The super-CI Hamiltonian matrix elements in calculations of the positron-electron correlated Hartree-Fock wavefunction

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Abstract

The super-CI Hamiltonian matrix elements in calculations of the positron-electron correlated Hartree-Fock (*pec*-HF) wavefunction are presented. The *pec*-HF wavefunction is the configuration interaction one which corresponds to a diatomic molecular Hartree-Fock wave function, and it is presented in our previous work [Chukyo Univ. Bull. Sch. Int. Liberal Studies 12 (2), 27 (2020)]. The super-CI Hamiltonian matrix elements are evaluated by the second quantization technique.

In our previous work[1], we considered diatomic molecule-like configuration interaction (CI) wave functions of positronium-atom complexes. Our simplest wavefunction is the positron-electron correlated Hartree-Fock (*pec*-HF) one. The *pec*-HF wavefunction corresponds to a diatomic molecular Hartree-Fock one, and it is written as

$$\Psi = (1 + T_2^{+})\Phi_0 \,. \tag{1}$$

Φ_0 is a wave function consisted of occupied orbitals obtained by variationally optimizing the total energy:

$$\Phi_0 = \psi_\xi(\boldsymbol{r}_0)\mathcal{A}[\chi_a(\boldsymbol{r}_1)\chi_b(\boldsymbol{r}_2)\cdots\chi_n(\boldsymbol{r}_n)]\,, \tag{2}$$

where ψ_ξ and $\{\chi_a\}$ are respectively positronic and electronic spin orbitals, and $\mathcal{A}$ is the antisymmetrizer. The positron is signified by 0, and the electrons by 1,2,3, ⋯ . The operator T_2^{+} is the positron-electron pair excitation operator

$$T_2^{+} = \sum_a \sum_{\rho r} C_{\xi a}^{\rho r}\, b_\rho^\dagger b_\xi a_r^\dagger a_a \,, \tag{3}$$

where $a_r^\dagger$ and a_a are respectively electronic creation and annihilation operators, $b_\rho^\dagger$ and b_ξ are respectively positronic creation and annihilation operators, and $\left\{C_{\xi a}^{\rho r}\right\}$ are linear coefficients which should be decided variationally. We employ the following convention for orbital indexes:

(i) ξ : the occupied positronic orbital,

(ii) $a, b, c, d, \cdots$: occupied electronic orbitals,

(iii) $r, s, t, u, \cdots$: virtual electronic orbitals,

(iv) $\rho, \sigma, \tau, \omega, \cdots$: virtual positronic orbitals,

and

(v) $i, j, k, l, \cdots$: arbitrary orbitals.

To obtain *pec*-HF wavefunctions, one must variationally optimize both the linear coefficients $\left\{C_{\xi a}^{\rho r}\right\}$ and the occupied orbitals. To this end, it is possible to apply procedures of multiconfiguration self-consistent field (MCSCF) calculations. MCSCF calculations can be carried out by three methods: (i) those that solve Hartree-Fock like equations; (ii) those that minimize the total energy directly by gradient techniques; and (iii) those based on the generalized Brillouin theorem[2]. This work employs the method based on the generalized Brillouin theorem.

The generalized Brillouin theorem for Ψ is

$$\langle\Psi|\mathcal{H}|\Psi(i \to j)\rangle = 0\,, \tag{4}$$

where $\mathcal{H}$ is the Hamiltonian, and $\Psi(i \to j)$ stands for one electron or one positron excited wavefunctions from occupied orbitals of Ψ. The generalized Brillouin theorem is applied in order to obtain Ψ from an arbitrary trial function Ψ'. It may be suitable to employ Ψ' with Φ_0 which is a Hartree-Fock wavefunction. Ψ is decided iteratively. The iterative procedure is the following steps:

(i) The linear coefficients $\left\{C_{\xi a}^{\rho r}\right\}$ are obtained by the standard variation procedure.

