
Exact Ensemble Exchange Potentials for Multiplets

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ABSTRACT

The approach of Gross, Oliveira, and Kohn for fractionally occupied states of ensembles is applied to determine ensemble exchange potentials for multiplets. A recently proposed method of the author is used to construct exact ensemble exchange potentials of multiplets. © 1995 John Wiley & Sons, Inc.

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. The extension of the theory to excited states was proposed by Theophilou [2] as a subspace theory. A more general treatment was suggested by Gross, Oliveira, and Kohn [3]. In this article, this method is applied to determine the exact exchange potential for ensembles of low-lying multiplets.

The multiplet structure has already been treated using the density functional theory. The most important approaches have been proposed by Bagus and Bennett [4], Ziegler, Rauk, and Baerends [5], and von Barth [6]. All these methods have the same feature of not being completely within the frame of the density functional theory.

The method of fractionally occupied states can also be used to treat the multiplet problem. How-

ever, the exchange energy and potential are not known even for the ground state. They are also unknown for the ensemble of excited states.

Recently, a method determining the exact exchange or exchange–correlation potential in the knowledge of the density was proposed [7]. (Similar approaches were introduced by Almladh and Pedroza [8], Stott et al. [9], and Zhao and Parr [10].) This method is now applied to calculate the ensemble exchange potential.

Fractional Approach of Multiplets

First, the theory of Gross, Oliveira, and Kohn [3] is summarized. Let us consider the lowest M eigenstates of the Hamiltonian:

$$\hat{H} |i, k\rangle = E_i |i, k\rangle \quad (k = 1, 2, \dots, g_i). \quad (1)$$

The energies are labeled as

$$E_1 \leq E_2 \leq \dots \quad (2)$$

g_i is the degeneracy of the i th multiplet. The ensemble energy is defined by

$$\mathcal{E}^I(w) = \frac{1 - wg_I}{M_{I-1}} (g_1 E_1 + \cdots + g_{I-1} E_{I-1}) + wg_I E_I, \quad (3)$$

while the ensemble density is given by

$$g_w^I(\mathbf{r}) = \frac{1 - wg_I}{M_{I-1}} \sum_{i=1}^{I-1} \sum_{k=1}^{g_i} \langle i, k | \hat{\rho}(\mathbf{r}) | i, k \rangle + w \sum_{k=1}^{g_I} \langle I, k | \hat{\rho}(\mathbf{r}) | I, k \rangle. \quad (4)$$

$\hat{\rho}(\mathbf{r})$ is the density operator. I is the total number of multiplets included in the M_I -state ensemble, where

$$M_I \equiv \sum_{i=1}^I g_i. \quad (5)$$

The parameter w interpolates between the equensembles of M_I and M_{I-1} :

$$0 \leq w \leq 1/M_I \quad (6)$$

Kohn–Sham equations can also be derived:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{KS}}(\mathbf{r}) \right] u_i(\mathbf{r}) = \varepsilon_i u_i(\mathbf{r}), \quad (7)$$

where

$$v_{\text{KS}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}^{M,g}(w, \rho; \mathbf{r}). \quad (8)$$

$v_{xc}^{M,g}(w, \rho; \mathbf{r})$ is the exchange–correlation potential of the ensemble characterized by the parameters M , g , and w .

Exact Ensemble Exchange Potential

There is a growing interest in determining the exact exchange, exchange–correlation, and Kohn–Sham potential in the knowledge of the density [7–10]. The present author has also proposed a method that enables one to calculate these potentials if the density is known [7]. All these efforts have been concentrated to the ground state. However, it can be generalized to ensemble states without any difficulty.

