On the evaluation of determinantal wave functions in open-shell Hartree-Fock theory

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Abstract

Slater method is modified for the evaluation of determinantal wave functions appearing in open-shell Hartree-Fock (HF) theory [1]. Using modified Slater method we have calculated, as an example, the orbital energies and the wave functions of terms obtained from the electronic configuration of a ground state of an N-atom system in the Hartree-Fock-Roothaan (HFR) approximation. The modified determinantal method introduced in this paper can be of considerable help and importance in the simplification and calculation of atomic and molecular electronic structure.

Key Words: Open-shell system; Hartree-Fock theory; Determinantal wave function.

1. Introduction

It is well known that Roothaan's open-shell method [2] does not seem to have been extended to arbitrary open-shell states. In Roothaan's treatment, which is an extension of HF-theory for closed-shell systems [3], and in the extensions to open-shell states by others [4-7], there are well-known complicating features which do not occur in the closed-shell equations. In Ref. [8], one of us eliminated these difficulties and derived HF and HFR equations applicable to any multi-determinantal state of a single configuration that has arbitrary open-shells. The Fock operator of these equations can be constructed from the wave functions of terms which are linear combinations of Slater determinants.

The general form of Slater determinants for an N-electron open-shell system may be written as

$$U(n_1 n_2 ... n_k) = \frac{1}{\sqrt{N!}}$$

$$\begin{vmatrix} u_{\mu_1}(x_1) & u_{\mu_2}(x_1) & \cdots & u_{\mu_{N-k}}(x_1) & u_{n_1}(x_1) & u_{n_2}(x_1) & \cdots & u_{n_k}(x_1) \\ u_{\mu_1}(x_2) & u_{\mu_2}(x_2) & \cdots & u_{\mu_{N-k}}(x_2) & u_{n_1}(x_2) & u_{n_2}(x_2) & \cdots & u_{n_k}(x_2) \\ . & . & \cdots & . & . & . & \cdots & . \\ . & . & \cdots & . & . & . & \cdots & . \\ . & . & \cdots & . & . & . & \cdots & . \\ u_{\mu_1}(x_N) & u_{\mu_2}(x_N) & \cdots & u_{\mu_{N-k}}(x_N) & u_{n_1}(x_N) & u_{n_2}(x_N) & \cdots & u_{n_k}(x_N) \end{vmatrix}$$

$$(1)$$

where $u_\mu(x)$ and $u_n(x)$ are a set of orthonormal spin-orbitals for closed and open shells, respectively and $u_{n_i}(x) \equiv u_{\mu_{N-k+i}}(x)$. Each of the spin-orbitals is assumed to be the product of a function of space coordinates and a spin function $u_{m_S}(\sigma)$. All determinants for a given configuration can be obtained from Eq. (1); k spin-orbitals of these determinants are different and all other $N - k$ spin orbitals are identical. For $k = 0$, Eq. (1), is the single Slater determinant for closed shell system. For $k = N$ all shells of a system are open.

The determinantal method is commonly used to evaluate the various properties of atoms and molecules when the HF and HFR approximations are employed. According to the determinantal method [8, 9] the total wave function of a system is constructed as a linear combination of Slater determinants (1), which are themselves constructed from an orthogonal spin-orbital basis set. However, by the use of determinantal method it is not only difficult, in general, to find independent Slater determinants but also to simplify the construction of a Fock operator as presented in Ref. [8] for open-shell systems. In this paper we have modified Slater's determinantal method for the evaluation of Slater determinants which are useful for the construction of Fock operator for open-shell systems.

2. Modified determinantal method

We have now to consider the problem of determining which of the independent Slater determiants occur in a given configuration. According to Refs. [9-10] we can write down the N individual sets comprising each complete set which occurs in the configuration. The number and nature of the closed shells is without effect on the values of quantum numbers in the open-shell spin-orbitals (see Eqs. (1) and (2) in Ref. [8]). We denote here a set of quantum numbers for open-shell spin-orbitals by n_i (where $i = 1, 2, ..., k$), namely,

$$n_i \equiv 1, 2, ..., N_i, \tag{2}$$

where N_i is the number of spin-orbitals in the shell i.

