PHYSICAL REVIEW A VOLUME 57, NUMBER 3 MARCH 1998

Kohn-Sham equations for multiplets

Á. Nagy
Institute of Theoretical Physics, Kossuth Lajos University, H–4010 Debrecen, Hungary

(Received 18 March 1997)

Kohn-Sham equations are derived for lowest-lying multiplets. A recently proposed method of the author is used to construct exchange potentials of multiplets. [S1050-2947(98)08902-1]

PACS number(s): 31.15.Ew

I. INTRODUCTION

The density-functional theory was originally developed for the ground state [1]. It can be applied only for the lowest-energy state in each symmetry class [2]. The symmetry problem in the density-functional theory was analyzed by several authors [3–6].

The multiplet structure was already treated using the density-functional theory. The most important approaches were proposed by Bagus and Bennett [7], Ziegler, Rauk, and Baerends [8], von Barth [9], and Wood [10]. All these methods have the same feature of not being completely within the frame of the density-functional theory. Recently, the method of fractionally occupied states of Gross, Oliveira, and Kohn [11] was used to treat the multiplet problem [12], and the exchange potential was determined for ensembles of low-lying multiplets.

In this paper another way of treating the multiplet problem is proposed. Görling [6] showed via the constrained search approach how the density-functional theory can be formalized for the lowest-energy state in each symmetry class. Here, instead of wave functions, density matrices are used. The constrained search is done not on the wave functions of a given symmetry, but on ''subspace density matrices'' constructed from the wave functions of the given multiplet.

Recently, a method determining the exchange or exchange-correlation potential in the knowledge of the density was proposed [13]. (Similar approaches were introduced by Almbladh and Pedroza [14], Stott and co-workers [15], Parr and co-workers [16], van Leeuwen and Baerends [17], and Görling [18].) This method is now applied to obtain the exchange potential for multiplets.

II. HOHENBERG-KOHN THEOREM FOR MULTIPLETS

Consider the lowest-lying solutions of the symmetry Γ of the Schrödinger equation

$$\hat{H}|\Psi_\gamma^\Gamma\rangle = E_0^\Gamma |\Psi_\gamma^\Gamma\rangle \quad (\gamma = 1,2,\ldots,g_\Gamma), \tag{1}$$

where g_Γ is the degeneracy. For case of simplicity, only one index is used to denote the symmetry both in spin and ordinary space. The subscript 0 in the energy E_0^Γ emphasizes the fact that only the lowest-lying solution of symmetry Γ is regarded. In a recent paper, Görling [6] applied the constrained search technique to these wave functions Ψ_γ^Γ. Now the space of all antisymmetric wave functions is divided into disjoint subspaces with different symmetries. The variation is done over a subspace S^Γ of a given symmetry Γ. This subspace is spanned by a set of wave functions of the given symmetry Γ. The dimension of the subspace is equal to the degeneracy g_Γ. In this case the constrained-search formalism can be used as follows:

$$\begin{aligned} E^\Gamma[\varrho^\Gamma] &= \min_{S^\Gamma} \sum_{\gamma=1}^{g_\Gamma} w_\gamma \langle \Psi_\gamma^\Gamma|\hat{H}|\Psi_\gamma^\Gamma\rangle \\ &= \min_{\varrho^\Gamma} \left\{ \min_{S^\Gamma \to \varrho^\Gamma} \sum_{\gamma=1}^{g_\Gamma} w_\gamma \langle \Psi_\gamma^\Gamma|\hat{H}|\Psi_\gamma^\Gamma\rangle \right\} \\ &= \min_{\varrho^\Gamma} \left\{ F^\Gamma[\varrho^\Gamma] + \int \varrho^\Gamma(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\}, \end{aligned} \tag{2}$$

where the weighting factors w_γ should satisfy the conditions

$$1 = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \tag{3}$$

and

$$w_\gamma \geqslant 0. \tag{4}$$

In principle, any set of weighting factors w_γ satisfying conditions (3) and (4), can be used. v is the external potential and

$$F^\Gamma[\varrho^\Gamma] = \min_{S^\Gamma \to \varrho^\Gamma} \sum_{\gamma=1}^{g_\Gamma} w_\gamma \langle \Psi_\gamma^\Gamma|\hat{T} + \hat{V}_{\mathrm{ee}})|\Psi_\gamma^\Gamma\rangle. \tag{5}$$

