of both the static polarizability and the frequency dependence of this property. In the present paper, it is shown that the errors in atomic static dipole and quadrupole polarizabilities are reduced by almost an order of magnitude, if a recently proposed model potential with correct Coulombic long-range behavior is used. The frequency dependence is improved similarly. The model potential also removes the overestimation in molecular polarizabilities, leading to slight improvements for average molecular polarizabilities and their frequency dependence. For the polarizability anisotropy we find that the model potential results do not improve over the LDA and GGA results. Our method for calculating frequency-dependent molecular response properties within time-dependent DFT, which we described in more detail elsewhere, is summarized. © *1996 American Institute of Physics.* [S0021-9606(96)02031-4]

I. INTRODUCTION

In recent years there has been a growing interest in density functional theory (DFT)[1,2] from the quantum chemistry community. Its time-dependent extension, time-dependent DFT[3–5] is not yet that well explored. It was given a firm theoretical basis in 1984, by Runge and Gross[6] and offers the possibility to calculate frequency-dependent response properties, whereas finite-field calculations[7–11] only give access to static properties. Most calculations with time-dependent DFT have been restricted to atoms.[12–19] Molecular calculations were, among others, performed by Levine and Soven,[20] in a single-center expansion. As this approach seems impractical for general systems, we recently developed a method which can be used for general molecules, although our present implementation can only handle closed-shell molecules. Our previous calculations with this method,[21] using the local density approximation (LDA) yielded satisfactory results for polarizabilities and van der Waals dispersion coefficients. However, the results for the atoms showed a clear overestimation of both the static polarizability and the frequency dependence, in agreement with results from previous papers.[12–18] The molecular results were more satisfactory, though the average polarizability is systematically overestimated here too, as is also well-known.[11,21] The overestimation seems more pronounced in lighter systems (He can serve as an example) than in heavy molecules.

In atomic calculations on properties which are even more sensitive to the outer region, such as quadrupole polarizabilities[22] and hyperpolarizabilities[16,23–25] the LDA error is more pronounced. The static quadrupole polarizabilities of the rare gases are overestimated by the LDA by about 25% on average. The static second hyperpolarizability γ is

overestimated by a factor of 2 approximately. The source of this error is well-known. The LDA potential is not attractive enough in the outer region, due to spurious self-interaction. This leads to valence electrons which are too loosely bound.

These results made it worthwhile to test a potential which has correct asymptotic behavior. There have been previous attempts to improve upon the LDA results for atomic response properties. In the book by Mahan and Subbaswamy[17] results for the static (hyper)polarizabilities with so-called self-interaction correction (SIC)[26] and partial self-interaction correction (PSIC) potentials are given. The disadvantage of this approach, is that the potential becomes orbital dependent, which makes all calculations significantly more time-consuming.

Zhong *et al.*[18] have considered the frequency dependence of the atomic polarizabilities in LDA. We agree with these authors upon the fact that occupied and unoccupied eigenvalues are too close together in LDA, which causes too high a frequency dependence. Their solution to this problem is inspired by the GW method,[27,28] which is popular in solid state physics. Their approach is simply to shift the unoccupied energies by a constant. The shift is obtained from a simple model or fitted in order to obtain the experimental static polarizability. This method is reminiscent of the more recent work of Malkin *et al.*,[29] who used a comparable procedure for the calculation of nuclear magnetic resonance (NMR) shielding tensors. We will compare our results to the papers mentioned above, and show that our results are at least of comparable quality, but are obtained in a more tractable or theoretically more satisfactory way.

First we will give a short outline of our implementation of the linear response equations of time-dependent DFT,

which has been described in more detail elsewhere.[21] Then the model potential with correct asymptotic behavior, proposed by two of the authors in Reference 30, will be presented. After this theoretical introduction, we present our atomic and molecular results in the next section, and we end with some concluding remarks.

II. THEORETICAL INTRODUCTION

A. Frequency-dependent linear response in DFT

We will use time-dependent DFT for our calculations in this paper. For reviews on time-dependent DFT we refer to References 3–5. Many atomic results are given in the book by Mahan and Subbaswamy.[17] A more detailed description of our approach has been given elsewhere.[21]

In time-dependent DFT, the frequency dependent linear density response $\delta\rho(\mathbf{r},\omega)$ due to a scalar electric external field $\delta v_{\text{ext}}(\mathbf{r},\omega)$ is given in terms of a single particle response function $\chi_s(\mathbf{r},\mathbf{r}',\omega)$ acting on an effective field $\delta v_{\text{eff}}(\mathbf{r}',\omega)$ (atomic units are used throughout the paper):

$$\delta\rho(\mathbf{r},\omega) = \int \chi_s(\mathbf{r},\mathbf{r}',\omega)\,\delta v_{\text{eff}}(\mathbf{r}',\omega)d\mathbf{r}'. \quad (1)$$

The Kohn–Sham response function $\chi_s(\mathbf{r},\mathbf{r}',\omega)$ is constructed from (real) orbitals, occupation numbers and one-electron energies, obtained in an ordinary DFT calculation:

