Study the Inter-Particle Function for Some Electronic System

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Abstract. Our studies deal with the inter-particle distribution function and their electron correlation for C⁺⁴ and O⁺⁶ ions. We consider variational approach based on uncorrelated wave function so-called the Zeta-Roothaan-Hartree-Fock (ZRHF) wave function and simply correlated wave function. We show how the average value, maximum location of the inter-particle, and the radius of coulomb hole change with the atomic number. All results are simulated via Mathematica package (2013).

1. Introduction

The independent particle is a subject that has paved the way for the electronic structure of atoms and molecules studies [1]. For N-electron the wave function had the antisymmetrised product of one-electron functions or orbitals basis set [2]. The distribution of inter-particle function, which describes the probability of finding two electrons separated by a distance, was first described by [3]. In particular, the electron correlation has been a wide range of quantum mechanics studies [4-7]. However, our paper deals with the typical issue of inter-particle function of C⁺⁴ and O⁺⁶ ions. Several correlated wave functions [8-12] were discussed very accurate results for energy eigenvalues and satisfy the cusp conditions fairly accurately, therefore, We consider two different wave functions single Zeta-Hartree-Fock [12] as well as simply correlated wave function [4,7,13]. Our results are obtained numerically via Mathematica package [14].

2. Computational details

For N-electron system the inter-particle function \( \Upsilon(r_{12}) \) has a form as follows

\[
\Upsilon(r_{12}) = \int \Pi(r_{1}, r_{2} | \hat{r}_{1}, \hat{r}_{2}) \frac{dr_{1}}{dr_{1}} \frac{dr_{2}}{dr_{2}}, \ldots, (1)
\]

With

\[
\Pi(r_{1}, r_{2} | \hat{r}_{1}, \hat{r}_{2}) = \left( \frac{N}{2} \right) \int \psi(x_{1}, x_{2}, x_{3}, \ldots, x_{N}) \psi^{*}(\hat{x}_{1}, \hat{x}_{2}, \hat{x}_{3}, \ldots, \hat{x}_{N}) dr_{12} dr_{12} dx_{1}, \ldots, (2)
\]

is the second density matrix of free spin from the corresponding normalized wave function [15]. Equation (2) corresponds the integration over spatial space and spin coordinates, respectively.
Furthermore, Eq. (1) discussed the probability of finding the separation distance for two electrons between \( r_{12} \) and \( r_{12} + dr_{12} \). In order to study the inter-particle function, we consider distinct wave functions.

A. The Hartree-Fock (HF) wave function is the best reasonable uncorrelated function. We have therefore consider the analytical expression obtained via Roothaan-Hartree-Fock based on a single \( \Psi \)-type orbitals which has form of linear combination of STOs [7,12], yielding

\[
\psi(r) = \sum_{i=1}^{N} C_{i} e^{-\alpha} \prod_{l=1}^{q-1} \left( \frac{I(q+l)}{I(q+l)!} \right)^{(q-1)} \left( \alpha \right)^{q-1} \tag{3}
\]

Here we consider Ref. [12] for all variational parameters \( C_{i} \), \( \alpha \), and \( q \) of Eq. (3).

B. Correlated wave function is defined as

\[
\psi(r_{1}, r_{2}, r_{3}) = \frac{N Z^{3}}{\pi} \left[ e^{-Zl} r_{1} s r_{2} \cosh(\alpha r_{1}) \cosh(\alpha r_{2}) \right] \times \left( 1 - e^{-A_{d} r_{1}} \right) \tag{4}
\]

this approximation was obtained in Ref. [16]. The factors \( \cosh(\alpha r_{1}) \) are point out the electron shielding 2 (1) on 1 (2) [4,7], while the second factor corresponds to the correlation function, that it depends only on \( r_{1} \). The mean value of \( r_{1}^{n} \) is given by

\[
\langle r_{1}^{n} \rangle = \int_{0}^{\infty} r_{1}^{n} \Psi(r_{1}) dr_{1} \tag{5}
\]

One of interesting features for various atomic system is electron correlation which can be described in terms of the Coulomb hole is corresponded to the region of surrounding each electron in atom in which the probability of finding another electron is small [15], i.e., the difference between the correlated and the Hartree-Fock interelectronic densities [17]. However Coulomb hole is written as

\[
\Delta \Pi(r_{1}) = \Pi(r_{1})_{C} - \Pi(r_{1})_{H} \tag{6}
\]