$\hat{T}$ and $\hat{V}_{\mathrm{ee}}$ are, respectively, the kinetic and the electron-electron repulsion operators. The density is given by

$$\varrho^\Gamma = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \int |\Psi_\gamma^\Gamma|^2 ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N, \tag{6}$$

where $\mathbf{x}$ stands for both the coordinates and the spin. The superscript Γ in ϱ^Γ and the subspace density matrix denotes that they are constructed from wave functions that belong to the subspace S^Γ. The densities do not generally have the symmetry Γ. Their symmetry also depends on the weighting factors w_γ. One is free to select the values of the weighting factors w_γ; they only should satisfy conditions (3) and (5). If the weighting factors w_γ are all equal, the density has the

1050-2947/98/57(3)/1672(6)/$15.00

property of transforming according to the first row of the character table. So, for instance, for atoms, the density will be spherically symmetric. But it is possible to select other values for the weighting factors w_{γ}.

The functional $F^{\Gamma}[\varrho^{\Gamma}]$ can be expressed with the density matrix defined in subspace S^{Γ},

$$\hat{D}^{\Gamma}=\sum_{\gamma=1}^{g_{\Gamma}} w_{\gamma}|\Psi_{\gamma}^{\Gamma}\rangle\langle\Psi_{\gamma}^{\Gamma}|, \tag{7}$$

as follows:

$$F^{\Gamma}[\varrho^{\Gamma}]=\min_{S^{\Gamma}\rightarrow\varrho^{\Gamma}} \mathrm{tr}\{\hat{D}^{\Gamma}(\hat{T}+\hat{V}_{\mathrm{ee}})\}. \tag{8}$$

Then the generalized Hohenberg-Kohn theorem has a form

$$F^{\Gamma}[\varrho^{\Gamma}]+\int \varrho^{\Gamma}(\mathbf{r})v(\mathbf{r})d\mathbf{r}\geqslant E_{0}^{\Gamma}, \tag{9}$$

that can be readily proved as follows:

$$\begin{aligned} F^{\Gamma}[\varrho^{\Gamma}]+\int \varrho^{\Gamma}(\mathbf{r})v(\mathbf{r})d\mathbf{r} &= \min_{S^{\Gamma}\rightarrow\varrho^{\Gamma}} \mathrm{tr}\{\hat{D}^{\Gamma}(\hat{T}+\hat{V}_{\mathrm{ee}})\} \\ &\quad +\int \varrho^{\Gamma}(\mathbf{r})v(\mathbf{r})d\mathbf{r} \\ &= \min_{S^{\Gamma}\rightarrow\varrho^{\Gamma}} \mathrm{tr}\{\hat{D}^{\Gamma}(\hat{T}+\hat{V}+\hat{V}_{\mathrm{ee}})\}\geqslant E_{0}^{\Gamma}, \end{aligned} \tag{10}$$

where the last inequality follows from the variational principle. The variational principle is valid here because we are considering the lowest-lying energy level of symmetry Γ. There is an equality if and only if the trial density ϱ^{Γ} is equal to the true density of the multiplet Γ.

