Theor Chem Acc (2006) 116: 608–613
DOI 10.1007/s00214-006-0106-4

REGULAR ARTICLE

Daniel Gómez · Eduardo V. Ludeña
Valentin Karasiev · Pedro Nieto

Application of exact analytic total energy functional for Hooke's atom to He, Li$^+$ and Be^{++}: an examination of the universality of the energy functional in DFT

Received: 2 January 2005 / Accepted: 15 September 2005 / Published online: 21 February 2006

Abstract We employ the recently generated energy density functional for Hooke's atom [Ludeña EV et al (2004) Intern J Quantum Chem 99:297], to which we introduce a simplification for the kinetic energy term, to evaluate the total energy of the helium atom and of the two-electron ions Li$^+$ and Be^{++}. Using accurate representations for the one-particle densities of these systems we show that the energy density functional for Hooke's atom leads, in these cases, to energy values that are below the exact ones. We discuss the implication of this finding with respect to the existence of a universal energy functional in DFT.

1 Introduction

In a previous work [1] we have advanced an exact expression for the energy of Hooke's atom expressed as a functional of the one-particle density $\rho(r)$. By Hooke's atom we denote an artificial two-electron system having infinite nuclear mass with harmonic electron-nuclear interaction and with the true Coulombic electron–electron interaction. This model system has been found useful in several areas including electron correlation [2–4], quantum dots [5], density functional theory [6–14] and reduced density matrix theory [15,16]. The importance of this model lies in that its Schrödinger equation can be separated in terms of the relative and center of mass coordinates of the electrons and that exact analytic solutions can be found for the ensuing equations.

In this previous work [1], relying precisely on this exact wavefunction, the Hooke's atom functional was explicitly constructed by applying local-scaling transformations. Various analytic approximations to the one-particle density were used to calculate the total energy of the Hookean atom and it was shown that it satisfies the variational principle (it attains the exact energy value of 2.0 hartrees when the functional is evaluated using the exact one-particle density of Hooke's atom and higher values for any other approximate density).

In the present work, we extend our previous results and apply the functional to evaluate the energy of other two-electron systems, which differ from Hooke's atom only in the external potential. We have selected as examples, the He atom and the two-electron ions Li$^+$ and Be^{2+}. Clearly, an important goal in the present work is to examine whether this exact functional for Hooke's atom can be transferred to systems with the same number of electrons but different external potentials.

A novel aspect we introduce in the present work is a simplified expression for the kinetic energy functional. The construction of this new expression was accomplished by judicious use of *Mathematica*.

In Sect. 2, we discuss some theoretical questions related to the construction of the functional $F[\rho]$. In Sect. 3, we apply local-scaling transformation in order to generate $F[\rho]$ for Hooke's atom and present a procedure that allows us to obtain a very compact expression for the kinetic energy functional. In Sect. 4, we present results of our calculations for He, Li$^+$ and Be^{2+} and some conclusions. In the Appendix we provide a listing of the programs written for *Mathematica* for the generation of the kinetic energy functional.

2 Construction of the functional $F[\rho]$

A basic problem in the Hohenberg-Kohn-Sham version of density functional theory [17] is the construction of the functional $F[\rho]$ comprising the total kinetic energy plus the electron–electron interaction energy. In view of the fact that the external potential does not appear explicitly in this expression, it has been assumed that this functional is universal,

---

Dedicated to Jean Paul Malrieu not only as a tribute to his scientific work, but chiefly, as a token of appreciation of his devotion to human, social and intellectual causes.

Daniel Gómez · Eduardo V. Ludeña (✉)
Valentin Karasiev · Pedro Nieto
Centro de Química, Instituto Venezolano de Investigaciones Científicas, IVIC, Apartado 21827, Caracas 1020-A, Venezuela
E-mail: eludena@ivic.ve

Eduardo V. Ludeña
Kimika Fakultatea
Euskal Herriko Unibertsitatea
P.K. 1072, 20080 Donostia, Spain

namely, that it is the same for any N-electron system. Moreover, since the number of electrons N is indirectly contained in the one-particle density, it has been conjectured that this functional is also N-independent.

