

## Self-consistent implementation of nonlocal exchange and correlation in a Gaussian density-functional method

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The gradient-expansion approximation (GEA) and the generalized gradient approximation (GGA) to nonlocal exchange energy in concert with the nonlocal correlation energy functional of Perdew [Phys. Rev. B **33**, 8822 (1986)] are analyzed when implemented in a fully self-consistent way in conjunction with the Vosko-Wilk-Nusair parametrization for the local exchange-correlation energy. It is shown that the lowest-order gradient expansion, even with corrected asymptotic behavior in the large-density-gradient limit, is still unsatisfactory in the chemically important region of electron densities where the basic assumption of the GEA ( $|\nabla n|/2k_F n < 1$ ) breaks down. In contrast, the GGA expansion behaves better. A shift by a constant additive term of an effective one-body Kohn-Sham potential in concert with the GGA nonlocal functional provides, within the framework of density-functional theory, a way of interpreting excitation energies. The nonlocal functionals significantly improve binding energies. The resulting nonlocal exchange-correlation potential is state independent; thus the present method is convenient from the computational point of view. Applications are presented for a number of atoms and small molecules, including O<sub>2</sub>, Mg<sub>2</sub>, CH<sub>2</sub>, and for a transition-metal cluster, Ni<sub>4</sub>.

### I. INTRODUCTION

In traditional *ab initio* quantum chemistry the problem of electronic correlation may be treated by expanding the wave function as a linear combination of Slater determinants. This configuration-interaction (CI) method,<sup>1</sup> while providing very accurate descriptions of various atomic and molecular properties, is usually restricted to small systems due to its numerical complexity. Thus, in transition-metal chemistry and physics, for example, alternative methods are needed. Density-functional theory (DFT) (Refs. 2 and 3) is showing great promise of providing such modern techniques. DFT provides an effective one-particle description of many-electron systems. Ground-state properties are given exactly by the theory. At the same time, the theory provides, in principle, a simple numerical scheme for determining these properties through the Kohn-Sham (KS) equations. Since its original formulation DFT has been extended onto spin densities, built for relativistic and finite-temperature systems, and it has a rigorous mathematical background.<sup>4-6</sup>

In practice, this theory needed approximations. The basic one—the local-density approximation (LDA)—has been surprisingly successful in determining the electronic properties of a wide class of systems.<sup>7</sup> At present, an efficient computational method based on DFT-LDA theory is the LCGTO-LSD one (linear combinations of Gaussian-type orbitals—local spin density). Originally proposed by Sambe and Felton<sup>8</sup> and further improved by Dunlap *et al.*<sup>9</sup> this method may be applied to atoms, molecules, and transition-metal clusters. The high accuracy of the LDA in determining molecular geometries, vibrational frequencies, electron densities, ionization po-

tentials, etc. has led to modern LCGTO-LSD programs that are highly efficient.<sup>10</sup>

Along with the success of the LDA, the limitations are also becoming progressively clear. For example, binding energies are typically too high, atomic exchange energies are underestimated by as much as 10–15%, while correlation energies are overestimated by as much as a factor of 2. By its definition the LDA is exact in the limit of a slowly varying electron gas. Because almost all systems to which the LDA is applied show inhomogeneities in electron density, the first natural way of going beyond the LDA is to investigate nonlocal corrections via density-gradient terms. From another viewpoint, one can observe that the local approximation to exchange and correlation leads to imperfect cancellation of electron self-interaction. Self-interaction corrections<sup>11,12</sup> (SIC), however, result in an orbital-dependent potential and are, therefore, outside of the Kohn-Sham formulation and we will not consider them further. Since the pioneering work of Langreth and Mehl (LM),<sup>13</sup> the essential aspects of nonlocal density-gradient corrections have been understood and new improved nonlocal gradient corrections to both exchange and correlation have been proposed. However, there are still many difficulties when incorporating these corrections into a computational scheme especially in a fully self-consistent way, i.e., introducing functional derivatives of these corrections to the exchange-correlation energy into an effective one-particle Kohn-Sham potential. Only recently has a self-consistent implementation of the original LM functional been reported in the literature.<sup>14</sup> It is, therefore, the purpose of this paper to investigate the recent nonlocal functionals to exchange and correlation energy, and choose those

which both satisfy the theoretical foundations of DFT and can be implemented into a computational scheme within the LCGTO method in a fully self-consistent way. In Sec. II we recall briefly the density-functional formalism presenting a minimum of formulas required to discuss the different schemes, which go beyond the LDA. Next, we present different nonlocal functionals, showing differences between them and we end that section with a review of our computational procedure. Section III presents results for total, exchange and correlation energies of a selection of atoms. These atomic values are necessary for determining the binding energies. This is done in Sec. IV, where we obtain also potential energy curves and vibrational frequencies for O<sub>2</sub> and Mg<sub>2</sub>. These cases are of particular interest because oxygen displays the largest nonspherical effect resulting in the worst LDA prediction of binding energy, whereas Mg<sub>2</sub> is very weakly bound and the binding is entirely due to correlation. The correlation effects play a key role in one other relatively simple molecular system, methylene. The singlet-triplet splitting in CH<sub>2</sub> as well as the geometry of its ground (<sup>1</sup>B<sub>3</sub>) and first excited (<sup>1</sup>A<sub>1</sub>) states are sensitive tests for the efficiency of different theoretical methods. Both these main features concerning methylene have been tested using the LDA and the nonlocal functionals of the exchange and correlation energy. At the end of Sec. IV, we compare the correlation energy for some simple molecules with other recently developed nonlocal correlation energy functionals. Finally, in Sec. V, we present the results of our method for a transition-metal cluster, Ni<sub>4</sub>, and discuss the physical meaning of the Kohn-Sham eigenvalues with the emphasis put on the effect of self-consistency of the nonlocal corrections.

## II. BEYOND THE LDA: ELABORATION OF THE METHOD

In DFT the basic quantities are the electron density  $n(r)$ , and the energy functional of  $n(r)$ :

$$E_v[n(r)] = \int v(r)n(r)d^3r + F[n(r)] , \quad (2.1)$$

where  $v(r)$  is some external potential (in most cases, the potential due to the nuclei), while  $F[n(r)]$  is a universal functional of the electron density, taken by Kohn and Sham to be

$$F[n] = T_s[n] + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{xc}[n(r)] , \quad (2.2)$$

where  $T_s[n]$  is the kinetic energy of a noninteracting-electron system of density  $n(r)$  in some external potential  $v_s(r)$ , the second term is the classical Coulomb repulsion energy, while  $E_{xc}[n(r)]$  is the exchange and correlation energy of the interacting system. Assuming that  $v_s(r)$  gives the same density in the noninteracting system as  $v(r)$  in the interacting system, and applying the variational principle to (2.1) with an additional condition conserving the number of particles,

$$\int n(r)d^3r = N , \quad (2.3)$$

one obtains a system of self-consistent equations:

$$v_s(r) = v(r) + \frac{1}{2} \int \frac{n(r')}{|r-r'|} d^3r' + v_{xc}(r) + C \equiv v_{\text{eff}}(r) , \quad (2.4a)$$

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(r) - \varepsilon_i\right]\psi_i = 0 , \quad (2.4b)$$

$$n(r) = \sum_{i=1}^N |\psi_i(r)|^2 , \quad (2.4c)$$

where

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} \quad (2.5)$$

is the functional derivative of the exchange and correlation energy functional. The ground-state energy is given by

$$E_N = \sum_{i=1}^N \varepsilon_i - \int v_{\text{eff}}(r)n(r)d^3r + \int v(r)n(r)d^3r + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{xc}[n(r)] . \quad (2.6)$$