III. KOHN-SHAM EQUATIONS FOR MULTIPLETS

Following the method proposed by Hadjisavvas and Theophilou [19], the Kohn-Sham equations can be derived. The noninteracting wave functions of symmetry Γ are constructed as a linear combination of Slater determinants Φ_{κ}:

$$\Psi_{s,\gamma}^{\Gamma}=\sum_{\kappa} c_{\gamma,\kappa}^{\Gamma}\Phi_{\kappa} \quad (\gamma=1,2,\ldots,g_{\Gamma}). \tag{11}$$

The noninteracting density matrix is defined as

$$\hat{D}_{s}^{\Gamma}=\sum_{\gamma=1}^{g_{\Gamma}} w_{\gamma}|\Psi_{s,\gamma}^{\Gamma}\rangle\langle\Psi_{s,\gamma}^{\Gamma}|. \tag{12}$$

The density corresponding to the density matrix $\hat{D}_{s}^{\Gamma}$ is ϱ^{Γ}:

$$\varrho^{\Gamma}=\sum_{\gamma=1}^{g_{\Gamma}} w_{\gamma}\int |\Psi_{s,\gamma}^{\Gamma}|^{2}ds_{1}d\mathbf{x}_{2}\cdots d\mathbf{x}_{N}, \tag{13}$$

The functionals of the Kohn-Sham scheme are now defined over the set of noninteracting density matrices $\hat{D}_{s}^{\Gamma}$. Following Hadjisavvas and Theophilou [19], we can state that to derive a minimum principle for a functional over $\hat{D}_{s}^{\Gamma}$, it is necessary to define a functional Q over $\hat{D}_{s}^{\Gamma}$ whose value is either (a) always equal to the expectation value of an operator $\hat{O}$ of the interacting system for some density matrix $\hat{D}^{\Gamma}$, i.e., $Q[\hat{D}_{s}^{\Gamma}]=\mathrm{tr}\{\hat{D}^{\Gamma}\hat{O}\}$; or (b) one can define $Q[\hat{D}_{s}^{\Gamma}]\neq\mathrm{tr}\{\hat{D}^{\Gamma}\hat{O}\}$, but the minimum value of $Q[\hat{D}_{s}^{\Gamma}]$ coincide with the minimum value of $\mathrm{tr}\{\hat{D}^{\Gamma}\hat{O}\}$. In the usual construction of the Kohn-Sham scheme, case (a) is followed. Here, however, just like in the paper by Hadjisavvas and Theophilou [19], the second case is used. So we define the following functional:

$$T_{s}^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}]=\min_{\hat{D}_{s}^{\Gamma}\rightarrow\varrho^{\Gamma}} \mathrm{tr}\{\hat{D}_{s}^{\Gamma}\hat{T}\}. \tag{14}$$

According to a theorem of Lieb [20], the minimum of the kinetic energy exists. This is a functional defined over all noninteracting density matrices $\hat{D}_{s}^{\Gamma}$ with the density ϱ^{Γ}. Then another functional is defined:

$$F^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}]=\min_{\hat{D}^{\Gamma}\rightarrow\varrho^{\Gamma}} \mathrm{tr}\{\hat{D}^{\Gamma}(\hat{T}+\hat{V}_{\mathrm{ee}})\}. \tag{15}$$

This can again be considered as a functional of noninteracting density matrices $\hat{D}_{s}^{\Gamma}$. Let us denote by $\hat{D}_{s,\min}^{\Gamma}$ and $\hat{D}_{\min}^{\Gamma}$ the noninteracting and interacting density matrices minimizing Eqs. (14) and (15), respectively. We can also define the following functionals:

$$T_{c}^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}]=\mathrm{tr}\{\hat{D}_{\min}^{\Gamma}\hat{T}\}-\mathrm{tr}\{\hat{D}_{s,\min}^{\Gamma}\hat{T}\} \tag{16}$$

and

$$V_{\mathrm{xc}}^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}]=\mathrm{tr}\{\hat{D}^{\Gamma}\hat{V}_{\mathrm{ee}}\}-\frac{1}{2}\int \frac{\varrho^{\Gamma}(\mathbf{r})\varrho^{\Gamma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'. \tag{17}$$

