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Density-functional-theory calculations of the total energies, ionization potentials, and optical response properties with the van Leeuwen–Baerends potential

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van Leeuwen and Baerends proposed a Becke-like nonlocal correction to the local-density-approximation (LDA) exchange-correlation potential so that its asymptotic structure becomes exact i.e., $-1/r$ [Phys. Rev. A **49**, 2421 (1994)]. They showed that it significantly improves the value of the highest occupied orbital eigenvalue of atoms and molecules. However, the correction is exchangelike in nature. With this in mind, in this paper we investigate how this correction affects the total energies and highest eigenvalues within the exchange-only approximation. We show that the potential also corrects the LDA errors substantially within this approximation, and leads to total energies and high eigenvalues which compare well with their Hartree-Fock counterparts. Improvement in the asymptotic behavior of the potential should also result in better values of the response properties of these systems. We show that with this correction one obtains better estimates, both within the exchange-only approximation and with correlation included, of the linear and nonlinear polarizabilities of inert gas atoms . This is quite significant, since the LDA is known to overestimate the nonlinear polarizabilities of these atoms by roughly 100%. On the other hand, for alkaline-earth atoms the values of polarizabilities obtained with this correction are not satisfactory. Nonetheless, hyperpolarizabilities show a marked improvement over the LDA results. [S1050-2947(99)06711-6]

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I. INTRODUCTION

Over the years, density-functional theory (DFT) [1,2] has emerged as a powerful method to determine the electronic structure of many-electron systems. Although the theory can be implemented only with approximate forms of the exchange and correlation energy functionals, its popularity stems from the fact that it is computaionally easy and leads to reasonably accurate results for a number of properties of interest. The most popular among the various approximations is the local-density approximation (LDA) [1,2], which has been the mainstay of DFT calculations since its inception [3,4]. However, one of the most serious drawbacks of the LDA is that it fails to describe the asymptotic region of a system accurately. This is because the tail of the LDA potential is exponential rather than $-1/r$, which is the correct asymptotic structure [5] of the exact potential. Thus, properties that depend primarily upon the density or orbitals in this region are not given as accurately as, for example, the total energy. As an example, the highest occupied orbital eigenvalues, which in principle should be equal to the negative of the ionization energies [5–7], are roughly only half as much. This implies that the LDA does not bind the outer electrons as tightly as they are in reality. This is also manifested clearly in the values of the response properties of atoms [8–10] and molecules [11,12]. For example, the linear polarizabilities of the noble gas atoms calculated from the LDA orbitals are always overestimates (by about 10%) of the experimental results. The nonlinear polarizabilities are much more sensitive and are overestimated by a much larger amount ($\approx 100\%$) when calculated from the LDA orbitals. Although over the past decade or so, many new functionals [13,14] have been constructed that improve upon the LDA by including the nonlocality in terms of the gradients of the density, they still do not give the asymptotic potential correctly. For example, the Becke [13] correction to the LDA gives the exact exchange-energy density in the asymptotic region, but the corresponding potential decays [15] as $-1/r^2$. Thus, whereas the total energies obtained from these functionals may be highly accurate, the highest occupied orbital eigenvalues still remain [16] way off from their exact values of the negative of the ionization potential. One way of rectifying this situation is to add to the LDA potential a term which leads to the correct asymptotic behavior. In the context of the $X\alpha$ [17] potential, this was done with the addition of Latter [18] correction. Recently van Leeuwen and Baerends (LB) [16] also took this approach to modify the LDA potential. They showed [16] that with the correction suggested by them accurate estimates of the highest occupied orbital eigenenergies and linear response properties [12,19] are obtained. However, whereas it is evident that the LB correction improves the orbitals and the density in the asymptotic region, it is not clear how the overall density is affected. In this paper we study the LB potential from this perspective, and show that it also describes a many-electron system well in this respect. We do this by calculating the total energies, highest occupied orbital eigenvalues, and static linear and nonlinear response properties of some atomic systems. In Sec. II below, we describe the LB correction and show within the exchange only, that both the total energies and the highest occupied orbital eigenvalues for these systems come out to be quite close to the corresponding Hartree-Fock (HF) values. In Sec. III we calculate the linear- and non-linear-response properties of these atoms and ions employing the orbitals obtained from this potential and demonstrate the effect of the LB correction both in the exchange-only (XO) case as well as in the fully correlated (XC) case. We conclude the paper with a discussion in Sec. IV.

