

# Calculation of Matrix Elements in the Hylleraas-CI Method for Positronium-atom Complexes

Shiro L. Saito\*

*School of International Liberal Studies, Chukyo University, Nagoya 466-8666, Japan*

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**Abstract:** Matrix elements used in the Hylleraas-CI method for positronium-atom complexes are derived. Our Hylleraas-CI wave function is a linear combination of determinants, each of which contains at most one power of the positron-electron distance. Electron-electron correlation effects are introduced into the wave function via electron excitations alone. In this work, correlation factors appearing in Hylleraas-CI determinants are expanded in complete sets to simplify the derivation of the matrix elements. As a result, each Hylleraas-CI determinant is transformed to a linear combination of determinants consisting only of orthonormal orbitals. By this means, the matrix elements can be obtained simply. An approximate method which can readily give the many-electron integrals in the matrix elements is also discussed.

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## 1 Introduction

The positron is the antiparticle of the electron and forms a bound state with one electron. This bound state is called positronium (Ps). Positronium can form complexes with several atoms, known as positronium-atom complexes. Positronium-atom complexes have been studied both experimentally [1–3] and theoretically [4–10], and their stability and the details of positron-electron pair annihilation have been determined. In particular, many theoretical studies have been made of the positronium-atom complexes.

Positronium hydride (PsH) is the simplest stable positronium-atom complex, and has been extensively studied by various quantum mechanical calculations [11–29]. Those studies reveal that explicitly correlated function methods, such as the Hylleraas-type method and explicitly correlated Gaussian function method, give very accurate results. It is very

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\* Email: luna@trinity.lets.chukyo-u.ac.jp

important to introduce the positron-electron distance explicitly into the wave function. The use of explicitly correlated functions is advantageous in the study of positronium-atom complexes. It is not practical to apply explicitly correlated functions to many-electron positronium-atom complexes, however, because many-electron integrals appear. Calculation of many-electron integrals becomes difficult as the number of electrons increases. As a result, there have been no calculations with explicitly correlated functions for many-electron positronium-atom complexes, except for complexes with one or two valence electrons.

Our purpose is to establish an applicable computational method using explicitly correlated functions for many-electron positronium-atom complexes. Hylleraas-CI is one possibility. This is a computational method for wave functions combining configuration interaction (CI) and Hylleraas-type functions, and was first applied by Sims and Hagstrom to the Be atom [30]. Their Hylleraas-CI wave function is a CI expansion with each configuration function which contains at most one power of the inter-electronic distance. Hylleraas-CI calculations for any many-electron atomic system require up to four-electron integrals. This is an advantage of the Hylleraas-CI method which was introduced by Sims and Hagstrom. Hylleraas-CI calculations for positronium-atom complexes have been carried out by Clary [24] alone: PsH, PsHe<sup>+</sup>, PsHe, and PsLi<sup>+</sup> have been calculated.

We consider the Hylleraas-CI wave function that comprises a linear combination of determinants, each containing at most one power of the positron-electron distance, because positron-electron distances are important for positronium-atom complex wave functions. Electron-electron correlation effects are introduced into the wave function only by electron excitations. In this work we derive the matrix elements between our Hylleraas-CI determinants. Since this derivation is very complicated and laborious, we adopt a procedure in which the correlation factors are expanded in complete sets [31]. This procedure transforms a Hylleraas-CI determinant to a linear combination of determinants consisting wholly of orthonormal orbitals. By this means we derive matrix elements between determinants without correlation factors.

Below, Section 2 sets out the theoretical aspect. Section 3 summarizes the resulting matrix elements relating to Hylleraas-CI wave functions for many-electron positronium-atom complexes. Section 4 discusses approximation for evaluating many-electron integrals that appear in the matrix elements.

## 2 Theoretical Aspects

In this section we define our Hylleraas-CI wave function, and transform a Hylleraas-CI determinant to a linear combination of determinants which consist only of orthonormal orbitals using complete sets. The formula including cofactors of the Hamiltonian matrix element is finally obtained.

The Hamiltonian of  $N$ -electron positronium-atom complexes in atomic units is given

by

$$\mathcal{H} = \sum_{i=1}^N h(i) + \sum_{i<j}^N r_{ij}^{-1} + h_+(0) - \sum_{i=1}^N r_{0i}^{-1}, \quad (1)$$

where

$$h(i) = -\frac{1}{2}\nabla_i^2 - Zr_i^{-1}, \quad (2)$$

$$h_+(0) = -\frac{1}{2}\nabla_0^2 + Zr_0^{-1}. \quad (3)$$

The positron is signified by 0, and the electrons by  $1, \dots, N$ . Here  $Z$  denotes the nuclear charge,  $r_0$  and  $r_i$  are distances from the nuclei to the positron and the  $i$ -th electron respectively, and  $r_{0i}$  and  $r_{ij}$  denote distances between the positron and the  $i$ -th electron, and between the  $i$ -th and  $j$ -th electrons.

We now consider the Hylleraas-CI wave function for  $N$ -electron positronium-atom complexes:

$$\Psi = \sum_{\alpha,p} \left( C_{\alpha p} + \sum_{\mu=1}^{N+1} T_{\mu} \right) \Psi_p^{\alpha}, \quad (4)$$

where  $T_{\mu}$  is a linear combination of all  $\mu$ -body excitation operators. Here,  $\Psi_p^{\alpha}$  is a determinant, as follows:

$$\Psi_p^{\alpha} = \mathcal{A} \psi_p^{\alpha}(\mathbf{x}_{0p}) \prod_{a(\neq p)}^N \chi_a(\mathbf{x}_a) \quad (5)$$

with

$$\psi_p^{\alpha}(\mathbf{x}_{0p}) = r_{0p}^{\alpha} \xi(\mathbf{x}_0) \chi_p(\mathbf{x}_p), \quad (6)$$

where  $\mathcal{A}$  is the antisymmetrization operator for  $N$  electrons,  $\mathbf{x}$  is a space-spin coordinate, and  $\mathbf{x}_{0p}$  stands for the set  $(r_{0p}, \mathbf{x}_0, \mathbf{x}_p)$ . In Eqs.(5) and (6),  $\{\chi_a\}$  are mutually orthogonal occupied electronic spin-orbitals and  $\xi$  is an occupied positronic spin-orbital. These functions span subspaces of the corresponding complete sets  $\{\chi_i\}$  and  $\{\xi_i\}$ . Occupied electronic orbitals are denoted by indexes  $a, b, c, \dots$ , and indexes of orbitals in both complete sets by  $i, j, k, \dots$ .