With the kinetic-energy difference T_{c} and the exchange-correlation energy V_{xc}, the total energy functional has the form

$$\begin{aligned} E^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}] &= T_{s}^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}]+T_{c}^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}] \\ &\quad +\int \varrho^{\Gamma}(\mathbf{r})v(\mathbf{r})d\mathbf{r}+V_{\mathrm{xc}}^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}] \\ &\quad +\frac{1}{2}\int \frac{\varrho^{\Gamma}(\mathbf{r})\varrho^{\Gamma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'. \end{aligned} \tag{18}$$

$E^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}]$ is a well-defined functional. It is really a functional of the noninteracting density matrix $\hat{D}_{s}^{\Gamma}$, as all terms in Eq. (18) can be considered as a functional of $\hat{D}_{s}^{\Gamma}$ through Eqs. (14) and (15).

One can easily see that the following theorem holds: The minimum of the functional $E^{\Gamma}[\varrho^{\Gamma};\hat{D}_{s}^{\Gamma}]$ exists, and its value is equal to E_{0}^{Γ}, the lowest energy of symmetry type Γ. The density coming from the noninteracting density matrix $\hat{D}_{s}^{\Gamma}$, minimizing the functional $E^{\Gamma}[\varrho^{\Gamma};\hat{D}_s^{\Gamma}]$, is equal to the density corresponding to the true density matrix $\hat{D}^{\Gamma}$.

To prove this theorem Eq.(18) is written in the form

$$E^{\Gamma}[\varrho^{\Gamma};\hat{D}_s^{\Gamma}]=\mathrm{tr}\{\hat{D}_s^{\Gamma}\hat{T}\}-\mathrm{tr}\{\hat{D}_{s,\mathrm{min}}^{\Gamma}\hat{T}\}+\mathrm{tr}\{\hat{D}^{\Gamma}(\hat{T}+\hat{V}_{\mathrm{ee}}+\hat{V})\}. \tag{19}$$

Equations (14) and (15) lead to the inequalities

$$\mathrm{tr}\{\hat{D}_s^{\Gamma}\hat{T}\}\geqslant\mathrm{tr}\{\hat{D}_{s,\mathrm{min}}^{\Gamma}\hat{T}\} \tag{20}$$

and

$$\mathrm{tr}\{\hat{D}^{\Gamma}(\hat{T}+\hat{V}_{\mathrm{ee}}+\hat{V})\}\geqslant E_0^{\Gamma}, \tag{21}$$

respectively. These relations, combining with Eq. (19), give the inequality

$$E^{\Gamma}[\varrho^{\Gamma};\hat{D}_s^{\Gamma}]\geqslant E_0^{\Gamma}. \tag{22}$$

The minimum of $E^{\Gamma}[\varrho^{\Gamma};\hat{D}_s^{\Gamma}]$ is E_0^{Γ}, as can readily be seen from the equalities in Eqs. (20), (21), and (22). From Eqs. (14) and (15) it follows that the density coming from the noninteracting density matrix $\hat{D}_s^{\Gamma}$, minimizing the functional $E^{\Gamma}[\varrho^{\Gamma};\hat{D}_s^{\Gamma}]$, is equal to the density corresponding to the true density matrix $\hat{D}^{\Gamma}$.

Now, the Kohn-Sham equations can be obtained from Eq. (14), carrying out the minimalization. Because of the fact that $\Psi_{s,\gamma}^{\Gamma}$ is a linear combination of several Slater determinants, the form of the Kohn-Sham equations is rather complicated for an arbitrarily selected set of weighting factors w_{γ} and have to be derived separately for each desired case. For a spherically symmetric case and equal weighting factors, however, the Kohn-Sham equations have a very simple form, as is shown in the Appendix. In this case the noninteracting kinetic energy is given by

$$T_s=\sum_{j=1}^{N}\lambda_j\int P_j^{\Gamma}\left[-\frac{1}{2}(P_j^{\Gamma})''+\frac{l_j(l_j+1)}{2r^2}P_j^{\Gamma}\right]dr, \tag{23}$$