In order to obtain from Eq. (1) all of the independent Slater determinants for a given atomic or molecular electronic configuration we modified the Slater's determinantal

method for the states of the same open-shell by taking into account in Eq. (1) only those values of n_i in the following form:

$$n_1 < n_2 < \cdots < n_k. \tag{3}$$

We refer to the Slater rule based on the inequality (3) as modified Slater's determinantal method for the evaluation of determinantal wave functions.

Now we can move on, as an example, to an application of modified determinantal method for the determination of Slater determinants for atoms. Having made a list of the complete sets which belong to an atomic electronic configuration we may classify them by values of $\sum m_l = M_L$ and $\sum m_s = M_S$. To make the argument concrete, let us consider the configuration N ($1s^2 2s^2 2p^3$) in which three p electrons occur outside closed shells. The complete sets for p^3 classified by M_L, M_S values and the independent determinants obtained from Eq. (1) by modified determinantal method are shown in Table 1.

Table 1. The determinantal wave functions for the electronic configuration N ($1s^2 2s^2 2p^3$).

n_1 : $m_{\ell_1}\, m_{s_1}$	n_2 : $m_{\ell_2}\, m_{s_2}$	n_3 : $m_{\ell_3}\, m_{s_3}$	M_L	M_S	$U(21 m_{\ell_1} m_{s_1}$	$21 m_{\ell_2} m_{s_2}$	$21 m_{\ell_3} m_{s_3})$
1 : 1 ½	2 : 1 ½	3 : 0 ½	2	½	U_1(2111/2	211-1/2	2101/2)
		4 : 0 - ½	2	- ½	U_2(2111/2	211-1/2	210-1/2)
		5 : -1 ½	1	½	U_3(2111/2	211-1/2	21-11/2)
		6 : -1 -½	1	-½	U_5(2111/2	211-1/2	21-1-1/2)
	3 : 0 ½	4 : 0 -½	1	½	U_4(2111/2	2101/2	210-1/2)
		5 : -1 ½	0	3/2	U_7(2111/2	2101/2	21-11/2)
		6 : -1 -½	0	½	U_8(2111/2	2101/2	21-1-1/2)
	4 : 0 -½	5 : -1 ½	0	½	U_9(2111/2	210-1/2	21-11/2)
		6 : -1 -½	0	-½	U_{11}(2111/2	210-1/2	21-1-1/2)
	5 : -1 ½	6 : -1 -½	-1	½	U_{14}(2111/2	21-11/2	21-1-1/2)
2 : 1 -½	3 : 0 ½	4 : 0 -½	1	-½	U_6(211-1/2	2101/2	210-1/2)
		5 : -1 ½	0	½	U_{10}(211-1/2	2101/2	21-11/2)
		6 : -1 -½	0	-½	U_{12}(211-1/2	2101/2	21-1-1/2)
	4 : 0 -½	5 : -1 ½	0	-½	U_{13}(211-1/2	210-1/2	21-11/2)
		6 : -1 -½	0	-3/2	U_{16}(211-1/2	210-1/2	21-1-1/2)
	5 : -1 ½	6 : -1 -½	-1	½	U_{17}(211-1/2	21-11/2	21-1-1/2)
3 : 0 ½	4 : 0 -½	5 : -1 ½	-1	½	U_{15}(2101/2	210-1/2	21-11/2)
		6 : -1 -½	-1	-½	U_{18}(2101/2	210-1/2	21-1-1/2)
	5 : -1 ½	6 : -1 -½	-2	½	U_{19}(2101/2	21-11/2	21-1-1/2)
4 : 0 -½	5 : -1 ½	6 : -1 -½	-2	-½	U_{20}(210-1/2	21-11/2	21-1-1/2)

It is easy to find from Table 1 the terms and the orthonormal sets of wave functions $\Psi_{M_L M_S}^{LS}$ which are egienfunctions of operators $\hat{L}^2, \hat{L}_z, \hat{S}^2$, and $\hat{S}_z$. The results are given in Table 2.

It should be noted that in the case of different open-shells the sets of quantum numbers in Eq. (1) are independent. Therefore it is easy to obtain the independent determinantal wave functions for these systems by the use of modified determinantal method. The results of calculation for the Slater determinants and the wave functions of terms for the electronic configuration C ($1s^2 2s^1 2p^3$) are presented in Tables 3 and 4, respectively.

Table 2. The terms of electronic configuration N ($1s^2 2s^2 2p^3$) and their wave functions.

