PHYSICAL REVIEW A **68**, 012505 (2003)

Correlation energy per particle from the coupling-constant integration

F. Colonna
Laboratoire de Chimie Théorique (CNRS) et Université Pierre et Marie Curie 4, Place Jussieu, Couloir 22-23, 1er Étage, Case Courrier 137, 75252 Paris, France

D. Maynau
Laboratoire de Physique Quantique, URA 505, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France

A. Savin*
Laboratoire de Chimie Théorique (CNRS) et Université Pierre et Marie Curie 4, Place Jussieu, Couloir 22-23, 1er Étage, Case Courrier 137, 75252 Paris, France

(Received 1 April 2003; published 15 July 2003)

The adiabatic connection can be used in density functional theory to define the unknown (exchange and) correlation density functional. Using conventional wave-function techniques, accurate estimates of thus defined (exchange and) correlation energy densities can be obtained for specified systems. In this paper, numerical results are presented for the He and the Be atom, as well as the isoelectron Ne ions. A generalized gradient approximation is tested against these results. The comparison shows that the generalized gradient approximation has the ability to detect local features (the shell structure). In one case (Ne^{6+}), however, it turns out that the accurate correlation energy per particle is lower than that obtained within the local-density approximation, and thus not properly corrected by the generalized gradient approximation.

DOI: 10.1103/PhysRevA.68.012505 PACS number(s): 31.15.Ew, 31.15.Ar, 31.25.Eb

INTRODUCTION

The unknown quantity in the Kohn-Sham density-functional theory is the universal correlation functional $E_c[n]$. It is the difference between the exact ground-state energy E of a system, having ground-state density n, and the expectation value of the Hamiltonian H, taken with the Kohn-Sham wave function Φ (the ground-state wave function of a system of *noninteracting* particles yielding density n).

$E_c[n]$ is approximated in practice by an expression of the type

$$E_c[n]=\int \varepsilon_c(r)n(r)d^3r, \tag{1}$$

where $\varepsilon_c(r)$ is constructed via $n(r)$ in the local-density approximation (LDA), or via $n(r)$ and $\nabla n(r)$ in the generalized gradient approximations.

Equation (1) is not sufficient to define ε_c when we know the exact E_c, the reason being that the latter is just a number, while the former is a function of r: adding to ε_c a function $g(r)$ satisfying

$$\int g(r)n(r)d^3r=0 \tag{2}$$

does not change the left-hand side of Eq. (1).

In order to understand approximations using an ansatz similar to Eq. (1), it has been proposed to look at it as the realization of an adiabatic connection process [1–3] in which a transition is made between the noninteracting, Kohn-Sham system, and the real, physical system by multiplying the electron-electron interaction by a factor λ (between 0, the value taken for the Kohn-Sham system, and 1, the value taken for the physical system). If the density is kept constant during this process (cf. Refs. [2,3] which is by no means necessary, cf. Refs. [1]), the correlation energy is given by

$$E_c[n]=\frac{1}{2}\int d^3r_1d^3r_2\int_0^1 d\lambda \times[P_2(r_1,r_2;\lambda)-P_2(r_1,r_2;\lambda=0)]\frac{1}{r_{12}}. \tag{3}$$

Here, $P_2(r_1,r_2;\lambda)$ is the reduced two-particle density matrix for the ground state at interaction strength λ.

If

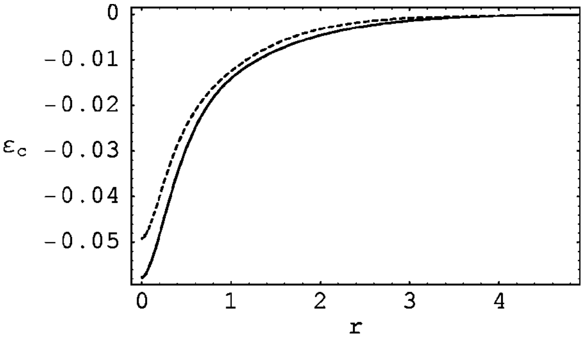

FIG. 1. The accurate correlation energy per particle, ε_c, as a function of r in the He atom (full curve) and in the atom with exponential density, $(2\zeta^3/\pi)\exp(-2\zeta r)$, for $\zeta=2$, dashed curve, in atomic units.