where P_j^{Γ} and λ_j are the radial wave functions and the occupation numbers corresponding to the given configuration, respectively. $''$ denotes the second derivative with respect to r. The density

$$\varrho^{\Gamma}=\sum_{j=1}^{N}\lambda_j(P_j^{\Gamma})^2 \tag{24}$$

in this particular case is spherically symmetric. The minimization of the noninteracting kinetic energy (23), keeping the density ϱ^{Γ} [Eq. (24)] fixed, leads to the radial Kohn-Sham equations

$$-\tfrac{1}{2}(P_j^{\Gamma})''+\frac{l_j(l_j+1)}{2r^2}P_j^{\Gamma}+v_{\mathrm{KS}}^{\Gamma}P_j^{\Gamma}=\varepsilon_j^{\Gamma}P_j^{\Gamma}, \tag{25}$$

where

$$v_{\mathrm{KS}}^{\Gamma}(\mathbf{r})=v(\mathbf{r})+\int\frac{\varrho^{\Gamma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}+v_{\mathrm{xc}}^{\Gamma}(\varrho^{\Gamma};\mathbf{r}), \tag{26}$$

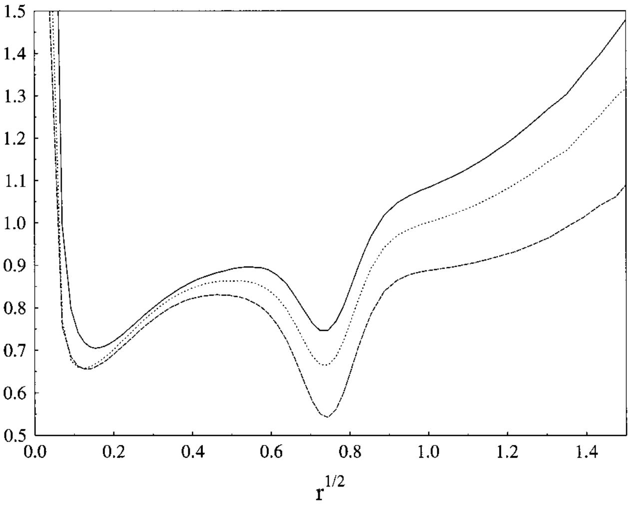

FIG. 1. The exchange factors α^{Γ} (in a.u.) of the C atom for the multiplets (^3P) (—), ^1D (...), and ^1S (- - -) as functions of the square root of the radius (in a.u.).

$$v_{\mathrm{xc}}^{\Gamma}(\varrho^{\Gamma};\mathbf{r})=\frac{\delta(V_{\mathrm{xc}}^{\Gamma}+T_c^{\Gamma})}{\delta n} \tag{27}$$

is the exchange-correlation potential of the lowest-lying multiplet of symmetry Γ. An essential point in the theory is that the exchange-correlation potential, and so the Kohn-Sham potential, depends on Γ, and we have different potentials for different multiplets. (The fact that the exchange-correlation potential must in general be different for each symmetry multiplet was first pointed out by Gunnarsson and Lundqvist [2], and later Weiner and Trickey [21].) The exchange-correlation potential also depends on the weighting factors w_{γ}.

We end this section by emphasizing the difference between the present approach and the subspace theory of Theophilou [22], the method of fractionally occupied states of Gross, Oliveira, and Kohn [11], and the symmetrized constrained-search procedure of Görling [6]. The present