According to Levy's constrained-search method [18], the functional $F[\rho]$ is obtained, in principle, as the extremum of the following variational principle:

$$F[\rho] = \inf\Big\{ < \Psi_\rho | \widehat{T} + \widehat{V}_{ee} | \Psi_\rho > \Big\} \tag{1}$$

$$\rho \in \mathcal{J}_N$$

$$\Psi_\rho \longrightarrow \rho(\text{fixed})$$

$$\Psi_\rho \in \mathcal{L}_N \tag{2}$$

where

$$\mathcal{J}_N \equiv \{\rho : \rho \geq 0, \int \rho = N, \rho^{1/2} \in H^1(\mathbf{R}^3)\} \tag{3}$$

and

$$\mathcal{L}_N \equiv (\text{ antisymmetric } N\text{-particle Hilbert space}) \tag{4}$$

Thus, in order to construct the energy functional $F[\rho]$ it is necessary to span all wavefunctions in an N-particle antisymmetric Hilbert space that yield the fixed density ρ. At the extremum, the following identity holds:

$$F[\rho] =< \Psi_\rho^{\min} | \widehat{T} + \widehat{V}_{ee} | \Psi_\rho^{\min} > \tag{5}$$

In particular, if the fixed $\rho \equiv \rho_0$ is the ground-state one-particle density of a given physical system, then

$$\Psi_{\rho_0}^{\min} = \Psi_0 \tag{6}$$

where Ψ_0 is the ground-state wavefunction for this system.

Levy's constrained search may be considered as an "implicit constructive procedure"since it does not provide the means for actually constructing this functional. In contrast to this situation, an "explicit constructive procedure", has been advanced in the context of the local-scaling transformation version of the DFT, LS-DFT, [19–22]. This procedure is based on the fact that through the introduction of density-dependent coordinates $r^T \equiv r^T([\rho]; \mathbf{r})$ it becomes possible to obtain density-dependent wavefunctions. In particular, if we know the exact ground-state wavefunction for a given physical system, then, by introducing these density-dependent coordinates into this exact wavefunction (this is accomplished in practice through the application of local-scaling transformations), we can generate the corresponding density-dependent wavefunction. For example, for an N-electron system, we have:

$$\Psi_0([\rho]; \mathbf{r}_1, \cdots, \mathbf{r}_N) = \sqrt{\frac{\rho(\mathbf{r}_1)}{\rho_\Psi(\mathbf{r}_1^T)}} \times \cdots \times \sqrt{\frac{\rho(\mathbf{r}_N)}{\rho_\Psi(\mathbf{r}_N^T)}} \Psi_0(\mathbf{r}_1^T, \cdots, \mathbf{r}_N^T) \tag{7}$$

The density-dependent coordinate r^T is obtained through the application of locally scaled transformations to the coordinate r. Explicitly, the transformed coordinate is given by

$$r^T = \sqrt{(x^T)^2 + (y^T)^2 + (z^T)^2} \tag{8}$$

where the Cartesian locally scaled components are:

$$x^T = \lambda(\mathbf{r})x, \qquad y^T = \lambda(\mathbf{r})y, \qquad \text{and} \qquad z^T = \lambda(\mathbf{r})z \tag{9}$$

In this expression, $\lambda(\mathbf{r})$ is the local-scaling transformation function, which is determined by solving the following first-order differential equation:

$$\lambda(\mathbf{r}) = \left(\frac{\rho(\mathbf{r})}{\rho_\Psi(\mathbf{r}^T)}\right)^{1/3} L1(\mathbf{r})^{-1/3} \tag{10}$$

where

$$L1(\mathbf{r}) = (1 + \mathbf{r} \cdot \nabla_{\mathbf{r}} \ln \lambda(\mathbf{r})) \tag{11}$$

