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In response to Professor Liu's Comment[1] on our recently published paper,[2] this article provides our responses to the raised questions. The Comment poses several questions, and the purpose of this article is to address and resolve those questions. Specifically, our focus encompasses three key aspects regarding the validity of our paper, referred to as Paper 2 in accordance with the assigned reference number (Ref. 2).

1. In Paper 2, we employed three types of contractions: the constantly null contraction (CNC), the charge-conjugated contraction (CCC), and the conventional contraction (cC). These contractions were utilized solely *formally* during the construction (definition) process of the QED Hamiltonians from the virtual pair approximation (VPA) Hamiltonian. Once the QED Hamiltonians, for the MO-CNC case as an example,

$$H^{\mathrm{QED(MO-CNC)}} = \sum_{pq}^{\mathrm{all}} h_{pq}\left\{a_p^\dagger a_q\right\}_n + \frac{1}{2}\sum_{pqrs}^{\mathrm{all}} (pq|rs)\left\{a_p^\dagger a_r^\dagger a_s a_q\right\}_n, \tag{1}$$

were defined, subsequent operator manipulations were consistently performed based on the usual fermion (anti)commutation relations,

$$\begin{aligned} a_i a_j + a_j a_i &= 0, \\ a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger &= 0, \\ a_i^\dagger a_j + a_j a_i^\dagger &= \delta_{ij}, \end{aligned} \tag{2}$$

$$\begin{aligned} b_i b_j + b_j b_i &= 0, & a_i b_j + b_j a_i &= 0, \\ b_i^\dagger b_j^\dagger + b_j^\dagger b_i^\dagger &= 0, & a_i^\dagger b_j^\dagger + b_j^\dagger a_i^\dagger &= 0, \\ b_i^\dagger b_j + b_j b_i^\dagger &= \delta_{ij}, & a_i^\dagger b_j + b_j a_i^\dagger &= 0, \\ & & b_i^\dagger a_j + a_j b_i^\dagger &= 0, \end{aligned} \tag{3}$$

where $a_i^\dagger$ and a_i represent the creation and annihilation operators for electrons, respectively, whereas $b_i^\dagger$ and b_i denote those for positrons.

In the picture where only electrons are treated regardless of their energy signs (i.e., the Dirac sea picture), the commutation relations (2) were used for both positive and negative energy electrons. [Equation (13) of Paper 2 was thus obtained from Eq. (1) using relations (2). Equations (16) and (19) of Paper 2 for the other contractions were also obtained through the same procedure.] On the other hand, in the picture where the holes in negative energy orbitals are replaced by positive energy positrons, commutation relations (2) and (3) were used for the commutation of the creation and annihilation operators of the positive energy particles. The Hamiltonians treated through these commutation relations are naturally (mathematically) equivalent to the original. In fact, difficulties would arise if CNC or CCC is used instead of the commutation relations of fermions after the definition of Hamiltonian. Appendix A is provided to supplement this fact. With respect

to the derivation of Eq. (22) of Paper 2 from Eq. (13) of Paper 2, the Comment mentions that it is an "inconsistence." However, in Paper 2, the equivalent deformations of Hamiltonian using the above-mentioned commutation relations have been applied, which is, of course, not an inconsistency. Consequently, the subsequent discussions including orbital invariance and nonrelativistic limits remain unaffected.

In the QED-based formulation of the molecular orbital method described in Sec. II C of Paper 2, identical expressions of the second-order Møller–Plesset (MP2) perturbation theory, the configuration interaction (CI) method, and the multi-configurational quasi-degenerate perturbation theory (MC-QDPT) can be derived from Eq. (13) and also from Eq. (22). As a result, their formulation in Sec. II C of Paper 2 is independent of the ordering of the operators.

