ORIGINAL PAPER

A comparison of efficiency and accuracy of two-electron integrals calculation between two methods in multi-configuration time-dependent hartree fock frame

Wenliang Li · Keli Han

Abstract An approach to the evaluation of the two-electron repulsion integrals exactly in sine finite basis representation is proposed. The two-electron coulomb potential integrals are calculated respectively in sine finite basis representation by using two-fold Gaussian quadrature rules and in discrete variable representation by using the natural potential expansion of coulomb potential r_{12}. The efficiency and accuracy of two methods to calculate the two-electron repulsion integrals are compared. Some demonstrative calculations indicate that both the two ways are effective methods to do two-electron integrals calculations in the multi-configuration time-dependent hartree fock (MCTDHF) frame. By using the method to calculate the two-electron integrals in sine FBR, the working equations of MCTDHF are propagated in imaginary time. The ground state energy of helium atom obtained in the imaginary propagation is close to the Full Configuration interaction energy calculated by Molpro.

1 Introduction

In recent years, there has been increasing interest in the correlated dynamics of many-electron systems. Theorists have developed a variety of explicit time-dependent versions of electronic structure methods [1–15]. Most of the explicitly time-dependent

W. Li (✉)· K. Han
State key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116023, China
e-mail: wenliangli.dicp@gmail.com

W. Li · K. Han
Xinjiang Institute of Engineering, Urumqi, Xinjiang 830091, China

approaches to quantum chemistry yet, were mainly carried out on the density functional (TD-DFT) [1,2], the Hartree–Fock (TD-HF) level of theory [3,4], or the configuration interaction (TD-CI) method [5]. An important method known as multi-configuration time-dependent Hartree Fock (MCTDHF) has been developed in the past few years [6–15]. It can either be seen as an explicitly time-dependent version of the complete active space self-consistent field method, or a specialization of the well established multi-configuration time-dependent Hartree (MCTDH) method [16–19] for distinguishable nuclei. Just recently, we have demonstrated the use of the MCTDHF method to compute the double ionization of helium atom [20].

The calculations of the so-called mean field operator matrix in MCTDHF frame are quite time-consuming [8,12]. The accurate and efficient calculations of mean field operator matrix are the crucial step to study the electron-electron correlated dynamics of the system interacting with laser field. The calculations of mean field are related to the two-electron spin orbital integrals in DVR or in sine FBR. The evaluation and manipulation of the two-electron integrals is a difficult major in the MCTDHF calculation. So the detailed studies of the methods to calculate the two-electron integrals are necessary and important. The properties of the approximate methods and accurate method are investigated respectively in this paper. The efficiency and accuracy of the two methods are compared.

2 State of the problem

To clear things up, we take helium atom in one dimension (1D) for example. The time dependent Hamiltonian for 1D helium atom irradiated by a laser fields $\varepsilon(t)$ reads,

$$H(x, y, t) = -\frac{1}{2}\frac{d^2}{dx^2} - \frac{1}{2}\frac{d^2}{dy^2} - \frac{2}{\sqrt{x^2 + b^2}} - \frac{2}{\sqrt{y^2 + b^2}}$$
$$+ \frac{1}{\sqrt{(x - y)^2 + b^2}} + (x + y)\varepsilon(t) \tag{1}$$

in where the electron-electron interaction and the electron-nucleus interaction are modeled by the usual 'smoothed Coulomb' potential with shielding parameter b. The sine DVR which was traditionally used in theoretical studies of molecular reactive dynamics has been chosen in the calculation. The sine DVR uses the particle-in-a-box eigenfunctions as a basis. The box boundaries are x_0 and x_{N+1}, and $L = x_{N+1} - x_0$ denotes the length of the box. The basis functions are thus,

$$\left\{\varphi_j(x) = \sqrt{2/L}\sin(j\pi(x - x0)/L), j = 1, 2, ...N\right\} \text{ for } \quad x_0 \leq x \leq x_{N+1} \tag{2}$$

The corresponding grid points basis functions are $\{\chi_i(x), i = 1, 2, ...N\}$, and the corresponding grid point values are $\{x_i, i = 1, 2, \ldots N\}$.