(ii) The linear coefficients $\left\{D_{\xi}^{\rho}\right\}$, $\{D_c^a\}$, and $\{D_c^r\}$ are obtained from the super-CI wavefunction[3]:

$$\Psi_{\mathrm{SCI}} = \Psi + \sum_{\rho} D_{\xi}^{\rho}\Psi_{\xi}^{\rho} + \sum_{ca} D_c^a\Psi_c^a + \sum_{cr} D_c^r\Psi_c^r \tag{5}$$

with

$$\Psi_{\xi}^{\rho} = b_{\rho}^{\dagger} b_{\xi}\Psi, \tag{6}$$

$$\Psi_c^a = a_a^{\dagger} a_c\Psi, \tag{7}$$

and

$$\Psi_c^r = a_r^{\dagger} a_c\Psi. \tag{8}$$

(iii) New sets of a positronic orbital ψ'_{ξ} and electronic orbitals $\{\chi'_a\}$ are obtained from

$$\psi'_{\xi} = \psi_{\xi} + \sum_{i} D_{\xi}^{i}\,\psi_i \tag{9}$$

and

$$\chi'_a = \chi_a + \sum_i D_a^i \chi_i \,. \tag{10}$$

(iv) These procedures are repeated until the desired convergence is obtained.

The super-CI wavefunction Ψ_{SCI} is solved by the variational procedure. In this work, we evaluate the matrix elements of $\langle \Psi_{\mathrm{SCI}} | \mathcal{H} | \Psi_{\mathrm{SCI}} \rangle$. The Hamiltonian matrix elements required are as follows:

$\langle \Psi | \mathcal{H} | \Psi \rangle$,

$\langle \Psi_\xi^\tau | \mathcal{H} | \Psi \rangle$, $\langle \Psi_\xi^\tau | \mathcal{H} | \Psi_\xi^\omega \rangle$,

$\langle \Psi_c^a | \mathcal{H} | \Psi \rangle$, $\langle \Psi_c^a | \mathcal{H} | \Psi_\xi^\omega \rangle$, $\langle \Psi_c^a | \mathcal{H} | \Psi_d^b \rangle$,

$\langle \Psi_c^t | \mathcal{H} | \Psi \rangle$, $\langle \Psi_c^t | \mathcal{H} | \Psi_\xi^\omega \rangle$, $\langle \Psi_c^t | \mathcal{H} | \Psi_d^b \rangle$, $\langle \Psi_c^t | \mathcal{H} | \Psi_d^u \rangle$.

Let us evaluate the Hamiltonian matrix elements between the super-CI wavefunctions. The non-relativistic Hamiltonian for positronium-atom complexes is written as

$$\mathcal{H} = \sum_{i=1} h(i) + \frac{1}{2} \sum_{i,j=1} r_{ij}^{-1} + h_+(0) - \sum_{i=1} r_{0i}^{-1}, \tag{11}$$

with

$$h(i) = -\frac{1}{2} \Delta_i - Z r_i^{-1} \tag{12}$$

and

$$h_+(0) = -\frac{1}{2} \Delta_0 + Z r_0^{-1}, \tag{13}$$

where Z is the nuclear charge, and $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$. We introduce the following notation for one-body and two-body integrals which appear in the Hamiltonian matrix elements:

$$\langle i | h | j \rangle = \int d\boldsymbol{r}_1 \, \chi_i^*(\boldsymbol{r}_1) h(1) \chi_j(\boldsymbol{r}_1), \tag{14}$$

$$\langle \xi | h_+ | \omega \rangle = \int d\boldsymbol{r}_0 \, \psi_\xi^*(\boldsymbol{r}_0) h_+(0) \psi_\omega(\boldsymbol{r}_0), \tag{15}$$

$$\langle ij | kl \rangle = \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 \chi_i^*(\boldsymbol{r}_1) \chi_j^*(\boldsymbol{r}_2) r_{12}^{-1} \chi_k(\boldsymbol{r}_1) \chi_l(\boldsymbol{r}_2), \tag{16}$$