Here, the method proposed earlier to the ground state [7] is applied to the ensemble state. The outline of the method is as follows: The ensemble density

$$\rho_w^I = \sum_i n_i |u_i|^2 \quad (9)$$

can be calculated with one-particle wave functions u_i of the Kohn–Sham equations (7). The occupation numbers can be determined from g_i and w [3]. If the ensemble density ρ_w^I is known, the ensemble 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 i th iteration can be given by

$$V^{(i)} = V^{(i-1)} \frac{\rho^{\text{input}}}{\rho^{(i-1)}} \quad (10)$$

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. (Here, the difference between the input and the output radial densities was taken to be less than 10^{-4} , which can be achieved in 400–500 iterations.) 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, the exact exchange potential is gained. Here, the ensemble exchange potentials for multiplets are calculated from the Hartree–Fock densities [11].

Results and Discussion

The ensemble exchange potentials are studied for the following multiplets: 3P , 1D , and 1S , for the atoms O and S and 4S , 2D , and 2P for the atoms N and P. The ensemble exchange potentials are written in the form

$$v_{xc}^{M,g}(w, \rho; r) = -3\alpha^{M,g}(w) \left(\frac{3}{8\pi} \rho_w \right)^{1/3}. \quad (11)$$

The factors $\alpha^{M,g}(w)$ are functions of the radial distance r . The exchange factors $\alpha^{M,g}(w)$ for the atoms O and S are presented in Figures 1 and 2 vs. the square of the radial distance. For comparison, the ground-state functional α is shown (solid line).

The upper line is for 3P . The exchange factor α of the ensemble obtained from 3P and 1D is the middle (point) line. The lower function corresponds to the ensemble arising from 3P , 1D , and 1S (dashed line). In these calculations, the maximum possible value of w is used, i.e., the ensemble density is given by

$$\rho = (g_1 \rho_1 + g_2 \rho_2) / (g_1 + g_2) \quad (12)$$

for the middle and

$$\rho = (g_1 \rho_1 + g_2 \rho_2 + g_3 \rho_3) / (g_1 + g_2 + g_3) \quad (13)$$

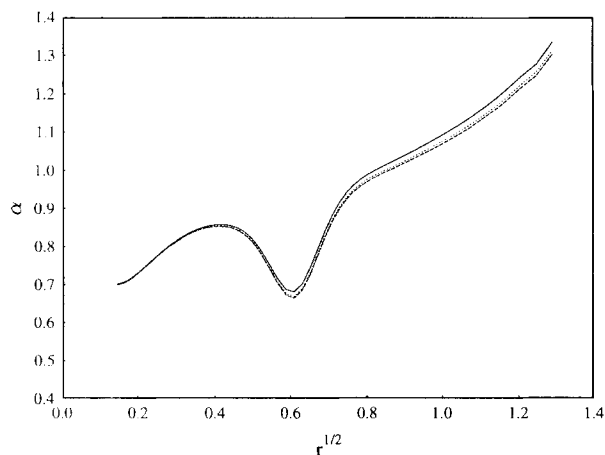


FIGURE 1. (—) The exchange factors α of the O atom for the ground state (3P), (\cdots) the ensemble obtained from 3P and 1D , and (---) the ensemble gained from 3P , 1D , and 1S as a function of the square of the radius.

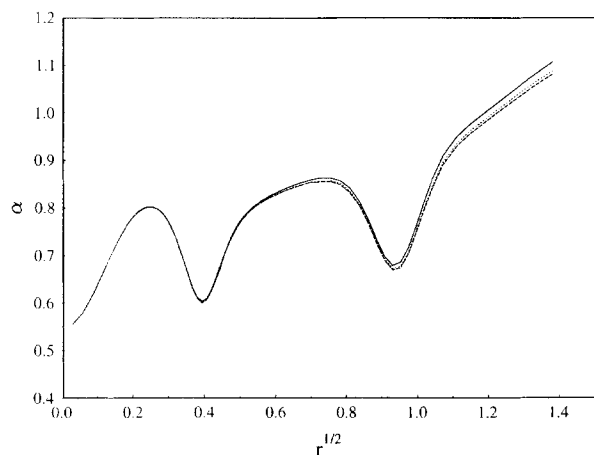


FIGURE 2. (—) The exchange factors α of the S atom for the ground state (3P), (\cdots) the ensemble obtained from 3P and 1D , and (---) the ensemble gained from 3P , 1D , and 1S as a function of the square of the radius.

