A new representation of the many body wave function and its application as a post Hartree-Fock energy variation method

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1 Introduction

In this paper, we introduce a new representation of many body electron wave function and a few calculation results of the ground state energies of many body systems using that representation, which is systematically better than the Hartree-Fock approximation.

The fundamental principle of condensed matter physics and chemistry is given in the many body Schrödinger equation, which is

\[ H = \sum_{i=1}^{N} \left[ -(1/2) \nabla_i^2 + v(r_i) \right] + \sum_{(i,j)} 1/|r_i - r_j|, \]

\[ H\psi(x_1 \cdots x_N) = E\psi(x_1 \cdots x_N). \]

This is a Schrödinger equation of \(N\) electrons in the external potential \(v(r)\) from nuclei under the Born-Oppenheimer approximation. The electron wave function \(\psi(x_1 \cdots x_N)\) must be antisymmetric in the exchange of arbitrary two spin coordinates \(x_i\) and \(x_j\). One of the central problems in condensed matter physics and chemistry is to find the solution of (2) and the ground state energy \(E_0\) of the given system. There are many attempts to solve this problem. In this section, we briefly look over the Hartree-Fock approximation (HF) and the Density functional theory (DFT) or Local density approximation (LDA).

In the Hartree-Fock approximation, the many body wavefunction \(\psi(x_1 \cdots x_N)\) is approximated by a single Slater determinant \(\psi_{SL}\), and this gives limitation to the accuracy of calculated ground state energy \(E_{HF}\). The reason is that an antisymmetric wave function \(\psi(x_1 \cdots x_N)\) is not always given as a single Slater determinant \(\psi_{SL}\). Rather, \(\psi(x_1 \cdots x_N)\) can be expanded in a linear combination of \(MC_N\) Slater determinants in the space of given orbital set \(\psi_1, \ldots, \psi_M\). In this way, one can rearrange the many body electron problem into the diagonalization of \(MC_N \times M C_N\) matrix. This method is known as Full CI method. Full CI always gives the exact ground state energy in the space of a given orbital set \(\psi_1, \ldots, \psi_M\). However, when the number of the electrons \(N\) and the orbitals \(M\) increases as much as a few dozens, the dimension of the matrix \(MC_N\) increases exponentially with \(N\) and \(M\) and Full CI calculation becomes practically impossible.

In the Hartree-Fock approximation, the variables of the variation are the \(N\) orbitals \(\psi_1, \ldots, \psi_N\). In contrast, in the density functional theory, the variable is the one electron density \(\rho(r)\). This \(\rho(r)\) can be uniquely deduced from the given antisymmetric wave function \(\psi(x_1 \cdots x_N)\). The essence of the DFT is that the expectation value of the sum of the kinetic energy \(T\) and the coulomb repulsion energy \(U\) in the ground state can be given by a unique functional of the one electron density, \(F[\rho(r)]\). However, the exact form of this functional \(F[\rho(r)]\) is not known until today. Therefore, in LDA calculation,
several approximated form of this functional is used and they are not exact. In LDA, the \( v \)-representability of \( \rho(\mathbf{r}) \) is generally assumed, if one uses integers for the occupation numbers. In this case, the calculated ground state energy \( E_{LDA} \) and the one electron density \( \rho(\mathbf{r}) \) are derived from a non interacting single slater determinant \( \psi_{SL} \). This may be the reason why the LDA calculation does not work well in the so called strongly correlated systems.

In the next section, we introduce a new representation of the antisymmetric wave function which is an extension of the slater determinant and therefore not always non interacting.

2 A new representation of many body wave function

In the many body schrodinger equation (12), the variable is the \( N \) body antisymmetric wave function \( \psi(x_1 \cdots x_N) \). However, this function is apparently not suited for any variational calculation because if one takes \( m \) spatial grids for one variable \( x_i \), then the total grids of the function is proportional to \( m^N \) and becomes progressively impossible to stock in the memory of the computer when he increases \( N \) to only a few dozens. One way to express this wave function \( \psi(x_1 \cdots x_N) \) is to expand it in a given \( M \) orbital set \( \psi_1, \ldots, \psi_M \). In this way, the wave function is expressed as

\[
\psi(x_1 \cdots x_N) = \sum_{i_1 \cdots i_N} A_{i_1 \cdots i_N} \psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N). \tag{3}
\]

In order to keep \( \psi(x_1 \cdots x_N) \) antisymmetric, the rank-\( N \) and dimension-\( M \) tensor \( A_{i_1 \cdots i_N} \) should be antisymmetric tensor. This antisymmetric tensor has \( M C_N \) degree of freedom and still be hard to take variation except for very small systems.