In view of Eq. (2.3), the functional derivative of (2.2) is defined only to within a constant since, for fixed  $N$ , we have

$$\int C \delta n(r)d^3r = 0 .$$

Therefore, the exact density-functional (DF) potential differs from  $V_{\text{eff}}$  by an  $r$ -independent additive constant, which is given<sup>15</sup> as

$$C = \varepsilon_{N+1} - E_{N+1} + E_N , \quad (2.7)$$

where  $\varepsilon$  denotes the highest eigenvalue of the  $(N+1)$ -particle system. Then, it follows from Eqs. (2.4a) and (2.7) that the exact DF potential of the KS scheme gives a precise physical meaning to its highest eigenvalue—it is an ionization potential of a given electron system. Up to now, the set of equations (2.4a)–(2.4c) is still exact  $E_{xc}[n(r)]$  remains unknown. The main approximation used in density-functional calculations—the local-density approximation assumes  $E_{xc}[n(r)]$  in the form

$$E_{xc}[n(r)] = \int n(r)\varepsilon_{xc}(n(r))d^3r , \quad (2.8)$$

where  $\varepsilon_{xc}(n(r))$  is the exchange and correlation energy per particle of a homogeneous electron gas with density  $n$ . Usually,  $\varepsilon_{xc}(n)$  is split into separate exchange and correlation terms. The exchange energy per particle is written as a Hartree-Fock (HF) contribution

$$\varepsilon_x = A_x n^{1/3} : A_x = -\frac{3}{4} \left[ \frac{3}{\pi} \right]^{1/3} \quad (2.9)$$

and a remainder, the correlation energy per particle  $\varepsilon_c$ , which has been given in various approximate forms. The most frequently used forms can be found in the works of Gunnarsson and Lundqvist (GL),<sup>16</sup> von Barth and Hedin

(vBH),<sup>17</sup> Perdew and Zunger (PZ),<sup>18</sup> and Vosko, Wilk, and Nusair (VWM).<sup>19</sup> The VWM parametrization using the Padé-approximant technique, gives an accurate interpolation of the quantum Monte Carlo results of Ceperley and Alder.<sup>20</sup> It is worthwhile to point out that the VWN parametrization goes beyond the usual RPA (random-phase approximation) treatment of the correlation energy. The RPA level is kept only in the spin dependence of  $\epsilon_c$ . The corresponding potential of the VWN parametrization of  $\epsilon_c$  is given by Painter.<sup>21</sup> As the electron density starts to vary slowly the exchange-correlation functional  $E_{xc}[n(r)]$  can be expressed in terms of the density and density gradients:<sup>2</sup>

$$E_{xc}[n(r)] = \int d^3r A_{xc}(n(r)) + \int d^3r B_{xc}(n(r))(\nabla n)^2 + \dots \quad (2.10)$$

Usually, the first term of this formal expansion is replaced by Eq. (2.8)—the local-density (LD) approximation as the limiting case for slow variations of the electron density. The expansion retaining only the lowest order of density gradients is called the gradient-expansion approximation (GEA). The GEA is applicable when the density is slowly varying, i.e., when

$$\frac{|\nabla n|}{2k_F n} \leq 1 \quad (2.11)$$

and

$$\frac{|\nabla^2 n|}{2k_F |\nabla n|} < 1, \quad (2.11a)$$

where  $k_F$  is the local Fermi wave vector:

$$k_F = (3\pi^2 n)^{1/3}. \quad (2.12)$$

On the other hand, it was shown<sup>22,23</sup> by dimensional analysis that in “exchange”-only DFT the exchange energy has a gradient expansion of the form

$$E_x[n] = E_x^{\text{LDA}} - b \int \frac{(\nabla n)^2}{n^{4/3}} d^3r, \quad (2.13)$$

where  $b$  is a constant and  $E_x^{\text{LDA}}$  is obtained by matching Eqs. (2.8) and (2.9):

$$E_x^{\text{LDA}} = A_x \int n^{4/3} d^3r. \quad (2.14)$$

Subtracting Eq. (2.14) from Eq. (2.8) one gets an expression for the correlation energy in the LDA:

$$E_c^{\text{LDA}} = \int n(r) \epsilon_c(n(r)) d^3r. \quad (2.15)$$

Therefore, Eqs. (2.14) and (2.15) not only determine the

$A_{xc}(n)$  function in the density-gradient expansion (2.10) but also its division into separate local exchange and correlation energies. Langreth and Mehl<sup>13</sup> have made a full wave-vector analysis of the  $B_{xc}$  function in the GEA. The correlation energy has been expressed as a sum of dynamic density fluctuations of various wave vectors  $\mathbf{k}$ . They have found a strong exponential peak around  $k=0$  in the  $B_{xc}$  function for correlation. Because the GEA is valid only if conditions (2.11) are satisfied, all contributions from the region where

$$k \leq \frac{f|\nabla n|}{n}, \quad f \sim 0.15$$

are spurious, and in the LM functional were replaced by zero. Also, their nonlocal correlation-only functional contained terms coming from the GEA expansion for exchange. Perdew<sup>24</sup> removed these two deficiencies of the LM functional and proposed a new nonlocal correlation energy functional, which, in contrast to LM, goes beyond the RPA parametrization for correlation. It is written as follows:

$$E_c(n_\alpha, n_\beta) = \int n \epsilon_c(n_\alpha, n_\beta) d^3r + \int d^{-1} e^{-\Phi} C(n) \frac{(\nabla n)^2}{n^{4/3}} d^3r. \quad (2.16a)$$

From now on, we use spin densities, i.e.,

$$n = n_\alpha + n_\beta,$$

where  $(\alpha, \beta)$  stand for spin-up and spin-down, respectively, and the spin polarization is defined in the usual way:

$$\xi = (n_\alpha - n_\beta) / n.$$

Also, in (2.16) we have

$$\Phi = 1.745 \tilde{f} [C(\infty) / C(n)] \frac{|\nabla n|}{n^{7/6}}, \quad (2.16b)$$

$$d = 2^{1/3} \left[ \left( \frac{1+\xi}{2} \right)^{5/3} + \left( \frac{1-\xi}{2} \right)^{5/3} \right]^{1/2}, \quad (2.16c)$$

$$C(n) = 0.001667 + \frac{0.002568 + \alpha r_s + \beta r_s^2}{1 + \gamma r_s + \delta r_s^2 + 10^4 \beta r_s^3}, \quad (2.16d)$$

where

$$n = (4\pi r_s^3 / 3)^{-1}, \quad (2.17)$$

$\alpha = 0.023266$ ,  $\beta = 7.389 \times 10^{-6}$ ,  $\gamma = 8.723$ , and  $\delta = 0.472$ .