It follows that using this density-dependent wavefunction we can construct a functional

$$\widetilde{F}[\rho] =< \Psi_0([\rho]) | \widehat{T} + \widehat{V}_{ee} | \Psi_0([\rho]) > \geq F[\rho] \tag{12}$$

which at the extremum (i.e., when $\rho = \rho_0$) coincides with Levy's functional

$$\widetilde{F}[\rho_0] = F[\rho_0] \tag{13}$$

This functional, in addition, minimizes the energy of the system under consideration (corresponding to the ground-state wavefunction Ψ_0):

$$E_o = \min\Big\{\widetilde{F}[\rho] + \int d^3\mathbf{r}\rho(\mathbf{r})v(\mathbf{r})\Big\} \tag{14}$$

$$\rho \in \mathcal{J}_N$$

3 Generation of $F[\rho]$ for Hooke's atom through local-scaling transformations

The Hamiltonian characterizing Hooke's atom [2,6,3] is

$$\widehat{H} = -\frac{1}{2}\left(\nabla^2_{\mathbf{r}_1} + \nabla^2_{\mathbf{r}_2}\right) + \frac{k}{2}(r_1^2 + r_2^2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{15}$$

showing that this is a two-electron atom differing from the true one in that a harmonic potential replaces the Coulomb electron–nuclear one.

The ground-state analytical solution for a coupling constant [3] $k = \frac{1}{4}$ is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = N_c b(r_1) b(r_2) C(r_{12}) \tag{16}$$

where

$$N_c = \frac{1}{2\pi\sqrt{5\pi + 8\sqrt{\pi}}} \tag{17}$$

$$b(r) = e^{-r^2/4} \tag{18}$$

$$C(r_{12}) = 1 + r_{12}/2 \tag{19}$$

The one-electron density associated with the exact ground-state wave function is

$$\rho_\Psi(r_1) = 2\int d^3\mathbf{r}_2 |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = N_c^2 b^2(r_1)\left(8b^2(r_1) + 7\sqrt{2\pi} + \frac{4\sqrt{2\pi}\mathrm{Erf}(r_1/\sqrt{2})}{r_1} + 4\sqrt{2\pi}\ \mathrm{Erf}(r_1/\sqrt{2})r_1 + \sqrt{2\pi}r_1^2\right) \tag{20}$$

(In what follows, we set $\rho_\Psi \equiv \rho_g$ where the latter is denoted as the "generating" density). According to Eq. (7) the locally scaled wave function, which depends on the arbitrary density $\rho(r)$ is given by:

$$\Psi([\rho]; \mathbf{r}_1, \mathbf{r}_2) = \sqrt{\frac{\rho(r_1)}{\rho_g(r_1^T)}}\sqrt{\frac{\rho(r_2)}{\rho_g(r_2^T)}}\Psi_g(\mathbf{r}_1^T, \mathbf{r}_2^T) \tag{21}$$

Defining the auxiliary function $a(r)$ as

$$a(r) = \sqrt{\frac{\rho(r)}{\rho_g(r^T)}} \tag{22}$$

and using Eq. (16), the locally scaled wave function can be written as:

$$\Psi([\rho]; \mathbf{r}_1, \mathbf{r}_2) = N_c a(r_1) a(r_2) b(r_1^T) b(r_2^T) C(r_{12}^T) \tag{23}$$

Similarly, the 1 - matrix is given by

$$D_\Psi^1([\rho]; \mathbf{r}_{1'}, \mathbf{r}_{1''}) = 2\int d^3 r_2 \Psi([\rho]; \mathbf{r}_{1'}, \mathbf{r}_2)\Psi([\rho]; \mathbf{r}_{1''}, \mathbf{r}_2) \tag{24}$$

Using Eq. (23) and the following equality between the volume elements of unscaled and locally-scaled coordinates

$$d^3\mathbf{r}\frac{\rho(\mathbf{r})}{\rho_g(\mathbf{r}^T)} = d^3\mathbf{r}^T \tag{25}$$

it can be rewritten as:

$$D_\Psi^1([\rho]; \mathbf{r}_{1'}, \mathbf{r}_{1''}) = 2N_c^2 a(r_{1'}) a(r_{1''}) b(r_{1'}^T) b(r_{1''}^T) \times \int d^3\mathbf{r}_2^T b^2(r_2^T) C(r_{1'2}^T) C(r_{1''2}^T) \tag{26}$$