In order to solve the MCTDHF working equations, the two-electron integrals in DVR or in FBR must be calculated. The two-electron integrals in DVR read,

$$TWO_{DVR} = \iint\limits_{x,y} \chi_\alpha^*(x)\chi_\beta(x)\frac{1}{\sqrt{((x-y)^2+b^2)}}\chi_\sigma^*(x)\chi_\delta(x)dxdy \qquad (3)$$

Those integrations will consume much time and memory traditionally [8]. Up to now, a significant approximation can be obtained with the natural potential expansion of coulomb potential r_{12},

$$V_{ee}(x,y) = \sum_{m=1}^{M} U_m(x) * V_m(y) \qquad (4)$$

with changing a two-dimensional integration into $2M$ one dimension integration. In the paper, we have attempted to do an accurate calculation of the integration in the sine FBR explicitly.

$$TWO_{FBR} = \iint\limits_{x,y} \varphi_i^*(x)\varphi_j(x)\frac{1}{\sqrt{((x-y)^2+b^2)}}\varphi_k^*(x)\varphi_l(x)dxdy \qquad (5)$$

which can be accomplished by using the Gaussian quadrature rule. The method can be used for a staff gauge to identify the accuracy of the above approximate method in Eq. 4. The Eq. 5 can also be written as $TWOP_{FBR} = [\varphi_i\varphi_j|\varphi_k\varphi_l]$ in Chemist's notation [21]. The two-fold Gaussian quadratrue formula with weigths ω_i and nodes x_i reads (nd is the number of nodes)

$$\int_{-1}^{1}\int_{-1}^{1} f(x,y)dxdy = \sum_{i=1}^{nd}\sum_{j=1}^{nd} \omega_i\omega_j f(x_i,y_i) \qquad (6)$$

3 Illustrative calculations and discussions

We have firstly studied the influence of the number of expansion terms M in Eq. 4 on the accuracy of the approximate expansion of coulomb potential. The approximate coulomb potential becomes better with the increment of the expansion length. The differences between the accurate coulomb potential and the approximate one are calculated with the following formula,

$$\sqrt{\sum_{i=1}^{N}\sum_{j=1}^{N}(V_{ee}(x_i,y_i) - V_{ee}(x_i,y_i)^2)/N^2} \qquad (7)$$

where x_i, y_i are grid points values, and N is the number of grid points. The calculated results are shown in Fig. 1. When the expressions of $U_m(x)$ and $V_m(y)$ are available, it is easy to calculate the two-electron integrals,
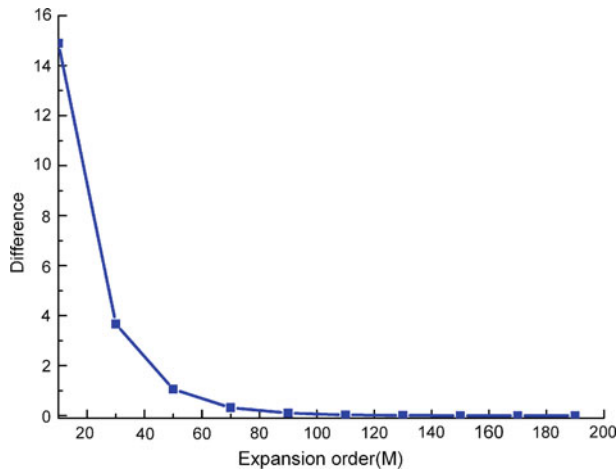
Fig. 1 Differences between the approximate potential and the exact potential as a function of the natural potential expansion size M. The total number of gird size is equal to 200. The gird range is $[-10a.u., 10a.u.]$.