The functional derivative of the correlation energy functional (2.16) is given as

$$\begin{aligned} \frac{\delta E_c}{\delta n_\sigma} = & v_c^L - d^{-1} e^{-\Phi} C(n) n^{-1/3} \left[ \frac{(2-\Phi)\nabla^2 n}{n} - \left[ \frac{4}{3} - \frac{11\Phi}{3} + \frac{7\Phi^2}{6} \right] \frac{|\nabla n|^2}{n^2} + \frac{\Phi(\Phi-3)(\nabla n \nabla)|\nabla n|}{n|\nabla n|} \right. \\ & \left. - \frac{(n_\sigma^{2/3} - n_{-\sigma}^{2/3})}{n^4} 2^{2/3} [(1-\Phi)n_{-\sigma}|\nabla n|^2 - (2-\Phi)n\nabla n_{-\sigma}\nabla n] \right] \\ & + d^{-1} e^{-\Phi} \frac{|\nabla n|^2}{n^{4/3}} (\Phi^2 - \Phi - 1) \frac{dC}{dn}. \end{aligned} \quad (2.18)$$

$v_c^L$  is the LDA correlation potential. In (2.16b),  $\tilde{f}$  plays the role of a fitting parameter and is equal to 0.11. In our self-consistent calculations we have used a slightly different value, 0.104, chosen so as to reproduce the correlation energy of the neon atom. The Perdew nonlocal correlation functional matches very well the VWN parametrization of the correlation energy per particle of the homogeneous electron gas in that they both go beyond the RPA level; however, the spin dependence of the correlation energy is still described within the RPA. For nonlocal terms this was done by Hue and Langreth.<sup>25</sup> Recently new correlation energy functionals have been reported. Becke's<sup>26</sup> correlation energy functional incorporating nonlocal effects is based on a coordinate-space model. The resulting expression, however, is orbital dependent and, therefore, does not belong to the family of pure density-gradient-corrected functionals. An interesting correlation energy functional has been proposed by Lee, Yang, and Parr.<sup>27</sup> They have converted the correlation energy formula due to Colle and Salvetti<sup>28</sup> into a purely density-dependent scheme, but it was done by making the local approximation to the kinetic energy and improving it by the addition of a gradient-type correction—a “Weizsacker” term, so this is not a KS scheme. A review as well as numerical results can be found in Ref. 29. We turn now to the exchange component.

In the context of condition (2.11) the GEA for exchange (2.13) is appropriate only for small density gradients. Also, its functional derivative, the corresponding exchange potential, becomes divergent in the large-gradient limit. LM removed this basic deficiency for a self-consistent scheme by multiplying this potential by a cutoff parameter:

$$\exp \left[ -h \frac{(\nabla n)^2}{n^{8/3}} \right], \quad (2.19)$$

where  $h$  was taken as  $10^{-4}$ .

There have been several post-LM attempts to remove the deficiencies of the GEA for the exchange energy. A summary of these works is given in Ref. 30. Becke<sup>31</sup> has found a form of exchange energy, which is correct in the large-gradient limit:

$$E_x \sim \text{const} \int n^{4/5} |\nabla n|^{2/5} d^3r. \quad (2.20)$$

Because the GEA is correct for small gradients, he proposed a modification of the GEA, which also recovers the limit of (2.20). Becke's “interpolated” GEA for the exchange energy has the following form:

$$E_x^{\text{MGC}} = E_x^{\text{LDA}} - \sum_{\sigma} \beta \int \frac{(\nabla n_{\sigma})^2}{n_{\sigma}^{4/3}} \left[ 1 + \gamma \frac{(\nabla n_{\sigma})^2}{n_{\sigma}^{8/3}} \right]^{-4/5}. \quad (2.21)$$

MGC denotes modified gradient correction,  $\gamma=0.007$ ,  $\beta=0.00375$ , and  $\sigma$  labels the spin density. The correct

behavior of (2.21) in the large-gradient limit makes its functional derivative free of divergence. Recently, Becke<sup>32</sup> reported another exchange energy functional which has similar asymptotic behavior in the large-gradient limit. On the other hand, Perdew<sup>33</sup> has proposed an approach to the exchange energy which is different from the GEA. His generalized gradient approximation (GGA), contrary to the GEA, satisfies two conditions which hold for the exact exchange hole:

$$n_x(r, r+R) \leq 0,$$

$$\int d^3R n_x(r, r+R) = -1,$$

where  $n_x(r, r+R)$  is the density at position  $r+R$  of the exchange hole about an electron at position  $r$ .

A suitable form of the GGA for practical applications is given in Ref. 34. The exchange energy is given as

$$E_x^{\text{GGA}} = A_x \int d^3r n^{4/3} F^{\text{GGA}}(s). \quad (2.22)$$

$A_x$  is given by (2.9)

$$F^{\text{GGA}}(s) = (1.0864s^2/m + bs^4 + cs^6)^m, \quad (2.23)$$

where  $m = \frac{1}{15}$ ,  $b = 14$ ,  $c = 0.2$ , and  $s$  is defined as

$$s = \frac{|\nabla n|}{2k_F n}. \quad (2.24)$$

The functional derivative of (2.22) is taken from<sup>34</sup>

$$\frac{\delta E_x}{\delta n} = A_x n^{1/3} \left[ \frac{4}{3} F - t s^{-1} \frac{dF}{ds} - \left( u - \frac{4}{3} s^3 \right) \frac{d}{ds} \left[ s^{-1} \frac{dF}{ds} \right] \right], \quad (2.25a)$$

where

$$t = (2k_F)^{-2} n^{-1} \nabla^2 n, \quad (2.25b)$$

$$u = (2k_F)^{-3} n^{-2} (\nabla n \nabla) |\nabla n|. \quad (2.25c)$$

For any spin polarization, we have an exact relation<sup>35</sup>

$$E_x[n_{\alpha}, n_{\beta}] = \frac{1}{2} E_x[2n_{\alpha}] + \frac{1}{2} E_x[2n_{\beta}], \quad (2.26)$$

thus

$$\frac{\delta E_x}{\delta n_{\sigma}} = \frac{\delta E_x}{\delta n} \Big|_{n=2n_{\sigma}}. \quad (2.27)$$

Perdew's exchange energy functional has also the same asymptotic behavior (2.20) in the large-gradient limit. Thus, it is interesting to compare these two different nonlocal exchange energy functionals using in both cases a fully self-consistent scheme. The functional derivative of Beck's exchange energy functional (2.21) after considerable but straightforward algebra is given as follows:

$$\frac{\delta E_x^{\text{MGC}}}{\delta n_\sigma} = v_x^{\text{LDA}} - \beta(1 + \gamma k)^{-9/5} \left[ \frac{4}{3} n_\sigma^{1/3} k \left( \frac{3}{5} \gamma k - 1 \right) + \frac{[(1 + \gamma k)(1 + \frac{3}{5} \gamma k) - \frac{18}{5} \gamma k (1 + \frac{1}{5} \gamma k)] B}{(1 + \gamma k)} \right], \quad (2.28a)$$

$$B = \frac{8}{3} \frac{(\nabla n_\sigma)^2}{n_\sigma^{7/3}} - \frac{2 \nabla^2 n_\sigma}{n_\sigma^{4/3}}, \quad (2.28b)$$

$$k = \frac{(\nabla n_\sigma)^2}{n_\sigma^{8/3}}. \quad (2.28c)$$

In order to compare the nonlocal exchange energy functionals of Becke [Eq. (2.21)] and Perdew [Eq. (2.22)], we obtained self-consistent densities for the Mg atom. In both cases the same nonlocal correlation energy functional of Perdew [Eq. (2.16)] has been used.