In terms of Eq. (26) the kinetic energy may be expressed as:

$$T[\Psi([\rho])] \equiv T[\rho] = \frac{1}{2}\int d^3\mathbf{r}_1 t([\rho]; \mathbf{r}_1) \tag{27}$$

where the kinetic energy density is given by:

$$t([\rho]; \mathbf{r}_1) = \nabla_{\mathbf{r}_{1'}} \nabla_{\mathbf{r}_{1''}} D_\Psi^1([\rho]; \mathbf{r}_{1'}, \mathbf{r}_{1''})\Big|_{\mathbf{r}_{1'}=\mathbf{r}_1, \mathbf{r}_{1''}=\mathbf{r}_1} \tag{28}$$

Bearing in mind the form of the wave function [Eq. (23)] the total kinetic energy density may be decomposed as [1]:

$$t([\rho]; r) = taa(r) + tbb(r) + tcc(r) + 2(tab(r) + tac(r) + tbc(r)) \tag{29}$$

where:

$$taa(r) = \rho_g(r^T)\, \nabla_{\vec{r}}\, a(r) \cdot\ \nabla_{\vec{r}}\, a(r) \tag{30}$$

$$tbb(r) = \rho_g(r^T) \left(\frac{a(r)}{b(r^T)}\right)^2 \nabla_{\vec{r}}\, b(r^T) \cdot \nabla_{\vec{r}}\, b(r^T) \tag{31}$$

$$tcc(r) = a(r)^2\, b(r^T)^2\, 2N_c^2 \times \int d^3\vec{r}_2^{\,T}\, b(r_2^T)^2\, \nabla_{\vec{r}_1}\, C(r_{12}^T) \cdot \nabla_{\vec{r}_1}\, C(r_{12}^T) \tag{32}$$

$$2(tab(r) + tbc(r)) = a(r)\, \nabla_{\vec{r}}\, a(r) \cdot\ \nabla_{\vec{r}}\, \rho_g(r^T) \tag{33}$$

$$tbb + tbc = \frac{a(r)^2}{2\, b(r^T)}\, \nabla_{\vec{r}}\, b(r^T) \cdot\ \nabla_{\vec{r}}\, \rho_g(r^T) \tag{34}$$

where the expressions show an implicit dependence on the density.

The *Mathematica* code for evaluating these expressions is given in the Appendix. This code when executed with the command *math*, produces as its output the following kinetic energy density functional:

$$T[\rho] = T_W[\rho] + 4\pi \times \int_0^\infty dr\, r^2\, \rho(r)^{5/3}\, L1(r)^{4/3}\, F_{5/3}(r^T(r)) \tag{35}$$

where:

$$F_{5/3}(x) = \frac{b(x)^2}{2\sqrt{2}(16\pi + 10\pi^{3/2})(\rho_g(x))^{5/3}} - \frac{x^2}{8(\rho_g(x))^{2/3}} - \frac{x(d\rho_g(x)/dx)}{4(\rho_g(x))^{5/3}} - \frac{(d\rho_g(x)/dx)^2}{8(\rho_g(x))^{8/3}} \tag{36}$$

and where $T_W[\rho]$ is the von Weizsäcker term:

$$T_W[\rho] = 4\pi \int_0^\infty dr\, r^2\, \frac{(d\rho(r)/dr)^2}{8\,\rho(r)} \tag{37}$$

The electron–electron interaction energy functional for the locally scaled wavefunction is given by

$$E_{ee}[\Psi([\rho])] = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 |\Psi([\rho]; \mathbf{r}_1, \mathbf{r}_2)|^2 \frac{1}{r_{12}} \tag{38}$$

Elsewhere [1], we have shown that upon application of local-scaling transformations we obtain the following density functional for the electron–electron interaction:

$$E_{ee}[\Psi([\rho])] \equiv E_{ee}[\rho] = \sum_{l=0}^{\infty} \int_0^\infty dr_1 r_1^2 \rho(r_1)^{(l+4)/3} F_{ee}^{(l)}([\rho]; r_1) \tag{39}$$