The aim of this work is to derive the Hamiltonian matrix element using a complete set expansion of  $\psi_p^{\alpha}$ , i.e.

$$\begin{aligned} \psi_p^{\alpha} &= \sum_{i,j} \xi_i(\mathbf{x}_0) \chi_j(\mathbf{x}_p) \int d\mathbf{x}_0 d\mathbf{x}_p \xi_i^*(\mathbf{x}_0) \chi_j^*(\mathbf{x}_p) \psi_p^{\alpha}(\mathbf{x}_{0p}) \\ &= \sum_{i,j} \langle \xi_i \chi_j | \psi_p^{\alpha} \rangle \xi_i(\mathbf{x}_0) \chi_j(\mathbf{x}_p). \end{aligned} \quad (7)$$

Eq.(7) is written using a simple integral notation. We denote integrals for an arbitrary

operator  $\mathcal{O}$  as

$$\langle \psi_p^\alpha \chi_a \cdots \chi_b | \mathcal{O} | \chi_c \psi_q^\beta \cdots \chi_d \rangle \quad (8)$$

$$\equiv \int d\mathbf{x}_0 d\mathbf{x}_1 \cdots d\mathbf{x}_N \psi_p^{\alpha*}(\mathbf{x}_{01}) \chi_a^*(\mathbf{x}_2) \cdots \chi_b^*(\mathbf{x}_N) \mathcal{O} \chi_c(\mathbf{x}_1) \psi_q^\beta(\mathbf{x}_{02}) \cdots \chi_d(\mathbf{x}_N). \quad (9)$$

We may write integrals omitting positronic and electronic coordinates; functions in the bra and the ket are arranged in order of the electron coordinate number. The integral (8) for  $\mathcal{O} = 1$  is written as

$$\langle \psi_p^\alpha \chi_a \cdots \chi_b | \chi_c \psi_q^\beta \cdots \chi_d \rangle. \quad (10)$$

By using Eq.(7), the Hylleraas-CI determinant (5) can be rewritten as

$$\Psi_p^\alpha = \sum_{i,j} \langle \xi_i \chi_j | \psi_p^\alpha \rangle \xi_i(\mathbf{x}_0) \Phi_{pj} \quad (11)$$

with

$$\Phi_{pj} = \mathcal{A} \chi_j(\mathbf{x}_p) \prod_{a(\neq p)} \chi_a(\mathbf{x}_a). \quad (12)$$

Next,  $\Psi_p^\alpha$  can be written as an electronic determinant  $\Phi_{pj}$  multiplied by a positronic orbital. Thus, our Hylleraas-CI wave function is expanded in terms of determinants consisting of orthonormal orbitals only.

The matrix elements between our Hylleraas-CI determinants can be derived using Löwdin's formula for non-orthogonal matrix elements [32–34]. Let us derive the matrix elements between  $\Psi_p^\alpha$  and  $\Psi_q^\beta$ , where

$$\Psi_q^\beta = \sum_{k,l} \langle \xi_k \chi_l | \psi_q^\beta \rangle \xi_k(\mathbf{x}_0) \Phi_{ql}. \quad (13)$$

The Hamiltonian matrix element is written as

$$\begin{aligned} & \langle \Psi_p^\alpha | \mathcal{H} | \Psi_q^\beta \rangle \\ &= \sum_{i,j,k,l} \langle \psi_p^\alpha | \xi_i \chi_j \rangle \langle \xi_k \chi_l | \psi_q^\beta \rangle \left[ \langle \xi_i | h_+ | \xi_k \rangle S_{pq} - \sum_{a,b} \langle \xi_i \chi_a | r_{01}^{-1} | \xi_k \chi_b \rangle S_{pq}^{(a,b)} \right. \\ & \left. + \sum_{a,b} \langle \chi_a | h | \chi_b \rangle \delta_{i,k} S_{pq}^{(a,b)} + \sum_{a<b,c<d} \langle \chi_a \chi_c | r_{12}^{-1} (1 - P_{12}) | \chi_b \chi_d \rangle \delta_{i,k} S_{pq}^{(a,b,c,d)} \right], \quad (14) \end{aligned}$$

where  $P_{12}$  is the permutation of electron 1 and 2.  $S_{pq}$  is the overlap integral of  $\Phi_{pj}^*$  and

$\Phi_{ql}$ :

$$S_{pq} = \begin{cases} \delta_{j,l} - \sum_{a(\neq p)} \delta_{j,a} \delta_{a,l} & (p = q) \\ \delta_{j,p} \delta_{q,l} & (p \neq q) \end{cases}, \quad (15)$$

where  $\delta$  is Kronecker's delta.  $S_{pq}^{(a,b)}$  and  $S_{pq}^{(a,b,c,d)}$  respectively denote the first- and second-order cofactors of  $S_{pq}$ . When  $S_{pq}^{-1}$  is non-zero,  $S_{pq}^{(a,b,c,d)}$  can be evaluated using Jacobi's theorem [35]:

$$S_{pq}^{(a,b,c,d)} = S_{pq}^{-1} (S_{pq}^{(a,c)} S_{pq}^{(b,d)} - S_{pq}^{(a,d)} S_{pq}^{(b,c)}). \quad (16)$$

Non-zero values of  $S_{pq}^{(a,b)}$  and  $S_{pq}^{(a,b,c,d)}$  in Eq.(14) are summarized in Tables 1 and 2, respectively.