$$TWO_{DVR} = \sum_{m=1}^{M} \int_x \chi_\alpha^*(x) U_m \chi_\beta(x) \int_y \chi_\sigma^*(y) V_m \chi_\delta(y) \tag{8}$$

The Eq. 5 of TWO_{FBR} are calculated by using the Gaussian quadratrue formula. What is the relationship between the two types of two-electron integrals? The relation between the basis of sine FBR and that of DVR is,

$$\varphi_j = \sum_\alpha^N U_{j\alpha} \chi_\alpha \tag{9}$$

in where U is the transform matrix between the two representations,

$$U_{j\alpha} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{j\alpha\pi}{N+1}\right) \tag{10}$$

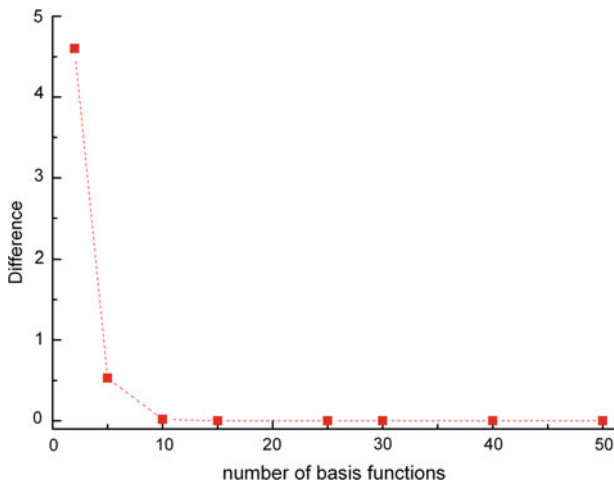So the two-electron integrals in sine FBR can also be written by

$$TWOP_{FBR} = [\varphi_i\varphi_j|\varphi_k\varphi_l] = \sum_{\alpha,\beta,\sigma,\delta} U_{i,\alpha} U_{j,\beta} U_{k,\sigma} U_{l,\delta} [\chi_\alpha \chi_\beta | \chi_\sigma \chi_\delta] \tag{11}$$

In order to compare the accuracy of the two calculation methods, parts of two-electron integrals in sine FBR basis are computed by using Eqs. 5 and 11, respectively. Some calculated results are listed in Table 1. It can be seen from the Table 1, the calculated results obtained in the DVR agree highly with that calculated in the sine FBR.

Table 1 The two-electron integrals calculated exactly in sine FBR and in DVR with the approximation of expansion of natural potential

$[\varphi_i \varphi_j | \varphi_k \varphi_l]$	TWO_{FBR}	$TWOP_{FBR}$
1,1,1,1	0.318643432071903	0.318643463927603
1,1,1,2	−7.408111778374694E−017	2.735586209130859E−016
1,1,2,1	−6.742133387088561E−017	2.737729731883004E−016
1,1,2,2	0.261054382191705	0.261054471929947
1,2,1,1	−2.471690484116814E−016	2.870896413732283E−016
1,2,1,2	0.108889374945507	0.108889430386525
1,2,2,1	0.108889374945507	0.108889430386525
1,2,2,2	−9.343384079075402E−017	4.918705236931349E−016
2,1,1,1	−2.471690484116814E−016	2.870896413732283E−016
2,1,1,2	0.108889374945507	0.108889430386525
2,1,2,1	0.108889374945507	0.108889430386525
2,1,2,2	−9.343384079075402E−017	4.918705236931349E−016
2,2,1,1	0.261054382191708	0.261054471929948
2,2,1,2	−5.276854780825608E−016	3.983361693387499E−016
2,2,2,1	−5.456962616415375E−016	3.985495157623396E−016
2,2,2,2	0.277553022073186	0.277553229882156

The grid range $[−10, 10]$. The number of grid point is equal to 50

Fig. 2 The differences between the two-electron integrals calculated in DVR and the exact ones calculated in sine FBR as a function of the number of the grid basis functions. The grid range is $[−10a.u., 10a.u.]$.