Since the densities obtained within the LDA are close to the exact ones, the differences between the densities calculated with two different exchange energy functionals can be measured with respect to the LDA density. In Fig. 1 the first natural observation is that the density obtained using Perdew's GGA approximation to exchange closely resembles the LDA density, whereas that of Becke differs more. Generally, the "oscillatory" character of these two curves shows density depletions in the regions between orbitals due to exchange repulsion. In the limit of small densities, i.e., when the density gradients are large relative to the density, both these functionals yield densities that approach the LDA limit, thus confirming that they have no divergence in that limit. However, there are big differences between them for "intermediate" density gradients. These differences become more apparent in the corresponding self-consistent exchange-correlation potentials, which are presented in Fig. 2(a). Following LM we display the change in potential associated with nonlocal effects, and we start the discussion with the first large positive peak occurring near 0.5 a.u. This peak arises from an exchange effect occur-

ring between 1s and 2s states. In the case of the Mg atom such peaks must appear, at larger  $r$ 's also due to the presence of 2p and 3s shells, but these effects should be smaller due to the fact that, except for the 1s region which gives the largest error in exchange, the following peaks are dominated and screened by correlation. Indeed, in the case of the GGA exchange functional the following

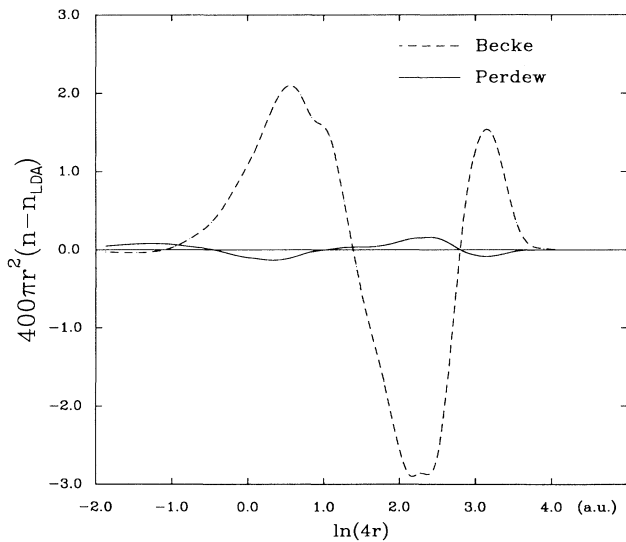


FIG. 1. Radial density difference between the LDA density and densities obtained using nonlocal exchange energy functionals: MGC (GEA) of Becke and GGA of Perdew for the Mg atom.

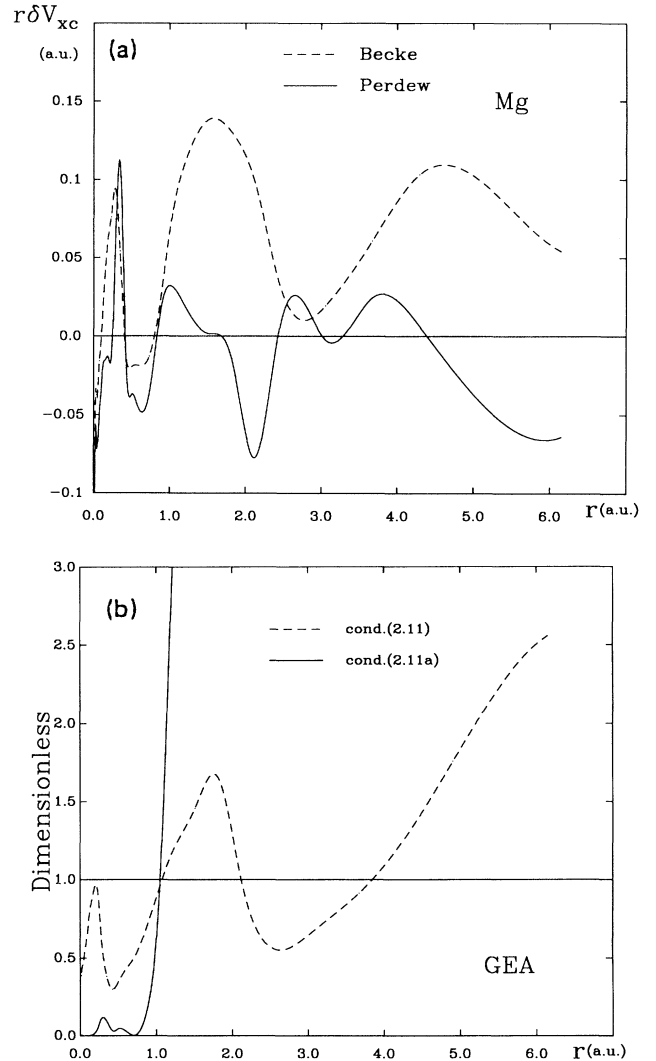


FIG. 2. (a) The difference with respect to the LDA in self-consistent exchange-correlation potentials for Mg using Becke and Perdew exchange energy functionals. (b) Plots of the necessary conditions for the GEA using Becke's MGC (GEA) exchange energy functional.

peaks are smaller. The third peak of Becke's functional appears near 4.5 a.u. This is exactly the region where the assumption of GEA validity (2.11) breaks down [see Fig. 2(b)]. Also, the second large peak of Becke's functional appears in the region where, again, condition (2.11) is not satisfied. For larger  $r$ 's (not seen in Fig. 2 but it can be inspected from Fig. 1) both nonlocal  $V_{xc}$  potentials match the LDA potential. Both GGA and GEA exchange functionals show the same and correct behavior in the limits of small and large density gradients, whereas they differ significantly in the intermediate range of density gradients, especially near the region where  $s \sim 1$  [Eq. (2.24)]. This is a fundamental failure of any GEA expression for the exchange energy, apart from any modification of the GEA leading to a correct behavior in the limit of large  $s$ . The differences between GGA and GEA approaches to exchange were also shown in Fig. 1 of Ref. 34.

The self-consistent implementation of any nonlocal correction to the local approximation of exchange and correlation energy raises the problem of the physical significance of the KS eigenvalues. The detailed discussion of that problem will be postponed until Sec. V, but now we recall briefly an earlier conclusion that the highest occupied KS eigenvalue corresponds to the first ionization potential. Unfortunately, there are few literature data which address this problem in the context of nonlocal density-gradient-type functionals, mainly because most of them have been tested in a non-self-consistent way. Once again, we turn to LM, where this problem is discussed. Their  $V_{xc}$  nonlocal potential based on the GEA approximation to exchange did not improve the position of the highest occupied orbital. With nonlocal corrections it even got worse. However, they have noticed that their highest eigenvalue could match the exact KS value if the potential would be shifted by a constant additive term  $\sim 0.2$  Ry. This constant remained uncertain in the large-gradient limit due to the fact that, in this region, the exchange-correlation potential has been multiplied by a cutoff parameter. This shift could affect only the positions of eigenvalues but not differences between them or other calculated properties such as the total energy.

In our calculations, Becke's functional also did not improve the position of the highest occupied orbital with respect to the LDA as can be seen in Table I. The GGA functional improves that eigenvalue slightly. The most likely reason that the GEA predicts a shift in the wrong direction for the highest occupied orbital is due to the fact that in the valence region the assumption (2.11)

TABLE I. Eigenvalues of the Mg atom taken with the opposite sign (in eV).

Orbital	LDA	GEA (Ref. 31)	GGA (Ref. 34)	GGA <sup>a</sup>
3s	4.80	4.37	4.92	7.30
2p	46.99	45.84	47.02	49.65
2s	79.22	78.82	80.00	82.50
1s	1251.4	1250.2	1260.0	1262.8

<sup>a</sup>Using the GGA functional for exchange, the SCF potential has been shifted by 0.17 Ry.

breaks down. Because the GGA functional behaves correctly over a wider range of densities in self-consistent calculations, it is more likely that an accurate ionization potential will be obtained from a simple shift of the effective one-body KS potential by a constant [following Eq. (2.4b)]. However, electron gas calculations applied to atoms are not appropriate for determining that constant, so this was done in Sec. V, using a Ni<sub>4</sub> cluster. The constant obtained was 0.17 Ry. The positions of KS orbitals with Perdew's GGA exchange functional and with this shift for the Mg atom are presented in the last column of Table I. This time the highest occupied orbital is placed at  $-7.3$  eV. The experimental IP for the Mg atom is 7.6 eV.