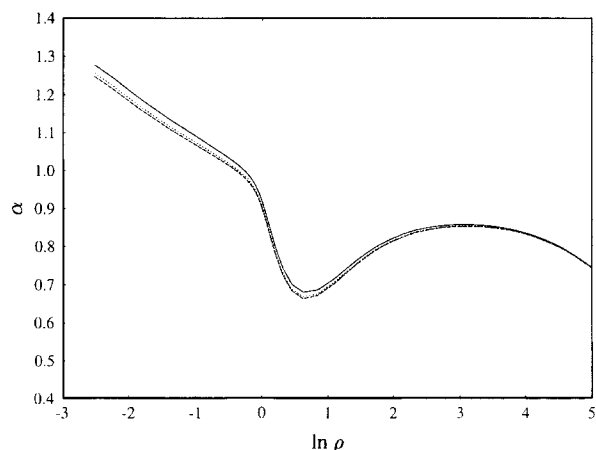


FIGURE 3. (—) The exchange factors α of the O atom for the ground state (3P), (\cdots) the ensemble obtained from 3P and 1D , and (---) the ensemble gained from 3P , 1D , and 1S as a function of the density.

for the lower line, respectively. It corresponds to the subspace theory of Theophilou [2].

These figures show a shell structure. (For the ground state, the shell structure has already been demonstrated [7]). Though the ensemble exchange potentials are different from the ground state one, the difference is not too much and the factors α show a very similar behavior.

The fact that the exact exchange potential has similar behavior for the ensemble of multiplets suggests that approximations might also be similar. Probably, a small change in the ground-state exchange functionals might lead to a good approximation for ensembles of multiplets.

Figures 3–6 present the factors α as functions of the density. The shell structure can also be clearly seen. If the ensemble exchange potential were a unique function of the ensemble density alone (for different ensembles), the curves α would be exactly the same. However, we can also see that the ensemble exchange potential is not the same function of the ensemble density. Though the curves are very close together, they are not exactly the same. So, the ensemble exchange potential has a different dependence on the ensemble densities for different ensembles. Moreover, comparing Figures 3 and 4 or 5 and 6, one can also observe that it is not a local function of ρ_w but some kind of functional of the ensemble density.

Figures 5–8 present exchange factors for atoms N and P. The upper lines correspond again to the ground state. The ensemble density leading to the

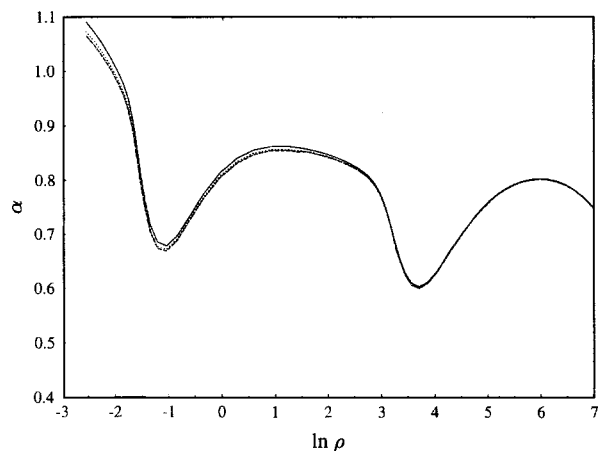


FIGURE 4. (—) The exchange factors α of the S atom for the ground state (3P), (\cdots) the ensemble obtained from 3P and 1D , and ($---$) the ensemble gained from 3P , 1D , and 1S as a function of the density.