---

*Electronic address: savin@lct.jussieu.fr

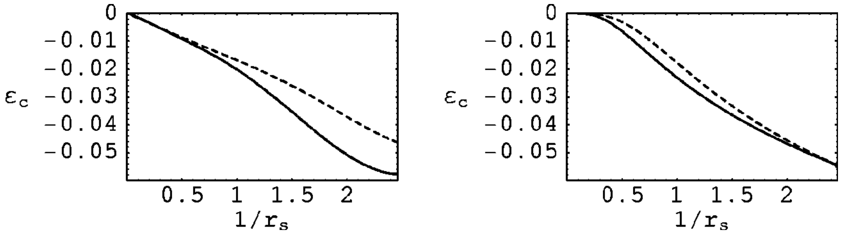

FIG. 2. The correlation energy per particle, ε_c, as a function of $1/r_s$ in the He atom (full curve) and in the atom with exponential density, $(2\zeta^3/\pi)\exp(-2\zeta r)$, for $\zeta=2$, dashed curve. The left-hand panel shows the accurate curves and the right-hand panel the approximate, generalized gradient approximation, PBE values [12], in atomic units.

$$\varepsilon_c(r_1)=\frac{1}{2n(r_1)}\int d^3r_2\int_0^1 d\lambda \times[P_2(r_1,r_2;\lambda)-P_2(r_1,r_2;\lambda=0)]\frac{1}{r_{12}}, \qquad (4)$$

then Eq. (1) is satisfied. [The reverse is not true, it may be that Eq. (1) holds without satisfying Eq. (4).]

As ε_c, as given by Eq. (4), is sometimes viewed as the paradigm of the density functional, we decided to compare more closely accurate and approximate (LDA, generalized gradient approximation) values for it. In a previous paper [4], we presented results for the He atom. In this paper, we will show results for the Be atom, and show the behavior in the series, by considering the ions of Ne, Ne^{8+}, and Ne^{6+}, respectively. Similar studies exist for a strongly inhomogeneous electron gas [5] and for the silicon crystal [6]. An accurate model for He has also been presented in Ref. [7].

Notice that in density-functional theory the exchange part ε_x,

$$\varepsilon_x(r_1)=\frac{1}{2n(r_1)}\int d^3r_2\int_0^1 d\lambda \times[P_2(r_1,r_2;\lambda=0)-n(r_1)n(r_2)]\frac{1}{r_{12}}, \qquad (5)$$

also plays an important role. We will not insist on it in this paper, since it is defined at $\lambda=0$, and was already explored by others (see, e.g., Ref. [8]).

The technique we use for producing the ground state of a system at interaction strength λ, having density n, has been described before ([9] and will not be repeated in detail here. We first generated an accurate density n by performing (multireference) configuration interaction calculations for these systems with Gaussian basis sets. At each λ, the density is kept constant within a high accuracy by using a supplementary λ-dependent potential $v(r;\lambda)$ described in terms of $r^{m_i}\exp(-\alpha_i r^2)$. The parameters of this potential are obtained in a way to ensure only second-order errors in the universal density functional (Legendre transform) by slightly modifying the program MOLPRO [10]. For each of the λ, $v(r;\lambda)$ and the modified interaction λ/r_{12} determine a Hamiltonian which has a ground state $\Psi(\lambda)$ and the reduced two-particle density matrix $P_2(r_1,r_2;\lambda)$, obtained with the program CASDI [11].

RESULTS

Figure 1 shows ε_c as a function of r, for the He atom and the system having the density $n_\zeta(r)=2\zeta^3/\pi\exp(-2\zeta r)$, for $\zeta=2$, which is the density of a noninteracting He atom. Notice that in both cases, ε_c behaves as one would expect in density-functional-theory approximations: as the density increases, so does ε_c, in absolute value. In order to emphasize this effect, we choose to plot ε_c also as a function of $1/r_s$, where $r_s=(3/(4\pi n(r)])^{1/3}$. As, in these examples, n is a monotonically decaying function of r, there is a one-to-one correspondence between n and r, or r_s and r, and we can produce such a plot. As large densities correspond to large $1/r_s$, the atomic center lies at the extreme right of the plot. Furthermore, in the $X\alpha$ approximation, or when using the Wigner crystal expression, the correlation energy is proportional to $n^{1/3}$, or to $1/r_s$ (a plot of ε_c in such an approximation is a straight line passing through the origin). Figure 2 shows ε_c as a function of $1/r_s$ in the left-hand panel for the same two-electron systems. The right-hand panel exemplifies that with increasing density, ε_c (in absolute value) also increases in density-functional approximations. In this paper, we compare with an approximate ε, in the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [12]. In spite of some details, the qualitative agreement between the accurate and approximate curves is good.