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \sum_i^{\text{occ.}} \sum_m^{\text{virt.}} n_i \phi_i(\mathbf{r})\phi_m(\mathbf{r})\phi_m(\mathbf{r}')\phi_i(\mathbf{r}')$$
$$\times\left(\frac{1}{(\varepsilon_i - \varepsilon_m) + \omega} + \frac{1}{(\varepsilon_i - \varepsilon_m) - \omega}\right). \quad (2)$$

Because of screening effects, the effective field in Equation (1) is not equal to the external field. It contains a Hartree and an exchange-correlation term due to the induced density:

$$\delta v_{\text{eff}}(\mathbf{r},\omega) = \delta v_{\text{ext}}(\mathbf{r},\omega) + \int d\mathbf{r}'\frac{\delta\rho(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|} + \delta v_{\text{xc}}(\mathbf{r},\omega), \quad (3)$$

where the last term is given by

$$\delta v_{\text{xc}}(\mathbf{r},\omega) = \int d\mathbf{r}'f_{\text{xc}}(\mathbf{r},\mathbf{r}';\omega)\delta\rho(\mathbf{r}',\omega). \quad (4)$$

Here the exchange-correlation kernel f_{xc} has been introduced. It is the functional derivative of the exchange-correlation potential with respect to the time-dependent density. As in our previous work,[21] we use the frequency-independent adiabatic LDA (ALDA) form of this kernel[3] for all our calculations. In this way we can assess the quality of different potentials, irrespective of the quality of their functional derivatives.

It should be noted that such a mixed scheme, where a different approximation for f_{xc} is made than for v_{xc}, has been used before. Mahan and Subbaswamy[17] prefer the partial SIC, which uses the self-interaction correction only for v_{xc} and not for f_{xc}, to full SIC, because the latter involves unphysical singularities. Stener et al.[19] have used the model potential, which we employ here and which they called

VLB-potential, in combination with time-dependent DFT to calculate autoionization resonances in noble gases. They used the simple X-α form for f_{xc}, claiming that the Coulombic term in Equation (3), which is the second term on the right-hand side, is much more important for the screening than the exchange-correlation term. We agree with this in general, though it should be observed that the last term is certainly not negligible. For this reason the exchange-correlation kernel has to be chosen with care.

We see no theoretical reason to prefer an f_{xc} derived from a generalized gradient approximation (GGA) potential or the model potential to the ALDA expression for f_{xc}. In the case of the GGAs, the energy functional E_{xc} is clearly superior to that of the LDA, but the functional derivative of this functional (v_{xc}) is not improved.[30] Because of this, there seems to be no reason to prefer the second functional derivative of a GGA energy functional to the ALDA kernel f_{xc}. On similar grounds, the model potential is not a priori expected to give an improvement, because it was obtained with some amount of fitting without considering the quality of the derivative of the potential. It should be noted that finite-field calculations can only be compared to schemes in which the exchange-correlation kernel f_{xc} is the functional derivative of the potential which is used.

The given set of equations (1), (2), (3), (4) is solved iteratively for a certain external potential v_{ext}, until self-consistency is reached. Then the first-order frequency dependent density change according to the external potential is known. By choosing the appropriate external field, one can calculate dipole, quadrupole and higher multipole polarizabilities.[3,17,21]

B. A model potential with correct asymptotic behavior

Recently, there has been much interest in constructing nearly exact exchange-correlation potentials from highly accurate ab initio densities.[30–35] The model potential used in this paper is supposed to approximate such an accurate exchange-correlation potential better than the GGA and LDA potentials do. It was recently proposed by two of the present authors.[30] It yields accurate values for the eigenvalue of the highest occupied Kohn–Sham orbital. This corrects the LDA and GGA values, which are typically several eV too high, causing the density to decrease too slowly in the outer region and the electrons to be too loosely bound. However, one should not look solely at this eigenvalue. We consider the difference between the highest occupied and lowest unoccupied eigenvalue to be a more important quantity for response properties. This can already be understood from Equation (2) for the response function, where only energy differences between occupied and unoccupied orbitals appear. In the work by Zhong et al.[18] this gap is also the main quantity.

One of the motivations for the direct modeling of the exchange-correlation potential, instead of taking the functional derivative of an energy functional, is that any exchange energy functional (the Becke functional[36] for example) of the form

$$E_x[\rho] = \int \rho^{4/3}(\mathbf{r}) f(x(\mathbf{r})) d\mathbf{r}, \tag{5}$$

with

$$x = \frac{|\nabla \rho|}{\rho^{4/3}}, \tag{6}$$

which satisfies the requirement that the exchange energy density per electron ε_x should behave asymptotically as

$$\varepsilon_x(\mathbf{r}) \sim -\frac{1}{2r} \quad (r \to \infty), \tag{7}$$

does not satisfy the requirement

$$v_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})} \sim -\frac{1}{r} \quad (r \to \infty). \tag{8}$$

The proof for this is given in References 37 and 30. The form of the model potential we use here is analogous to Becke's functional for the exchange energy density.[36] In spin-restricted form it is given by Ref. 30:

$$v_{\text{model}}(\mathbf{r}) = -\beta \rho^{1/3} \frac{x^2}{1 + 3\beta x \sinh^{-1}(x)}, \tag{9}$$

where β has the value 0.05, which is an order of magnitude larger than the value used by Becke in his energy functional.[36] This potential is a correction to the normal LDA potential, for which we use the Vosko–Wilk–Nusair parametrization.[38] This form of the model potential ensures the correct Coulombic decay at large distances. Furthermore, it reduces to the LDA potential in the weak inhomogeneity limit $(x \to 0)$.

