

Hyperpolarizabilities of closed-shell atoms and ions in the local-density approximation

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The local-density approximation (LDA) of density-functional theory is applied to the computation of static hyperpolarizabilities of rare-gas atoms. It is found that simple LDA predicts cubic hyperpolarizabilities γ that are too large by approximately a factor of 2. It is argued that the excessive deformability of the electronic clouds in atoms predicted by LDA is an artifact of the way this approximation treats the tail of the electronic distribution. One of the causes for the poor performance of LDA in the tail region of an atom is ascribed to the presence in such a scheme of interactions of the electrons with themselves. Therefore, a modification of the LDA is considered in which self-interactions are subtracted. When applied to He, the method yields both linear and cubic dipole polarizabilities in reasonable agreement with experiments. The modified scheme is also applied to heavier rare gases and to some negative ions (H^- , F^- , Cl^-). Difficulties that are encountered in dealing with atoms (ions) with more than two electrons are overcome by limiting the self-interaction corrections to the unperturbed atom problem. A systematic reduction of the discrepancies between the calculated static hyperpolarizabilities and those inferred from recent finite frequency measurements is found.

I. INTRODUCTION

The local-density approximation¹ (LDA) to the density-functional theory of Hohenberg and Kohn² constitutes the most popular technique for studying the properties of a many-electron system.^{3,4} One of the reasons for this success lies in the simplicity of the associated computational scheme. This, in fact, only requires the solution of Hartree-like equations, in contrast with the more complex form of Hartree-Fock equations which involve a nonlocal potential. The present availability of the "exact" exchange and correlation energy of the homogeneous electron gas, as obtained by Monte Carlo simulations,⁵ eliminates the only additional source of approximation present in the LDA.

In principle, the LDA should work well in situations in which the electronic density is slowly varying. However, it has turned out to be successful in a much larger number of physical situations ranging from atoms and molecules⁶ to surfaces⁷ and bulk solids.⁶ The quality of the results depends largely on the nature of the quantities under consideration. Integrated properties such as total energies of atoms, for instance, are reproduced in most cases within 1%.⁸ On the opposite end, atomic correlation energies, which depend on the details of the electronic distribution,⁹ are off by about a factor of 2.⁸

In the case of the atomic dipole polarizability α , it has been found that LDA predictions for closed-shell atoms agree with experiments within a few percent.¹⁰⁻¹² The helium atom constitutes an extreme case with a discrepancy of 17%. In principle, an amplification of such errors would be expected in the calculations of higher polarizabilities due to the increasingly important role played by the tail of the electronic distribution, which in turn is not well treated in LDA.

In this paper we study the ability of the local-density

approximation to describe the nonlinear response of atoms to an applied electric field. The motivation for such an investigation is not only one of principle. Atomic hyperpolarizabilities have been measured, with a variety of techniques,¹³⁻¹⁷ for all rare gases up to xenon, whereas *ab initio* calculations have been performed only for lighter atoms, within the Hartree-Fock scheme.¹⁸ Also, hyperpolarizabilities are important for describing Raman scattering in ionic solids such as alkali halides.¹⁹ Of course, in this latter case in-crystal hyperpolarizabilities are needed.²⁰

Here, we limit our study to the case of closed-shell atoms or ions in a static uniform electric field. With F denoting the external field, the induced dipole moment of the atom reads²¹

$$P_\mu = \alpha F_\mu + \frac{1}{6} \gamma_{\mu\beta\gamma\delta} F_\beta F_\gamma F_\delta + \dots, \quad (1)$$

and the ground-state energy shift is given by

$$\Delta E = -\frac{1}{2} \alpha F^2 - \frac{1}{24} \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots. \quad (2)$$

The presence of the electric field also induces a quadrupole moment,

$$q_{\mu\nu} = \frac{1}{6} B_{\mu\nu,\alpha\beta} F_\alpha F_\beta. \quad (3)$$

In writing Eqs. (1)–(3) only a partial use has been made of the symmetry of the unperturbed atom. In fact, the two tensors appearing in Eqs. (1) and (3) can be written in terms of one constant each. One explicitly has

$$\begin{aligned} \gamma_{\alpha\alpha\alpha\alpha} &= \gamma, \\ \gamma_{\alpha\alpha\beta\beta} &= \gamma_{\alpha\beta\alpha\beta} = \gamma/3, \\ B_{\alpha\alpha\alpha\alpha} &= B, \\ B_{\alpha\alpha\beta\beta} &= -3B_{\alpha\beta\alpha\beta}/2 = -B/2. \end{aligned} \quad (4)$$

All the other components of the tensors are zero.

In the following, we report on LDA calculations for the static hyperpolarizabilities γ and B in some atoms and ions. The more general case of the nonlinear response to an oscillating field is at present under investigation and will be presented elsewhere.²² The main reason for this is that for the time-dependent problem we have found it convenient to use the response function technique,¹² whereas a straightforward expansion of the Kohn-Sham equations is employed here.^{11,23} A preliminary study of helium along these lines has already appeared.²³

The outline of the paper is as follows. In Sec. II we briefly describe the expansion of the Kohn-Sham equations and of the total energy in powers of the perturbing field. This yields simple formulas for B and γ . Modifications of the above scheme to take into account self-interaction corrections along the lines proposed by Perdew and Zunger²⁴ are also outlined. In Sec. III we examine the numerical consequences of adopting the simple LDA for the calculation of B and γ for rare gases. This is done through a detailed comparison with both the most recent and reliable experimental data and the results of other calculations. The effects of self-interaction corrections on the calculated hyperpolarizabilities are then critically examined in Sec. IV. Implications of these results on the present form²⁴ of self-interaction corrections are also discussed. Section V presents the results of calculation of α, B, γ for three negative ions, i.e., H^- , F^- , and Cl^- . These calculations are only performed in the scheme with self-interaction corrections, since the bare LDA does not predict binding for negative ions.^{24,25} Section VI finally summarizes the main conclusions of our analysis. Some details on the angular decomposition of Kohn-Sham equations are given in the Appendixes.

II. HYPERPOLARIZABILITIES FROM THE PERTURBATION EXPANSION OF KOHN-SHAM EQUATIONS

It has been shown by Kohn and Sham¹ that the total density of a system of N electrons in an external potential can be represented as

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2, \quad (5)$$

with the one-particle orbitals ψ_i satisfying the self-consistent equations

$$[-\nabla^2 + V(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (6)$$

where the local self-consistent potential

$$V(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + 2 \int d^3r' n(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| + V_{\text{xc}}(\mathbf{r}) \quad (7)$$

is determined by the external potential, the Hartree term, and exchange and correlation interactions. Above and throughout this paper, energies are in rydbergs and dis-

tances in Bohr radii. The exchange and correlation potential is obtained from the exchange and correlation energy functional $U_{\text{xc}}[n]$,

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta U_{\text{xc}}}{\delta n(\mathbf{r})}. \quad (8)$$

In terms of the quantities introduced above, the ground-state energy of the electron system reads

$$E = \sum_{i=1}^N \epsilon_i - \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + U_{\text{xc}} - \int d^3r n(\mathbf{r})V_{\text{xc}}(\mathbf{r}). \quad (9)$$

