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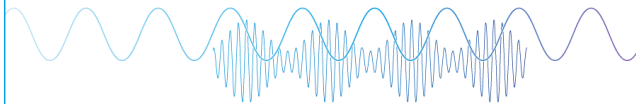
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## ABSTRACT

Theoretical discussions are given on issues in relativistic molecular orbital theory to which the quantum electrodynamics (QED) Hamiltonian is applied. First, several QED Hamiltonians previously proposed are sifted by the orbital rotation invariance, the charge conjugation and time reversal invariance, and the nonrelativistic limit. The discussion on orbital rotation invariance shows that orbitals giving a stationary point of total energy should be adopted for QED Hamiltonians that are not orbital rotation invariant. A new total energy expression is then proposed, in which a counter term corresponding to the energy of the polarized vacuum is subtracted from the total energy. This expression prevents the possibility of total energy divergence due to electron correlations, stemming from the fact that the QED Hamiltonian does not conserve the number of particles. Finally, based on the Hamiltonian and energy expression, the Dirac–Hartree–Fock (DHF) and electron correlation methods are reintroduced. The QED-based DHF equation is shown to give information on positrons from negative-energy orbitals while having the same form as the conventional DHF equation. Three electron correlation methods are derived: the QED-based configuration interactions and single- and multireference perturbation methods. Numerical calculations show that the total energy of the QED Hamiltonian indeed diverged and that the counter term is effective in avoiding the divergence. The relativistic molecular orbital theory presented in this article also provides a methodology for dealing with systems containing positrons based on the QED Hamiltonian.

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## I. INTRODUCTION

The relativistic electronic structure theory, which is based on the Dirac equation, is a powerful tool to understand the properties of systems containing heavy or superheavy elements.<sup>1</sup> Nowadays, the relativistic Hartree–Fock (HF) method<sup>2,3</sup> and electron correlation methods, such as density functional theory,<sup>4</sup> Møller–Plesset (MP) perturbation method,<sup>5</sup> configuration interaction (CI) method,<sup>6</sup> multiconfiguration self-consistent field method,<sup>7</sup> multireference perturbation method,<sup>8–10</sup> multireference coupled-cluster method,<sup>11</sup> two-time Green’s function method,<sup>12</sup> and polarization propagator method,<sup>13</sup> have been developed and used. The relativistic electronic structure theory is also useful to understand magnetic phenomena because the spin–orbit interaction is naturally included through the Dirac equation. In fact, the nuclear magnetic resonance (NMR) shielding constants can be reproduced by taking into account the spin–orbit interaction.<sup>14</sup> One of the major differences between the Dirac equation and the nonrelativistic Schrödinger equation is that the former has negative kinetic energy solutions as well as positive kinetic energy solutions. This is based on the fact that the relativistic dispersion relationship between energy and momentum is

a quadratic equation:  $E^2 = m^2 c^4 + p^2 c^2$ , i.e.,  $E = \pm(m^2 c^4 + p^2 c^2)^{1/2}$ . This negative kinetic energy is conventionally referred to simply as “negative energy,” and we, hereafter, follow this convention. The problem of the negative-energy solution itself has already been solved by the relativistic quantum field theory.<sup>15–18</sup> The relativistic quantum field theory assumed that all negative-energy levels are filled with unobservable electrons and regard holes in negative energy levels as positrons. This interpretation not only solved the aforementioned negative energy solution problem but also predicted the pair-creation/annihilation of electron–positron pairs.

In the relativistic molecular orbital method, the basic Hamiltonian is the Dirac–Coulomb (DC) Hamiltonian,

$$H^{\text{DC}} = \sum_i \left( \begin{bmatrix} \mathbf{0}_2 & \mathbf{c}\boldsymbol{\sigma} \cdot \mathbf{p}_i \\ \mathbf{c}\boldsymbol{\sigma} \cdot \mathbf{p}_i & -2mc^2 \mathbf{1}_2 \end{bmatrix} - \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \begin{bmatrix} \mathbf{1}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & \mathbf{1}_2 \end{bmatrix} \right) + \sum_{i>j} \frac{\mathbf{1}_4(i)\mathbf{1}_4(j)}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1)$$

which introduces the Dirac Hamiltonian and Coulomb repulsion as the one-electron Hamiltonian and two-electron potential, respectively. The second-quantized Hamiltonian, which is represented simply by the electron creation/annihilation operators, regardless of whether the energies of the orbitals expressing the Hamiltonian are positive or negative, is the virtual pair approximation (VPA) Hamiltonian,<sup>19</sup>

$$H^{\text{VPA}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q, \quad (2)$$

where  $a_p^\dagger$  and  $a_r^\dagger$  are electron creation operators, and  $a_q$  and  $a_s$  are electron annihilation operators. The orbital sums are taken for all the orbitals. The integrals  $h_{pq}$  and  $(pq|rs)$  are defined as

$$h_{pq} = \int d^3\mathbf{r} \psi_p^\dagger(\mathbf{r}) \left( \begin{bmatrix} \mathbf{0}_2 & c\boldsymbol{\sigma} \cdot \mathbf{p} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} & -2mc^2 \mathbf{1}_2 \end{bmatrix} - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \begin{bmatrix} \mathbf{1}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & \mathbf{1}_2 \end{bmatrix} \right) \psi_q(\mathbf{r}), \quad (3)$$

$$(pq|rs) = \int \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \psi_p^\dagger(\mathbf{r}_1) \psi_q(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_r^\dagger(\mathbf{r}_2) \psi_s(\mathbf{r}_2). \quad (4)$$

Alternatively, the second-quantized Hamiltonian, restricted to include only positive-energy orbitals, is the no virtual pair approximation (NVPA) Hamiltonian, often used in relativistic molecular orbital theory,<sup>20</sup>

$$H^{\text{NVPA}} = \sum_{pq}^{(+)} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{(+)} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q, \quad (5)$$

where the orbital sums (+) are taken only for the positive-energy orbitals. The VPA and NVPA Hamiltonians have their own theoretical problems when applied to relativistic electron correlation theory. The VPA Hamiltonian is problematic because it does not employ the remedy to the aforementioned negative energy problem. The NVPA Hamiltonian also has the problem that the Fock space used is not complete.

In contrast to the VPA and NVPA Hamiltonians, which have these problems, a second-quantized Hamiltonian that applies the aforementioned remedy for the negative energy problem is the quantum electrodynamics (QED) Hamiltonian.<sup>21–25</sup> Note that the QED in this paper is the so-called no-photon QED and that the quantum effects of an electromagnetic field, the other important aspect of the QED,<sup>26–32</sup> are not treated in this paper. Even in the QED Hamiltonian, several issues need to be investigated. The first is the choice of the QED Hamiltonian to be employed. Several different QED Hamiltonians have been proposed to date,<sup>21–25,33,34</sup> depending on the type of contraction of the creation/annihilation operators and the representing orbitals. Because there should be only one “legitimate” Hamiltonian describing nature, we need to examine which one should be adopted through theoretical requirements. Second, since the choice of orbitals used to describe the second quantized Hamiltonian can be directly related to the division of electron and positron space in the QED Hamiltonian, the necessity of choosing orbitals beyond the HF method should also

be discussed. Third, it is not known whether the combination of the QED Hamiltonian and electron correlation theory works properly. Since the QED Hamiltonian can describe the pair-creation of electrons and positrons, electron correlation can cause the total number of particles in the system to fluctuate. The effects of this fluctuation in the number of particles should be verified. Relativistic molecular orbital methods based on the QED Hamiltonian may also provide an effective way to utilize negative-energy orbitals, which have been “nuisances” in conventional relativistic molecular orbital methods. In this article, we attempt to provide theoretical considerations for these issues. The proper way to partition the electron and positron space will be considered along with orbital rotational invariance.

The arrangement of this article is as follows: In Sec. II, QED Hamiltonians are examined and then sifted for proper QED Hamiltonians that satisfy the physical requirements [orbital rotation invariance, charge conjugation and time reversal (CT) invariance, and the nonrelativistic limit], and a total energy expression that can exclude divergences by the electron correlations from pair-created configurations is proposed. The issue of the partitioning of the space between electrons and positrons is discussed along with orbital rotational invariance. Based on the sifted QED Hamiltonian and the proposed total energy expression, the relativistic molecular orbital theory is rederived. In Sec. III, some of the theoretical considerations in Sec. II are confirmed numerically. The conclusions are presented in Sec. IV.

## II. THEORY

In this section, we discuss several issues of relativistic molecular orbital methods applying the QED Hamiltonian and propose remedies if the existence of the problems is confirmed. First, we systematically list the QED Hamiltonians treated in this paper, including the already proposed QED Hamiltonians and some new ones considered as variations of them. Which of these QED Hamiltonians should be adopted is sifted according to whether it satisfies the three physical requirements associated with positrons. We also propose new total energy expressions for the QED-based electron correlation methods. Based on these arguments, the relativistic molecular orbital method will be re-derived in a form based on the QED Hamiltonian.

### A. Examination of QED Hamiltonians

In this subsection, we examine the expression of the QED Hamiltonian. The QED Hamiltonian here is a Hamiltonian that is based on the picture that the negative energy levels are filled with electrons or that the holes in the negative energy levels are regarded as antiparticles. Several different formulations of the QED Hamiltonian have been proposed, depending on the reference vacuums and other factors. Here, determining the reference vacuum is essentially the same as determining the *representing orbitals* that represent the creation/annihilation operators. In this subsection, considering the possibility that there may be other candidates for the QED Hamiltonians, we will reconsider the systematic derivation and classification of the QED Hamiltonians. The change from the VPA Hamiltonian to the QED Hamiltonian has been treated in a number of references (Refs. 35–37), but we employ the method described in Refs. 24

and 36. This change is also regarded as the change from the configuration space to the Fock space.<sup>38</sup> The VPA Hamiltonian (2) can be rewritten as follows:

$$H^{\text{VPA}} = \sum_{pq}^{\text{all}} h_{pq} \{a_p^\dagger a_q\}_n + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) \{a_p^\dagger a_r^\dagger a_s a_q\}_n + \sum_{pqrs}^{\text{all}} [(pq|rs) - (ps|rq)] \{a_p^\dagger a_q\}_n \langle 0_0 | a_r^\dagger a_s | 0_0 \rangle + \sum_{pq}^{\text{all}} h_{pq} \langle 0_0 | a_p^\dagger a_q | 0_0 \rangle + \frac{1}{2} \sum_{pqrs}^{\text{all}} [(pq|rs) - (ps|rq)] \times \langle 0_0 | a_p^\dagger a_q | 0_0 \rangle \langle 0_0 | a_r^\dagger a_s | 0_0 \rangle, \quad (6)$$

where  $|0_0\rangle$  is the single configuration vacuum and the subscript “0” indicates “single configuration,” and  $\{\}_n$  is the normal ordering and the subscript “n” indicates “normal.” Note that the single configuration vacuum does not include the electron correlation and is not the true vacuum state.

By eliminating the constant terms [the fourth and fifth terms in Eq. (6)], we obtain a QED Hamiltonian. To obtain specific forms, it is necessary to specify the contraction  $\langle 0_0 | a_p^\dagger a_q | 0_0 \rangle$ , and furthermore, the representing orbitals defining integrals and creation/annihilation operators. There are three choices for the contraction. One is

$$\langle 0_0 | a_p^\dagger a_q | 0_0 \rangle \equiv 0, \quad (7)$$

which we, hereafter, refer to as the “constantly null contraction (CNC).” Another is the charge-conjugate contraction (CCC) as proposed by Liu *et al.*,<sup>25,34,39</sup>

$$\langle 0_0 | a_p^\dagger a_q | 0_0 \rangle \equiv \begin{cases} (-1/2)\delta_{pq} & (p, q \in \{(+)\}), \\ (1/2)\delta_{pq} & (p, q \in \{(-)\}), \\ 0 & (\text{other cases}), \end{cases} \quad (8)$$

and the last one is the conventional contraction (cC),

$$\langle 0_0 | a_p^\dagger a_q | 0_0 \rangle \equiv \begin{cases} \delta_{pq} & (p, q \in \{(-)\}), \\ 0 & (\text{other cases}). \end{cases} \quad (9)$$

There are also three choices for representing orbitals. One is the so-called molecular orbitals (MOs), which are orbitals that are solutions of the Hartree–Fock or multi-configurational self-consistent field (MCSCF) method. Another is free-particle orbitals, which are eigenfunctions of kinetic energy part of the one electron Dirac Hamiltonian, and the last one is the Furry orbitals, which are eigenfunctions of the one-electron Dirac Hamiltonian. Hereinafter, the MOs are not enclosed with brackets, the free-particle orbitals are enclosed with square brackets “[],” and the Furry orbitals are enclosed with double square brackets “[[]]” to distinguish them. Note that if the free-particle or Furry orbitals are adopted as the representing orbitals, the normal ordering and the contraction must be redefined for the free-particle or Furry orbitals rather than the MOs (e.g.,  $p \rightarrow [p]$  or

$p \rightarrow [[p]]$ ). The single configuration vacuum  $|0_0\rangle$  are also redefined accordingly,

$$|0_0\rangle \equiv |0_0^{(\text{MO})}\rangle = a_{-1}^\dagger a_{-2}^\dagger \cdots a_{-\infty}^\dagger |\text{empty}\rangle, \quad (10)$$

$$|0_0\rangle \equiv |0_0^{(\text{free})}\rangle = a_{[-1]}^\dagger a_{[-2]}^\dagger \cdots a_{[-\infty]}^\dagger |\text{empty}\rangle, \quad (11)$$

and

$$|0_0\rangle \equiv |0_0^{(\text{Furry})}\rangle = a_{[[ -1 ]]}^\dagger a_{[[ -2 ]]}^\dagger \cdots a_{[[ -\infty ]]}^\dagger |\text{empty}\rangle, \quad (12)$$

when the representing orbitals are MOs, free-particles, and Furry orbitals, respectively. Here,  $|\text{empty}\rangle$  is the *completely empty state*; in other words, the state that vanishes by an operation of any (i.e., regardless of positive- or negative-electron energy) electron annihilation operators.