To perform Hylleraas-CI calculations, the matrix elements over electronic singly, doubly, and triply excited determinants are required. The corresponding determinants are denoted as  $\Psi_q^\beta(r)$ ,  $\Psi_q^\beta(rs)$ , and  $\Psi_q^\beta(rst)$ . Here,  $\Psi_q^\beta(rst\dots)$  is any electron excited determinant in which electrons have been excited from  $\chi_a, \chi_b, \chi_c, \dots$  to  $\chi_r, \chi_s, \chi_t, \dots$ . Those excited determinants are written as

$$\Psi_q^\beta(r) = \sum_{k,l} \langle \xi_k \chi_l | \psi_q^\beta \rangle \xi_k(\mathbf{x}_0) \Phi_{ql}(r), \quad (17)$$

$$\Psi_q^\beta(rs) = \sum_{k,l} \langle \xi_k \chi_l | \psi_q^\beta \rangle \xi_k(\mathbf{x}_0) \Phi_{ql}(rs), \quad (18)$$

and

$$\Psi_q^\beta(rst) = \sum_{k,l} \langle \xi_k \chi_l | \psi_q^\beta \rangle \xi_k(\mathbf{x}_0) \Phi_{ql}(rst). \quad (19)$$

The electronic singly, doubly, and triply excited determinants  $\Phi_q(r)$ ,  $\Phi_q(rs)$ , and  $\Phi_q(rst)$ , are written as

$$\Phi_{ql}(r) = \mathcal{A} \chi_l(\mathbf{x}_q) \chi_r(\mathbf{x}_a) \prod_{b(\neq q,a)} \chi_b(\mathbf{x}_b), \quad (20)$$

$$\Phi_{ql}(rs) = \mathcal{A} \chi_l(\mathbf{x}_q) \chi_r(\mathbf{x}_a) \chi_s(\mathbf{x}_b) \prod_{c(\neq q,a,b)} \chi_c(\mathbf{x}_c), \quad (21)$$

and

$$\Phi_{ql}(rst) = \mathcal{A} \chi_l(\mathbf{x}_q) \chi_r(\mathbf{x}_a) \chi_s(\mathbf{x}_b) \chi_t(\mathbf{x}_c) \prod_{d(\neq q,a,b,c)} \chi_d(\mathbf{x}_d). \quad (22)$$

The terms  $\langle \Psi_p^\alpha | \mathcal{H} | \Psi_q^\beta(r) \rangle$ ,  $\langle \Psi_p^\alpha | \mathcal{H} | \Psi_q^\beta(rs) \rangle$ , and  $\langle \Psi_p^\alpha | \mathcal{H} | \Psi_q^\beta(rst) \rangle$  also require second-order cofactors, but these cannot be evaluated by Jacobi's theorem because their  $S_{pq}$  vanish. These second-order cofactors have to be evaluated step by step. Summaries of these cofactor values are omitted in this paper.

### 3 Results

This section exhibits the resulting overlap and the Hamiltonian matrix elements. All matrix elements between  $\Psi_p^{\alpha*}$  and  $\Psi_q^\beta$  have different forms for the cases  $p = q$  and  $p \neq q$ . Most matrix elements include summations over occupied orbitals. We denote summation over all values of  $a$  except  $p$  by  $\sum'_a$  and summation over all values of  $a$  except  $p$  and  $q$  by  $\sum''_a$ . If additional conditions are required for summations, then we write these explicitly, e.g.  $\sum'_{b(\neq a)}$  for a summation over all values of  $b$  except  $a$ .

The overlap matrix element between  $\Psi_p^{\alpha*}$  and  $\Psi_p^\beta$  is

$$\begin{aligned}
 \langle \Psi_p^\alpha | \Psi_p^\beta \rangle &= \sum_{i,j,k,l} \langle \psi_p^\alpha | \xi_i \chi_j \rangle \langle \xi_k \chi_l | \psi_p^\beta \rangle \delta_{i,k} \langle \Phi_{pj} | \Phi_{pl} \rangle \\
 &= \sum_{i,j} \langle \psi_p^\alpha | \xi_i \chi_j \rangle \langle \xi_i \chi_j | \psi_p^\beta \rangle - \sum_i \sum'_a \langle \psi_p^\alpha | \xi_i \chi_a \rangle \langle \xi_i \chi_a | \psi_p^\beta \rangle \\
 &= \langle \psi_p^\alpha | \psi_p^\beta \rangle - \sum'_a \langle \psi_p^\alpha \chi_a | \chi_a \psi_p^\beta \rangle,
 \end{aligned} \tag{23}$$

Eq.(23) is obtained by applying Eq.(15) and the completeness condition

$$\sum_i^\infty |\xi_i\rangle \langle \xi_i| = \sum_j^\infty |\chi_j\rangle \langle \chi_j| = 1. \tag{24}$$

Similarly, the overlap matrix element between  $\Psi_p^{\alpha*}$  and  $\Psi_q^\beta$  ( $p \neq q$ ) is obtained as follows:

$$\langle \Psi_p^\alpha | \Psi_q^\beta \rangle = \langle \psi_p^\alpha \chi_q | \chi_p \psi_q^\beta \rangle. \tag{25}$$

The Hamiltonian matrix element  $\langle \Psi_p^\alpha | \mathcal{H} | \Psi_q^\beta \rangle$  can be obtained by using  $S_{pq}^{(a,b)}$  and  $S_{pq}^{(a,b,c,d)}$  as summarized in Tables 1 and 2 and Eq.(24). The resulting matrix elements for each operator are shown below.