For an atom placed in a static electric field \mathbf{F} the external potential is

$$V_{\text{ext}}(\mathbf{r}) = -\frac{2Z}{r} + fr \cos\theta, \quad (10)$$

where Z is the nuclear charge and $f = F/F_0$ is the field in our units, with $F_0 = e/(2a_0^2)$. The effect of the electric field is to cause changes of the electronic density and ground-state energy with respect to those of the isolated atom ($f=0$). If these changes are written as an (asymptotic) expansion around $f=0$,

$$n = n^{(0)} + fn^{(1)} + f^2n^{(2)} + f^3n^{(3)} + \dots, \quad (11)$$

$$E = E^{(0)} + fE^{(1)} + f^2E^{(2)} + f^3E^{(3)} + f^4E^{(4)} + \dots, \quad (12)$$

the polarizabilities α , B , and γ may be expressed in terms of the appropriate moments of the density changes as

$$\alpha = - \int d^3r n^{(1)}(\mathbf{r})r \cos\theta, \quad (13)$$

$$B = -2 \int d^3r n^{(2)}(\mathbf{r})r^2 P_2(\cos\theta), \quad (14)$$

$$\frac{\gamma}{6} = - \int d^3r n^{(3)}(\mathbf{r})r \cos\theta. \quad (15)$$

We notice, at this point, that α and γ may also be written in terms of the energy shifts,

$$\alpha = -2E^{(2)}, \quad (16)$$

$$\gamma = -24E^{(4)}. \quad (17)$$

Thus, the calculation of α , B , and γ requires the knowledge of $n^{(1)}$, $n^{(2)}$, and $n^{(3)}$ or $E^{(4)}$. This, in turn, may be achieved in a straightforward way by expanding all quantities appearing in Eqs. (5)–(7) and Eq. (9) in powers of f . In particular,

$$\psi_i = \psi_i^{(0)} + f\psi_i^{(1)} + f^2\psi_i^{(2)} + f^3\psi_i^{(3)} + f^4\psi_i^{(4)} + \dots, \quad (18)$$

$$\epsilon_i = \epsilon_i^{(0)} + f\epsilon_i^{(1)} + f^2\epsilon_i^{(2)} + f^3\epsilon_i^{(3)} + f^4\epsilon_i^{(4)} + \dots, \quad (19)$$

$$V = V^{(0)} + fV^{(1)} + f^2V^{(2)} + f^3V^{(3)} + f^4V^{(4)} + \dots. \quad (20)$$

By substituting Eq. (11) and Eqs. (18)–(20) in Eq. (6) and collecting all the terms of the same order, one obtains

$$(H_0 - \epsilon_i^{(0)})\psi_i^{(0)} = 0, \quad (21a)$$

$$(H_0 - \epsilon_i^{(0)})\psi_i^{(1)} + (V^{(1)} - \epsilon_i^{(1)})\psi_i^{(0)} = 0, \quad (21b)$$

$$(H_0 - \epsilon_i^{(0)})\psi_i^{(2)} + (V^{(1)} - \epsilon_i^{(1)})\psi_i^{(1)} + (V^{(2)} - \epsilon_i^{(2)})\psi_i^{(0)} = 0, \quad (21c)$$

$$(H_0 - \epsilon_i^{(0)})\psi_i^{(3)} + (V^{(1)} - \epsilon_i^{(1)})\psi_i^{(2)} + (V^{(2)} - \epsilon_i^{(2)})\psi_i^{(1)} + (V^{(3)} - \epsilon_i^{(3)})\psi_i^{(0)} = 0, \quad (21d)$$

$$(H_0 - \epsilon_i^{(0)})\psi_i^{(4)} + (V^{(1)} - \epsilon_i^{(1)})\psi_i^{(3)} + (V^{(2)} - \epsilon_i^{(2)})\psi_i^{(2)} + (V^{(3)} - \epsilon_i^{(3)})\psi_i^{(1)} + (V^{(4)} - \epsilon_i^{(4)})\psi_i^{(0)} = 0. \quad (21e)$$

In the above $H_0 \equiv -\nabla^2 + V^{(0)}(\mathbf{r})$, and

$$V^{(j)}(\mathbf{r}) = -\delta_{0,j} \frac{2Z}{r} + \delta_{1,j} r \cos\theta + 2 \int d^3r' \frac{n^{(j)}(r')}{|\mathbf{r}-\mathbf{r}'|} + V_{xc}^{(j)}(\mathbf{r}). \quad (22)$$

The exchange-correlation term $V_{xc}^{(j)}(\mathbf{r})$ can be explicitly obtained by expanding $V_{xc}(\mathbf{r})$ in a functional series around $n^{(0)}(\mathbf{r})$ and collecting all the terms of order j in f . If the local-density approximation is made, then $V_{xc}(\mathbf{r}) = v_{xc}(n(\mathbf{r}))$ and $V_{xc}^{(j)}(\mathbf{r})$ can be expressed through derivatives of v_{xc} . For instance, in LDA one has

$$V_{xc}^{(1)}(\mathbf{r}) = v'_{xc}(n^{(0)}(\mathbf{r}))n^{(1)}(\mathbf{r}), \quad (23)$$

$$V_{xc}^{(2)}(\mathbf{r}) = v'_{xc}(n^{(0)}(\mathbf{r}))n^{(2)}(\mathbf{r}) + \frac{1}{2}v''_{xc}(n^{(0)}(\mathbf{r}))[n^{(1)}(\mathbf{r})]^2. \quad (24)$$

In the above equations, $v'_{xc}(n)$ and $v''_{xc}(n)$ are, respectively, the first and second derivatives of $v_{xc}(n)$ with the respect to n . Expressions for the densities of the various

$$E^{(4)} = \frac{1}{2} \int d^3r \left[\sum_{i=1}^N \{ |\psi_i^{(1)}(\mathbf{r})|^2 V^{(2)}(\mathbf{r}) + [\psi_i^{(1)*}(\mathbf{r})\psi_i^{(2)}(\mathbf{r}) + \text{c.c.}] V^{(1)}(\mathbf{r}) - \epsilon_i^{(2)} |\psi_i^{(1)}(\mathbf{r})|^2 \} + \frac{1}{12} \{ [n^{(1)}(\mathbf{r})]^4 v'''_{xc}(n^{(0)}(\mathbf{r})) + 6n^{(2)}(\mathbf{r})[n^{(1)}(\mathbf{r})]^2 v''_{xc}(n^{(0)}(\mathbf{r})) \} \right]. \quad (26)$$

To obtain Eq. (26), one proceeds as follows. First, Eq. (9) is expanded in powers of f to obtain the coefficient of f^4 , i.e., $E^{(4)}$. This contains the $\epsilon_i^{(4)}$'s. By taking a suitable combination of Eqs. (21a)–(21e) one obtains an expression for $\epsilon_i^{(4)}$ that contains $\psi_i^{(3)}$ and $\psi_i^{(4)}$ only implicitly through $V^{(3)}$ and $V^{(4)}$. This expression is then substituted back in $E^{(4)}$ and advantage is taken of the explicit definition of $V^{(j)}$ in Eq. (22). One finds that all the terms containing $\psi_i^{(3)}$ and $\psi_i^{(4)}$ cancel. We notice that Eq. (25) has been written in LDA only for convenience. One obtains a similar result for any $U_{xc}[n]$ with symmetric second-order functional derivatives. The only difference with the LDA expression (25) is the presence of functional derivatives of $V_{xc}(\mathbf{r}, [n])$ instead of derivatives of v_{xc} .

