

# Local spin-density approximation for spin eigenspaces and its application to the excited states of atoms

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The main objective of this paper is to investigate the applicability of the subspace density-functional theory (SDFT) for the calculation of excited-state energies. The exchange and correlation energy density functionals,  $E_{xc}(\rho)$ , used in the present calculation are local and depend on the polarizability parameter  $\zeta=2S/N$ . The deviations of the calculated excited-state energies from their corresponding experimental values range from 0.1% to 0.8% for systems with more than two electrons, while for the helium isoelectronic series the corresponding range is from 0.1% to 1.9%. Thus the SDFT accuracy compares well in most cases with that of the ground-state local-density approximation calculations. Virial theorem and other relations concerning atoms are verified in the context of SDFT calculations. In this paper we also present a new formulation of the SDFT. Our new formulation alleviates the initial Kohn and Sham (KS) theory from the constraint of densities representable by single Slater determinants. This is an essential development as there are eigenstates of spin and other quantum operators, not representable by single Slater determinants.

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## I. INTRODUCTION

Although the excited-state Kohn and Sham (KS) theory was established long ago [1–3], its applications are very limited. Kohn, Oliveira, and Gross (KOG) [2] used the subspace (equiensemble) exchange and correlation functional  $E_{xc}(\rho)$  derived by Kohn [4] to calculate the energies of light atoms. Most of their results compare well with experiment, indicating that the  $E_{xc}(\rho)$  used has sufficient accuracy. However, the nonlocal dependence of this functional makes the calculations practically difficult. This is one of the reasons, in our view, that this method did not become popular. To our knowledge, after the work of Kohn [4] only Nagy [5] tried to determine explicit forms of  $E_{xc}(\rho)$  and do applications. However, her efforts were on the general ensemble theory [2], and thus the advantages derived from the geometric features of the subspace density-functional theory (SDFT) [6] were not taken into account.

One of these advantages is that in the SDFT the subspace density has the symmetry of the external potential, whereas in the KOG theory this is not the case. The consequence of this asymmetry is catastrophic in the case of degeneracy, as no solutions of the KS equations exist, transforming according to the irreducible representations (irreps) of the symmetry group of the exact Hamiltonian [7]. In the present paper, we do not deal with universal functionals but attention is focused on the more moderate problem of functionals appropriate for subspaces having definite spin  $S$  and total angular momentum  $L$ . The role of the spin parameter is apparent in the kinetic-energy functional of a two-particle noninteracting system, where the kinetic-energy functional for the  $S=0$  states is

$$\int d^3r \frac{[\nabla\rho(\mathbf{r})]^2}{8\rho(\mathbf{r})},$$

whereas the  $S=1$  state has a complicated expression which includes a phase factor, the explicit form of which can be

determined by solving a differential equation [8]. Thus, the universality of the ground-state functionals of the initial KS theory does not imply universality of the functional forms. In fact, for some cases it is not possible to express the noninteracting state of definite spin with a single Slater determinant (SLD) [9].

The most difficult task in density-functional theory (DFT) is the determination of the functional form of  $E_{xc}(\rho)$ . Although hundreds of papers have been written on this problem, the effort is essentially on the ground-state theory. Older work in this field can be found in DFT text books [10,11,3,12]. The methods employed to derive approximations for  $E_{xc}(\rho)$  are based on three overlapping methodologies: (a) scale transformations, sum rules, and variational principles [13–16]; (b) the electron gas and other model systems [17–20]; and (c) the hierarchy equations for the density matrices [8,21,22].

All these methods are also applicable in the SDFT. For this reason, in the present paper we propose a local  $E_{xc}(\rho, \zeta)$ , parametrized by the spin polarizability  $\zeta=2S/N$ , which can be viewed as a subspace generalization of the von Barth and Hedin functional, which was based on a random-phase approximation (RPA) of the spin-polarized electron gas [3,23].

The existence of accurate experimental and theoretical results for atoms and atomic ions was the reason that we attempted to apply our theory initially to these systems. Another reason for this choice is that the Hartree and  $E_{xc}(\rho)$  potentials are spherically symmetric, as in this case one can prove that the spherical part of the density is sufficient to determine uniquely the exchange and correlation potential [24]. This property of the KS potential leads to an additional advantage as one needs to determine only the radial part of the wave function, i.e., one has to solve one variable KS equations for which simple numerical procedures can be used. Hence, one has to deal with differential equations of a single variable, making it easier to have control over the computer programs and the accuracy of the computations.

In Sec. II, we derive the SDFT single-particle equations, without using the one-to-one correspondence between density and subspace, i.e., without using a Hohenberg and Kohn (HK) theorem for subspaces. The advantage of the new formulation is that there is no restriction of the KS states to single Slater determinants, nor to any noninteracting state. This is an essential feature which makes the present theory different from the initial KS theory, where one insists on a single SLD. We emphasize here that the HK theorem [25], although not necessary, is valuable for deriving general properties of the density functionals. Another feature of the present formulation is that it does not use functional differentiation. This is a big advantage as the functional derivatives of the energy with respect to the density may not exist [26].

In Sec. III we formulate our subspace local-density approximation (SLDA) scheme. The proposed functional  $E_{xc}(\rho, \zeta)$  is justified through an alternative treatment of the homogeneous electron gas (HEG). In this treatment, we deal with states of the HEG having not only well-defined total spin ( $S$ ) but also well-defined angular momentum ( $L$ ).

Finally, in Sec. IV we apply our method to the excited states of atoms and compare our results with those derived through the KOG method and draw some conclusions. We also compare them with those of von Barth, which refer to the lower-energy states of each symmetry [27].

## II. DERIVATION OF THE SUBSPACE KS EQUATIONS

### A. The subspace minimum principle

The initial DFT for excited states (SDFT) [1] was based on the one-to-one correspondence between the minimizing subspace and the subspace density. This is the subspace equivalent of the Hohenberg and Kohn theorem for the ground state [25], on which the initial KS theory was based [28]. As was shown in a previous paper [24], this theorem is not necessary for the ground-state formulation, and a more elegant rigorous formulation is possible. In this paper, we show that a derivation of the KS equations for the subspace theory of excited states is also possible. This formulation has certain advantages over the previous rigorous formulation [29] as no problem of representability of densities by Slater determinants arises. In fact, in the new formulation there is no need for the constraint of densities representable by single determinants.