A more complicated case is that of the Be atom. The shell structure there produces a double-minimum structure in the accurate $\varepsilon_c(r)$. The maximum around $r=1$ bohr corresponds to the separation between the shells. As can be seen

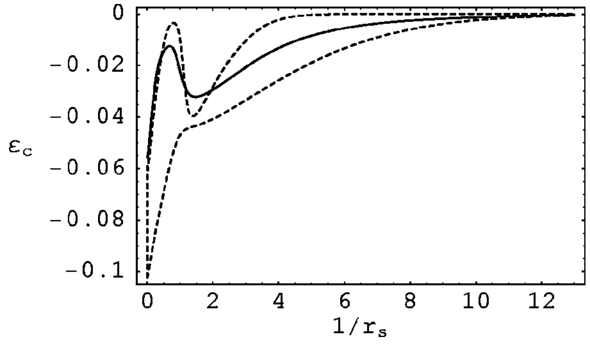

FIG. 3. The correlation energy per particle, ε_c, as a function of r in the Be atom. Accurate (full curve) and two approximate results: in the local-density approximation (lower dashed curve) and in the generalized gradient approximation, PBE values [12] (upper dashed curve), in atomic units.

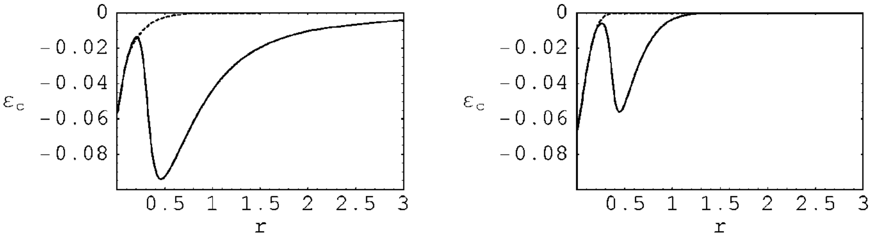

FIG. 4. The correlation energy per particle, ε_c, as a function of r in the Ne^{6+}(full curve) and Ne^{8+}(dashed curve) ions, in atomic units. The left-hand panel shows the accurate results and the right-hand panel those obtained in the PBE approximation [12].

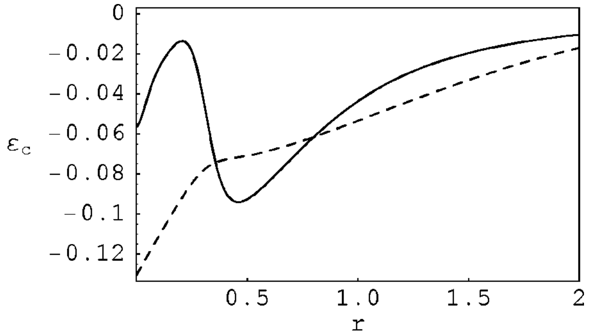

FIG. 5. The correlation energy per particle, ε_c, as a function of r, in atomic units, for the Ne^{6+} ion: accurate (full curve), within the local-density approximation (dashed curve).

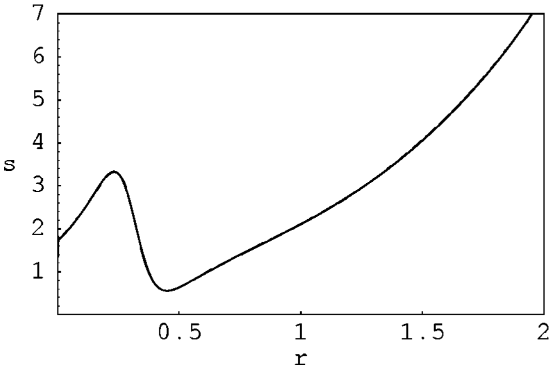

FIG. 6. The reduced gradient in Ne^{6+}, as a function of r, in atomic units.

