Going beyond "no-pair relativistic quantum chemistry"

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The current field of relativistic quantum chemistry (RQC) has been built upon the no-pair and no-retardation approximations. While retardation effects must be treated in a time-dependent manner through quantum electrodynamics (QED) and are hence outside RQC, the no-pair approximation (NPA) has to be removed from RQC for it has some fundamental defects. Both configuration space and Fock space formulations have been proposed in the literature to do this. However, the former is simply wrong, whereas the latter is still incomplete. To resolve the old problems pertinent to the NPA itself and new problems beyond the NPA, we propose here an effective many-body (EMB) QED approach that is in full accordance with standard methodologies of electronic structure. As a first application, the full second order energy E_2 of a closed-shell many-electron system subject to the instantaneous Coulomb-Breit interaction is derived, both algebraically and diagrammatically. It is shown that the same E_2 can be obtained by means of 3 Goldstone-like diagrams through the standard many-body perturbation theory or 28 Feynman diagrams through the S-matrix technique. The NPA arises naturally by retaining only the terms involving the positive energy states. The potential dependence of the NPA can be removed by adding in the QED one-body counter terms involving the negative energy states, thereby leading to a "potential-independent no-pair approximation" (PI-NPA). The NPA, PI-NPA, EMB-QED, and full QED then span a continuous spectrum of relativistic molecular quantum mechanics. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4811795]

I. INTRODUCTION

The last decade has witnessed fast developments of relativistic quantum chemistry (RQC), as symbolized by the advent of the so-called exact two-component (X2C)[1] relativistic Hamiltonians (for recent reviews see Refs. 2–4). What is equally important in this context is the observation that, under very mild conditions, four- and two-component relativistic approaches can be made fully equivalent in all the aspects of simplicity, accuracy, and efficiency through the generic ideas of "quasi-four-component" (Q4C)[5] and "from atoms/fragments to molecules"[6–8] (or something similar[9,10]). In essence, the no-pair projected Dirac-Coulomb-Breit (DCB) Hamiltonian H_+^{DCB} and its Q4C (H_+^{Q4C}) and X2C (H_+^{X2C}) variants share the same generic second-quantized normal-ordered form[7] as the Schrödinger-Coulomb (SC) Hamiltonian (H_+^{SC}), viz.,

$$H_+^{\mathrm{X}}\Psi^{\mathrm{X}} = E\Psi^{\mathrm{X}}, \quad \Psi^{\mathrm{X}} = W^{\mathrm{X}}|0\rangle, \qquad \mathrm{X} = \mathrm{SC, X2C, Q4C, DCB}, \tag{1}$$

$$H_+^{\mathrm{X}} = H_0^{\mathrm{X}} + H_1^{\mathrm{X}} + H_2^{\mathrm{X}}, \tag{2}$$

$$H_0^{\mathrm{X}} = \langle 0|H_+^{\mathrm{X}}|0\rangle, \tag{3}$$

$$H_1^{\mathrm{X}} = (f^{\mathbf{X}})_p^q\{a_q^p\}, \quad a_q^p = a_p^\dagger a_q, \tag{4}$$

$$H_2^{\mathrm{X}} = \tfrac{1}{4}\bar{g}_{pq}^{rs}\{a_{rs}^{pq}\}, \quad a_{rs}^{pq} = a_p^\dagger a_q^\dagger a_s a_r, \qquad \bar{g}_{pq}^{rs} = g_{pq}^{rs} - g_{pq}^{sr} = g_{pq}^{rs} - g_{qp}^{rs}, \tag{5}$$

$$g_{pq}^{rs} = \int\int d\vec{r}_1^3 d\vec{r}_2^3 \varphi_p^\dagger(\vec{r}_1)\varphi_q^\dagger(\vec{r}_2) g(1,2)\varphi_r(\vec{r}_1)\varphi_s(\vec{r}_2). \tag{6}$$

They differ formally only in the Fock operator f^{X} generating the orbitals. Yet, a subtlety lies in that the bare Coulomb, Coulomb-Gaunt, or Coulomb-Breit operators, viz.,

$$g(1,2) = g_{\mathrm{C}}(1,2) + g_{\mathrm{B}}(1,2), \tag{7}$$

$$g_{\mathrm{C}}(1,2) = \frac{I_4 I_4}{r_{12}}, \tag{8}$$

$$g_{\mathrm{B}}(1,2) = g_{\mathrm{G}}(1,2) + g_{\mathrm{g}}(1,2), \tag{9}$$

$$g_{\mathrm{G}}(1,2) = -\frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{r_{12}}, \tag{10}$$

$$g_{\mathrm{g}}(1,2) = \frac{\vec{\alpha}_1 \cdot \vec{\alpha}_2}{2r_{12}} - \frac{(\vec{\alpha}_1 \cdot \vec{r}_{12})(\vec{\alpha}_2 \cdot \vec{r}_{12})}{2r_{12}^3} \tag{11}$$

can all directly be used for $g(1,2)$ (6) in the case of Q4C, but they must be transformed appropriately in the case

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of X2C. As a very good approximation,[11] the Gaunt or Breit interaction can be treated at the mean-field level through $f^{\mathrm{X2C/Q4C}}$, while only the bare Coulomb term is adopted for the fluctuation potential (5) of X2C/Q4C. Then, X2C/Q4C is computationally very similar to those approximate two-comment (A2C) approaches[12,13] that combine some approximately transformed one-electron operator h^{A2C} with the bare Coulomb operator. Although defined only algebraically, the spin separations of the no-pair DCB, Q4C, and X2C Hamiltonians are still possible, leading to a series of new Hamiltonians that are infinite order in scalar relativity and finite order in spin-orbit coupling.[14] In this regard, the sf-X2C+DKH$_n$ Hamiltonian by combining the spin-free (sf) part of X2C with the nth order Douglas-Kroll-Hess[12] (DKH$_n$) type of spin-dependent (sd) terms is particularly promising.[15] The no-pair Hamiltonian axis,[16] going from SC through sf-A2C, sf-X2C, A2C, sf-X2C+DKH$_n$, X2C, and Q4C to DCB, can now be regarded as completed. Any orbital-based correlation methods for parameterizing the wave function Ψ^{X} through the wave operator W^{X} can directly be used (for recent reviews see Ref. 17). However, one has to be aware that the no-pair approximation (NPA) itself has several drawbacks: (a) Being defined only at matrix level, the H_+^{X} (X = DCB, Q4C, X2C) Hamiltonians are incompatible with the so-called explicitly correlated methods[18–20] because of two reasons. First, integrals like $\langle pq|\hat{h}_{rel} f_{12}|rs\rangle$ and $\langle pq| f_{12}\hat{h}_{rel} f_{12}|rs\rangle$ must be evaluated analytically to achieve fast convergence,[21] but the required relativistic operator $\hat{h}_{rel}$ is not available in such Hamiltonians. Second and more seriously, just like any second-quantized Hamiltonian, such Hamiltonians have only a finite spectrum limited by the given basis such that the effect of the correlation factor f_{12} is just null for an obvious reason: The r_{12}-dependent two-electron basis functions try to simulate an orthogonal complementary correlation space but which is not part of the Hamiltonians. (b) At variance with the nonrelativistic full configuration interaction (FCI), the no-pair FCI (more precisely, complete active space CI) energy is always dependent on the potential used to generate the orbitals.[22] This is a direct consequence of ignoring the correlation space spanned by the negative energy states (NES) of the Dirac operator. An immediate question is then whether the combination of a no-pair calculation with only radiative quantum electrodynamics (QED) corrections is meaningful at all: The missing contribution of NES to correlation[23] is of the same order of $(Z\alpha)^3$ as the leading QED corrections. A recent numerical study[24] indeed shows that, for the ionization potential of the gold atom, the already good agreement between the no-pair calculation[25] and experiment is worsened instead of improved when the corrections due to one-electron self-energy and vacuum polarization are included. This is likely due to the missing correlation of NES, approximately 3% of the total correlation.

It turns out that the two problems in (a) can be resolved by introducing an *extended* no-pair DCB Hamiltonian,[16,26] viz.,

$$\tilde{H}_+ = \begin{pmatrix} PH_{CS}P & PH_{CS}Q \\ QH_{CS}P & QH_{CS}Q \end{pmatrix}, \tag{12}$$

$$P_{12} = (O^+(1) + V^+(1))(O^+(2) + V^+(2)), \tag{13}$$

$$Q_{12} = (1 - O^+(1) - V^-(1))(1 - O^+(2) - V^-(2)) \times (1 - V^+(1)V^+(2)). \tag{14}$$

Here, H_{CS} is the first-quantized configuration space (CS) DCB Hamiltonian for N-electrons moving in the field of the clamped nuclei

$$H_{\mathrm{CS}} = \sum_i^N D(i) + \sum_{i<j}^N g(i,j), \tag{15}$$

$$D = D_0 + V_{ext}, \tag{16}$$

$$D_0 = c\vec{\alpha}\cdot\vec{p} + \beta mc^2, \tag{17}$$

$$V_{ext}(\vec{r}) = q\phi_{ext}(\vec{r}), \quad \phi_{ext}(\vec{r}) = \sum_A \frac{Z_A e}{|\vec{r} - \vec{R}_A|}, \quad q = -e = -1, \tag{18}$$

where D_0 is the free particle Dirac operator, V_{ext} is the nuclear attraction, $c = 1/\alpha$ is the speed of light, $\vec{p} = -i\vec{\nabla}$ is the linear momentum operator, and $\vec{\alpha}$ and β are the usual 4×4 Dirac matrices. The O^+, V^+, and V^- operators in Eqs. (13) and (14) are the respective projectors for the occupied positive energy states (PES), unoccupied PES and NES defined by the given basis. The projectors P_{12} and Q_{12} are to act on the conventional and explicitly correlated subspaces, respectively. The so-defined Q_{12} is formally in line with the filled Dirac picture: Both O^+ and V^- can be viewed as occupied. It ensures strong orthogonality to the "reference" $O^+ + V^-$ as well as orthogonality to the conventional correlation subspace spanned by orbital products. Moreover, it has minimal unphysical contamination from the NES and the correct nonrelativistic limit. Further combined with the coalescence conditions of relativistic wave functions,[26,27] four-component relativistic explicitly correlated methods can then be made fully parallel to the nonrelativistic counterparts.[26] A first implementation along this line was just reported by Ten-no and Yamaki.[28] It can be envisaged that the treatment of no-pair correlation shall soon reach an accuracy of approximately 10^{-2} eV for systems containing heavy elements. At that stage, the intrinsic $\mathcal{O}(Z\alpha)^3$ uncertainty of the no-pair correlation energy must be removed to make the accuracy really valid. This can only be achieved by further accounting for the contribution of NES to correlation. The question is how. This is probably the single final issue left with RQC from a formal point of view.[29] It is also related to the exponible as how to bridge seamlessly RQC and QED, the two mutually exclusive subfields.