Before proceeding to the derivation of the excited-state KS equations, we make a brief review of the subspace theory minimum principle, as it is essential for understanding the rest. By means of this theory [1] one can reduce the excited-state problem to a minimum principle problem, although the retrieval of information about the excited state corresponding to the energy eigenvalue  $E_j$  is not direct, but through subspaces of dimension  $j$  and  $j-1$  to be defined below: Let  $H$  be a Hamiltonian and  $M$  any linear subspace of the Hilbert space of dimension  $j$ .

Then one can define the functional

$$E(M) = \text{Tr}_M(H) = \sum_{i=1}^j \langle \Psi_i | H | \Psi_i \rangle, \quad |\Psi_i\rangle \in M. \quad (1)$$

Note that the above functional does not depend on the choice of basis in  $M$  as the trace ( $\text{Tr}$ ) of an operator in a subspace does not depend on the basis. Let us find the minima of this functional for all subspaces of the Hilbert space of dimension  $j$ . We take into account that by varying a single state  $|\Psi_i\rangle$  to  $|\Psi_i\rangle + \epsilon|u\rangle$ , where  $|u\rangle$  is a state with zero projection in the subspace  $M$ , one produces a different subspace  $M'$ . Then, if  $M$  is the minimizing subspace of dimension  $j$ , one gets for the first-order variations

$$\langle u | H | \Psi_i \rangle = 0, \quad |\Psi_i\rangle \in M,$$

and therefore  $H|\Psi_i\rangle$  has only a projection in  $|\Psi_i\rangle$ , i.e.,

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle \quad (2)$$

and

$$E(M) = \sum_{i=1}^j E_i, \quad E_i \leq E_{i+1}, \quad (3)$$

i.e.,  $E(M)$  is the sum of the  $j$  lowest-energy eigenvalues of  $H$ . Then if  $M_j$  and  $M_{j-1}$  are minimizing subspaces, over the set of subspaces of dimension  $j$  and  $j-1$ , the  $j$ th eigenvalue in ascending order is

$$E_j = E(M_j) - E(M_{j-1}).$$

Thus, by using an indirect method, one can calculate the energy eigenvalues and eigenstates by applying a minimum principle. The space of eigenstates will be referred to as the *eigenspace*. To calculate the expectation value of an operator  $A$ , corresponding to the energy eigenstate  $|\Psi_j\rangle$ , we need the subspace functional

$$Q_A(M) = \text{Tr}_M(A) = \sum_{i=1}^j \langle \Psi_i | A | \Psi_i \rangle, \quad |\Psi_i\rangle \in M \quad (4)$$

for subspaces of dimension  $j$  and dimension  $j-1$ . Thus, given the minimizing subspaces  $M_j$  and  $M_{j-1}$ , the expectation value of  $A$  can be determined by the relation

$$\langle \Psi_j | A | \Psi_j \rangle = Q_A(M_j) - Q_A(M_{j-1}). \quad (5)$$

If the Hamiltonian is invariant under a group of transformations  $G$ , one can choose subspaces transforming according to a definite irrep of  $G$  and find the minima in this class of subspaces. In this way there is no problem of degeneracy as one considers the whole space of degeneracy and not a single state.

### B. The new SDFT formulation

The Hamiltonian considered here is the many-electron Hamiltonian

$$H_V = T + H_{\text{int}} + \hat{V}, \quad (6)$$

where  $T$  is the kinetic-energy operator,

$$T = \frac{1}{2} \int d^3r \sum_s \nabla \psi^{s\dagger}(\mathbf{r}) \nabla \psi^s(\mathbf{r}), \quad (7)$$

$H_{\text{int}}$  is the interaction energy,

$$H_{\text{int}} = \frac{1}{2} \int d^3r \int d^3r' \sum_{st} \frac{\psi^{s\dagger}(\mathbf{r}) \psi^{t\dagger}(\mathbf{r}') \psi^t(\mathbf{r}') \psi^s(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (8)$$

$$\hat{V} = \int d^3r \hat{\rho}(\mathbf{r}) V(\mathbf{r}), \quad (9)$$

and  $\hat{\rho}(\mathbf{r})$  is the density operator,

$$\hat{\rho}(\mathbf{r}) = \sum_s \psi^{s\dagger}(\mathbf{r}) \psi^s(\mathbf{r}). \quad (10)$$

The summation over  $s$  and  $t$  indicates summation with respect to the spin indices.

We next define the functionals  $K$  and  $L$  in the same way as in the case of the ground-state formulation [24], the difference being that the arguments of the new functionals are  $j$ -dimensional subspaces. In the case of degeneracy, the dimensionality  $j$  must be an integral multiple of the dimension of the irrep of the symmetry group of the Hamiltonian and will be denoted by a suffix, e.g., for the case of spin symmetry by  $M^S$  we denote the subspaces of the  $2S+1$  eigenstates of  $\mathbf{S}^2$ . The upper index will be omitted in the following as subspaces  $M^S$  of definite spin will be considered, i.e., our Hamiltonian will not involve any spin-orbit interaction. In this way the energy eigenstates are simultaneously eigenstates of  $\mathbf{S}^2$  and the variational principle can be limited to variations in this space, as variations to other subspaces of spin  $S'$  satisfy the relation

$$\langle u^{s'} | H | \Psi_i^s \rangle = c \delta_{ss'}$$

and thus variations out of the subspace under consideration vanish identically as they are orthogonal to any state of the form  $H | \Psi_i^s \rangle$ .

The minimum kinetic-energy functional is

$$K(M) = \inf\{Q_T(M') : \rho_{M'}(\mathbf{r}) = \rho_M(\mathbf{r})\}, \quad (11)$$

where

$$\rho_M(\mathbf{r}) = Q_{\rho(\mathbf{r})}(M) = \sum_{i=1}^j \langle \Psi_i | \hat{\rho}(\mathbf{r}) | \Psi_i \rangle, \quad (12)$$

$$|\Psi_i\rangle \in M, \quad \langle \Psi_i | \Psi_j \rangle = \delta_{ij}.$$

The above definition implies that for each subspace  $M$  we consider the set of subspaces  $M'$ , having the same density as  $M$ . To each such subspace we assign a kinetic energy  $Q_T(M') = \text{Tr}_{M'}(T)$ . Then the functional  $K(M)$  is the minimum of the kinetic energy in this set of subspaces. Note that the value of the functional  $K(M)$  is the same for all subspaces having the same density. This is an essential difference with respect to our previous rigorous formulations [29]