Here we introduce a new representation of this antisymmetric tensor \( A_{i_1 \cdots i_N} \):

\[
A_{i_1 \cdots i_N} = \sum_{i=1}^{K} c_i^1 c_i^2 \cdots c_i^K \epsilon_{i_1 i_2} \epsilon_{i_1 i_3} \cdots \epsilon_{i_{N-1} i_N}, \tag{4}
\]

In this representation, each \( c_i^1, \ldots, c_i^K \) represents a vector of dimension \( M \). For this reason, let us tentatively call this representation as the vector product. \( c_1, \ldots, c_K \) are arbitrary coefficients. \( \epsilon_{ij} \) is a rank-2 and dimension-\( M \) tensor which is defined by

\[
\epsilon_{ij} = \begin{cases} 
1 & (i < j), \\
-1 & (i > j), \\
0 & (i = j).
\end{cases} \tag{5}
\]

It is easy to verify that \( \epsilon_{i_1 \cdots i_N} \equiv \epsilon_{i_1 i_2} \cdots \epsilon_{i_{N-1} i_N}, N(N-1)/2 \) product of \( \epsilon_{ij} \), is rank-\( N \) and dimension-\( M \) antisymmetric tensor which takes the value of only 1, -1 or 0 for any indices \( i_1 \cdots i_N \). Here we give the proof. If \( N = 2 \), it is obvious from the definition that \( \epsilon_{i_1 i_2} \) is antisymmetric. Let us assume that \( \epsilon_{i_1 \cdots i_N} \equiv \epsilon_{i_1 i_2} \cdots \epsilon_{i_{N-1} i_N} \) is now antisymmetric and consider about the rank-\( N + 1 \) tensor

\[
\epsilon_{i_1 \cdots i_{N+1}} \equiv \epsilon_{i_1 \cdots i_N} \cdot \epsilon_{i_1 i_{N+1}} \cdots \epsilon_{i_{N-1} i_{N+1}}. \tag{6}
\]

We only need to prove that this tensor is antisymmetric for indices \( i_1 \) and \( i_{N+1} \). One can rewrite the above form to

\[
\epsilon_{i_1 \cdots i_{N+1}} = \epsilon_{i_2 \cdots i_N} \cdot \epsilon_{i_1 i_2} \cdots \epsilon_{i_1 i_{N+1}} \cdots \epsilon_{i_N i_{N+1}} \cdot \epsilon_{i_1 i_{N+1}}. \tag{7}
\]
When one exchanges the indices $i_1$ and $i_{N+1}$, tensor $\epsilon_{i_2 \cdots i_N}$ does not change. Tensor $\epsilon_{i_1i_2} \cdots \epsilon_{i_{N+1}}$ and $\epsilon_{i_2i_{N+1}} \cdots \epsilon_{i_Ni_{N+1}}$ change into each other with the same factor $(-1)^{N-1}$, so their product does not change. And finally, the tensor $\epsilon_{i_1i_{N+1}}$ changes its sign by $-1$. Therefore, the tensor $\epsilon_{i_1 \cdots i_N}$ changes its sign by $-1$ in this operation. Thus the argument is proved. It is trivial from the definition that the value of the tensor $\epsilon_{i_1 \cdots i_N}$ takes only $1$, $-1$ or $0$.

From this, one can conclude that the tensor $A_{i_1 \cdots i_N}$ is antisymmetric. We have proved that $\epsilon_{i_1 \cdots i_N}$ is antisymmetric. Therefore, $c_{i_1} \cdots c_{i_N} \epsilon_{i_1 \cdots i_N}$ is antisymmetric. $A_{i_1 \cdots i_N}$ is a linear combination of these antisymmetric tensors for $i = 1, \cdots, K$, then antisymmetric.