In fact, as has been described in Paper 2, it is readily confirmed that the combination of Eq. (22) of Paper 2 and the Hartree–Fock (HF) configuration, Eq. (65) of Paper 2,

$$|\Psi_0\rangle = \prod_i^{\mathrm{occ(ele.)}} a_i^\dagger \prod_p^{\mathrm{occ(pos.)}} b_p^\dagger |\mathrm{empty}\rangle, \tag{4}$$

and the combination Eq. (13) of Paper 2 and the following HF configuration:

$$\begin{aligned}|\Psi_0\rangle &= \prod_i^{\mathrm{occ(ele.)}} a_i^\dagger \prod_p^{\mathrm{occ(pos.)}} a_p \left|0^{(\mathrm{MO})}\right\rangle \\ &= \prod_i^{\mathrm{occ(ele.)}} a_i^\dagger \prod_p^{\mathrm{occ(pos.)}} a_p \prod_q^{(-)} a_q^\dagger |\mathrm{empty}\rangle,\end{aligned} \tag{5}$$

both result in the identical energy expression as follows:

$$\begin{aligned}E &= \left\langle \Psi_0 \middle| H^{\mathrm{QED}} \middle| \Psi_0 \right\rangle \\ &= \sum_i^{\mathrm{occ(ele.)}} h_{ii} - \sum_p^{\mathrm{occ(pos.)}} h_{pp} + \frac{1}{2} \sum_{ij}^{\mathrm{occ(ele.)}} [(ii|jj) - (ij|ji)] \\ &\quad - \sum_i^{\mathrm{occ(ele.)}} \sum_p^{\mathrm{occ(pos.)}} [(ii|pp) - (ip|pi)] \\ &\quad + \frac{1}{2} \sum_{pq}^{\mathrm{occ(pos.)}} [(pp|qq) - (pq|qp)].\end{aligned} \tag{6}$$

This equivalence holds true for the MP2, CI, and MC-QDPT cases. Appendix B provides examples for the CI methods.

2. In Subsection II B 3 of Paper 2, we required that the limit of the QED Hamiltonian when $c \to +\infty$ agrees with the nonrelativistic multicomponent molecular orbital (NR-MCMO) Hamiltonian[3] except for a constant term, and it was shown that only QED (MO-CNC) can satisfy this requirement. In other words, the other eight QED Hamiltonians include operators that are independent of c and not included in the MCMO Hamiltonian.

In the Comment, a different view on the nonrelativistic limit of the Hamiltonian from our view has been shown. The difference lies in the nonrelativistic limit of the Q_p^q term of QED(MO-CCC). In Paper 2, the limit was to be nonzero, whereas in Eq. (45) of the Comment, the limit is to be zero.

The expression for Q_p^q is as follows:

$$\begin{aligned}Q_p^q = &\sum_r^{(-)} \frac{1}{2}[(pq|rr) - (pr|rq)] \\ &- \sum_r^{(+)} \frac{1}{2}[(pq|rr) - (pr|rq)].\end{aligned} \tag{7}$$

From this expression, in the nonrelativistic limit, for $p, q \in \{(+)\}$,

$$\begin{aligned}Q_p^q \xrightarrow{c\to+\infty} &\sum_r^{(-)} \frac{1}{2}\left(\psi_p^{(\mathrm{ele.})}\psi_q^{(\mathrm{ele.})}\middle|\psi_r^{(\mathrm{pos.})}\psi_r^{(\mathrm{pos.})}\right) \\ &- \sum_r^{(+)} \frac{1}{2}\left[\left(\psi_p^{(\mathrm{ele.})}\psi_q^{(\mathrm{ele.})}\middle|\psi_r^{(\mathrm{ele.})}\psi_r^{(\mathrm{ele.})}\right)\right. \\ &\left. - \left(\psi_p^{(\mathrm{ele.})}\psi_r^{(\mathrm{ele.})}\middle|\psi_r^{(\mathrm{ele.})}\psi_q^{(\mathrm{ele.})}\right)\right] = \left(Q_{\mathrm{NR}}^{(+)}\right)_p^q,\end{aligned} \tag{8}$$