as our definitions here do not demand details about the space of densities, i.e., in this formulation only subspace representable densities are involved. In the same way as above, one can define for every subspace  $M$  the minimum internal energy functional for the operator  $H_0 = T + H_{\text{int}}$ ,

$$L(M) = \inf\{Q_{H_0}(M) : \rho_{M'}(\mathbf{r}) = \rho_M(\mathbf{r})\}, \quad (13)$$

which is the equivalent of the minimum kinetic-energy functional  $K$ . Here, one can show that the infima of these functionals are minima, i.e., minimizing subspaces of the Hilbert space belonging to the irrep of the symmetry group of  $H$  exist [30]. The procedure followed is similar to that of Lieb [26] and Hadjisavvas *et al.* [29]. Thus one can use the minima under the constraint in place of the infima. Finally, we define the functional

$$G(M) = L(M) + Q_T(M) - K(M) + \int d^3r \rho_M(\mathbf{r}) V(\mathbf{r}), \quad (14)$$

where  $Q_T(M) = \text{Tr}_M(T)$ , according to the notation introduced by Eq. (4).

Since  $Q_T(M) - K(M) \geq 0$ , one concludes that the minimum of  $G(M)$  is obtained when equality holds. Further, one can show, following the same proving procedure used for the single state [24], that

$$\min G(M) = \min\{\text{Tr}_{M'}(H_V) : \rho_{M'}(\mathbf{r}) = \rho_M(\mathbf{r})\} = \sum_{i=1}^j E_i. \quad (15)$$

Thus, the minimum value of the functional  $G(M)$  is equal to the sum of the  $j$  lowest-energy eigenvalues of the initial Hamiltonian  $H_V$ , whereas the minimizing subspace is not the subspace  $S$  which minimizes the initial Hamiltonian, i.e., the one for which the equality  $\text{Tr}_S(H_V) = \min\{\text{Tr}_{M'}(H_V)\}$  holds, but a noninteracting system  $j$ -dimensional subspace which minimizes the kinetic energy under the density constraint since  $Q_T(M) = K(M)$ . Thus, the following equation is satisfied:

$$Q_T(M) = \min\left\{ \sum_{i=1}^j \langle \Psi_i | T | \Psi_i \rangle : \sum_{i=1}^j \langle \Psi_i | \hat{\rho}(\mathbf{r}) | \Psi_i \rangle = \rho_S(\mathbf{r}), |\Psi_i\rangle \in M, \langle \Psi_i | \Psi_j \rangle = \delta_{ij} \right\}, \quad (16)$$

where  $\rho_S(\mathbf{r})$  is the density corresponding to the subspace  $S$  defined above.

As is well known, minimization of the kinetic energy under the density constraint leads to the following equation [18,29]:

$$T | \Phi_i \rangle + \int d^3r \hat{\rho}(\mathbf{r}) V_{\text{eff}}(\mathbf{r}) | \Phi_i \rangle = E'_i | \Phi_i \rangle \quad (17)$$

with the potential  $V_{\text{eff}}$  entering as a Lagrange multiplier, to be determined by the density constraint. These are equations

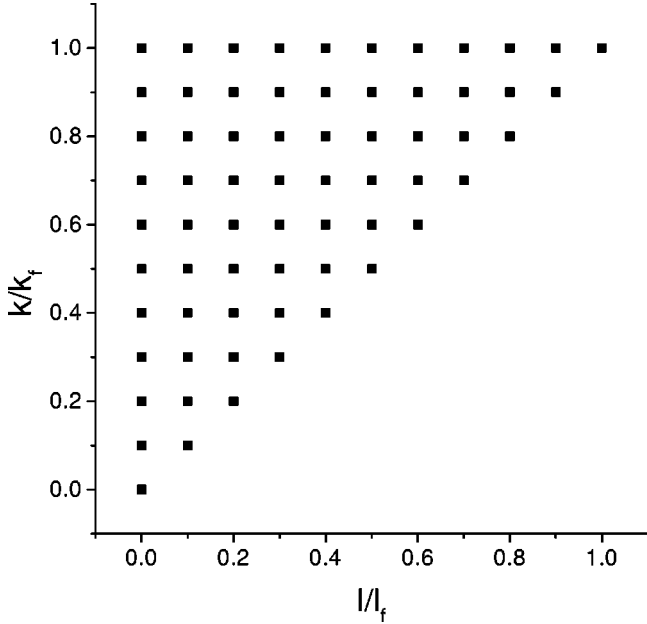


FIG. 1. Occupied spin orbitals for the ground state of a jellium model confined by a spherical surface. Note that the values of  $k$  are limited on the right because of the relation  $kR \leq l$ .

of a noninteracting system and for this reason the eigenstates  $|\Phi_i\rangle$  will be referred to as *noninteracting states*. Thus for a given external potential  $V$ , there is a noninteracting Hamiltonian with an effective potential  $V_{\text{eff}}$ , with the same density as that of the minimizing subspace of the initial Hamiltonian  $H_V$ . As no constraint was imposed, the states  $|\Phi_i\rangle$  need not be single Slater determinants but a linear combination of them. Thus, one can choose states which transform according to the irreps of a group and not representable by single SLD.

We next proceed in a more conventional way to define  $E_{\text{xc}}$ ,

$$E_{\text{xc}}(M) = L(M) - K(M) - E_H(M), \quad (18)$$

where

$$E_H(M) = \frac{j}{2} \int d^3r \int d^3r' \frac{\rho_M(\mathbf{r})\rho_M(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \quad (19)$$

is the Hartree energy and the density normalization here and in the following is to the particle number  $N$ .

We note that all quantities on the right are determined uniquely by the subspace density, because of their definitions. Thus since all subspaces with the same density have the same minimum internal energy and kinetic energy, one can write  $L(M) = U(\rho_M)$ ,  $K(M) = T(\rho_M)$ , and in this way the exchange and correlation energy can be expressed in terms of the subspace density. Then

$$G(M) = Q_M(M) + E_H(\rho_M) + E_{\text{xc}}(\rho_M) + j \int d^3r \rho_M(\mathbf{r})V(\mathbf{r}). \quad (20)$$