Notice that the representation (4) is an approximative form of general antisymmetric tensor. Antisymmetric tensor $A_{i_1 \cdots i_N}$ has $M C_N$ elements, and belongs to the dimension $M C_N$ vector space. Therefore, if $K = M C_N$ and all $c_{i_1} \cdots c_{i_N} \epsilon_{i_1 \cdots i_N}$ are linearly independent for $i = 1, \cdots, K$, then any $A_{i_1 \cdots i_N}$ can be expanded in the form of (4). However, in the following section we will see that one can well approximate at least some antisymmetric tensors which are solutions of the many body problem, with the condition $K = 1$.

Apparently, the vector product for $K = 2$ is an extension of the vector product for $K = 1$. Generally, the vector product for $K + 1$ is an extension of the vector product for $K$. Here we see that the vector product for $K = 1$ includes all slater determinants for a given orbital set $\psi_1, \cdots, \psi_M$. When $K = 1$, the vector product is given as

$$A_{i_1 \cdots i_N} = c c_{i_1} \cdots c_{i_N} \epsilon_{i_1i_2} \cdots \epsilon_{i_{N-1}i_N}. \quad (8)$$

We only need to consider the case which $i_1 = 1, \cdots, i_N = N$. When it is possible to expand the wave function $\psi(x_1 \cdots x_N)$ in the orbital set $\psi_1, \cdots, \psi_N$, the antisymmetric tensor $A_{i_1 \cdots i_N}$ has degree of $N C_N = 1$ and thus uniquely determined under the antisymmetric condition, with an arbitrary factor. The slater determinant for $\psi_1, \cdots, \psi_N$ is of course antisymmetric. Therefore, we only need to show that the vector product for $K = 1$ can be antisymmetric when expanded in orbitals $\psi_1, \cdots, \psi_N$ and zero when expanded in other orbitals. This condition is satisfied when one takes the vector $c_{i_1}$ for

$$c_{i_1} = \begin{cases} 1 & (i_1 = 1, \cdots, N), \\ 0 & (\text{others}). \end{cases} \quad (9)$$

Thus the argument is proved.

It is not difficult to see that the vector product with $K = 1$ ($\psi_{VP}^1$) is indeed an extension of the slater determinant if the number of the orbital $M$ is larger than the number of electrons $N$. In other words, there are wave functions which are representable in the form of $\psi_{VP}^1$ but not in a slater determinant. The characteristic of the slater determinant is that the first order reduced density matrix ($\gamma_1$) of the slater determinant has the same eigenvalues $1/N$ for $N$ natural orbitals. One can easily see that $\gamma_1$ of an arbitrary wave function which is representable as $\psi_{VP}^1$ has generally different eigenvalues $\lambda_i < 1/N$ by simply take random values for the vector $c_{i_1}$ and calculate $\gamma_1$ and its eigenvalues. This fact indicates that $\psi_{VP}^1$ is generally interacting and not always representable by a single slater determinant.

As we discussed above, the vector product with $K = 1$ is an extension of a single slater determinant. For this reason, one can obtain the same or lower ground state energy $E_0$ by using $c_{i_1}$ as variational parameters, compared to the Hartree-Fock approximation.
This is possible when one uses an orbital set \( \psi_1, \ldots, \psi_M \) which includes the Hartree-Fock derived orbitals \( \psi_1, \ldots, \psi_N \). One can obtain further lower energy by the vector product method when he takes variation also for orbitals \( \psi_1, \ldots, \psi_M \). This variation of orbitals is possible in various ways. One way is to take unitary transform of these orbitals and take variation for the elements of the unitary matrix. The details of this transform are to be explained in the following section.

### 3 Energy calculation in the vector product method

Generally, the expectation value of the energy \( E \) of the \( N \) electron system in the normalized state \( \psi(x_1, \ldots, x_N) \) is given as

\[
E = \int \cdots \int dx_1 \cdots dx_N \psi^* (x_1, \ldots, x_N) H \psi(x_1, \ldots, x_N).
\]  

(10)

However, the Hamiltonian of electrons is generally two-body and in the following form:

\[
H = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 + v(r_i) \right) + \sum_{(i,j)} \frac{1}{|r_i - r_j|},
\]

(11)