We first display the matrix elements of one-body operators. The matrix elements of a one-positron operator  $h_+(0)$  are

$$\langle \Psi_p^\alpha | h_+(0) | \Psi_p^\beta \rangle = \langle \psi_p^\alpha | h_+ | \psi_p^\beta \rangle - \sum'_a \langle \psi_p^\alpha \chi_a | h_+ | \chi_a \psi_p^\beta \rangle \tag{26}$$

and

$$\langle \Psi_p^\alpha | h_+(0) | \Psi_q^\beta \rangle = \langle \psi_p^\alpha \chi_q | h_+ | \chi_p \psi_q^\beta \rangle, \quad (p \neq q). \tag{27}$$

The matrix elements of a one-electron operator  $\sum_i h(i)$  are

$$\begin{aligned} & \left\langle \Psi_p^\alpha \left| \sum_i h(i) \right| \Psi_p^\beta \right\rangle \\ &= \sum_a' \langle \chi_a | h | \chi_a \rangle \left[ \langle \psi_p^\alpha | \psi_p^\beta \rangle - \sum_b' \langle \psi_p^\alpha \chi_b | \chi_b \psi_p^\beta \rangle \right] + \sum_{a,b}' \langle \chi_a | h | \chi_b \rangle \langle \psi_p^\alpha \chi_b | \chi_a \psi_p^\beta \rangle \\ & \quad + \langle \psi_p^\alpha | h | \psi_p^\beta \rangle - \sum_a' \langle \psi_p^\alpha \chi_a | h(1) + h(2) | \chi_a \psi_p^\beta \rangle \end{aligned} \quad (28)$$

and

$$\begin{aligned} & \left\langle \Psi_p^\alpha \left| \sum_{i=1} h(i) \right| \Psi_q^\beta \right\rangle \\ &= -\langle \chi_q | h | \chi_p \rangle \left[ \langle \psi_p^\alpha | \psi_q^\beta \rangle - \sum_a'' \langle \psi_p^\alpha \chi_a | \chi_a \psi_q^\beta \rangle \right] \\ & \quad + \sum_a'' \left[ \langle \chi_a | h | \chi_a \rangle \langle \psi_p^\alpha \chi_q | \chi_p \psi_q^\beta \rangle \langle \chi_a | h | \chi_p \rangle \langle \psi_p^\alpha \chi_q | \chi_a \psi_q^\beta \rangle \right. \\ & \quad \left. - \langle \chi_q | h | \chi_a \rangle \langle \psi_p^\alpha \chi_a | \chi_p \psi_q^\beta \rangle \right] + \langle \psi_p^\alpha \chi_q | h(1) + h(2) | \chi_p \psi_q^\beta \rangle, \quad (p \neq q). \end{aligned} \quad (29)$$

The matrix elements of an operator  $\sum_i r_{0i}^{-1}$  are given next. This operator is a positron-electron interaction with sign reversed. The resulting matrix elements are

$$\begin{aligned} & \left\langle \Psi_p^\alpha \left| \sum_{i=1} r_{0i}^{-1} \right| \Psi_p^\beta \right\rangle \\ &= \langle \psi_p^\alpha | r_{01}^{-1} | \psi_p^\beta \rangle + \sum_a' \langle \psi_p^\alpha \chi_a | r_{02}^{-1} | \psi_p^\beta \chi_a \rangle \\ & \quad - \sum_a' \langle \psi_p^\alpha \chi_a | r_{01}^{-1} + r_{02}^{-1} | \chi_a \psi_p^\beta \rangle + \sum_{a,b}' \langle \psi_p^\alpha \chi_a \chi_b | R_{02} | \chi_a \chi_b \psi_p^\beta \rangle \end{aligned} \quad (30)$$

and

$$\begin{aligned} & \left\langle \Psi_p^\alpha \left| \sum_{i=1} r_{0i}^{-1} \right| \Psi_q^\beta \right\rangle \\ &= -\langle \psi_p^\alpha \chi_q | r_{02}^{-1} | \psi_q^\beta \chi_p \rangle + \langle \psi_p^\alpha \chi_q | r_{01}^{-1} + r_{02}^{-1} | \chi_p \psi_q^\beta \rangle \\ & \quad + \sum_a'' \left[ \langle \psi_p^\alpha \chi_q \chi_a | R_{02} | \chi_a \chi_p \psi_q^\beta \rangle \langle \psi_p^\alpha \chi_a \chi_q | R_{02} | \chi_p \chi_a \psi_q^\beta \rangle \right], \quad (p \neq q), \end{aligned} \quad (31)$$

where  $R_{ij} = r_{ij}^{-1}(1 - P_{12})$ .

The electron-electron interaction matrix element is complicated as a result of electron

exchange. The electron-electron interaction matrix elements are

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i < j} r_{ij}^{-1} \right| \Psi_p^\beta \right\rangle \\
&= \frac{1}{2} \sum'_{a,b} \langle \chi_a \chi_b | R_{12} | \chi_a \chi_b \rangle \left[ \langle \psi_p^\alpha | \psi_p^\beta \rangle - \sum_c \langle \psi_p^\alpha \chi_c | \chi_c \psi_p^\beta \rangle \right] \\
&+ \sum'_{a,b,c} \langle \chi_a \chi_b | R_{12} | \chi_c \chi_b \rangle \langle \psi_p^\alpha \chi_c | \chi_a \psi_p^\beta \rangle + \sum'_a \langle \psi_p^\alpha \chi_a | R_{12} | \psi_p^\beta \chi_a \rangle \\
&+ \sum'_{a,b} \langle \psi_p^\alpha \chi_a \chi_b | R_{12} + R_{23} | \chi_a \chi_b \psi_p^\beta \rangle
\end{aligned} \tag{32}$$