Nine different QED Hamiltonians are possible from three different contractions and three different representing orbitals. We will give systematic names to these nine QED Hamiltonians for convenience in this paper.

If CNC is employed, and, in addition, the representing orbitals of MOs, free-particle orbitals, and Furry orbitals are employed, then the QED(MO-CNC) Hamiltonian,<sup>21–25</sup>

$$H^{\text{QED(MO-CNC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{pp} + \frac{1}{2} \sum_{pq}^{(-)} [(pp|qq) - (pq|qp)] - \sum_{pq}^{\text{all}} \sum_r^{(-)} [(pq|rr) - (pr|rq)] a_p^\dagger a_q, \quad (13)$$

QED(free-CNC) Hamiltonian,<sup>33</sup>

$$H^{\text{QED(free-CNC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{[pp]} + \frac{1}{2} \sum_{pq}^{(-)} \{([pp][qq]) - ([pq][qp])\} - \sum_{pq}^{\text{all}} \sum_r^{(-)} \{(pq|[rr]) - (p[r][r]q)\} a_p^\dagger a_q, \quad (14)$$

and QED(Furry-CNC) Hamiltonian,

$$H^{\text{QED(Furry-CNC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{[[pp]]} + \frac{1}{2} \sum_{pq}^{(-)} \{([[pp]][[qq]]) - ([[pq]][[qp]])\} - \sum_{pq}^{\text{all}} \sum_r^{(-)} \{(pq[[rr]]) - (p[[r]][[r]q])\} a_p^\dagger a_q, \quad (15)$$

are obtained, respectively.

Then, if CCC is employed, and, in addition, the representing orbitals of MOs, free-particle orbitals, and Furry orbitals are employed, then the QED(MO-CCC) Hamiltonian,

$$H^{\text{QED(MO-CCC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{pp} + \frac{1}{2} \sum_p^{(-)} \sum_q^{(+)} [(pp|qq) - (pq|qp)] - \frac{1}{2} \sum_{pq}^{\text{all}} \sum_r^{\text{all}} [(pq|rr) - (pr|rq)] a_p^\dagger a_q, \quad (16)$$

QED(free-CCC) Hamiltonian,

$$H^{\text{QED(free-CCC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{[pp]} + \frac{1}{2} \sum_p^{(-)} \sum_q^{(+)} \{([pp]||[qq]) - ([pq]||[qp])\} - \frac{1}{2} \sum_{pq}^{\text{all}} \sum_r^{\text{all}} \{(pq|[rr]) - (p[r]||[r]q)\} a_p^\dagger a_q, \quad (17)$$

and QED(Furry-CCC) Hamiltonian,

$$H^{\text{QED(Furry-CCC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{[pp]} + \frac{1}{2} \sum_p^{(-)} \sum_q^{(+)} \{([pp]||[qq]) - ([pq]||[qp])\} - \frac{1}{2} \sum_{pq}^{\text{all}} \sum_r^{\text{all}} \{(pq|[rr]) - (p[[r]||[r]q)\} a_p^\dagger a_q, \quad (18)$$

are obtained, respectively.

Finally, if cC is employed, and, in addition, the representing orbitals of MOs, free-particle orbitals, and Furry orbitals are employed, then the QED(MO-cC) Hamiltonian,

$$H^{\text{QED(MO-cC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{pp} - \frac{1}{2} \sum_{pq}^{(-)} [(pp|qq) - (pq|qp)], \quad (19)$$

QED(free-cC) Hamiltonian,

$$H^{\text{QED(free-cC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{[pp]} - \frac{1}{2} \sum_p^{(-)} \{([pp]||[qq]) - ([pq]||[qp])\}, \quad (20)$$

and QED(Furry-cC) Hamiltonian,

$$H^{\text{QED(Furry-cC)}} = \sum_{pq}^{\text{all}} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - \sum_p^{(-)} h_{[[pp]]} - \frac{1}{2} \sum_{pq}^{(-)} \{([pp]||[qq]) - ([pq]||[qp])\}, \quad (21)$$

are obtained, respectively.

Here, four of the nine QED Hamiltonians are already reported in important previous studies. QED(MO-CNC) is equivalent to the widely known "QED Hamiltonian,"<sup>21-25</sup>

$$H^{\text{QED(MO-CNC)}} = \sum_{pq}^{(+)} h_{pq} a_p^\dagger a_q - \sum_{pq}^{(-)} h_{pq} b_q^\dagger b_p + \sum_p^{(+)} \sum_q^{(-)} h_{pq} a_p^\dagger b_q^\dagger + \sum_q^{(+)} \sum_p^{(-)} h_{pq} b_p b_q + \frac{1}{2} \left( \sum_{pqrs}^{(+)} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q - 2 \sum_{pq}^{(+)} \sum_{rs}^{(-)} (pq|rs) a_p^\dagger b_s^\dagger b_r a_q + 2 \sum_{ps}^{(+)} \sum_{qr}^{(-)} (pq|rs) a_p^\dagger b_q^\dagger b_r a_s + \sum_{pqrs}^{(-)} (pq|rs) b_s^\dagger b_q^\dagger b_p b_r + 2 \sum_{pqr}^{(+)} \sum_s^{(-)} (pq|rs) a_p^\dagger a_r^\dagger b_s^\dagger a_q - 2 \sum_r^{(+)} \sum_{pq}^{(-)} (pq|rs) a_r^\dagger b_s^\dagger b_q^\dagger b_p + 2 \sum_{pq}^{(+)} \sum_r^{(-)} (pq|rs) a_p^\dagger b_r a_s a_q - 2 \sum_s^{(+)} \sum_{pqr}^{(-)} (pq|rs) b_q^\dagger b_p b_r a_s + \sum_{pr}^{(+)} \sum_{qs}^{(-)} (pq|rs) a_p^\dagger a_r^\dagger b_s^\dagger b_q^\dagger + \sum_{pr}^{(+)} \sum_{qs}^{(-)} (pq|rs) b_p b_r a_s a_q \right), \quad (22)$$

where  $b_p^\dagger$  and  $b_p$  are creation and annihilation operators of a positron, respectively. As a footnote, Eq. (13) can also be obtained by replacing the operators in Eq. (22) as  $b_p^\dagger \rightarrow a_p$  and  $b_p \rightarrow a_p^\dagger$  and ordering them with the anticommutation relations. The reference vacuum corresponding to Eq. (22) is  $|empty\rangle$  and that corresponding to Eq. (13) is  $|0_0^{(\text{MO})}\rangle$ , which is the same reference vacuum but apparently different. In addition, QED(free-CNC) is already proposed by Saue and Visscher,<sup>33</sup> QED(MO-CCC) is equivalent to Eq. (27) in Ref. 34, and QED(free-CCC) is equivalent to Eq. (98) in Ref. 34. The Hamiltonian of Eq. (67) in Ref. 34 differ only in constant terms from QED(free-CCC); hence, they are essentially identical.

We need to choose the most proper QED Hamiltonians. The discussion that follows requires some conditions that seem physically appropriate for many-body systems of electrons and positrons.

## B. Fundamental requirements for the QED Hamiltonian: Orbital rotation invariance, CT invariance, and nonrelativistic limit

In this section, we discuss the orbital rotation invariance, CT invariance, and nonrelativistic limit of the Hamiltonian as requirements for the second-quantized relativistic Hamiltonian. We focus on these three requirements because the orbital rotation invariance is closely related to the partitioning of the orbital space describing electrons and positrons, the CT invariance is related to the symmetry between electrons and positrons, and, in the nonrelativistic limit, the symmetry between electrons and positrons must also hold. After sifting the candidates for the Hamiltonian using these three requirements, we discuss the expression of total energy for the Hamiltonian.

### 1. Orbital rotation invariance

First, we discuss the orbital rotation invariance of the Hamiltonian. Orbital rotation including negative-energy orbitals was first considered in Ref. 40. Consider the orbital rotation, namely, the unitary transformation for MOs,

$$\varphi_i \rightarrow \varphi'_i = \sum_n U_{ni} \varphi_n. \quad (23)$$

The corresponding unitary transformation for the annihilation operators is given by

$$a_i \rightarrow a'_i = \sum_n (U^\dagger)_{in} a_n. \quad (24)$$

Using these expressions, the one- and two-electron terms of the VPA Hamiltonian are transformed as follows:

$$\begin{aligned} \sum_{ij}^{\text{all}} h_{ij} a_i^\dagger a_j &\rightarrow \sum_{ij}^{\text{all}} h'_{ij} a_i'^\dagger a'_j = \sum_{ijmn}^{\text{all}} (U^\dagger)_{im} h_{mn} U_{nj} U_{mi} a_m^\dagger (U^\dagger)_{jn} a_n \\ &= \sum_{mn}^{\text{all}} h_{mn} a_m^\dagger a_n, \end{aligned} \quad (25)$$

$$\begin{aligned} \sum_{ijkl}^{\text{all}} (ij|kl) a_i^\dagger a_k^\dagger a_l a_j &\rightarrow \sum_{ijkl}^{\text{all}} (ij|kl)' a_i'^\dagger a_k'^\dagger a_l' a_j' \\ &= \sum_{ijklpqrs}^{\text{all}} (U^\dagger)_{ip} U_{qj} (pq|rs) (U^\dagger)_{kr} \\ &\quad \times U_{si} U_{pi} a_p^\dagger U_{rk} a_r^\dagger (U^\dagger)_{ls} a_s (U^\dagger)_{jq} a_q \\ &= \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q. \end{aligned} \quad (26)$$

These results show that the VPA Hamiltonian is invariant for the orbital rotation. In the same manner, we can easily show that the QED(free-CNC), QED(Furry-CNC), QED(free-CCC), QED(Furry-CCC), QED(free-cC), and QED(Furry-cC) Hamiltonians are also invariant for orbital rotation.

In contrast, the QED(MO-CNC) Hamiltonian is not invariant for the transformation. To see how the QED Hamiltonian is transformed, we take a term  $\sum_{ij}^{\text{all}} \sum_k^{(-)} [(ij|kk) - (ik|kj)] a_i^\dagger a_j$  in  $H^{\text{QED(MO-CNC)}}$  as an example. This term is transformed by the orbital rotation as follows:

$$\begin{aligned} \sum_{ij}^{\text{all}} \sum_k^{(-)} [(ij|kk) - (ik|kj)] a_i^\dagger a_j &\rightarrow \sum_{ijrs}^{\text{all}} \sum_k^{(-)} [(ij|kk)' - (ik|kj)'] a_i'^\dagger a'_j \\ &= \sum_{ijpqrs}^{\text{all}} \sum_k^{(-)} (U^\dagger)_{ip} U_{qj} [(pq|rs) - (ps|rq)] (U^\dagger)_{kr} \\ &\quad \times U_{sk} U_{pi} a_p^\dagger (U^\dagger)_{jq} a_q \\ &= \sum_{pqrs}^{\text{all}} \sum_k^{(-)} (U^\dagger)_{kr} U_{sk} [(pq|rs) - (ps|rq)] a_p^\dagger a_q \\ &\neq \sum_{pq}^{\text{all}} \sum_r^{(-)} [(pq|rr) - (pr|rq)] a_p^\dagger a_q. \end{aligned} \quad (27)$$

This is clearly not invariant because the summation for  $k$  is taken not for all the orbitals but only for the negative-energy orbitals. The same is true for the other terms, showing that the total QED Hamiltonian is not orbital rotation invariant. In other words, QED(MO-CNC), QED(MO-CCC), and QED(MO-cC) Hamiltonians are orbital rotation invariant only for special orbital rotations that do not mix positive- and negative-energy orbitals, i.e., orbital rotations represented by block diagonal matrices for the positive- and negative-energy orbital parts. The general orbital rotations obviously have no such special properties and consequently change the QED(MO-CNC), QED(MO-CCC), and QED(MO-cC) Hamiltonians. This fact is easily understood as follows: In the case that the representing orbitals are MOs, the partitioning of the electron and positron orbital spaces is variable for the orbital rotation, whereas in the case that the representing orbitals are the free particle or Furry orbitals, the partitioning is fixed. This difference in the variable and fixed partitioning between the electron and positron orbital space is responsible for the orbital rotation invariance of the Hamiltonian.

If a Hamiltonian does not have orbital rotation invariance, even if we construct the wave function with all possible configurations, namely, excitations, pair creations, and pair annihilations, we cannot obtain unique energy spectra. This is in sharp contrast to the nonrelativistic Hamiltonian, for which we can obtain the unique spectra using the full CI for any orbital sets made from a common basis set. These situations are also the case for the NVPA Hamiltonian.

The discussion thus far has shown that some QED Hamiltonians are not orbital rotation invariant. This fact seems to indicate that some QED Hamiltonians have a problem giving different spectra depending on the orbital sets. However, this problem is resolved by considering the time dependency of the states. As the spectra are the expectation values of the total energy in the stationary state, the orbitals used to calculate the spectra must be ones capable of constituting the stationary state, and such orbitals must themselves be stationary: i.e., they must not evolve in time. In other words, by

using the stationary orbitals, the spectra are uniquely determined even without orbital rotation invariance in stationary states, which is in contrast to general (nonstationary) states, where any orbitals are allowed. Therefore, the orbital rotation invariance for the QED Hamiltonians itself is not necessarily essential. Note here that in this paper, the term “stationary” is used in two senses: one is used to mean that a variable does not evolve in time, and the other is used to mean that the derivative of a function or functional derivative is zero (i.e., at the maximum, minimum, or saddle point). We write simply “stationary” when we use it in the former sense and “stationary point” in the latter sense.