There have been two approaches in the field of RQC for handling the NES, i.e., the configuration space (CS) approach[30–35] associated with the empty Dirac picture and the Fock space (FS) approach[37–41] associated with the filled Dirac picture. While they yield identical results for one-electron properties of any order, the two approaches are completely different in the contribution of NES to two-electron properties beyond first order, including electron correlation.[16] In the latter regard, the CS approach is completely illegitimate for both mathematical and physical reasons. Mathematically, it suffers

from the (in)famous continuum dissolution problem,[42] which implies essentially that the first-quantized configuration space DC/DCB Hamiltonian (15) does *not* have any bound electronic states and even its discrete states are characterized by complex energies and are hence resonances of finite life times. The latter further implies that the DC/DCB Hamiltonian is *not* self-adjoint (Hermitian). Although deduced only from a crude model[42] and numerical experimentations,[32–35] such deductions are further confirmed by firmer formal evidence.[26,43] The CS approach is also physically wrong: It conserves the number of electrons, at variance with the true physics where it is the charge instead of the number of particles that is conserved. In other words, the CS approach treats the NES as if they were energetically positive, just like the unoccupied $1s$ spin orbitals of He$2s^2$. This is more clearly seen from the "recovery"[16] of the CS approach from QED by replacing the Feynman electron propagator

$$S_F(x_2, x_1) = -i\langle 0|T[\phi(x_2)\phi^\dagger(x_1)]|0\rangle, \qquad \phi(x) = b_p\varphi_p(\vec{r})e^{-i\epsilon_p t} + b^{\tilde{p}}\varphi_{\tilde{p}}(\vec{r})e^{-i\epsilon_{\tilde{p}} t} \tag{19}$$

$$= -i\langle 0|\Theta(t_2 - t_1)\phi(x_2)\phi^\dagger(x_1) - \Theta(t_1 - t_2)\phi^\dagger(x_1)\phi(x_2)|0\rangle \tag{20}$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{\varphi_t(\vec{r}_2)\varphi_t^\dagger(\vec{r}_1)}{\omega - \epsilon_t + i\eta\epsilon_t} e^{-i\omega(t_2 - t_1)}, \quad t \in \{p, \tilde{p}\} \tag{21}$$

with the "configuration space propagator"

$$S_C(x_2, x_1) = -i\langle 0|T[\phi(x_2)\phi^\dagger(x_1)]|0\rangle, \qquad \phi(x) = a_p\varphi_p(\vec{r})e^{-i\epsilon_p t} + a_{\tilde{p}}\varphi_{\tilde{p}}(\vec{r})e^{-i\epsilon_{\tilde{p}} t} \tag{22}$$

$$= -i\Theta(t_2 - t_1)\langle 0|\phi(x_2)\phi^\dagger(x_1) + \phi^\dagger(x_1)\phi(x_2)|0\rangle \tag{23}$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{\varphi_t(\vec{r}_2)\varphi_t^\dagger(\vec{r}_1)}{\omega - \epsilon_t + i\eta|\epsilon_t|} e^{-i\omega(t_2 - t_1)}, \quad t \in \{p, \tilde{p}\}. \tag{24}$$

Here, the implicit summations over t in Eqs. (21) and (24) include both PES (p) and NES ($\tilde{p}$), whether occupied or not. While $S_F(x_2, x_1)$ (21) propagates the PES forward in time (through the Heaviside function $\Theta(t_2 - t_1)$ or equivalently the lower-half-plane poles $\epsilon_p - i\eta$) and the NES backward in time (through the Heaviside function $\Theta(t_1 - t_2)$ or equivalently the upper-half-plane poles $\epsilon_{\tilde{p}} + i\eta$), $S_C(x_2, x_1)$ (24) propagates both the PES and NES forward in time. Since the replacement of $S_F(x_2, x_1)$ with $S_C(x_2, x_1)$ changes the nature of NES completely, it is clear that the CS approach is *not* an approximation of QED, the Holy Grail of electromagnetic interactions between charged particles. In particular, the *anti-correlating* contribution of NES in the CS approach (i.e., energy increasing when included in the correlation treatment)[30–35] is *not* part of QED effects, sometimes claimed though. Again, this should not be confused with the anti-correlating contribution of $1s$ to He$2s^2$: While the Schrödinger He$2s^2$ is truly unstable, the Dirac He$1s^2$ is certainly stable even in the presence of NES. In sum, the CS approach should definitely be dumped even if the DC/DCB Hamiltonian were self-adjoint and had bound states. In other words, the first-quantized configuration space DC/DCB equation cannot be solved as it stands. Instead, the NPA is here a conceptual must instead merely of a technical means[44] to avoid the continuum dissolution problem.

Rather unexpectedly, as far as the correlation contribution of NES is concerned,[23] the FS approach[37–41] differs also from QED although they share the same framework. It will be shown here that the previous comparison[16] of FS with QED was "unfair": The FS second order energy contains some radiative terms that were not ascribed to correlation and were hence excluded deliberately from QED.[16,22] The two approaches do agree with each other when the same radiative and non-radiative Feynman diagrams are considered. Therefore, the FS approach should be regarded as an important step for going beyond the no-pair RQC. Nonetheless, the FS approach is still incomplete: Only those radiative Feynman diagrams featured by photon self-energy and vertex correction are captured, whereas those radiative Feynman diagrams featured by electron self-energy and vacuum polarization are all missed. Note in particular that the former appear at second and higher orders, whereas the latter enter already at first order. It will be shown here that the missing electron vacuum polarization and self-energy can be captured in a natural manner through an effective one-body potential. Here, the newly introduced "charge-conjugated contraction" of Fermion fields plays the key role, see Sec. II A. The resulting Schrödinger-Coulomb-like effective Hamiltonian can account for all kinds of virtual-pair effects due to non-retarded interactions, and meanwhile is fully compatible with with the standard many-body theories of electronic structure. To confirm this, the full second order energy of a closed-shell system of N-electrons are to be derived in three different ways in Sec. II B. The present findings lead naturally to a new definition of RQC as "theory for anything due to non-retarded interactions," whereas QED accordingly as "theory for anything due to retarded interactions."

Apart from the Einstein summation convention over repeated indices, the following convention is to be adopted throughout the work: The occupied PES are to be denoted by $\{i, j, \dots\}$, whereas the unoccupied PES and NES by $\{a, b, \dots\}$ and $\{\tilde{i}, \tilde{j}, \cdots\}$, respectively. Unspecified orbitals are denoted as $\{p, q, r, s\}$. When necessary, the NES will explicitly be designated by $\{\tilde{p}, \tilde{q}, \tilde{r}, \tilde{s}\}$.

II. EFFECTIVE MANY-BODY QED APPROACH

A. The non-retarded QED Hamiltonian

The so-called no-photon FS Hamiltonian is defined as[36–41]

$$H_{\rm FS}[b] = \int d\vec{r}\{\phi^\dagger(\vec{r})D\phi(\vec{r})\} + \frac{1}{2}\iint d\vec{r}_1 d\vec{r}_2\{\phi^\dagger(\vec{r}_1)\phi^\dagger(\vec{r}_2) \times g(r_1, r_2)\phi(\vec{r}_2)\phi(\vec{r}_1)\}, \tag{25}$$

where the curly brackets indicate normal ordering. The field operator $\phi(\vec{r})$ is defined as

$$\phi(\vec{r}) = b_p\varphi_p(\vec{r}) + b^{\tilde{p}}\varphi_{\tilde{p}}(\vec{r}), \quad b_p|0;\tilde{0}\rangle = b_{\tilde{p}}|0;\tilde{0}\rangle = 0, \tag{26}$$

where b_p (b^p) annihilates (creates) an electron of positive energy ϵ_p, whereas $b^{\tilde{p}}$ ($b_{\tilde{p}}$) creates (annihilates) a positron of positive energy $|\epsilon_{\tilde{p}}| = -\epsilon_{\tilde{p}}$. Inserting the expression (26) for $\phi(\vec{r})$ into $H_{\rm FS}[b]$ (25) leads to 4 and 16 terms for the one- and two-body parts, respectively. Close inspections reveal that the Hamiltonian (25) is based on three essential ingredients:

(I) Second-quantize the matter field $\phi(\vec{r})$ in terms of the PES and NES of a mean-field operator h, viz.,

$$h\varphi_p = \epsilon_p\varphi_p, \quad h = D + U. \tag{27}$$

Various choices can be made for the counter potential U: (a) $U = -V_{ext}$, the free-particle picture;[45] (b) $U = 0$, the Furry picture;[46] (c) $U = V_{HF}$, the Fuzzy picture;[47] (d) $U = V_{loc}$, the extended Furry picture. It appears that the appearance of unoccupied NES imposes no particular problem on solving Eq. (27) represented in a finite basis, as long as the basis is constructed according to, e.g., the restricted kinetic balance (RKB) condition[48] and meanwhile the electrons are, in each iteration cycle, assigned to the lowest PES. Even full variational safety[49] can be guaranteed via the dual kinetic balance (DKB) condition.[50]

(II) Introduce the particle-hole picture. That is, the NES are reinterpreted as holes (virtual positrons). This is dictated by the charge conjugation symmetry. The charge conservation further dictates that the operator $b^{\tilde{p}}$ (instead of $b_{\tilde{p}}$) must accompany b_p in the field operator $\phi(\vec{r})$ (26). This can be seen as follows. Both b_p and $b^{\tilde{p}}$ increase the charge of a state by one unit; b_p does this by destroying an electron, whereas $b^{\tilde{p}}$ does this by creating a positron. Thus, the field operator $\phi(\vec{r})$ always increases one unit of charge. Similarly, the field operator $\phi^\dagger(\vec{r})$ always decreases one unit of charge. Therefore, the operator $\phi^\dagger(\vec{r})\phi(\vec{r})$ conserves the charge.