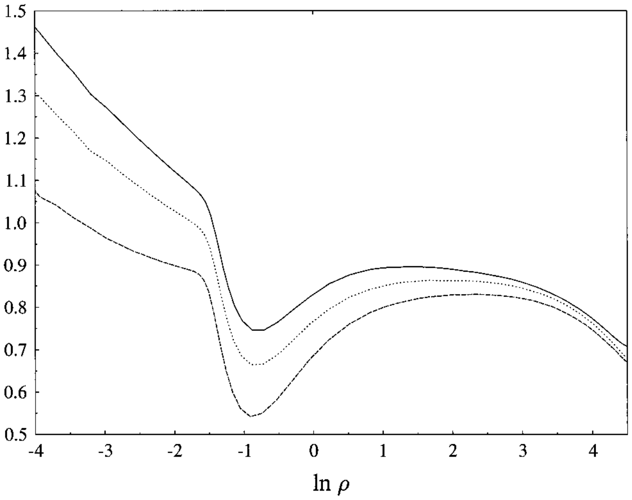

FIG. 2. The exchange factors α^{Γ} (in a.u.) of the C atom for the multiplets (^3P) (—), ^1D (...), and ^1S (- - -) as functions of the density (in a.u.).

TABLE I. One-electron, kinetic, and total energies for the multiplet ^3P of the C atom calculated with the Hartree-Fock [24] (HF) and the exchange-only density functional (DF) (this work) methods (in Ry).

ε_i		HF	DF
	$1s$	-22.651	-20.707
	$2s$	-1.411	-1.505
	$2p$	-0.867	-0.867
T		75.377	75.372
E		-75.377	-75.372

TABLE II. One-electron, kinetic, and total energies for the multiplet ^1D of the C atom calculated with the Hartree-Fock [24] and the exchange-only density functional, (this work) methods (in Ry).

ε_i		HF	DF
	$1s$	-22.703	-20.607
	$2s$	-1.437	-1.398
	$2p$	-0.763	-0.763
T		75.264	75.259
E		-75.263	-75.258

method can be considered a generalization of the subspace theory of Theophilou [22]. Here the space of all antisymmetric wave functions is divided into disjoint subspaces with different symmetries, and the variation is done over a subspace S^Γ of a given symmetry Γ. In the subspace theory of Theophilou [22], subspaces are constructed over wave functions of all kinds of symmetries. However, in a recent paper [23] considering noninteracting systems, he mentioned the advantages of constructing subspace densities from all eigenstates of a given symmetry.

Comparing the present approach with the method of fractionally occupied states of Gross, Oliveira, and Kohn [11], the main difference is that, in an ensemble-constrained search, the search is done over all density matrices which give a certain density, while here the search is over a subspace of a given symmetry. There is a similarity in the fact, however, that the construction contains weighting factors in both methods. The freedom in selecting the value of the weighting factors may come useful in practice. It has the consequence, however, that the exchange-correlation potential depends on these weighting factors.

There are several differences between the present method and the symmetrized constrained-search procedure of Görling [6]. In the latter approach, the search is also over the subspace of all antisymmetric wave functions of a given symmetry. However, the wave functions do not have to give a certain density; only the totally symmetric part of the density is specified. The Kohn-Sham wave function has the same symmetry as the corresponding full interacting wave function. In the present method, on the other hand, density matrices and not wave functions are considered both in the interacting and noninteracting systems. This approach has the advantage that with equal weighting factors the density has the symmetry of the external potential.

IV. EXCHANGE POTENTIAL FOR MULTIPLETS

There is a growing interest in determining the exact exchange, exchange-correlation, and Kohn-Sham potentials in the knowledge of the density [14–18]. The present author has also proposed a method [13] that enables one to calculate these potentials if the density is known. The method has also been generalized to ensemble states [12]. Now we show that it can be applied to the lowest-lying multiplets of each symmetry class.

The method proposed earlier is outlined for the present problem. If the density ϱ^Γ of the multiplet of symmetry Γ is known, the exchange and the exchange-correlation potentials are calculated as follows: Starting out from an appropriate (e.g., a local density) potential, the Kohn-Sham equations are solved, and the density of the first iteration is calculated. The potential of the ith iteration can be given by

$$V^\Gamma_{(i)} = V^\Gamma_{(i-1)} \frac{\varrho^\Gamma_{\mathrm{input}}}{\varrho^\Gamma_{(i-1)}}, \tag{28}$$

and an appropriate damping is applied to obtain a stable convergence. Then the Kohn-Sham potential of the second iteration is constructed. The process goes on until the density equals the input density. If the input density is the exact density, the exact Kohn-Sham potential and the exact exchange-correlation potential are obtained. If the input density is the Hartree-Fock density a potential very close to the exact exchange potential is gained. Here, the exchange potentials for multiplets are calculated from the Hartree-Fock densities [24].