Then, how can the stationary orbitals that are suitable for the QED-level MO calculations be obtained? The answer to this question lies in finding the MOs giving a stationary point of total energy, as we usually do in the nonrelativistic electronic structure calculations. In fact, from the time-dependent variational principle, it can be shown that MOs (and CI coefficients) giving a stationary point of total energy do not evolve in time, but the derivation itself is left to the Appendix. Consequently, the problem of the QED Hamiltonian not being orbital rotation invariant is solved by using these optimal MOs.

Thus, we have determined the orbital rotation invariance/noninvariance of the Hamiltonians. By employing the proper MOs, even orbital rotation invariant Hamiltonians are not sifted out, but it should be noted that it is not possible to choose arbitrary MOs when using such Hamiltonians for stationary state calculations.

## 2. CT invariance

We next discuss the CT invariance. The CT transformation is a composite transformation of the charge conjugation<sup>25</sup> and time reversal<sup>41</sup> (C and T) transformations, defined as

$$\hat{C}\hat{K} = \hat{K}\hat{C} = \begin{bmatrix} 0 & \mathbf{1}_2 \\ -\mathbf{1}_2 & 0 \end{bmatrix} \quad (28)$$

in matrix form, where

$$\hat{C} = \begin{bmatrix} 0 & i\sigma_y \\ -i\sigma_y & 0 \end{bmatrix} \hat{K}_0 \quad (29)$$

and

$$\hat{K} = \begin{bmatrix} -i\sigma_y & 0 \\ 0 & -i\sigma_y \end{bmatrix} \hat{K}_0 \quad (30)$$

are the C and T transformation operators, respectively. Here,  $\hat{K}_0$  is the complex conjugation operator. Applying the CT transformation [Eq. (28)] to the Dirac equation,

$$\begin{bmatrix} V\mathbf{1}_2 & \mathbf{c}\boldsymbol{\sigma} \cdot \mathbf{p} \\ \mathbf{c}\boldsymbol{\sigma} \cdot \mathbf{p} & V\mathbf{1}_2 - 2mc^2\mathbf{1}_2 \end{bmatrix} \begin{bmatrix} \Psi^L \\ \Psi^S \end{bmatrix} = E \begin{bmatrix} \Psi^L \\ \Psi^S \end{bmatrix}, \quad (31)$$

we obtain the CT-transformed Dirac equation,

$$\begin{bmatrix} -V\mathbf{1}_2 & \mathbf{c}\boldsymbol{\sigma} \cdot \mathbf{p} \\ \mathbf{c}\boldsymbol{\sigma} \cdot \mathbf{p} & -V\mathbf{1}_2 - 2mc^2\mathbf{1}_2 \end{bmatrix} \begin{bmatrix} \Psi^S \\ -\Psi^L \end{bmatrix} = (-E - 2mc^2) \begin{bmatrix} \Psi^S \\ -\Psi^L \end{bmatrix} = \tilde{E} \begin{bmatrix} \Psi^S \\ -\Psi^L \end{bmatrix}, \quad (32)$$

where  $\tilde{E} = -E - 2mc^2$  is *reinterpreted energy*: if  $E$  is negative,  $\tilde{E}$  gives positive (normal) energy. This CT-transformed Dirac equation [Eq. (32)] contains a potential of inverse sign that gives antiparticle solutions,<sup>42,43</sup> and the associated eigen spinor has the form of exchanged large and small components. The *reinterpreted energy* corresponds to the energy of positrons without the rest mass energy. Therefore, negative-energy orbitals with negative and positive *reinterpreted energy* represent the bound and unbound positrons, respectively. Here, the fact that the negative-energy solutions are associated with antiparticles by  $\tilde{E}$  rather than  $E$  indicates that the particle-hole relationship is inverted in the negative-energy solutions.

Based on the properties of the CT transformation for the one-particle Dirac equation, we next discuss the CT transformation for the multiparticle (DC) Hamiltonian. Here, as preparation before CT transformation, we rewrite Eq. (13). Because the indices in the sums run over all the orbitals, including both Kramers pairs ( $p$  and  $\bar{p}$ ), we can rewrite Eq. (13) by changing the order of the orbitals in the sums,

$$\begin{aligned} H^{\text{QED(MO-CNC)}} &= \sum_{pq}^{\text{all}} h_{\bar{p}\bar{q}} a_{\bar{p}}^\dagger a_{\bar{q}} + \frac{1}{2} \sum_{pqrs}^{\text{all}} (\bar{p}\bar{q}|\bar{r}\bar{s}) a_{\bar{p}}^\dagger a_{\bar{r}}^\dagger a_s a_{\bar{q}} \\ &\quad - \sum_p^{(-)} h_{\bar{p}\bar{p}} + \frac{1}{2} \sum_{pq}^{(-)} [(\bar{p}\bar{p}|\bar{q}\bar{q}) - (\bar{p}\bar{q}|\bar{q}\bar{p})] \\ &\quad - \sum_{pq}^{\text{all}} \sum_r^{(-)} [(\bar{p}\bar{q}|\bar{r}\bar{r}) - (\bar{p}\bar{r}|\bar{r}\bar{q})] a_{\bar{p}}^\dagger a_{\bar{q}}. \end{aligned} \quad (33)$$

It should be noted that it is simply a change in the order of the sum. This manipulation is done to make it easier to see the final result of the CT transformation. Applying CT transformation to the Hamiltonian, the creation/annihilation operators and molecular integrals change as follows:

$$a_p^\dagger \rightarrow a_{\bar{p}}, \quad a_p \rightarrow a_{\bar{p}}^\dagger, \quad h_{pq} \rightarrow -h_{\bar{p}\bar{q}}^{\text{CT}} \quad \text{and} \quad (pq|rs) \rightarrow (pq|rs)^{\text{CT}}, \quad (34)$$

and we obtain

$$\begin{aligned} (H^{\text{QED(MO-CNC)}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs)^{\text{CT}} a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{pp}^{\text{CT}} + \frac{1}{2} \sum_{pq}^{(+)} [(pp|qq)^{\text{CT}} - (pq|qp)^{\text{CT}}] \\ &\quad - \sum_{pq}^{\text{all}} \sum_r^{(+)} [(pq|rr)^{\text{CT}} - (pr|rq)^{\text{CT}}] a_p^\dagger a_q \end{aligned} \quad (35)$$

with

$$h_{pq}^{\text{CT}} = \int d^3\mathbf{r} \psi_p^\dagger(\mathbf{r}) \begin{bmatrix} -V\mathbf{1}_2 + 2mc^2\mathbf{1}_2 & \mathbf{c}\boldsymbol{\sigma} \cdot \mathbf{p} \\ \mathbf{c}\boldsymbol{\sigma} \cdot \mathbf{p} & -V\mathbf{1}_2 \end{bmatrix} \psi_q(\mathbf{r}), \quad (36)$$

$$(pq|rs)^{\text{CT}} = (pq|rs).$$

This CT-transformed Hamiltonian includes the external field potential of the inverse sign, and the rest mass energy is attached to the particles, not the antiparticles. This means that the CT-transformed Hamiltonian is essentially the same as if it were formulated by simply swapping the particles and antiparticles. Hence, it gives the same solutions as those of the original Hamiltonian. In this meaning, the QED(MO-CNC) Hamiltonian is CT invariant. In a similar way, QED(free-CNC), QED(Furry-CNC), QED(MO-CCC), QED(free-CCC), and QED(Furry-CCC) Hamiltonians are shown to be CT invariant, as follows:

$$\begin{aligned} (H^{\text{QED(free-CNC)}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{[pp]}^{\text{CT}} + \frac{1}{2} \sum_p^{(+)} \{([pp][qq]) - ([pq][qp])\} \\ &\quad - \sum_{pq}^{\text{all}} \sum_r^{(+)} \{(pq|[rr]) - (p[r][r]q)\} a_p^\dagger a_q, \quad (37) \end{aligned}$$

$$\begin{aligned} (H^{\text{QED(Furry-CNC)}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{[pp]}^{\text{CT}} + \frac{1}{2} \sum_p^{(+)} \\ &\quad \times \{([pp][qq]) - ([pq][qp])\} \\ &\quad - \sum_{pq}^{\text{all}} \sum_r^{(+)} \{(pq|[rr]) - (p[r][r]q)\} a_p^\dagger a_q, \quad (38) \end{aligned}$$

$$\begin{aligned} (H^{\text{QED(MO-CCC)}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{pp}^{\text{CT}} + \frac{1}{2} \sum_p^{(+)} \sum_q^{(-)} \{(pp|qq) - (pq|qp)\} \\ &\quad - \frac{1}{2} \sum_{pq}^{\text{all}} \sum_r^{\text{all}} \{(pq|rr) - (pr|rq)\} a_p^\dagger a_q, \quad (39) \end{aligned}$$

$$\begin{aligned} (H^{\text{QED(free-CCC)}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{[pp]}^{\text{CT}} + \frac{1}{2} \sum_p^{(+)} \sum_q^{(-)} \\ &\quad \times \{([pp][qq]) - ([pq][qp])\} \\ &\quad - \frac{1}{2} \sum_{pq}^{\text{all}} \sum_r^{\text{all}} \{(pq|[rr]) - (p[r][r]q)\} a_p^\dagger a_q, \quad (40) \end{aligned}$$

$$\begin{aligned} (H^{\text{QED(Furry-CCC)}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{[pp]}^{\text{CT}} + \frac{1}{2} \sum_p^{(+)} \sum_q^{(-)} \\ &\quad \times \{([pp][qq]) - ([pq][qp])\} - \frac{1}{2} \sum_{pq}^{\text{all}} \sum_r^{\text{all}} \\ &\quad \times \{(pq|[rr]) - (p[r][r]q)\} a_p^\dagger a_q. \quad (41) \end{aligned}$$

In contrast, the VPA, NVPA, QED(MO-cC), QED(free-cC), and QED(Furry-cC) Hamiltonians are not CT invariant—they change forms by CT transformation, beyond the mere exchange of particles and antiparticles. In fact, the CT-transformed VPA, NVPA, and QED(MO-cC), QED(free-cC), and QED(Furry-cC) Hamiltonians are given as

$$\begin{aligned} (H^{\text{VPA}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_q^\dagger a_p + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{\text{all}} h_{pp}^{\text{CT}} - \sum_{pqr}^{\text{all}} [(pq|rr) - (pr|rq)] a_p^\dagger a_q \\ &\quad + \frac{1}{2} \sum_{pq}^{\text{all}} [(pp|qq) - (pq|qp)], \quad (42) \end{aligned}$$

$$\begin{aligned} (H^{\text{NVPA}})^{\text{CT}} &= \sum_{pq}^{(+)} h_{qp}^{\text{CT}} a_q^\dagger a_p + \frac{1}{2} \sum_{pqrs}^{(+)} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{pp}^{\text{CT}} - \sum_{pqr}^{(+)} [(pq|rr) - (pr|rq)] a_p^\dagger a_q \\ &\quad + \frac{1}{2} \sum_{pq}^{(+)} [(pp|qq) - (pq|qp)], \quad (43) \end{aligned}$$

$$\begin{aligned} (H^{\text{QED(MO-cC)}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{pp}^{\text{CT}} - \frac{1}{2} \sum_{pq}^{(+)} \{(pp|qq) - (pq|qp)\} \\ &\quad - \sum_{pqr}^{\text{all}} [(pq|rr) - (pr|rq)] a_p^\dagger a_q \\ &\quad + \sum_{pq}^{(+)} \{(pp|qq) - (pq|qp)\} \\ &\quad + \frac{1}{2} \sum_p^{(+)} \sum_q^{(-)} \{(pp|qq) - (pq|qp)\}, \quad (44) \end{aligned}$$

$$\begin{aligned} (H^{\text{QED(free-cC)}})^{\text{CT}} &= \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad - \sum_p^{(+)} h_{[pp]}^{\text{CT}} - \frac{1}{2} \sum_{pq}^{(+)} \{([pp][qq]) \\ &\quad - ([pq][qp])\} - \sum_{pqr}^{\text{all}} [(pq|rr) - (pr|rq)] \end{aligned}$$



$$\begin{aligned} & \times a_p^\dagger a_q + \sum_{pq}^{(+)} \{ ([pp][qq]) - ([pq][qp]) \} \\ & + \frac{1}{2} \sum_p^{(+)} \sum_q^{(-)} \{ ([pp][qq]) - ([pq][qp]) \}, \end{aligned} \quad (45)$$

and

$$\begin{aligned} & (H^{\text{QED(Furry-cC)}})^{\text{CT}} \\ & = \sum_{pq}^{\text{all}} h_{pq}^{\text{CT}} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ & - \sum_p^{(+)} h_{[pp]}^{\text{CT}} - \frac{1}{2} \sum_{pq}^{(+)} \{ ([pp][qq]) - ([pq][qp]) \} \\ & - \sum_{pqr}^{\text{all}} [(pq|rr) - (pr|rq)] a_p^\dagger a_q \\ & + \sum_{pq}^{(+)} \{ ([pp][qq]) - ([pq][qp]) \} \\ & + \frac{1}{2} \sum_p^{(+)} \sum_q^{(-)} \{ ([pp][qq]) - ([pq][qp]) \}, \end{aligned} \quad (46)$$

respectively. In the Hamiltonians (42)–(46), new terms have been generated by the CT transformation. Of these new terms, the constant terms are permitted as they only shift the energy spectra, but the one-electron operator terms clearly violate the CT invariance. Thus, of the eleven second-quantized relativistic Hamiltonians, QED(MO-CNC), QED(free-CNC), QED(Furry-CNC), QED(MO-CCC), QED(free-CCC), and QED(Furry-CCC) are CT invariant.