Terms	$\Psi^{LS}_{M_L M_S}$	
^{2}D	$\Psi^{2\ 1/2}_{2\ 1/2} = U_1$	$\Psi^{2\ 1/2}_{2\ -1/2} = U_2$
	$\Psi^{2\ 1/2}_{1\ 1/2} = \frac{1}{\sqrt{2}}(U_3 - U_4)$	$\Psi^{2\ 1/2}_{1\ -1/2} = \frac{1}{\sqrt{2}}(U_5 - U_6)$
	$\Psi^{2\ 1/2}_{0\ 1/2} = \frac{1}{\sqrt{6}}(-U_8 + 2U_9 - U_{10})$	$\Psi^{2\ 1/2}_{0\ -1/2} = \frac{1}{\sqrt{6}}(U_{11} - 2U_{12} + U_{13})$
	$\Psi^{2\ 1/2}_{-1\ 1/2} = \frac{1}{\sqrt{2}}(-U_{14} + U_{15})$	$\Psi^{2\ 1/2}_{-1\ -1/2} = \frac{1}{\sqrt{2}}(-U_{17} + U_{18})$
	$\Psi^{2\ 1/2}_{-2\ 1/2} = -U_{19}$	$\Psi^{2\ 1/2}_{-2\ -1/2} = -U_{20}$
^{4}S	$\Psi^{0\ 3/2}_{0\ 3/2} = U_7$	$\Psi^{0\ 3/2}_{0\ 1/2} = \frac{1}{\sqrt{3}}(U_8 + U_9 + U_{10})$
	$\Psi^{0\ 3/2}_{0\ -1/2} = \frac{1}{\sqrt{3}}(U_{11} + U_{12} + U_{13})$	$\Psi^{0\ 3/2}_{0\ -3/2} = U_{16}$
^{2}p	$\Psi^{1\ 1/2}_{1\ 1/2} = \frac{1}{\sqrt{2}}(U_3 + U_4)$	$\Psi^{1\ 1/2}_{1\ -1/2} = \frac{1}{\sqrt{2}}(U_5 + U_6)$
	$\Psi^{1\ 1/2}_{0\ 1/2} = \frac{1}{\sqrt{2}}(U_8 - U_{10})$	$\Psi^{1\ 1/2}_{0\ -1/2} = \frac{1}{\sqrt{2}}(U_{11} - U_{13})$
	$\Psi^{1\ 1/2}_{-1\ 1/2} = \frac{1}{\sqrt{2}}(U_{14} + U_{15})$	$\Psi^{1\ 1/2}_{-1\ -1/2} = \frac{1}{\sqrt{2}}(U_{17} + U_{18})$

3. Numerical results and discussion

As can be seen from the Tables 1-4, the modified determinantal method can be of considerable importance in the simplification and calculation of determinantal wave functions for open-shell systems. As an application of modified determinantal method, we have solved HFR equations (see: Ref. [8]) for the ground state of an N-atom system using Slater-type atomic orbitals as a basis. The results of computer calculations for

the linear-combination coefficients, orbital energies, total energy and virial coefficient are given in Tables 5, 6 and 7 (the data for the Slater atomic orbitals were taken from Ref. [11]). The results given in these tables agree well with published data [11].

Table 3. The determinantal wave functions for the electronic configuration C $(1s^2 2s^1 2p^3)$.