(III) Introduce the concept of normal ordering. Effectively, this will change the sign of the negative energy $\epsilon_{\tilde{p}}$ and meanwhile get rid of the infinite energy of the otherwise filled Dirac sea.

Additional remarks should be made here.

(1) At first glance, it is quite puzzling that the mean-field equation (27) is usually solved under the empty Dirac picture but the field quantization (26) actually adopts the filled Dirac picture. Yet, as shown by Dyall and Fægri,[40] variation of the expectation value of $H_{\rm FS}[b]$ over a single determinant wave function $|\alpha\rangle = |N;\tilde{0}\rangle^{(0)}$ leads to precisely the same equation (27), provided that the vacuum $|0;\tilde{0}\rangle$ itself is "floating," i.e., updated self-consistently. Therefore, the mean-field calculation with the empty Dirac picture is perfectly justified. The situation would be different if a frozen vacuum (e.g., the free particle one) is considered. In this case, (unrenormalized) vacuum polarizations would arise from the one-body potential $V_{ext} + U$ already at the mean-field level. Therefore, the Hamiltonian $H_{\rm FS}[b]$ (25) should be classified into two types, with the associated vacuum $|0;\tilde{0}\rangle$ frozen[37–39] or floating.[40,41] The latter is more appealing for bound states, where virtual pairs are only created by the fluctuation potential and represent pure correlation effects when the screening potential U is chosen to be the Hartree-Fock potential V_{HF}.

(2) The same Hamiltonian $H_{\rm FS}[b]$ (25) along with a floating vacuum $|0;\tilde{0}\rangle$ was discussed by both Dyall[40] and Kutzelnigg.[41] However, the former focused only on the stationarity conditions for mean-field calculations, whereas the latter advocated strongly that the Hamiltonian $H_{\rm FS}[b]$ is the only acceptable relativistic many-body Hamiltonian under the no-photon approximation, provided that the polarization of the floating $|0;\tilde{0}\rangle$ is also taken into account.

(3) As explained before,[16] the Hamiltonian $H_{\rm FS}[b]$ (25) can be rewritten as

$$H_{\rm FS}[a] = D_p^q\{a_q^p\}_n + \frac{1}{2}g_{pq}^{rs}\{a_{rs}^{pq}\}_n \tag{28}$$

$$= \epsilon_p\{a_p^p\}_n - U_p^q\{a_q^p\}_n + \frac{1}{2}g_{pq}^{rs}\{a_{rs}^{pq}\}_n, \tag{29}$$

where the subscript n emphasizes that the normal ordering is taken with respect to the vacuum $|0;\tilde{N}\rangle = \Pi_{\tilde{i}}^{\tilde{N}}a^{\tilde{i}}|0;\tilde{0}\rangle$, manifesting the filled Dirac picture. This form is more akin to nonrelativistic quantum mechanics and is operationally much easier when deriving the energy expressions (cf. Sec. II B 1).

In short, the Hamiltonian $H_{\rm FS}[b]$ (25) together with the polarization of the floating $|0;\tilde{0}\rangle$, or equivalently the Hamiltonian $H_{\rm FS}[a]$ (28) together with the polarization of the floating $|0;\tilde{N}\rangle$, defines the no-photon Fock space approach proposed by Kutzelnigg.[41] However, the so-introduced "vacuum polarization" refers actually to "photon self-energy" rather than "electron vacuum polarization," as clearly seen from the analysis in Sec. II B 2. Both electron vacuum polarization and electron self-energy are missed by taking only the normal-ordered two-body interaction, the second term of Eq. (25) or (28). The question is how to incorporate such terms into the Hamiltonian in the same way as above. To achieve this goal, we first notice that the normal-ordered Hamiltonian (28) arises actually as follows:

$$H_{\rm FS}[a] = H - \langle 0;\tilde{N}|H|0;\tilde{N}\rangle \tag{30}$$

$$= \epsilon_p\{a_p^p\}_n - U_p^q\{a_q^p\}_n + \frac{1}{2}g_{pq}^{rs}\{a_{rs}^{pq}\}_n, \tag{31}$$

where the unnormal-ordered Hamiltonian H reads

$$H = D_p^q a_q^p + \frac{1}{2}g_{pq}^{rs}a_{rs}^{pq} = \epsilon_p a_p^p - U_p^q a_q^p + \frac{1}{2}g_{pq}^{rs}a_{rs}^{pq}. \tag{32}$$

Going from Eqs. (30) to (31) is the usual normal ordering, apart from that the contractions among the occupied NES are excluded. Otherwise, we would obtain the following

Hamiltonian:

$$H_{\rm CS}[a] = H_{\rm FS}[a] + \bar{g}^{q\tilde{j}}_{p\tilde{j}}\{a^p_q\}_n. \tag{33}$$

This is just the second-quantized Schrödinger-Coulomb Hamiltonian if the NES $\tilde{j}$ are interpreted as the occupied HF orbitals. For the present case, it can readily be shown that even the first order energy $\tilde{E}^{(1)}$ of $H_{\rm CS}[a]$ (33), i.e.,

$$\tilde{E}^{(1)} = E^{(1)}_{\rm np} + \bar{g}^{i\tilde{j}}_{i\tilde{j}}, \tag{34}$$

$$E^{(1)}_{\rm np} = \frac{1}{2}\bar{g}^{ij}_{ij} - U^i_i \tag{35}$$

is incorrect, as compared either to $E^{(1)}_{\rm np}$ (35) or $E^{(1)}$ (62). As a matter of fact, $H_{\rm CS}[a]$ (33) corresponds to a truly filled Dirac sea, at variance with $H_{\rm FS}[a]$ (28) where the filled Dirac sea is introduced only as a formal step to avoid conceptually the so-called radiation catastrophe associated with the empty Dirac sea. The second term of Eq. (33) arising from the contractions only within the NES amounts to treating the PES and NES asymmetrically. If we start with the free-particle Dirac equation, we usually interpret the PES (q_1) as electrons and the NES (q_2) as positrons, but we can equally interpret the PES as positrons and the NES as electrons. The situation remains unchanged when switching on the internal Coulomb interaction $\frac{q_1 q_2}{r_{12}}$, which is exchangeable with respect to the charges: $q_1q_2 = +1$ for both $q_1 = q_2 = -1$ and $q_1 = q_2 = +1$; $q_1q_2 = -1$ for both $q_1 = -1$, $q_2 = +1$ and $q_1 = +1$, $q_2 = -1$. The charge conjugation symmetry is broken only when an external field $\phi_{ext}(\vec{r})$ is introduced through the minimal coupling principle, i.e., $q\phi_{ext}(\vec{r})$, which is different for different charges. The question is: What is the mean-field interaction between the PES and NES before the external field is switched on? Such a mean-field, generated from the contractions of the Coulomb interaction through normal ordering, must be symmetric with respect to the PES and NES. To achieve this, we introduce here a "charge-conjugated contraction" (CCC) of the Fermion operators, viz.,

$$\underbrace{AB} = \langle vac|\frac{1}{2}[A, B]|vac\rangle, \tag{36}$$

such that

$$AB = \{AB\} + \underbrace{AB}. \tag{37}$$

It is understood that the expansion (37) includes all possible numbers and combinations of contractions. For the present case, we have $|vac\rangle = |0; \tilde{N}\rangle$ and hence

$$a^p a_q = \{a^p a_q\}_n - \frac{1}{2}\delta^p_q, \quad \epsilon_p, \epsilon_q > 0, \tag{38}$$

$$a^{\tilde{p}} a_{\tilde{q}} = \{a^{\tilde{q}} a_{\tilde{p}}\}_n + \frac{1}{2}\delta^{\tilde{p}}_{\tilde{q}}, \quad \epsilon_{\tilde{p}}, \epsilon_{\tilde{q}} < 0, \tag{39}$$

which can generally be written as

$$a^p_q = \{a^p a_q\}_n - \frac{1}{2}\delta^p_q {\rm sgn}(\epsilon_q), \quad \forall {\rm PES, NES}. \tag{40}$$

By applying this relation repeatedly we obtain

$$\begin{aligned} a^{pq}_{rs} = \{a^{pq}_{rs}\}_n &- \frac{1}{2}\{\delta^p_r a^q_s {\rm sgn}(\epsilon_r) + \delta^q_s a^p_r {\rm sgn}(\epsilon_s) \\ &- \delta^q_r a^p_s {\rm sgn}(\epsilon_r) - \delta^p_s a^q_r {\rm sgn}(\epsilon_s)\}_n \\ &+ \frac{1}{4}(\delta^p_r\delta^q_s - \delta^q_r\delta^p_s){\rm sgn}(\epsilon_r){\rm sgn}(\epsilon_s), \end{aligned} \tag{41}$$

which leads to

$$\frac{1}{2}g^{rs}_{pq}a^{pq}_{rs} = \frac{1}{2}g^{rs}_{pq}\{a^{pq}_{rs}\}_n + Q^q_p\{a^p_q\}_n + \frac{1}{8}\bar{g}^{pq}_{pq}{\rm sgn}(\epsilon_p){\rm sgn}(\epsilon_q), \tag{42}$$

where

$$Q^q_p = \tilde{Q}^q_p + \bar{Q}^q_p = -\frac{1}{2}\bar{g}^{q\omega}_{p\omega}{\rm sgn}(\epsilon_\omega), \tag{43}$$

$$\tilde{Q}^q_p = -\frac{1}{2}g^{q\omega}_{p\omega}{\rm sgn}(\epsilon_\omega), \tag{44}$$

$$\bar{Q}^q_p = \frac{1}{2}g^{\omega q}_{p\omega}{\rm sgn}(\epsilon_\omega). \tag{45}$$