From the discussion on the CT invariance for the Hamiltonians, we can expect that the negative-energy virtual orbitals describe the distribution of a positron and that by using an appropriate basis set, we can describe the positronic orbitals in systems including positrons using negative-energy orbitals. In order to verify these predictions, the exact solutions for the hydrogen-like ion need to be examined in detail. The exact solution of the Dirac equation for the hydrogen-like ion is written in the following form:<sup>22</sup>

$$\psi = \frac{1}{r} \begin{bmatrix} P_{n\kappa}(r) \xi_{\kappa m}(\theta, \phi) \\ iQ_{n\kappa}(r) \xi_{-\kappa m}(\theta, \phi) \end{bmatrix}. \quad (47)$$

Applying the CT transformation to Eq. (47) yields a spinor with the large and small components interchanged in Eq. (47),

$$\psi^{\text{CT}} = \frac{1}{r} \begin{bmatrix} iQ_{n\kappa}(r) \xi_{-\kappa m}(\theta, \phi) \\ -P_{n\kappa}(r) \xi_{\kappa m}(\theta, \phi) \end{bmatrix}. \quad (48)$$

By comparing Eqs. (47) and (48) in terms of angular symmetry only, it is shown that the CT transformation is equivalent to reversing the sign of  $\kappa = (l - j)(2j + 1)$ . Thus, we can explicitly represent the

positronic orbitals with the basis functions that have angular symmetry with the sign of  $\kappa$  reversed from that of the electrons ( $s_{1/2} \rightleftharpoons p_{1/2}, p_{3/2} \rightleftharpoons d_{3/2}, d_{5/2} \rightleftharpoons f_{5/2}, f_{7/2} \rightleftharpoons g_{7/2}, \dots$ ). Moreover, angular symmetry of the negative-energy orbitals obtained as positronic virtual orbitals can be interpreted in the same way. One might think that there is still a concern that the extra  $r^2$  term in the positive  $\kappa$  case included in the following small component:

$$\sigma \cdot \mathbf{p} r^l e^{-\zeta r^2} \xi_{\kappa m} \propto \begin{cases} r^{l+1} e^{-\zeta r^2} \xi_{-\kappa m} & (\text{negative } \kappa), \\ r^{l-1} \left( 1 - \frac{\zeta}{l+1/2} r^2 \right) e^{-\zeta r^2} \xi_{-\kappa m} & (\text{positive } \kappa), \end{cases} \quad (49)$$

which is obtained by imposing strict kinetic balance in the Gaussian basis functions, may break the CT symmetry and interfere with the description of the positronic orbitals. This concern is not an essential problem, however, because remedies are possible; e.g., (i) using a sufficiently rich basis set, (ii) using a *restricted kinetic balance* (RKB)<sup>44–46</sup> for negative  $\kappa$  orbitals and an *inverse kinetic balance* (IKB)<sup>47</sup> for positive  $\kappa$  orbitals as in Ref. 48, and (iii) using a *dual kinetic balance* (DKB).<sup>49</sup>

### 3. Nonrelativistic limit of QED Hamiltonians

We now discuss the nonrelativistic limit of the QED Hamiltonians. The QED Hamiltonian solves the problem of negative-energy solutions by considering the electrons in the negative-energy solution as positron holes. Therefore, the proper QED Hamiltonian must be capable of describing electron–positron many-body systems. In particular, the nonrelativistic limit of the QED Hamiltonian must coincide with an appropriate nonrelativistic Hamiltonian, except for the difference in the constant terms. Based on this requirement, we verify the nonrelativistic limit of the QED Hamiltonians.

For the description of electron–positron systems, a method called the multicomponent (MC)-MO method has been successfully applied to a number of systems.<sup>50,51</sup> The MC-MO method is an extension of the nonrelativistic MO method and can handle multiple types of particles in a system, namely, electrons and positrons in this context. The Hamiltonian of this nonrelativistic MC (NRMC)-MO method is given by the following:<sup>51</sup>

$$\begin{aligned} H^{(\text{NRMC})} & = \sum_{pq}^{(+)} h_{pq}^{(\text{ele.NR})} a_p^\dagger a_q + \sum_{pq}^{(-)} h_{pq}^{(\text{pos.NR})} b_p^\dagger b_q \\ & + \frac{1}{2} \sum_{pqrs}^{(+)} \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} \middle| \psi_r^{(\text{ele.})} \psi_s^{(\text{ele.})} \right) a_p^\dagger a_r^\dagger a_s a_q \\ & + \frac{1}{2} \sum_{pqrs}^{(-)} \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} \middle| \psi_r^{(\text{pos.})} \psi_s^{(\text{pos.})} \right) b_p^\dagger b_r^\dagger b_s b_q \\ & - \sum_{pq}^{(+)} \sum_{rs}^{(-)} \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} \middle| \psi_r^{(\text{pos.})} \psi_s^{(\text{pos.})} \right) a_p^\dagger b_r^\dagger b_s a_q \end{aligned} \quad (50)$$

with

$$\begin{aligned} h_{pq}^{(\text{ele.NR})} & = \left\langle \psi_p^{(\text{ele.})} \middle| V^{(\text{ext.})} \middle| \psi_q^{(\text{ele.})} \right\rangle \\ & + \left\langle \psi_p^{(\text{ele.})} \middle| -\nabla^2 / (2m) \middle| \psi_q^{(\text{ele.})} \right\rangle, \end{aligned} \quad (51)$$

$$h_{pq}^{(\text{pos.NR})} = -\langle \psi_p^{(\text{pos.})} | V^{(\text{ext.})} | \psi_q^{(\text{pos.})} \rangle + \langle \psi_p^{(\text{pos.})} | -\nabla^2 / (2m) | \psi_q^{(\text{pos.})} \rangle, \quad (52)$$

where the sum ranges (+) and (−) run over the nonrelativistic MOs of the electron and positron, respectively, rather than the positive- and negative-energy orbitals in the relativistic case. If the negative-energy solution holes in the QED Hamiltonian correctly represent the positron, then the nonrelativistic limit of the QED Hamiltonian should be identical to  $H^{(\text{NRMC})}$ , except for the difference in the constant terms. The procedure for obtaining the nonrelativistic limit is to first set

$$\psi_p = \begin{bmatrix} \psi_p^{(\text{ele.})} \\ (\boldsymbol{\sigma} \cdot \mathbf{p} / (2mc)) \psi_p^{(\text{ele.})} \end{bmatrix} \quad (53)$$

for the  $p$ th spinor with positive energy and

$$\psi_p = \begin{bmatrix} -(\boldsymbol{\sigma} \cdot \mathbf{p} / (2mc)) \psi_p^{(\text{pos.})} \\ \psi_p^{(\text{pos.})} \end{bmatrix} \quad (54)$$

for the  $p$ th spinor with negative energy and then take the limit  $c \rightarrow +\infty$ .

The resulting nonrelativistic limits for one-electron Hamiltonian matrix elements are

$$h_{pq} \rightarrow h_{pq}^{(\text{ele.NR})} + o(c^{-2}) \quad (55)$$

for the case of  $p, q \in (+)$ ,

$$\begin{aligned} h_{pq} &\rightarrow \langle \psi_p^{(\text{pos.})} | V^{(\text{ext.})} | \psi_q^{(\text{pos.})} \rangle - 2mc^2 \langle \psi_p^{(\text{pos.})} | \psi_q^{(\text{pos.})} \rangle \\ &\quad - 2 \langle \psi_p^{(\text{pos.})} | -\nabla^2 / (2m) | \psi_q^{(\text{pos.})} \rangle + o(c^{-2}) \\ &= -h_{pq}^{(\text{pos.NR})} - 2mc^2 \delta_{pq} + o(c^{-2}) \end{aligned} \quad (56)$$

for the case of  $p, q \in (-)$ , and  $h_{pq} \sim c^{-1}$  for the case of  $p \in (+)$ ,  $q \in (-)$  or  $p \in (-)$ ,  $q \in (+)$ . Note that the result in Eq. (56) is obtained by the normalization condition for Eq. (54). For the two-electron integrals, the nonrelativistic limit is obtained by extracting the terms independent of  $c$ , considering that the inner product between the positive- and negative-energy spinors necessarily yields a term with a negative power of  $c$ .

The resulting nonrelativistic limit of the QED(MO-CNC) Hamiltonian is

$$H^{\text{QED(MO-CNC)}} \rightarrow H^{(\text{NRMC})} + 2mc^2 \times (\text{number of positrons}) + o(c^{-1}). \quad (57)$$

The term proportional to  $c^2$  on the rhs can be neglected because it is the relativistic rest energy. In the relativistic molecular orbital method, the origin of the energy is shifted in advance so that there is no rest energy of the electron, so the rest energy neglected here should be understood that contribution by both the electrons and positrons. Since the negative power term of  $c$  vanishes in the nonrelativistic limit, the nonrelativistic limit of the QED(MO-CNC) Hamiltonian coincides with Eq. (50).

The nonrelativistic limit of the QED(free-CNC) Hamiltonian is

$$\begin{aligned} H^{\text{QED(free-CNC)}} &\rightarrow H^{(\text{NRMC})} - \sum_p^{(-)} \left( h_{pp}^{(\text{pos.NR})} - h_{[pp]}^{(\text{pos.NR})} \right) \\ &\quad + \frac{1}{2} \sum_{pq}^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_p^{(\text{pos.})} | \psi_q^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right. \\ &\quad \left. - \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} | \psi_q^{(\text{pos.})} \psi_p^{(\text{pos.})} \right) \right\} \\ &\quad - \sum_{pq}^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_p^{(\text{pos.})} | \psi_{[q]}^{(\text{pos.})} \psi_{[q]}^{(\text{pos.})} \right) \right. \\ &\quad \left. - \left( \psi_p^{(\text{pos.})} \psi_{[q]}^{(\text{pos.})} | \psi_{[q]}^{(\text{pos.})} \psi_p^{(\text{pos.})} \right) \right\} \\ &\quad + \frac{1}{2} \sum_{pq}^{(-)} \left\{ \left( \psi_{[p]}^{(\text{pos.})} \psi_{[p]}^{(\text{pos.})} | \psi_{[q]}^{(\text{pos.})} \psi_{[q]}^{(\text{pos.})} \right) \right. \\ &\quad \left. - \left( \psi_{[p]}^{(\text{pos.})} \psi_{[q]}^{(\text{pos.})} | \psi_{[q]}^{(\text{pos.})} \psi_{[p]}^{(\text{pos.})} \right) \right\} \\ &\quad + \sum_{pq}^{(+)} \sum_r^{(-)} \left\{ \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} | \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) \right. \\ &\quad \left. - \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} | \psi_{[r]}^{(\text{pos.})} \psi_{[r]}^{(\text{pos.})} \right) \right\} a_p^\dagger a_q \\ &\quad + \sum_{pq}^{(-)} \sum_r^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} | \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) \right. \\ &\quad \left. - \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} | \psi_{[r]}^{(\text{pos.})} \psi_{[r]}^{(\text{pos.})} \right) \right. \\ &\quad \left. - \left( \psi_p^{(\text{pos.})} \psi_r^{(\text{pos.})} | \psi_r^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right. \\ &\quad \left. + \left( \psi_p^{(\text{pos.})} \psi_{[r]}^{(\text{pos.})} | \psi_{[r]}^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right\} b_p^\dagger b_q \\ &\quad + 2mc^2 \times (\text{number of positrons}) + o(c^{-1}). \end{aligned} \quad (58)$$

This Hamiltonian contains operators in terms that do not depend on  $c$ ; hence, it does not coincide with  $H^{(\text{NRMC})}$  in the nonrelativistic limit. Similarly, the QED(MO-CCC), QED(free-CCC), QED(MO-cC), and QED(free-cC) Hamiltonians in the nonrelativistic limit are as follows:

$$\begin{aligned} H^{\text{QED(MO-CCC)}} &\rightarrow H^{(\text{NRMC})} - \frac{1}{2} \sum_{pq}^{(+)} \sum_r^{(+)} \left\{ \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} | \psi_r^{(\text{ele.})} \psi_r^{(\text{ele.})} \right) \right. \\ &\quad \left. - \left( \psi_p^{(\text{ele.})} \psi_r^{(\text{ele.})} | \psi_r^{(\text{ele.})} \psi_q^{(\text{ele.})} \right) \right\} a_p^\dagger a_q \\ &\quad + \frac{1}{2} \sum_{pq}^{(+)} \sum_r^{(-)} \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} | \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) a_p^\dagger a_q \\ &\quad + \frac{1}{2} \sum_{pq}^{(-)} \sum_r^{(+)} \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} | \psi_r^{(\text{ele.})} \psi_r^{(\text{ele.})} \right) b_p^\dagger b_p \\ &\quad - \frac{1}{2} \sum_{pq}^{(-)} \sum_r^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} | \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) \right. \\ &\quad \left. - \left( \psi_p^{(\text{pos.})} \psi_r^{(\text{pos.})} | \psi_r^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right\} b_p^\dagger b_p \\ &\quad + 2mc^2 \times (\text{number of positrons}) + o(c^{-1}), \end{aligned} \quad (59)$$