V. RESULTS AND DISCUSSION

The exchange potentials are studied for the multiplets ^3P, ^1D, and ^1S for the atom C. The exchange potentials are written in the form

$$v^\Gamma_{\mathrm{xc}}(r;\varrho^\Gamma) = -3\alpha^\Gamma \left(\frac{3}{8\pi} \varrho^\Gamma \right)^{1/3}. \tag{29}$$

The factors α^Γ are functions of the radial distance r. The exchange factors α^Γ for the atom C is presented in Fig. 1 versus the square of the radial distance. The upper (solid)

TABLE III. One-electron, kinetic, and total energies for the multiplet ^1S of the C atom calculated with the Hartree-Fock [24] and the exchange-only density-functional (this work) methods (in Ry).

ε_i		HF	DF
	$1s$	-22.782	-20.481
	$2s$	-1.479	-1.252
	$2p$	-0.620	-0.623
T		75.101	75.099
E		-75.099	-75.094

line is for ^3P, the middle (point) line is obtained for ^1D, and the lower function arises from ^1S (dashed line).

These figures show a shell structure. (For the ground and ensemble states the shell structure has already been demonstrated [13,12].) The fact that the exchange potentials behave similarly for the multiplets suggests that approximating expressions for these potentials might also be similar. Probably, a small change in the presently used ground-state exchange functionals might lead to a good approximation for multiplets.

Figure 2 presents the factor α^Γ as a function of the density. The shell structure can also be clearly seen. Though the curves are very close together, they are not exactly the same. So the exchange potential has a different dependence on the density for different multiplets.

The method described in Sec. IV makes it possible to calculate the one-electron and total energies. (Details can be found in Refs. [13,12].) Table I–III present the results for the multiplets ^3P, ^1D, and ^1S of the C atom. For comparison, the Hartree-Fock values [24] are also included in Table I. The exchange-only density functional and the Hartree-Fock total energies are very close together, the latter being somewhat lower, as is expected. However, the one-electron energies are different (except the highest orbital energies) [13].

ACKNOWLEDGMENTS

The grant ''Széchenyi'' from the Hungarian Ministry of Culture and Education is gratefully acknowledged. This work was supported by Grant MTA-NSF No. 93, and Grant Nos. OTKA T 16623 and FKFP 0314/1997.

APPENDIX

It can be easily shown that for a spherically symmetric case and equal weighting factors and supposing LS coupling, the Kohn-Sham equations have a very simple form. In this case the noninteracting kinetic energy is given by

$$T_s = \mathrm{tr}\,\{\hat{D}_s^\Gamma \hat{T}\}. \tag{A1}$$

Substituting Eqs. (11) and (12) into Eq. (A1), we obtain

$$T_s = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \sum_\kappa \sum_\mu c^{\Gamma *}_{\gamma,\kappa} c^\Gamma_{\gamma,\mu} \times \int \Phi^*_\kappa \left(-\sum_{i=1}^{N} \tfrac{1}{2} \nabla_i^2 \right) \Phi_\mu d\mathbf{x}_1 \cdots d\mathbf{x}_N. \tag{A2}$$