Therefore, one can obtain \( E \) from the normalized second order reduced density matrix \( \gamma_2 \):

\[
E = N \int dx_1 [(-\frac{1}{2} \nabla_1^2 + v(r_1))\gamma_1 (x_1', x_1)]_{x_1' = x_1}
+ N(N - 1)/2 \int \int dx_1 dx_2 \frac{1}{|r_1 - r_2|} \gamma_2 (x_1 x_2, x_1 x_2),
\]

(12)

\[
\gamma_2 (x_1', x_2, x_1 x_2) \equiv \int \cdots \int dx_3 \cdots dx_N \psi^* (x_1' x_2 x_3 \cdots x_N) \psi (x_1 x_2 x_3 \cdots x_N),
\]

(13)

\[
\gamma_1 (x_1', x_1) \equiv \int dx_2 \gamma_2 (x_1' x_2, x_1 x_2).
\]

(14)

One can obtain the tensor representation of \( \gamma_2 \) by substituting (13) for (12):

\[
\gamma_2 (x_1 x_2, x_3 x_4) = \sum_{i_1 i_2 i_3 i_4} C_{i_1 i_2 i_3 i_4} \psi_{i_1}^* (x_1) \psi_{i_2}^* (x_2) \psi_{i_3} (x_3) \psi_{i_4} (x_4),
\]

(15)

\[
C_{i_1 i_2 i_3 i_4} \equiv \sum_{i_3 \cdots i_N} A_{i_1 i_2 i_3 \cdots i_N}^* A_{i_1 i_2 i_3 \cdots i_N}.
\]

(16)

Here, orbitals \( \psi_1, \ldots, \psi_M \) are assumed to be orthonormal. One can write down the tensor representation of \( E \) as following:

\[
E = \sum_{i_1 i_2 i_3 i_4} h_{i_1 i_2 i_3 i_4} C_{i_1 i_2 i_3 i_4} / n,
\]

(17)

\[
n \equiv \langle \psi(x_1 \cdots x_N) | \psi(x_1 \cdots x_N) \rangle
= \sum_{i_1 i_2} C_{i_1 i_2 i_1 i_2},
\]

(18)

\[
h_{i_1 i_2 i_3 i_4} \equiv N (t_{i_1 i_3} + v_{i_1 i_3}) \delta_{i_2 i_4} + \frac{N(N - 1)}{2} w_{i_1 i_2 i_3 i_4},
\]

(19)
\[ t_{i_1i_3} \equiv \int dx_1 \psi_{i_1}^* (x_1) (-1/2) \nabla_1^2 \psi_{i_3} (x_1), \quad (20) \]
\[ v_{i_1i_3} \equiv \int dx_1 \psi_{i_1}^* (x_1) v(r_1) \psi_{i_3} (x_1), \quad (21) \]
\[ w_{i_1i_2i_3i_4} \equiv \int \int dx_1 dx_2 \psi_{i_1}^* (x_1) \psi_{i_2}^* (x_2) \frac{1}{|r_1 - r_2|} \psi_{i_3} (x_1) \psi_{i_4} (x_2). \quad (22) \]

Next, we will see the representation of \( \gamma_2 \) in vector product. Here we assume real values for the components of the vector product \( c_i \) and \( c_i^j \) for simplicity. We need to substitute \( \mathbb{I} \) for \( \mathbb{F} \). The result is

\[
C_{i_1i_2i_3i_4} = \sum_{i,j=1}^{K} c_i c_j c_{i_1} c_{i_2} c_{i_3} c_{i_4} \epsilon_{i_1i_2} \epsilon_{i_3i_4} \\
\quad \cdot \sum_{j_3 \cdots j_N} c_{j_3} c_{j_3} \epsilon_{i_1j_3} \epsilon_{i_2j_3} \epsilon_{i_3j_3} \cdots c_{j_N} c_{j_N} \epsilon_{i_1j_N} \epsilon_{i_2j_N} \epsilon_{i_3j_N} \epsilon_{i_4j_N} d_{j_3 \cdots j_N} \\
\equiv \sum_{i,j=1}^{K} c_i c_j c_{i_1} c_{i_2} c_{i_3} c_{i_4} \epsilon_{i_1i_2} \epsilon_{i_3i_4} \cdot I_{i_1i_2i_3i_4}^{ij}, \quad (23) \]

\[
d_{j_3 \cdots j_N} \equiv \epsilon_{j_3 \cdots j_N}^2 = \begin{cases} 
1 & (j_3 \cdots j_N : \text{all different}), \\
0 & (\text{others}). \quad (24) 
\end{cases}
\]