$$\begin{aligned}
 H^{\text{QED}(\text{free}-\text{CCC})} &\rightarrow H^{(\text{NRM})} - \sum_p^{(-)} \left( h_{pp}^{(\text{pos.NR})} - h_{[pp]}^{(\text{pos.NR})} \right) \\
 &+ \frac{1}{2} \sum_{pq}^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_p^{(\text{pos.})} \middle| \psi_q^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right. \\
 &- \left. \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} \middle| \psi_q^{(\text{pos.})} \psi_p^{(\text{pos.})} \right) \right\} \\
 &- \frac{1}{2} \sum_{pq}^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_p^{(\text{pos.})} \middle| \psi_{[q]}^{(\text{pos.})} \psi_{[q]}^{(\text{pos.})} \right) \right. \\
 &- \left. \left( \psi_p^{(\text{pos.})} \psi_{[q]}^{(\text{pos.})} \middle| \psi_{[q]}^{(\text{pos.})} \psi_p^{(\text{pos.})} \right) \right\} \\
 &+ \frac{1}{2} \sum_p^{(-)} \sum_q^{(+)} \left\{ \left( \psi_{[p]}^{(\text{pos.})} \psi_{[p]}^{(\text{pos.})} \middle| \psi_{[q]}^{(\text{ele.})} \psi_{[q]}^{(\text{ele.})} \right) \right. \\
 &- \left. \left( \psi_p^{(\text{pos.})} \psi_p^{(\text{pos.})} \middle| \psi_{[q]}^{(\text{ele.})} \psi_{[q]}^{(\text{ele.})} \right) \right\} \\
 &- \frac{1}{2} \sum_{pq}^{(+)} \sum_r^{(+)} \left\{ \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} \middle| \psi_{[r]}^{(\text{ele.})} \psi_{[r]}^{(\text{ele.})} \right) \right. \\
 &- \left. \left( \psi_p^{(\text{ele.})} \psi_{[r]}^{(\text{ele.})} \middle| \psi_{[r]}^{(\text{ele.})} \psi_q^{(\text{ele.})} \right) \right\} a_p^\dagger a_q \\
 &+ \sum_{pq}^{(+)} \sum_r^{(-)} \left\{ \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} \middle| \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) \right. \\
 &- \left. \frac{1}{2} \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} \middle| \psi_{[r]}^{(\text{pos.})} \psi_{[r]}^{(\text{pos.})} \right) \right\} a_p^\dagger a_q \\
 &+ \frac{1}{2} \sum_{pq}^{(-)} \sum_r^{(+)} \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} \middle| \psi_{[r]}^{(\text{ele.})} \psi_{[r]}^{(\text{ele.})} \right) b_p^\dagger b_q \\
 &- \sum_{pq}^{(-)} \sum_r^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} \middle| \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) \right. \\
 &- \left. \left( \psi_p^{(\text{pos.})} \psi_r^{(\text{pos.})} \middle| \psi_r^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right\} b_p^\dagger b_q \\
 &+ \frac{1}{2} \sum_{pq}^{(-)} \sum_r^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} \middle| \psi_{[r]}^{(\text{pos.})} \psi_{[r]}^{(\text{pos.})} \right) \right. \\
 &- \left. \left( \psi_p^{(\text{pos.})} \psi_{[r]}^{(\text{pos.})} \middle| \psi_{[r]}^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right\} b_p^\dagger b_q \\
 &+ 2mc^2 \times (\text{number of positrons}) + o(c^{-1}), \quad (60)
 \end{aligned}$$

$$\begin{aligned}
 H^{\text{QED}(\text{MO}-\text{cC})} &\rightarrow H^{(\text{NRM})} \\
 &+ \sum_{pq}^{(+)} \sum_r^{(-)} \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} \middle| \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) a_p^\dagger a_q \\
 &- \sum_{pq}^{(-)} \sum_r^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} \middle| \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) \right. \\
 &- \left. \left( \psi_p^{(\text{pos.})} \psi_r^{(\text{pos.})} \middle| \psi_r^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right\} b_p^\dagger b_q \\
 &+ 2mc^2 \times (\text{number of positrons}) + o(c^{-1}), \quad (61)
 \end{aligned}$$

$$\begin{aligned}
 H^{\text{QED}(\text{free}-\text{cC})} &\rightarrow H^{(\text{NRM})} - \sum_p^{(-)} \left( h_{pp}^{(\text{pos.NR})} - h_{[pp]}^{(\text{pos.NR})} \right) \\
 &+ \frac{1}{2} \sum_{pq}^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_p^{(\text{pos.})} \middle| \psi_q^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right.
 \end{aligned}$$

TABLE I. Properties of various DC Hamiltonians.

	Orbital rotation invariance	CT invariance	Nonrelativistic limit
VPA	✓	×	N/A
NVPA	×	×	N/A
QED(MO-CNC)	×	✓	✓
QED(free-CNC)	✓	✓	×
QED(Furry-CNC)	✓	✓	×
QED(MO-CCC)	×	✓	×
QED(free-CCC)	✓	✓	×
QED(Furry-CCC)	✓	✓	×
QED(MO-cC)	×	×	×
QED(free-cC)	✓	×	×
QED(Furry-cC)	✓	×	×

$$\begin{aligned}
 &- \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} \middle| \psi_q^{(\text{pos.})} \psi_p^{(\text{pos.})} \right) \right\} \\
 &- \frac{1}{2} \sum_{pq}^{(-)} \left\{ \left( \psi_{[p]}^{(\text{pos.})} \psi_{[p]}^{(\text{pos.})} \middle| \psi_{[q]}^{(\text{pos.})} \psi_{[q]}^{(\text{pos.})} \right) \right. \\
 &- \left. \left( \psi_{[p]}^{(\text{pos.})} \psi_{[q]}^{(\text{pos.})} \middle| \psi_{[q]}^{(\text{pos.})} \psi_{[p]}^{(\text{pos.})} \right) \right\} \\
 &+ \sum_{pq}^{(+)} \sum_r^{(-)} \left( \psi_p^{(\text{ele.})} \psi_q^{(\text{ele.})} \middle| \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) a_p^\dagger a_q \\
 &- \sum_{pq}^{(-)} \sum_r^{(-)} \left\{ \left( \psi_p^{(\text{pos.})} \psi_q^{(\text{pos.})} \middle| \psi_r^{(\text{pos.})} \psi_r^{(\text{pos.})} \right) \right. \\
 &- \left. \left( \psi_p^{(\text{pos.})} \psi_r^{(\text{pos.})} \middle| \psi_r^{(\text{pos.})} \psi_q^{(\text{pos.})} \right) \right\} b_p^\dagger b_q \\
 &+ 2mc^2 \times (\text{number of positrons}) + o(c^{-1}), \quad (62)
 \end{aligned}$$

which do not coincide with  $H^{(\text{NRM})}$  in the nonrelativistic limit. Furthermore, QED(Furry-CNC), QED(Furry-CCC), and QED(Furry-cC), obtained from the replacement of parentheses (the parentheses  $[\ ]$  replaced by  $[[\ ]]$ ) in Eqs. (58), (60), and (62), respectively, also do not coincide with  $H^{(\text{NRM})}$  in the nonrelativistic limit. Thus, all the QED Hamiltonians except QED(MO-CNC) have extra one-electron operators not included in the NRM. These are caused by the differences in the representing orbitals and contractions adopted.

Thus, only the QED(MO-CNC) Hamiltonian properly describes the electron-positron interactions in the nonrelativistic limit. The properties of the Hamiltonians with respect to the three criteria, namely, the orbital rotation invariance, CT invariance, and nonrelativistic limit, are summarized in Table I. Hereafter, we refer to the QED(MO-CNC) Hamiltonian simply as the QED Hamiltonian, unless otherwise noted.

#### 4. Total energy expression for QED Hamiltonian

In the discussions in Subsections II B 1–II B 3 of Sec. II B, we have shown that the QED(MO-CNC) Hamiltonian is a candidate for relativistic Hamiltonians that can describe many-body systems including both electrons and positrons. However, in addition, we

need to define the total energy expressions for the QED Hamiltonian. Because the QED Hamiltonian does not conserve the number of particles, the number of particles fluctuates, even in vacuum, i.e., the lowest energy state. This indicates that the energy of the vacuum, defined as the expectation value of the QED(MO-CNC) Hamiltonian, may diverge if an infinite number of electron-positron pairs are created, albeit with a very low probability. Therefore, to guarantee finite total energy, an offset of the vacuum energy is required. Thus, we define the following as the expression of the total energy of state  $|\Psi\rangle$ :

$$E^{\text{QED}} = \langle \Psi | H^{\text{QED}} | \Psi \rangle - \langle 0^{(\text{MO})} | H^{\text{QED}} | 0^{(\text{MO})} \rangle, \quad (63)$$

where the first term represents the un-offset total energy and the second term represents the total energy of the vacuum—these refer to as the main term and the counter term, respectively. Since electron-positron pair creations are described as excitations from a negative-energy orbital to a positive-energy orbital, the intensity of the divergence depends on the calculation levels of electron correlation. Thus, to properly cancel the total energy divergence, the level of electron correlation in the counter term should be identical to the main term. For example, at the Dirac-Hartree-Fock (DHF) level, the vacuum state is defined in Eq. (10). At this level, the counter term is zero, and there is no need to consider it. In another case, at the CI level, the Furry vacuum state is defined by

$$|0_{\text{CI}}^{(\text{MO})}\rangle = \left( \tilde{C}_0 + \sum_i^{(+)} \tilde{C}_i^j a_i^\dagger a_j + \sum_{ik}^{(+)} \sum_{jl}^{(-)} \tilde{C}_{jl}^{ik} a_i^\dagger a_j a_k^\dagger a_l + \dots \right) \times |0_0^{(\text{MO})}\rangle, \quad (64)$$

where  $\tilde{C}_0, \tilde{C}_j^i, \tilde{C}_{jl}^{ik}, \dots$  are the CI coefficients for the vacuum state, which should be determined so that  $\langle 0_{\text{CI}}^{(\text{MO})} | H^{\text{QED}} | 0_{\text{CI}}^{(\text{MO})} \rangle$  is minimized. In this case, this minimum value itself is the counter term.

We should mention here that expressions of Eqs. (27), (67), and (98) in Ref. 34, or Eq. (7–98) in Ref. 52, look formally similar to the total energy Eq. (63). However, the terms subtracted from the referenced Hamiltonians are single Slater determinants and cannot remove total energy divergence caused by the generalized electron correlation. Thus, these subtracted terms are not counter terms but the terms that are subtracted as the vacuum expectation value that is discarded in the normal ordering procedure described in Sec. II A. Although not explicitly introduced for the purpose of eliminating divergence, an expression for subtracting the vacuum containing electron correlation is given in Eq. (113) of Ref. 34. This expression, which can be regarded as an extension of Eq. (27) in Ref. 34, differs from Eq. (63), in that it employs the QED(MO-CCC) Hamiltonian. Here, one might argue that, given that the vacuum is a system without real electrons and positrons, it could be appropriate to employ the Furry orbitals instead of MOs for its description. The total energy expression and the concrete expressions for MP2, CI, and MCQDPT of this case are given in the supplementary material.

We have now narrowed down the Hamiltonian to QED(MO-CNC) [Eq. (13)] and obtained a total energy expression [Eq. (63)] necessary to formulate a QED-based MO theory. We next derive the QED-level DHF, CI, MP2, and multireference second order perturbation methods based on Eq. (63).

## C. QED-based MO theory

### 1. QED-based DHF method

In previous discussions, we have shown that the relativistic MO method rederived based on the QED(MO-CNC) Hamiltonian can describe positrons reasonably when using negative-energy solutions. In this subsection, we derive the DHF method, including explicit positrons in the configuration, based on the QED(MO-CNC) Hamiltonian (22). The ground configuration explicitly including positrons is written using creation operators  $a_i^\dagger$  and  $b_p^\dagger$  as

$$|\Psi_0\rangle = \prod_i^{\text{occ(ele.)}} a_i^\dagger \prod_p^{\text{occ(pos.)}} b_p^\dagger |\text{empty}\rangle. \quad (65)$$

The expectation value of the QED(MO-CNC) Hamiltonian for this configuration is the total energy already shown in Eq. (53) of Ref. 48. The QED-based Fock operator

$$\hat{f} = \hat{h} + \sum_j^{\text{occ(ele.)}} (\hat{f}_j - \hat{K}_j) - \sum_p^{\text{occ(pos.)}} (\hat{f}_p - \hat{K}_p) \quad (66)$$

was also obtained by taking the variation of this total energy with respect to the electron orbitals in Ref. 48. Note that this Fock operator is shown in matrix notation in Eq. (60) of Ref. 48.