and for $p, q \in \{(-)\}$,

$$\begin{aligned}Q_p^q \xrightarrow{c\to+\infty} &\sum_r^{(-)} \frac{1}{2}\left[\left(\psi_p^{(\mathrm{pos.})}\psi_q^{(\mathrm{pos.})}\middle|\psi_r^{(\mathrm{pos.})}\psi_r^{(\mathrm{pos.})}\right)\right. \\ &\left. - \left(\psi_p^{(\mathrm{pos.})}\psi_r^{(\mathrm{pos.})}\middle|\psi_r^{(\mathrm{pos.})}\psi_q^{(\mathrm{pos.})}\right)\right] \\ &- \sum_r^{(+)} \frac{1}{2}\left(\psi_p^{(\mathrm{pos.})}\psi_q^{(\mathrm{pos.})}\middle|\psi_r^{(\mathrm{ele.})}\psi_r^{(\mathrm{ele.})}\right) = -\left(Q_{\mathrm{NR}}^{(-)}\right)_p^q,\end{aligned} \tag{9}$$

neither of which generally vanish. Hence, Eq. (45) of the Comment is not satisfied, and in the nonrelativistic limit, there remains a one-electron operator that is not included in the NR-MCMO method,

$$\sum_{pq}^{\mathrm{all}} Q_p^q \left\{a_p^\dagger a_q\right\} \xrightarrow{c\to+\infty} \sum_{pq}^{(+)} \left(Q_{\mathrm{NR}}^{(+)}\right)_p^q \left\{a_p^\dagger a_q\right\} - \sum_{pq}^{(-)} \left(Q_{\mathrm{NR}}^{(-)}\right)_p^q \left\{a_p^\dagger a_q\right\}, \tag{10}$$

indicating that the QED Hamiltonian with the CCC still does not give a nonrelativistic limit consistent with the NR-MCMO. The typical QED effects have a negative order of the speed of light, c, as can be seen in the Uehling potential,[4] and should go to zero in the nonrelativistic limit. Thus, we consider that it is unnatural to attribute the non-vanishing effect in the nonrelativistic limit as a QED effect.

3. In Subsection II B 4 of Paper 2, the total energy divergence arising from generalized electron correlations involving electron–positron pair creations and the removal of the divergence by a counter term were discussed. The Comment asserts that the description in Subsection II B 4 in Paper 2, which states, "the terms subtracted from the referenced Hamiltonians are single Slater determinants and cannot remove

total energy divergence caused by the generalized electron correlation" is a "complete misunderstanding." However, the content of the Comment does not lead us to conclude that the description in Paper 2 is a misunderstanding. In fact, the single-configuration vacuum in Eq. (49) of the Comment was replaced by a multiconfigurational vacuum in Eq. (50) of the Comment,

$$\langle 0;\tilde{N}|H|0;\tilde{N}\rangle \to \langle \Psi(0;\tilde{N})|H|\Psi(0;\tilde{N})\rangle. \tag{11}$$

This does not contradict the description in Paper 2 quoted above. The procedures of subtracting the counter term after the derivation of the Hamiltonian and replacing the single-configuration vacuum with the multiconfigurational vacuum are intended to be offset with respect to the vacuum state, and both give essentially the same total energy expression,

$$\begin{aligned}&\langle \Psi(N;\tilde{N})|H'|\Psi(N;\tilde{N})\rangle - \langle \Psi(0;\tilde{N})|H'|\Psi(0;\tilde{N})\rangle \\ &= \langle \Psi(N;\tilde{N})|H|\Psi(N;\tilde{N})\rangle - \langle \Psi(0;\tilde{N})|H|\Psi(0;\tilde{N})\rangle,\end{aligned} \tag{12}$$

with

$$H' = H - \langle 0;\tilde{N}|H|0;\tilde{N}\rangle. \tag{13}$$

Thus, it is not an essential issue which procedure is used to derive the total energy expression.