The implicit summations over ω in $\tilde{Q}$ and $\bar{Q}$ include all the PES and NES, whether occupied or not. Together with the one-body term of Eq. (32), we obtain the desired Hamiltonian

$$H_{\rm QED}[a] = \epsilon_p\{a^p_p\}_n - U^q_p\{a^p_q\}_n + \frac{1}{2}g^{rs}_{pq}\{a^{pq}_{rs}\}_n + Q^q_p\{a^p_q\}_n \tag{46}$$

$$= H_{\rm FS}[a] + Q, \quad Q = Q^q_p\{a^p_q\}_n \tag{47}$$

normal ordered with respect to the Dirac vacuum $|0; \tilde{N}\rangle$. By further introducing the particle-hole picture we would obtain a Hamiltonian $H_{\rm QED}[b]$ normal ordered with respect to the genuine vacuum $|0; \tilde{0}\rangle$. It is seen that $H_{\rm QED}[a]$ (or $H_{\rm QED}[b]$) is just an extension of the original FS Hamiltonian $H_{\rm FS}[a]$ (29) (or $H_{\rm FS}[b]$) by adding in the one-body term Q. Since it is in full agreement with the non-retarded part of QED (vide post), it may legitimately be called "effective QED Hamiltonian." It differs from $H_{\rm CS}[a]$ (33) only in the second term. That is, only the Q term of $H_{\rm QED}[a]$ (47) arising from the CCC (36) looks peculiar as compared with nonrelativistic quantum mechanics. To reveal the physical meaning of this term, we calculate the induced charge density

$$\rho_{vp}(\vec{r}) = -\frac{|e|}{2}\langle 0; \tilde{N}|[\phi^\dagger(\vec{r}), \phi(\vec{r})]0; \tilde{N}\rangle, \tag{48}$$

$$\begin{aligned} \phi(\vec{r}) &= a_p\varphi_p(\vec{r}) + a_{\tilde{p}}\varphi_{\tilde{p}}(\vec{r}) \\ &= -\frac{|e|}{2}(n_-(\vec{r}) - n_+(\vec{r})), \\ n_+ &= \sum_p \varphi^\dagger_p\varphi_p, \quad n_- = \sum_{\tilde{p}}\varphi^\dagger_{\tilde{p}}\varphi_{\tilde{p}}, \end{aligned} \tag{49}$$

where the summations in n_+ and n_- involve the whole PES and NES, respectively. By virtue of the identity $n_+ + n_- = \bar{n}_+ + \bar{n}_- = 2\bar{n}_-$ with $\bar{n}_+$ and $\bar{n}_-$ ($= \bar{n}_+$) being the free-particle number densities, we have

$$\rho_{vp}(\vec{r}) = -|e|(n_-(\vec{r}) - \bar{n}_-(\vec{r})), \tag{50}$$

which is clearly the vacuum charge polarization. It is hence clear that the $\tilde{Q}$ term (44) corresponds to the electron vacuum polarization. Equation (49) implies that the NES are occupied by electrons, whereas the PES by positrons. Since the two pictures are equivalent thanks to charge conjugation symmetry, they should be averaged with an equal weight, viz., 1/2. The $\bar{Q}$ term (45) then corresponds to the electron self-energy as the exchange of $\tilde{Q}$. It is also clear that, in the case of Coulomb interaction, the vacuum polarization is larger in magnitude than the self-energy. However, the opposite is true for the exchange of a transverse photon not considered here, which contributes to the self-energy but not to the vacuum polarization. When both contributions are considered, the electron self-energy becomes larger than the vacuum polarization typically by one order of magnitude for light atoms. However, the vacuum polarization increases more sharply as the nuclear charge increases, such that it becomes comparable with the self-energy for heavy atoms, see Ref. 24 for most recent numerical results. It also deserves to be mentioned here that the formally quadratically divergent $\tilde{Q}$ can readily be regularized and renormalized, whereas the regularization and renormalization of the linearly divergent $\bar{Q}$ are only possible together with the transverse-photon contribution. Nevertheless, this will not affect the subsequent discussions: One can simply regard $\bar{Q}$ as the total electron self-energy wheresoever it appears.

In summary, in addition to the three ingredients (I)–(III) mentioned in the beginning, a fourth ingredient, i.e., the charge-conjugated contraction (36), should also be invoked to make the no-photon FS approach[41] complete.

B. The second order energy

The previously defined Hamiltonian (46) taking $|0;\tilde{N}\rangle$ as the vacuum is fully compatible with standard many-body theories. To show this, we derive the lowest order energies in different ways.

1. Treating the occupied PES as holes

To follow nonrelativistic quantum mechanics as closely as possible, we first calculate the energy as the difference between the $\Psi(N;\tilde{N})$ and $\Psi(0;\tilde{N})$ states[16]

$$E = \langle\Psi(N;\tilde{N})|\bar{H}|\Psi(N;\tilde{N})\rangle - \langle\Psi(0;\tilde{N})|\bar{H}|\Psi(0;\tilde{N})\rangle, \tag{51}$$

$$\bar{H} = \bar{H}_0 + \bar{V}_0 + V_1 + V_2, \tag{52}$$

$$\bar{H}_0 = \sum_m^{N+\tilde{N}} \epsilon_m + \epsilon_p\{a_p^p\}, \tag{53}$$

$$\bar{V}_0 = \frac{1}{2}(V_{HF})_i^i - \sum_m^{N+\tilde{N}} U_m^m + \sum_m^{N+\tilde{N}} Q_m^m, \tag{54}$$

$$V_1 = (V_1)_p^q\{a_q^p\}, \tag{55}$$

$$V_2 = \frac{1}{2}g_{pq}^{rs}\{a_{rs}^{pq}\}, \tag{56}$$

where the one-electron integrals are defined as

$$(V_1)_p^q = (V_{HF})_p^q + (\bar{V}_1)_p^q, \tag{57}$$

$$(V_{HF})_p^q = \bar{g}_{pi}^{qi}, \tag{58}$$

$$(\bar{V}_1)_p^q = -U_p^q + Q_p^q, \quad Q_p^q = \tilde{Q}_p^q + \bar{Q}_p^q. \tag{59}$$

Note that the normal ordering has been taken with respect to the reference $|N;\tilde{N}\rangle$, as indicated by the summation over m in (53) and (54). Since the V_{HF} term in (54) and (55) emerges only for systems of more than one positive energy electrons, it does not apply to the $\Psi(0;\tilde{N})$ state. The analogy with nonrelativistic formulation is revealed by regarding the second term on the right hand side of Eq. (51) as the HF reference energy and the left hand side as the correlation energy. Therefore, following the standard many-body perturbation theory (MBPT) we obtain immediately

$$E^{(0)} = \sum_m^{N+\tilde{N}} \epsilon_m - \sum_m^{\tilde{N}} \epsilon_m = \sum_i^N \epsilon_i, \tag{60}$$

$$E^{(1)} = \left[\frac{1}{2}(V_{HF})_i^i - \sum_m^{N+\tilde{N}} U_m^m + \sum_m^{N+\tilde{N}} Q_m^m\right] - \left[-\sum_m^{\tilde{N}} U_m^m + \sum_m^{\tilde{N}} Q_m^m\right] \tag{61}$$

$$= \left(\frac{1}{2}V_{HF} - U + Q\right)_i^i, \tag{62}$$

$$E^{(2)} = E_1^{(2)} + E_2^{(2)}, \tag{63}$$

$$E_1^{(2)} = (V_1)_i^a(V_1)_a^i\Delta_i^a + (V_1)_{\tilde{i}}^a(V_1)_a^{\tilde{i}}\Delta_{\tilde{i}}^a - (\bar{V}_1)_{\tilde{i}}^i(\bar{V}_1)_i^{\tilde{i}}\Delta_{\tilde{i}}^i - (\bar{V}_1)_{\tilde{i}}^a(\bar{V}_1)_a^{\tilde{i}}\Delta_{\tilde{i}}^a, \tag{64}$$

$$E_2^{(2)} = \frac{1}{4}\bar{g}_{mn}^{ab}\bar{g}_{ab}^{mn}\Delta_{mn}^{ab}|_{m,n=i,j,\tilde{i},\tilde{j}} - \frac{1}{4}\bar{g}_{\tilde{i}\tilde{j}}^{pq}\bar{g}_{pq}^{\tilde{i}\tilde{j}}\Delta_{\tilde{i}\tilde{j}}^{pq}|_{p,q=i,j,a,b} \tag{65}$$

$$= \frac{1}{4}\bar{g}_{ij}^{ab}\bar{g}_{ab}^{ij}\Delta_{ij}^{ab} + \frac{1}{2}\bar{g}_{i\tilde{j}}^{ab}\bar{g}_{ab}^{i\tilde{j}}\Delta_{i\tilde{j}}^{ab} - \frac{1}{2}\bar{g}_{\tilde{i}\tilde{j}}^{ia}\bar{g}_{ia}^{\tilde{i}\tilde{j}}\Delta_{\tilde{i}\tilde{j}}^{ia} - \frac{1}{4}\bar{g}_{\tilde{i}\tilde{j}}^{ij}\bar{g}_{ij}^{\tilde{i}\tilde{j}}\Delta_{\tilde{i}\tilde{j}}^{ij}, \tag{66}$$

$$\Delta_p^q = \frac{1}{\epsilon_p - \epsilon_q}, \quad \Delta_{pq}^{rs} = \frac{1}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s}. \tag{67}$$

Here, all the terms with a global negative sign stem from the $\Psi(0;\tilde{N})$, whereas the others from the $\Psi(N;\tilde{N})$ state. The two terms of Eq. (65) can nicely be represented by the same Goldstone-like diagrams shown in Fig. 1. It is just that the particles and holes as well as the one-body potential are interpreted differently.

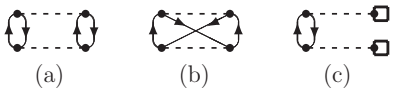

FIG. 1. Diagrammatical representation of the second order energy (65). (a) two-body direct; (b) two-body exchange; (c) one-body. The horizontal dashed line represents the instantaneous Coulomb/Breit interaction. For the $\Psi(N;\tilde{N})$ state, the particles (upgoing lines) and holes (downgoing lines) are $\{a, b\}$ and $\{i, j, \tilde{i}, \tilde{j}\}$, respectively. The one-body potential represented by the square is V_1 (57). For the $\Psi(0;\tilde{N})$ state, the particles and holes are $\{a, b, i, j\}$ and $\{\tilde{i}, \tilde{j}\}$, respectively. The one-body potential is $\bar{V}_1$ (59). A global negative sign should be inserted to the terms of $\Psi(0;\tilde{N})$.

2. Treating the occupied PES as particles

The previous derivation of the energy is truly simple and can readily be extended to arbitrary orders. Yet, the expressions are too compact to elucidate the various contributions. For this purpose, the occupied PES should be treated as particles. This amounts to directly calculating the left hand side of Eq. (51) by using the $H_{\rm QED}[a]$ Hamiltonian (46) yet without explicitly referring to the vacuum $|0;\tilde{N}\rangle$.