Following the conventional HF procedure, we introduce the Lagrangian to take into account the orthonormality of the orbitals:

$$\begin{aligned} \mathcal{L} = E &- \sum_{ij}^{\text{occ(ele.)}} (\langle i|j\rangle - \delta_{ij}) \varepsilon_{ji} - \sum_{pq}^{\text{occ(pos.)}} (\langle p|q\rangle - \delta_{pq}) (-\varepsilon_{qp}) \\ &- \sum_i^{\text{occ(ele.)}} \sum_p^{\text{occ(pos.)}} \langle i|p\rangle \varepsilon_{pi} - \sum_i^{\text{occ(ele.)}} \sum_p^{\text{occ(pos.)}} \langle p|i\rangle (-\varepsilon_{ip}). \end{aligned} \quad (67)$$

The signs of the Lagrange multipliers in Eq. (67) were chosen so that proper physical interpretation of the multipliers is assured, which simplifies the final form of the DHF equation. Taking the variations of the  $k$ th orbital of electrons for  $\mathcal{L}$ , we have

$$\delta\mathcal{L}(\delta k) = \langle \delta k | \hat{f} | k \rangle - \sum_j^{\text{occ(ele.)}} \langle \delta k | j \rangle \varepsilon_{jk} - \sum_p^{\text{occ(pos.)}} \langle \delta k | p \rangle \varepsilon_{pk} + \text{c.c.} \quad (68)$$

Using a similar procedure, we can obtain the results for variations of the  $s$ th orbital of positrons,

$$\delta\mathcal{L}(\delta s) = \langle \delta s | -\hat{f} | s \rangle - \sum_j^{\text{occ(ele.)}} \langle \delta s | j \rangle (-\varepsilon_{js}) - \sum_p^{\text{occ(pos.)}} \langle \delta s | p \rangle (-\varepsilon_{ps}) + \text{c.c.} \quad (69)$$

Setting the  $\delta\mathcal{L}$  in Eqs. (68) and (69) to zero, we obtain the following DHF equations:

$$\hat{f}|k\rangle = \sum_j^{\text{occ}(\text{ele.})} |j\rangle \varepsilon_{jk} + \sum_p^{\text{occ}(\text{pos.})} |p\rangle \varepsilon_{pk}, \quad (70)$$

$$\hat{f}|s\rangle = \sum_j^{\text{occ}(\text{ele.})} |j\rangle \varepsilon_{js} + \sum_p^{\text{occ}(\text{pos.})} |p\rangle \varepsilon_{ps}. \quad (71)$$

Now, we have two equations, (70) and (71), but they are actually equivalent. Therefore, we only have to solve either of the eigen equations of  $\hat{f}$ . If the solution is considered an electron solution, then it is a result of Eq. (70), and if it is considered a positron solution, then it is a result of Eq. (71). These solutions are readily achieved by using the canonical orbitals to define *orbital energies*, as in the case of non-QED. We can easily distinguish the electron and positron solutions by checking whether the orbital energy is greater or less than  $-mc^2$ . Canonicalizing and applying the LCAO approximation to Eqs. (70) and (71), we have the Dirac–Hartree–Fock–Roothaan (DHFR) equation,

$$\mathbf{F}\mathbf{c} = \mathbf{S}\mathbf{c}\boldsymbol{\varepsilon}, \quad (72)$$

where  $\mathbf{c}$  is the MO coefficients,  $\mathbf{S}$  is the overlap integral matrix, and  $\mathbf{F}$  is the Fock matrix,

$$\begin{aligned} (\mathbf{F})_{\mu\nu} &= (\mathbf{h})_{\mu\nu} + \sum_{\lambda\rho} \left( (\mathbf{P}^{(\text{ele.})})_{\lambda\rho} - (\mathbf{P}^{(\text{pos.})})_{\lambda\rho} \right) \\ &\times [(\mu\nu|\lambda\rho) - (\mu\rho|\lambda\nu)], \end{aligned} \quad (73)$$

with

$$(\mathbf{F})_{\mu\nu} = \langle \mu | \hat{f} | \nu \rangle, \quad (\mathbf{h})_{\mu\nu} = \langle \mu | \hat{h} | \nu \rangle. \quad (74)$$

The total energy expression in the LCAO approximation is written as

$$E = \frac{1}{2} \sum_{\mu\nu} \left[ (\mathbf{P}^{(\text{ele.})})_{\mu\nu} - (\mathbf{P}^{(\text{pos.})})_{\mu\nu} \right] [(\mathbf{h})_{\mu\nu} + (\mathbf{F})_{\mu\nu}]. \quad (75)$$

Here,  $\mathbf{P}^{(\text{ele.})}$  and  $\mathbf{P}^{(\text{pos.})}$  are electronic and positronic density matrices, respectively,

$$\begin{aligned} (\mathbf{P}^{(\text{ele.})})_{\mu\nu} &= \sum_i^{\text{occ}(\text{ele.})} (\mathbf{c})_{\mu i}^* (\mathbf{c})_{\nu i}, \\ (\mathbf{P}^{(\text{pos.})})_{\mu\nu} &= \sum_i^{\text{occ}(\text{pos.})} (\mathbf{c})_{\mu i}^* (\mathbf{c})_{\nu i}, \end{aligned} \quad (76)$$

They are characteristic of the QED-based DHF method. For a system without positrons, the positronic density matrix is equal to the null matrix. In this case, the QED-based DHFR equation becomes identical to the conventional (NVPA- or VPA-based) DHFR equation. Nevertheless, even in such a case, our QED-based DHF formalism can give various information about positronic virtual orbitals

from the negative-energy orbitals. According to the discussion in Subsection II B 2, the *reinterpreted orbital energy*,

$$\tilde{\varepsilon}_p = -\varepsilon_p - 2mc^2, \quad (77)$$

obtained from the negative orbital energy represents the effective one-particle energy of the positron, and the form of the small component reflects the symmetry (e.g., *s*-type, *p*-type, and so on) of the orbitals of positrons.

## 2. QED-based CI method

The derivation of the basic equation of the QED-based CI method using the DHF wave function is straightforward. In the QED-based MO theory, the electronic state in nonrelativistic theory, which involves only electrons, is generalized to the state that includes both electrons and positrons. This generalized electronic state is expressed as a linear combination of configurations (Slater determinants)  $|\Psi_J\rangle$  in the CI method,

$$|\Psi_\alpha^{\text{CI}}\rangle = \sum_J C_{J\alpha} |\Psi_J\rangle, \quad (78)$$

where subscript  $\alpha$  denotes a generalized electronic state. The generalized configurations  $|\Psi_J\rangle$  are conventional electronic configurations or configurations including both electrons and positrons due to pair creations, and the coefficients  $C_{J\alpha}$  are obtained as eigenvectors of the CI Hamiltonian matrix,

$$H_{IJ} = \langle \Psi_I | H^{\text{QED}} | \Psi_J \rangle. \quad (79)$$

Note that the QED Hamiltonian mixes the DHF configuration with pair-created/annihilated configurations as well as the electron-excited configurations. From Eqs. (13) and (79), the diagonal and nondiagonal matrix elements of the QED-based CI Hamiltonian matrix are written as

$$\begin{aligned} H_{IJ} &= \sum_p^{\text{occ}(\text{ele.})} h_{pp} - \sum_r^{\text{occ}(\text{pos.})} h_{rr} + \frac{1}{2} \sum_{pq}^{\text{occ}(\text{ele.})} [(pp|qq) - (pq|qp)] \\ &- \sum_p^{\text{occ}(\text{ele.})} \sum_r^{\text{occ}(\text{pos.})} [(pp|rr) - (pr|rp)] \\ &+ \frac{1}{2} \sum_{rs}^{\text{occ}(\text{pos.})} [(rr|ss) - (rs|sr)] \end{aligned} \quad (80)$$

and

$$\begin{aligned} H_{IJ} &= \sum_{pq}^{\text{all}} \langle \Psi_I | a_p^\dagger a_q | \Psi_J \rangle \left\{ h_{pq} - \sum_r^{(-)} [(pq|rr) - (pr|rq)] \right\} \\ &+ \frac{1}{2} \sum_{pqrs}^{\text{all}} \langle \Psi_I | a_p^\dagger a_r^\dagger a_s a_q | \Psi_J \rangle (pq|rs), \end{aligned} \quad (81)$$

respectively. Here,  $\text{occ}(\text{ele.})$  and  $\text{occ}(\text{pos.})$  in the summations indicate that the orbital labels run over the electronic and positronic occupied orbitals in  $|\Psi_J\rangle$ , respectively. The CI energies  $E_\alpha$  are obtained from the counter term and the eigenvalues of the Hamiltonian matrix,

$$E_\alpha = \sum_{IJ} C_{I\alpha}^* H_{IJ} C_{J\alpha} - \langle 0_{\text{CI}}^{(\text{MO})} | H^{\text{QED}} | 0_{\text{CI}}^{(\text{MO})} \rangle. \quad (82)$$

### 3. QED-based MP2 method

The perturbation method differs from the CI method, in that the counter term is not straightforward but is treated perturbatively, as is the main term. The MP2 formula at the QED level has already been derived in Refs. 24, 35, and 36 for general orbitals as well as the canonical MOs. However, in the perturbation energies presented in these references, the case involving real (occupied) positrons, which is the focus of our interest, is not considered. We, therefore, attempted a formulation based on the QED(MO-CNC) Hamiltonian and the counter term Eq. (63), including the case with positronic occupied orbitals.

The energy up to the second order for the DHF configuration, including the counter term, is given by the following formula:

$$E^{\text{MP2}} = E^{\text{DHF}} + E^{(2)} - E_{\text{counter}}^{(2)}, \quad (83)$$

$$E^{(2)} = \sum_{n(\neq \text{DHF})} \frac{\langle \Psi_{\text{DHF}} | V | \Psi_n \rangle \langle \Psi_n | V | \Psi_{\text{DHF}} \rangle}{E_{\text{DHF}}^{(0)} - E_n^{(0)}}, \quad (84)$$

where the counter term in Eq. (63) is expressed by the second-order perturbation energy. Note that the zeroth-plus first-order contributions to the counter term are zero, as discussed for the DHF method.

As mentioned in Sec. II A, we can choose either expression Eq. (13) or Eq. (22) to derive a more specific energy expression for MP2. Here, we use the expression Eq. (13) for simplicity in the derivation. Since the Brillouin theorem is satisfied for the QED-based DHF method, the intermediate states  $|\Psi_n\rangle$  in Eq. (84) are double excitation configurations,

$$|\Psi_n\rangle = a_s^\dagger a_b a_r^\dagger a_a |\Psi_{\text{DHF}}\rangle = |\Psi_{ab}^{rs}\rangle, \quad (85)$$

where these excitations include not only conventional electron excitations but also pair creations. The partitioning of the Hamiltonian into the unperturbed Hamiltonian and perturbation is given as

$$\begin{aligned} H^{\text{QED}} &= H_0^{\text{QED}} + V, \\ H_0^{\text{QED}} &= \sum_p^{\text{all}} \varepsilon_p a_p^\dagger a_p - \sum_p^{(-)} \varepsilon_p, \\ V &= H^{\text{QED}} - H_0^{\text{QED}} \\ &= \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q \\ &\quad + (\text{constant and } 1 - \text{electron operator}). \end{aligned} \quad (86)$$

According to this partitioning, the energy denominator and numerator in Eq. (84) are

$$\begin{aligned} E_{\text{DHF}}^{(0)} - E_n^{(0)} &= \langle \Psi_{\text{DHF}} | H_0^{\text{QED}} | \Psi_{\text{DHF}} \rangle - \langle \Psi_n | H_0^{\text{QED}} | \Psi_n \rangle \\ &= \left\langle \Psi_{\text{DHF}} \left| \sum_p^{\text{all}} \varepsilon_p a_p^\dagger a_p \right| \Psi_{\text{DHF}} \right\rangle - \left\langle \Psi_{ab}^{rs} \left| \sum_p^{\text{all}} \varepsilon_p a_p^\dagger a_p \right| \Psi_{ab}^{rs} \right\rangle \\ &= \varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s \end{aligned} \quad (87)$$

and

$$\langle \Psi_{\text{DHF}} | V | \Psi_{ab}^{rs} \rangle = (ar|bs) - (as|br), \quad (88)$$

respectively. Thus, the second term on the rhs of Eq. (83) becomes

$$E_{\text{counter}}^{(2)} = \frac{1}{2} \sum_{ab}^{\text{occ}} \sum_{rs}^{\text{vir}} \left[ \frac{(ar|bs)(ra|sb)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{(ar|bs)(rb|sa)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right], \quad (89)$$

which looks like the familiar MP2 formula in the nonrelativistic theory. However, the ranges in the summations are

$$\begin{aligned} \{\text{occ}\} &= \{\text{occ}(\text{ele.})\} \cup \{\text{vir}(\text{pos.})\}, \\ \{\text{vir}\} &= \{\text{vir}(\text{ele.})\} \cup \{\text{occ}(\text{pos.})\}. \end{aligned} \quad (90)$$

When the system includes no positrons,  $\{\text{vir}(\text{pos.})\} = \{(-)\}$  and  $\{\text{occ}(\text{pos.})\} = \emptyset$  are satisfied. For comparison, the ranges in the summation for VPA-based MP2 are

$$\begin{aligned} \{\text{occ}\} &= \{\text{occ}(\text{ele.})\}, \\ \{\text{vir}\} &= \{\text{vir}(\text{ele.})\} \cup \{(-)\}. \end{aligned} \quad (91)$$

Note that negative-energy orbitals are treated differently in QED and VPA. In addition to this difference, the counter term  $E_{\text{counter}}^{(2)}$  is also needed in the QED-based MP2. Since the counter term is the second-order energy for the vacuum configuration, it is obtained by adopting the following ground configuration and intermediate states for Eqs. (84) and (87), respectively:

$$|\Psi_{\text{DHF}}\rangle \rightarrow |0_0^{(\text{MO})}\rangle, \quad (92)$$

$$|\Psi_n\rangle \rightarrow a_s^\dagger a_b a_r^\dagger a_a |0_0^{(\text{MO})}\rangle. \quad (93)$$

These substitutions are equivalent to adopting  $\{(-)\}$  and  $\{(+)\}$  for  $\{\text{occ}\}$  and  $\{\text{vir}\}$  in Eq. (89), respectively. Thus, the counter term for MP2 is obtained as

$$E_{\text{counter}}^{(2)} = \frac{1}{2} \sum_{ab}^{(-)} \sum_{rs}^{(+)} \left[ \frac{(ar|bs)(ra|sb)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{(ar|bs)(rb|sa)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right]. \quad (94)$$

From Eqs. (83), (89), and (94), the final energy expression of the QED-based MP2 is

$$\begin{aligned} E^{\text{MP2}} &= E^{\text{DHF}} + \frac{1}{2} \sum_{ab}^{\text{occ}} \sum_{rs}^{\text{vir}} \left[ \frac{(ar|bs)(ra|sb)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{(ar|bs)(rb|sa)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right] \\ &\quad - \frac{1}{2} \sum_{ab}^{(-)} \sum_{rs}^{(+)} \left[ \frac{(ar|bs)(ra|sb)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{(ar|bs)(rb|sa)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right]. \end{aligned} \quad (95)$$

The main and counter terms in Eq. (95) contain the common sum,

$$\frac{1}{2} \sum_{ab}^{\text{vir}(\text{pos.})} \sum_{rs}^{\text{vir}(\text{ele.})} \left[ \frac{(ar|bs)(ra|sb)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{(ar|bs)(rb|sa)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \right], \quad (96)$$

which can be excluded in advance from both the main and counter terms.

It should be noted that there are some previous studies of second-order perturbation energy expressions<sup>34,38,39,53,54</sup> that include a term corresponding to the counter term, although they were not introduced explicitly to suppress the divergence of the perturbation energy.