It is clear from the above discussion that the computation of α , B , and γ only requires the solution of the first- and second-order problems, in addition to the ground-state one. We notice at this point that $\epsilon_i^{(1)}$ vanishes by symmetry and

$$\epsilon_i^{(2)} = \int d^3r [|\psi_i^{(0)}(\mathbf{r})|^2 V^{(2)} + \psi_i^{(0)*}(\mathbf{r})\psi_i^{(1)}(\mathbf{r})V^{(1)}]. \quad (27)$$

Details of the angular decomposition of Eqs. (21b)–(21c), which are useful for practical applications, are given in the Appendixes.

orders may be obtained by substituting Eq. (18) in Eq. (5). The sets of equations (21a)–(21e) need to be solved in sequence and under the condition that the orbitals remain suitably normalized at each order in f^{23} . Thus, in first order with a perturbation that behaves as $\cos(\theta)$ such a condition is automatically satisfied. In second order one has to impose it explicitly:

$$\int d^3r [|\psi_i^{(1)}(\mathbf{r})|^2 + \psi_i^{(0)*}(\mathbf{r})\psi_i^{(2)}(\mathbf{r}) + \psi_i^{(0)}(\mathbf{r})\psi_i^{(2)*}(\mathbf{r})] = 0. \quad (25)$$

Also, each one of the sets of differential equations (21a)–(21e) must be solved in a self-consistent manner. The potential $V^{(j)}$, in fact, contains $n^{(j)}$ and this in turn contains all of the $\psi_i^{(j)}$, $i=1, N$.

So far, it would seem that the calculation of γ requires the knowledge of $\psi_i^{(j)}$'s up to the third order, at least. However, by using the alternative definition of γ given in Eq. (12) it can be easily shown that this is not the case. The fourth-order energy only requires the knowledge of $\psi_i^{(j)}$ up to second order,²⁶

The computational scheme that we have described in the foregoing paragraphs can be practically implemented when a choice for $V_{xc}(\mathbf{r})$ is made. In the following we shall use the local-density approximation. For the exchange-correlation potential of the homogeneous unpolarized electron gas, we utilize the Ceperly-Alder Monte Carlo results⁵ as parametrized by Perdew and Zunger.²⁴

The above computational scheme is simply modified to correct the LDA for self-interactions, in the manner proposed by Perdew and Zunger.²⁴ We just list, here, the necessary changes. The potentials of Eqs. (21a)–(21e) become orbital dependent,

$$V_i^{(j)} = V^{(j)} + \delta V_i^{(j)}, \quad (28)$$

with $V^{(j)}$ still given by Eq. (22) and

$$\delta V_i^{(j)} = -2 \int d^3r' \frac{n_i^{(j)}(r')}{|\mathbf{r}-\mathbf{r}'|} - \delta V_{xc,i}^{(j)}(\mathbf{r}). \quad (29)$$

Above, $n_i^{(j)}$ is the coefficient of f^j in the expansion of

$$n_i(\mathbf{r}) = |\psi_i(\mathbf{r})|^2 \quad (30)$$

and within the LDA,

$$\delta V_{xc,i}^{(1)}(\mathbf{r}) = \bar{v}'_{xc}(n_i^{(0)}(\mathbf{r}))n_i^{(1)}(\mathbf{r}), \quad (31)$$

$$\delta V_{xc,i}^{(2)}(\mathbf{r}) = \bar{v}'_{xc}(n_i^{(0)}(\mathbf{r}))n_i^{(2)}(\mathbf{r}) + \frac{1}{2}\bar{v}''_{xc}(n_i^{(0)}(\mathbf{r}))[n_i^{(1)}(\mathbf{r})]^2, \quad (32)$$

with $\bar{v}_{xc}(n)$ the exchange correlation potential of a homo-

geneous polarized electron gas. The fourth-order energy is changed to

$$E_{\text{SIC}}^{(4)} = E^{(4)} + \delta E^{(4)}, \quad (33)$$

with $E^{(4)}$ still given by Eq. (26), and

$$\delta E^{(4)} = \frac{1}{2} \int d^3r \sum_{i=1}^N [|\psi_i^{(1)}(\mathbf{r})|^2 \delta V_i^{(2)}(\mathbf{r}) + [\psi_i^{(1)*}(\mathbf{r})\psi_i^{(2)}(\mathbf{r}) + \text{c.c.}] \delta V_i^{(1)}(\mathbf{r}) + \frac{1}{12} \{ [n_i^{(1)}(\mathbf{r})]^4 \bar{v}'''_{xc}(n_i^{(0)}(\mathbf{r})) + 6n_i^{(2)}(\mathbf{r})[n_i^{(1)}(\mathbf{r})]^2 \bar{v}''_{xc}(n_i^{(0)}(\mathbf{r})) \}]. \quad (34)$$

For \bar{v}_{xc} in the application of this modified scheme, we shall consistently use the parametrization²⁴ of the results of Monte Carlo simulations.⁵

Before turning to the analysis of the predictions of LDA and self-interaction-correlated LDA (SIC-LDA) for hyperpolarizabilities, it is worth noting that the present formulation is easily extended to the spin-density-functional theory²⁷ to treat open-shell systems. However, such an extension requires an additional approximation—that of spherical averaging over magnetic quantum numbers.

III. LDA HYPERPOLARIZABILITIES OF RARE GASES

Solutions to Eqs. (21a)–(21c) have been obtained by using the Numerov method. For the ground-state problem, self-consistency in energy within one part in 10^6 was readily achieved. First- and second-order equations were then solved, requiring an accuracy of one part in 10^4 on α , B , and γ , respectively. Values of α, B, γ calculated from Eqs. (13) and (14), Eq. (17), and Eq. (26), are given in units of $a_0^3, a_0^6/e$ and a_0^7/e^2 , respectively.

We have first performed calculations with the Gunnarsson-Lundquist parametrization²⁷ of v_{xc} to reproduce the published values for the dipole polarizability α of rare gases.^{10–12} After this preliminary result all subsequent calculations were performed using a suitable parametrization²⁴ of the “exact” Monte Carlo results⁵ for v_{xc} .

This choice was motivated by the obvious consideration that, to assess the accuracy of LDA, one should avoid any additional approximation. We find, in fact, that the use of the exact v_{xc} increases the value of the dipole polarizability of rare gases between 2% and 4%, compared to those obtained from the Gunnarsson-Lundquist v_{xc} . This makes the agreement with experiments a little worse, yielding relative discrepancies ranging from a minimum of 5% for Xe, to a maximum of 20% for He.

Our results for the static dipole hyperpolarizability γ of rare gases from He to Xe are reported in Table I. Four sets of experimental data are also shown. The experimental static hyperpolarizabilities reported in Table I have been obtained by extrapolation from the original data, which were at finite frequencies, in the range between 4880 and 10550 Å. For this purpose, the measured dispersion of $\gamma(\omega)$ for Ar, Kr, and Xe as observed by Mizrahi and Shelton¹⁶ and Shelton,¹⁶ was used. Also, the one-resonance model put forward by Shelton¹⁶ was utilized to transfer the dispersion of $\gamma(\omega)$ from the first data set to the other ones. Such a model is expected to have an accuracy¹⁶ of only 10–20%. This should be enough for our present purposes. The dispersion of $\gamma(\omega)$ for He was taken from the accurate variational results of Sitz and Yaris.²⁸ These results are commonly quoted as having a relative accuracy of 1%. In addition, they were used in the electric-field-induced second-harmonic generation (ESHG) experiment of Mizrahi and Shelton,¹⁶ to get abso-

TABLE I. Hyperpolarizability $\gamma/6$ of rare gases. Comparison of local-density-approximation results with experiments. All numbers are in units of 10^{-39} esu. The experimental static hyperpolarizabilities (with footnote indicators (a–d) have been obtained by extrapolation from finite frequency measurements. For details about the extrapolation and meaning of the symbols see text.