Most exchange-correlation potentials do not show the correct asymptotic behavior. In fact, the only examples known to us which have not yet been mentioned, are a potential based upon the computationally expensive weighted density approximation (WDA),[39,40] and another model potential developed by some of us.[41,42] We will make some comments on our results with the latter potential in the final section of the paper.

A comparison of the accurate exchange-correlation potential and the model potential from Reference 30 with the LDA potential shows the erroneous behavior of the LDA potential in the outer region. These potentials are compared in Figure 1 for the neon atom. In the outer region, the model potential is clearly much closer to the accurate potential than the LDA potential is. In the core region there is room for improvement, because the model potential does not exhibit the peak at the boundary of the $1s$ and $2s$ shells. The relatively poor quality of the model potential near the nucleus might be the reason why the results for geometries obtained with the model potential are not so good, as was recently shown by Neumann et al.[43]

For polarizabilities, the outer region is of greater importance however, and in this region the LDA potential is not attractive enough. This leads to too high values for the ei-
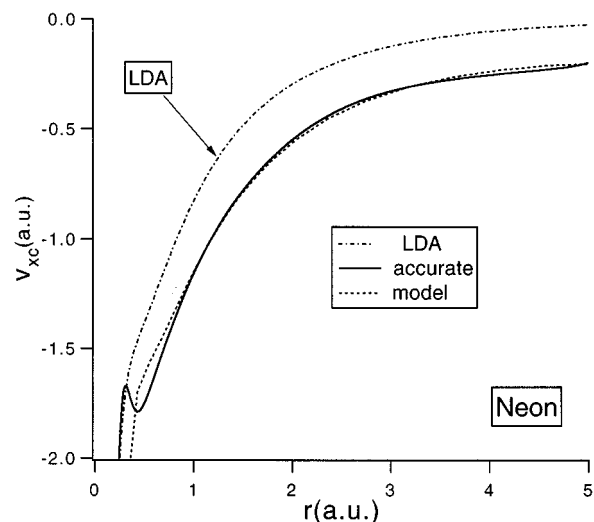

FIG. 1. A comparison, for the neon atom, of the model potential and the LDA potential to an accurate potential, constructed from a high quality configuration interaction density.

genvalue of the highest occupied orbital and overestimation of polarizabilities. The characteristics of Figure 1 also appear for other atoms.

III. DETAILS OF CALCULATION AND ATOMIC RESULTS

A. Description of the program and details of the calculations

All calculations were performed with the Amsterdam density functional (ADF) package.[44–48] Its characteristics include the use of Slater type orbitals, the possibility to use a frozen core approximation, the use of fit functions (also called auxiliary basis functions) for the density and an accurate numerical integration scheme.[46,47] The basis sets we use for our calculations are at least as extensive as those we used previously.[21] These basis sets consisted of a valence triple zeta basis with two polarization functions, augmented with two s, two p and two d functions, all with diffuse exponents. These diffuse functions are essential in obtaining results which are close to the basis set limit. The basis sets for atoms which we did not include in our previous publication were constructed in a similar fashion.

For most molecules (H_2, HF, F_2, N_2, CO, Cl_2, HCl, CO_2, N_2O, SO_2, CH_4) we have added diffuse f functions to the basis sets. A comparison with the results with slightly smaller basis sets shows, that in most (but not all) cases this addition causes only very small changes in the dipole polarizabilities. For the other molecules we did not include the diffuse f functions in the bases, because of technical problems due to linear dependencies in the basis sets. Because of the large basis sets we use, we can expect to be close to the basis set limit in all the calculations presented in this paper. This is also shown by the fact that our atomic and molecular results are close to those obtained with basis set free methods[17] and to other results with high quality basis sets.[11]

TABLE I. Static atomic dipole polarizabilities (in a.u.), calculated with various exchange-correlation potentials.

Atom	LDA[a]	LDA (lit)	BP[b]	PSIC[c]	Model[d]	Expt.[e]
He	1.65	1.67[f]	1.59	1.32	1.40	1.38
Ne	3.02	3.05[f]	2.98	2.56	2.55	2.67
Ar	11.94	12.01[f]	11.66	11.67	11.40	11.07
Kr	17.67	18.02[f], 17.88[g]	17.39	17.95	16.48	16.74

[a]Reference 21.
[b]References 36 and 49.
[c]References 2417.
[d]Reference 30.
[e]Reference 68.
[f]Reference 17.
[g]Reference 18.

We made sure that all our fit sets were nearly saturated and that the integration accuracy was sufficiently high. We used the frozen core approximation for most of the atoms. The outermost frozen shell was $3d$ for Kr, $2p$ for Si, P, S, Cl, Ar and $1s$ for C, N, O, F, Ne. This approximation is assumed to change the results only insignificantly, especially for molecules. We have tested this before.[21] We demanded at least six significant digits for a set of test integrals from the numerical integration routine, which is more than sufficient.