#### 4. QED-based multiconfigurational quasi-degenerate perturbation theory (MCQDPT)

The same procedure as for the single-reference perturbation theory can also be applied to derive a QED-based multireference perturbation theory. A brief explanation follows.

In the multiconfigurational quasi-degenerate perturbation theory (MCQDPT),<sup>55</sup> the effective Hamiltonian up to the second order is given by

$$H_{\alpha\beta}^{\text{MCQDPT}} = H_{\alpha\beta} + \frac{1}{2} \times \sum_{I(\neq \text{CAS})} \left\{ \frac{\langle \Psi_{\alpha} | V | \Psi_I \rangle \langle \Psi_I | V | \Psi_{\beta} \rangle}{E_{\beta}^{(0)} - E_I^{(0)}} + (\alpha \leftrightarrow \beta) \right\}, \quad (97)$$

where  $\Psi_{\alpha}$  and  $\Psi_{\beta}$  are states functions composed of the determinants inside the complete active space (CAS), and  $\Psi_I$  are the determinants outside CAS. Here, the perturbation Hamiltonian  $V$  of MCQDPT is identical to that given in Eq. (86), but the one-electron term should be explicitly specified,

$$V = \frac{1}{2} \sum_{pqrs}^{\text{all}} (pq|rs) a_p^{\dagger} a_r^{\dagger} a_s a_q + \sum_{pq}^{\text{all}} \{ h_{pq} - \bar{f}_{pq} \} a_p^{\dagger} a_q + \text{const.}, \quad (98)$$

where  $\bar{f}_{pq}$  is the elements of the modified Fock matrix,

$$\bar{f}_{pq} = f_{pq} + \sum_r^{(-)} [(pq|rr) - (pr|rq)]. \quad (99)$$

In brief, by treating negative-energy orbitals as occupied orbitals as well as substituting the Fock matrix with the modified Fock matrix, we can perform MCQDPT calculations for the QED Hamiltonian. If the active orbital space of the main term does not include both positive- and negative-energy orbitals, the counter term of second-order MCQDPT is identical to that of MP2 because the corresponding active space for the counter term does not contain any particles in this case. Due to the very large energy gap between the positive- and negative-energy solutions, there is almost no non-dynamical correlation between the electron and positron. If one needs to consider both the electron–electron and positron–positron non-dynamical correlations, it is recommended to use, for example, the product space (quasi-complete active space<sup>56,57</sup>) of the electron CAS and the positron CAS instead of the CAS across the positive- and negative-energy orbitals. In the cases of using the product spaces, the counter term of second-order MCQDPT is identical to that of MP2.

### III. NUMERICAL RESULTS AND DISCUSSION

#### A. QED-based DHF calculations: Hydride ion and positronium

In Subsection II C 1, we generalized the DHF method to a method in QED-based form. An important point of the generalization is that it is extended to handle the systems containing positrons. Therefore, the validity of the generalization is tested by whether the method can describe the properties of positrons. In other words, the orbital shapes and energies of negative-energy solutions must be proper as the occupied or virtual orbitals of a positron. To confirm

this point, we performed calculations for the hydride ion and the positronium.

#### 1. Hydride ion

We calculated the hydride ion using the DHF method described in Subsection II C 1 with  $s$ ,  $p$ ,  $d$ ,  $f$ , and  $g$  being orbital-type even-tempered Gaussian basis functions, the exponents of which are given by  $\{\zeta = 0.01(1/45)^3(2.0)^{n-1}, n = 1, 2, \dots, 45\}$ . Here, we focus on the negative-energy virtual orbitals rather than the occupied orbitals of electrons. This is because, for systems without positrons, our formulation is identical to the conventional DHF method, which only gives the physical interpretation of negative-energy solutions. In Fig. 1, the reinterpreted energy levels of the negative-energy orbital  $\tilde{\epsilon}_k$ , which is defined in Eq. (77), are shown. The orbitals with energy  $\tilde{\epsilon}_k < 0$  are regarded as bound levels of a positron. The degeneracy pattern of the bounded negative-energy levels is not at all similar to the single-center Coulombic field. Referring to the discussion in Subsection II B 2, we see the relationship between the symmetry of the original basis functions and that of the negative-energy solutions when they are regarded as positronic orbitals. These orbitals are constructed from the basis functions originally used to describe the  $p_{1/2}$  orbital of the electrons, but both correspond to the  $s$  orbitals of the positron. The shapes of the small component of the two orbitals with the first- and second-lowest reinterpreted orbital energies are shown in Fig. 2. The curve shown on the left side of Fig. 2 corresponds to the  $1s_{1/2}$  orbital of a positron. On the left side of Fig. 2, the function value at the origin is 0.026 356, and the slope is 0.024 353. The curve on the right side of Fig. 2 corresponds to the  $2s_{1/2}$  orbital of a positron. On the right side of Fig. 2, the function value at the origin is 0.015 954, and the slope is 0.016 820. The fact that the function values and the slopes are almost equal indicates that these orbitals follow the nuclear cusp conditions for  $Z = -1$ . Thus, the particles corresponding to these orbitals behave repulsively with the central proton and can be interpreted as actually having a positive charge. This is consistent with the interpretation that these orbitals are positronic virtual orbitals ( $1s_{1/2}$  and  $2s_{1/2}$  orbitals of the positrons), which are caused by the attractive potential created by the two electrons occupying the  $1s_{1/2}$  orbital of the electron. Therefore, our reinterpretation in Subsection II C 1 holds no inconsistency regarding the virtual orbitals of positrons.

#### 2. Positronium

We calculated the singlet configuration of the positronium (para-positronium) using  $s$  and  $p_{1/2}$  orbital-type even-tempered RKB Gaussian basis functions, the exponents of which are given by  $\{\zeta = 0.01(10/45)^3(2.0)^{n-1}, n = 1, 2, \dots, 35\}$ . In this system, no point charge was placed at the center of the basis functions, and the bound state was formed only by the electron–positron attraction. The radial functions of the calculated (relativistic) orbitals corresponding to the nonrelativistic  $1s_{1/2}$  orbitals of electrons and positrons are shown in Fig. 3 (left). Here, the nonrelativistic  $1s$  orbital of an electron corresponds to the large component of the  $s$  orbital with the lowest positive energy, while the nonrelativistic  $1s$  orbital of a positron corresponds to the small component of the  $p_{1/2}$  orbital with the highest negative energy. As described in Subsection II B 2, basis functions employing RKB of the large component of the  $s$  orbitals and the small component of the  $p_{1/2}$

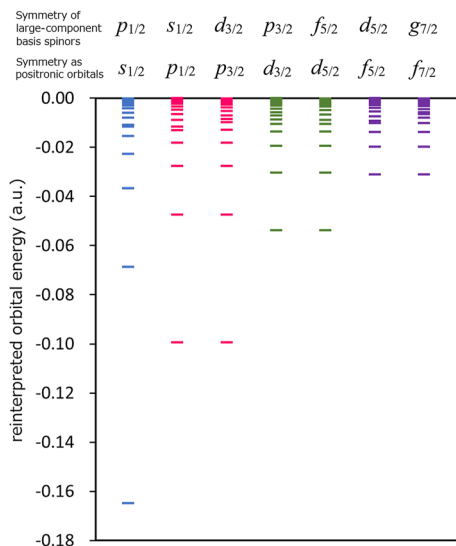


FIG. 1. Energy level of negative-energy orbitals for the hydride ion.

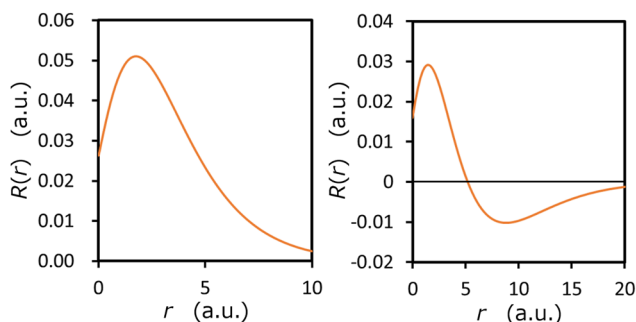


FIG. 2. Radial functions of positronic  $1s_{1/2}$  (left) and  $2s_{1/2}$  (right) orbitals for the hydride ion.

orbitals have different function forms in the radial direction. Nevertheless, these orbitals are in good agreement, and this indicates that the CT invariance can be recovered by employing a sufficient number of basis functions. The calculated orbital energies corresponding to the  $1s_{1/2}$  orbitals of an electron was  $-0.162773$  a.u. and that of a positron was  $-37557.562071$  a.u., which is equal to  $-0.162765$  a.u. in reinterpreted orbital energy. Thus, the CT invariance of the one-particle energy is almost preserved to the fifth decimal place.

The DHF total energy for this system was  $-0.100846$  a.u., which is considerably higher than the exact nonrelativistic total energy of  $-0.25$  a.u. In general, in precise calculations of the total energy of systems with explicit positrons, the electron–positron correlations are taken into account by highly correlated methods, such as the MO method using a Hylleraas-type basis and the diffusion Monte Carlo method. However, since the aim of the numerical calculations in this section is not to calculate positronium compounds accurately but to show that the negative-energy solution

describes the positron, we performed HF calculations for positronium based on the NRMCMO method. The basis functions used were the  $s$ -orbital Gaussian basis set with the same exponents as in the DHF calculations above and common to the electron and positron. The  $1s$  orbital radial functions obtained from the calculation were the same for electron and positron, as shown in Fig. 3 (right). The HF total energy was  $-0.108513$  a.u. The radial function in Fig. 3 (right) is similar to both the large component of the electronic  $1s_{1/2}$  spinor and the small component of the positronic  $1s_{1/2}$  spinor in Fig. 3 (left). Thus, the results of the DHF calculation and NRMCMO HF calculation are in good agreement. This indicates that the reinterpretation for negative-energy orbitals shown in Subsection II C 1 is plausible for the occupied orbitals of positrons.

## B. QED-based MP2 and MCQDPT2 calculations: Helium-like ion

We have expressed our concern about the divergence of the total energy of QED-based electron correlation methods in Subsection II B 4, and our prediction that the problem of this divergence can be solved by a counter term. These concerns and predictions could be shown to exist by numerical calculation of the electron correlation theory in an appropriate system. As a system suitable for the verification, we employed the helium-like ion with  $Z = 100$ . As discussed in Subsection II B 4, the QED-level electron correlation methods involve wave functions consisting of generalized electronic excited configurations, such as pair creations, conventional excitations, and their combinations. Because the number of pair creation configurations becomes very large, even for a system with few electrons, the CI calculations at the QED level are not an easy task. In contrast, second-order perturbation calculations are readily performed. We, therefore, performed the second-order perturbation calculations (MP2 and MCQDPT2) as a test of the QED-level electron correlation theory.

To verify whether the MP2 energy converges to a finite value, we observed the change in energy while varying the range of absolute values of the momentum of the orbitals included in the MP2 calculation. For this calculation, we first performed the DHF calculation to obtain the MOs. The basis functions used were  $s$ -type Gaussian functions with their exponents given by  $\{\zeta = 0.01(100/45)^3(2.0)^{n-1}, n = 1, 2, \dots, 45\}$ . The square momenta of the MOs were calculated from the relativistic kinetic energy as

$$\langle p^2 \rangle_i = (\langle T_R \rangle_i / c + mc)^2 - m^2 c^2, \quad (100)$$

where  $\langle T_R \rangle_i$  is the relativistic kinetic energy of the  $i$ th orbital. We then performed the MP2 calculation by varying the cutoff momentum  $p^2$  (i.e., the MOs with  $\langle p^2 \rangle_i < p^2$  were included in the orbital summation in the MP2 formula). The results of MP2 calculations are shown in Fig. 4. The horizontal axis indicates the cutoff momentum  $p^2$ , and the vertical axis indicates the second-order perturbation energy. Note that QED and QED(renormalized) mean  $E^{(2)}$  and  $E^{(2)} - E_{\text{counter}}^{(2)}$ , respectively. With the increase of  $p^2$ , the perturbation energies of NVPA, VPA, and QED(renormalized) converge to the finite values  $-0.03176$ ,  $-0.02687$ , and  $-0.03733$  a.u., respectively, while the perturbation energies of QED diverge to minus infinity.



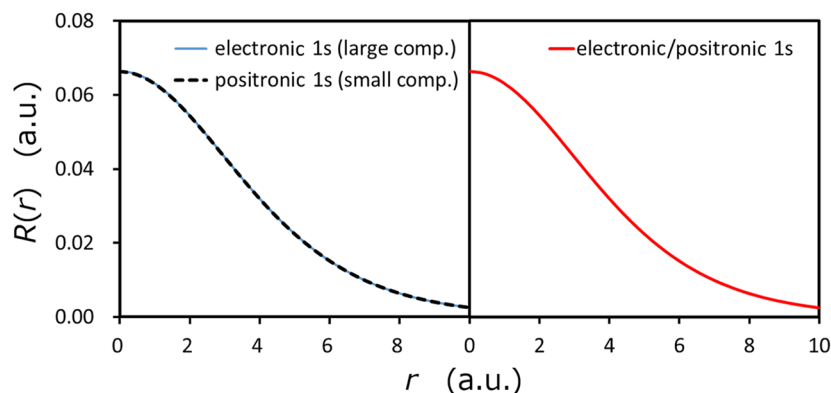


FIG. 3. Radial functions of the electronic and positronic  $1s_{1/2}$  orbitals of positronium calculated by the QED-based DHF (left) and the nonrelativistic multicomponent HF (right) methods.