	$\gamma/6$ (10^{-39} esu)				
	He	Ne	Ar	Kr	Xe
LDA	7.40	17.7	156	332	769
ESHG ^a	3.58 ^c		92±2	188±4	404±8
THG ^b	3.5±0.4	5.9±0.6	72±7	174±17	403±40
FWM ^c	3.0±0.7		105±19	229±41	
dc Kerr ^d	4.4±0.3	8.0±0.6	91±6	202±14	489±38

^aReference 16.

^bReference 17.

^cReference 15.

^dReference 14.

^eAccurate theoretical value by Sitz and Yaris (Ref. 28) used as reference value in the electric-field-induced second-harmonic generation (ESHG) measurements (Ref. 16).

lute values for $\gamma_{Ar}(\omega)$. The measurements for Ar of these workers were in fact relative to γ_{He} . Similarly, Shelton¹⁶ measured the ratios γ_{Kr}/γ_{Ar} and γ_{Xe}/γ_{Ar} . For Ne we took an ESHG dispersion coefficient lying between those of He and Ar. We notice that if one chooses either extreme (He or Ar) one would still obtain for Ne numbers agreeing with those of Table I, within the reported uncertainties. We should also add that in the uncertainties reported for the last three data sets [third-harmonic generation (THG), four-wave mixing (FWM), and dc-Kerr] no allowance was made for the uncertainties due to the use of the one-resonance model. In spite of this, if we restrict ourselves to the most recent experiments, i.e., ESHG, THG, FWM, we find agreement within the quoted uncertainties for all the rare gases, with the exception of the THG value for Ar. This gives confidence in the reliability of these latter experimental data.

The comparison of the LDA predictions for γ with the experimental values from four different kinds of measurements presented in Table I clearly shows a systematic tendency of the theory to overestimate γ by about a factor of 2. This appears as a large amplification of the discrepancies previously found in the case of the dipole polarizability α . We have found that the use of the Gunnarsson-Lundquist parameterization only lowers the LDA values of Table I by about 10%, leaving the substantial disagreement shown in Table I unchanged.

Thus, LDA makes atoms too easy to deform. It is tempting to argue, that such a failure of LDA is due to its deficiency in describing the tail of the electronic distribution. The ground-state LDA potential approaches zero exponentially rather than as r^{-1} . One clear mark of such a failure is the large values of the LDA energy of the uppermost occupied atomic orbital.²⁴ Also, the LDA values²⁹ for the second density moment $\langle r^2 \rangle$ are too large. A simple modification of the LDA, which has proven successful in dealing with the above problems,^{24,29} is due to Perdew and Zunger.²⁴ They have proposed a new scheme for the subtraction of self-interactions from approximate density functionals. We shall study the applicability and the effect of such self-interaction correlations (SIC) in the calculation of atomic hyperpolarizabilities in the next section.

The calculated values of the quadrupole hyperpolarizability B turn out to be negative, ranging from -5.75×10^{-40} esu for He to -421×10^{-40} esu for Xe. One would expect them to be too large in absolute value, in analogy with the results of α and γ . However, no experimental data are available for this hyperpolarizability. We notice that the value of B for He reported in Ref. 23 should be multiplied by -2 .

IV. THE EFFECT OF SELF-INTERACTION CORRECTIONS ON THE POLARIZABILITIES OF RARE GASES

Self-interaction corrections may be taken into account in the LDA with simple modifications, as we have discussed in Sec. II. For closed-shell atoms or ions they amount to having shell-dependent potentials in the Kohn-Sham equations. This causes the complication that

one should explicitly impose the orthogonality for orbitals with the same angular momentum. However, it has been found that the degree of nonorthogonalization is very small.²⁴ Also, the changes in orbital energy resulting from the orthogonalization are practically negligible^{24,30} for isolated atoms. Since we are looking for major changes in our calculated hyperpolarizabilities, we will completely neglect the orthogonalization problem in the following. With such a choice numerical computations proceed essentially as for the bare LDA, apart from the need of calculating a potential for each shell at each iteration of the self-consistent equations (21a)–(21c).

In the case of He, however, the orthogonalization problem does not arise due to the presence of the $1S$ shell only. On the other hand, in the case of heavier rare gases a much more serious problem is encountered in the application of the self-interaction-corrected LDA (SIC-LDA). It is found, in fact, that the self-interaction corrections as proposed by Perdew and Zunger²⁴ cannot be consistently carried out beyond the isolated-atom problem. They would yield, in fact, first- and second-order potentials with divergences at the locations of the zeros of the isolated-atom orbitals. This is easily understood. Near a zero of the density n , the exchange-correlation potential of the homogeneous electron gas has a leading term that behaves as $n^{1/3}$. The first- and second-order potentials [Eqs. (23) and (24) and Eqs. (31) and (32)] will then have terms like $\sim n^{(1)}/(n^{(0)})^{2/3}$ and $\sim n^{(2)}/(n^{(0)})^{2/3}$, $(n^{(1)})^2/(n^{(0)})^{4/3}$, respectively. In bare LDA this does not cause any problem. The total density vanishes only at infinity where $n^{(1)}$ and $n^{(2)}$ also vanish. In SIC-LDA, on the other hand, the zero-order orbital densities appear explicitly. This yields denominators that vanish near a node. Unless the first- and second-order orbitals vanish at the same point in a suitable manner, the corresponding exchange and correlation potential blows up. We have not found any reason for such a vanishing of higher-order orbitals, nor have we found it in numerical calculations.

Because of the difficulties discussed above, in the case of heavier rare gases we have corrected the LDA for self-interactions only in the zero-order problem. Thus, to gain some orientation as to the effects of such partial corrections, we first discuss below the case of He.

In Table II we report α, B, γ from two different calculations for He. The calculation labeled SIC was carried out taking into account self-interaction corrections in all orders according to the formulas given at the end of Sec. II. The results labeled partial SIC (PSIC) were obtained by dropping such corrections from the first- and second-order problem, namely, neglecting $\delta V_i^{(1)}$ and $\delta V_i^{(2)}$. It is clear that at least for helium, the major effect of self-interaction corrections are reflected in the polarizabilities through the modification of the free-atom orbitals. Let us first consider the dipole polarizability α . The experimental value for He is 0.205×10^{-24} cm³, whereas LDA gave 0.246×10^{-24} cm³. As expected, the effect of the self-interaction subtraction is to make the atom more rigid. The value of α decreases by 27%, improving the agreement with experiments from +20% to -7%. The effect of changing from SIC to PSIC has an effect of only 2%.

TABLE II. Effect of full self-interaction correction (SIC) and partial self-interaction correction (PSIC) in the calculation of the polarizabilities α, B, γ for He.

	α (10^{-24} cm ³)	B (10^{-40} esu)	$\gamma/6$ (10^{-39} esu)
SIC	0.191	-2.82	2.77
PSIC	0.195	-3.03	2.92

The comparison of the values of γ reported in Tables I and II reveals a much more dramatic effect. Changing from LDA to SIC, the discrepancy with the accurate value of Sitz and Yaris²⁸ changes from 107% to -23%. Again, dropping the self-interaction corrections in the first- and second-order equations has an effect of only 4%. Similar changes are found for B . The overall effect of self-interaction corrections, in the LDA calculation of He, is to make this atom a little more rigid than experimentally found. This is also reflected in the fact that the SIC-LDA total energy of He is lower than the experimental one. The agreement with experiments, however, is substantially improved over that of bare LDA.

