

Improved tensor-product expansions for the two-particle density matrix

Gábor Csányi,^{1,*} Stefan Goedecker,² and T. A. Arias³

¹*Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

²*Département de Recherche Fondamentale sur la Matière Condensée, SP2M/NM, CEA-Grenoble, 38054 Grenoble cedex 9, France*

³*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853*

(Received 20 July 2001; published 20 February 2002)

We present a density-matrix functional within the recently introduced framework for tensor-product expansions of the two-particle density matrix. It performs well both for the homogeneous electron gas as well as atoms. For the homogeneous electron gas, it performs significantly better than all previous density-matrix functionals, becoming very accurate for high densities and outperforming the Hartree-Fock method at metallic valence electron densities. For isolated atoms and ions, it is on par with generalized-gradient approximations to the density-functional theory. We also present analytic results for the correlation energy in the low-density limit of the free-electron gas for a broad class of such functionals.

DOI: 10.1103/PhysRevA.65.032510

PACS number(s): 31.15.Ew

INTRODUCTION

The long-standing quest for an accurate description of electronic correlation with effective single-particle theories has renewed interest in density-matrix functionals in recent years. The success of density-functional approaches, based on the Hohenberg-Kohn-Sham theory [1,2], is well established [3]. Unfortunately, the known approximations to the requisite universal energy functional of the density are not sufficiently accurate to predict the rates of chemical and physical processes at room temperatures. This theory can easily be generalized to show that there is a universal correlation-energy functional of the single-particle density matrix as well [4–9]. A density-matrix functional requires an expression of the two-body matrix in terms of the one-body density matrix. An ansatz for the two-body matrix containing one free parameter was proposed by Müller [10], and the case where this parameter is set to 1/2 has been discussed by Buijse [11]. In addition, Buijse attempted to perform self-consistent calculations but optimized only the lowest two natural orbitals and occupation numbers and only for the H₂ molecule. Independently, Goedecker and Umrigar [12] proposed a functional based on a very similar, but self-interaction corrected, two-body matrix and derived the Euler-Lagrange formalism necessary for the numerical minimization of the functional. Optimizing typically 50 natural orbitals and occupation numbers, necessary to achieve convergence, for a variety of atoms and ions it was found that the Goedecker-Umrigar (GU) functional yielded energies that were comparable or better than those from the generalized-gradient approximation (GGA) in the density-functional theory and densities that were better than those from GGA. Following these first encouraging numerical results, several groups of authors have recently proposed and studied the accuracy of various new approximations to the density-matrix functional [13,14,16–25]. However, numerical studies [14] demonstrate that density-matrix functionals,

to date, give poor correlation energies for the homogeneous electron gas.

It has been shown analytically that the *per particle* correlation energy of the homogeneous electron gas in the low-density limit approaches a nonzero constant [16] for these initial functionals. Building on our tensor-product formalism [14], below we extend this proof and demonstrate this shortcoming for a broad class of functionals. As regions of low densities contribute relatively little to the total energies of solids and molecules, we focus our attention on improving the results for the high- and intermediate-density regimes. We present a density-matrix functional that is more than an order of magnitude more accurate in the high-density limit for the homogeneous electron gas than those proposed previously and also represents a significant improvement in the intermediate regime. In atoms, the functional performs similarly to the GGA [26] in the density-functional theory but not as well as the GU functional. Because self-interaction corrections complicate numerical calculations, we do not enforce them on our functional in the present work.