The results as discussed above have led us to choose the GGA expression for the nonlocal exchange energy and the Perdew nonlocal correlation energy functional as nonlocal (NL) corrections, which have been built into our LCGTO computational scheme. Also, the constant (0.17 Ry) term has been added in our self-consistent potential.

### III. ATOMIC TESTS

Calculations of total atomic energies are necessary to determine binding energies in molecules or cohesive energies in solids. In DFT these calculations raise the problem of determining the total energy of atoms with open shells. Usually, in that case, the approximation is made of spherically averaging the electron density. Generally, the problem of obtaining multiplet energies within DFT is still open. The exchange and correlation energy functional approximated through electron gas data at both local and nonlocal levels is symmetry independent. So, for a given state the symmetry can be inferred only through charge and spin densities.<sup>36</sup> In the present calculations the ground state of an atom with an open shell is described by a single Slater determinant with  $M_s = S$  and  $M_L = L$ , where  $S, L$  describe the multiplet with highest spin  $S$  and the highest orbital angular momentum  $L$  corresponding to  $S$ . In total-energy calculations the electron density has been spherically averaged, except for oxygen, where the total energy has been obtained using both spherical and nonspherical densities. Gaussian basis sets of moderate size have been used. The contraction pat-

TABLE II. Orbital basis sets and auxiliary sets used in the present work.

Atom	Orbital	Auxiliary
H	(41/1)	(5,1,1;4,1,1)
C	(5211/411/1)	(6,2,3;6,2,3)
O	(521/41/1)	(6,2,2;5,2,2)
Ni <sup>a</sup>	(43 321/4211/311)	(13,3,3;13,3,3)
Ni <sup>b</sup>	(311/31/311)	(7,3,4;7,3,3)
Si	(5321/521/1)	(10,3,4;10,3,4)
Mg	(5321/411)	(9,4,4;9,4,4)

<sup>a</sup>Two basis sets with the same contraction patterns have been optimized for  $d^8s^2$  and  $d^9s^1$  atomic configurations of nickel atom (Ref. 37).

<sup>b</sup>A 16-electron valence basis set used with a model core potential (Ref. 38).

TABLE III. (a) Total energy:  $-E_{\text{tot}}$  (in hartrees). (b) Total (nonrelativistic) energy of nickel atom (in hartrees).  $3d^8s^2(^3F)-3d^9s^1(^3D)$  excitation energy (in eV).

Atom	LDA	NL	Expt. <sup>a</sup>	HF <sup>a</sup>	SIC <sup>a</sup>
		(a)			
C	37.451	37.864	37.844	37.688	37.928
O <sup>b</sup>	74.484	75.109	75.063	74.808	75.252
O <sup>c</sup>	74.482	75.094			
Mg	199.044	200.086	200.042	199.608	200.524
Si	288.128	289.402	289.349	288.849	289.950
	LDA	NL	SDC <sup>d</sup>		
		(b)			
Ni ( $3d^9s^1$ )	-1504.221 515	-1507.165 95	-1507.164 48		
Ni ( $3d^8s^2$ )	-1504.206 938	-1507.167 81	-1507.166 89		
$^3F-^3D$	+0.40	-0.05	-0.02		

<sup>a</sup>Harrison, Ref. 39.

<sup>b</sup>Nonspherical electron density has been used.

<sup>c</sup>Spherical density.

<sup>d</sup>Bauschlicher, Siegbahn, and Pettersson, Ref. 40. From that reference the experimental (nonrelativistic) excitation energy:  $-0.03$  eV.

terns for both orbital and auxiliary basis sets are presented in Table II. The total energies of a few selected atoms are given in Table III.

The total energy of an oxygen atom when using a spherically averaged density is 0.413 eV higher than that obtained with a nonspherical density. Oxygen shows the highest nonspherical effect at the nonlocal level. Within the LDA this effect is reduced to 0.06 eV.<sup>41</sup> The present NL results confirm that nonlocal corrections significantly improve the total energies of atoms with respect to the LDA and show that our self-consistent Gaussian implementation is functioning correctly. Also, they are in better agreement with experimental total energies than SIC corrections. The total energy of the nickel atom is presented in Table III(b). Nickel is a transition-metal atom and any theoretical description of the electronic states arising from  $sd^{n+1}$  and  $s^2d^n$  configurations must include important valence correlation effects.<sup>40,42</sup> Table III(b) shows that DFT, with its "single-determinant" approach to the multiplet problem and with the use of spherically averaged densities in concert with the present

choice of nonlocal corrections to the LDA, is comparable with the single-reference-configuration CI method when predicting the  $d^n s^2-d^{n+1}s^1$  excitation energy. At the same time, the very good quality of the basis sets is also confirmed. Using spherically averaged self-consistent densities, exchange and correlation energies have been obtained. They are presented in Tables IV and V, respectively.

For that selection of atoms and ions the nonlocal exchange energies agree with exact ones within 0.2%, the correlation energies are determined with  $\sim 3\%$  accuracy as has been found previously with different techniques.<sup>30,44</sup>

#### IV. "LIGHT" MOLECULES: BINDING ENERGY

The LDA calculations overestimate binding energies for dimers of the first row of the Periodic Table. In the worst case, for the oxygen molecule, the LDA is about

TABLE IV. Exchange energy:  $-E_x$  (in hartrees).

Atom and ion	LDA	NL	Exact <sup>(a)</sup>
C	4.42	5.08	5.05
C <sup>+</sup>	4.09	4.73	4.72
O	7.29	8.21	8.18
O <sup>+</sup>	7.02	7.91	7.90
Mg	14.55	16.02	15.99
Mg <sup>+</sup>	14.41	15.88	15.86
Si	18.52	20.31	20.28
Si <sup>+</sup>	18.29	20.07	20.05
Ni	57.96	61.76	61.68 <sup>(b)</sup>

<sup>a</sup>Vosko and Lagowski, Ref. 43.

<sup>b</sup>HF exchange energy for nickel atom taken from Ref. 31.

TABLE V. Correlation energy:  $-E_c$  (in mhartrees).

Atom and ion	LDA	NL	Expt. <sup>a</sup>
C	358	158	157
C <sup>+</sup>	321	128	139
O	538	260	258
O <sup>+</sup>	460	210	194
Mg	891	451	444
Mg <sup>+</sup>	845	413	406
Si	1042	531	521
Si <sup>+</sup>	1011	505	502
Ni	2438	1390	

<sup>a</sup>Lagowski and Vosko, Ref. 44. From the same reference correlation energy for nickel atom with LM functional: 1280 mhartrees and with SIC approximation 1540 mhartrees.

2.3 eV higher than the experimental value, 5.21 eV. Nevertheless, the LDA predicts equilibrium distances and ground-state vibrational frequencies for these dimers with good accuracy. Thus, it is interesting to see how the present nonlocal corrections can improve this basic LDA deficiency. The self-consistent implementation of the LM nonlocal functional generally improves binding energies, giving slightly better vibrational frequencies,<sup>14</sup> however, the choice of cutoff parameters which have to be incorporated in the LM scheme leaves a 0.3 eV uncertainty in the binding energy. The LM result for the binding energy of the oxygen molecule with spherically averaged atomic density is 6.87 eV, still too big. Our potential energy curve for oxygen has been obtained using both the LDA and the present NL functional. In the case of nonlocal corrections, spherical and nonspherical atomic densities have been used. The spin-polarized version has been used also in the molecular calculations. The binding-energy curves are presented in Fig. 3. Table VI summarizes our results

The binding energy obtained using the spherical density is 6.22 eV. Further improvement is made if the spherical density constraint is removed. It lowers the binding energy to 5.39 eV. The equilibrium distance is 0.02 a.u. smaller than the LDA distance, which in that case agrees with experiment. Standard procedures<sup>14</sup> have been used for determining the vibrational frequencies. The NL vibrational frequency is lowered with respect to LDA by  $\sim 90 \text{ cm}^{-1}$ , however, this NL value itself is very close to the experimental one.