$$\langle \xi i | \omega j \rangle = \iint d\boldsymbol{r}_0 d\boldsymbol{r}_1 \psi_\xi^*(\boldsymbol{r}_0) \chi_i^*(\boldsymbol{r}_1) r_{01}^{-1} \psi_\omega(\boldsymbol{r}_0) \chi_j(\boldsymbol{r}_1), \tag{17}$$

and

$$\langle ij \| kl \rangle = \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 \chi_i^*(\boldsymbol{r}_1) \chi_j^*(\boldsymbol{r}_2) r_{12}^{-1} A_{12} \chi_k(\boldsymbol{r}_1) \chi_l(\boldsymbol{r}_2), \tag{18}$$

where $A_{12}=1-P_{12}$, and P_{12} is the permutation operator of indexes 1 and 2. Below, this operator is also used for the permutation of orbital indexes.

The Hamiltonian matrix elements are evaluated using the second quantized Hamiltonian:

$$\mathcal{H}=\sum_{ij}\langle i|h|j\rangle a_i^\dagger a_j+\frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\, a_i^\dagger a_j^\dagger a_l a_k$$
$$+\sum_{ij}\langle i|h_+|j\rangle b_i^\dagger b_j-\sum_{ijkl}\langle ij|kl\rangle\, b_i^\dagger a_j^\dagger b_k a_l\,. \tag{19}$$

Moreover, we rewrite the Hamiltonian to the normal product form relative to the Fermi vacuum Φ_0 :

$$\mathcal{H}=\sum_{ij}\langle i|h|j\rangle\{a_i^\dagger a_j\}+\frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\,\{a_i^\dagger a_j^\dagger a_l a_k\}+\sum_{aij}\langle ia\|ja\rangle\,\{a_i^\dagger a_j\}$$
$$+\sum_{ij}\langle i|h_+|j\rangle\{b_i^\dagger b_j\}-\sum_{ijkl}\langle ij|kl\rangle\,\{b_i^\dagger b_k\}\{a_j^\dagger a_l\}$$
$$-\sum_{aij}\langle ia|ja\rangle\,\{b_i^\dagger b_j\}-\sum_{ij}\langle\xi i|\xi j\rangle\,\{a_i^\dagger a_j\}$$
$$+\sum_{a}\langle a|h|a\rangle+\frac{1}{2}\sum_{ab}\langle ab\|ab\rangle+\langle\xi|h_+|\xi\rangle-\sum_{a}\langle\xi a|\xi a\rangle\,, \tag{20}$$

where curly brackets stand for the normal product relative to the Fermi vacuum Φ_0. The generalized Wick's theorem[4] simplifies evaluation of the Hamiltonian matrix elements because only normal products with fully contracted terms survive[5,6]. For example, a matrix element of a normal product one-body operator

$$h_N=\sum_{ij}\langle i|h|j\rangle\,\{a_i^\dagger a_j\} \tag{21}$$

between two determinants Φ_a^r and Φ_b^s singly excited from the Fermi vacuum Φ is

$$\langle\Phi_a^r|h_N|\Phi_b^s\rangle=\sum_{ij}\langle i|h|j\rangle\,\langle\Phi|\{a_a^\dagger a_r\}\{a_i^\dagger a_j\}\{a_s^\dagger a_b\}|\Phi\rangle$$
$$=\sum_{ij}\langle i|h|j\rangle\,\langle\Phi|\{a_a^\dagger a_r\}\{a_i^\dagger a_j\}\{a_s^\dagger a_b\}+\{a_a^\dagger a_r\}\{a_i^\dagger a_j\}\{a_s^\dagger a_b\}|\Phi\rangle$$
$$=\sum_{ij}\langle i|h|j\rangle\,\langle\Phi|-\delta_{aj}\delta_{rs}\delta_{ib}+\delta_{ab}\delta_{ri}\delta_{js}|\Phi\rangle$$
$$=-\delta_{rs}\langle b|h|a\rangle+\delta_{ab}\langle r|h|s\rangle\,. \tag{22}$$

A matrix element of a normal product two-body operator can be evaluated in the same way though it is very tedious work.