B. Atomic results

In Table I we compare the static dipole polarizability for the rare gases, calculated with different potentials. Our LDA results are close to accurate literature values, testifying to the quality of our basis and fit sets. The LDA values are substantially larger than the experimental values. The literature LDA values[17] are on average 12.8% too high. Compared to this, the results with the model potential are excellent. They differ on average by only 2.6% from the experimental values. Results with the partial SIC method,[17] another scheme to remove the LDA self-interaction, are worse than our results with the model potential. The average deviation from experiment is 5.3% in this case. Using full SIC (not shown in the table) hardly improves this (4.7% average deviation). Another interesting result is that the Becke–Perdew (BP)[36,49] generalized gradient potential overestimates the polarizability somewhat less (9.0%) than the LDA potential does.

The frequency dependence of the dipole polarizability of the rare gases is sometimes given in the form[17]

$$\alpha(\omega) = \alpha_0(1 + C_2\omega^2). \tag{10}$$

In this formulation, which is only applicable for small values of ω, the coefficient C_2 is a measure for the frequency dependence which is independent of the static value. Zhong et al.[18] have devoted an article to the problem of the overestimation of the frequency dependence in atomic time-dependent LDA (TDLDA) calculations. They use two semi-empirical models to increase the gap between occupied and unoccupied Kohn-Sham energies. They call this the modified TDLDA approach. One model is based on a single-oscillator model, the other one simply applies a scissors operator to the gap. In both cases one imposes that the static polarizability should equal the experimental value. Their results have been included in Table II. In this table, our LDA values are again close to the basis set free results. These LDA results show a large overestimation of the C_2 coefficient (24%). The semi-empirical values obtained with the scissors operator are already much closer to experiment (12%), but they show a systematic underestimation of the frequency dependence. Both the single-oscillator model and the use of the model potential increase the agreement with experiment significantly. They respectively differ by only 4.3% and 4.5% from the experimental numbers. However, we stress that our results were obtained without any fitting or modeling. Merely the quality of the model potential in the outer region of the atom assures the good description of the frequency dependence.

We have also performed calculations on atomic quadrupole polarizabilities. For these calculations the inclusion of the diffuse f functions to the basis sets was much more important than for dipole polarizabilities and had a significant influence on the results. The calculations can be assumed to

TABLE II. Frequency dependence C_2 of atomic dipole polarizability, as defined by Equation (10).

Atom	TDLDA[a]	TDLDA lit.[e]	Mod. TDLDA[b] scissors	Mod. TDLDA[b] single oscil.	Model[c]	Expt.[d]
He	1.46	1.49	0.94	1.01	1.11	1.16
Ne	1.49	1.49	0.95	1.10	1.05	1.11
Ar	3.07	3.13	2.35	2.62	2.63	2.60
Kr	4.02	4.10	3.28	3.52	3.35	3.61

[a]Reference 21.
[b]Modified time-dependent LDA approach, as described in the text, Reference 18.
[c]Reference 30.
[d]Reference 68.
[e]Reference 16.

TABLE III. Atomic quadrupole polarizabilities (in a.u.) with different potentials.

Atom	LDA	LDA (lit.)[a]	Model[b]	*Ab initio*
He	3.56	3.35	2.52	2.445[c]
Ne	9.47	9.35	7.12	7.52[d], 7.3276[e]
Ar	61.81	59.6	55.61	53.58[f], 51.862[e]
Kr	111.42	108.5	96.53	99.86[g], 99.296[e]

[a]References 22 and 17.   [e]MBPT, Reference 70.
[b]Reference 30.   [f]Finite-field MP4, Reference 71.
[c]Reference 50.   [g]Finite-field MP4, Reference 72.
[d]CCSD(T), Reference 69.

be equally close to the basis set limit as the calculations for dipole polarizabilities. The static results are given in Table III. Again, the LDA values severely overestimate the results from reliable *ab initio* calculations. They are on average 25% too large, with He as the worst case. The model potential brings major improvement for this property too. The results are only about 5% from the *ab initio* reference values, on average.

One of the major advantages of the model potential is that the one-electron energies of the highest occupied[30] and lowest unoccupied orbital are quite well predicted. Only the highest occupied eigenvalue has strict physical significance (it should equal minus the ionization potential), but the gap between the highest occupied and lowest unoccupied orbital determines the frequency dependence to a great extent. Especially in the region near the first excitation energy this plays an important role.

This can clearly be seen from Figure 2, where the quadrupole polarizability of He has been calculated on a wide range of real frequencies. The time-dependent LDA result and the result with the model potential are compared to an extremely accurate *ab initio* calculation.[50] It was already known from Table III that the static LDA value for the quadrupole polarizability was not very good. In addition to this, Figure 2 shows that the LDA result has a much too high frequency dependence and that the first excitation energy lies too low (these facts are of course interrelated). In comparison, the model potential performs quite well. It follows the accurate theoretical curve closely, along the entire frequency range. Note that this frequency range extends to 0.6 Hartree!