n_1 : $m_{\ell_1}\ m_{s_1}$	n_2 : $m_{\ell_2}\ m_{s_2}$	n_3 : $m_{\ell_3}\ m_{s_3}$	n_4 : $m_{\ell_4}\ m_{s_4}$	M_L	M_S	$U(20m_{\ell_1}m_{s_1}\ 21m_{\ell_2}m_{s_2}\ 21m_{\ell_3}m_{s_3}$ $21m_{\ell_4}\ m_{s_4})$			
1 : 0 $1/2$	3 : 1 $1/2$	4 : 1 -$1/2$	5 : 0 $1/2$	2	1	U_1(2001/2	2111/2	211-1/2	2101/2)
			6 : 0 -$1/2$	2	0	U_2(2001/2	2111/2	211-1/2	210-1/2)
			7 : -1 $1/2$	1	1	U_4(2001/2	2111/2	211-1/2	21-11/2)
			8 : -1 -$1/2$	1	0	U_6(2001/2	2111/2	211-1/2	21,1-1/2)
		5 : 0 $1/2$	6 : 0 -$1/2$	1	1	U_5(2001/2	2111/2	2101/2	210-1/2)
			7 : -1 $1/2$	0	2	U_{10}(2001/2	2111/2	2101/2	21-11/2)
			8 : -1 -$1/2$	0	1	U_{11}(2001/2	2111/2	2101/2	21-1-1/2)
		6 : 0 -$1/2$	7 : -1 $1/2$	0	1	U_{12}(2001/2	2111/2	210-1/2	21-11/2)
			8 : -1 -$1/2$	0	0	U_{15}(2001/2	2111/2	210-1/2	21-1-1/2)
		7 : -1 $1/2$	8 : -1 - $1/2$	-1	1	U_{21}(2001/2	2111/2	21-11/2	21-1-1/2)
	4 : 1 - $1/2$	5 : 0 $1/2$	6 : 0 -$1/2$	1	0	U_7(2001/2	211-1/2	2101/2	210-1/2)
			7 : - 1 $1/2$	0	1	U_{13}(2001/2	211-1/2	2101/2	21-11/2)
			8 : -1 -$1/2$	0	0	U_{16}(2001/2	211-1/2	2101/2	21-1-1/2)
		6 : 0 -$1/2$	7 : -1 $1/2$	0	0	U_{17}(2001/2	211-1/2	210-1/2	21-11/2)
			8 : -1 -$1/2$	0	-1	U_{23}(2001/2	211-1/2	210-1/2	21-1-1/2)
		7 : -1 $1/2$	8 : -1 -$1/2$	-1	0	U_{27}(2001/2	211-1/2	21-11/2	21-1-1/2)
	5 : 0 $1/2$	6 : 0 -$1/2$	7 : - 1 $1/2$	-1	1	U_{22}(2001/2	2101/2	210-1/2	21-11/2)
			8 : -1 -$1/2$	-1	0	U_{28}(2001/2	2101/2	210-1/2	21-1-1/2)
		7 : -1 -$1/2$	8: -1 -$1/2$	-2	1	U_{31}(2001/2	2101/2	21-11/2	21-1-1/2)
	6: 0 -$1/2$	7 : -1 $1/2$	8 : -1 -$1/2$	-2	0	U_{32}(2001/2	210-1/2	21-11/2	21-1-1/2)
2 : 0 -$1/2$	3 : 1 $1/2$	4 : 1 -$1/2$	5 : 0 $1/2$	2	0	U_3(200-1/2	2111/2	211-1/2	2101/2)
			6 : 0 -$1/2$	2	-1	U_{34}(200-1/2	2111/2	211-1/2	210-1/2)
			7 : -1 $1/2$	1	0	U_8(200-1/2	2111/2	211-1/2	21-11/2)
			8 : -1 –$1/2$	1	-1	U_{35}(200-1/2	2111/2	211-1/2	21-1-1/2)
		5: 0 $1/2$	6 : 0 –$1/2$	1	0	U_9(200-1/2	2111/2	2101/2	210-1/2)
			7 : -1 $1/2$	0	1	U_{14}(200-1/2	2111/2	2101/2	21-11/2)
			8 : -1 –$1/2$	0	0	U_{18}(200-1/2	2111/2	2101/2	21-1-1/2)
		6 : 0 -$1/2$	7 : -1 $1/2$	0	0	U_{19}(200-1/2	2111/2	210-1/2	21-11/2)
			8 : -1 –$1/2$	0	-1	U_{24}(200-1/2	2111/2	210-1/2	21-1-1/2)
		7: -1 $1/2$	8: -1 - $1/2$	-1	0	U_{29}(200-1/2	2111/2	21-11/2	21-1-1/2)
	4 : 1 -$1/2$	5 : 0 $1/2$	6 : 0 -$1/2$	1	-1	U_{36}(200-1/2	211-1/2	2101/2	210-1/2)
			7 : -1 $1/2$	0	0	U_{20}(200-1/2	211-1/2	2101/2	21-11/2)
			8 : -1 –$1/2$	0	-1	U_{25}(200-1/2	211-1/2	2101/2	21-1-1/2)
		6 : 0 –$1/2$	7 : -1 $1/2$	0	-1	U_{26}(200-1/2	211-1/2	210-1/2	21-11/2)
			8 : -1 –$1/2$	0	-2	U_{37}(200-1/2	211-1/2	210-1/2	21-1-1/2)
		7: -1 $1/2$	8: -1 - $1/2$	-1	-1	U_{38}(200-1/2	211-1/2	21-11/2	21-1-1/2)
	5 : 0 $1/2$	6 : 0 –$1/2$	7 : -1 $1/2$	-1	0	U_{30}(200-1/2	2101/2	210-1/2	21-11/2)
			8 : -1 –$1/2$	-1	-1	U_{39}(200-1/2	2101/2	210-1/2	21-1-1/2)
		7: -1 $1/2$	8: -1 - $1/2$	-2	0	U_{33}(200-1/2	2101/2	21-11/2	21-1-1/2)
	6: 0 - $1/2$	7 : -1 $1/2$	8 : -1 - $1/2$	-2	-1	U_{40}(200-1/2	210-1/2	21-11/2	21-1-1/2)