In Table III, results for the hyperpolarizability γ of heavier rare gases are recorded. They were obtained with partial self-interaction corrections. The values of the quadrupole hyperpolarizability B are also shown. Compared to the LDA values of Table I, a systematic lowering of γ is found. This improves the agreement with the experimental data. However, the relative effect of the self-interaction corrections becomes smaller for the heavier atoms as expected. Thus, for Ne and Ar a reasonable agreement is now found with the experimental data, with discrepancies reduced to $\sim 20\%$. On the other hand the PSIC values of γ for Kr and Xe are still too large. They overestimate the experimental data by $\sim 40\%$ and $\sim 70\%$, respectively.

An important difference has to be noticed between LDA and PSIC hyperpolarizabilities of rare gases. The local-density approximation consistently predicts in all cases atoms that are too soft. The effect of our partial self-interaction correction is to make them more rigid. It appears as if the size of the correction becomes progressively smaller in moving from He to Xe. While there are reasons to expect this we feel that one cannot rule out the possibility that this is an artifact of the present form of self-interaction corrections; in particular, because of the fact that for heavier atoms it is not possible to fully correct for self-interactions in the higher-order calcula-

TABLE III. Hyperpolarizabilities γ and B for heavier rare gases; the calculations were performed with partial self-interaction correction (PSIC).

	Ne	Ar	Kr	Xe
$\gamma/6$ (10^{-39} esu)	7.18	112	269	701
B (10^{-40} esu)	-6.95	-81.2	-176	-417

tions.

The only other *ab initio* calculations of the hyperpolarizability γ for rare gases appearing in the literature have been carried out at the Hartree-Fock level. Here, we refer to the most recent calculation due to Sitter and Hurst.¹⁸ Their values for $\gamma/6$ are 3.02×10^{-39} cm for He, 3.52×10^{-39} cm for Ne, and 84.8×10^{-39} cm for Ar. These show roughly the same degree of agreement with experiments as the PSIC results.

V. POLARIZABILITIES OF SOME FREE NEGATIVE IONS

Negative ions represent a very difficult test for atomic theories. The bare LDA does not give any binding unless the ion is artificially placed in a spherical box.²⁵ Hartree-Fock³² predicts binding energies that are too small, in some cases, and fails completely in other cases, such as for H^- . It has been found, however, that with the inclusion of self-interaction corrections LDA is able to predict binding²⁴ for negative ions, yielding binding energies that are in good agreement with experiments.

Here, we shall examine the predictions of the SIC-LDA for the polarizabilities α, B, γ of three free negative ions: H^- , F^- , and Cl^- . We stress that the present results should not be compared with polarizabilities obtained from measurement on ions in crystals. Large differences are, in fact, to be expected in the two cases, due to crystal-field and overlap effects.³¹⁻³³

The results of the present calculations are shown in Tables IV and V. We draw attention to the fact that for F^- and Cl^- only a partial account of self-interaction corrections was feasible, for the same reasons discussed at length for rare gases. However, for H^- the predictions of both full and partial SIC-LDA are reported. The results for the dipole polarizability α are compared with the predictions of full (or coupled) Hartree-Fock (CHF) with and without many-body perturbation (MP) corrections. It is found that the present modified LDA yields predictions that are comparable to those of CHF. In fact, they are somewhat better. The present value of α for Cl^- practically coincides with that of the corrected Hartree-Fock calculation. For H^- , results of a variational calculation provide exact upper and lower bound for the dipole polarizability, $\alpha = 30.5 \pm 0.4$. A comparison with the values in Table IV, shows a substantial underestimate of α for H^- by the SIC-LDA. As in the case of He, the present form of self-interaction corrections make the ion H^- too rigid. It is illuminating, in this respect, to look at the value of the uppermost (which in this case is also the first) Kohn-Sham eigenvalue. It has been shown that this coincides with the negative of the ionization potential of the atom or ion³⁴ in question and determines the long-distance decay of the electronic density. We find that in the SIC-LDA calculation of H^- the Kohn-Sham eigenvalue is more than twice larger, in absolute value, than the measured ionization potential (which in the present case is the same as the affinity of the hydrogen atom). We also notice that for He a discrepancy in the same direction was found: it was, however, of only 5%.

The results of the present calculation for B and γ are recorded in Table V. We notice that for F^- in Hartree-

TABLE IV. Dipolar polarizability α of negative ions from local-density approximation with partial self-interaction corrections. All numbers are in unit of 10^{-24} cm³.

	α (10^{-24} cm ³)		
	H ⁻	F ⁻	Cl ⁻
PSIC ^a	12.0 (10.8)	1.80	5.47
CHF ^b		1.58	4.66
CHF + MP ^b		2.48	5.49

^aThe value in parentheses is from a full SIC calculation.

^bResults from full Hartree-Fock calculations (Ref. 31) with and without many-body perturbation corrections (MP). The many-body perturbation corrections were included up to second order.

Fock it was found³¹ that $\gamma/6 > 836 \times 10^{-39}$ esu. This agrees with the present value of 1200×10^{-39} cm. Also, we argue that our values of B and γ for H⁻ should provide, respectively, an upper and lower bound for the true values.

VI. SUMMARY AND CONCLUSIONS

In this paper we have investigated the adequacy of the local-density approximation in describing the static response of an atom or ion to an applied electric field. We have shown that the calculation of nonlinear polarizabilities represents a very severe test for the theory in that a greater sensitivity to the details of the approximate description arises. In particular, it has been found that the LDA largely overestimates the cubic dipole polarizability of rare-gas atoms.

In an attempt to compensate for the excessive softness of LDA atoms, we have considered the effect of self-interaction corrections to LDA. We have indeed obtained a systematic reduction of the calculated polarizabilities of rare gases. However, severe difficulties related to the present form of self-interaction corrections have been encountered. These, in turn, pose some questions about the general validity of self-interaction corrections as proposed by Perdew and Zunger.²⁴ Calculation in this modified LDA scheme have been carried out also for the very delicate case of negative ions.

The comparison of the results of the present study with those of other *ab initio* calculations shows that the present modified LDA scheme yields polarizabilities and hyperpolarizabilities that overall are of a quality comparable to

TABLE V. Hyperpolarizabilities B and γ for negative ions from local-density approximation with partial self-interaction correction.

	H ⁻	F ⁻	Cl ⁻
B (10^{-40} esu)	-0.242×10^5 -0.179×10^5 ^a	-318	-0.168×10^4
$\gamma/6$ (10^{-39} esu)	0.288×10^6 0.196×10^6 ^a	0.120×10^4	0.723×10^4

^aResults of a full SIC calculations.

that of Hartree-Fock calculations. This is obtained, however, with a fraction of the effort required for the solution of Hartree-Fock equations.

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APPENDIX A: ANGULAR DECOMPOSITION OF THE FIRST-ORDER KOHN-SHAM EQUATIONS

The special cases of *s*-, *p*-, and *d*-shell ions have been considered by Mahan.¹¹ The discussion given in this appendix is not only for any general *l*, but also paves the way for the more complicated higher-order equations. We consider the first-order equation (21b) in the case in which the closed-shell atom or ion is perturbed by a potential of the form

$$V'(r) = fg_M(r)P_M(\cos\theta). \quad (A1)$$

The dipole perturbation is obtained by choosing $M=1$ and $g_M(r)=r$.