IV. MOLECULAR RESULTS

A. Average polarizabilities

It has been remarked many times that both the LDA and the GGAs systematically overestimate polarizabilities. Because the atomic results with the model potential are promising, we are now going to study molecular polarizabilities. We remark that the overestimation of the polarizability is less pronounced in molecules than in atoms. Other effects, such as charge transfer from one atom to another, become important, which makes the asymptotic behavior of the potential less crucial. In order to be able to draw reliable conclusions from our calculations, we decided to perform calculations on a fairly large number (19) of small and medium-sized molecules. We took the molecules we already

performed calculations on previously[21] and added those from Reference 11. This should yield a list of molecules which is representative and large enough.

We performed our calculations at the experimental geometries, gathered from different sources, such as References 51 and 52. For the sake of reproducibility and for ease of reference, we listed the used geometries in Table IV. In our previous work,[21] we used the same geometries, except for H_2, for which we used the optimized geometry of $r(HH) = 0.767$ Å. For PH_3 we listed both the experimental geometry and the geometry which was optimized with the Becke–Perdew potential. We performed calculations at the optimized geometry as well, in order to be able to explain a discrepancy between our results and the results obtained by McDowell *et al.*[11] for the same molecule.

In Table V the average polarizabilities for the molecules are presented. We show our results with the LDA potential, the BP potential and the model potential and compare them to literature values with LDA and GGAs, as well as to experimental values and values obtained with the accurate constrained dipole oscillator strength distribution (DOSD) method.[53,54]

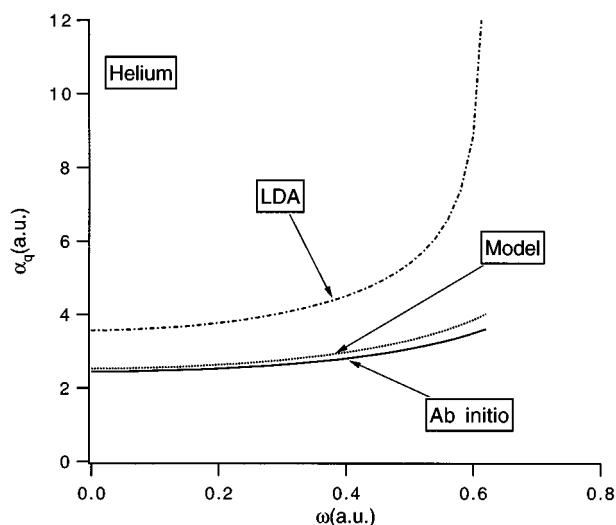In general, our LDA values agree well with previous

FIG. 2. The frequency-dependent quadrupole polarizability of He. Comparison of results with the LDA and model potentials to benchmark *ab initio* results.

TABLE IV. Molecular geometries used in this paper.

Molecule	Bond length(Å)	Angle(degrees)
H_2	$r(HH) = 0.7461$	
HF	$r(HF) = 0.917$	
HCl	$r(HCl) = 1.2746$	
N_2	$r(NN) = 1.0976$	
CO	$r(CO) = 1.1283$	
F_2	$r(FF) = 1.417$	
Cl_2	$r(ClCl) = 1.9871$	
H_2O	$r(OH) = 0.957$	$\angle(HOH) = 104.5$
H_2S	$r(SH) = 1.3455$	$\angle(HSH) = 93.3$
CO_2	$r(CO) = 1.160$	
N_2O	$r(NO) = 1.186$, $r(NN) = 1.1257$	
SO_2	$r(SO) = 1.4321$	$\angle(OSO) = 119.54$
NH_3	$r(NH) = 1.008$	$\angle(HNH) = 107.3$
PH_3[a]	$r(PH) = 1.4166$	$\angle(HPH) = 93.1$
PH_3[b]	$r(PH) = 1.437$	$\angle(HPH) = 91.5$
CH_4	$r(CH) = 1.091$	
SiH_4	$r(SiH) = 1.4798$	
C_2H_4	$r(CH) = 1.071$, $r(CC) = 1.344$	$\angle(HCH) = 119.9$
C_2H_6	$r(CH) = 1.107$, $r(CC) = 1.533$	$\angle(HCH) = 109.3$
c-C_3H_6	$r(CH) = 1.089$, $r(CC) = 1.510$	$\angle(HCH) = 115.0$

[a]Experimental geometry.
[b]Becke–Perdew optimized geometry.

work in which high quality basis sets were used,[11] except for our PH_3 results at the experimental geometry, which are 37.63, 36.42 and 35.44 for the LDA, BP and model potentials respectively. In the table the results with the optimized

geometry for PH_3 have been presented, which agree well with the literature values.

The LDA results are higher than the experimental ones, without exception. The average overestimation of the LDA values is 5.3%, which is close to the 5.7% overestimation found by McDowell et al.[11] for a subset of the molecules in our table.