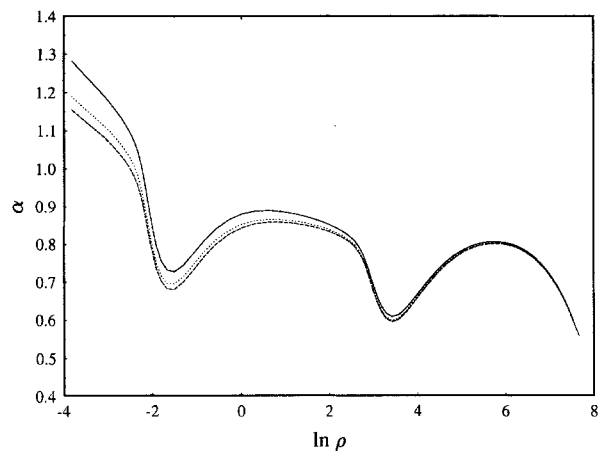


FIGURE 6. (—) The exchange factors α of the P atom for the ground state (4S), (\cdots) the ensemble obtained from 4S and 2D , and ($---$) the ensemble gained from 4S , 2D , and 2P as a function of the density.

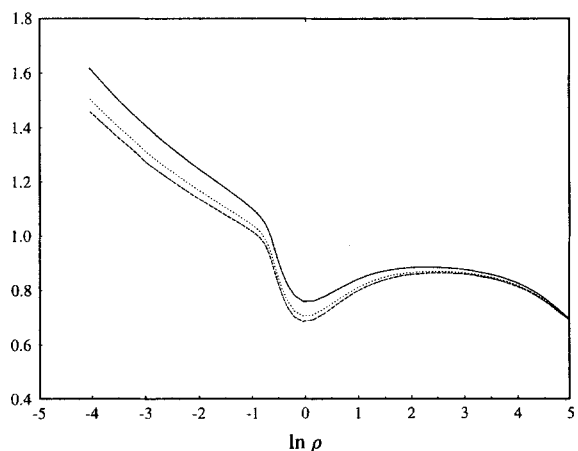


FIGURE 5. (—) The exchange factors α of the N atom for the ground state (4S), (\cdots) the ensemble obtained from 4S and 2D , and ($---$) the ensemble gained from 4S , 2D , and 2P as a function of the density.

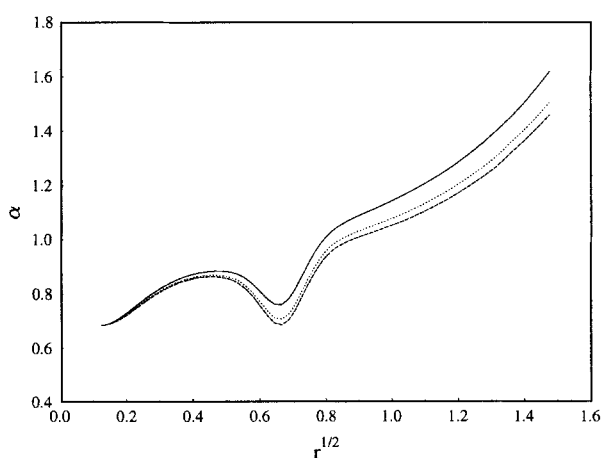


FIGURE 7. (—) The exchange factors α of the N atom for the ground state (4S), (\cdots) the ensemble obtained from 4S and 2D , and ($---$) the ensemble gained from 4S , 2D , and 2P as a function of the square of the radius.

middle line is obtained from Eq. (12), while the lower curve arises from the ensemble density of Eq. (13).

Figures 1–8 show the exchange factors for ensembles of maximum weighting factors w . Figure 9 presents the exchange factor for ensembles obtained from 4S and 2D with different weighting factors: $w = 0, 0.238, 0.476$, and 0.714 . The ensemble density is defined by

$$\rho_w = \rho_1(1 - w) + \rho_2 w, \quad (14)$$

where ρ_1 and ρ_2 are the 4S and 2D densities, respectively. The ensemble exchange potential can be given by Eq. (11). The ensemble exchange factors are presented in Figure 9. According to the theory of Gross, Oliveira, and Kohn [3], any value of w satisfying the condition (6) can be used to generate an ensemble. Figure 9 shows that the ensemble exchange factor is different for different values of w . It was emphasized in the theory of Gross, Oliveira, and Kohn [3] that the ensemble exchange potential depends on w .