and

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i < j} r_{ij}^{-1} \right| \Psi_q^\beta \right\rangle \\
&= - \sum''_a \langle \chi_a \chi_q | R_{12} | \chi_a \chi_p \rangle \left[ \langle \psi_p^\alpha | \psi_q^\beta \rangle - \sum_b \langle \psi_p^\alpha \chi_b | \chi_b \psi_q^\beta \rangle \right] \\
&+ \sum''_{a,b} \left[ \langle \chi_a \chi_b | R_{12} | \chi_p \chi_a \rangle \langle \psi_p^\alpha \chi_q | \chi_b \psi_q^\beta \rangle + \langle \chi_q \chi_a | R_{12} | \chi_a \chi_b \rangle \langle \psi_p^\alpha \chi_b | \chi_p \psi_q^\beta \rangle \right. \\
&+ \langle \chi_q \chi_a | R_{12} | \chi_b \chi_p \rangle \langle \psi_p^\alpha \chi_b | \chi_a \psi_q^\beta \rangle + \left. \frac{1}{2} \langle \chi_a \chi_b | R_{12} | \chi_a \chi_b \rangle \langle \psi_p^\alpha \chi_q | \chi_p \psi_q^\beta \rangle \right] \\
&- \langle \psi_p^\alpha \chi_q | R_{12} | \psi_q^\beta \chi_p \rangle + \sum''_a \left[ \langle \psi_p^\alpha \chi_q \chi_a | R_{12} + R_{23} | \chi_a \chi_p \psi_q^\beta \rangle \right. \\
&+ \left. \langle \psi_p^\alpha \chi_a \chi_q | R_{12} + R_{23} | \chi_p \chi_a \psi_q^\beta \rangle \right], \quad (p \neq q).
\end{aligned} \tag{33}$$

We now give the overlap and Hamiltonian matrix elements between  $\Psi_p^{\alpha*}$  and single, double, and triple electron excited determinants of  $\Psi_q^\beta$ ,  $\Psi_q^\beta(r)$ ,  $\Psi_q^\beta(rs)$ , and  $\Psi_q^\beta(rst)$ . These matrix elements have non-vanishing terms.

The non-vanishing matrix elements between  $\Psi_p^{\alpha*}$  and  $\Psi_q^\beta(r)$  are as follows:

$$\langle \Psi_p^\alpha | \Psi_p^\beta(r) \rangle = - \langle \psi_p^\alpha \chi_a | \chi_r \psi_p^\beta \rangle, \tag{34}$$

$$\langle \Psi_p^\alpha | h_+(0) | \Psi_p^\beta(r) \rangle = - \langle \psi_p^\alpha \chi_a | h_+ | \chi_r \psi_p^\beta \rangle, \tag{35}$$



$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i=1} h(i) \right| \Psi_p^\beta(r_a) \right\rangle \\
&= \langle \chi_a | h | \chi_r \rangle \left[ \langle \psi_p^\alpha | \psi_p^\beta \rangle - \sum_b' \langle \psi_p^\alpha \chi_b | \chi_b \psi_p^\beta \rangle \right] \\
&+ \sum_b' \left[ \langle \chi_a | h | \chi_b \rangle \langle \psi_p^\alpha \chi_b | \chi_r \psi_p^\beta \rangle + \langle \chi_b | h | \chi_r \rangle \langle \psi_p^\alpha \chi_a | \chi_b \psi_p^\beta \rangle \right. \\
&\left. - \langle \chi_b | h | \chi_b \rangle \langle \psi_p^\alpha \chi_a | \chi_r \psi_p^\beta \rangle \right] - \langle \psi_p^\alpha \chi_a | h(1) + h(2) | \chi_r \psi_p^\beta \rangle, \quad (36)
\end{aligned}$$

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i=1} h(i) \right| \Psi_q^\beta(r_a) \right\rangle \\
&= \langle \chi_a | h | \chi_r \rangle \langle \psi_p^\alpha \chi_q | \chi_p \psi_q^\beta \rangle - \langle \chi_a | h | \chi_p \rangle \langle \psi_p^\alpha \chi_q | \chi_r \psi_q^\beta \rangle \\
&- \langle \chi_q | h | \chi_r \rangle \langle \psi_p^\alpha \chi_a | \chi_p \psi_q^\beta \rangle + \langle \chi_q | h | \chi_p \rangle \langle \psi_p^\alpha \chi_a | \chi_r \psi_q^\beta \rangle, \quad (p \neq q), \quad (37)
\end{aligned}$$

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i=1} r_{0i}^{-1} \right| \Psi_p^\beta(r_a) \right\rangle \\
&= \langle \psi_p^\alpha \chi_a | r_{02}^{-1} | \psi_p^\beta \chi_r \rangle - \langle \psi_p^\alpha \chi_a | r_{01}^{-1} + r_{02}^{-1} | \chi_r \psi_p^\beta \rangle \\
&+ \sum_b' \left[ \langle \psi_p^\alpha \chi_a \chi_b | R_{02} | \chi_r \chi_b \psi_p^\beta \rangle + \langle \psi_p^\alpha \chi_b \chi_a | R_{02} | \chi_b \chi_r \psi_p^\beta \rangle \right], \quad (38)
\end{aligned}$$

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i=1} r_{0i}^{-1} \right| \Psi_q^\beta(r_a) \right\rangle \\
&= \langle \psi_p^\alpha \chi_a \chi_q | R_{02} | \chi_p \chi_r \psi_q^\beta \rangle + \langle \psi_p^\alpha \chi_q \chi_a | R_{02} | \chi_r \chi_p \psi_q^\beta \rangle, \quad (p \neq q), \quad (39)
\end{aligned}$$