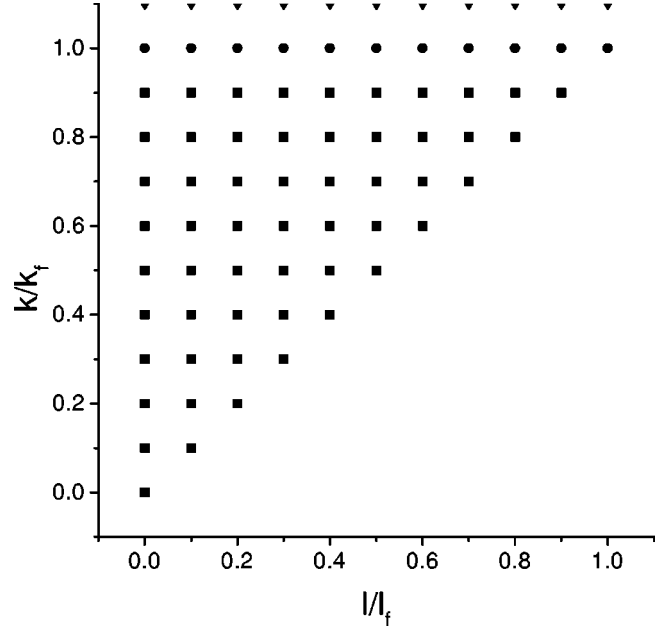


FIG. 2. Occupied spin orbitals of a high angular momentum excited state for the jellium model confined by a spherical surface. The triangles correspond to spin orbitals with positive  $L_z$  while the circles have  $m$  positive or 0.

In varying the subspace  $M$  by variations of  $|\Phi_i\rangle$ , we can write

$$\delta E_{\text{xc}}(\rho_M) = \frac{\delta E_{\text{xc}}(\rho_M)}{\delta \rho_M} \langle \delta \Psi_i | \hat{\rho}(\mathbf{r}) | \Psi_i \rangle$$

and in this way retrieve Eq. (17), where  $V_{\text{eff}} = V + V_H + V_{\text{xc}}$ , with exchange and correlation potential

$$V_{\text{xc}}(\rho_M) = \frac{\delta E_{\text{xc}}(\rho_M)}{\delta \rho_M(\mathbf{r})} \quad (21)$$

and Hartree potential

$$V_H(\rho_M) = \int d^3r' \frac{\rho_M(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}. \quad (22)$$

However, this derivation is at the expense of mathematical rigor as we used the functional derivative of the exchange and correlation energy with respect to the density and one has to prove the existence of this derivative, after defining the space of densities [26].

### III. THE SPIN-INDEXED SUBSPACE FUNCTIONALS

When no magnetic field and spin-orbit interactions are present, the total spin operator  $\mathbf{S}$  commutes with the Hamiltonian. Therefore, one can restrict the search of the energy eigenstates in the subspace of the Hilbert space spanned by eigenstates of  $\mathbf{S}^2$  and  $\mathbf{S}_z$ , having fixed  $S$  and  $M_S$ . Thus one can develop a SDFT theory with fixed quantum numbers  $S$ . As usual, in order to get an approximation for  $E_{\text{xc}}(\rho)$ , we derive some conclusions for systems with a large number of

TABLE I. Subspaces with the expressions of their densities, their dimension (dim), particle number ( $N$ ), spin ( $S$ ), and total angular momentum ( $L$ ).

Subspace	dim	$N$	$S$	$L$	Subspace density
$M_1 = \{1s^2\ ^1S\}$	1	2	0	0	$2\phi_{10}^2$
$M_2 = \{1s2s; \ ^1S\} + M_1$	2	2	0	0	$\frac{3}{2}\phi_{10}^2 + \frac{1}{2}\phi_{20}^2$
$M_3 = \{1s2s; \ ^3S\}$	3	2	1	0	$\phi_{10}^2 + \phi_{20}^2$
$M_4 = \{1s2p; \ ^1P\}$	3	2	0	1	$\phi_{10}^2 + \phi_{21}^2$
$M_5 = \{1s2p; \ ^3P\}$	9	2	1	1	$\phi_{10}^2 + \phi_{21}^2$
$M_6 = \{1s3s; \ ^1S\} + M_2$	3	2	0	0	$\frac{4}{3}\phi_{10}^2 + \frac{1}{3}\phi_{20}^2 + \frac{1}{3}\phi_{30}^2$
$M_7 = \{1s3s; \ ^3S\} + M_3$	6	2	1	0	$\phi_{10}^2 + \frac{1}{2}\phi_{20}^2 + \frac{1}{2}\phi_{30}^2$
$M_8 = \{1s3p; \ ^3P\} + M_5$	18	2	1	1	$\phi_{10}^2 + \frac{1}{2}\phi_{21}^2 + \frac{1}{2}\phi_{31}^2$
$M_9 = \{1s3d; \ ^3D\}$	15	2	1	2	$\phi_{10}^2 + \phi_{32}^2$
$M_{10} = \{1s^22s; \ ^2S\}$	2	3	$\frac{1}{2}$	0	$2\phi_{10}^2 + \phi_{20}^2$
$M_{11} = \{1s^22p; \ ^2P\}$	6	3	$\frac{1}{2}$	1	$2\phi_{10}^2 + \phi_{21}^2$
$M_{12} = \{1s^22s^2; \ ^1S\}$	1	4	0	0	$2\phi_{10}^2 + 2\phi_{20}^2$
$M_{13} = \{1s^22s, 2p; \ ^3P\}$	9	4	1	1	$2\phi_{10}^2 + \phi_{20}^2 + \phi_{21}^2$
$M_{14} = \{1s^22s, 2p; \ ^1P\}$	3	5	0	1	$2\phi_{10}^2 + \phi_{20}^2 + \phi_{21}^2$
$M_{15} = \{1s^22s^22p; \ ^2P\}$	6	5	$\frac{1}{2}$	1	$2\phi_{10}^2 + 2\phi_{20}^2 + \phi_{21}^2$
$M_{16} = \{1s^22s, 2p^2; \ ^4P\}$	12	5	$\frac{3}{2}$	1	$2\phi_{10}^2 + \phi_{20}^2 + 2\phi_{21}^2$
$M_{17} = \{1s^22s^22p^2; \ ^1D\}$	5	6	0	2	$2\phi_{10}^2 + 2\phi_{20}^2 + 2\phi_{21}^2$
$M_{18} = \{1s^22s^22p^2; \ ^3P\}$	9	6	1	1	$2\phi_{10}^2 + 2\phi_{20}^2 + 2\phi_{21}^2$
$M_{19} = \{1s^22s2p^3; \ ^5S\}$	5	6	2	0	$2\phi_{10}^2 + \phi_{20}^2 + 3\phi_{21}^2$
$M_{20} = \{1s^22s^22p^4; \ ^3P\}$	9	8	1	1	$2\phi_{10}^2 + 2\phi_{20}^2 + 4\phi_{21}^2$
$M_{21} = \{1s^22s2p^5; \ ^3P\} + M_{20}$	18	8	1	1	$2\phi_{10}^2 + \frac{3}{2}\phi_{20}^2 + \frac{9}{2}\phi_{21}^2$
$M_{22} = \{1s^22s2p^5; \ ^1P\}$	3	8	0	1	$2\phi_{10}^2 + \phi_{20}^2 + 5\phi_{21}^2$
$M_{23} = M_2 + M_4$	5	2	0		$\frac{6}{5}\phi_{10}^2 + \frac{1}{5}\phi_{20}^2 + \frac{3}{5}\phi_{21}^2$

TABLE II. Total energies for atoms and ions for two electrons (helium isoelectronic series).