In the papers[5–7] indicated in the Comment as being on the removal of total energy divergence, Refs. 5 and 6 actually mentioned removal of the infinite energy value resulting from the normal ordering of the Hamiltonian. This is understood also from the fact that the vacuum expectation value being subtracted in the equations [Eq. (14) of Ref. 5 and Eq. (2.13) of Ref. 6] in these papers stems from a single configuration vacuum. They differ in origin from the divergence of the total energy due to generalized electron correlations and its suppression of divergence using the counter term we presented in Paper 2. Furthermore, Ref. 7 discusses variational stability with respect to changes in the fine structure constant, which we also do not think is related to the divergence of the generalized electron correlation. In addition, Paper 2 provided initial numerical examples of the divergence due to the generalized electron correlations and its removal.

As indicated above, Paper 2 has no internal inconsistency that the Comment raised. Other points raised in the Comment are not explicitly addressed in this response, because they do not directly pertain to the validity of Paper 2 (or are outside the scope of Paper 2 in the first place).

Paper 2 adopted the three criteria and examined the QED Hamiltonian in accordance with them. However, it is important to note that the consideration of alternative criteria for the QED Hamiltonians is not ruled out. Exploring these possibilities, however, was not in the scope of Paper 2 and should be considered as a subject for future research.

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APPENDIX A: ON THE INCOMPATIBILITY OF CNC AND CCC WITH THE COMMUTATION RELATIONS OF FERMIONS

In Appendix A, for the readers' convenience, we briefly describe the fact that CNC and CCC are incompatible with the commutation relations of fermions.

Let $\mathrm{c}(ab)$ denote the contraction of operators a and b. The CNC and CCC are defined as follows:

$$\mathrm{c}\left(a_p^\dagger a_q\right) = 0, \qquad \mathrm{c}\left(a_p a_q^\dagger\right) = 0, \tag{A1}$$

and

$$\mathrm{c}\left(a_p^\dagger a_q\right) = -(1/2)\delta_{pq}\,\mathrm{sgn}\,(\varepsilon_p), \mathrm{c}\left(a_p a_q^\dagger\right) = (1/2)\delta_{pq}\,\mathrm{sgn}\,(\varepsilon_p). \tag{A2}$$

The contraction is the difference between the product ab of two creation/annihilation operators and their normal product $\{ab\}_n$,

$$\mathrm{c}(ab) = ab - \{ab\}_n. \tag{A3}$$

Therefore, in the case of CNC,

$$a_p^\dagger a_p + a_p a_p^\dagger = a_p^\dagger a_p + \left\{a_p a_p^\dagger\right\}_n = a_p^\dagger a_p - a_p^\dagger a_p = 0, \tag{A4}$$

for p such that $\varepsilon_p > 0$, and

$$a_p^\dagger a_p + a_p a_p^\dagger = \left\{a_p^\dagger a_p\right\}_n + a_p a_p^\dagger = -a_p a_p^\dagger + a_p a_p^\dagger = 0, \tag{A5}$$

for p such that $\varepsilon_p < 0$. Thus, the commutation relations consistent with CNC are

$$\begin{aligned}a_p a_q + a_q a_p &= 0,\\ a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger &= 0,\\ a_p^\dagger a_q + a_q a_p^\dagger &= 0,\end{aligned} \tag{A6}$$

which are obviously contradictory to the commutation relations of fermions,

$$\begin{aligned}a_p a_q + a_q a_p &= 0,\\ a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger &= 0,\\ a_p^\dagger a_q + a_q a_p^\dagger &= \delta_{pq}.\end{aligned} \tag{A7}$$