Consider a one-dimensional model space defined by the projector $P = |\tilde{\alpha}\rangle\langle\tilde{\alpha}|$ with $\tilde{\alpha} = |N;\tilde{N}\rangle$. The zeroth and first order energies of $|\tilde{\alpha}\rangle$ can readily be obtained as

$$E^{(0)} = \langle\tilde{\alpha}|\epsilon_p\{a_p^p\}_n|\tilde{\alpha}\rangle = \langle\tilde{\alpha}|\epsilon_i a_i^i|\tilde{\alpha}\rangle = \sum_i^N \epsilon_i, \quad (68)$$

$$E^{(1)} = \langle\tilde{\alpha}|(Q-U)_p^q\{a_q^p\}_n + \frac{1}{2}g_{pq}^{rs}\{a_{rs}^{pq}\}_n|\tilde{\alpha}\rangle \quad (69)$$

$$= \langle\tilde{\alpha}|(Q-U)_i^j a_j^i + \frac{1}{2}g_{ij}^{kl}a_{kl}^{ij}|\tilde{\alpha}\rangle \quad (70)$$

$$= \left(\frac{1}{2}V_{HF} - U + Q\right)_i^i. \quad (71)$$

The first order wave operator $\Omega^{(1)} \equiv (1-P)\Omega^{(1)}P$ normal ordered with respect to $|0;\tilde{N}\rangle$ contains a^p, a_q and $a_{\tilde{q}}$ types of operators but no $a^{\tilde{p}}$, viz.,

$$\Omega^{(1)} = X_t^u\{a_u^t\}_n + X_{\tilde{t}}^{\tilde{u}}\{a_{\tilde{u}}^t\}_n + \frac{1}{2}X_{tu}^{vw}\{a_{vw}^{tu}\}_n + X_{tu}^{v\tilde{w}}\{a_{v\tilde{w}}^{tu}\}_n + \frac{1}{2}X_{tu}^{\tilde{v}\tilde{w}}\{a_{\tilde{v}\tilde{w}}^{tu}\}_n + \tilde{X}\{a_u^t\}_n + \tilde{X}_t^{\tilde{u}}\{a_{\tilde{u}}^t\}_n + \bar{X}_t^u\{a_u^t\}_n + \bar{X}_t^{\tilde{u}}\{a_{\tilde{u}}^t\}_n, \quad (72)$$

where

$$X_t^u = W_t^u\Delta_u^t, \quad W \equiv -U, \quad (73)$$

$$\tilde{X}_t^u = \tilde{Q}_t^u\Delta_u^t, \quad (74)$$

$$\bar{X}_t^u = \bar{Q}_t^u\Delta_u^t, \quad (75)$$

$$X_{tu}^{vw} = g_{tu}^{vw}\Delta_{vw}^{tu}. \quad (76)$$

The corresponding potential that can be contracted with $\Omega^{(1)}$ reads

$$V = W_p^q\{a_q^p\}_n + W_{\tilde{p}}^q\{a_q^{\tilde{p}}\}_n + \frac{1}{2}g_{pq}^{rs}\{a_{rs}^{pq}\}_n + g_{p\tilde{q}}^{rs}\{a_{rs}^{p\tilde{q}}\}_n + \frac{1}{2}g_{\tilde{p}\tilde{q}}^{rs}\{a_{rs}^{\tilde{p}\tilde{q}}\}_n + \tilde{Q}_p^q\{a_q^p\}_n + \tilde{Q}_{\tilde{p}}^q\{a_q^{\tilde{p}}\}_n + \bar{Q}_p^q\{a_q^p\}_n + \bar{Q}_{\tilde{p}}^q\{a_q^{\tilde{p}}\}_n. \quad (77)$$

The terms in V (77) and $\Omega^{(1)}$ (72) can be represented by the diagrams shown in Figs. 2 and 3, respectively, in the same ordering as they appear in the equations. The following rules for contracting the V and $\Omega^{(1)}$ operators should be followed up: (1) The NES must all be contracted; (2) Zero contractions leading to unlinked terms should be discarded; (3) At least one pair of particle creation and annihilation operators should be retained. Further using the relations given in Appendix A, we obtain

$$H_{eff}^{(2)} = PV(1-P)\Omega^{(1)}P = \sum_{I=1}^{28}\mathrm{S}(I), \quad (78)$$

where

$$\mathrm{S}(1) = W_p^q X_q^u\{a_u^p\}_n - W_{\tilde{p}}^q X_t^{\tilde{p}}\{a_q^t\}_n, \quad (79)$$

$$\mathrm{S}(2) = W_p^q X_{qu}^{vw}\{a_{vw}^{pu}\}_n - g_{p\tilde{q}}^{rs}X_t^{\tilde{q}}\{a_{rs}^{pt}\}_n, \quad (80)$$

$$\mathrm{S}(3) = g_{pq}^{rs}X_s^u\{a_{ru}^{pq}\}_n - W_{\tilde{p}}^q X_{tu}^{v\tilde{p}}\{a_{vq}^{tu}\}_n, \quad (81)$$

$$\mathrm{S}(4) = \frac{1}{2}g_{pq}^{rs}X_{rs}^{vw}\{a_{vw}^{pq}\}_n + \frac{1}{2}g_{\tilde{p}\tilde{q}}^{rs}X_{tu}^{\tilde{p}\tilde{q}}\{a_{rs}^{tu}\}_n, \quad (82)$$

$$\mathrm{S}(5) = g_{pq}^{rs}X_{ru}^{vw}\{a_{vsw}^{pqu}\}_n - g_{p\tilde{q}}^{rs}X_{tu}^{v\tilde{q}}\{a_{rsv}^{put}\}_n, \quad (83)$$

$$\mathrm{S}(6) = -W_{\tilde{p}}^q X_{qu}^{v\tilde{p}}\{a_v^u\}_n - g_{p\tilde{q}}^{rs}X_r^{\tilde{q}}\{a_s^p\}_n, \quad (84)$$

$$\mathrm{S}(7) = g_{p\tilde{q}}^{rs}X_s^{\tilde{q}}\{a_r^p\}_n + W_{\tilde{p}}^q X_{tq}^{v\tilde{p}}\{a_v^t\}_n, \quad (85)$$

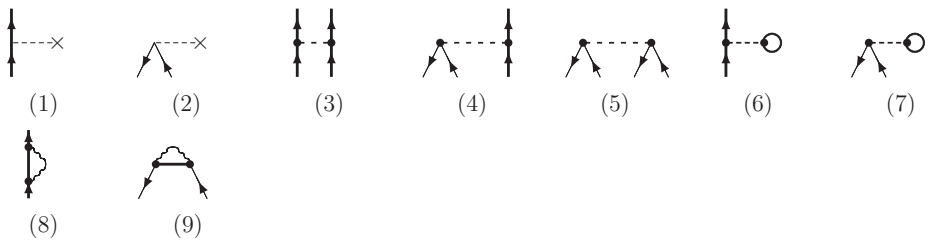

FIG. 2. Diagrammatical representation of the potential (77). Free orbital lines directed upwards and downwards represent PES and NES, respectively. The internal orbital lines for the electron vacuum polarization (6) and (7) and self-energy (8) and (9) can be both PES and NES, whether occupied or not. Both the dashed and wavy lines represent the instantaneous Coulomb/Breit interaction. The cross indicates the counter potential $-U$.

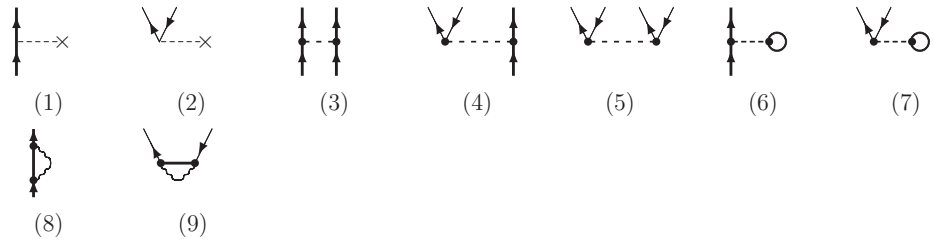

FIG. 3. Diagrammatical representation of the first order wave operator $\Omega^{(1)}$ (72). Free orbital lines directed upwards and downwards represent PES and NES, respectively. The internal orbital lines for the electron vacuum polarization (6) and (7) and self-energy (8) and (9) can be both PES and NES, whether occupied or not. Both the dashed and wavy lines represent the instantaneous Coulomb/Breit interaction. The cross indicates the counter potential $-U$.

$$\mathrm{S}(8) = g^{rs}_{p\tilde{q}} X^{v\tilde{q}}_{rs} \{a^p_v\}_n - g^{rs}_{\tilde{p}\tilde{q}} X^{\tilde{p}\tilde{q}}_{ru} \{a^u_s\}_n, \tag{86}$$

$$\mathrm{S}(9) = -g^{rs}_{p\tilde{q}} X^{v\tilde{q}}_{sr} \{a^p_v\}_n + g^{rs}_{\tilde{p}\tilde{q}} X^{\tilde{q}\tilde{p}}_{ru} \{a^u_s\}_n, \tag{87}$$

$$\mathrm{S}(10) = -g^{rs}_{p\tilde{q}} X^{v\tilde{q}}_{su} \{a^{pu}_{rv}\}_n - g^{rs}_{p\tilde{q}} X^{v\tilde{q}}_{tr} \{a^{pt}_{sv}\}_n, \tag{88}$$

$$\mathrm{S}(11) = g^{rs}_{p\tilde{q}} X^{v\tilde{q}}_{ts} \{a^{pt}_{rv}\}_n, \tag{89}$$

$$\mathrm{S}(12) = -g^{rs}_{p\tilde{q}} X^{v\tilde{q}}_{ru} \{a^{pu}_{vs}\}_n. \tag{90}$$

$$\mathrm{S}(13) = g^{rs}_{pq} \tilde{X}^u_r \{a^{pq}_{us}\}_n - \tilde{Q}^q_{\tilde{p}} X^{v\tilde{p}}_{tu} \{a^{tu}_{vq}\}_n, \tag{91}$$

$$\mathrm{S}(14) = g^{rs}_{pq} \bar{X}^u_r \{a^{pq}_{us}\}_n - \bar{Q}^q_{\tilde{p}} X^{v\tilde{p}}_{tu} \{a^{tu}_{vq}\}_n, \tag{92}$$