The electron-electron interaction enhancement factors are:

$$F_{ee}^{(l)}([\rho]; r_1) = \frac{4\pi}{2l+1} \times \frac{e^{-(r_1^T)^2/2}}{(r_1^T)^{l+1}\rho_\Psi(r_1^T)^{(l+4)/3} L1(r_1)^{(l+1)/3}} I_l([\rho]; r_1) \tag{40}$$

where the auxiliary integral $I_l([\rho]; r_1)$ is given by

$$I_l([\rho]; r_1) = 2N_c^2 \frac{2\pi}{r_1^T} \int_0^{r_1^T} dr_2^T r_2^T r_2^l b^2(r_2^T) \times \left[\int_{r_1^T - r_2^T}^{r_1^T + r_2^T} dr_{12}^T r_{12}^T P_l^0\big(\cos\theta_{12}\big)(1 + r_{12}^T/2)^2 + \int_{r_2^T - r_1^T}^{r_1^T + r_2^T} dr_{12}^T r_{12}^T P_l^0\big(\cos\theta_{12}\big) \times (1 + r_{12}^T/2)^2\right] \tag{41}$$

and where $\cos\theta_{12} = ((r_1^T)^2 + (r_2^T)^2 - (r_{12}^T)^2)/(2r_1^T r_2^T)$.

Table 1 Evaluation of the exact energy functional for Hooke's atom using Hylleraas' [23] and Koga's [24] densities for the He atom and Koga's [24] densities for the two-electron ions Li$^+$ and Be^{+2}. For comparison, the exact results for Hooke's atom are included and the exact energies for the systems considered

Energies	Hooke	He(Hylleraas)	He(Koga)	Li$^+$(Koga)	Be^{+2}(Koga)
$T_c[\rho]$	0.029172	0.141246	0.096929	0.247715	0.471255
$T_s[\rho]$	0.635245	2.873206	2.867259	7.240085	13.614083
$T[\rho] = T_c[\rho] + T_s[\rho]$	0.664418	3.014453	2.964187	7.487800	14.085338
$E_{ee}[\rho]^a$	0.447443	0.774102	0.775188	0.749477	0.738870
$\widetilde{F}[\rho] = T[\rho] + E_{ee}[\rho]$	1.111861	3.788555	3.739375	8.237277	14.824208
$E_{\text{ext}}[v_{\text{ext}}, \rho]$	0.888139	−6.760337	−6.753459	−16.127542	−29.501996
$E_{\text{total}}[v_{\text{ext}}, \rho]$	2.000000	−2.971782	−3.014083	−7.890265	−14.677789
E_{exact}	2.000000	−2.903724	−2.903724	−7.279913	−13.655566
$E_{\text{ext}}[v_{\text{ext}}^{\text{Hooke}}, \rho]$	0.888139	0.296349	0.298365	0.111570	0.058017
$E_{\text{total}}[v_{\text{ext}}^{\text{Hooke}}, \rho]$	2.000000	4.084941	4.037741	7.609306	14.882224

[a] For this energy component we set $l_{\max} = 8$.

4 Results and discussion

The expressions for Hooke's atom functionals $T[\rho]$, given by Eqs. (35) and (37) and for $E_{ee}[\rho]$ given by Eq. (39) have been evaluated using the Hylleraas [23] and Koga [24] one-particle densities for the He atom and Koga's densities [24] for the two-electron systems Li$^+$ and Be^{2+}.

Also, calculations have been performed to evaluate the total energy functional

$$E_{\text{total}}[v_{\text{ext}}, \rho] = T[\rho] + E_{ee}[\rho] + E_{ext}[v_{\text{ext}}, \rho] \tag{42}$$

where the energy due to the external is defined as

$$E_{\text{ext}}[v_{\text{ext}}, \rho] = \int d^3\mathbf{r}\rho(\mathbf{r})v_{\text{ext}}(\mathbf{r}) \tag{43}$$

In Table 1 we list, for these densities, the values of $T[\rho]$ and of its components $T_s[\rho]$, – the kinetic energy for a non-interacting system, which in the present two-electron case is just the von Weizsäcker contribution $T_s[\rho] = T_W[\rho]$–, and of $T_c[\rho]$ the correlation contribution to the kinetic energy, defined by the relation $T_c[\rho] = T[\rho] - T_W[\rho]$. In this table, $E_{\text{total}}[v_{\text{ext}}, \rho]$ and $E_{\text{ext}}[v_{\text{ext}}, \rho]$ are the total and the external energies, defined by Eqs. (42) and (43), respectively. In this table we also list $E_{\text{total}}[v_{\text{ext}}^{\text{Hooke}}, \rho]$ and $E_{\text{ext}}[v_{\text{ext}}^{\text{Hooke}}, \rho]$ which are the total and the external energies, respectively, evaluated with the density of the system under consideration but with the Hooke's atom external potential. For comparison purposes, we have included the values for Hooke's atom and the exact energies for the systems under consideration.