There is a method to calculate the tensor \( I_{i_1i_2i_3i_4}^{ij} \). When one omits the indices \( i_1i_2i_3i_4 \) and \( ij \), \( I_{i_1i_2i_3i_4}^{ij} \) has a following form:

\[
I = \sum_{j_3 \cdots j_N} a_{j_3} \cdots a_{j_N} d_{j_3 \cdots j_N}, \quad (25) \]

\[
a_{j_k} \equiv c_{j_k} c_{j_k} \epsilon_{i_1j_k} \epsilon_{i_2j_k} \epsilon_{i_3j_k} \epsilon_{i_4j_k}. \quad (26) \]

From the definition of the tensor \( d_{j_3 \cdots j_N} \), one can conclude that the sum in \( (25) \) is taken over all permutation \( (j_3 \cdots j_N) \) for \( j_3 \cdots j_N = 1, \cdots, M \) with the condition that all \( j_3 \cdots j_N \) are different. Therefore, the value of \( I \) in \( (25) \) can be represented as the \( M - (N - 2) \)-th order coefficients of the following polynomial:

\[
f(t) \equiv (N - 2)! (t + a_1) \cdots (t + a_M). \quad (27) \]

Then the problem is how to calculate the \( M - (N - 2) \)-th order coefficients of a given polynomial \( f(t) \). Notice that now \( f(t) \) is an \( M \)-th order polynomial of \( t \). Then \( f(t) \) can be expanded in a following form:

\[
f(t) = b_0 + b_1 t + \cdots + b_M t^M, \quad (28)\]

\[
I = b_{M - (N - 2)}. \quad (29)\]

One can derive the \( M - (N - 2) \)-th order coefficients \( b_{M - (N - 2)} \) by solving a linear algebra problem. One can define a vector \( b \) of \( M + 1 \) dimension from the unknown coefficients \( b_0, \cdots, b_M \). One can have arbitrary \( M + 1 \) different values for \( t_0, \cdots, t_M \). Then he has

\[
f(t_0) = b_0 + b_1 t_0 + \cdots + b_M t_0^M, \quad (29)\]

\[
f(t_M) = b_0 + b_1 t_M + \cdots + b_M t_M^M. \quad (30)\]
One can solve this linear algebra problem with given values for $t_0, \ldots, t_M$ and $f(t_0), \ldots, f(t_M)$ and find all the coefficients $b_i$. To do that, one only need to calculate the inverse matrix of a matrix $T_{ij} \equiv t_i^2$ and multiplies it to a vector composed of $f(t_0), \ldots, f(t_M)$. In this way, one can calculate the value of $b_{M-(N-2)}$, and therefore the value of tensor $I$ for each indices $i, i_2, i_3, i_4, i_j$. Then one can calculate the matrix element $C_{i_1 i_2 i_3 i_4}$ from $c_i$ and $c_j$.

One has to take calculation steps proportional to $M^2$ for each calculation of $I_{i_1 i_2 i_3 i_4}^{ij}$, because he has to calculate the value of $M$-th order polynomial $f(t)$ for about $M$ times. To calculate $C_{i_1 i_2 i_3 i_4}$, one has to take this $M^2$ step for $M^4$ times for each indices, therefore he needs calculation steps proportional to $M^6$ for each calculation of the matrix $C_{i_1 i_2 i_3 i_4}$.

4 Variation of orbitals

In this section, we will consider about the variation of orbitals used in the expansion of many body wave function. The result of the vector product method is depending of the choice of orbitals, then one has to take variation for orbitals in the vector product method in order to obtain lower energy. Let us assume that we use orbitals $\psi_1, \ldots, \psi_M$ and a basis set $\phi_1, \ldots, \phi_B$. Here, $B \geq M$ and orbitals are expanded in the basis set:

$$\psi_i(x) = \sum_{j=1}^{B} U_{ij} \phi_j(x). \quad (31)$$

We assume that the basis set is orthonormal. Then, dimension-$B$ vectors $U_{ij}, \ldots, U_{Mj}$ should be orthonormal in order to maintain orbitals $\psi_1, \ldots, \psi_M$ to be orthonormal. Next, we will see how this expansion is applied on the expression of the energy matrix $h_{i_1 i_2 i_3 i_4}$ appeared in (17). The definition of $h_{i_1 i_2 i_3 i_4}$ is