Our values with the Becke–Perdew potential are not strictly comparable to GGA values in previous studies, because our mixed-scheme results need not be identical to finite-field results. In fact, our results with the Becke–Perdew potential correct the LDA overestimation somewhat. The agreement with the experimental values is improved (2.7%). The values are still too high, though in three cases it is slightly lower than experiment. Finite-field Becke–Lee–Yang–Parr (BLYP)[36,55] values slightly increase the LDA overestimation.[11]

The results with the model potential in Table V are also slightly better than the LDA results. The average absolute error is somewhat reduced, to 3.5%. More important, the overestimation which is present in the LDA and GGA results, is removed. No large systematic over- or underestimation of the experimental results remains. Part of the remaining underestimation of 0.9% might be due to the fact that the basis set limit has not been fully reached.

It is well-known that LDA and GGA potentials underestimate the eigenvalue of the highest occupied Kohn–Sham orbital by typically 5 eV. This error is greatly reduced by the

TABLE V. Average molecular polarizabilities calculated with different potentials.

Molecule	LDA	LDA (lit)[a]	BP[b]	BLYP[c]	Model[d]	DOSD / Expt.[e]
NH_2	5.89		5.54		5.61	5.43
HF	6.20	6.17	6.08	6.26	5.31	5.60
HCl	18.63	18.43	18.09	18.54	17.86	17.39
N_2	12.27		12.04		11.46	11.74
CO	13.87		13.36		12.62	13.08
F_2	8.87	8.82	8.70	8.96	8.02	8.38
Cl_2	32.00	31.70	31.29	31.97	30.96	30.35
H_2O	10.53	10.54	10.28	10.63	9.20	9.64
H_2S	26.34	26.13	25.49	25.94	25.39	24.71
CO_2	17.72	17.80	17.46	17.97	16.63	17.51
N_2O	19.91		19.63		18.71	19.77
SO_2	26.49	26.41	26.21	26.75	24.59	25.61
NH_3	15.62	15.57	15.25	15.62	13.85	14.56
PH_3[f]	32.80	32.52	31.56	32.14	32.12	32.03
CH_4	18.19	18.01	17.40	17.82	17.98	17.27
SiH_4	34.04	34.28	32.34	33.14	33.91	31.90
C_2H_4	28.30	29.10	27.77	29.31	27.12	27.70
C_2H_6	30.74		29.72		30.54	29.54
c-C_3H_6	39.19		38.91		37.91	38.0
Mean error	+5.3%		+2.4%		-0.9%	
Mean absolute error	5.3%		2.7%		3.5%	

[a]Reference 11.
[b]Becke–Perdew potential (References 36 and 49).
[c]Becke–Lee–Yang–Parr potential, (References 36 and 55) results obtained by McDowell et al. (Reference 11).
[d]Reference 30.
[e]Experimental and constrained dipole oscillator strength distribution results, as gathered in References 11 and 21.
[f]Optimized geometry was used in our calculations.

TABLE VI. Polarizability anisotropies γ (in a.u.), as in Equation (11). Comparison of results with different exchange-correlation potentials to experimental data.

Molecule	LDA	LDA (lit)[a]	BP[b]	BLYP[c]	Model[d]	DOSD / Expt.[e]
H_2	2.04		2.00		2.13	2.04
HF	0.93	1.10	0.96	1.160	1.28	1.33
HCl	1.29	1.30	1.32	1.329	2.29	1.45
N_2	4.62		4.69		4.67	4.45
CO	3.26		3.40		3.23	3.57
F_2	5.69	5.49	5.75	5.784	5.94	
Cl_2	16.60	16.11	16.46	16.455	17.33	17.53
H_2O	0.07	0.24	0.15	0.296	1.25	0.66
H_2S	0.84	1.24	0.67	1.664	0.81	0.65
CO_2	13.37	13.96	13.22	14.026	13.49	13.3
N_2O	18.73		18.63		18.35	19.10
SO_2	13.36	13.16	13.35	13.427	13.02	13.0
NH_3	3.09	2.67	3.09	2.676	0.25	1.94
PH_3[f]	2.25	2.38	2.03	2.337	0.76	
C_2H_4	11.31		10.95		12.82	11.4
C_2H_6	4.37		4.10		3.82	5.2
$C-C_3H_6$	−5.25		−4.95		−5.52	−5.4

[a]Reference 11.
[b]Becke–Perdew potential (References 36 and 49).
[c]Becke–Lee–Yang–Parr potential (References 36 and 55), results obtained by McDowell *et al.* (Reference 11).
[d]Reference 30.
[e]Experimental and constrained dipole oscillator strength distribution results, as gathered in References 11 and 21.
[f]Optimized geometry was used.

model potential we employ. The average error is a few tenths of an eV in this case.[30] One might wonder how it is possible that the LDA and GGA values for molecular polarizabilities are only a few percent too high, compared to experiment, when the highest eigenvalue is predicted so erroneously. In order to answer this question, we calculated the eigenvalue of the lowest unoccupied orbital as well. It appears that the gap between these eigenvalues is not so different for the three potentials considered here. Typically, they are identical to within a few tenths of an eV. The correct asymptotic behavior of the model potential affects the highest occupied and lowest unoccupied eigenvalues in similar fashion. They both become more bound, being shifted by almost the same amount. This is true for molecules, but it does not hold for atoms, as can be seen from Figure 2. This is due to the different nature of the lowest unoccupied orbital in the atomic and molecular cases. For a more detailed analysis, the knowledge of the exact Kohn–Sham values for these eigenvalues would be desirable. However, we presume that the model potential yields accurate values for the first unoccupied eigenvalue as well, because of its asymptotically correct behavior.