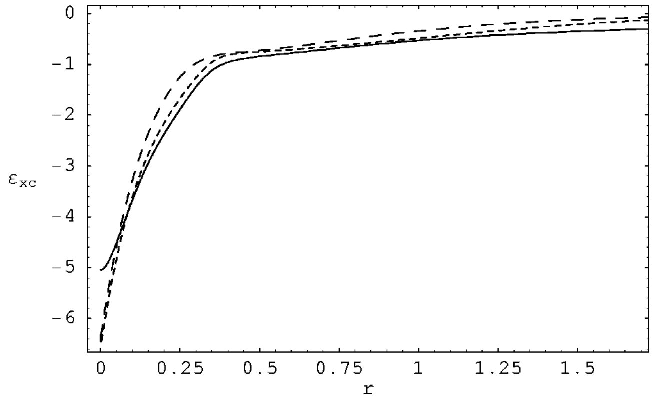

FIG. 7. Exchange and correlation energy per particle, ε_{xc}, as a function of r, for the Ne^{6+} ion, in atomic units: accurate (full curve), in the local-density approximation (long-dashed curve), and a generalized gradient approximation (PBE, short-dashed curve).

in Fig. 3, this feature is also present in the PBE approximation (the upper dashed curve following the trends of the accurate, full curve). The local-density approximation, also shown in Fig. 3, not only yields significantly too low ε_c, but only gives a hint to the shell structure. Figure 3 shows that the PBE approximation works better for the core region of Be than for the intershell and valence region.

We show in Fig. 4 similar curves for Ne^{8+} and Ne^{6+}, isoelectronic with He and Be, respectively. Notice that Ne^{8+} is quite well described by the approximation and that ε_c is transferable from Ne^{8+} to the Ne^{6+} core. The valence correlation is underestimated, however, in the approximation.

The description of the double minimum of ε_c is not present in the local-density approximation, as can be seen in Fig. 5. It appears within the PBE approximate functional due to the presence of the reduced gradient, $t = |\nabla n|/[n^{7/6}4(3/\pi)^{1/6}]$, shown in Fig. 6 for Ne^{6+}. It is not able to fully correct the local-density approximation: normally, the gradient correction reduced the effect of LDA; from Fig. 5 it is evident, however, that the effect of LDA should be enhanced in the valence region (around 0.5 bohr).

It is often believed that using exchange and correlation together improves on the results. We show in Fig. 7 the exchange and correlation energy density for Ne^{6+}, by comparing the accurate values with those obtained within the local-density and a generalized gradient approximation. The definition of the accurate ε_{xc} is given by the sum of ε_x [Eq. (5)], and ε_c [Eq. (4)]. Although the agreement is not perfect, the PBE curve follows significantly better the accurate one than the curve obtained within the local-density approximation.

A more detailed analysis is presented in Fig. 8, which

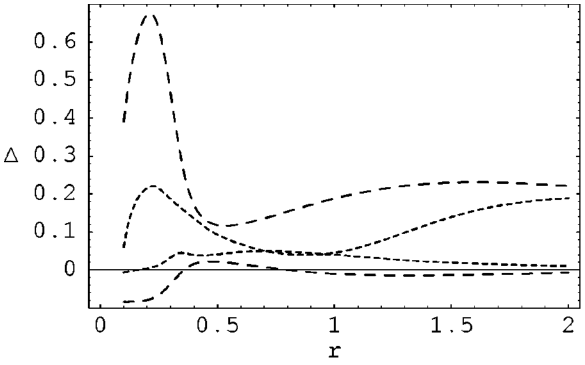

FIG. 8. Errors of the energy per particle of Ne^{6+}, as a function of r, in the local-density (long-dashed curves) and a generalized gradient approximation (PBE, short-dashed curves): exchange and correlation (upper pair of curves) and correlation only (lower pair of curves), in atomic units.