In the isolated atom the orbitals are labeled by $i \equiv (n, l, m, \sigma)$. However, in the following we shall drop the spin-projection quantum number and introduce factors of 2 in the sums over occupied states. The explicit form of the unperturbed orbitals is

$$\psi_{nlm}^{(0)}(r) = \frac{R_{nl}(r)}{r} Y_l^m(\Omega), \quad (A2)$$

and the corresponding unperturbed density is

$$\begin{aligned} n^{(0)}(r) &= 2 \sum_{n,l,m}^{\text{occ}} |\psi_{nlm}^{(0)}(r)|^2 \\ &= \frac{1}{2\pi r^2} \sum_{n,l}^{\text{occ}} (2l+1) R_{nl}^2(r). \end{aligned} \quad (A3)$$

Since the magnetic quantum number m is conserved with a perturbation like that in Eq. (A1), we can write

$$\psi_{nlm}^{(1)}(r) = \sum_j \frac{u_{nlmj}^{(1)}(r)}{r} Y_j^m(\Omega). \quad (A4)$$

It immediately follows that

$$\begin{aligned} n^{(1)}(r) &= 4 \sum_{n,l,m} \text{Re}[\psi_{nlm}^{(0)*}(r)\psi_{nlm}^{(1)}(r)] \\ &= \sum_h n_h^{(1)}(r) P_h(\cos\theta), \end{aligned} \quad (A5)$$

where

$$n_h^{(1)}(r) = \frac{2h+1}{\pi r^2} \sum_{n,l,m,j} C(lj, m|h) R_{nl}(r) U_{nlmj}^{(1)}(r). \quad (A6)$$

Above, the coefficient $C(lj, m|h)$ originates from the decomposition of the product of two spherical harmonics and can be written in terms of Wigner 3-*j* symbols³⁵ as

$$C(lj, m | h) = (-1)^m [(2l+1)(2j+1)]^{1/2} \times \begin{bmatrix} l & j & h \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & j & h \\ m & -m & 0 \end{bmatrix}. \quad (\text{A7})$$

Notice that it is invariant both under the interchange of l with j and of m to $-m$. From Eqs. (22) and (23) and Eq. (A5) one easily gets

$$V^{(1)}(\mathbf{r}) = \sum_h V_h^{(1)}(r) P_h(\cos\theta), \quad (\text{A8})$$

with

$$V_h^{(1)}(r) = \delta_{h,M} g_M(r) + \frac{8\pi}{2h+1} \int dr' r'^2 n_h^{(1)}(r') \frac{r_{<}^h}{r_{>}^{h+1}} + v'_{xc}(n^0(r)) n_h^{(1)}(r) \quad (\text{A9})$$

and $r_{>}$ ($r_{<}$) the greater (the smaller) of r and r' . We also define

$$H_0^j = -\frac{d^2}{dr^2} + \frac{j(j+1)}{r^2} + V^{(0)}(r) \quad (\text{A10})$$

In terms of the quantities defined above, Eq. (21b) becomes equivalent to a set of equations

$$(H_0^j - \epsilon_{nl}^{(0)}) \tilde{U}_{nlhj}^{(1)} = [(2l+1)(2j+1)/(2h+1)]^{1/2} \begin{bmatrix} l & j & h \\ 0 & 0 & 0 \end{bmatrix} R_{nl} (\delta_{j,l} \epsilon_{nlh}^{(1)} - V_h^{(1)}). \quad (\text{A15})$$

An important feature of such equations is that they are "diagonal in h ." This means that $V_h^{(1)}$ only contains functions $\tilde{U}_{nlh'j}^{(1)}$ with $h'=h$. One immediate consequence of this property is that the radial functions $\tilde{U}_{nlhj}^{(1)}$ with $h \neq M$ do not depend in anyway on the external perturbation g_M and, therefore, they must vanish. For the same reason when $h=M$ the only nonzero radial functions are those for which

$$\begin{bmatrix} l & j & M \\ 0 & 0 & 0 \end{bmatrix} \neq 0, \quad (\text{A16})$$

which requires that $j=l+M$, $l+M-2, \dots, |l-M|$. One can further write

$$\tilde{U}_{nlhj}^{(1)} = [(2l+1)(2j+1)/(2h+1)]^{1/2} \begin{bmatrix} l & j & h \\ 0 & 0 & 0 \end{bmatrix} U_{nlj}^{(1)} \delta_{h,M}, \quad (\text{A17})$$

where, for the allowed values of j , $U_{nlj}^{(1)}$ satisfy the equation

$$(H_0^j - \epsilon_{nl}^{(0)}) U_{nlj}^{(1)} = R_{nl} (\delta_{j,l} \epsilon_{nlM}^{(1)} - V_M^{(1)}). \quad (\text{A18})$$

In terms of the new radial functions one has

$$U_{nlmj}^{(1)} = C(lj, m | M) U_{nlj}^{(1)} \quad (\text{A19})$$

and

$$n_h^{(1)} = \delta_{h,M} \sum_{n,l,j} [(2l+1)(2j+1)]^{1/2} C(lj, 0 | M) \frac{R_{nl} U_{nlj}^{(1)}}{\pi r^2}. \quad (\text{A20})$$

$$(H_0^j - \epsilon_{nl}^{(0)}) U_{nlmj}^{(1)} = R_{nl} \sum_h C(lj, m | h) (\delta_{j,l} \epsilon_{nlh}^{(1)} - V_h^{(1)}), \quad (\text{A11})$$

for the radial functions $U_{nlmj}^{(1)}$. For arbitrary M the first-order energy appearing in Eq. (A11) is defined as

$$\epsilon_{nlh}^{(1)} = \int_0^\infty dr R_{nl}^2(r) V_h^{(1)}(r). \quad (\text{A12})$$

Equation (A11) can be put in a simpler form by noting that only a particular linear combination of the $U_{nlmj}^{(1)}$ enters $n_h^{(1)}$. This suggests setting

$$\tilde{U}_{nlhj}^{(1)} = \sum_m [A(lj)]_{hm} U_{nlmj}^{(1)}, \quad (\text{A13})$$

with

$$[A(lj)]_{hm} = (-1)^m (2h+1)^{1/2} \begin{bmatrix} l & j & h \\ m & -m & 0 \end{bmatrix}. \quad (\text{A14})$$

The matrix $A(lj)$ is orthogonal, as can easily be checked using the known properties of the 3- j symbols.³⁶ Therefore, one can work with the functions $\tilde{U}_{nljh}^{(1)}$'s. They obey the equations

It should be noticed that for $2l > M$ and M even, j can take the value l . In such a case the conditions $U_{nl}^{(1)}(0) = U_{nl}^{(1)}(\infty) = 0$ do not completely fix $U_{nl}^{(1)}(r)$. One has the freedom of adding to $U_{nl}^{(1)}$ a function of the form CR_{nl} with C being a constant, since R_{nl} is a solution of the homogeneous equation which is obtained from Eq. (A18) by putting the right-hand side to zero. The normalization of the orbital (nlm), however, requires $U_{nlm}^{(1)}$ to be orthogonal to R_{nl} . This condition fixes $U_{nl}^{(1)}$ completely.