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II. VAN LEEUWEN AND BAERENDS CORRECTION TO THE POTENTIAL AND THE ENERGY

Taking a cue from Becke's correction [13] to the exchange energy density, LB proposed [16] a similar correction to the LDA potential directly instead of modifying the energy functional and then taking its functional derivative. As noted above, Becke's correction gives the correct exchange-energy density in the asymptotic region but fails to give the exact behavior for the corresponding potential (derived as the functional derivative). To rectify this, LB wrote the effective exchange-correlation potential as

$$v_{\rm xc}(\mathbf{r})=v_{xc}^{\rm LDA}(\mathbf{r})+v^{\rm LB}(\mathbf{r}), \tag{1}$$

where

$$v^{\rm LB}(\mathbf{r})=-\beta\rho^{1/3}\frac{x^2}{1+3\beta x\,\sinh^{-1}(x)}, \tag{2}$$

with $x=|\nabla\rho|/\rho^{4/3}$, and $\beta=0.05$. With this correction term added to the LDA, the effective potential does go as $-1/r$ asymptotically. Since the extra term added to the LDA potential is like the Becke term, it represents the correction to only the exchange component of the potential. In fact, it scales [20] like the exchange potential. To investigate its accuracy, it is therefore important that it be assessed at the level of exchange only. The total potential is then given as in Eq. (1) with $v_{\rm xc}^{\rm LDA}(\mathbf{r})$ replaced by its XO counterpart. Thus the effective exchange potential is

$$v_x(\mathbf{r})=-\left(\frac{3\rho(\mathbf{r})}{\pi}\right)^{1/3}+v^{\rm LB}(\mathbf{r}). \tag{3}$$

Since the potential above has not been derived as a functional derivative, it is not clear what the corresponding energy is. However, the exchange energy can be evaluated by applying the virial theorem based Levy-Perdew sum rule [20]

$$E_x[\rho]=-\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r}\cdot\nabla v_x(\mathbf{r}), \tag{4}$$

and is given as

$$E_x[\rho]=E_x^{\rm LDA}[\rho]-\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r}\cdot\nabla v^{\rm LB}(\mathbf{r}). \tag{5}$$

With this, the prescription for performing DFT calculations with the LB potential is complete. Within the XO case, the potential and the energy are given by Eqs. (3) and (5), respectively. If the fully correlated problem is to be solved, the LDA correlation functional and the corresponding functional derivative are added to the respective XO quantities. The results of these calculations are described below.

In Table I we present the exchange-only ground-state energies and $-\epsilon_{\rm max}$ obtained from the LB potential and the corresponding functional [see Eq. (5)] for the noble gas atoms He, Ne, and Ar, the alkaline earths Be, Mg, and Ca, and the halogen anions F$^-$ and Cl$^-$ along with their LDA and HF values [21]. As is evident, the LB potential improves upon the LDA total energies and $\epsilon_{\rm max}$ substantially. The magnitude of the total energies are, however, slightly overestimated. Significantly, whereas no stable solutions for negative ions are obtained within the LDA, the LB potential gives stable solutions for both F$^-$ and Cl$^-$ ions. However, the highest occupied orbital eigenvalue for both the ions is much smaller in magnitude than the corresponding HF value.

TABLE I. Total energies and the highest occupied eigenvalues of inert gas atoms, alkaline earths, and halogen anions in the exchange-only LDA, LDA+LB and Hartree-Fock theory.