3. Results and Discussion

Our results have been obtained via Mathematica Package [14]. In particular, we consider the date of Ref. [12] for single Zeta-Roothaan-Hartree-Fock based on Beta-type orbital, while Ref. [6] for correlated wave function.

| Ions | Wave functions | \( \langle r_{1}^{n} \rangle \) | \( \alpha \) | \( \mu \) |
|------|----------------|------------------|-----|-----|
|      |                | \( n = -2 \) | \( n = -1 \) | \( n = 0 \) | \( n = 1 \) | \( n = 2 \) |
|      | ZRHF           | 21.379           | 3.527 | 1.000 | 0.39 | 0.191 |
| C+4  | Correlated     | 20.252           | 3.393 | 1.000 | 0.416 | 0.223 |
|      | Ref. [8]       | 3.444            |       | 0.395 |
|      | Ref. [18,19]   | 3.4700           |       | 0.3898 | 0.1892 |
| O+6  | ZRHF           | 39.149           | 4.778 | 1.000 | 0.287 | 0.104 |

Table 1: The inter-particle expectation value in unit of (a.u) for C+4and O+6 ions for single Zeta-Roothaan-Hartree-Fock and correlated wave functions.
Tab. 1 Shows the expectation value of the inter-particle function in unit of (a.u.) versus the exponent of C\textsuperscript{+4} and O\textsuperscript{+6} ions for single Zeta-Roothaan-Hartree-Fock and correlated wave functions, respectively. According to the electron correlation of Eq. (4), we see that force between two-electron, \( n = 2 \) larger than the force of Eq. (3) and correlated wave function Eq. (4) has the largest mean separation distance \( \langle r_1 \rangle \). The repulsion energy \( n = -1 \) increases by increasing the atomic number. The expectation value for \( n = 0 \) equal to unity due to the normalization condition. Indeed, the values of \( \langle r_1 \rangle \) and \( \langle r_1^{-1} \rangle \) refer to the accuracy correlation level of the wave functions and closely approaching the values mentioned by Refs. [8,18,19].

|       | Correlated | Ref. [8] | Ref. [18,19] |
|-------|------------|----------|--------------|
|       | 37.612     | 4.692    | 4.7187       |
|       | 4.644      | --       | --           |
|       | 1.000      | 0.290    | 0.2874       |
|       | 0.301      | --       | 0.1030       |
|       | 0.116      | --       | --           |

In Fig. 1 shows the probability of the inter-particle function \( f(r_1) \) versus the separation distance \( r_1 \) for C\textsuperscript{+4} and O\textsuperscript{+6} ions, respectively. We read off the maximum value of inter-particle function for correlated wave function Eq. (4) is smaller than the uncorrelated wave function Eq. (3) according to the correlation motion of electrons that reduced the repulsion force. This turns out that these particles are closer than nucleus. The inter-particle function increase as increase the atomic number as well as close to the nucleus due to the attraction force between the electrons and nucleus. In Fig. 2, We estimate the Coulomb correlation for C\textsuperscript{+4} and O\textsuperscript{+6} ions, that expressed from the ZRHF wave function Eq. (3) and correlated wave function Eq. (4). The total charge amount in Fig. 2a which moved by Eq. (6) is equal to the area under the curve between \( r_1 = 0 \) and \( r_1 = 0.53 \) a\(_t\) for C\textsuperscript{+4} ion as well as \( r_1 = 0 \) and \( r_1 = 0.39 \) a\(_t\) for O\textsuperscript{+6} ion. Evidently, the hole describes the decreasing in the probability of finding the electrons close together with a concomitant increase of the probability of their being further apart. Furthermore, as the atomic number increases, the electrons are drowning closer to the nucleus and the inter-particle function and Coulomb holes’ contract toward the origin.
Figure 2: Coulomb hole (a) $\Delta (r_{12})$ versus the separation distance $r_{12}$ and (b) $\Delta (\hat{r}_{12})$ versus $\hat{r}_{12}$, respectively, for $C^{+4}$ and $O^{+6}$ ions. The solid gray curves correspond to $C^{+4}$ ion, while black curves represent to $O^{+6}$ ion.

4. Conclusions

We have studied and discussed the inter-particle function for $C^{+4}$ and $O^{+6}$ ions. Different wave function has been considered Roothaan-Hartree-Fock based on single beta-type orbitals as well as correlated wave function. We have estimated the mean value of the separation distance between two-electron $\langle \hat{r}_{12}^N \rangle$ and Coulomb hole. Via increasing the atomic number, the inter-particle increase and close to the nucleus. In particular, the electron correlation reduces the probability of the two electrons which is located at large separations distance.

5. Reference

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