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i < j} r_{ij}^{-1} \right| \Psi_p^\beta(r_a) \right\rangle \\
&= \sum'_{b(\neq a)} \langle \chi_a \chi_b | R_{12} | \chi_r \chi_b \rangle \left[ \langle \psi_p^\alpha | \psi_p^\beta \rangle - \sum'_{c(\neq a)} \langle \psi_p^\alpha \chi_c | \chi_c \psi_p^\beta \rangle \right] \\
&+ \sum'_{b,c(\neq a)} \left[ \langle \chi_a \chi_b | R_{12} | \chi_r \chi_c \rangle \langle \psi_p^\alpha \chi_c | \chi_b \psi_p^\beta \rangle \right. \\
&+ \langle \chi_a \chi_b | R_{12} | \chi_c \chi_b \rangle \langle \psi_p^\alpha \chi_c | \chi_r \psi_p^\beta \rangle + \langle \chi_b \chi_c | R_{12} | \chi_b \chi_r \rangle \langle \psi_p^\alpha \chi_a | \chi_c \psi_p^\beta \rangle \\
&\left. - \frac{1}{2} \langle \chi_b \chi_c | R_{12} | \chi_b \chi_c \rangle \langle \psi_p^\alpha \chi_a | \chi_r \psi_p^\beta \rangle \right] + \langle \psi_p^\alpha \chi_a | R_{12} | \psi_p^\beta \chi_r \rangle \\
&+ \sum'_{b(\neq a)} \left[ \langle \psi_p^\alpha \chi_a \chi_b | R_{12} + R_{23} | \chi_r \chi_b \psi_p^\beta \rangle + \langle \psi_p^\alpha \chi_b \chi_a | R_{12} + R_{23} | \chi_b \chi_r \psi_p^\beta \rangle \right], \quad (40)
\end{aligned}$$

and

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i < j} r_{ij}^{-1} \right| \Psi_q^\beta(r_a) \right\rangle \\
&= \langle \chi_q \chi_a | R_{12} | \chi_r \chi_p \rangle \left[ \langle \psi_p^\alpha | \psi_q^\beta \rangle - \sum''_b \langle \psi_p^\alpha \chi_b | \chi_b \psi_q^\beta \rangle \right] \\
&+ \sum''_b \left[ \langle \chi_a \chi_b | R_{12} | \chi_r \chi_b \rangle \langle \psi_p^\alpha \chi_q | \chi_p \psi_q^\beta \rangle + \langle \chi_a \chi_b | R_{12} | \chi_p \chi_r \rangle \langle \psi_p^\alpha \chi_q | \chi_b \psi_q^\beta \rangle \right. \\
&+ \langle \chi_a \chi_b | R_{12} | \chi_b \chi_p \rangle \langle \psi_p^\alpha \chi_q | \chi_r \psi_q^\beta \rangle + \langle \chi_q \chi_a | R_{12} | \chi_r \chi_b \rangle \langle \psi_p^\alpha \chi_b | \chi_p \psi_q^\beta \rangle \\
&+ \langle \chi_q \chi_a | R_{12} | \chi_b \chi_p \rangle \langle \psi_p^\alpha \chi_b | \chi_r \psi_q^\beta \rangle + \langle \chi_b \chi_q | R_{12} | \chi_r \chi_b \rangle \langle \psi_p^\alpha \chi_a | \chi_p \psi_q^\beta \rangle \\
&+ \langle \chi_b \chi_q | R_{12} | \chi_p \chi_r \rangle \langle \psi_p^\alpha \chi_a | \chi_b \psi_q^\beta \rangle + \langle \chi_b \chi_q | R_{12} | \chi_b \chi_p \rangle \langle \psi_p^\alpha \chi_a | \chi_r \psi_q^\beta \rangle \\
&\left. + \langle \psi_p^\alpha \chi_q \chi_a | R_{12} + R_{23} | \chi_r \chi_p \psi_q^\beta \rangle + \langle \psi_p^\alpha \chi_a \chi_q | R_{12} + R_{23} | \chi_p \chi_r \psi_q^\beta \rangle \right], \quad (p \neq q). \quad (41)
\end{aligned}$$

The matrix elements of the overlap and  $h_+(0)$  operator for  $p \neq q$  vanish.

The matrix elements of the overlap and  $h_+(0)$  between  $\Psi_p^\alpha$  and  $\Psi_q^\beta(r_{ab}^{rs})$  do not appear.  $\langle \Psi_p^\alpha | \sum_i r_{0i}^{-1} | \Psi_q^\beta(r_{ab}^{rs}) \rangle$  ( $p \neq q$ ) also vanish. The resulting matrix elements are as follows:

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_i h(i) \right| \Psi_p^\beta(r_{ab}^{rs}) \right\rangle \\
&= \langle \chi_a | h | \chi_s \rangle \langle \psi_p^\alpha \chi_b | \chi_r \psi_p^\beta \rangle - \langle \chi_a | h | \chi_r \rangle \langle \psi_p^\alpha \chi_b | \chi_s \psi_p^\beta \rangle \\
&+ \langle \chi_b | h | \chi_r \rangle \langle \psi_p^\alpha \chi_a | \chi_s \psi_p^\beta \rangle - \langle \chi_b | h | \chi_s \rangle \langle \psi_p^\alpha \chi_a | \chi_r \psi_p^\beta \rangle, \quad (42)
\end{aligned}$$

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_i r_{0i}^{-1} \right| \Psi_p^\beta(r_{ab}^{rs}) \right\rangle \\
&= \langle \psi_p^\alpha \chi_a \chi_b | R_{02} | \chi_r \chi_s \psi_p^\beta \rangle + \langle \psi_p^\alpha \chi_b \chi_a | R_{02} | \chi_s \chi_r \psi_p^\beta \rangle, \quad (43)
\end{aligned}$$