$$\mathrm{S}(15) = \tilde{Q}^q_p X^{vw}_{qu} \{a^{pu}_{vw}\}_n - g^{rs}_{p\tilde{q}} \tilde{X}^{\tilde{q}}_t \{a^{pt}_{rs}\}_n, \tag{93}$$

$$\mathrm{S}(16) = \bar{Q}^q_p X^{vw}_{qu} \{a^{pu}_{vw}\}_n - g^{rs}_{p\tilde{q}} \bar{X}^{\tilde{q}}_t \{a^{pt}_{rs}\}_n, \tag{94}$$

$$\mathrm{S}(17) = \tilde{Q}^q_p \tilde{X}^u_q \{a^p_u\}_n - \tilde{Q}^q_{\tilde{p}} \tilde{X}^{\tilde{p}}_t \{a^t_q\}_n, \tag{95}$$

$$\mathrm{S}(18) = \tilde{Q}^q_p \bar{X}^u_q \{a^p_u\}_n - \tilde{Q}^q_{\tilde{p}} \bar{X}^{\tilde{p}}_t \{a^t_q\}_n, \tag{96}$$

$$\mathrm{S}(19) = \bar{Q}^q_p \tilde{X}^u_q \{q^p_u\}_n - \bar{Q}^q_{\tilde{p}} \tilde{X}^{\tilde{p}}_t \{a^t_q\}_n, \tag{97}$$

$$\mathrm{S}(20) = \bar{Q}^q_p \bar{X}^u_q \{a^p_u\}_n - \bar{Q}^q_{\tilde{p}} \bar{X}^{\tilde{p}}_t \{a^t_q\}_n, \tag{98}$$

$$\mathrm{S}(21) = g^{rs}_{p\tilde{q}} \tilde{X}^{\tilde{q}}_s \{a^p_r\}_n + \tilde{Q}^q_{\tilde{p}} X^{v\tilde{p}}_{tq} \{a^t_v\}_n, \tag{99}$$

$$\mathrm{S}(22) = g^{rs}_{p\tilde{q}} \bar{X}^{\tilde{q}}_s \{a^p_r\}_n + \bar{Q}^q_{\tilde{p}} X^{v\tilde{p}}_{tq} \{a^t_v\}_n, \tag{100}$$

$$\mathrm{S}(23) = -g^{rs}_{p\tilde{q}} \bar{X}^{\tilde{q}}_r \{a^p_s\}_n - \bar{Q}^q_{\tilde{p}} X^{v\tilde{p}}_{qu} \{a^u_v\}_n, \tag{101}$$

$$\mathrm{S}(24) = -g^{rs}_{p\tilde{q}} \tilde{X}^{\tilde{q}}_r \{a^p_s\}_n - \tilde{Q}^q_{\tilde{p}} X^{v\tilde{p}}_{qu} \{a^u_v\}_n, \tag{102}$$

$$\mathrm{S}(25) = W^q_p \tilde{X}^u_q \{a^p_u\}_n - \tilde{Q}^q_{\tilde{p}} X^{\tilde{p}}_t \{a^t_q\}_n, \tag{103}$$

$$\mathrm{S}(26) = W^q_p \bar{X}^u_q \{a^p_u\}_n - \bar{Q}^q_{\tilde{p}} X^{\tilde{p}}_t \{a^t_q\}_n, \tag{104}$$

$$\mathrm{S}(27) = \tilde{Q}^q_p X^u_q \{a^p_u\}_n - W^q_{\tilde{p}} \tilde{X}^{\tilde{p}}_t \{a^t_q\}_n, \tag{105}$$

$$\mathrm{S}(28) = \bar{Q}^q_p X^u_q \{a^p_u\}_n - W^q_{\tilde{p}} \bar{X}^{\tilde{p}}_t \{a^t_q\}_n. \tag{106}$$

Every term of the S(I) operators can be represented by a time-ordered Feynman diagram shown in Fig. 4. Reversely, each term of S(I) can also be obtained by joining systematically the bottom lines of the diagrams in Fig. 2 and the top lines of the diagrams in Fig. 3, demonstrating the equivalence of the diagrammatic and algebraic derivations. Note in passing that the number of the so-joined diagrams can considerably be reduced if the Q and $-U$ potentials are summed up in Figs. 2 and 3. However, the "primitive diagrams" in Fig. 4 are more transparent for a detailed analysis. They are also closely related to the time-unordered Feynman diagrams shown in Fig. 5. The calculation of the second order energy

$$E^{(2)} = \langle\tilde{\alpha}|H^{(2)}_{eff}|\tilde{\alpha}\rangle = \langle\tilde{\alpha}|VQ\Omega^{(1)}|\tilde{\alpha}\rangle \tag{107}$$

is further facilitated by the following identity:

$$\begin{aligned}
&\langle\tilde{\alpha}|\{a^{p_1 p_2\cdots p_{m-1} p_m}_{q_1 q_2\cdots q_{m-1} q_m}\}_n|\tilde{\alpha}\rangle \\
&= \langle\tilde{\alpha}|\{\delta^{p_m}_{q_m} a^{p_1 p_2\cdots p_{m-2} p_{m-1}}_{q_1 q_2\cdots q_{m-2} q_{m-1}} - \delta^{p_m}_{q_{m-1}} a^{p_1 p_2\cdots p_{m-2} p_{m-1}}_{q_1 q_2\cdots q_{m-2} q_m} \\
&\quad - \delta^{p_m}_{q_{m-2}} a^{p_1 p_2\cdots p_{m-2} p_{m-1}}_{q_1 q_2\cdots q_m q_{m-1}} - \cdots - \delta^{p_m}_{q_2} a^{p_1 p_2\cdots p_{m-2} p_{m-1}}_{q_1 q_m\cdots q_{m-2} q_{m-1}} \\
&\quad - \delta^{p_m}_{q_1} a^{p_1 p_2\cdots p_{m-2} p_{m-1}}_{q_m q_2\cdots q_{m-2} q_{m-1}}\}_n|\tilde{\alpha}\rangle n_{p_1} n_{p_2}\cdots n_{p_m},
\end{aligned} \tag{108}$$

where $\{n_{p_i}\}$ are the occupation numbers (0 or 1) of the PES in $|\tilde{\alpha}\rangle$. Repeated use of Eq. (108) can be made to obtain the fully contracted result. Moreover, intermediate states leading to zero energy denominators are excluded because of the underlying intermediate renormalization. The results read

$$E^{(2)}(1) = W^a_i W^i_a \Delta^a_i - W^i_{\tilde{i}} W^{\tilde{i}}_i \Delta^i_{\tilde{i}}, \quad W = -U, \tag{109}$$

$$E^{(2)}(2) = W^a_i (V_{HF})^i_a \Delta^a_i - (V_{HF})^i_{\tilde{i}} W^{\tilde{i}}_i \Delta^i_{\tilde{i}}, \tag{110}$$

$$E^{(2)}(3) = (V_{HF})^a_i W^i_a \Delta^a_i - W^i_{\tilde{i}} (V_{HF})^{\tilde{i}}_i \Delta^i_{\tilde{i}}, \tag{111}$$

$$\begin{aligned}
E^{(2)}(4) &= \frac{1}{4} \bar{g}^{pq}_{ij} \bar{g}^{ij}_{pq} \Delta^{pq}_{ij}\big|_{p,q=k,l,a,b} + \frac{1}{4} \bar{g}^{ij}_{\tilde{i}\tilde{j}} \bar{g}^{\tilde{i}\tilde{j}}_{ij} \Delta^{ij}_{\tilde{i}\tilde{j}} \\
&= \frac{1}{4} \bar{g}^{ab}_{ij} \bar{g}^{ij}_{ab} \Delta^{ab}_{ij} + \frac{1}{2} \bar{g}^{ak}_{ij} \bar{g}^{ij}_{ak} \Delta^{ak}_{ij}\big|_{i\neq j\neq k} + \bar{g}^{aj}_{ij} \bar{g}^{ij}_{aj} \Delta^{aj}_{ij} \\
&\quad + \frac{1}{4} \bar{g}^{ij}_{\tilde{i}\tilde{j}} \bar{g}^{\tilde{i}\tilde{j}}_{ij} \Delta^{ij}_{\tilde{i}\tilde{j}},
\end{aligned} \tag{112}$$