The difference between the two-electron integrals calculated in the two representation is equal to $\sqrt{\sum_{i,j,k,l}^{num} (TWO_{FBR} − TWOP_{FBR})^2}$, in where num is the number of two-electron integrals. To make things more convenient and simple, $num = 5$ are
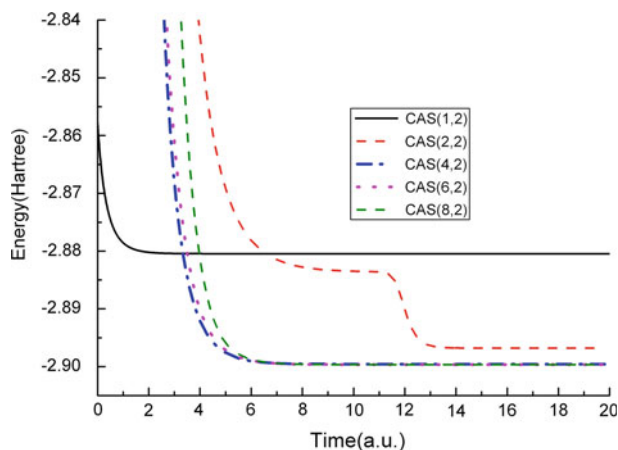
Fig. 3 The influences of the number of the active space on the imaginary time process and the relaxed ground state energy. We have used the traditional complete active space SCF method notation (*Num, Numelectron*) to refer to a system with *Numelectron* electrons and *Num* spatial orbitals.

used in our calculation. We have plotted those as the function of the number of grid points in Fig. 2. It is obvious that the two-electron integrals calculated by using the accurate scheme in sine FBR are quite in agreement with those results obtained by using the approximate method in DVR when the number of basis function are large enough.

By taking advantage of the properties of the grid basis functions in DVR, Eq.8 can be simplified by

$$TWO_{DVR} = \sum_{m=1}^{M} \delta_{\alpha,\beta} U_m(x_\alpha) \delta_{\sigma,\delta} V_m(x_\sigma) \tag{12}$$

It is evident that not all the two-electron integrals are necessarily required in DVR, only parts of the two-electron integrals which are non-zero are necessary. For example, there are number of N grid points and number of M terms in the natural potential expansion. Only $N(N + 1)/2$ non-zero integrals are required when the symmetry is considered. So there are about $2M * N(N + 1)/2(1 \leq M \leq N)$ one-electron integrals when the two-electron integrals are calculated in DVR. As for the calculation of Eq.12 in sine FBR, there are about $(N^4 + 2N^3 + 3N^2 + 2N)/8$ two-fold integrals. Obviously, we can draw a conclusion that the computing time of two-electron integrals in sine FBR is much more expensive than that in DVR when the number of the grid points increases.

To further test the accuracy and the stability of our scheme to calculate the two-electron integrals in sine FBR, we take typical two-electron system, such as helium atom, for example. We have obtained the ground state energy of helium atom through the propagation of MCTDHF equations in imaginary time (PIT) in the absence of an external laser field. We have considered the influence of the numbers of the active space on the atom relaxation energy when the guess wave function propagates in imaginary time. The calculated results are shown in Fig. 3. We have increased the

active space from 1 spatial orbital to 8 spatial orbitals. When the active space increases, the relaxed ground energy becomes lower and lower. The relaxed energy of the PIT with the number of 8 spatial orbital is 2.8999 hartree which is nearly equal to the Full Configuration energy 2.90 hartree of helium atom calculated by Molpro [22].

4 Conclusions

We have proposed an approach for evaluating the two-electron repulsion integrals exactly in sine FBR. This approach has been found to be an efficient and accurate method which can be used for a staff gauge to identify the accuracy of the above approximate method. We have also demonstrated the use of the new method to propagate the MCTDHF working equations in imaginary time. The accurate ground state energy of helium atom is obtained.

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