As another example, the  $\text{Mg}_2$  molecule provides a

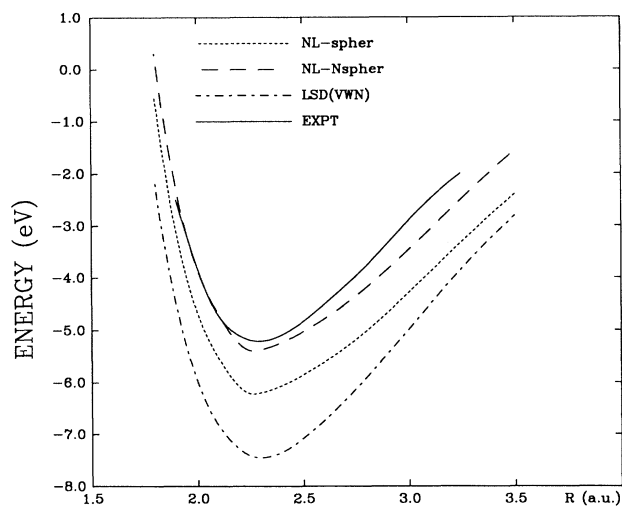


FIG. 3. Potential energy curves for the oxygen molecule obtained with LDA and NL functionals. In the case of NL calculations, the total energy of the oxygen atom has been calculated with (NL-spher) and without (NL-Nspher) spherical averaging of the electron density. The experimental curve has been taken from Ref. 45.

TABLE VI. Equilibrium distances, vibrational frequencies, and binding energies for  $\text{O}_2$  and  $\text{Mg}_2$  molecules: Nuclear separations are in a.u., vibrational frequencies are in  $\text{cm}^{-1}$ , and binding energies are in eV.

$\text{O}_2$	LDA	NL	Expt. <sup>a</sup>
$r_e$	2.28	2.26	2.28
$\omega_e$	1657	1568	1580
$E_b$	7.46	6.22 <sup>b</sup>	5.21
$\text{Mg}_2$		5.39 <sup>c</sup>	
$r_e$	6.50	6.95	7.35 <sup>d</sup>
$\omega_e$	114.1	76.6	51.1 <sup>d</sup>
$E_b$	0.171	0.034	0.05 <sup>d</sup>

<sup>a</sup>Experimental values taken from Ref. 45.

<sup>b</sup>The spherical density has been used for atom.

<sup>c</sup>The nonspherical density.

<sup>d</sup>Experimental values taken from Ref. 46.

stringent test for the nonlocal exchange and correlation functional. In the usual terms, the bonding is entirely due to correlation. The HF level gives a repulsive curve, as for any other van der Waals molecule. The natural extension is to use CI methods, but due to the strong coupling between intra- and inter-atomic correlations during the formation of  $\text{Mg}_2$ , the conventional CI approach taking into account all double excitations (DECI) is not entirely satisfactory. However, the use of many-body perturbation theory (MBPT), which properly describes the mentioned coupling, gives a potential energy curve (Ref. 46) which is in very good agreement with experiment. Our results for that molecule are presented in the second part of Table VI. In the present calculations the basis set for the Mg atom had no  $d$ -type polarization functions. The NL binding energy of  $\text{Mg}_2$  is in much better agreement with experiment than the LDA value. It is even better than the reported binding energy of the DECI calculation,<sup>46</sup> 0.018 eV, but worse than the MBPT (Ref. 46) result, 0.045 eV. The NL equilibrium distance is closer to the experimental one than the LDA result but still 0.4 a.u. less, while both DECI and MBPT methods predict bond distances greater than experiment: 8.0 and 7.65 a.u., respectively.

As the final test for the present NL scheme we took the  $\text{CH}_2$  molecule, which is known to present some demanding correlation effects. The geometry of methylene and the energy gap between its two lowest states have been the subject of extensive experimental and theoretical studies. While the controversy in the interpretation of experimental results has already been removed and there are excellent experimental data,  $\text{CH}_2$  is still an interesting case for different *ab initio* methods.<sup>47</sup> Also a comprehensive study on methylene has been made using the density-functional approach within the LD approximation.<sup>48</sup> Both the LDA and CI methods confirm the importance of including polarization functions in the basis sets. Therefore, in the present calculations, basis sets of double  $\zeta$  plus polarization quality have been extended with additional  $d$ - and  $p$ -type polarization functions for



TABLE VII. Geometries, total energies, and the energy difference ( $\Delta E$ ) between singlet and triplet states in methylene. Angles are in degrees, bond lengths in Å,  $E_T$  in hartrees, and  $\Delta E$  in kcal/mol. Contraction patterns for orbital and auxiliary basis sets used in calculations upon methylene: Carbon, (5211/411/11), (8,3,4;6,3,4). Hydrogen (311/11), (5,2,2;4,2,2).

Method	${}^3B_1$			${}^1A_1$			$\Delta E$ $-E_T$
	H-C-H	$R_{C-H}$	$R_{C-H}$	$-E_T$	H-C-H	$R_{C-H}$	
LDA	137	1.08	38.745 54	102	1.12	38.724 57	13.2
NL	130	1.08	39.179 39	99	1.12	39.164 88	9.1
expt.	134	1.07		102	1.11		9.1

the carbon and hydrogen atoms, respectively. The exponents were taken from Ref. 49. The auxiliary basis sets for C and H atoms were the same as those of Ref. 48. The present results are summarized in Table VII. The LDA already gives a good estimate of the  ${}^3B_1$ - ${}^1A_1$  energy gap, 13.2 kcal/mol (Hartree-Fock yields 25 kcal/mol). The NL functional decreases this gap to 9.1 kcal/mol, which is in this case equal to the experimental value. While the ground ( ${}^3B_1$ ) state of methylene can be described by a single determinant, the first excited state ( ${}^1A_1$ ) requires two configurations to describe properly the  $\sigma$ - and  $\pi$ -electron pairs. However, the KS scheme, a one-configuration method, in concert with a large polarization space is able to describe the geometry of both states of methylene to high accuracy.

We end this section with the results of the correlation energy for some simple molecules using both LDA and NL functionals at the experimental geometries.<sup>50</sup> We compare our results with the correlation energy functionals of Becke (B) (Ref. 26) and of Lee, Yang, and Parr (LYP) (Ref. 27) which, although outside of the KS formalism, have gained popularity. This is given in Table VIII. Our NL results agree within a few mhartrees with those of B and LYP.

### V. Ni<sub>4</sub> CLUSTER: ORBITAL ENERGIES

The Ni<sub>4</sub> cluster, when viewed as a model for the electronic properties of transition-metal surfaces, is a small one, however, as a "simple" transition-metal complex it helps to provide a wider basis of tests for different computational methods. Indeed, this cluster was the subject of a detailed study by Messmer and Lamson.<sup>51</sup> Using a very extensive basis set they have obtained their results within the  $X\alpha$  approximation to exchange correlation both in linear combination of atomic orbitals (LCAO) and scattered-wave (SW) techniques. Within each

TABLE VIII. Correlation energy  $-E_c$  of some simple molecules (in mhartrees).