Ion	Configuration	$M$	$E_{xc}$	$E_{calc}$	$E_{expt.}$	% error
He	$\{1s^2\ ^1S\}$	$M_1$	-1.003	-2.871	-2.904	1.1
C (V)	$\{1s^2\ ^1S\}$	$M_1$	-3.186	-32.087	-32.406	1.4
O (VII)	$\{1s^2\ ^1S\}$	$M_1$	-4.254	-58.690	-59.156	0.8
He	$\{1s2s\ ^1S\}$	$M_2$	-0.772	-2.182	-2.147	1.6
C (V)	$\{1s2s\ ^1S\}$	$M_2$	-2.431	-21.253	-21.232	0.1
O (VII)	$\{1s2s\ ^1S\}$	$M_2$	-3.232	-38.284	-38.232	0.1
He	$\{1s2s\ ^3S\}$	$M_3$	-0.700	-2.156	-2.176	0.9
C (V)	$\{1s2s\ ^3S\}$	$M_3$	-2.165	-21.235	-21.431	0.9
O (VII)	$\{1s2s\ ^3S\}$	$M_3$	-2.882	-38.275	-38.522	0.6
He	$\{1s2p\ ^1P\}$	$M_4$	-0.674	-2.082	-2.124	1.9
He	$\{1s2p\ ^3P\}$	$M_5$	-0.687	-2.115	-2.134	0.8
C (V)	$\{1s2p\ ^1P\}$	$M_4$	-1.807	-20.762	-21.103	1.6
C (V)	$\{1s2p\ ^1P\}$	$M_{23}$	-2.042	-20.742	-21.231	1.7
O (VII)	$\{1s3s\ ^1S\}$	$M_6$	-2.806	-34.519	-34.736	0.6
O (VII)	$\{1s3s\ ^3S\}$	$M_7$	-2.647	-34.613	-34.812	0.6
C (V)	$\{1s3p\ ^3P\}$	$M_8$	-2.013	-19.286	-19.428	0.7
C (V)	$\{1s3d\ ^3D\}$	$M_9$	-1.875	-19.207	-19.401	1.0
He	$\{1s2p\} \ ^3P$	$M_{24}$	-0.689	-2.111	-2.134	1.0
C (V)	$\{1s2p\} \ ^3P$	$M_5$	-2.196	-21.140	-21.231	0.4
C (V)	$\{1s2p\} \ ^3P$	$M_{24}$	-2.185	-21.109	-21.231	0.6

TABLE III. Total energies for atoms and ions for  $N=3$ .

Ion	Configuration	$M$	$E_{xc}$	$E_{calc}$	$E_{expt.}$	% error
Li (I)	$\{1s^2 2s; ^2S\}$	$M_{10}$	-1.720	-7.418	-7.478	0.8
C (IV)	$\{1s^2 2s; ^2S\}$	$M_{10}$	-3.646	-34.516	-34.745	0.6
Li (I)	$\{1s^2 2p; ^2P\}$	$M_{11}$	-1.691	-7.352	-7.410	0.8
C (IV)	$\{1s^2 2p; ^2P\}$	$M_{11}$	-3.643	-34.451	-34.451	0.6

electrons and try to extend their validity to systems with a small number of electrons.

A well-known property of a solid is the dependence of its intensive properties on the magnetization  $\zeta=2S/N$ . Thus if we consider another piece of the same material with volume  $V'=qV$ , number of electrons  $N'=qN$ , and spin  $S'=qS$ , its intensive properties such as, e.g., its bulk density, will not change. The same holds for the surface density. Hence, the main dependence of  $E_{xc}(\rho)$  is on the parameter  $\zeta$ . Thus by using the new set of parameters  $\zeta$  and  $n=NS$ , the new functional of the exchange and correlation energy  $E_{xc}(\rho; \zeta, n)$  will have a strong dependence on  $\zeta$  and a weak one on  $n$ , which in the first-order approximation can be neglected. If we consider now the spectroscopic properties of the above two pieces of solid, we find that they are also the same. We therefore conclude that in a subspace local-density approximation, the functional of the exchange and correlation energy must not have a strong explicit dependence on  $S$  and  $N$  independently, but on  $\zeta$ .

Similarly, in a metal with a spherical shape, where the total angular momentum  $L$  is a good quantum number, the main dependence of its properties is on  $\zeta_L=L/N$ . We also claim that our functionals must not depend strongly on the subspace dimension  $j$ , since, should such a dependence exist, then a finite excitation energy would result for metals enclosed in spherical surfaces, which is in contradiction to the well-known fact that the spectrum of the low-lying excitations is continuous. Symmetry breaking does not change the essential features of the energy spectrum either. Thus, e.g., by enclosing the same metal volume in a cube instead of a sphere, where the new many-particle wave functions become linear combinations of the older ones, involving different total angular momenta, we have the same excitation spectrum. In the next paragraph we derive quantitative relations on this matter. The procedure usually followed for the derivation of the local-density approximation of  $E_{xc}$  is to extend the validity of the jellium model and write

$$E_{xc}(\rho; \zeta, \zeta_L) = \int \rho(r) \varepsilon_{xc}^{\text{HOM}}(\rho; \zeta, \zeta_L) d^3 r, \quad (23)$$

TABLE IV. Total energies for atoms and ions for  $N=4$ .

Ion	Configuration	$M$	$E_{xc}$	$E_{calc}$	$E_{expt.}$	% error
C (III)	$\{1s^2 2s^2; ^1S\}$	$M_{12}$	-3.993	-36.230	-36.535	0.8
C (III)	$\{1s^2 2s 2p; ^3P\}$	$M_{13}$	-4.167	-36.107	-36.295	0.5
C (III)	$\{1s^2 2s 2p; ^1P\}$	$M_{14}$	-3.974	-35.923	-36.068	0.4
C (III)	$\{1s^2 2s 2p; ^1P\}$	$M_{25}$	-3.978	-35.923	-36.068	0.4

TABLE V. Total energies for atoms and ions for  $N=5$ .