NOTATION

For a system of N electrons, the exact energy functional of the *two*-body density matrix $\gamma(\mathbf{x}_1\mathbf{x}_2, \mathbf{x}'_1\mathbf{x}'_2) \equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}^\dagger(\mathbf{x}'_2) \hat{\psi}(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1) | \Psi \rangle / 2$ is

$$E = \int d\mathbf{x}_1 \left(\left[-\frac{1}{2} \nabla_{\mathbf{r}_1}^2 + U(\mathbf{r}_1) \right] n(\mathbf{x}_1, \mathbf{x}'_1) \right) \Big|_{\mathbf{x}'_1 = \mathbf{x}_1} + \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\gamma(\mathbf{x}_1\mathbf{x}_2, \mathbf{x}_1\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (1)$$

Here and throughout, we work in atomic units, and the \mathbf{x}_i are compound coordinates representing both position \mathbf{r}_i and spin s_i , so that integration over \mathbf{x}_i represents integration over space and summation over spin channels. In the above expression, the external potential and one-body density matrix are $U(\mathbf{r})$ and $n(\mathbf{x}_1, \mathbf{x}'_1) \equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) | \Psi \rangle$, respectively.

*Present address: TCM Group, Cavendish Laboratory, Madingley Rd., Cambridge CB3 0HE, United Kingdom.

Finally, we note that simple integration of the definitions reveals the sum rule, which connects the one- and two-body matrices,

$$\left(\frac{N-1}{2}\right)n(\mathbf{x}_1, \mathbf{x}'_1) = \int d\mathbf{x}_2 \gamma(\mathbf{x}_1 \mathbf{x}_2, \mathbf{x}'_1 \mathbf{x}_2). \quad (2)$$

As in [14], we expand γ into Hartree and exchange-correlation contributions,

$$\hat{\gamma} = \hat{\gamma}_H + \hat{\gamma}_{XC}. \quad (3)$$

By separation of variables, it is always possible to expand the unknown exchange-correlation part as a (potentially infinite) sum of tensor products,

$$\hat{\gamma}_{XC} = \sum_i \hat{u}_i \otimes \hat{v}_i. \quad (4)$$

In this context we view the two-body density matrix as a two-body operator (a function of four variables) and \hat{u}_i and \hat{v}_i as one-body operators (functions of two variables). Note that throughout we employ the twisted tensor product (denoted as a “type-III” product in [14]),

$$[u \otimes v](\mathbf{x}_1 \mathbf{x}'_1, \mathbf{x}_2 \mathbf{x}'_2) \equiv u(\mathbf{x}_1, \mathbf{x}'_2)v(\mathbf{x}'_1, \mathbf{x}_2),$$

to combine the one-body operators.

Remarkably, given such an expansion truncated to finite order, the combination of the symmetry constraints on γ with the sum rule is sometimes sufficient to determine the full four-variable function γ directly in terms of the two-variable density matrix n . Under these conditions, one can then evaluate the energy as an explicit functional of the density matrix using Eq. (1). Minimizing the density-matrix functional over all physical density matrices then yields the ground state of the system under this approximation. In this context it is irrelevant that all approximate $\hat{\gamma}_{XC}$ do not correspond to N -representable [15] density matrices.

NEW FUNCTIONAL

Considerable freedom remains in the terms for the expansion (4). Previously, we explored two choices, the “corrected Hartree-Fock” (CHF) [14] and the “corrected Hartree” (CH) functional,

$$\hat{\gamma}_{XC}^{\text{CHF}} = -\frac{1}{2}(\hat{n} \otimes \hat{n}) - \frac{1}{2}[\sqrt{\hat{n}(1-\hat{n})} \otimes \sqrt{\hat{n}(1-\hat{n})}],$$

$$\hat{\gamma}_{XC}^{\text{CH}} = -\frac{1}{2}(\sqrt{\hat{n}} \otimes \sqrt{\hat{n}}),$$

respectively. The latter is identical to the one proposed by Buijse [11] and a special case of the one proposed by Müller [10]. The GU functional is the CH functional with a self-interaction correction. In the case of the homogeneous electron gas at high densities the GU and CH functionals become identical since the self-interaction correction vanishes, but at