Table 4. The terms of electronic configuration C $(1s^2 2s^1 2p^3)$ and their wave functions.

Terms	$\Psi_{M_L M_S}^{LS}$
^{3}D	$\Psi_{21}^{21} = U_1 \qquad \Psi_{20}^{21} = \frac{1}{\sqrt{2}}(U_2 + U_3) \qquad \Psi_{2-1}^{21} = U_{34}$ $\Psi_{11}^{21} = \frac{1}{\sqrt{2}}(U_4 - U_5) \qquad \Psi_{10}^{21} = \frac{1}{2}(U_6 - U_7 + U_8 - U_9)$ $\Psi_{1-1}^{21} = \frac{1}{\sqrt{2}}(U_{35} - U_{36})$ $\Psi_{01}^{21} = \frac{1}{\sqrt{6}}(-U_{11} + 2U_{12} - U_{13})$ $\Psi_{00}^{21} = \frac{1}{\sqrt{12}}(U_{15} - 2U_{16} + U_{17} - U_{18} + 2U_{19} - U_{20})$ $\Psi_{0-1}^{21} = \frac{1}{\sqrt{6}}(U_{24} - 2U_{25} + U_{26})$ $\Psi_{-11}^{21} = \frac{1}{\sqrt{2}}(-U_{21} + U_{22}) \qquad \Psi_{-10}^{21} = \frac{1}{2}(-U_{27} + U_{28} - U_{29} + U_{30})$ $\Psi_{-1-1}^{21} = \frac{1}{\sqrt{2}}(-U_{38} + U_{39})$ $\Psi_{-21}^{21} = -U_{31} \qquad \Psi_{-20}^{21} = -\frac{1}{\sqrt{2}}(U_{32} + U_{33}) \qquad \Psi_{-2-1}^{21} = -U_{40}$
^{1}D	$\Psi_{20}^{20} = \frac{1}{\sqrt{2}}(U_2 - U_3) \qquad \Psi_{10}^{20} = \frac{1}{2}(U_6 - U_7 - U_8 + U_9)$ $\Psi_{00}^{20} = \frac{1}{\sqrt{12}}(U_{15} - 2U_{16} + U_{17} + U_{18} - 2U_{19} + U_{20})$ $\Psi_{-10}^{20} = \frac{1}{2}(-U_{27} + U_{28} + U_{29} - U_{30}) \qquad \Psi_{-20}^{20} = \frac{1}{\sqrt{2}}(-U_{32} + U_{33})$
^{3}P	$\Psi_{11}^{11} = \frac{1}{\sqrt{2}}(U_4 + U_5) \qquad \Psi_{10}^{11} = \frac{1}{2}(U_6 + U_7 + U_8 + U_9)$ $\Psi_{1-1}^{11} = \frac{1}{\sqrt{2}}(U_{35} + U_{36})$ $\Psi_{01}^{11} = \frac{1}{\sqrt{2}}(U_{11} - U_{13}) \qquad \Psi_{00}^{11} = \frac{1}{2}(U_{15} - U_{17} + U_{18} - U_{20})$ $\Psi_{0-1}^{11} = \frac{1}{\sqrt{2}}(U_{24} - U_{26})$ $\Psi_{-11}^{11} = \frac{1}{\sqrt{2}}(U_{21} + U_{22}) \qquad \Psi_{-10}^{11} = \frac{1}{2}(U_{27} + U_{28} + U_{29} + U_{30})$ $\Psi_{-1-1}^{11} = \frac{1}{\sqrt{2}}(U_{38} + U_{39})$
^{1}P	$\Psi_{10}^{10} = \frac{1}{2}(U_6 + U_7 - U_8 - U_9) \qquad \Psi_{00}^{10} = \frac{1}{2}(U_{15} - U_{17} - U_{18} + U_{20})$ $\Psi_{-10}^{10} = \frac{1}{2}(U_{27} + U_{28} - U_{29} - U_{30})$
^{5}S	$\Psi_{02}^{02} = U_{10} \qquad \Psi_{01}^{02} = \frac{1}{2}(U_{11} + U_{12} + U_{13} + U_{14})$ $\Psi_{00}^{02} = \frac{1}{\sqrt{6}}(U_{15} + U_{16} + U_{17} + U_{18} + U_{19} + U_{20})$ $\Psi_{0-1}^{02}\frac{1}{2}(U_{23} + U_{24} + U_{25} + U_{26}) \qquad \Psi_{0-2}^{02} = U_{37}$
^{3}S	$\Psi_{01}^{01} = \frac{1}{\sqrt{12}}(U_{11} + U_{12} + U_{13} - 3U_{14})$ $\Psi_{00}^{01} = \frac{1}{\sqrt{6}}(U_{15} + U_{16} + U_{17} - U_{18} - U_{19} - U_{20})$ $\Psi_{0-1}^{01} = \frac{1}{\sqrt{12}}(3U_{23} - U_{24} - U_{25} - U_{26})$