Ion	Configuration	$M$	$E_{xc}$	$E_{calc}$	$E_{expt.}$	% error
O (IV)	$\{1s^2 2s^2 2p; ^2P\}$	$M_{15}$	-6.264	-70.788	-71.208	0.6
O (IV)	$\{1s^2 2s 2p^2; ^4P\}$	$M_{16}$	-6.652	-70.648	-70.883	0.3

where  $\varepsilon_{xc}^{\text{HOM}}(\rho; \zeta, \zeta_L)$  is the exchange and correlation energy per particle of a homogeneous electron gas of density  $\rho$ . Under these considerations, the ground state of an unpolarized ( $\zeta=0$ ) HEG enclosed in a sphere of radius  $R$ , with zero angular momentum ( $\zeta_L=0$ ), is not described by the familiar Fermi sphere but by a Fermi prism whose cross section with the  $M=0$  plane,  $M$  being the quantum number corresponding to  $L_Z$ , is given in Fig. 1. Each dot of the graph represents a KS state with degeneracy  $2(2l+1)$ . It is straightforward to verify the validity of the following relations, known from the traditional treatment of the jellium model:

$$k_f R = (9\pi/4)^{1/3} N^{1/3}, \quad t = T/N = (3/10)(3\pi^2)^{2/3} \rho^{2/3}, \quad (24)$$

where  $T$  stands for the jellium kinetic energy.

We claim that, unlike the strong dependence of  $\varepsilon_{xc}$  on the spin polarization  $\zeta$ , the dependence on the angular momentum polarization  $\zeta_L$  is negligible in a first-order approximation. This is because in the second case, unlike the first, it is possible to create high angular momentum excited states with small excitation energies. For example, by annihilating an electron at the Fermi level ( $k=k_f$ ,  $l=0$ ,  $m=0$ ) and creating one at ( $k'=k_f+\Delta k$ ,  $l=l_f$ ,  $m=l_f$ ), we can form a many-electron jellium state with  $L=l_f \sim \rho^{1/3} R$ , which is very large and for  $N$  tending to infinity it goes to infinity, while the corresponding excitation energy  $\Delta E$  tends to zero in the first-order approximation as  $\Delta E \approx k_f \Delta k \sim \rho^{1/3}/R$ . This is obviously *not* the case with the spin polarization since the same excitation energy can only give an increment of the total spin  $S$  equal to 1, if we flip a spin-down to a spin-up orbital.

In order to get further insight, we consider an excitation of a whole layer of electrons, reversing the sign of the  $z$  component of the total angular momentum of negative  $m$  from  $k_f - \Delta k$  to  $k_f + \Delta k$ , while we keep fixed the values of  $l$  and  $m_s$  (see Fig. 2). (Note that the values of  $k$  are limited on the right because of the relation  $kR \leq l$  [31].) The resulting jellium state can be represented by a Slater determinant which can be written in the second quantization representation as

TABLE VI. Total energies for atoms and ions for  $N=6$ .

Ion	Configuration	$M$	$E_{xc}$	$E_{calc}$	$E_{expt.}$	% error
O (III)	$\{1s^2 2s^2 2p^2; ^1D\}$	$M_{17}$	-6.852	-72.746	-73.132	0.5
O (III)	$\{1s^2 2s^2 2p^2; ^3P\}$	$M_{18}$	-7.000	-72.885	-73.224	0.5
O (III)	$\{1s^2 2s 2p^3; ^5S\}$	$M_{19}$	-7.441	-72.782	-72.949	0.2

TABLE VII. Total energies for atoms and ions for  $N=7$ .

Ion	Configuration	$M$	$E_{xc}$	$E_{calc}$	$E_{expt.}$	% error
F (III)	$\{1s^2 2s^2 2p^3; ^4S\}$	$M_{26}$	-8.882	-97.408	-97.801	0.4
F (III)	$\{1s^2 2s^2 2p^3; ^2D\}$	$M_{27}$	-8.606	-97.147	-97.645	0.5

$$|\Phi\rangle = \prod_{l=1}^{l_f} \prod_{m=1}^l \alpha_{k_f + \Delta k, l, m, m_s}^+ \alpha_{k_f, l, -m, m_s} |\Phi_0\rangle, \quad (25)$$

where  $|\Phi_0\rangle$  stands for the ground state of jellium. One can easily verify that  $L^+|\Phi\rangle=0$ , which means that  $|\Phi\rangle$  is an eigenstate of  $L^2$  and  $L_z$  with corresponding eigenvalues

$$L = M^* = 2 \sum_1^{l_f} \sum_{m=1}^l m = \sum_1^{l_f} l(l+1) \sim l_f^3/4 \sim N$$

giving a finite  $\zeta_l$ .

Then, in order to get jellium excitations with  $\zeta_L$  finite, appropriate to extend our results for atoms and molecules, it is enough to excite a single layer making thus an increase of the excitation energy of the order of

$$\begin{aligned} \Delta T &= \sum_1^{l_f} \sum_{m=1}^l k_f \Delta k = l_f(l_f+1)k_f \Delta k \\ &\sim N^{1/3} \quad \text{and} \quad \Delta T/N = N^{-2/3}. \end{aligned}$$

In contrast, in order to create a jellium excitation with spin polarization  $\zeta \sim 1$ , we must raise half of the total population of the electrons, thus creating a state with a very high excitation energy of order  $N$ . Consequently, we can ignore, in a first approximation, the dependence of the  $E_{xc}$  functional on  $\zeta_L$  and keep only the dependence on the global spin-polarization parameter,  $\zeta$ . Thus, we write

$$E_{xc}(\rho; \zeta) \int \rho(r) \varepsilon_{xc}^{\text{HOM}}(\rho; \zeta) d^3r. \quad (26)$$

The explicit form of  $\varepsilon_{xc}^{\text{HOM}}(\rho; \zeta)$  can be derived through the common RPA approximation. In this work, we adopted the widely used von Barth and Hedin approximation [27], with the Hedin and Lundqvist parametrization [32]. The corresponding exchange potential is given by  $V_{xc}(\rho) = \delta E_{xc}(\rho) / \delta \rho(\mathbf{r})$ .