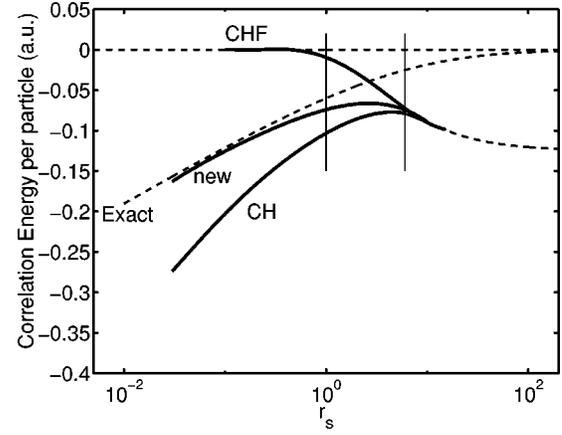


FIG. 1. Correlation energies of the three functionals in the text and the exact result [27–29], versus the mean particle separation. The solid lines are numerical calculations, the dashed lines are exact results. The vertical lines indicate the range of typical metallic valence densities.

low densities they could differ if the natural orbitals are localized. One way to view these functionals is in terms of the coefficient of the Fock term $\hat{n} \otimes \hat{n}$, which is $-1/2$ in the CHF functional and zero in the CH functional. Under truncation of the expansion to one additional term, the value of this coefficient, through the sum rule, then uniquely determines the form of the remaining tensor product.

HOMOGENEOUS ELECTRON GAS

Figure 1 shows the correlation energies of the resulting functionals for the spin-unpolarized homogeneous electron gas. The corrected Hartree-Fock functional leads to no improvement in the correlation energy over the Hartree-Fock functional, and approaches zero for high electron density. The CH functional is a little better, and represents an improvement by a factor of 2 over the Hartree-Fock functional at high densities, where it is overcorrelated. Both functionals are overcorrelated at low densities, where they perform badly, with the per particle correlation energy approaching a *nonzero* constant. This property of the CH functional has been demonstrated analytically in [16].

Having seen the behavior of the above two functionals in the high-density regime, it is natural to look for a form with a Fock coefficient intermediate to those above. A coefficient of $-1/4$ for the Fock term results in the following functional:

$$\hat{\gamma}_{XC} = -\frac{1}{4}[\hat{n} \otimes \hat{n} + \sqrt{\hat{n}(2-\hat{n})} \otimes \sqrt{\hat{n}(2-\hat{n})}]. \quad (5)$$

Figure 1 shows that this new functional results in a dramatic improvement at high densities (low r_s) and significant improvement at metallic valence densities ($1 < r_s < 6$). At low density, the behavior of *all three* functionals becomes the same, resulting in unrealistically large correlation energies *per particle*. Note that because this happens at low density, the contribution of these regions to the total energy is likely to be small in an inhomogeneous system. We now explore

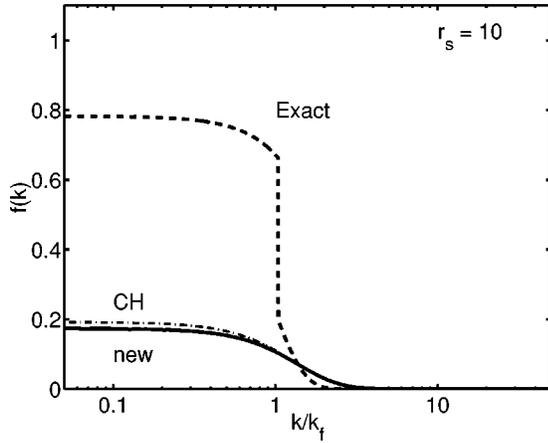


FIG. 2. The momentum distribution $f(k)$ as a function of the wave vector k : exact [30] (dashed line), CH functional [16] (dash-dotted line), and our new functional (solid line) at $r_s=10$. The Fermi wave vector is denoted k_f

the reasons for this behavior to ascertain the feasibility of making improvements in this regime as well.