Below, the resulting Hamiltonian matrix elements are listed:

$$\begin{aligned}\langle\Psi|\mathcal{H}|\Psi\rangle &= \sum_e \langle e|h|e\rangle + \frac{1}{2}\sum_{ef}\langle ef\|ef\rangle + \langle\xi|h_+|\xi\rangle - \sum_e \langle\xi e|\xi e\rangle \\ &\quad - \sum_b\sum_{\sigma s} C_{\xi b}^{\sigma s}\langle\xi b|\sigma s\rangle - \sum_a\sum_{\rho r} C_{\xi a}^{\rho r}\langle\rho r|\xi a\rangle \\ &\quad + \sum_{ab}\sum_{\rho r}\sum_{\sigma s} C_{\xi a}^{\rho r} C_{\xi b}^{\sigma s}\left[\delta_{ab}\delta_{rs}\left(\delta_{\rho\sigma}\sum_e\langle e|h|e\rangle + \frac{1}{2}\delta_{\rho\sigma}\sum_{ef}\langle ef\|ef\rangle\right.\right. \\ &\qquad \left. + \langle\rho|h_+|\sigma\rangle - \sum_e\langle\rho e|\sigma e\rangle\right) \\ &\qquad + \delta_{ab}\left(\delta_{\rho\sigma}\langle r|h|s\rangle + \delta_{\rho\sigma}\sum_e\langle re\|se\rangle - \langle\rho r|\sigma s\rangle\right) \\ &\qquad \left. - \delta_{rs}\left(\delta_{\rho\sigma}\langle b|h|a\rangle + \delta_{\rho\sigma}\sum_e\langle be\|ae\rangle - \langle\rho b|\sigma a\rangle\right) + \delta_{\rho\sigma}\langle br\|sa\rangle\right],\end{aligned} \tag{23}$$

$$\begin{aligned}\langle\Psi_\xi^\tau|\mathcal{H}|\Psi\rangle &= \langle\tau|h_+|\xi\rangle - \sum_e\langle\tau e|\xi e\rangle \\ &\quad + \sum_b\sum_{\sigma s} C_{\xi b}^{\sigma s}\left[\delta_{\tau\sigma}\left(\langle b|h|s\rangle + \sum_e\langle be\|se\rangle\right) - \langle\tau b|\sigma s\rangle\right],\end{aligned} \tag{24}$$

$$\langle\Psi_\xi^\tau|\mathcal{H}|\Psi_\xi^\omega\rangle = \delta_{\tau\omega}\left(\sum_e\langle e|h|e\rangle + \frac{1}{2}\sum_{ef}\langle ef\|ef\rangle\right) + \langle\tau|h_+|\omega\rangle - \sum_e\langle\tau e|\omega e\rangle\,, \tag{25}$$

$$\begin{aligned}\langle\Psi_c^a|\mathcal{H}|\Psi\rangle &= \sum_a\sum_{\rho r} C_{\xi a}^{\rho r}\langle\rho r|\xi c\rangle \\ &- \sum_b\sum_{\rho r}\sum_{\sigma s} C_{\xi a}^{\rho r}\, C_{\xi b}^{\sigma s}\Bigg[\delta_{bc}\delta_{rs}\Bigg(\delta_{\rho\sigma}\sum_e\langle e|h|e\rangle + \frac{1}{2}\delta_{\rho\sigma}\sum_{ef}\langle ef\|ef\rangle \\ &\quad + \langle\rho|h_+|\sigma\rangle - \sum_e\langle\rho e|\sigma e\rangle\Bigg) \\ &\quad + \delta_{bc}\Bigg(\delta_{\rho\sigma}\langle r|h|s\rangle + \delta_{\rho\sigma}\sum_e\langle re\|se\rangle - \langle\rho r|\sigma s\rangle\Bigg) \\ &\quad - \delta_{rs}\Bigg(\delta_{\rho\sigma}\langle b|h|c\rangle + \delta_{\rho\sigma}\sum_e\langle be\|ce\rangle - \langle\rho b|\sigma c\rangle\Bigg) + \delta_{\rho\sigma}\langle br\|sc\rangle\Bigg],\end{aligned} \tag{26}$$