Note that in our global spin local-density approximation, only a single potential is necessary, contrary to the familiar ground-state local spin-density approximation (LSD) in which two KS potentials are necessary, one for the spin-up

and another for the spin-down electrons. This is an advantage of the method proposed, since the involvement of two different KS potentials in the familiar ground-state LSD approximation requires higher computational effort, as two potentials must be calculated selfconsistently. Finally, we note that our spin polarization parameter,  $\zeta = 2S/N$ , is a global one and not a function of the space variable  $\zeta(r) = \rho^\dagger(r) - \rho^\downarrow(r) / \rho^\dagger(r) + \rho^\downarrow(r)$ , the local spin polarization function, involved in the ground-state LSD approximation. These two different approaches coincide in the jellium approximation, but in nonuniform densities they are different.

We conclude this section by noting that the present theory has certain advantages for systems with definite spin and spacial angular momentum, but cannot be applied to electron systems with nonuniform magnetic interactions and systems not having spherically symmetry such as, e.g., molecules.

### A. Application of the method to light atoms

The SDFT one-particle KS equations corresponding to the many-particle KS equation (17) for the particular case we are dealing with have the form

$$\frac{1}{2} \left( -\nabla_r^2 + \frac{l(l+1)}{r^2} \right) \phi_{i,l}(r) + V_{\text{eff}}(r) \phi_{i,l}(r) = \epsilon_{i,l} \phi_{i,l}(r), \quad (27)$$

where

$$\nabla_r^2 = r^{-2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \quad (28)$$

and the density of the subspace of degeneracy is

$$\rho_M(r) = \sum_{i,l} n_i (2l+1) \phi_{i,l}^2(r), \quad (29)$$

$n_i$  being the occupation numbers, which depend on the configuration and the total spin and angular momentum. We emphasize here that in the SDFT the occupation numbers  $n_i$  are fixed and are derived from the subspace [33], whereas in other theories such as, e.g., the general ensemble theory of Gross, Oliveira, and Kohn [2], these numbers vary as the statistical weights for the states of the ensemble can change. However, to our knowledge up to the present time calculations have been limited to the equiensemble case.

We applied our subspace theory, using the widely used von Barth and Hedin approximation [27] with the Hedin and Lundqvist parametrization [32] functional, to the excited states of atoms and ions with nuclear charge  $Z$  ranging from two to ten and the number of electrons two to eight. Calculations

 TABLE VIII. Total energies for atoms and ions for  $N=8$ .

Ion	Configuration	$M$	$E_{xc}$	$E_{calc}$	$E_{expt.}$	% error
Ne (III)	$\{1s^2 2s^2 2p^4; ^3P\}$	$M_{20}$	-10.648	-126.111	-126.674	0.4
Ne (III)	$\{1s^2 2s^2 2p^5; ^3P\}$	$M_{21}$	-10.615	-125.278	-125.719	0.3
Ne (III)	$\{1s^2 2s^2 2p^5; ^1P\}$	$M_{22}$	-10.487	-125.155	-125.331	0.1

TABLE IX. Comparison of SDFT and KOG results, where  $\Delta E$  is the excitation energy.

State	dim	$E$ (SDFT)	$\Delta E$ (SDFT)	$E$ (KOG)	$\Delta E$ (KOG)	$E$ (Expt.)	$\Delta E$ (Expt.)
$1s^2$	1	-2.871		-2.836		-2.904	
$1s2s$	4	-2.163	0.709	-2.073	0.763	-2.169	0.735
$1s2p$	12	-2.114	0.757	-1.985	0.851	-2.131	0.773

lations for such systems, being highly inhomogeneous, represent together with metallic surfaces the most harsh test for any LDA approximation scheme, both for the ground and the excited states. We used a wide spectrum of configurations and subspaces in order to test our theory. The results of our calculations appear in Table II, where we also give the experimental values of the energies for comparison. All experimental data in our tables were taken from the NIST database for Atomic Spectroscopy (National Institute of Standards and Technology, U.S. Department of Commerce, 1995). We also give the percent deviation of the calculated from the corresponding experimental values.

In Table I we define the subspaces through which the excited-state energies of atoms have been derived. In the last column of Table I we give the expression of the subspace density in terms of the occupied orbitals, normalized to the number of particles  $N$ . The dimensions  $M$  of our subspaces ranged from 1 to 18, the total spin  $S$  from 0 to 2, the polarizability  $\zeta$  from 0 to 1, and the total angular momentum  $L$  from 0 to 2. The atomic orbitals involved in our calculations are of the type  $1s$ ,  $2s$ ,  $3s$ ,  $2p$ ,  $3p$ , and  $3d$ .

Our results for the excited-state energies appear in Tables II–VIII. All results are given in a.u. (hartrees). The accuracy of the calculated energies is comparable to that of the ground state, as the deviations from the experimental values are in the range of 0.1–0.8% for a number of electrons larger than two, while for the helium isoelectronic series the corresponding numbers are from 0.2% to 1.9%. As expected, the accuracy increases with the number of particles, since when the number of particles becomes larger, the deviations from the HEG, by means of which the density functional was derived, become smaller although still strongly inhomogeneous. The accuracy of the excited energies calculated by our method is in most cases the same with that of the ground state, when a local-density approximation is used. As one can conclude from the recent ground-state calculations of Jarzecki and

TABLE X. Comparison of von Barth and SDFT error of energies  $E$  and excitation energies  $\Delta E$  with respect to the corresponding experimental values.

State	Err. (%) of $E$ (SDFT)	Err. (%) of $E$ (Barth)	Err. (%) of $\Delta E$ (SDFT)	Err. (%) of $\Delta E$ (Barth)
$1s2s\ ^3S\ m_s=1$	0.9	1.2	1.78	3.73
$1s2s\ ^3S\ m_s=0$	0.9	3.6	1.78	10.49
$1s2s\ ^1S$	1.6	2.2	8.92	6.21

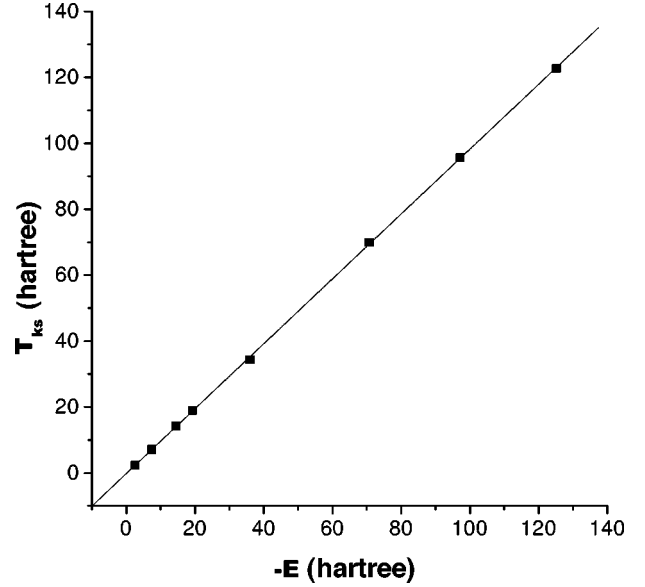


FIG. 3. The KS kinetic energy vs the total subspace energy calculated by the SDFT theory. The calculated values fit a straight line of slope equal to 1.01.