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i<j} r_{ij}^{-1} \right| \Psi_p^\beta(rs) \right\rangle \\
&= \langle \chi_a \chi_b | R_{12} | \chi_r \chi_s \rangle \left[ \langle \psi_p^\alpha | \psi_p^\beta \rangle - \sum_c' \langle \psi_p^\alpha \chi_c | \chi_c \psi_p^\beta \rangle \right] \\
&+ \sum_c' [\langle \chi_a \chi_b | R_{12} | \chi_c \chi_s \rangle \langle \psi_p^\alpha \chi_c | \chi_r \psi_p^\beta \rangle + \langle \chi_a \chi_b | R_{12} | \chi_r \chi_c \rangle \langle \psi_p^\alpha \chi_c | \chi_s \psi_p^\beta \rangle \\
&+ \langle \chi_a \chi_c | R_{12} | \chi_r \chi_s \rangle \langle \psi_p^\alpha \chi_b | \chi_c \psi_p^\beta \rangle + \langle \chi_a \chi_c | R_{12} | \chi_c \chi_r \rangle \langle \psi_p^\alpha \chi_b | \chi_s \psi_p^\beta \rangle \\
&+ \langle \chi_a \chi_c | R_{12} | \chi_s \chi_c \rangle \langle \psi_p^\alpha \chi_b | \chi_r \psi_p^\beta \rangle + \langle \chi_b \chi_c | R_{12} | \chi_c \chi_s \rangle \langle \psi_p^\alpha \chi_a | \chi_r \psi_p^\beta \rangle \\
&+ \langle \chi_b \chi_c | R_{12} | \chi_r \chi_c \rangle \langle \psi_p^\alpha \chi_a | \chi_s \psi_p^\beta \rangle + \langle \chi_b \chi_c | R_{12} | \chi_s \chi_r \rangle \langle \psi_p^\alpha \chi_a | \chi_c \psi_p^\beta \rangle] \\
&+ \langle \psi_p^\alpha \chi_a \chi_b | R_{12} + R_{23} | \chi_r \chi_s \psi_p^\beta \rangle + \langle \psi_p^\alpha \chi_b \chi_a | R_{12} + R_{23} | \chi_s \chi_r \psi_p^\beta \rangle, \tag{44}
\end{aligned}$$

and

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i<j} r_{ij}^{-1} \right| \Psi_q^\beta(rs) \right\rangle \\
&= \langle \chi_a \chi_b | R_{12} | \chi_r \chi_s \rangle \langle \psi_p^\alpha \chi_q | \chi_p \psi_q^\beta \rangle + \langle \chi_a \chi_b | R_{12} | \chi_p \chi_r \rangle \langle \psi_p^\alpha \chi_q | \chi_s \psi_q^\beta \rangle \\
&+ \langle \chi_a \chi_b | R_{12} | \chi_s \chi_p \rangle \langle \psi_p^\alpha \chi_q | \chi_r \psi_q^\beta \rangle + \langle \chi_q \chi_a | R_{12} | \chi_r \chi_s \rangle \langle \psi_p^\alpha \chi_b | \chi_p \psi_q^\beta \rangle \\
&+ \langle \chi_q \chi_a | R_{12} | \chi_p \chi_r \rangle \langle \psi_p^\alpha \chi_b | \chi_s \psi_q^\beta \rangle + \langle \chi_q \chi_a | R_{12} | \chi_s \chi_p \rangle \langle \psi_p^\alpha \chi_b | \chi_r \psi_q^\beta \rangle \\
&+ \langle \chi_b \chi_q | R_{12} | \chi_r \chi_s \rangle \langle \psi_p^\alpha \chi_a | \chi_p \psi_q^\beta \rangle + \langle \chi_b \chi_q | R_{12} | \chi_p \chi_r \rangle \langle \psi_p^\alpha \chi_a | \chi_s \psi_q^\beta \rangle \\
&+ \langle \chi_b \chi_q | R_{12} | \chi_s \chi_p \rangle \langle \psi_p^\alpha \chi_a | \chi_r \psi_q^\beta \rangle, \quad (p \neq q). \tag{45}
\end{aligned}$$

The matrix element between  $\Psi_p^\alpha$  and  $\Psi_p^\beta(rs)$  is nonzero only for electron-electron interactions, and the formula is

$$\begin{aligned}
& \left\langle \Psi_p^\alpha \left| \sum_{i<j} r_{ij}^{-1} \right| \Psi_p^\beta(rst) \right\rangle \\
&= \langle \chi_a \chi_b | R_{12} | \chi_s \chi_r \rangle \langle \psi_p^\alpha \chi_c | \chi_t \psi_p^\beta \rangle + \langle \chi_a \chi_b | R_{12} | \chi_t \chi_s \rangle \langle \psi_p^\alpha \chi_c | \chi_r \psi_p^\beta \rangle \\
&+ \langle \chi_a \chi_b | R_{12} | \chi_r \chi_t \rangle \langle \psi_p^\alpha \chi_c | \chi_s \psi_p^\beta \rangle + \langle \chi_a \chi_c | R_{12} | \chi_t \chi_r \rangle \langle \psi_p^\alpha \chi_b | \chi_s \psi_p^\beta \rangle \\
&+ \langle \chi_a \chi_c | R_{12} | \chi_s \chi_t \rangle \langle \psi_p^\alpha \chi_b | \chi_r \psi_p^\beta \rangle + \langle \chi_a \chi_c | R_{12} | \chi_r \chi_s \rangle \langle \psi_p^\alpha \chi_b | \chi_t \psi_p^\beta \rangle \\
&+ \langle \chi_b \chi_c | R_{12} | \chi_t \chi_s \rangle \langle \psi_p^\alpha \chi_a | \chi_r \psi_p^\beta \rangle + \langle \chi_b \chi_c | R_{12} | \chi_r \chi_t \rangle \langle \psi_p^\alpha \chi_a | \chi_s \psi_p^\beta \rangle \\
&+ \langle \chi_b \chi_c | R_{12} | \chi_s \chi_r \rangle \langle \psi_p^\alpha \chi_a | \chi_t \psi_p^\beta \rangle. \tag{46}
\end{aligned}$$