$$\langle\Psi_c^a|\mathcal{H}|\Psi_\xi^\omega\rangle = -\sum_{\rho r} C_{\xi a}^{\rho r}\Bigg[\delta_{\rho\omega}\Bigg(\langle r|h|c\rangle + \sum_e\langle re\|ce\rangle\Bigg) - \langle\rho r|\omega c\rangle\Bigg], \tag{27}$$

$$\begin{aligned}\langle\Psi_c^a|\mathcal{H}|\Psi_d^b\rangle &= \sum_{\rho r}\sum_{\sigma s} C_{\xi a}^{\rho r}\, C_{\xi b}^{\sigma s}\Bigg[\delta_{cd}\delta_{rs}\Bigg(\delta_{\rho\sigma}\sum_e\langle e|h|e\rangle + \frac{1}{2}\delta_{\rho\sigma}\sum_{ef}\langle ef\|ef\rangle + \langle\rho|h_+|\sigma\rangle \\ &\quad - \sum_e\langle\rho e|\sigma e\rangle\Bigg) + \delta_{cd}\Bigg(\delta_{\rho\sigma}\langle r|h|s\rangle + \delta_{\rho\sigma}\sum_e\langle re\|se\rangle - \langle\rho r|\sigma s\rangle\Bigg) \\ &\quad - \delta_{rs}\Bigg(\delta_{\rho\sigma}\langle d|h|c\rangle + \delta_{\rho\sigma}\sum_e\langle de\|ce\rangle - \langle\rho d|\sigma c\rangle\Bigg) + \delta_{\rho\sigma}\langle dr\|sc\rangle\Bigg],\end{aligned} \tag{28}$$

$$\begin{aligned}\langle\Psi_c^t|\mathcal{H}|\Psi\rangle &= \langle t|h|c\rangle + \sum_e\langle te\|ce\rangle - \langle\xi t|\xi c\rangle \\ &+ \sum_b\sum_{\sigma s} C_{\xi b}^{\sigma s}\Bigg[\delta_{st}\langle\xi b|\sigma c\rangle - \delta_{bc}\langle\xi t|\sigma s\rangle + \delta_{bc}\delta_{st}\Bigg(\langle\xi|h_+|\sigma\rangle - \sum_e\langle\xi e|\sigma e\rangle\Bigg)\Bigg] \\ &+ \sum_{ab}\sum_{\rho r}\sum_{\sigma s} C_{\xi a}^{\rho r}\, C_{\xi b}^{\sigma s}\Bigg[\delta_{\rho\sigma}(A_{rt}\delta_{st}\langle rb\|ca\rangle + A_{ac}\delta_{ab}\langle rt\|sc\rangle) \\ &\quad + A_{ac}A_{rt}\delta_{ab}\delta_{rs}\Bigg(\delta_{\rho\sigma}\langle t|h|c\rangle + \delta_{\rho\sigma}\sum_e\langle te\|ce\rangle - \langle\rho t|\sigma c\rangle\Bigg)\Bigg],\end{aligned} \tag{29}$$

$$\left\langle \Psi_c^t \middle| \mathcal{H} \middle| \Psi_\xi^\omega \right\rangle = -\langle \xi t | \omega c \rangle + \sum_a \sum_r C_{\xi a}^{\omega r} \langle rt \| ac \rangle , \tag{30}$$