The results of the present decomposition of the first-order Kohn-Sham equations (21b) are equivalent to the explicit forms for s , p , and d shells given by Mahan.¹¹ However, our formulas are valid for any l and M . Also, the present analysis is preliminary to that of the more involved second-order equations. We notice that the coefficients $C(lj, m | M)$, defined in Eq. (A7), can be easily calculated from tables of 3- j symbols such as those by Rotenberg *et al.*³⁶

APPENDIX B: ANGULAR DECOMPOSITION OF THE SECOND-ORDER KOHN-SHAM EQUATIONS

We start by writing the second-order orbitals as

$$\psi_{nlm}^{(2)}(\mathbf{r}) = \sum_k \frac{U_{nlmk}^{(2)}(r)}{r} Y_k^m(\Omega). \quad (\text{B1})$$

Hence, the second-order density reads

$$\begin{aligned} n^{(2)}(\mathbf{r}) &= \sum_{n,l,m} \{ 2 |\psi_{nlm}^{(1)}(\mathbf{r})|^2 + 4 \operatorname{Re}[\psi_{nlm}^{(0)*}(\mathbf{r})\psi_{nlm}^{(2)}(\mathbf{r})] \} \\ &= \sum_h n_h^{(2)}(r) P_h(\cos\theta), \end{aligned} \quad (\text{B2})$$

where

$$n_h^{(2)}(r) = \bar{n}_h^{(2)}(r) + \bar{\bar{n}}_h^{(2)}(r), \quad (\text{B3})$$

and

$$\bar{n}_h^{(2)}(r) = \frac{2h+1}{2\pi r^2} \sum_{n,l,j,j'} B^M(l,j,j'|h) U_{nlj}^{(1)}(r) U_{nlj'}^{(1)}(r), \quad (\text{B4})$$

$$\bar{\bar{n}}_h^{(2)}(r) = \frac{2h+1}{\pi r^2} \sum_{n,l,m,k} C(lk,m|h) R_{nl}(r) U_{nlmk}^{(2)}(r). \quad (\text{B5})$$

The new coefficient in Eq. (B4) has the explicit expression

$$B^M(l,j,j'|h) = (-1)^{l+j+j'} (2l+1)(2j+1)(2j'+1) \begin{Bmatrix} l & j & M \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} l & j' & M \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} j & j & h \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} M & M & h \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} M & M & h \\ j & j' & l \end{Bmatrix}, \quad (\text{B6})$$

where the last symbol on the right-hand side of Eq. (B6) is a 6- j symbol.^{35,36} Equation (B2) implies

$$V^{(2)}(\mathbf{r}) = \sum_h V_h^{(2)}(r) P_h(\cos\theta), \quad (\text{B7})$$

with

$$V_h^{(2)}(r) = \frac{8\pi}{2h+1} \int dr' r'^2 n_h^{(2)}(r') \frac{r'^h}{r^{h+1}} + v'_{xc}(n^{(0)}(r)) n_h^{(2)}(r) + \frac{1}{6} v''_{xc}(n^{(0)}(r)) [n^{(1)}(r)]^2 \frac{2h+1}{2M+1} C(MM,0|h). \quad (\text{B8})$$

For future reference, we notice that last term on the right-hand side of the above equation has a nonvanishing coefficient only for $h=0,2,\dots,2M$.

In analogy with the first-order case we now write the equation obeyed by $U_{nlmk}^{(2)}$:

$$\begin{aligned} (H_0^k - \varepsilon_{nl}^{(0)}) U_{nlmk}^{(2)} &= C(lk,m|M) C(ll,m|M) \varepsilon_{nlM}^{(1)} U_{nlmk}^{(1)} - \sum_j C(jk,m|M) C(lj,m|M) V_M^{(1)} U_{nlj}^{(1)} \\ &\quad + \delta_{k,l} \sum_h \left[C(ll,m|h) \int_0^\infty dr R_{nl}^2 V_h^{(2)} + \delta_{n,M} \sum_j C(lj,m|h) C(lj,m|M) \int_0^\infty dr R_{nl} U_{nlj}^{(1)} V_M^{(1)} \right] R_{nl} \\ &\quad - R_{nl} \sum_h C(lk,m|h) V_h^{(2)}. \end{aligned} \quad (\text{B9})$$

The third term on the right-hand side of the above equation is the second-order energy, which has been written explicitly. We then consider the orthogonal transformation

$$\tilde{U}_{nlhk}^{(2)} = \sum_m [A(lk)]_{hm} U_{nlmk}^{(2)}, \quad (\text{B10})$$

where the matrix $A(lk)$ has been defined in Eq. (A14). The equation for the new radial functions reads

$$\begin{aligned} (H_0^k - \varepsilon_{nl}^{(0)}) \tilde{U}_{nlhk}^{(2)} &= \delta_{h,M} [(2l+1)(2k+1)/(2h+1)]^{1/2} \begin{Bmatrix} l & k & h \\ 0 & 0 & 0 \end{Bmatrix} C(ll,m|M) \varepsilon_{nlk}^{(1)} U_{nlk}^{(1)} \\ &\quad - \sum_j \left[\sum_m [A(lk)]_{hm} C(lj,m|M) C(jk,m|M) \right] \left[V_M^{(1)} U_{nlj}^{(1)} - \delta_{k,l} \int_0^\infty dr R_{nl} U_{nlj}^{(1)} V_M^{(1)} \right] \\ &\quad + [(2l+1)(2k+1)/(2h+1)]^{1/2} \begin{Bmatrix} l & k & h \\ 0 & 0 & 0 \end{Bmatrix} R_{kl} \left[\delta_{k,l} \int_0^\infty dr R_{nl}^2 V_h^{(2)} - V_h^{(2)} \right]. \end{aligned} \quad (\text{B11})$$

We note that for $\begin{pmatrix} l & k & h \\ 0 & 0 & 0 \end{pmatrix} = 0$ the first and third terms on the right side of Eq. (B11) vanish. It can be shown that the same happens to the second term. Thus, for $\begin{pmatrix} l & k & h \\ 0 & 0 & 0 \end{pmatrix} = 0$ and $k \neq l$ the functions $\tilde{U}_{nlhk}^{(2)}$ must vanish. In the particular case in which $\begin{pmatrix} l & k & h \\ 0 & 0 & 0 \end{pmatrix} = 0$ and $k=l$, one would get a solution of the form $\tilde{U}_{nlhk}^{(2)} = C R_{nl}$. However, the normalization condition for the Kohn-Sham orbitals in second order forces $C=0$. One condition on the indices k and h in order to obtain nonvanishing solutions to Eq. (B11) is

$$\begin{Bmatrix} l & k & h \\ 0 & 0 & 0 \end{Bmatrix} \neq 0. \quad (\text{B12})$$

Because of the condition (B12) one can define

$$\tilde{\bar{U}}_{nlhk}^{(2)} = [(2l+1)(2k+1)/(2h+1)]^{1/2} \begin{Bmatrix} l & k & h \\ 0 & 0 & 0 \end{Bmatrix} \tilde{U}_{nlhk}^{(2)} \quad (\text{B13})$$

and, in terms of the new functions $\tilde{\bar{U}}_{nlhk}^{(2)}$, write Eq. (B11) as

$$\begin{aligned}
 (H_0^k - \varepsilon_{nl}^{(0)}) \bar{U}_{nlhk}^{(2)} &= \delta_{h,M} C(l, m | M) \varepsilon_{nlM}^{(1)} U_{nlk}^{(1)} & B^M(l, jj' | h) \neq 0 & \quad (B22) \\
 &- \sum_j D^M(j, lk | h) V_M^{(1)} U_{nlj}^{(1)} & \text{or} & \\
 &+ (\delta_{l,k} \varepsilon_{nlh}^{(2)} - V_h^{(2)}) R_{nl} . & \delta_{h,M} C(l, m | M) \neq 0 , & \quad (B23)
 \end{aligned}
 \tag{B14}$$