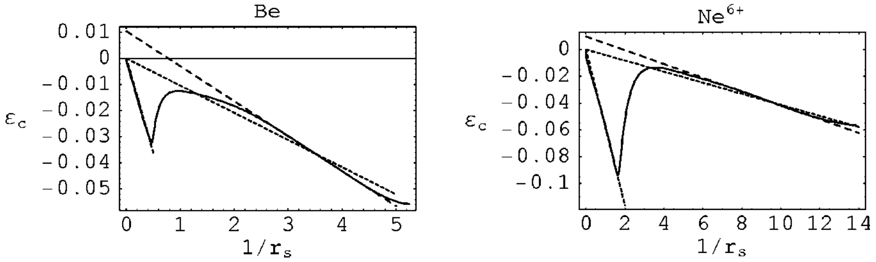

FIG. 9. Accurate correlation energy per particle, ε_c, of Be (left panel), and Ne^{6+}, as a function of $1/r_s$, together with linear fits to segments of it, in atomic units.

shows the errors in the local-density and the generalized gradient correction for Ne^{6+}. The generalized gradient correction always improves on ε_{xc}. As mentioned before, the gradient correction on the correlation energy per particle, ε_c, is not always improving on the local approximation. As the exchange and the correlation gradient correction work in opposite directions, it is possible to compensate errors in the gradient correction correlation part by that in the exchange part.

A further investigation is shown by analyzing the correlation energy per particle, ε_c, plotted as a function of $1/r_s$, cf. Fig. 9. (Please note that in this figure the scale is different on the two plots shown.) An attempt to find a simple form of ε_c shows that for each atomic region, core and valence, a linear fit shows a reasonable agreement. This reminds one of the $X\alpha$ approximation, giving a linear dependence on $1/r_s$, too, and having an atom-dependent coefficient of $1/r_s$. Here, the coefficient becomes also shell dependent. It is not so surprising that the shells behave differently, since chemical and pseudopotential experience shows that they behave like nearly independent subsystems. The coefficients seem roughly proportional to the nuclear charge for the core, but show a much smaller dependence on it for the valence region. An even better fit seems possible when the correlation energy per particle, ε_c, is not forced to vanish for the inner-shell part, if a constant term ($\approx$0.01 au) is included in the fit.

CONCLUSIONS

The present calculations support with numerical evidence (absent up to now) the view, defended by many active researchers in the field of density-functional theory, that the success of density-functional theory is based upon the ability to successfully model the two-body density matrix averaged along the adiabatic connection. We hope that calculations of this kind could be further pursued and provide more hints for the construction of approximations.

ACKNOWLEDGMENTS

We are grateful to Professor Thierry Leininger (Université Paul Sabatier, Toulouse) for helpful discussions. We would like to thank Professor Kieron Burke (Rutgers University, Piscataway, USA) and Professor John Perdew (Tulane University, New Orleans, USA) for comments on the manuscript.

---

[1] J. Harris and R.O. Jones, J. Phys. F: Met. Phys. **4**, 1170 (1974).
[2] D.C. Langreth and J.P. Perdew, Solid State Commun. **17**, 1425 (1975).
[3] O. Gunnarsson and B.I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
[4] A. Savin, F. Colonna, and R. Pollet, Int. J. Quantum Chem. **93**, 166 (2003).
[5] M. Nekovee, W.M.C. Foulkes, and R.J. Needs, Phys. Rev. Lett. **87**, 036401 (2001).
[6] A.C. Cancio, M.Y. Chou, and R.Q. Hood, Phys. Rev. B **64**, 115112 (2001).
[7] J. Tao and J.P. Perdew, in *Reviews of Modern Quantum Chemistry*, edited by K.D. Sen (World Scientific, Teaneck, NJ, 2002).
[8] O.V. Gritsenko and E.J. Baerends, J. Phys. Chem. A **30**, 5383 (1997).
[9] F. Colonna and A. Savin, J. Chem. Phys. **110**, 2828 (1999).
[10] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P.J. Knowles, with contributions from R.D. Amos, A. Bernhardsson, A. Berning, P. Celani, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A.W. Lloyd, S.J. McNicholas, F.R. Manby, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A.J. Stone, R. Tarroni, and T. Thorsteinsson.
[11] N. Ben Amor and D. Maynau, Chem. Phys. Lett. **286**, 211 (1998).
[12] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).