B. Anisotropy in the polarizability

Our results for the static polarizability anisotropy are presented in Table VI. The anisotropy γ is defined for diagonal polarizability tensors in the usual way[56] as:

$$\gamma^2 = \tfrac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{yy})^2], \quad (11)$$

where we use $\gamma = \alpha_{zz} - \alpha_{xx}$ for symmetric top molecules with their main symmetry axis along the z axis. For this property the LDA and GGA results are more satisfactory and the model potential offers no improvement.

The results with LDA and Becke–Perdew, which are similar to each other, are slightly preferable. In most cases the different potentials yield similar results, but for a few molecules (notably HCl, H_2O, NH_3 and PH_3) the model potential gives markedly different results. (Here the results for PH_3 at the experimental geometry are 8.17, 8.07 and 3.13 respectively.)

The polarizability anisotropy suffers much less from the incorrect asymptotic behavior of the LDA and GGA potentials, because the overestimation of the different polarizability tensor components partially cancels in Equation (11). This means that the correct description of the outer region is not as important as for the average polarizability. Other parts of the potential curve gain in importance. Because the model potential only improves the outer region and is not so good near the nucleus, one would not necessarily expect an improvement from this potential for the polarizability anisotropy. For this, one would need an exchange-correlation potential which improves upon the LDA near the nucleus as well.

The agreement between our LDA anisotropies and those obtained by McDowell *et al.*[11] is somewhat less than for the average polarizabilities, especially for the molecules with small anisotropies. This can be understood from the fact that the polarizability anisotropy is a more sensitive property than the average polarizability. It has been noted before[11] that

TABLE VII. Frequency dependence of average polarizability α, with different potentials. Here, Δ gives the difference between the results at the two different wavelengths.

Molecule	$\lambda(\text{Å})$	ALDA	BP[a]	Model[b]	Expt.[c]
H_2	3251.3	6.44	6.02	6.06	5.86
	6329.9	6.03	5.66	5.72	5.54
	Δ	**0.41**	**0.36**	**0.34**	**0.32**
CO_2	3251.3	18.83	18.68	17.57	18.62
	6329.9	18.00	17.85	16.85	17.78
	Δ	**0.83**	**0.82**	**0.72**	**0.84**
N_2O	3251.3	21.50	21.18	20.78	21.32
	6329.9	20.29	20.01	19.67	20.09
	Δ	**1.21**	**1.17**	**1.11**	**1.23**
NH_3	3251.3	19.02	18.25	15.33	16.35
	6329.9	16.34	15.82	14.19	14.96
	Δ	**2.68**	**2.43**	**1.14**	**1.39**
C_2H_6	3251.3	33.45	32.21	33.07	31.92
	6329.9	31.39	30.33	31.16	30.13
	Δ	**2.06**	**1.88**	**1.91**	**1.79**
c-C_3H_6	3251.3	43.16	43.01	41.29	40.577
	6329.9	40.12	39.84	38.71	38.107
	Δ	**3.04**	**3.17**	**2.57**	**2.47**
Mean error in Δ		+26.1%	+18.9%	-4.2%	
Mean absolute error in Δ		27.0%	21.3%	9.9%	

[a]Becke–Perdew potential (References 36 and 49).
[b]Reference 30.
[c]Reference 57.

LDA and GGA polarizability anisotropies are of higher quality than Hartree–Fock anisotropies.

C. Frequency dependence of molecular polarizabilities

Because the model potential improves the frequency dependence of the atomic polarizabilities remarkably, we have investigated the frequency dependence of average molecular polarizabilities as well. It is known that Hartree–Fock calculations underestimate the frequency dependence of the polarizability considerably. The Cauchy moment $S(-4)$ in the expansion $\alpha(\omega)=\Sigma_k S(-2k-2)\omega^{2k}$, which dominates the frequency dependence in usual frequency ranges, was underestimated by 27.6% with respect to experiment in a study by Spackman on a large number of molecules.[56] To our knowledge, it has never been investigated how well different potentials in DFT describe this frequency dependence for molecules. For these two reasons we have calculated some frequency-dependent molecular polarizabilities with the same potentials we have used in the rest of this work. We compare to recent experimental values of high accuracy.[57] We could not perform calculations on O_2, for which measurements were also performed,[57] because it is an open-shell molecule. The results at $\omega = 0.140$ and 0.072 a.u. are shown in Table VII.

As was to be expected, the LDA and BP potentials tend to overestimate the frequency dependence. The LDA values differ from the experimental ones by 27.0% on average and

the Becke–Perdew values differ by 21.3%. The overestimation is especially clear in the cases of ammonia and cyclopropane. The model potential yields better results for these molecules. Its average error is 9.9%, which makes it a more reliable choice than Hartree–Fock, LDA or Becke–Perdew. The error in the model potential results seems to be less systematic, which is reflected by the fact that the mean error is about two times as small as the mean absolute error.