Atom	$E_{\rm ground\ state}$			$-\epsilon_{\rm max}$		
	LDA	LDA+LB	HF [a]	LDA	LDA+LB	HF [a]
He	2.724	2.810	2.862	0.517	0.796	0.918
Ne	127.491	129.426	128.547	0.443	0.725	0.850
Ar	524.518	529.045	526.817	0.334	0.528	0.591
Be	14.223	14.533	14.573	0.170	0.283	0.309
Mg	198.249	200.890	199.615	0.142	0.254	0.253
Ca	674.160	679.615	676.758	0.111	0.208	0.196
F$^-$		100.433	99.459		0.097	0.181
Cl$^-$		461.827	459.577		0.103	0.150

[a] Reference [21].

Next we ask what happens if the LDA correlation potential is added to the XO LB potential. For this purpose we employ the Gunnarsson-Lundquist [22] correlation functional and then perform our calculations. As already demonstrated in Ref. [16], this leads to a highly accurate orbital energy for the highest occupied orbital. For completeness, and also because we have used a functional different from that in Ref. [16], we present the results for $\epsilon_{\rm max}$ in Table II. As expected the values obtained are quite accurate. In fact, these eigenvalues are in better agreement with experimental ionization energies [23] than the XO eigenvalues are with their HF counterparts. Thus, whereas the LB correction to the exchange-potential does not correct the XO eigenvalues fully, though bringing them close to the HF values, its combination with the local correlation potential does much better

TABLE II. Comparison of the highest occupied eigenvalues of the inert gas atoms, alkaline earths, and halogen anions obtained in the fully correlated LDA and LDA+LB, with their experimental ionization energies.

Atom	$-\epsilon_{\rm max}$		Ionization energy
	LDA	LDA+LB	(expt.) [a]
He	0.583	0.866	0.904
Ne	0.511	0.796	0.793
Ar	0.393	0.591	0.579
Be	0.213	0.329	0.343
Mg	0.182	0.298	0.281
Ca	0.146	0.248	0.225
F$^-$		0.152	0.125
Cl$^-$		0.154	0.133

[a] Reference [23].

TABLE III. Polarizabilities and hyperpolarizabilities of inert gas atoms, alkaline-earth atoms, and halogen anions in the exchange-only (XO) approximation with and without the LB correction to the LDA.

Atom		α			γ	
	LDA	LDA+LB	HF	LDA	LDA+LB	HF
He	1.77	1.49	1.32 [a]	114.24	54.31	36.2 [a]
Ne	3.26	2.78	2.38 [a]	268.31	116.55	71.20 [a]
Ar	12.76	12.24	10.76 [a]	2436	1476	966 [a]
Be	47.13	46.19	45.61 [b]	8.15×10^4	5.58×10^4	3.88×10^4 [b]
Mg	77.82	65.38	81.59 [c]	2.48×10^5	1.24×10^5	1.49×10^5 [c]
Ca	162.55	132.46	185.45 [c]	10.9×10^5	5.12×10^5	7.97×10^5 [c]
F^-		14.71	10.67 [d]		3.83×10^4	9×10^3 [e]
Cl^-		39.05	31.48 [d]		1.09×10^5	

[a] Reference [28].
[b] Reference [30].
[c] Reference [31].
[d] Reference [32].
[e] Reference [33].

in this respect. As such we expect the asymptotic density obtained from the full LB potential to be close to the exact density of the system, although the same may not be the case for the XO density in comparison with the HF density. Note that in Table II we have not shown the total energies, since the accuracy of the functional was already demonstrated in Table I. From the above comparison we anticipate that the fully correlated orbitals obtained from the LB potential should give accurate polarizabilities and hyperpolarizabilities for these systems. On the other hand, when compared with the LDA, the XO polarizabilities would come closer to, although still remain larger than their HF counterparts. These results are discussed in detail in Sec. III.

III. RESPONSE PROPERTIES

As noted above, we expect the LB potential to describe the response properties better than the LDA. This has already been demonstrated in connection with the linear polarizability of the Be atom, inert gas atoms, and some molecules [12,19]. In this section we obtain the linear and nonlinear polarizabilities of the atoms and ions considered above with the LB potential, and evaluate its accuracy with respect to these properties also.