$$h_{i_1 i_2 i_3 i_4} = \int \int dx_1 dx_2 \psi_{i_1}(x_1) \psi_{i_2}(x_2) \left[ N(-\frac{1}{2}\nabla^2_1 + v(r_1)) + \frac{N(N-1)}{2} \frac{1}{|r_1 - r_2|} \right] \psi_{i_3}(x_1) \psi_{i_4}(x_2). \quad (32)$$

By substituting (31) for (32), one gets following expression:

$$h_{i_1 i_2 i_3 i_4} = \sum_{j_1,j_2,j_3,j_4=1}^{B} U_{i_1 j_1} U_{i_2 j_2} U_{i_3 j_3} U_{i_4 j_4} H_{j_1 j_2 j_3 j_4}, \quad (33)$$

$$H_{j_1 j_2 j_3 j_4} = \int \int dx_1 dx_2 \phi_{j_1}(x_1) \phi_{j_2}(x_2) \left[ N(-\frac{1}{2}\nabla^2_1 + v(r_1)) + \frac{N(N-1)}{2} \frac{1}{|r_1 - r_2|} \right] \phi_{j_3}(x_1) \phi_{j_4}(x_2). \quad (34)$$

This matrix $h_{i_1 i_2 i_3 i_4}$ can be calculated by taking proportional to $MB^4$ steps from the fixed matrix $H_{j_1 j_2 j_3 j_4}$. The variation of orbitals is possible when one takes variation for the matrix $U_{ij}$ with maintaining vectors $U_{ij}, \ldots, U_{Mj}$ to be orthonormal. Notice that when $B = M$, $U_{ij}$ is a unitary matrix or orthogonal matrix.
5 Results of calculation

In this section, we will report on the results of the calculation of ground state energy of carbon ($^6\text{C}$) and oxygen ($^8\text{O}$) atom, using the vector product method with $K = 1$. The author of this paper admits that he is not a specialist of computational physics. He does not emphasize the numerical accuracy of the results shown in this section. The purpose of this section is to show that the calculation of the expectation energy with the vector product is possible and one can obtain better results with the vector product compared to the Hartree-Fock. For calculations of the diagonalization in Hartree-Fock and Full CI, we used CLAPACK which is LAPACK usable in C.

First, we will report on the results of $^6\text{C}$ ($E_{VP}$) by using the vector product method with $K = 1$ with 14 atomic orbitals as a basis set, which is $1s^2, \cdots, 3s^2$ and $3p_x^2$. We set $B$ to 14. We took variation for dimension-14 vector $c^1_i$ and a $14 \times 14$ orthogonal matrix $U_{ij}$. The expectation value of the energy $E$ is given explicitly as a polynomial of $c^1_i$ and $U_{ij}$. Therefore, we can explicitly define the differential value of $E$ for each $c^1_i$ and $U_{ij}$. Then, we took variation for $c^1_i$ and $U_{ij}$ by using the steepest descent method. We started from randomly chosen value for $c^1_i$ and a unit matrix for $U_{ij}$ as an initial value. We also calculated the ground state energy in this basis set by the Hartree-Fock method ($E_{HF}$) and Full CI method ($E_{FCI}$). The results are following:

| $M=14$ $^6\text{C}$ | $E_{HF}$ | $-37.661$ |
|----------------------|----------|------------|
| $M=14$ $^6\text{C}$ | $E_{VP}$ | $-37.688$ |
| $M=14$ $^6\text{C}$ | $E_{FCI}$ | $-37.708$ |

In this results, one can see that even though we set $K = 1$ and used only one $\psi_{VP}$ as many body wave function, he can obtain well better results compared to the Hartree-Fock. If one takes $K$ larger than 1, then it is sure that he will obtain further better results. This result $E_{VP} = -37.688$ is obtained by the steepest descent method and not yet converged. Therefore we may rather say $E_{VP} \leq -37.688$.