LOW-DENSITY LIMIT

To understand the approach of the three functionals shown in Fig. 1 to one another in the low-density limit, we recall that Cioslowski and Pernal [16] have determined the predictions of the CH functional analytically for $r_s \gtrsim 5.769$. Their analysis applies, provided that $\hat{\gamma}_{XC}$ is represented as a single tensor product of a specific homogeneous form. As an illustration of the anomalous correlation behavior which these functionals exhibit in the low-density limit, Fig. 2 compares the known many-body momentum distribution with numerical results for our new functional and the analytic distribution from [16] derived for the CH functional for $r_s = 10$. Both density-matrix functionals have very low occupation numbers, and lose the characteristic signature of the sharp drop near the Fermi wave vector evident in the exact curve.

We now show that as a consequence of the sum rule, all of the above functionals reduce to this particular form in the limit of high r_s . Fourier transforming Eq. (1), the total energy in the homogeneous electron gas becomes

$$E = 2 \int \frac{V d\mathbf{k}}{(2\pi)^3} \frac{\mathbf{k}^2}{2} f_{\mathbf{k}} - \frac{1}{V} \int \frac{V^2 d\mathbf{k} d\mathbf{k}'}{(2\pi)^6} g_{\mathbf{k}\mathbf{k}'} \frac{4\pi}{|\mathbf{k}' - \mathbf{k}|^2}, \quad (6)$$

where $g_{\mathbf{k}\mathbf{k}'}$ is the momentum-space representation of $\hat{\gamma}_{XC}$. In the case that $\hat{\gamma}_{XC}$ is expanded as a sum of tensor products of single-particle operators, its momentum-space representation will be a sum of tensor products of the momentum-space representation of those operators. Because our one-body operators are explicit functions of the density matrix, which for the homogeneous electron gas is diagonal in the momentum representation, their momentum-space representations are also diagonal. Thus, their tensor products become simple products, and we have

$$g_{\mathbf{k}\mathbf{k}'} = \Omega_1[n(\mathbf{k}), n(\mathbf{k}')] + \Omega_2[n(\mathbf{k}), n(\mathbf{k}')] + \dots, \quad (7)$$

where the Ω are the same functions of the density matrix that appear in the tensor products expressing $\hat{\gamma}_{XC}$, but with the tensor-product operator replaced with simple multiplication. For example, for the CH functional $g_{\mathbf{k}\mathbf{k}'} = -\frac{1}{2} \sqrt{n(\mathbf{k})n(\mathbf{k}')}$.

We now show that, in the low-density limit, the analytic solution presented in [16] for the case when $g_{\mathbf{k}\mathbf{k}'}$ consists of a *single* Ω function of the homogeneous form

$$\Omega[\lambda n(\mathbf{k}), \lambda n(\mathbf{k}')] = \lambda^\beta \Omega[n(\mathbf{k}), n(\mathbf{k}')] \quad (8)$$

applies more generally to cases with multiple tensor products. The analysis of [16] begins with the scaling ansatz

$$n(\mathbf{k}) = \rho^\Delta \eta(\rho^\nu \mathbf{k}),$$

where ρ is the total electron density per spin channel, ν is a constant, η is a universal function that does not depend on the density explicitly, and $\Delta = 1 - 3\nu$ due to the constraint of the total particle density. Note that as $\rho \rightarrow 0$, $n(\mathbf{k}) \rightarrow 0$ uniformly (provided that $\Delta > 0$). This behavior, evident in Fig. 2, forms the crux of our argument; we verify it self-consistently below.