Similarly, in the case of CCC, the same procedure gives

$$a_p^\dagger a_p + a_p a_p^\dagger = a_p^\dagger a_p + \left[\left\{a_p a_p^\dagger\right\}_n + 1/2\right] = 1/2, \tag{A8}$$

for p such that $\varepsilon_p > 0$, and

$$a_p^\dagger a_p + a_p a_p^\dagger = \left[\left\{a_p^\dagger a_p\right\}_n + 1/2\right] + a_p a_p^\dagger = 1/2, \tag{A9}$$

for p such that $\varepsilon_p < 0$. However, CCC also gives $\mathrm{c}\left(a_p^\dagger a_p\right) = a_p^\dagger a_p - \left\{a_p^\dagger a_p\right\}_n = -(1/2)$ $(\varepsilon_p > 0)$. This relation seems inconsistent with the usual normal product $\left\{a_p^\dagger a_p\right\}_n = a_p^\dagger a_p$ $(\varepsilon_p > 0)$. In either case, Eqs. (A6), (A8), and (A9) are contradictory to the commutation relations of fermions, Eq. (A7).

This incompatibility can also be seen from the following example, even without involving commutation relations. For a vacuum $|\text{vac}\rangle = a^\dagger_{-1}a^\dagger_{-2}\cdots a^\dagger_{-N}|\text{empty}\rangle$, if we annihilate a negative energy electron with the annihilation operator a_{-1} and then create a negative energy electron with the creation operator $a^\dagger_{-1}$, we obtain

$$a^\dagger_{-1}(a_{-1}|\text{vac}\rangle) = a^\dagger_{-1}a_{-1}|\text{vac}\rangle = |\text{vac}\rangle, \tag{A10}$$

by the nature of creation/annihilation operators. However, with CNC, $a^\dagger_{-1}a_{-1} = \{a^\dagger_{-1}a_{-1}\}_n + c(a^\dagger_{-1}a_{-1}) = -a_{-1}a^\dagger_{-1}$, we have

$$a^\dagger_{-1}a_{-1}|\text{vac}\rangle = 0, \tag{A11}$$

and with CCC, $a^\dagger_{-1}a_{-1} = \{a^\dagger_{-1}a_{-1}\}_n + c(a^\dagger_{-1}a_{-1}) = -a_{-1}a^\dagger_{-1} + 1/2$, we have

$$a^\dagger_{-1}a_{-1}|\text{vac}\rangle = (1/2)|\text{vac}\rangle, \tag{A12}$$

both of which clearly differ from the result of the creation/annihilation operators of fermions, Eq. (A10).

Therefore, CNC, CCC, and the standard commutation relations of fermions cannot coexist within a single framework. Since electrons/positrons are fermions, a physical system of electrons/positrons must be described by creation/annihilation operators satisfying the commutation relations (and the standard contractions compatible with these commutation relations). If Eq. (A11) or Eq. (A12), for example, occurs during the computation in many-body theory calculations, it is evident that proper calculations cannot be performed. For this reason, we strictly separate the use of CNC or CCC from the use of standard commutation relations of fermions. That is, the use of CNC or CCC is limited to the purely formal-theoretical process of constructing the Hamiltonians, and the commutation relations of fermions are used for many-body theory calculations once the definition of the Hamiltonian is established.

APPENDIX B: MATRIX ELEMENTS FOR CI METHOD

In response to a request during the review process, this appendix shows that matrix elements of the CI method for the Hamiltonians (13) and (22) of Paper 2 are equivalent.

1. Diagonal elements

First, we present the most basic diagonal element "DHF total energy." It was shown in Paper 2 that the total energy (6) is derived using Hamiltonian (22) of Paper 2 and Slater determinant (4). In this appendix, we show that total energy (6) is also derived using Hamiltonian (13) of Paper 2 and Slater determinant (5),