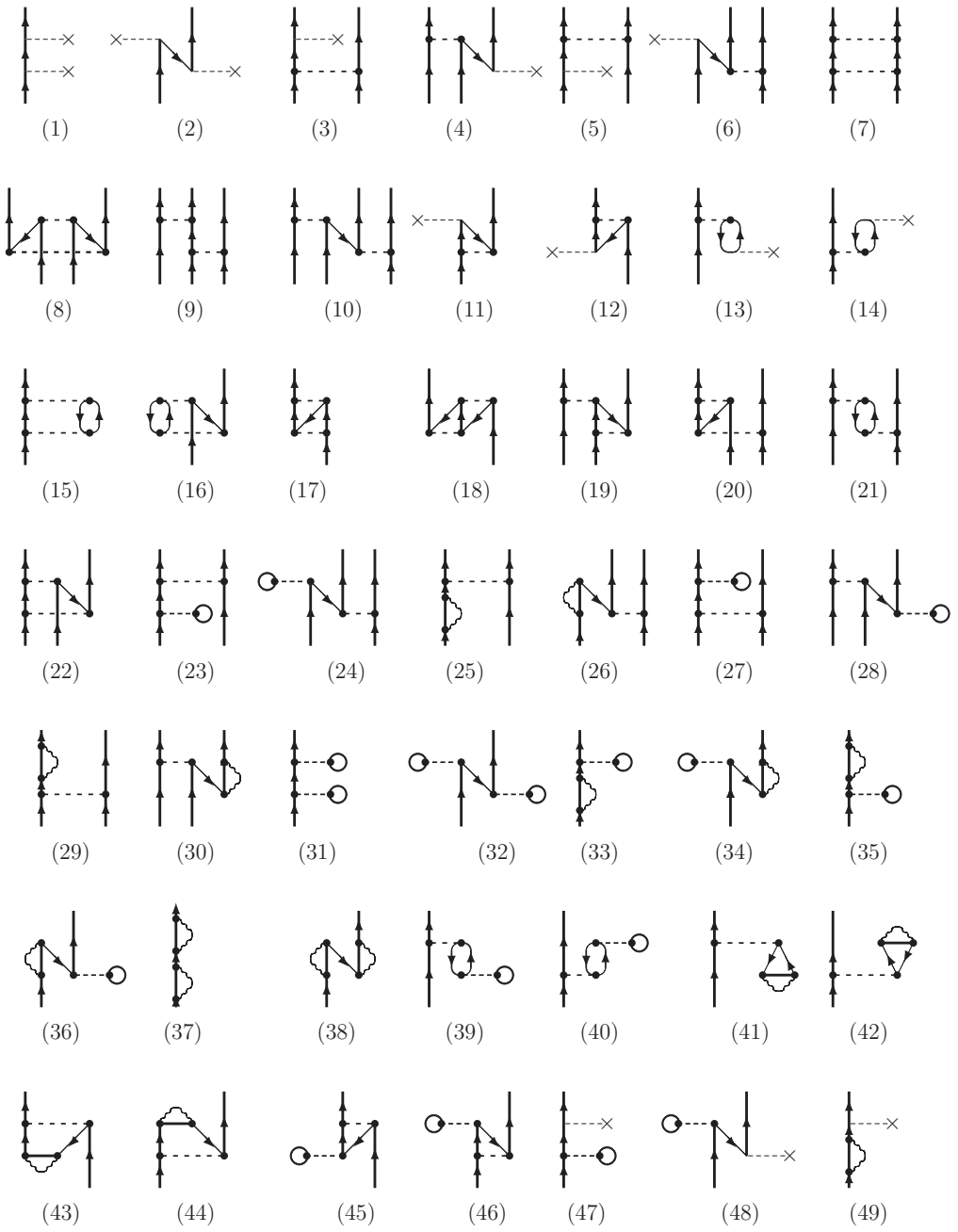

FIG. 4. Time-ordered Feynman diagrams for the S-operators (79)–(106) with instantaneous interactions.

$$E^{(2)}(5) = \left[\bar{g}^{pj}_{ij}\bar{g}^{ik}_{pk}\Delta^{pk}_{ik} - \frac{1}{2}\bar{g}^{pk}_{ij}\bar{g}^{ij}_{pk}\Delta^{pk}_{ij}\right]\Big|_{p=l,a}$$

$$-\left[\bar{g}^{ij}_{i\tilde{j}}\bar{g}^{k\tilde{j}}_{kj}\Delta^{kj}_{k\tilde{j}} - \frac{1}{2}\bar{g}^{kj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{kj}\Delta^{kj}_{i\tilde{j}}\right], \quad i \neq j \neq k$$

$$= \left[\bar{g}^{aj}_{ij}\bar{g}^{ik}_{ak}\Delta^{ak}_{ik} - \frac{1}{2}\bar{g}^{ak}_{ij}\bar{g}^{ij}_{ak}\Delta^{ak}_{ij}\right] - \left[\bar{g}^{ij}_{i\tilde{j}}\bar{g}^{k\tilde{j}}_{kj}\Delta^{kj}_{k\tilde{j}}\right.$$

$$\left. - \frac{1}{2}\bar{g}^{kj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{kj}\Delta^{kj}_{i\tilde{j}}\right], \quad i \neq j \neq k$$

$$= \left[(V_{HF})^a_i(V_{HF})^i_a\Delta^a_i - \bar{g}^{aj}_{ij}\bar{g}^{ij}_{aj}\Delta^{aj}_{ij}\right.$$

$$\left. - \frac{1}{2}\bar{g}^{ak}_{ij}\bar{g}^{ij}_{ak}\Delta^{ak}_{ij}|_{i\neq j\neq k}\right]$$

$$-\left[(V_{HF})^{\tilde{i}}_{\tilde{i}}(V_{HF})^{\tilde{i}}_{i}\Delta^{i}_{\tilde{i}} - \bar{g}^{ij}_{\tilde{i}j}\bar{g}^{\tilde{i}j}_{ij}\Delta^{ij}_{\tilde{i}j}\right.$$

$$\left. - \frac{1}{2}\bar{g}^{kj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{kj}\Delta^{kj}_{i\tilde{j}}|_{i\neq j\neq k}\right], \tag{113}$$

$$E^{(2)}(6) = -W^p_{\tilde{j}}g^{i\tilde{j}}_{pi}\Delta^{pi}_{i\tilde{j}} - g^{pi}_{i\tilde{j}}W^{\tilde{j}}_{p}\Delta^{p}_{\tilde{j}}, \quad p = j, a, \tag{114}$$

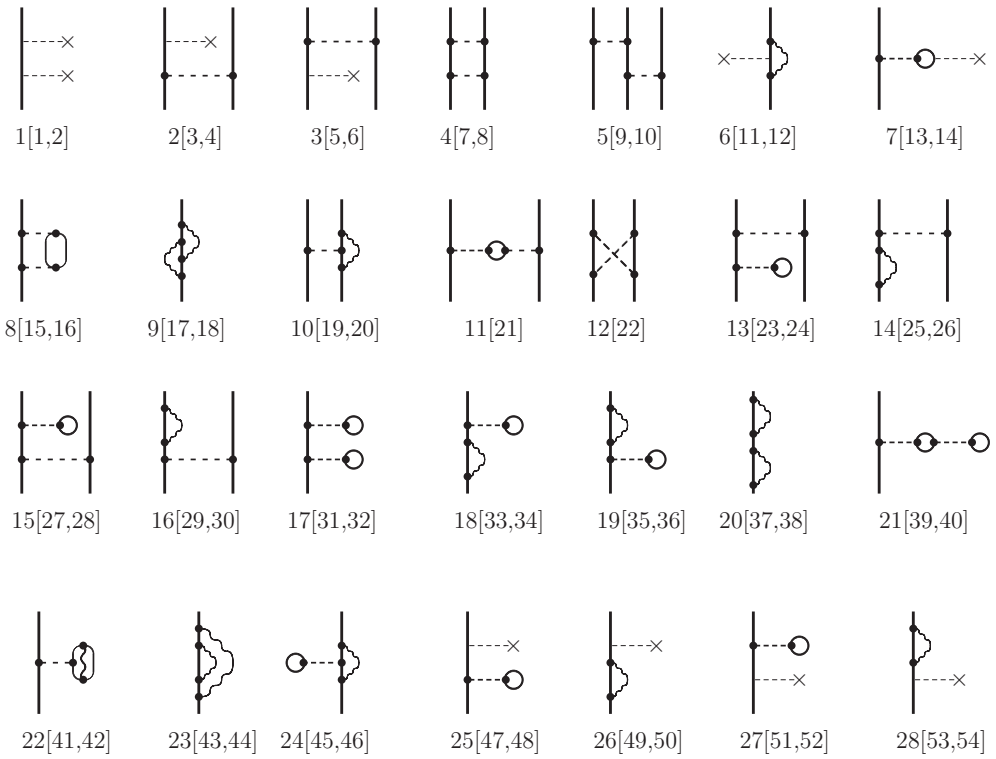

FIG. 5. Non-retarded Feynman diagrams for the second order energy. The numbers in brackets refer to the diagrams in Fig. 4. The retarded diagrams are obtained by replacing one or two Coulomb photons with transverse photons.

$$E^{(2)}(7) = W_{\tilde{j}}^{p} g_{ip}^{i\tilde{j}} \Delta_{i\tilde{j}}^{ip} + g_{i\tilde{j}}^{ip} W_{p}^{\tilde{j}} \Delta_{\tilde{j}}^{p}, \quad p = j, a, \tag{115}$$

$$E^{(2)}(8) = g_{i\tilde{j}}^{pq} g_{pq}^{i\tilde{j}} \Delta_{i\tilde{j}}^{pq} - g_{\tilde{i}\tilde{j}}^{pi} g_{pi}^{\tilde{i}\tilde{j}} \Delta_{\tilde{i}\tilde{j}}^{pi}, \quad p, q = k, l, a, b, \tag{116}$$

$$E^{(2)}(9) = -g_{i\tilde{j}}^{pq} g_{qp}^{i\tilde{j}} \Delta_{i\tilde{j}}^{qp} + g_{\tilde{i}\tilde{j}}^{pi} g_{ip}^{\tilde{i}\tilde{j}} \Delta_{\tilde{i}\tilde{j}}^{ip}, \quad p, q = k, l, a, b, \tag{117}$$

$$E^{(2)}(10) = -g_{i\tilde{j}}^{ip} g_{pj}^{j\tilde{j}} \Delta_{j\tilde{j}}^{pj} + g_{i\tilde{j}}^{jp} g_{pj}^{i\tilde{j}} \Delta_{i\tilde{j}}^{pj} - g_{i\tilde{j}}^{pi} g_{jp}^{j\tilde{j}} \Delta_{j\tilde{j}}^{jp} + g_{i\tilde{j}}^{pj} g_{jp}^{i\tilde{j}} \Delta_{i\tilde{j}}^{jp}, \quad i \neq j, p = k, a, \tag{118}$$

$$E^{(2)}(11) = g_{i\tilde{j}}^{ip} g_{jp}^{j\tilde{j}} \Delta_{j\tilde{j}}^{jp} - g_{i\tilde{j}}^{jp} g_{jp}^{i\tilde{j}} \Delta_{i\tilde{j}}^{jp}, \quad i \neq j, p = k, a, \tag{119}$$

$$E^{(2)}(12) = g_{i\tilde{j}}^{pi} g_{pj}^{j\tilde{j}} \Delta_{j\tilde{j}}^{pj} - g_{i\tilde{j}}^{pj} g_{pj}^{i\tilde{j}} \Delta_{i\tilde{j}}^{pj}, \quad i \neq j, p = k, a, \tag{120}$$

$$E^{(2)}(13) = (V_{HF})_{i}^{a} \tilde{Q}_{a}^{i} \Delta_{i}^{a} - \tilde{Q}_{\tilde{i}}^{i} (V_{HF})_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \tag{121}$$

$$E^{(2)}(14) = (V_{HF})_{i}^{a} \bar{Q}_{a}^{i} \Delta_{i}^{a} - \bar{Q}_{\tilde{i}}^{i} (V_{HF})_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \tag{122}$$

$$E^{(2)}(15) = \tilde{Q}_{i}^{a} (V_{HF})_{a}^{i} \Delta_{i}^{a} - (V_{HF})_{\tilde{i}}^{i} \tilde{Q}_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \tag{123}$$

$$E^{(2)}(16) = \bar{Q}_{i}^{a} (V_{HF})_{a}^{i} \Delta_{i}^{a} - (V_{HF})_{\tilde{i}}^{i} \bar{Q}_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \tag{124}$$