In the above limit, all of the Ω_i in the above functionals approach homogeneous functions with their own exponents β_i . Substituting $n(\mathbf{k})$ into Eq. (7), we then find that a single homogeneous function dominates $g_{\mathbf{k}\mathbf{k}'}$, the one with the smallest β_i ($\equiv \beta_{\min}$). Therefore, all the conditions for the analysis of [16] apply, in particular, that

$$\nu = \frac{1 - \beta_{\min}}{3\beta_{\min} - 2}.$$

One can show that not only the above functionals but any functional satisfying the sum rule and dominated by a *single* homogeneous term in the low-density limit will exhibit $\beta_{\min} = 1$ in that limit. If indeed a single tensor-product term dominates $\hat{\gamma}$, then the symmetry arguments presented in [14] imply that $\hat{\gamma}_{XC}$ must take the form

$$\hat{\gamma}_{XC} = \hat{u}[\hat{n}] \otimes \hat{u}[\hat{n}]. \quad (9)$$

The sum rule (2) then implies

$$\int d\mathbf{x}'_2 \hat{\gamma}_{XC} = \hat{n}, \quad (10)$$

which, using Eq. (9), can be written as an operator equation,

$$(u[\hat{n}])^2 = \hat{n}, \quad (11)$$

which implies that $u[\]$ must be a homogeneous function with exponent 1/2 and therefore that $\hat{\gamma}_{XC}$ is dominated by a term of homogeneous exponent $\beta_{\min} = 1$. Therefore $\nu = 0$ and $\Delta = 1$; the fact that $\Delta > 0$ confirms the self-consistency and the validity of the above analysis.

Reference [16] analyzes the case $\beta = 1$ in detail, finding for the correlation energy per particle the result

TABLE I. Error in the total energies of atoms for the new functional, in hartrees. For comparison, results are included for the CH and the GU functionals and for the LDA and PBE-GGA approximations within density-functional theory. The root-mean-square error is listed in the last line.

| Atom | Present | CH | GU | LDA | PBE |
|------------------|---------|--------|-------|------|------|
| He | 0.01 | -0.01 | 0.006 | 0.07 | 0.01 |
| Be | -0.07 | -0.1 | -0.02 | 0.2 | 0.04 |
| Ne | 0.1 | -0.07 | 0.05 | 0.7 | 0.07 |
| Be ²⁺ | -0.02 | -0.005 | 0.004 | 0.2 | 0.04 |
| C ⁴⁺ | -0.02 | -0.003 | 0.003 | 0.4 | 0.06 |
| C ²⁺ | 0.1 | -0.2 | 0.01 | 0.4 | 0.07 |
| O ⁴⁺ | 0.1 | -0.2 | 0.02 | 0.6 | 0.1 |
| RMS | 0.07 | 0.1 | 0.02 | 0.4 | 0.06 |

$$\epsilon_c \rightarrow -\frac{1}{8},$$

as $\rho \rightarrow 0$. Figure 1 verifies that, in the low-density limit, indeed the correlation energy of all three functionals approach one another and, in particular, that they all approach a non-zero constant correlation energy of $-1/8$ hartree per particle.

ATOMS

The electrons in solids exhibit both free-electronlike and localized atomic-orbital behavior. Thus, another important limiting case for assessing new functionals is their behavior in atoms. Table I presents energies obtained from the new functional for light atoms and ions. For comparison, we include energies obtained from the CH and GU functionals as well as from the local-density approximation (LDA), and the Perdew-Burke-Ernzerhof (PBE) [26] generalized-gradient approximation.

The atomic natural orbitals were represented as a product of a radial part and spherical harmonics. For a given maximal value of the angular momentum l , the program can calculate the total energies with a precision that is close to the machine precision. Thus, the only approximation is, in prac-

tice, the number of natural orbitals included in the calculation. In addition to the occupied orbitals we have included 55 virtual orbitals, which corresponds to all the shells up to $l=4$.

Table I reveals that, on the whole, the new functional performs for atoms quite comparably to both the CH functional and to PBE. In particular, for the two-electron series, the new functional is somewhat worse, but for the four-electron series, it is somewhat better. All density-matrix functionals are generally much better than LDA. For the neutral atoms, CH and the present functional are not quite as good as PBE, but, for the ions both are better or in some cases similar to PBE. Note that the CH functional always overestimates the correlation energy, which is not the case for the new functional. In the GU functional this overcorrelation is corrected by the self-interaction correction and this functional yields the best energies for atoms and ions. Thus, we feel that the density-matrix functionals provide an adequate description of atomlike systems.