Here,

$$D^M(j, lk | h) = \frac{(2h+1)B^M(j, lk | h)}{(2k+1)^{1/2}(2l+1)^{1/2}C(lk, 0 | h)} \tag{B15}$$

and

$$\begin{aligned}
 \varepsilon_{nlh}^{(2)} &= \int_0^\infty dr R_{nl}^2 V_h^{(2)} \\
 &+ \int_0^\infty dr R_{nl} V_M^{(1)} \sum_j D^M(j, ll | h) U_{nlj}^{(1)} .
 \end{aligned}
 \tag{B16}$$

We also notice that

$$U_{nlmk}^{(2)} = C(lk, m | h) \bar{U}_{nlhk}^{(2)} , \tag{B17}$$

$$\begin{aligned}
 \bar{n}_h^{(2)}(r) &= \sum_{n,l,k} [(2l+1)(2k+1)]^{1/2} C(lk, 0 | h) \\
 &\times \frac{R_{nl}(r)}{\pi r^2} \bar{U}_{nlhk}^{(2)}(r) ,
 \end{aligned}
 \tag{B18}$$

and that the normalization condition for the Kohn-Sham orbitals is equivalent, in second order, to

$$\int_0^\infty dr R_{nl} \bar{U}_{nlhl}^{(2)} = -\frac{1}{2} \sum_j D^M(j, ll | h) \int_0^\infty dr [U_{nlj}^{(1)}]^2 .
 \tag{B19}$$

In order to fully determine the values of k and h for which $\bar{U}_{nlhk}^{(2)}$ does not vanish, we make the following observations. Equation (B14) is diagonal in h . The dependence of the second-order radial functions on the perturbation potential is present on the right-hand side of Eq. (B14) explicitly through $V_M^{(1)}$ and implicitly through the first-order orbitals, which also appear in $\varepsilon_{nlh}^{(2)}$ and $V_h^{(2)}$. This implies that for nonvanishing $U_{nlhk}^{(2)}$, k and h must satisfy one of the following conditions in addition to that given in Eq. (B12):

$$D^M(j, lk | h) \neq 0 , \tag{B20}$$

or

$$C(MM, 0 | h) \neq 0 \tag{B21}$$

or

where j and j' take the values $l+M$, $l+M-2, \dots, |l-M|$. Using the explicit expression for the coefficients appearing in the above equations, one finds that to satisfy any one of the conditions in Eqs. (B20)–(B22) it is necessary that h takes one of the following values: $0, 2, \dots, 2M$. This, in turn, is sufficient to have $C(MM, 0 | h) \neq 0$ and $B^M(l, jj' | h) \neq 0$ for some j, j' .

The condition given by Eq. (B23) can be satisfied only when M is even $2l \geq M$, in which case it does not yield any new value for h . In conclusion, the nonvanishing radial functions $\bar{U}_{nlhk}^{(2)}$'s are those for which $h=0, 2, \dots, 2M$ and for given h , $k=l+h$, $l+h-2, \dots, |l-h|$, to satisfy the condition in Eq. (B12).

Before turning to the explicit form for the fourth-order energy change, in terms of the working functions introduced in this appendix and Appendix A, we would like to make one comment about the numerical solutions of Eqs. (B14) and (A18). We have employed a straightforward Numerov method. If U is one radial function we have to solve for, one has $U(0)=U(\infty)=0$. Inward integration from a large value of r (r_∞) and outward integration from $r=0$ are performed with arbitrary slopes, say, A and B . The matching of U and its first derivative, at a suitably chosen intermediate distance, allows us to determine A and B . However, this is not always true. Equations (B16) and (A18) are linear nonhomogeneous integro-differential equations. It can be easily shown that, whenever the associated homogeneous differential equations allow a solution (R) with the same boundary condition that we have specified above for U , the conditions of the continuity of U and its first derivative become degenerate. On the other hand, in such cases it also happens that the normalization condition for the Kohn-Sham orbitals is not satisfied automatically through the vanishing of the angular integral $\int_0^\infty dr RU$. One has to impose it in terms of the value of $\int_0^\infty dr RU$. This provides the second independent condition that, together, say, with the continuity of U , fully determines A and B . In these particular cases, in order not to “see” the round-off error of the numerical integration it is safer to use, in the higher-order differential equations, the same matching point that was used in the solution of the zero-order equation.

Finally, we give below the fourth-order energy in terms of the functions defined in the Appendixes:

$$\begin{aligned}
 E^{(4)} &= \pi \int_0^\infty dr r^2 \left[2 \frac{\bar{n}_M^{(3)}(r)}{2M+1} V_M^{(1)}(r) + 2 \sum_{s=0}^M \frac{\bar{n}_{2s}^{(2)}(r)}{4s+1} V_{2s}^{(2)}(r) + v_{xc}'''(n^{(0)}(r)) [n_M^{(1)}(r)]^4 \sum_{s=0}^M \frac{4s+1}{6(2M+1)^2} C^2(MM, 0 | 2s) \right. \\
 &\quad \left. + v_{xc}''(n^{(0)}(r)) [n_M^{(1)}(r)]^2 \sum_{s=0}^M \frac{C(MM, 0 | 2s)}{2M+1} n_{2s}^2(r) \right] - \sum_{n,l,j} p_{nlj} \bar{\varepsilon}_{nlj}^{(2)} .
 \end{aligned}
 \tag{B24}$$

In the above

$$\bar{n}_M^{(3)} = \frac{2M+1}{\pi r^2} \sum_{n,l,j,k,h} B^M(j,lK|h) U_{nlj}^{(1)} \bar{U}_{nhk}^{(2)}, \quad (\text{B25})$$

$$p_{nlj} = \int_0^\infty dr [U_{nlj}^{(1)}(r)]^2 \quad (\text{B26})$$

and

$$\begin{aligned} \bar{\epsilon}_{nlj}^{(2)} &= \sum_h B^M(j,ll|h) \int_0^\infty dr R_{nl}^2 V_h^{(1)} \\ &+ \sum_{j'} F^M(l,jj') \int_0^\infty dr R_{nl} U_{nlj'}^{(1)} V_M^{(1)}. \end{aligned} \quad (\text{B27})$$

The new coefficient $F^M(l,jj')$ is defined by

$$\begin{aligned} F^M(l,jj') &= (2l+1)[(2j+1)(2j'+1)]^{1/2} \\ &\times C(lj,0|M)C(lj',0|M)\bar{F}^M(l,jj'), \end{aligned} \quad (\text{B28})$$

and

$$\begin{aligned} \bar{F}^M(l,jj') &= \sum_m \begin{Bmatrix} l & j & M \\ m & -m & 0 \end{Bmatrix}^2 \begin{Bmatrix} l & j' & M \\ m & -m & 0 \end{Bmatrix}^2 \\ &= \sum_{s=0}^M (4s+1) \begin{Bmatrix} M & M & 2s \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} j & l & M \\ l & j' & M \\ M & M & 2s \end{Bmatrix}. \end{aligned} \quad (\text{B29})$$

The last symbol on the right-hand side of Eq. (B29) is a 9-j coefficient.^{35,36}

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