We perform our calculations by employing [10] the variation-perturbation method [24] within the Kohn-Sham scheme. The method has been used extensively [10,25] in the past, and the details about the variational form for the orbitals, their orthonormalization, etc., are given in the literature. As such, we do not describe these here and discuss the results directly. We note here, though, that irrespective of the potential being employed to obtain the ground-state orbitals, the second- and fourth-order energy changes are always calculated [10] with the LDA for the exchange and correlation. Further, we have chosen the variational form for the induced densities to be a linear combination of the Slater-type orbitals optimized to give the best LDA results [8,26]. We point out that our LDA results for hyperpolarizabilities of inert gas atoms are around 10% less than that from the values of Refs. [8,9] due to the use of a different (Gunnarsson-Lundquist) functional for the correlation energy.

Shown in Table III are the polarizabilities (α) and hyperpolarizabilities (γ) for the systems under consideration within the XO approximation, along with the corresponding HF values [28–33]. We have put the noble gas atoms, the alkaline earths, and the negative ions in separate groups as their response properties behave differently in the approximations considered. For the noble gas atoms, the LDA orbitals lead to numbers which are overestimates of their exact values. The error is not so large ($\approx 10\%$) for the linear polarizabilities as it is for the hyperpolarizabilities ($\approx 100\%$). This shows the high sensitivity of nonlinear polarizabilities toward the nature of the orbitals or, equivalently, toward the structure of the approximate potential. When the LB correction is added to the LDA, the resulting values of both the polarizability and the hyperpolarizability shift toward the exact HF numbers. Moreover, the correction is substantial for the nonlinear polarizabilities. On the other hand, for alkaline-earth atoms (except Be) the LDA polarizabilities are closer to the HF numbers than the results obtained with LB corrections to the LDA. However, for the nonlinear polarizabilities the trend is opposite: compared to their LDA values, they move towards the HF with the LB correction to the LDA. Results for the polarizabilities of the inert gas atoms, along with the fact that the ground-state energies are also improved (Table I), indicate that the LB correction improves the potential all over the space including the asymptotic region. Although the energies and the highest occupied orbital eigenvalues for the other atoms are also as close to the exact values as they are for the inert gas atoms, the response properties show a different behavior. A possible explanation for this is given later in the paper.

Next, we include the correlation via the LDA (Gunnarsson-Lundquist parametrization [22]), and study its effect on the response properies. The results of these calculations are presented in Table IV. As is evident, the values of linear polarizability of inert gas atoms thus obtained are quite

TABLE IV. Same as Table III, with correlation included (XC).

Atom	α			γ		
	LDA	LDA+LB	*Ab initio*/ (Expt.)	LDA	LDA+LB	*Ab initio*/ (Expt.)
He	1.63	1.40	$1.384^{a,b}$ (1.39^{c})	82.84	42.84	43.104^{a} $(35.7^{d}, 41.7^{e})$ $(42.6^{f}, 52.4^{g})$
Ne	3.00	2.61	2.63 ± 0.03^{b} (2.67^{c})	184.89	89.87	$119\pm4^{b}, 106\pm5^{h}$ $(70.3^{e}, 95.3^{g})$
Ar	11.80	11.52	11.20 ± 0.1^{b} $(11.08)^{c}$	1631	1104	1220 ± 30^{b} $(858^{d}, 1084^{e})$ $(1096^{f}, 1251^{g})$
Be	42.97	43.28	37.30^{i}	4.59×10^{4}	3.67×10^{4}	$3.15\times10^{4\ i}$
Mg	69.78	60.55	71.69^{j} (75.0 ± 3.5^{k})	13.2×10^{4}	7.95×10^{4}	$10.18\times10^{4\ j}$
Ca	145.0	122.5	163.25^{j} 169 ± 17^{l}	5.24×10^{5}	3.15×10^{5}	$3.83\times10^{5\ j}$
F^{-}		11.93	15.50^{m}		1.35×10^{4}	$5.8\times10^{4\ m}$
Cl^{-}		33.09	36.4^{n}		4.61×10^{4}	