Davidson [34], more sophisticated approximations to  $\varepsilon_{xc}(\rho)$  give better agreement with experiment. One expects that the same holds for the excited-state theory.

In Table IX, one can see a comparison between SDFT and KOG results, where the calculations concern the helium atom. One should take into account that, in the KOG approach, the subspace (equiensemble) theory and not the general ensemble theory is used. However, this theory uses the  $E_{xc}(\rho)$  derived by Kohn [4] and the difference of energy splitting due to electronic spin is not taken into account. Instead, the statistical averages between  $S=0$  and 1 states (with weights 1 and 3, respectively) are calculated. In this table, we denote by  $E$  the average of the total energy of each configuration while  $\Delta E$  stands for the excitation energy. The comparison is in favor of the SDFT scheme as far as the total energies are concerned, whereas the errors in the excitation energies are practically the same in the case of the  $1s2s$  configuration and in favor of the SDFT method in the  $1s2p$  one. Thus, although the Kohn exchange [4] goes beyond the local-density approximation, its advantages are outweighed by the symmetry considerations of the present treatment.

TABLE XI. Comparison of  $E$ ,  $T_{KS}$ , and  $V_{ne}$ .

Ion	Conf.	$T_{KS}$	$-E$	$-V_{ne}$
He	$\{1s2s; ^1S\}$	2.348	2.527	5.564
Be	$\{1s^22s^2; ^1S\}$	14.213	14.518	33.250
O (IV)	$\{1s^22s2p^2; ^4P\}$	69.922	70.648	155.771
C (V)	$\{1s3d; ^3D\}$	18.884	19.207	38.831
Li	$\{1s^22s; ^2S\}$	7.158	7.418	16.810
Li	$\{1s^22s; ^2P\}$	7.089	7.352	16.585
C (III)	$\{1s^22s2p; ^1P\} - M_{25}$	34.322	35.923	78.088
F (III)	$\{1s^22s^22p^3; ^2D\}$	95.608	97.147	221.495
Ne (III)	$\{1s^22s2p^5; ^1P\}$	122.720	125.155	288.319



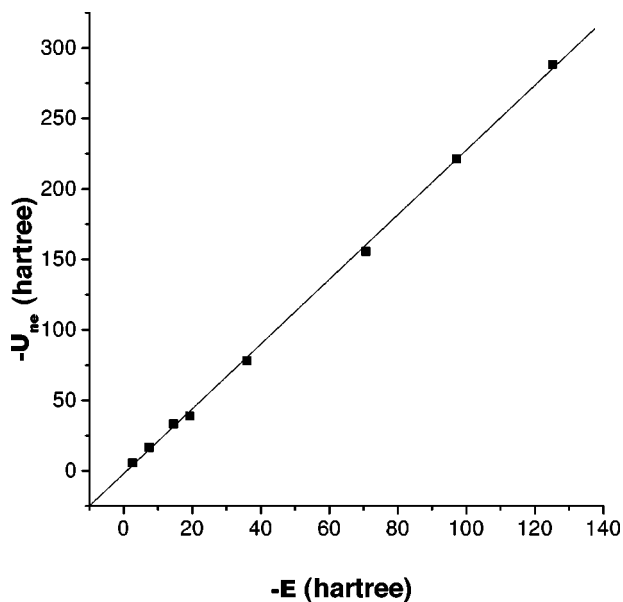


FIG. 4. Relation between the nucleus-electron energy  $U_{ne}$  vs the total energy. The calculated values fit a straight line with slope 2.31 which is very near to  $7/3=2.33$ , derived by the statistical Thomas-Fermi model.

In Table X we compare our SDFT results with those of von Barth [27], noting that the latter refers to the lowest-energy state of each symmetry. Although the numbers available for comparison are limited, we can conclude that the comparison is in favor of SDFT.

An important feature of our results is that excited-state energies calculated by using different subspaces gave almost identical results, with deviations ranging from 0% to 0.09% (compare  $M_4 - M_{23}$ ,  $M_5 - M_{24}$ , and  $M_{14} - M_{25}$ ). This observation is in favor of the validity of the proposed functional.

It is also worth noting that the calculated excited-state energies preserve almost in all cases the order relation of the experimental ones. The only exception is the one of the  $\{1s2s, {}^1S\}$  and  $\{1s2s, {}^3S\}$  states.

To test the accuracy of our results, we plotted in Fig. 3 the KS kinetic energy versus the total subspace energy (see Table XI) and found an almost straight line with slope equal to 1.01. This is in accordance to the virial theorem (which holds in the framework of subspace theory as well), according to which the interacting kinetic energy is equal to the absolute value of the total energy. The difference between real (interacting) and KS (noninteracting) kinetic energies is systematically equal to 1% of the total energy. As shown in an earlier paper [1],  $T_{KS} < T$ , their difference usually being called KS correlation energy  $E_c$ . This is of the order of the usual correlation energy defined as the difference between the Hartree-Fock energy and the exact one.

As a second test we plotted in Fig. 4 the relation between the nucleus-electron energy,  $U_{ne}$ , and the total subspace energy. This graph is a straight line with slope equal to 2.31, which is very close to the value  $7/3=2.333$  given by the scaling relation of the statistical Thomas-Fermi theory [8],

$$E_{\text{int}} = -\frac{1}{7} F_{ne}, \quad (30)$$

by means of which the relation  $E_{ne} = -\frac{7}{3} E$  can be easily derived after using the relation  $T = -E$ . Numerical values are given in Table XI.

We found that in all our calculations, Hund's rule was obeyed. This is not only due to the lower-energy occupation by spin orbitals but also to the deepening of  $V_{xc}$  due to the increase of  $\zeta$ .

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