$$\begin{aligned}
\left\langle\Psi_0\middle|H^{\text{QED(MO}-\text{CNC)}}_{\text{(Eq. (13) of Paper 2)}}\middle|\Psi_0\right\rangle &= \sum_i^{\text{occ(ele.)}} h_{ii} + \left(\sum_p^{(-)} h_{pp} - \sum_p^{\text{occ(pos.)}} h_{pp}\right) \\
&+ \frac{1}{2}\sum_{ij}^{\text{occ(ele.)}} [(ii|jj) - (ij|ji)] + \frac{1}{2}\sum_{pq}^{(-)} [(pp|qq) - (pq|qp)] \\
&+ \frac{1}{2}\sum_{pq}^{\text{occ(pos.)}} [(pp|qq) - (pq|qp)] + \sum_i^{\text{occ(ele.)}}\sum_p^{(-)} [(ii|pp) - (ip|pi)] \\
&- \sum_p^{(-)}\sum_q^{\text{occ(pos.)}} [(pp|qq) - (pq|qp)] \\
&- \sum_i^{\text{occ(ele.)}}\sum_p^{\text{occ(pos.)}} [(ii|pp) - (ip|pi)] \\
&- \sum_q^{(-)} h_{qq} + \frac{1}{2}\sum_{pq}^{(-)} [(pp|qq) - (pq|qp)] \\
&- \sum_i^{\text{occ(ele.)}}\sum_r^{(-)} [(ii|rr) - (ir|ri)] - \sum_{pr}^{(-)} [(pp|rr) - (pr|rp)] \\
&+ \sum_p^{\text{occ(pos.)}}\sum_r^{(-)} [(pp|rr) - (pr|rp)] \\
&= (\text{Eq. (6)}).
\end{aligned} \tag{B1}$$

In the same way as in Eq. (B1), it can be shown that for the other diagonal elements, identical elements [Eq. (80) of Paper 2] result from the combinations of Hamiltonian (22) of Paper 2 and the general Slater determinant,

$$|\Psi_J\rangle = \prod_i^{\text{occ}J\text{(ele.)}} a^\dagger_i \prod_p^{\text{occ}J\text{(pos.)}} b^\dagger_p|\text{empty}\rangle, \tag{B2}$$

as well as from the combination of Hamiltonian (13) of Paper 2 and the general Slater determinant,

$$|\Psi_J\rangle = \prod_i^{\text{occ}J\text{(ele.)}} a^\dagger_i \prod_p^{\text{occ}J\text{(pos.)}} a_p \prod_q^{(-)} a^\dagger_q|\text{empty}\rangle. \tag{B3}$$

2. Off-diagonal elements

Second, we present examples of off-diagonal matrix elements. Note that in the following, it is assumed that the phase of $|\Psi_J\rangle$ in the case of Hamiltonian (13) is adjusted to match the phase of $|\Psi_J\rangle$ in the case of Hamiltonian (22).

- Matrix element between $|\Psi_I\rangle$ and one-electron excitation determinant $|\Psi_J\rangle$.
  For Hamiltonian (22) of Paper 2, $|\Psi_I\rangle$ is given by Eq. (B2), and $|\Psi_J\rangle = a^\dagger_i a_b|\Psi_I\rangle$,

$$
\begin{aligned}
H_{IJ} &= \left\langle \Psi_I \middle| H^{\mathrm{QED(MO-CNC)}}_{\text{(Eq. (22) of Paper 2)}} \middle| \Psi_J \right\rangle \\
&= \sum_{q}^{(+)} \sum_{p}^{(-)} \left\langle \Psi_I \middle| a_p^\dagger a_q a_i^\dagger a_b \middle| \Psi_I \right\rangle h_{pq} \\
&\quad + \frac{1}{2} \sum_{pqrs}^{(+)} \left\langle \Psi_I \middle| a_p^\dagger a_r^\dagger a_s a_q a_i^\dagger a_b \middle| \Psi_I \right\rangle (pq|rs) \\
&= h_{bi} + \sum_{a}^{\mathrm{occ}I(\mathrm{ele.})} [(bi|aa) - (ba|ai)] - \sum_{p}^{\mathrm{occ}I(\mathrm{pos.})} [(bi|pp) - (bp|pi)].
\end{aligned} \tag{B4}
$$