As we have previously discussed, the computation of the local-scaling transformation function $r^T(r)$ is implicit in the evaluation of the energy functional (42). This implies finding the roots of the following transcendental equation expressing the conservation of charge:

$$\int_0^{r^T} x^2\,\rho_g(x) - \int_0^{r} x^2\,\rho(x) = 0, \tag{44}$$

This step was accomplished using the command *FindRoot* in *Mathematica*.

Once the function $r^T(r)$ has been determined, the remaining task is the numerical computation of the integrals of the kinetic and electron–electron energy densities. The former can still be computed with the aid of *Mathematica* (by using the *NIntegrate* command), for the latter the run-time becomes very large therefore making it more convenient to evaluate this energy component with a Fortran program. In this Fortran program (as in the *Mathematica* case) the infinite sum of Eq. (39) was truncated after an arbitray given number of $l_{\max}$ terms, and each integration was carried out using a Newton-Cotes quadrature. The results obtained with this program are shown in Table 1.

As we can see from Table 1, $E_{\text{total}}[v_{\text{ext}}^{\text{Hooke}}, \rho]$ (which is the energy of the complete Hooke's energy functional evaluated with densities of two-electron systems) satisfies the variational principle. In all cases, it is above the extremum value of 2.00000 hartrees. It attains this value only when the energy functional is computed using the exact Hooke's atom density. Similarly, one can see that the values of the functional $\widetilde{F}[\rho] = T[\rho] + E_{ee}[\rho]$ also satisfy the variational principle. The lowest value of 1.111861 hartrees is attained for $\widetilde{F}[\rho_{\text{Hooke}}]$. It is interesting to notice that there are considerable differences between the densities of these two-electron systems. This fact is reflected in the values of $E_{\text{ext}}[v_{\text{ext}}^{\text{Hooke}}, \rho]$, namely, in the values of the external energies calculated using the same Hooke's atom external potential but different one-particle densities.

The total energies obtained by adding to $\widetilde{F}[\rho]$ the contribution coming from the external energy $E_{\text{ext}}[v_{\text{ext}}, \rho]$ evaluated using the external potential that corresponds to the one-particle density, give values which are below the exact values for these two-electron systems. In other words, for these cases, the variational principle does not hold and in consequence, energy values lower than the exact ones can be obtained. This shows that the exact energy density functional for Hooke's atom, cannot be used to compute the total energy of other two-particle systems differing from Hooke's atom in just the external potential.

We address now the question of whether the functional $\widetilde{F}[\rho]$, which by construction is the exact functional for Hooke's atom, should also be the exact functional for other two-electron systems. The answer is certainly not. The reason is that the exact Hooke's functional which we have generated by applying local-scaling transformations on the exact wavefunction for Hooke's atom, only coincides with Levy's functional at the extremum, namely, at the point when the arbitrary density becomes equal to the exact density of Hooke's atom. Clearly, at other points of the variational scheme, any other given and fixed density will select among the wavefunctions in Hilbert space that particular wavefunction, which both minimizes $F[\rho]$ and yields the density ρ. And, in fact, if that given and fixed density is the exact density of any other two-particle system differing from Hooke's atom in just the external potential, then the wavefunction that minimizes $F[\rho]$ must certainly be the exact ground-state wavefunction for that particular system. Now, if we had at our disposal exact wavefunctions for two-particle systems corresponding to a reasonable sampling of external potentials, then we could construct using the same local-scaling transformation method employed for the case of Hooke's atom, the corresponding exact energy functional $\widetilde{F}[\rho]$ for all these systems. This would allow us to ascertain the common characteristics that should be present in the common (or universal) functional of Levy.