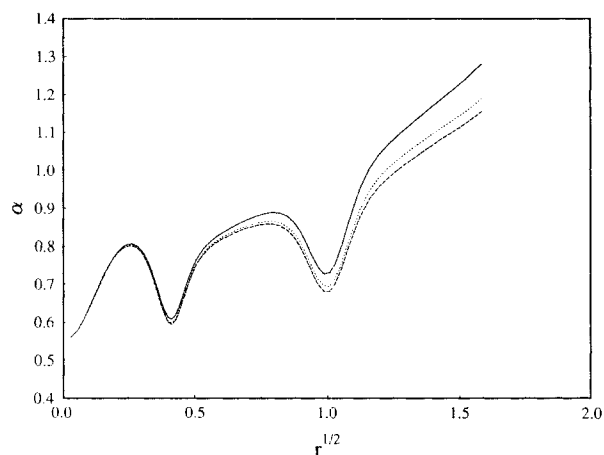


FIGURE 8. (—) The exchange factors α of the P atom for the ground state (4S), (\cdots) the ensemble obtained from 4S and 2D , and ($---$) the ensemble obtained from 4S , 2D , and 2P as a function of the square of the radius.

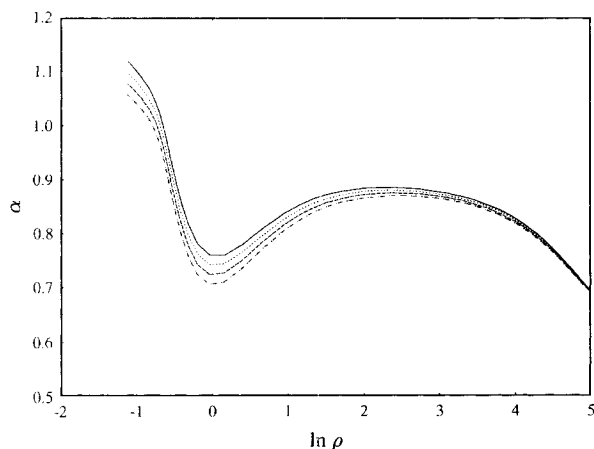


FIGURE 9. The exchange factors α of the N atom for the ensembles obtained from 4S and 2D states for $w =$ (—) 0, (\cdots) 0.238, ($---$) 0.476, and ($- \cdot -$) 0.714.

Figure 9 demonstrates the dependence of the ensemble exchange potential on w . There is a slight monotonic dependence on w . We can conclude again that a slight change in the ground-state functionals might lead to adequate approximations for ensembles of different weighting factors.

The method described in the third section makes it possible to calculate the ensemble energy. (Details can be found in [7]) Table I presents the results for the atoms N, O, P, and S. The calculations were done for the ensemble densities given in Eqs. (12) and (13) with the maximum possible weighting factors. For comparison, the Hartree-Fock values obtained from [11] are also included

TABLE I
Hartree-Fock and exchange-only density functional ensemble energies (in Ry).

Atom	HF	DF	
N	$^4S, ^2D$	-108.652	-108.650
	$^4S, ^2D, ^2P$	-108.593	-108.591
O	$^3P, ^1D$	-149.561	-149.559
	$^3P, ^1D, ^2S$	-149.539	-149.536
P	$^4S, ^2D$	-681.337	-681.292
	$^4S, ^2D, ^2P$	-681.298	-681.255
S	$^3P, ^1D$	-794.972	-794.920
	$^3P, ^1D, ^2S$	-794.957	-794.906

in Table I. The exchange-only density functional and the Hartree-Fock ensemble are very close together, the latter being somewhat lower, as expected.

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