## 4 Discussion

The key feature of this work is derivation of the matrix elements by complete set expansions of correlation factors in Hylleraas-CI determinants. This procedure transforms a Hylleraas-CI determinant to a linear combination of determinants consisting of orthonormal orbitals, and hence simplifies the derivation of the matrix elements. The resulting matrix elements are given by very complicated formulas which include up to four-electron

integrals. In the same way, the matrix elements in the Hylleraas-CI method for usual atoms can be derived.

Computation of many-electron integrals is laborious, and requires very large storage. There may be procedures which reduce the computational load and storage of many-electron integrals. One procedure is to use the incomplete resolution of identity operators [31]:

$$P(01) = \sum_i^N \sum_j^N |\xi_i(\mathbf{x}_0)\chi_j(\mathbf{x}_1)\rangle \langle \xi_i(\mathbf{x}'_0)\chi_j(\mathbf{x}'_1)|. \quad (47)$$

In this procedure, three- and four-electron integrals are calculated as finite sums of products of two-electron integrals, e.g.

$$\begin{aligned} & \langle \psi_p^\alpha \chi_a \chi_b | R_{02} | \chi_c \chi_d \psi_q^\beta \rangle \\ &= \langle \psi_p^\alpha \chi_a \chi_b | P(01) R_{02} P(03) | \chi_c \chi_d \psi_q^\beta \rangle \\ &= \sum_i^N \sum_j^N \langle \psi_p^\alpha | \xi_i \chi_c \rangle \langle \xi_i \chi_a | R_{01} | \xi_j \chi_d \rangle \langle \xi_j \chi_b | \psi_q^\beta \rangle. \end{aligned} \quad (48)$$

From this point, only necessary two-electron integrals have to be calculated and stored. Although these summations are carried out only approximately, it is possible to obtain highly accurate many-electron integrals by using very flexible basis functions, e.g. the *B*-spline set [36]. The *B*-spline set comprises piecewise polynomials, and is very flexible. The flexibility of the *B*-splines has been demonstrated in the atomic Hartree–Fock [37] and third Douglas-Kroll self-consistent calculations [38]. Work is in progress for these approximate computations of many-electron integrals.

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**Table 1** First-order cofactors in  $\langle \Psi_p | \mathcal{H} | \Psi_q \rangle$  ( $a \neq b$ )

$S_{pp}^{(p,p)} = 1$	$S_{pq}^{(p,q)} = \delta_{q,l}$
$S_{pp}^{(p,a)} = -\delta_{a,l}$	$S_{pq}^{(q,q)} = \delta_{j,p}$
$S_{pp}^{(a,p)} = -\delta_{j,a}$	$S_{pq}^{(q,p)} = -\delta_{j,l} + \sum_{c(\neq p,q)} \delta_{j,c} \delta_{c,l}$
$S_{pp}^{(a,a)} = \delta_{j,l} - \sum_{c(\neq p,a)} \delta_{j,c} \delta_{c,l}$	$S_{pq}^{(a,p)} = -\delta_{j,a} \delta_{q,l}$
$S_{pp}^{(a,b)} = \delta_{j,a} \delta_{b,l}$	$S_{pq}^{(q,a)} = -\delta_{j,p} \delta_{a,l}$
	$S_{pq}^{(a,a)} = \delta_{j,p} \delta_{q,l}$

**Table 2** Second-order cofactors in  $\langle \Psi_p | \mathcal{H} | \Psi_q \rangle$  ( $a < b < c$  and  $p < q$ )

$S_{pp}^{(p,a,p,a)} = 1$	$S_{pq}^{(p,q,p,q)} = 1$
$S_{pp}^{(p,a,a,b)} = \delta_{b,l}$	$S_{pq}^{(p,q,p,a)} = -\delta_{a,l}$
$S_{pp}^{(p,b,a,b)} = -\delta_{a,l}$	$S_{pq}^{(q,a,p,q)} = \delta_{j,a}$
$S_{pp}^{(a,b,p,a)} = \delta_{j,b}$	$S_{pq}^{(p,a,p,a)} = \delta_{q,l}$
$S_{pp}^{(a,b,p,b)} = \delta_{j,a}$	$S_{pq}^{(q,a,q,a)} = \delta_{j,p}$
$S_{pp}^{(a,b,a,b)} = \delta_{j,l} - \sum_{d(\neq p,a,b)} \delta_{j,d} \delta_{d,l}$	$S_{pq}^{(q,a,p,a)} = -\delta_{j,l} + \sum_{d(\neq p,q,a)} \delta_{j,d} \delta_{d,l}$
$S_{pp}^{(a,b,a,c)} = -\delta_{j,b} \delta_{c,l}$	$S_{pq}^{(q,a,p,b)} = -\delta_{j,a} \delta_{b,l}$
$S_{pp}^{(a,b,b,c)} = -\delta_{j,a} \delta_{c,l}$	$S_{pq}^{(a,b,p,a)} = \delta_{j,b} \delta_{q,l}$
	$S_{pq}^{(a,b,p,b)} = -\delta_{j,a} \delta_{q,l}$
	$S_{pq}^{(q,a,a,b)} = \delta_{j,p} \delta_{b,l}$
	$S_{pq}^{(q,b,a,b)} = -\delta_{j,p} \delta_{b,l}$
	$S_{pq}^{(a,b,a,b)} = \delta_{j,b} \delta_{q,l}$