The Slater determinants Φ_κ are built of one-electron orbitals,

$$u_j^\Gamma = P_{nl}^\Gamma Y_{lm_l} \sigma_{m_s}, \tag{A3}$$

corresponding to the given electron configuration. P_{nl}^Γ are radial wave functions with quantum numbers n and l, Y_{lm_l} are the spherical harmonics, and σ_{m_s} stands for the spin eigenfunction. The Slater determinants Φ_κ and Φ_μ may differ only in orbitals of the open shells; that is, in the quantum numbers m_l and m_s. Taking into consideration that the spherical harmonics are eigenfunctions of the Laplacian and the orthogonality of the wave functions in Eq. (A3) we notice that the integrals taken with different determinants disappear in Eq. (A2). So the noninteracting kinetic energy is given by

$$T_s = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \sum_\kappa |c^\Gamma_{\gamma,\kappa}|^2 \sum_{j=1}^{N} \lambda^\Gamma_{\kappa,j} \langle u_j^\Gamma | -\tfrac{1}{2}\nabla^2 | u_j^\Gamma \rangle. \tag{A4}$$

Now, the occupation numbers $\lambda^\Gamma_{\kappa,j}$ do not depend on κ, because we have the same electron configuration. (e.g., in the case studied in Sec. V we have p^2; i.e., the occupation numbers are 2 for the p electrons in each determinant.) Making use of the orthogonality of the wave functions $\Psi^\Gamma_{s,\gamma}$ and the equality of the weighting factors w_γ we arrive at Eq. (23).

Equation (24) can be similarly derived. The density is given by

$$\varrho^\Gamma = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \sum_\kappa \sum_\mu c^{\Gamma *}_{\gamma,\kappa} c^\Gamma_{\gamma,\mu} \int \Phi^*_\kappa \Phi_\mu ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N. \tag{A5}$$

Taking into account that Φ_κ and Φ_μ should correspond to the same quantum numbers M_L and M_S and the orthogonality of the wave functions in Eq. (A3), we arrive at Eq. (24).

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).
[2] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
[3] B. I. Dunlap, Adv. Chem. Phys. **69**, 287 (1987).
[4] R. McWeeney, Philos. Mag. B **69**, 727 (1994).
[5] J. P. Perdew, A. Savin, and K. Burke, Phys. Rev. A **51**, 4531 (1995).
[6] A. Görling, Phys. Rev. A **47**, 2783 (1993).
[7] P. S. Bargus and B. I. Bennett, Int. J. Quantum Chem. **9**, 143 (1975).
[8] T. Ziegler, A. Rauk, and E. J. Baerends, Theor. Chim. Acta **43**, 261 (1977).
[9] U. von Barth, Phys. Rev. A **20**, 1693 (1979).
[10] J. H. Wood, J. Phys. B **13**, 1 (1980).
[11] E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2805 (1988); **37**, 2809 (1988); **37**, 2821 (1988).
[12] Á. Nagy, Int. J. Quantum Chem. **29**, 297 (1995).
[13] Á . Nagy, J. Phys. B **26**, 43 (1993); Philos. Mag. B **69**, 779 (1994).
[14] C. O. Almbladth and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1994).
[15] F. Aryasetiawan and M. J. Stott, Phys. Rev. B **38**, 2974 (1988); J. Chen and M. J. Stott, Phys. Rev. A **44**, 2816 (1991); J. Chen,

R. O. Esquivel, and M. J. Stott, Philos. Mag. B **69**, 1001 (1994).

[16] Q. Zhao and R. G. Parr, J. Chem. Phys. **98**, 543 (1993); R. G. Parr, Philos. Mag. B **69**, 737 (1994).

[17] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).

[18] A. Görling, Phys. Rev. A **46**, 3753 (1992); **51**, 4501 (1995).

[19] N. Hadjisavvas and A. K. Theophilou, Phys. Rev. A **30**, 2183 (1984).

[20] E. Lieb, Int. J. Quantum Chem. **24**, 243 (1982).

[21] B. Weiner and S. Trickey (unpublished).

[22] A. K. Theophilou, J. Phys. C **12**, 5419 (1979).

[23] A. K. Theophilou, Philos. Mag. B **69**, 771 (1994).

[24] E. Clementi and A. Roetti, At. Data **14**, 177 (1974).