CONCLUSIONS

We have introduced a density-matrix functional, which represents a major improvement over existing functionals of the density matrix. It is very accurate in the high-density regime of the homogeneous electron gas, significantly improves the correlation energies at typical valence densities, and it is comparable to the generalized-gradient approximation in atoms. Although it is not as accurate as the GU functional for atoms, we expect it to perform better than the GU functional for solids. We have also shown that, in our tensor-product expansion of the two-body density matrix, little further improvement can be expected at the present truncation of two terms. Our test systems span the range of environments encountered in solids and molecules, so we conclude that this new functional is a good candidate to be used in electronic-structure calculations of condensed matter.

ACKNOWLEDGMENT

We thank Cyrus Umrigar for interesting discussions and helpful comments on the manuscript.

-
- [1] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, B864 (1964).
 [2] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
 [3] M.C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).
 [4] E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976).
 [5] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).
 [6] S.M. Valone, J. Chem. Phys. **73**, 1344 (1980); **73**, 4653 (1980).
 [7] R.A. Donnelly and R.G. Parr, J. Chem. Phys. **69**, 4431 (1978).
 [8] G. Zumbach and K. Maschke, J. Chem. Phys. **82**, 5604 (1985).
 [9] M. Levy, in *Density Matrices and Density Functionals*, edited by R. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987), p. 479.
 [10] A.K.M. Müller, Phys. Lett. **105A**, 446 (1984).
 [11] M. A. Buijse, Ph.D. thesis, Department of Chemistry, Free University of Amsterdam, Amsterdam, 1991.
 [12] S. Goedecker and C.J. Umrigar, Phys. Rev. Lett. **81**, 866 (1998).
 [13] S. Goedecker and C. J. Umrigar, in *Many-electron Densities and Reduced Density Matrices*, edited by J. Cioslowski (Kluwer Academic, Dordrecht, 2000).
 [14] Gábor Csányi and T.A. Arias, Phys. Rev. B **61**, 7348 (2000).
 [15] A. J. Coleman, in *Reduced Density Operators with Applications to Physical and Chemical Systems*, edited by R. M. Erdahl (Queen's University, Kingston, Ontario, 1974).
 [16] J. Cioslowski and K. Pernal, J. Chem. Phys. **111**, 3396 (1999); Phys. Rev. A **61**, 034503 (2000).
 [17] J. Cioslowski, P. Ziesche, and K. Pernal, Phys. Rev. B **63**, 205105 (2001).

- [18] R. Lopez-Sandoval and G.M. Pastor, Phys. Rev. B **61**, 1764 (2000).
- [19] R.G. Hennig and A.E. Carlsson, Phys. Rev. B **63**, 115116 (2001).
- [20] B. Barbiellini, J. Phys. Chem. Solids **61**, 341 (2000).
- [21] B. Barbiellini and A. Bansil, J. Phys. Chem. Solids **62**, 2181 (2001).
- [22] J. Cioslowski and R. Lopez-Boada, J. Chem. Phys. **109**, 4156 (1998).
- [23] J. Cioslowski and K. Pernal, J. Chem. Phys. **115**, 5784 (2001).
- [24] J. Cioslowski, P. Ziesche, and K. Pernal, Phys. Rev. B **63**, 205105 (2001).
- [25] K. Yasuda, Phys. Rev. A **63**, 032517 (2001).
- [26] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [27] G. D. Mahan, *Many-Particle Physics* (Plenum Press, New York, 1990).
- [28] D.M. Ceperley and B.J. Alder, J. Phys. C **7**, 295 (1980); Phys. Rev. Lett. **45**, 566 (1980).
- [29] M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).
- [30] B. Farid *et al.*, Phys. Rev. B **48**, 11 602 (1993).