But from our present results, we may readily infer that each such functional will depend on particular characteristics of the system at hand. The question of the universality of the functional $F[\rho]$ can be stated, therefore, as that of whether it is possible to have a single expression that fulfills all the characteristics of particular exact functionals when these characteristics can be made to vary at wish. Most likely, the answer to this question is again negative. But this question, it seems to us, deserves to be explored. In this respect the lack of exact wavefunctions from which to obtain these functionals may be circumvented by resorting to highly approximate wavefunctions. Currently, work is underway to construct these explicit functionals through application of local-scaling transformations to these quasi-exact wavefunctions.

Let us finish by mentioning that, recently, one of us has shown [26] that the questions of the still unsolved problem of the N-representability of the two-matrix and that of the construction of the universal functional $F[\rho]$ are intimately related. Certainly this connection opens the way to exploring the effect that approximate N-representability conditions of the two-matrix have on the actual form of approximate functionals.

Acknowledgements We gratefully acknowledge support by FONACIT of Venezuela through Group Project No. G-97000741.

Appendix: Mathematica code

```
(*LST Wave function form: Nc*a[r1]*a[r2]*b[r1]
*b[r2]*c[r12]*)
Off[General::spell];
Off[General::spell1];
<< Calculus‘VectorAnalysis‘
b[r_] = Exp[-f[r]^2/4]
c[r_] = 1 + r/2
a[r_]   = Sqrt[R[r]/Rg[f[r]]];
lst[r_] = R[r]^(1/3)*Rg[f[r]]^(-1/3)*L[r]^(2/3);
df12d1 = f[r]/f12 -f2/f12*((f[r]^2+f2^2-f12^2)/
(2*f[r]*f2));
SetCoordinates[Spherical[r,t,p]];
gR=Simplify[Grad[Rg[f[r]]]/.D[f[r],r]->lst
[r]];
ga=Simplify[Grad[a[r]]/.D[f[r],r]->lst[r]];
gaga=Collect[Expand[Dot[ga,ga]],{R,Rg,L}];
gb=Simplify[Grad[b[r]]/.D[f[r],r]->lst[r]];
gbgb=Collect[Expand[Dot[gb,gb]],{R,Rg,L}];
gc=Simplify[Grad[c[f12[f[r]]]]/.{D[f[r],r]
->lst[r],
D[f12[f[r]],f[r]]->df12d1}];
SetCoordinates[Cartesian[x1,y1,z1]];
r12 = Sqrt[(x1-x2)^2 +(y1-y2)^2+(z1-z2)^2];
G1=Simplify[Grad[c[r12]]];
G2=Simplify[lst[r]^2*Dot[G1,G1]];
Clear[r12];
Simplify[G2/.{Sqrt[(x1-x2)^2 +(y1-y2)^2+
(z1-z2)^2]->f12},
f12>0];
gcgc=Simplify[%/.{(x1^2-2 x1 x2+x2^2+y1^2
- 2 y1 y2 + y2^2  + z1^2  - 2 z1 z2 + z2^2 )
->f12^2}];
taa = Collect[Expand[gaga*Rg[f[r]]],{R,Rg,L}];
tabac= Collect[Expand[a[r]*Dot[ga,gR]],
{R,Rg,L}];
tbb = Collect[Expand[gbgb*Rg[f[r]]*(a[r]/
b[r])^2],{R,Rg,L}];
tbbbc= Collect[Expand[(a[r]^2/(2*b[r]))
*Dot[gb,gR]],{R,Rg,L}];
tbc = Simplify[tbbbc - tbb];
tcc = Simplify[2*a[r]^2*b[r]^2*2*Pi*Nc^2/
f[r]*(Integrate[
Integrate[f[r2]*f12*b[r2]^2*gcgc,{f12,f[r]-
f[r2],f[r]+f[r2]}],
{f[r2],0,f[r]}]+Integrate[Integrate[f[r2]
*f12*b[r2]^2*gcgc,
{f12,f[r2]-f[r],f[r]+f[r2]}],{f[r2],f[r],
Infinity}]),{A>0,B>0,B1>0}];
t[r_]= Collect[PowerExpand[(taa +
tbb + tcc + tabac
+ 2*tbc)/2], {R[r],R[r]^(5/3)}]
```