Molecule	LDA	NL	B (Ref. 26) <sup>a</sup>	LYP (Ref. 27) <sup>a</sup>
O <sub>2</sub>	1110	579	586	572
H <sub>2</sub> O	662	350	347	341
C <sub>2</sub> H <sub>2</sub>	872	441	451	444

<sup>a</sup>Calculated using HF density.

method, Slater's transition-state concept was used in calculations of ionization potentials. Also, using an all-electron basis set optimized for the present VWN-LSD method, results for the Ni<sub>4</sub> cluster have been reported.<sup>52</sup> In the present calculations we apply our (NL) method along with a recently developed model-core potential for the Ni atom.<sup>38</sup> All results were obtained using a spin restricted framework,  $T_d$  symmetry, and the bulk Ni-Ni distance, 4.707 a.u. A 16-electron split-valence basis set has been chosen, thus taking into account important  $3p$ - $3d$  interactions.

As can be seen in Fig. 4 the ordering of levels and their relative spacing are similar in the present LDA calculation and the cited  $X\alpha$ -LCAO results; however, all eigenvalues are shifted toward more negative values in the LDA variant because of the correlation term. The  $X\alpha$ -SW eigenvalues are placed even below the LDA ones. Also, there is a reordering in orbital energies with respect to both LDA and  $X\alpha$ -LCAO results. One of the most important features of the eigenvalue spectra is their relation to ionization potentials. Sometimes, Koopmans'

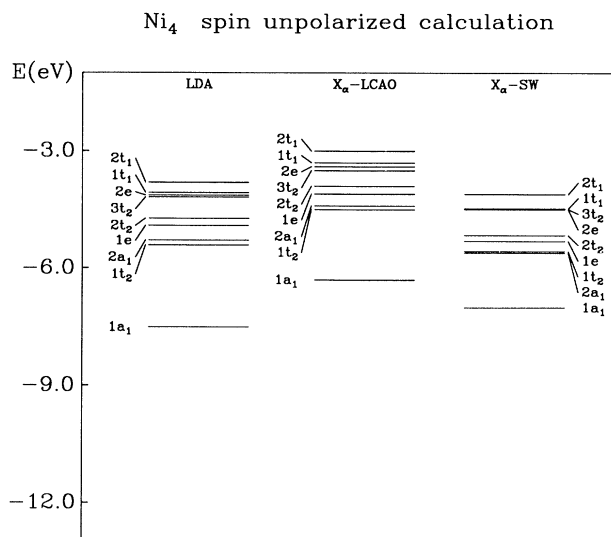


FIG. 4. Eigenvalues of the Ni<sub>4</sub> cluster obtained within the LD approximation. For comparison,  $X\alpha$  results of Messmer and Lamson are also shown. The positions of  $X\alpha$  eigenvalues were found with Figs. 2 and 3 of Ref. 51 and may be in error by  $+0.1$  eV.

theorem is used as the first estimate of ionization potentials for an atomic or molecular system. However, this does not apply to  $X\alpha$  eigenvalues because the local exchange approximation introduces a spurious Coulomb self-interaction term; Slater's transition-state method removes this, approximately.<sup>53</sup>

The present self-consistent-field (SCF) method, which introduces nonlocal corrections to both local exchange and local correlation, provides a physically appealing way to interpret eigenvalue spectra. It avoids, in a natural way, the use of the transition-state method. Also, this is a fully correlated treatment for a molecular system. Following the discussion given in Sec. II on the correspondence between highest eigenvalue and the ionization potential of a given system, we shifted our effective one-body potential in the nonlocal version to get the highest eigenvalue equal to the difference between total energies of neutral and singly ionized  $Ni_4$  clusters. This was obtained when the constant shift was  $-0.17$  Ry (a value close to that reported in the LM work:  $-0.2$  Ry) giving the position of the highest eigenvalue of the neutral  $Ni_4$  cluster at  $-6.26$  eV. For comparison, the total-energy difference of these nickel clusters within the LDA was  $6.47$  eV, while the position of the highest eigenvalue was  $-3.81$  eV.

The entire eigenvalue spectrum obtained in the present nonlocal method with a  $-0.17$  Ry potential shift and both  $X\alpha$ -LCAO and  $X\alpha$ -SW transition-state (TS) orbital energies are presented in Fig. 5. All eigenvalues move down in the nonlocal treatment with respect to those obtained within the local approximation (the vertical energy scale is the same in Figs. 4 and 5). The global positioning of NL orbital energies is comparable with those of  $X\alpha$ -LCAO[TS]; however, there are some differences in the relative positions of particular eigenvalues and a reorder-

ing of closely spaced levels.

Finally, we close this section by emphasizing that we have used a spin-restricted formalism. Also the geometry of  $Ni_4$  has not been optimized. We did this in order to compare our results with other calculations reported in the literature. In general, a spin-polarized version is required if one wants to investigate magnetic properties of transition-metal clusters along with geometry optimization. Both these factors are essential for magnetic phenomena. Also, it will be interesting to investigate these properties with respect to cluster size, using a nonlocal treatment of exchange and correlation. Such calculations are in progress.

## VI. CONCLUSIONS

In the present paper nonlocal corrections to the LCGTO-LSD method have been incorporated. There was an initial constraint that any step beyond the LD approximation should retain in a reasonable manner the high efficiency of the present computational method based on the Kohn-Sham scheme and fitting procedures used to reduce the  $N^4$  problem for the integrals. Our primary area of interest is usually molecular clusters containing several transition-metal atoms. Any *ab initio* treatment of such systems is nontrivial. If the basic feature of the KS approach to practical DFT is satisfied, then any improvement over the LDA should be, in principle, incorporated in a self-consistent way. The nonlocal corrections involving electron density gradients are natural candidates for such improvements. The formal density-gradient expansion of the exchange-correlation functional usually has the form of a GEA. This is an approximation and as we have shown in the present study, using the Mg atom as an example, its SCF implementation, which requires functional derivatives of nonlocal functionals is not entirely satisfactory. The highest occupied KS eigenvalue, which has direct physical meaning as the IP for a given electron system, corresponds to the valence region in electron density where the basic assumption of GEA validity breaks down. Modifications of the GEA which correctly predict the asymptotic behavior in the large-gradient limit remove the artificial asymptotic divergence of the nonlocal potential, but still the electron density which controls the highest occupied eigenvalue is not improved. From a chemical point of view, this is the most important region. It is worthwhile to point out that any nonlocal corrections which have the form of a GEA, when applied in a non-self-consistent way, i.e., using, for example, HF densities, predict total, exchange and correlation energies for atoms and simple dimers with high accuracy. This is, however, an approximation, which works very well for small systems like atoms or simple molecules. For larger systems, this has not been tested, since HF densities are less available and they are also likely to be less accurate due to increasing correlation effects. A possible way out is to use the LDA density instead, but in that case the exchange and correlation energy functional does not correspond to its functional derivative, i.e., the exchange and correlation potential.