However, when considering the frequency dependence of the polarizability, another point is of importance. We made an adiabatic approximation for the exchange-correlation kernel f_{xc} in Equation (4). This means that the exchange-correlation screening is assumed to be frequency independent. In the present context it is relevant to assess the validity of this approximation. To this purpose, we have performed some test calculations with the frequency-dependent Gross–Kohn exchange-correlation kernel,[58–60,3] which is based upon the frequency-dependent linear response of the homogeneous electron gas. Although some principal objections can be raised against it (such as the violation of the so-called ''harmonic potential theorem''[61]), it provides at present the only practical way to go beyond the adiabatic approximation.

As a check on our implementation, we compared to Reference 3 and reproduced Figures 1 and 2 of that paper. We also compared numerically to another implementation of the

same kernel,[62] finding agreement in the first five digits over a wide frequency range.

The Gross–Kohn parametrization of f_{xc} decreases the frequency dependence which is found in the ALDA. This is due to the fact that the exchange-correlation screening, which increases the polarizability, becomes smaller with increasing frequency in the Gross–Kohn parametrization.

In the literature,[3,16] it has been assumed that the adiabatic approximation is not a severe one. Our preliminary results for the frequency dependence of the average polarizability indicate that this is not true in general. We find that the ALDA results in Table VII for the quantities Δ are reduced by roughly 15–30% with the Gross–Kohn kernel, thus increasing the agreement with experiment. This indicates that the adiabatic approximation cannot be applied thoughtlessly in the optical region and that its use will lead to a frequency dependence which is too high. It is important to note here that if the Gross–Kohn kernel is used in combination with the model potential, the resulting frequency dependence in Table VII will be too low in comparison with experiment. This may be due to the fact that the Gross–Kohn kernel was derived from the frequency-dependent linear response of the homogeneous electron gas, which might not be a realistic model for the frequency dependence in molecules.

We conclude that both the quality of the exchange-correlation potential in the outer region of the molecule and the frequency dependence of the exchange-correlation screening need to be considered in order to obtain accurate DFT results for frequency-dependent polarizabilities. We emphasize however, that the restricted number of molecules for which we performed these calculations does not allow definite generalizations and that more work is needed in order to further clarify the importance of the adiabatic approximation and the importance of the outer region of the exchange-correlation potential on the frequency dependence.

V. CONCLUDING REMARKS

We have presented calculations with a model exchange-correlation potential, which possesses the correct long-range behavior. Our approach allows an analytic determination of frequency-dependent polarizabilities for closed-shell molecules. A mixed scheme was used, in which the adiabatic LDA approximation was used for the exchange-correlation kernel f_{xc}, regardless of the approximation made for the exchange-correlation potential v_{xc}. Our atomic results (static and dynamic dipole and quadrupole polarizabilities) are substantial improvements on previous results with LDA and GGA potentials. In our molecular calculations, the model potential removes the systematic overestimation in the average polarizability, which is obtained in calculations with LDA or GGA potentials. Both the results with the model potential and the results with the Becke–Perdew potential provide improvements on the LDA results. More subtle modeling for the exchange-correlation potential is needed to obtain satisfactory results for the anisotropy, for which the LDA and GGA results are slightly better.

In general, we observe that the asymptotic behavior of the potential is more critical for polarizability calculations than the correct description of the core region. This is shown by test calculations with a model potential which was introduced more recently.[41,42] This potential gives a better description of the core region (it exhibits the required peaks between the atomic shells) and also possesses the correct long-range behavior. It yields accurate values for the highest occupied Kohn–Sham orbital as well, but it did not yield good results in preliminary calculations which we performed. The polarizabilities were consistently underestimated, thus overcorrecting the LDA results. Subsequent analysis showed that the gap between the highest occupied and lowest unoccupied orbital was larger for this potential than for the model potential used in this work. This was due to the fact that the Coulombic asymptotic behavior was reached too slowly, showing that the problems in the modeling of potentials can be quite subtle.

In future work, it would seem desirable to improve the quality of the potential in the core region. This might help to improve the results for other response properties as well, such as NMR shielding tensors, in which the poor quality of the LDA or GGA eigenvalues is also important.[29,63,64] Furthermore, the quality of the exchange-correlation kernel is of importance, as shown by our finite-field test calculations.

The frequency dependence of average molecular polarizabilities was also best described by the model potential. The LDA and Becke–Perdew potentials tend to overestimate this frequency dependence. The importance of the frequency dependence of the exchange-correlation screening should not be underestimated, as shown by our preliminary results with the Gross–Kohn parametrization for f_{xc}. We have shown that the direct modeling of the exchange-correlation potential yields promising improvements in our calculations on response properties, and we hope to have encouraged further work in this direction.

In the final stages of this work, the work of Casida and co-workers[5,65,66] came to our attention. They also have an implementation capable of calculating molecular frequency-dependent linear response within DFT. They present results for the N_2 molecule for which they calculated excitation energies and the frequency-dependent average polarizability, suggesting that their results might be improved by using an accurate exchange-correlation potential. We learned very recently that Castro, Casida and Salahub[67] obtained very similar results for polarizabilities with the model potential.

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