Next, we will report on the results of $^6\text{C}$ and $^8\text{O}$ atom using the vector product method with $K = 1$ ($E_{VP}$) with 19 atomic orbitals as a basis set, which is $1s^2, \cdots, 3p^6$ and $3d_{3z^2-r^2}$ set. We set the effective nuclear charge as $Z = 5.5$ for $^6\text{C}$ and $Z = 7.5$ for $^8\text{O}$. We also calculated the ground state energy in this basis set by the Hartree-Fock method ($E_{HF}$). We also compare these results with results in a literature $E_{HF}^{G}, E_{DFT}^{G}$ and $E_{EXP}^{G}$, which are results in Hartree-Fock, Density functional theory and experiment, respectively. The results are following:

| $M=19$ $^6\text{C}$ | $E_{HF}$ | $-37.666$ |
|----------------------|----------|------------|
| $M=19$ $^6\text{C}$ | $E_{VP}$ | $-37.790$ |
| $^6\text{C}$ | $E_{HF}^{G}$ | $-37.702$ |
| $^6\text{C}$ | $E_{DFT}^{G}$ | $-37.479$ |
| $^6\text{C}$ | $E_{EXP}^{G}$ | $-37.858$ |
| $M=19$ $^8\text{O}$ | $E_{HF}$ | $-74.908$ |
| $M=19$ $^8\text{O}$ | $E_{VP}$ | $-74.956$ |
| $^8\text{O}$ | $E_{HF}^{G}$ | $-74.858$ |
| $^8\text{O}$ | $E_{DFT}^{G}$ | $-74.532$ |
| $^8\text{O}$ | $E_{EXP}^{G}$ | $-75.113$ |
Here, $E_{VP}$ is not converged for both $^6$C and $^8$O. From these results, one can conclude that the results of the vector product method with $K=1$ can be better than the results of Hartree-Fock. If one takes $K$ larger than 1 then he will obtain further lower results for $E_{VP}$.

In the calculation of the vector product method, one needs proportional to $M^6$ steps for an evaluation of the matrix $\gamma_2$ in $c_{i1}$. There are $M$ variables for variation. Therefore we took proportional to $M^7$ steps for the variation of matrix $\gamma_2$. In the variation of the orthogonal matrix $U_{ij}$, one needs to take proportional to $M^5$ ($MB^4$) steps for each transformation of the energy matrix $h_{i1jzizi4}$. We took variation for each rows of the matrix. Therefore we spend proportional to $M^6$ ($M^2B^4$) steps for the variation of orbitals. Then the estimated calculation time $T$ for the vector product method is

$$ T \sim O(M^7) + O(M^2B^4). \quad (35) $$

The total amount of the calculation time for $E_{VP}$ was about a few hours for $^6$C and $^8$O ($M = 19$) with a $\sim 3$GHz CPU. In our calculation, we spend larger amount of time for the term $O(M^6) = O(M^2B^4)$ compared to $O(M^7)$.

6 Conclusion

We propose a new representation of many body electron wave function, namely the vector product. We also propose its application as a post Hartree-Fock method to evaluate the ground state energy of many body electron systems. The results of the vector product method will converge to the results of the Full CI method when one takes sufficiently large value for the parameter $K$ and keeps each vector products $\psi_{iVP}$ linearly independent. We obtained systematically better energy results compared to the results of the Hartree-Fock method for $^6$C and $^8$O atoms. The estimated calculation time $T$ for the vector product method is $T \sim O(M^7)$ as a function of orbital number $M$. It is expected that using higher spec CPUs, one can obtain the ground state energy better than Hartree-Fock in more big systems. In the vector product method, one can simultaneously variate the orbitals used in the calculation. This is an advantage of the vector product method compared to other methods such as CI method in which orbitals are fixed during the calculation. In the vector product method, one can simultaneously obtain the many body wave function of the system. This means that one can obtain many physical quantities of the system at the ground state. For example, the off diagonal long range order (ODLRO) in solid which is related to the superconductivity can be explained in a way that the maximum eigenvalue of the second order reduced density matrix ($\lambda_{max}^2$) satisfies the following condition:\[3\]$

N^2\lambda_{max}^2 \sim O(N). \quad (36)$

Calculated wave functions and second order reduced density matrices in the vector product method are not non-interacting in general. Then there is a possibility that the superconductivity of solid can be explained by the results of the vector product method.

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