For Hamiltonian (13) of Paper 2, $|\Psi_I\rangle$ is given by Eq. (B3), and $|\Psi_J\rangle = a_i^\dagger a_b |\Psi_I\rangle$ ($b \in \{\mathrm{occ}I(\mathrm{ele.})\}$),

$$
\begin{aligned}
H_{IJ} &= \left\langle \Psi_I \middle| H^{\mathrm{QED(MO-CNC)}}_{\text{(Eq. (13) of Paper 2)}} \middle| \Psi_J \right\rangle \\
&= \sum_{pq}^{\mathrm{all}} \left\langle \Psi_I \middle| a_p^\dagger a_q a_i^\dagger a_b \middle| \Psi_I \right\rangle \left\{ h_{pq} - \sum_{r}^{(-)} [(pq|rr) - (pr|rq)] \right\} \\
&\quad + \frac{1}{2} \sum_{pqrs}^{\mathrm{all}} \left\langle \Psi_I \middle| a_p^\dagger a_r^\dagger a_s a_q a_i^\dagger a_b \middle| \Psi_I \right\rangle (pq|rs) \\
&= h_{bi} - \sum_{r}^{(-)} [(bi|rr) - (br|ri)] + \sum_{a}^{\mathrm{occ}I(\mathrm{ele.})} [(bi|aa) - (ba|ai)] \\
&\quad + \sum_{p}^{(-)} [(bi|pp) - (bp|pi)] - \sum_{p}^{\mathrm{occ}I(\mathrm{pos.})} [(bi|pp) - (bp|pi)] \\
&= h_{bi} + \sum_{a}^{\mathrm{occ}I(\mathrm{ele.})} [(bi|aa) - (ba|ai)] - \sum_{p}^{\mathrm{occ}I(\mathrm{pos.})} [(bi|pp) - (bp|pi)] \\
&= (\text{Eq. (B4)}).
\end{aligned} \tag{B5}
$$

- Matrix element between $|\Psi_I\rangle$ and pair creation determinant $|\Psi_J\rangle$.
  For Hamiltonian (22) of Paper 2, $|\Psi_I\rangle$ is given by Eq. (B2), and $|\Psi_J\rangle = a_i^\dagger b_b^\dagger |\Psi_I\rangle$,

$$
\begin{aligned}
H_{IJ} &= \left\langle \Psi_I \middle| H^{\mathrm{QED(MO-CNC)}}_{\text{(Eq. (22) of Paper 2)}} \middle| \Psi_J \right\rangle \\
&= \sum_{q}^{(+)} \sum_{p}^{(-)} \left\langle \Psi_I \middle| b_p a_q a_i^\dagger b_b^\dagger \middle| \Psi_I \right\rangle h_{pq} \\
&\quad + \sum_{pqs}^{(+)} \sum_{r}^{(-)} \left\langle \Psi_I \middle| a_p^\dagger b_r a_s a_q a_i^\dagger b_b^\dagger \middle| \Psi_I \right\rangle (pq|rs) \\
&= h_{bi} + \sum_{a}^{\mathrm{occ}I(\mathrm{ele.})} [(bi|aa) - (ba|ai)] - \sum_{p}^{\mathrm{occ}I(\mathrm{pos.})} [(bi|pp) - (bp|pi)].
\end{aligned} \tag{B6}
$$