Table 5. The linear combination coefficients and orbital energies of ^{2}P term for the ground state of N-atom.

ε_i	-15.676226	-0.86873201	-0.2639832	-0.22034108	-0.12316354
	C_{p1}	C_{p2}	C_{p3}	C_{p4}	C_{p5}
1s	0.99915072	-0.2027468	0.00000000	0.00000000	0.00000000
2s	0.00431561	1.0195046	0.00000000	0.00000000	0.00000000
2p$_x$	0.00000000	0.00000000	0.00000000	1.00000000	0.00000000
2p$_y$	0.00000000	0.00000000	1.00000000	0.00000000	0.00000000
2p$_z$	0.00000000	0.00000000	0.00000000	0.00000000	1.00000000

E = -54.010966418 Hartree T = 52.148768 Hartree V = -106.15973223 Hartree **Virial = -2.0366**

Table 6. The linear combination coefficients and orbital energies of ^{2}D term for the ground state of N-atom.

ε_i	-15.6762268	-0.86873201	-0.21893107	-0.21470107	-0.21470107
	C_{p1}	C_{p2}	C_{p3}	C_{p4}	C_{p5}
1s	0.99915072	-0.2027468	0.00000000	0.00000000	0.00000000
2s	0.00431561	1.0195046	0.00000000	0.00000000	0.00000000
2p$_x$	0.00000000	0.00000000	0.00000000	1.00000000	0.00000000
2p$_y$	0.00000000	0.00000000	1.00000000	0.00000000	0.00000000
2p$_z$	0.00000000	0.00000000	0.00000000	0.00000000	1.00000000

E = -54.05181 Hartree T = 52.148876 Hartree V = -106.200577 Hartree **Virial = -2.0364**

Table 7. The linear combination coefficients and orbital energies of ^{4}S term for the ground state of N-atom.

ε_i	-15.676226	-0.86873201	-0.2696911	-0.2696911	-0.2696911
	C_{p1}	C_{p2}	C_{p3}	C_{p4}	C_{p5}
1s	0.99915072	-0.2027468	0.00000000	0.00000000	0.00000000
2s	0.00431561	1.0195046	0.00000000	0.00000000	0.00000000
2p$_x$	0.00000000	0.00000000	0.00000000	1.00000000	0.00000000
2p$_y$	0.00000000	0.00000000	1.00000000	0.00000000	0.00000000
2p$_z$	0.00000000	0.00000000	0.00000000	0.00000000	1.00000000

E = -54.2125497 Hartree T = 52.148769 Hartree V = -106.361317 Hartree **Virial = -2.0396**

Its should be noted that the modified determinantal method presented in this paper can also be used to obtain the independent determinantal wave functions for open-shell

molecules. Work is in progress in our group for the computation of electronic structure of atoms and molecules with multi-determinantal state of a single configuration that has arbitrary open-shells.

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