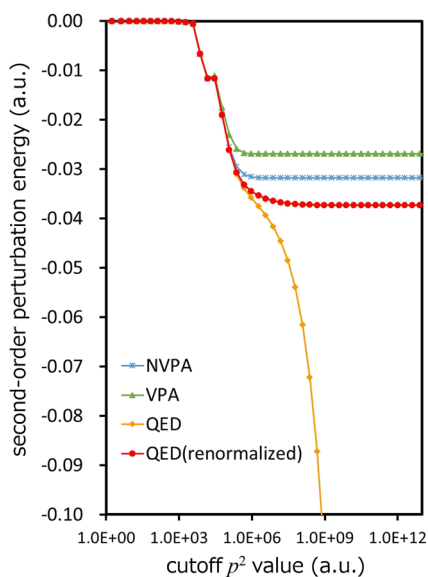


FIG. 4. Second-order perturbation energy of MP2 for helium-like ion ( $Z = 100$ ). The zeroth- and first-order energies (DHF total energy) are  $-11\,796.856\,33$  a.u.

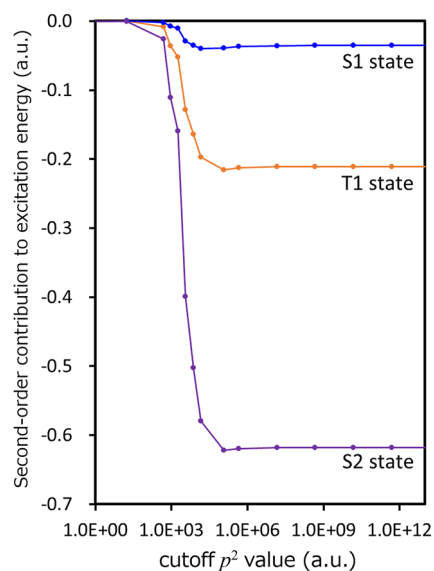


FIG. 5. Second-order contribution of MCQDPT2 to excitation energies for the  $T_1$ ,  $S_1$ , and  $S_2$  excited states of a helium-like ion ( $Z = 100$ ).

Thus, in Fig. 4, the perturbation energy of VPA is higher than that of NVPA and that of QED is lower than that of NVPA. This can be understood from the fact that for second-order perturbations involving negative-energy orbitals, the sign of the denominator of the perturbation is opposite since VPA considers excitation configurations from positive-energy orbitals to negative-energy orbitals and QED considers excitation configurations from negative-energy orbitals to positive-energy orbitals. In Fig. 4, the perturbation energy of QED(renormalized) is lower than that of NVPA due to perturbations that do not cancel with the counter term and have a negative value contribution. The excited configurations giving such perturbations are combinations of a single excitation and a single-pair creation.

Subsequently, we performed MCQDPT2 calculations for the helium-like ion with  $Z = 100$  to observe the behavior of the excited state energies. The MOs are identical to those in the MP2 calculations. The reference space of MCQDPT2 was the CAS-CI composed of two electrons and the  $1s$  and  $2s$  orbitals, and the target states were the ground ( $S_0$ ) and three excited ( $T_1$ ,  $S_1$ , and  $S_2$ ) states, of which the main configurations were the  $1s^2$ ,  $1s^1 2s^1$  (triplet),  $1s^1 2s^1$  (singlet), and  $2s^2$ , respectively. The results are shown in Fig. 5 and Table II. In Fig. 5, the horizontal axis is the same as in Fig. 4, and the vertical axis shows the second-order perturbation contributions of the excitation energies. As in the case of the MP2 energy, the perturbation energy of each state diverges with the addition of large momentum configurations. The renormalized total energy

**TABLE II.** Second-order contributions to excitation energies by MCQDPT. The reference CI (zeroth-plus first-order) excitation energies for the  $T_1$ ,  $S_1$ , and  $S_2$  states are 4334.0179, 4342.2433, and 8719.7062 a.u., respectively, and the  $S_0$  state total energies of QED (renormalized), NVPA, and VPA are  $-11\,796.893\,74$ ,  $-11\,796.888\,17$ , and  $-11\,796.883\,29$ , respectively.

	QED(renormalized)	NVPA	VPA
$T_1$	-0.2107	-0.2091	-0.2123
$S_1$	-0.0355	-0.0339	-0.0357
$S_2$	-0.6178	-0.6123	-0.6163

of each state is the MCQDPT2 energy minus the counter term energy used in the MP2 calculation, which shows a converged finite value as in the MP2 case. As the counter terms of each state are common, the excitation energies, which are the energy differences from the ground state energy, are the values of the second-order perturbation as it is. The obtained excitation energy cancels out the divergence of energy in each state in the same way that the counter terms cancel out each other. In fact, as seen in Fig. 4, the values of the excitation energies for the  $T_1$ ,  $S_1$ , and  $S_2$  states converged to  $-0.2107$ ,  $-0.0355$ , and  $-0.6178$  a.u., respectively, with the increase of  $p^2$ . Thus, it is shown that the QED-based MP2 and MCQDPT give stable and finite values for the total and excitation energies.

#### IV. CONCLUSIONS

We have discussed proper forms of the second-quantized relativistic many-body Hamiltonian in relativistic MO theory. We theoretically investigated the properties of the QED Hamiltonians in terms of the orbital rotation invariance, CT invariance, and non-relativistic limit. First, we examined the orbital rotation invariance of the QED Hamiltonians. We showed that three out of nine QED Hamiltonians are not orbital rotation invariant. This noninvariance may lead to indefinite eigenvalues. However, we also showed that this problem does not arise if the orbitals are fixed to those proper for a stationary state, and that such proper orbitals are determined as MOs giving a stationary point of the total energy surface. Such orbitals are optimal for QED Hamiltonians without rotational invariance, while for QED Hamiltonians with rotational invariance, there is no optimal one and any orbitals can be adopted. Second, we examined the CT invariance of the QED Hamiltonian. We confirmed that the virtual negative-energy orbitals indicate the virtual orbitals of positrons and that the negative-energy orbitals can be used to describe the occupied orbitals of positrons when CT invariance holds and showed that six out of nine QED Hamiltonians are CT invariant. Third, we examined the nonrelativistic limit of the QED Hamiltonians. We showed that only the QED(MO-CNC) Hamiltonian has the nonrelativistic limit consistent with conventional (nonrelativistic) MCMO theory. Among our candidates for the QED Hamiltonians, the only Hamiltonian that meets our requirements is the QED(MO-CNC) Hamiltonian. In addition, we mention the possibility of divergence of the total energy obtained from the QED Hamiltonian, which allows an infinite number of pair creations. To avoid the divergence, we proposed a total energy expression including a counter term, which adjusts the energy origin so that the vacuum energy is zero.

Based on these considerations, we discussed the DHF and electron correlation methods. We confirmed that the conventional DHF equation can also be regarded as the DHF equation for the QED Hamiltonian, keeping the same form, and showed that the DHF equation for positrons is also derived simultaneously. In addition, we presented CI, single-reference perturbation (MP2), and multi-reference perturbation (MCQDPT) methods based on the QED Hamiltonian.

In the results of the DHF calculations of the hydride ion, the negative-energy orbital with negative reinterpreted orbital energy can be interpreted as a bound positron. It was also found that, although the function forms of the basis functions using RKB lack CT invariance, the CT invariance of the QED Hamiltonian itself can be recovered by using a sufficiently rich basis function set. The results of MP2 calculations for the helium-like ion showed that the total energy of the QED Hamiltonian without the counter term diverges to minus infinity, and the introduction of the counter term leads to a proper finite total energy. The MCQDPT calculations for the helium-like ion also showed that the QED Hamiltonian gives finite excitation energies; in this case, the counter term does not affect the excitation energies since they are the energy differences between the total energies of the states. From these considerations and results for a relativistic MO theory without the theoretical inconsistency we mentioned, it is appropriate to use the QED (MO-CNC) Hamiltonian, MOs that give a stationary point of total energy, and to introduce a counter term that suppresses divergence.

#### SUPPLEMENTARY MATERIAL

See the supplementary material for the explanation of the formulation of counter terms that differ from those presented in the main text.

#### ACKNOWLEDGMENTS

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#### AUTHOR DECLARATIONS

##### Conflict of Interest

The authors have no conflicts to disclose.

#### Author Contributions

**Nobuki Inoue:** Conceptualization (equal); Funding acquisition (equal); Methodology (equal); Software (equal); Writing – original draft (equal). **Yoshihiro Watanabe:** Software (equal); Supervision (equal); Writing – review & editing (equal). **Haruyuki Nakano:** Funding acquisition (equal); Project administration (equal); Software (equal); Supervision (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

## APPENDIX: PROOF OF NO TIME EVOLUTION OF WAVE FUNCTION GIVING STATIONARY POINT

In this appendix, we show that MOs (and CI coefficients) giving a stationary point of total energy do not evolve in time from the time-dependent variational principle.

Let  $|\Psi(t)\rangle$  be the wave function of a state and express its time dependence as a linear combination of determinants  $|\Phi_I(t)\rangle$ ,

$$|\Psi(t)\rangle = \sum_I C_I(t) |\Phi_I(t)\rangle. \quad (\text{A1})$$

The time dependence of the determinants  $|\Phi_I(t)\rangle$  is further expressed using time-dependent MO coefficients  $q_{mi}(t)$  for the MOs  $\varphi_i(t)$ ,

$$\varphi_i(t) = \sum_m q_{mi}(t) \varphi_m(0), \quad (\text{A2})$$

and creation operators  $a_m^\dagger(0)$  at  $t = 0$  as

$$|\Phi_I(t)\rangle = \prod_i^{\text{occ.}I} \left( \sum_m q_{mi}(t) a_m^\dagger(0) \right) |\text{empty}\rangle, \quad (\text{A3})$$

where  $i$  in the multiplication runs over the occupied MOs in determinant  $I$ . To describe the time evolution of the state  $|\Psi(t)\rangle$ , we define the following Lagrangian:

$$\begin{aligned} L = & \frac{i}{2} \langle \Psi(t) | \dot{\Psi}(t) \rangle - \frac{i}{2} \langle \dot{\Psi}(t) | \Psi(t) \rangle - \langle \Psi(t) | H | \Psi(t) \rangle \\ & - \sum_{ij} \lambda_{ij} \left( \frac{d}{dt} \sum_k (q_{ki}^*(t) q_{kj}(t)) \right) \\ & - \Lambda \left( \frac{d}{dt} \sum_I (C_I^*(t) C_I(t)) \right), \end{aligned} \quad (\text{A4})$$

where the “over-dot” means the time derivative, as usual. Because the ket  $|\Psi(t)\rangle$  depends only on  $q_{pq}$  and  $C_I$  but not on their complex conjugate  $q_{pq}^*$  and  $C_I^*$ , and vice versa for the bra  $\langle \Psi(t) |$ , the time derivative of the state  $|\dot{\Psi}(t)\rangle$  is written as

$$\begin{aligned} |\dot{\Psi}(t)\rangle &= \sum_{pq} \left( \frac{\partial \Psi}{\partial q_{pq}}(t) \right) \dot{q}_{pq} + \sum_I \left( \frac{\partial \Psi}{\partial C_I}(t) \right) \dot{C}_I, \\ \langle \dot{\Psi}(t) | &= \sum_{pq} \left( \frac{\partial \Psi}{\partial q_{pq}}(t) \right) \dot{q}_{pq}^* + \sum_I \left( \frac{\partial \Psi}{\partial C_I}(t) \right) \dot{C}_I^*. \end{aligned} \quad (\text{A5})$$

Then, applying the Euler–Lagrange equation to the Lagrangian (A4) gives the equation of motions for the MOs,

$$\begin{aligned} \frac{\partial L}{\partial q_{pq}^*} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_{pq}^*} &= i \sum_{rs} A_{pq,rs} \dot{q}_{rs}(t) + i \sum_I a_{I,pq}^* \dot{C}_I(t) - \frac{\partial E}{\partial q_{pq}^*} \\ &= 0, \end{aligned} \quad (\text{A6})$$

as well as that for CI coefficients,

$$\begin{aligned} \frac{\partial L}{\partial C_I^*} - \frac{d}{dt} \frac{\partial L}{\partial \dot{C}_I^*} &= i \sum_{rs} a_{I,rs} \dot{q}_{rs}(t) + i \dot{C}_I(t) - \frac{\partial E}{\partial C_I^*} \\ &= 0, \end{aligned} \quad (\text{A7})$$

where we have used the following as shorthand notations:

$$\begin{aligned} E &\equiv \langle \Psi(t) | H | \Psi(t) \rangle, \\ A_{pq,rs} &\equiv \left\langle \frac{\partial \Psi}{\partial q_{pq}}(t) \left| \frac{\partial \Psi}{\partial q_{rs}}(t) \right. \right\rangle, \\ a_{I,pq} &\equiv \left\langle \frac{\partial \Psi}{\partial C_I}(t) \left| \frac{\partial \Psi}{\partial q_{pq}}(t) \right. \right\rangle. \end{aligned} \quad (\text{A8})$$

By combining Eqs. (A6) and (A7) into a matrix representation, we have

$$\begin{bmatrix} \mathbf{A} & \mathbf{a}^\dagger \\ \mathbf{a} & \mathbf{1} \end{bmatrix} \begin{bmatrix} \dot{\mathbf{q}} \\ \dot{\mathbf{C}} \end{bmatrix} = \begin{bmatrix} \partial E / \partial \mathbf{q}^* \\ \partial E / \partial \mathbf{C}^* \end{bmatrix}, \quad (\text{A9})$$

which shows that if  $\partial E / \partial q_{pq}^* = 0$  and  $\partial E / \partial C_I^* = 0$ , then  $\dot{q}_{rs}(t) = 0$  because the inverse of the coefficient matrix of Eq. (A9) exists under usual conditions. In other words, if  $E$  is at a stationary point with respect to changes in MO coefficients  $q_{pq}(t)$  and CI coefficients  $C_I(t)$ , the orbital coefficients  $q_{pq}(t)$  do not evolve in time.

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