For Hamiltonian (13) of Paper 2, $|\Psi_I\rangle$ is given by Eq. (B3), and $|\Psi_J\rangle = a_i^\dagger a_b |\Psi_I\rangle$ ($b \in \{(-)\}$),

$$
\begin{aligned}
H_{IJ} &= \left\langle \Psi_I \middle| H^{\mathrm{QED(MO-CNC)}}_{\text{(Eq. (13) of Paper 2)}} \middle| \Psi_J \right\rangle \\
&= \sum_{pq}^{\mathrm{all}} \left\langle \Psi_I \middle| a_p^\dagger a_q a_i^\dagger a_b \middle| \Psi_I \right\rangle \left\{ h_{pq} - \sum_{r}^{(-)} [(pq|rr) - (pr|rq)] \right\} \\
&\quad + \frac{1}{2} \sum_{pqrs}^{\mathrm{all}} \left\langle \Psi_I \middle| a_p^\dagger a_r^\dagger a_s a_q a_i^\dagger a_b \middle| \Psi_I \right\rangle (pq|rs) \\
&= h_{bi} - \sum_{r}^{(-)} [(bi|rr) - (br|ri)] + \sum_{a}^{\mathrm{occ}I(\mathrm{ele.})} [(bi|aa) - (ba|ai)] \\
&\quad + \sum_{p}^{(-)} [(bi|pp) - (bp|pi)] - \sum_{p}^{\mathrm{occ}I(\mathrm{pos.})} [(bi|pp) - (bp|pi)] \\
&= h_{bi} + \sum_{a}^{\mathrm{occ}I(\mathrm{ele.})} [(bi|aa) - (ba|ai)] - \sum_{p}^{\mathrm{occ}I(\mathrm{pos.})} [(bi|pp) - (bp|pi)] \\
&= (\text{Eq. (B6)}).
\end{aligned} \tag{B7}
$$

Similarly, the agreement of the matrix elements between $|\Psi_I\rangle$ and two-particle difference determinants $|\Psi_K\rangle$ can be confirmed. For Hamiltonian (13) of Paper 2, determinants $|\Psi_K\rangle = a_j^\dagger a_c a_i^\dagger a_b |\Psi_I\rangle$ are the two-electron excitation ($b, c \in \{\mathrm{occ}I(\mathrm{ele.})\}$), the one-pair creation and one-electron excitation ($b \in \{\mathrm{occ}I(\mathrm{ele.})\}$ and $c \in \{(-)\}$), and the two-pair creation ($b, c \in \{(-)\}$),

$$
\begin{aligned}
H_{IJ} &= \left\langle \Psi_I \middle| H^{\mathrm{QED(MO-CNC)}}_{\text{(Eq. (13) of Paper 2)}} \middle| \Psi_K \right\rangle \\
&= \frac{1}{2} \sum_{pqrs}^{\mathrm{all}} \left\langle \Psi_I \middle| a_p^\dagger a_r^\dagger a_s a_q a_j^\dagger a_c a_i^\dagger a_b \middle| \Psi_I \right\rangle (pq|rs) \\
&= (bi|cj) - (bj|ci),
\end{aligned} \tag{B8}
$$

which is also obtained from Hamiltonian (22) of Paper 2 and determinants $|\Psi_K\rangle = a_j^\dagger a_c a_i^\dagger a_b |\Psi_I\rangle$, $a_j^\dagger b_c^\dagger a_i^\dagger a_b |\Psi_I\rangle$, and $a_j^\dagger b_c^\dagger a_i^\dagger b_b^\dagger |\Psi_I\rangle$.

REFERENCES

[1] W. Liu, J. Chem. Phys. **160**, 187101 (2024).
[2] N. Inoue, Y. Watanabe, and H. Nakano, J. Chem. Phys. **159**, 054105 (2023).
[3] T. Udagawa and M. Tachikawa, *Multi-Component Molecular Orbital Theory* (Nova Science Publishing, Inc., 2008).
[4] E. A. Uehling, Phys. Rev. **48**, 55 (1935).
[5] C. Hainzl, M. Lewin, E. Séré, and J. P. Solovej, Phys. Rev. A: At., Mol., Opt. Phys. **76**, 052104 (2007).
[6] P. Chaix and D. Iracane, J. Phys. B: At., Mol. Opt. Phys. **22**, 3791 (1989).
[7] P. Chaix, D. Iracane, and P. L. Lions, J. Phys. B: At., Mol. Opt. Phys. **22**, 3815 (1989).