In this code, $R[r]$ and $Rg[r]$ are the final and initial densities $\rho(r)$ and $\rho_g(r)$, respectively. The locally scaled coordinate $r^T(r)$ is denoted by $f(r)$ and $D[f[r], r]$ is the first derivative of the locally scaled coordinate, which is replaced by $lst[r]$ (line 8), the chain rule for the LST. The function $L1(r)$ has its origin in the Jacobian of the LST [22] and is given by:

$$L1(r) = \left(\frac{r}{f}\right)^3 \frac{\rho(r)}{\rho_g(f)} \tag{45}$$

In this code, the calculation of the gradient of the correlation function is done first through the use of the definition of the f_{12} variable and its first derivative with respect to f_1 (df12d1 in the source):

$$f_{12}^2 = f_1^2 + f_2^2 - 2\, f_1\, f_2\, \cos(\theta_{12}) \tag{46}$$

$$\frac{df_{12}}{df_1} = \frac{f_1}{f_{12}} - \frac{f_2}{f_{12}} \frac{(f_1^2 + f_2^2 - f_{12}^2)}{(2\, f_1\, f_1)} \tag{47}$$

é1 where the following substitution was made: $\cos(\theta_{12}) = (f_1^2 + f_2^2 - f_{12}^2)/(2 f_1 f_2)$

For evaluating the scalar product of such gradients, Cartesian coordinates were employed because in such coordinates it is easier to carry out the simplifications (lines 16–22).

In line 30, the integral of Eq. (32) is evaluated by means of the procedure described by Calais and Lödwin [26].

References

1. Ludeña EV, Gómez D, Karasiev V, Nieto P (2004) Int J Quantum Chem 99:297
2. Kestner NR, Sinanoğlu O (1962) Phys Rev 128:2687
3. Taut M (1993) Phys Rev A 48:3561
4. Kais S, Hershbach DR, Levine RD (1989) J Chem Phys 91:7791
5. Merkt U, Huser J, Wagner M (1991) Phys Rev B 43:7320
6. Laufer PM, Krieger JB (1986) Phys Rev A 33:1480
7. Samanta A, Ghosh SK (1991) Phys Rev A 43:6395
8. Kais S, Hershbach DR, Handy NC, Murray CW, Laming GJ (1993) J Chem Phys 99:417
9. Filippi C, Umrigar CJ, Taut M (1994) J Chem Phys 100:1290
10. Burke K, Perdew JP, Levy M (1995) In: Modern density functional theory. A tool for chemistry, Seminario JM, Politzer P (Eds.) Elsevier: Amsterdam p. 29
11. Huang CJ, Umrigar CJ (1997) Phys Rev A 56:290
12. Sahni V (1997) Phys Rev A 55:1846
13. Cioslowski J, Pernal K (2000) J Chem Phys 11:8434
14. Karwowski J, Cyrnek L (2004) Ann Phys (Leipzig) 13:181
15. Ludeña EV, Karasiev V, Artemyev A, Gómez D (2000) In: Many-electron densities and reduced density matrices, Cioslowski J (Ed.) Kluwer:Dordrecht p. 209
16. Artemyev A, Ludeña EV, Karasiev V (2002) J Mol Struct (Theochem) 580:47
17. Hohenberg PC, Kohn W (1964) Phys Rev 136:B864
18. Levy M (1979) Proc Nat Acad Sci USA 76:6062
19. Kryachko ES, Ludeña EV (1990) Energy density functional theory of many-electron systems, Kluwer:Dordrecht
20. Ludeña EV, López-Boada R (1996) Topics Curr Chem 180:169
21. Ludeña EV, López-Boada R, Karasiev V, Pino R, Valderrama E, Maldonado J, Colle R, Hinze J (1999) Adv Quant Chem 33:49
22. Ludeña EV, Karasiev V, López-Boada R, Valderrama E Maldonado J (1999) J Comput Chem 20:155
23. Hylleraas EA (1929) Z Phys 54:347; see also, Koga T (1990) J Chem Phys 93:3720
24. Koga T, Kasai Y, Thakkar AJ (1993) Int J Quantum Chem 46:689
25. Ludeña EV (2004) J Mol Struct (Theochem) 709:25
26. Calais JL, Löwdin P-O (1962) J Mol Spect 8:203