[a] Reference [27].
[b] Reference [28].
[c] Reference [34].
[d] Reference [37].
[e] Reference [36].
[f] Reference [35].
[g] Reference [38].
[h] Reference [29].
[i] Reference [30].
[j] Reference [31].
[k] Reference [39].
[l] Reference [40].
[m] Reference [33].
[n] Reference [32].

close to the *ab initio* results [27–29], and match well with the experimental results [34]. Similarly, the values of hyperpolarizabilities of these atoms show substantial improvement over the LDA results when compared with both the *ab initio* [27–29] and experimental numbers [35–38]. Therefore, we conclude that the combination of LB correction with LDA exchange-correlation potential produces highly accurate densities in the outer regions of these atoms. On the other hand, for alkaline-earth atoms the trend in polarizabilities and hyperpolarizabilities are similar to their XO counterpart. Thus, compared to the LB-corrected results, their LDA polarizabilities are closer to the experimental [39,40] values, whereas the hyperpolarizabilities show the opposite trend. From these results we infer that for loosely bound atoms the use of the LDA in the calculation of second- and fourth-order energy changes is not as accurate as it is for the inert gas atoms. In this connection we mention that we have employed the LDA for calculating energy changes, since it is the simplest form of the exchange-correlation energy for which the functional derivatives to any order are easily calculated. We are not aware of any other functionals for which higher-order functional derivatives are nonsingular and can be calculated as easily as for the LDA.

In Tables III and IV we also present results for F^{-} and Cl^{-}. The polarizabilities of these ions are estimated reasonably accurately both in XO and XC cases. For example, in the XC case the value of polarizability of F^{-} and Cl^{-} are lower by 23% and 9%, respectively, from their *ab initio* results [32]. In contrast, the hyperpolarizability of F^{-} is 76% smaller than its accurate value [33]. For Cl^{-} no *ab initio* hyperpolarizability result exists in the literature. But we expect that the error in the hyperpolarizabilty for this ion would also be of the same order. The large error in the results for hyperpolarizabilies of negative ions is attributed to the fact that although these anions have closed-shell structure like inert gas atoms, the valence electrons in these ions are very loosely bound. Thus the exchange and correlation play an important role in binding them [33], and the LDA may not be adequate in calculating the higher-order energy changes. This is similar to the case of the alkaline-earth atoms discussed above. Therefore, to obtain accurate response properties of such systems, one needs to go beyond the LDA in solving the higher-order equations too.

Finally, we note that recently hyperpolarizabilities of some small molecules have also been calculated [41] with the unperturbed orbitals obtained from the LB potential. These calculations also lead to nonlinear polarizabilities better than those calculated with the LDA orbitals.

IV. DISCUSSION AND CONCLUSION

In this paper we have considered the VLB correction to the LDA, and demonstrated that the potential gives accurate ground-state densities. This is reflected by the ground-state energies calculated by evaluating the exchange-energy via the virial-theorem sum rule. Moreover this potential also determines accurately the value of the highest occupied orbital eigenvalue, which is the negative of the ionization energy. In the calculation of response properties we find that LB correction to the LDA leads to significant improvement in the values of linear and nonlinear polarizabilities of inert gas atoms. The polarizabilities of the alkaline-earth atoms and the hyperpolarizabilities of the halogen anions F^- and Cl^- are not obtained satisfactorily with LB correction to the LDA. This is attributed to the use of the LDA for the exchange-correlation energy in calculating the higher-order energy changes. Motivated by the results obtained for the inert gas atoms, we are now employing the LB potential to determine the frequency-dependent response properties of these systems by using the variation-perturbation method [42,43] of the time-dependent DFT [44,45]. Further, we expect this to lead to reasonably accurate estimates of the excited states via the time-dependent DFT route [46,47].

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