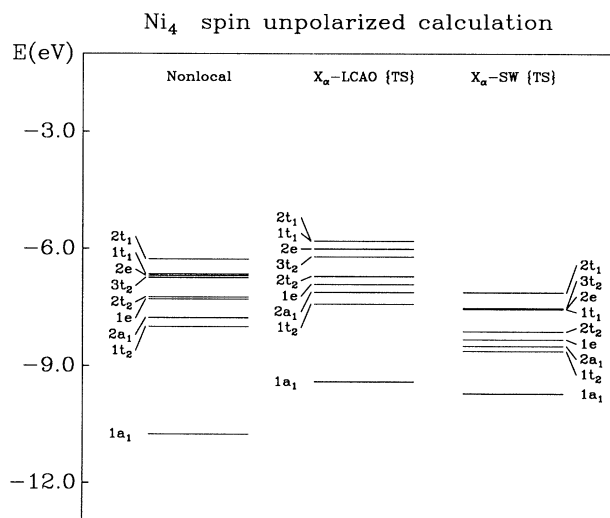


FIG. 5. Eigenvalues of the  $Ni_4$  cluster obtained by NL calculations. Also shown are results of  $X\alpha$  calculations obtained using the transition-state method, from Ref. 51. Values of  $X\alpha$  orbital energies were found in the same way as in Fig. 4.

The choice of nonlocal corrections made here is a very promising one. The GGA exchange energy and correlation energy functionals of Perdew and Wang are free of the basic GEA deficiency. The resulting nonlocal exchange-correlation potential is orbital independent. Moreover, an effective one-body self-consistent KS potential could be shifted by a constant additive term, thus approaching the exact DF "local" (state-independent) potential more closely. Atomic tests confirm the resulting quality of the nonlocal corrections, the efficiency of basis sets used in the present calculations, and the particular choice of a single Slater determinant to describe the multiplets considered. The numerical results of the  $s^2d^n-s^1d^{n+1}$  excitation energy for nickel, the binding energies of oxygen and magnesium dimers as well as the singlet-triplet splitting in methylene, are comparable with corresponding CI results. The VWN parametrization of local correlation energy in concert with Perdew's nonlocal correlation energy functional offers a very good and

practical representation of the correlation energy of the inhomogeneous electron gas, especially in the range of metallic densities. In practical applications, the self-consistent implementation of nonlocal corrections provides increased accuracy for a variety of systems and yet still retains the convenience of the LCGTO method.

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<sup>1</sup>A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (MacMillan, New York, 1982).

<sup>2</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

<sup>3</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

<sup>4</sup>*Density Functional Methods in Physics*, edited by R. M. Dreizler and J. Providencia, Vol. 123 of *NATO Advanced Study Institute Series B: Physics* (Plenum, New York, 1985).

<sup>5</sup>M. Levy and J. P. Perdew, *Phys. Rev. A* **32**, 2010 (1985).

<sup>6</sup>V. Sahni and M. Levy, *Phys. Rev. B* **33**, 3869 (1986).

<sup>7</sup>R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989), and references therein.

<sup>8</sup>H. Sambe and R. H. Felton, *J. Chem. Phys.* **62**, 1122 (1975).

<sup>9</sup>B. I. Dunlap, J. W. Connolly, and J. R. Sabin, *J. Chem. Phys.* **71**, 3396 (1979).

<sup>10</sup>A. St-Amant and D. R. Salahub, *Chem. Phys. Lett.* **169**, 387 (1990), and references therein.

<sup>11</sup>A. Zunger, J. P. Perdew, and G. L. Oliver, *Solid State Commun.* **34**, 933 (1980).

<sup>12</sup>S. H. Vosko and L. Wilk, *J. Phys. B* **16**, 3687 (1983).

<sup>13</sup>D. C. Langreth and M. J. Mehl, *Phys. Rev. B* **28**, 1809 (1983).

<sup>14</sup>F. W. Kutzler and G. S. Painter, *Phys. Rev. B* **37**, 2850 (1988).

<sup>15</sup>U. von Barth, in *Many-Body Phenomena at Surfaces*, edited by D. Langreth and H. Suhl (Academic, New York, 1984).

<sup>16</sup>O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976).

<sup>17</sup>U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).

<sup>18</sup>J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

<sup>19</sup>S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).

<sup>20</sup>D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).

<sup>21</sup>G. S. Painter, *Phys. Rev. B* **24**, 4264 (1981).

<sup>22</sup>F. Herman, J. P. van Dyke, and I. B. Ortenburger, *Phys. Rev. Lett.* **22**, 807 (1969).

<sup>23</sup>F. Herman, I. B. Ortenburger, and J. P. van Dyke, *Int. J. Quant. Chem.* **3**, 827 (1970).

<sup>24</sup>J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).

<sup>25</sup>C. D. Hu and D. C. Langreth, *Phys. Scr.* **32**, 391 (1985).

<sup>26</sup>A. D. Becke, *J. Chem. Phys.* **88**, 1053 (1988).

<sup>27</sup>C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).

<sup>28</sup>R. Colle and O. Salvetti, *Theor. Chim. Acta* **37**, 329 (1975).

<sup>29</sup>B. Miehlich, A. Savin, H. Stoll, and H. Preuss, *Chem. Phys. Lett.* **157**, 200 (1989).

<sup>30</sup>A. E. DePristo and J. D. Kress, *J. Chem. Phys.* **86**, 1425 (1987).

<sup>31</sup>A. D. Becke, *J. Chem. Phys.* **85**, 7184 (1986).

<sup>32</sup>A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).

<sup>33</sup>J. P. Perdew, *Phys. Rev. Lett.* **55**, 1665 (1985).

<sup>34</sup>J. P. Perdew and Y. Wang, *Phys. Rev. B* **33**, 8800 (1986).

<sup>35</sup>G. L. Oliver and J. P. Perdew, *Phys. Rev. A* **20**, 397 (1979).

<sup>36</sup>U. von Barth, *Phys. Rev. A* **20**, 1693 (1979).

<sup>37</sup>J. Andzelm, E. Radzio, and D. R. Salahub, *J. Comput. Chem.* **6**, 520 (1985).

<sup>38</sup>A. Peluso, D. R. Salahub, and A. Goursot, *Inorg. Chem.* **29**, 1544 (1990).

<sup>39</sup>J. G. Harrison, *J. Chem. Phys.* **78**, 4562 (1983).

<sup>40</sup>C. W. Bauschlicher, P. Sieghban, and L. G. M. Pettersson, *Theor. Chim. Acta* **74**, 479 (1988).

<sup>41</sup>F. W. Kutzler and G. S. Painter, *Phys. Rev. Lett.* **59**, 1285 (1987).

<sup>42</sup>B. H. Botch, T. H. Dunning, and J. F. Harrison, *J. Chem. Phys.* **75**, 3466 (1981).

<sup>43</sup>S. H. Vosko and J. B. Lagowski, in *Density Matrices and Density Functionals*, edited by R. M. Erdahl and V. H. Smith (Reidel, Dordrecht, 1986).

<sup>44</sup>J. B. Lagowski and S. H. Vosko, *J. Phys. B* **21**, 203 (1988).

<sup>45</sup>H. F. Schaefer III, *J. Chem. Phys.* **54**, 2207 (1971), and references therein.

<sup>46</sup>G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **68**, 2114 (1978).

<sup>47</sup>I. Shavitt, *Tetrahedron* **41**, 1531 (1985).

<sup>48</sup>E. Radzio and D. R. Salahub, *Int. J. Quant. Chem.* **29**, 241

- (1986).
- <sup>49</sup>H. J. Werner and E. A. Reinsch, *J. Chem. Phys.* **76**, 3144 (1982).
- <sup>50</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1979).
- <sup>51</sup>R. P. Messmer and S. H. Lamson, *Chem. Phys. Lett.* **90**, 31 (1982).
- <sup>52</sup>E. Radzio, J. Andzelm, and D. R. Salahub, *J. Comput. Chem.* **6**, 533 (1985).
- <sup>53</sup>M. S. Gopinathan, *J. Phys. B* **12**, 521 (1979).