$$\begin{aligned}
\left\langle \Psi_c^t \middle| \mathcal{H} \middle| \Psi_d^b \right\rangle = &-\sum_{\sigma s} C_{\xi b}^{\sigma s} \left[\delta_{st} \langle \xi d | \sigma c \rangle - \delta_{cd} \langle \xi t | \sigma s \rangle + \delta_{cd} \delta_{st} \left(\langle \xi | h_+ | \sigma \rangle - \sum_e \langle \xi e | \sigma e \rangle \right) \right] \\
&- \sum_a \sum_{\rho r} \sum_{\sigma s} C_{\xi a}^{\rho r} C_{\xi b}^{\sigma s} \Bigg[\delta_{\rho\sigma} (A_{rt} \delta_{st} \langle rd \| ca \rangle + A_{ac} \delta_{ad} \langle rt \| sc \rangle) \\
&\quad + A_{ac} A_{rt} \delta_{ad} \delta_{rs} \left(\delta_{\rho\sigma} \langle t | h | c \rangle + \delta_{\rho\sigma} \sum_e \langle te \| ce \rangle - \langle \rho t | \sigma c \rangle \right) \Bigg],
\end{aligned} \tag{31}$$

$$\begin{aligned}
\langle \Psi_c^t | \mathcal{H} | \Psi_d^u \rangle = &-\langle td \| uc \rangle + \delta_{cd} \left(\langle t | h | u \rangle + \sum_e \langle te \| ue \rangle - \langle \xi t | \xi u \rangle \right) \\
&- \delta_{tu} \left(\langle d | h | c \rangle + \sum_e \langle de \| ce \rangle - \langle \xi d | \xi c \rangle \right) \\
&+ \delta_{cd} \delta_{tu} \left(\sum_e \langle e | h | e \rangle + \frac{1}{2} \sum_{ef} \langle ef \| ef \rangle + \langle \xi | h_+ | \xi \rangle - \sum_e \langle \xi e | \xi e \rangle \right) \\
&- \sum_b \sum_{\sigma s} C_{\xi b}^{\sigma s} A_{bd} A_{su} \delta_{bc} \delta_{st} \langle \xi d | \sigma u \rangle - \sum_a \sum_{\rho r} C_{\xi a}^{\rho r} A_{ac} A_{rt} \delta_{ad} \delta_{ru} \langle \rho t | \xi c \rangle \\
&+ \sum_{ab} \sum_{\rho r} \sum_{\sigma s} C_{\xi a}^{\rho r} C_{\xi b}^{\sigma s} \Bigg[-\delta_{\rho\sigma} A_{bd} A_{su} \delta_{ab} \delta_{rs} \langle td \| uc \rangle \\
&\quad + A_{ac} A_{bd} A_{su} \delta_{ab} \delta_{ru} \delta_{st} \left(\delta_{\rho\sigma} \langle d | h | c \rangle + \delta_{\rho\sigma} \sum_e \langle de \| ce \rangle - \langle \rho d | \sigma c \rangle \right) \\
&\quad + A_{bd} A_{su} A_{rt} \delta_{ab} \delta_{cd} \delta_{rs} \left(\delta_{\rho\sigma} \langle t | h | u \rangle + \delta_{\rho\sigma} \sum_e \langle te \| ue \rangle - \langle \rho t | \sigma u \rangle \right) \\
&\quad + A_{bd} A_{su} \delta_{ab} \delta_{cd} \delta_{rs} \delta_{tu} \Bigg(\delta_{\rho\sigma} \sum_e \langle e | h | e \rangle + \frac{1}{2} \delta_{\rho\sigma} \sum_{ef} \langle ef \| ef \rangle \\
&\quad + \langle \rho | h_+ | \sigma \rangle - \sum_e \langle \rho e | \sigma e \rangle \Bigg) \Bigg].
\end{aligned} \tag{32}$$

As seen in Eqs. (23)–(32), the super-CI Hamiltonian matrix elements are expressed in long linear combinations of various integrals. However, Eqs. (23)–(32) are written as short as possible with the aid of the operator A_{ab}.

We are preparing test calculations of the *pec*-HF wavefunction using the generalized Brillouin theorem.

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