$$E^{(2)}(17) = \tilde{Q}_{i}^{a} \tilde{Q}_{a}^{i} \Delta_{i}^{a} - \tilde{Q}_{\tilde{i}}^{i} \tilde{Q}_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \tag{125}$$

$$E^{(2)}(18) = \tilde{Q}_{i}^{a} \bar{Q}_{a}^{i} \Delta_{i}^{a} - \tilde{Q}_{\tilde{i}}^{i} \bar{Q}_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \tag{126}$$

$$E^{(2)}(19) = \bar{Q}_{i}^{a} \tilde{Q}_{a}^{i} \Delta_{i}^{a} - \bar{Q}_{\tilde{i}}^{i} \tilde{Q}_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \tag{127}$$

$$E^{(2)}(20) = \bar{Q}_{i}^{a} \bar{Q}_{a}^{i} \Delta_{i}^{a} - \bar{Q}_{\tilde{i}}^{i} \bar{Q}_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \tag{128}$$

$$E^{(2)}(21) = g_{i\tilde{j}}^{ip} \tilde{Q}_{p}^{\tilde{j}} \Delta_{\tilde{j}}^{p} + \tilde{Q}_{\tilde{j}}^{p} g_{ip}^{i\tilde{j}} \Delta_{i\tilde{j}}^{ip}, \quad p = j, a, \tag{129}$$

$$E^{(2)}(22) = g_{i\tilde{j}}^{ip} \bar{Q}_{p}^{\tilde{j}} \Delta_{\tilde{j}}^{p} + \bar{Q}_{\tilde{j}}^{p} g_{ip}^{i\tilde{j}} \Delta_{i\tilde{j}}^{ip}, \quad p = j, a, \tag{130}$$

$$E^{(2)}(23) = -g_{i\tilde{j}}^{pi} \bar{Q}_{p}^{\tilde{j}} \Delta_{\tilde{j}}^{p} - \bar{Q}_{\tilde{j}}^{p} g_{pi}^{i\tilde{j}} \Delta_{i\tilde{j}}^{pi}, \quad p = j, a, \tag{131}$$

$$E^{(2)}(24) = -g_{i\tilde{j}}^{pi} \tilde{Q}_{p}^{\tilde{j}} \Delta_{\tilde{j}}^{p} - \tilde{Q}_{\tilde{j}}^{p} g_{pi}^{i\tilde{j}} \Delta_{i\tilde{j}}^{pi}, \quad p = j, a, \tag{132}$$

$$E^{(2)}(25) = W_{i}^{p} \tilde{Q}_{p}^{i} \Delta_{i}^{p} - \tilde{Q}_{\tilde{i}}^{i} W_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \quad p = j, a, \tag{133}$$

$$E^{(2)}(26) = W_{i}^{p} \bar{Q}_{p}^{i} \Delta_{i}^{p} - \bar{Q}_{\tilde{i}}^{i} W_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \quad p = j, a, \tag{134}$$

$$E^{(2)}(27) = \tilde{Q}_{i}^{p} W_{p}^{i} \Delta_{i}^{p} - W_{\tilde{i}}^{i} \tilde{Q}_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \quad p = j, a, \tag{135}$$

$$E^{(2)}(28) = \bar{Q}_{i}^{p} W_{p}^{i} \Delta_{i}^{p} - W_{\tilde{i}}^{i} \bar{Q}_{i}^{\tilde{i}} \Delta_{\tilde{i}}^{i}, \quad p = j, a. \tag{136}$$

The terms from $E^{(2)}(4)$ to $E^{(2)}(28)$ can be regrouped as

$$\sum_{I=4}^{5} E^{(2)}(I) = (V_{HF})^a_{\tilde{i}}(V_{HF})^{\tilde{i}}_a\Delta^a_{\tilde{i}} - (V_{HF})^i_{\tilde{i}}(V_{HF})^{\tilde{i}}_i\Delta^i_{\tilde{i}} + \frac{1}{4}\bar{g}^{ab}_{ij}\bar{g}^{ij}_{ab}\Delta^{ab}_{ij} + \frac{1}{4}\bar{g}^{ij}_{\tilde{i}\tilde{j}}\bar{g}^{\tilde{i}\tilde{j}}_{ij}\Delta^{ij}_{\tilde{i}\tilde{j}} + \bar{g}^{ij}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{ij}\Delta^{ij}_{i\tilde{j}} + \frac{1}{2}\bar{g}^{kj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{kj}\Delta^{kj}_{i\tilde{j}}\big|_{i\neq j\neq k}, \quad (137)$$

$$\sum_{I=6}^{7} E^{(2)}(I) = W^a_{\tilde{i}}(V_{HF})^{\tilde{i}}_a\Delta^a_{\tilde{i}} + (V_{HF})^a_{\tilde{i}}W^{\tilde{i}}_a\Delta^a_{\tilde{i}} + W^i_{\tilde{i}}(V_{HF})^{\tilde{i}}_i\Delta^i_{\tilde{i}} + (V_{HF})^i_{\tilde{i}}W^{\tilde{i}}_i\Delta^i_{\tilde{i}}, \quad (138)$$

$$\begin{aligned}\sum_{I=8}^{9} E^{(2)}(I) &= \frac{1}{2}\bar{g}^{pq}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{pq}\Delta^{pq}_{i\tilde{j}} - \frac{1}{2}\bar{g}^{pi}_{\tilde{i}\tilde{j}}\bar{g}^{\tilde{i}\tilde{j}}_{pi}\Delta^{pi}_{\tilde{i}\tilde{j}}, \quad p,q = k,l,a,b \\ &= \bar{g}^{ia}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{ia}\Delta^{ia}_{i\tilde{j}} + \frac{1}{2}\bar{g}^{ab}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{ab}\Delta^{ab}_{i\tilde{j}} - \frac{1}{2}\bar{g}^{ij}_{\tilde{i}\tilde{j}}\bar{g}^{\tilde{i}\tilde{j}}_{ij}\Delta^{ij}_{\tilde{i}\tilde{j}} - \frac{1}{2}\bar{g}^{ia}_{\tilde{i}\tilde{j}}\bar{g}^{\tilde{i}\tilde{j}}_{ia}\Delta^{ia}_{\tilde{i}\tilde{j}} \\ &\quad + \bar{g}^{aj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{aj}\Delta^{aj}_{i\tilde{j}}\big|_{i\neq j} + \bar{g}^{ij}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{ij}\Delta^{ij}_{i\tilde{j}} + \frac{1}{2}\bar{g}^{kj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{kj}\Delta^{kj}_{i\tilde{j}}\big|_{i\neq j\neq k}, \end{aligned} \quad (139)$$

$$\begin{aligned}\sum_{I=10}^{12} E^{(2)}(I) &= \bar{g}^{ip}_{i\tilde{j}}\bar{g}^{j\tilde{j}}_{jp}\Delta^{jp}_{j\tilde{j}} - \bar{g}^{pj}_{ij}\bar{g}^{i\tilde{j}}_{pj}\Delta^{pj}_{i\tilde{j}}, \quad i\neq j,\ p = k,a \\ &= \bar{g}^{ia}_{i\tilde{j}}\bar{g}^{j\tilde{j}}_{ja}\Delta^{ja}_{j\tilde{j}}\big|_{i\neq j} + (V_{HF})^i_{\tilde{i}}(V_{HF})^{\tilde{i}}_i\Delta^i_{\tilde{i}} - \bar{g}^{aj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{aj}\Delta^{aj}_{i\tilde{j}}\big|_{i\neq j} \\ &\quad - 2\bar{g}^{ij}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{ij}\Delta^{ij}_{i\tilde{j}} - \bar{g}^{kj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{kj}\Delta^{kj}_{i\tilde{j}}\big|_{i\neq j\neq k}, \end{aligned} \quad (140)$$

$$\sum_{I=13}^{16} E^{(2)}(I) = (V_{HF})^a_i Q^i_a\Delta^a_i + Q^a_i(V_{HF})^i_a\Delta^a_i - Q^i_{\tilde{i}}(V_{HF})^{\tilde{i}}_i\Delta^i_{\tilde{i}} - (V_{HF})^i_{\tilde{i}}Q^{\tilde{i}}_i\Delta^i_{\tilde{i}}, \quad (141)$$

$$\sum_{I=17}^{20} E^{(2)}(I) = Q^a_i Q^i_a\Delta^a_i - Q^i_{\tilde{i}}Q^{\tilde{i}}_i\Delta^i_{\tilde{i}}, \quad (142)$$

$$\sum_{I=21}^{24} E^{(2)}(I) = (V_{HF})^a_{\tilde{i}}Q^{\tilde{i}}_a\Delta^a_{\tilde{i}} + Q^a_{\tilde{i}}(V_{HF})^{\tilde{i}}_a\Delta^{\tilde{i}}_a + Q^i_{\tilde{i}}(V_{HF})^{\tilde{i}}_i\Delta^{\tilde{i}}_i + (V_{HF})^i_{\tilde{i}}Q^{\tilde{i}}_i\Delta^i_{\tilde{i}}, \quad (143)$$

$$\sum_{I=25}^{28} E^{(2)}(I) = W^a_i\tilde{Q}^i_a\Delta^a_i + \tilde{Q}^a_i W^i_p\Delta^a_i - W^i_{\tilde{i}}\tilde{Q}^{\tilde{i}}_i\Delta^i_{\tilde{i}} - \tilde{Q}^i_{\tilde{i}}W^{\tilde{i}}_i\Delta^i_{\tilde{i}}. \quad (144)$$

The one-body terms in Eqs. (109)–(111) and (137)–(144) can be summed up, leading to

$$E^{(2)}_1 = E^{(2)}_{\mathrm{FS},1} + E^{(2)}_{\mathrm{VS},1}, \quad (145)$$

$$E^{(2)}_{\mathrm{FS},1} = (V_{HF}-U)^a_i(V_{HF}-U)^i_a\Delta^a_i + (V_{HF}-U)^a_{\tilde{i}}(V_{HF}-U)^{\tilde{i}}_a\Delta^a_{\tilde{i}} - U^a_{\tilde{i}}U^{\tilde{i}}_a\Delta^a_i - U^i_{\tilde{i}}U^{\tilde{i}}_i\Delta^i_{\tilde{i}}, \quad (146)$$

$$E^{(2)}_{\mathrm{VS},1} = \left[(V_{HF}-U)^a_i Q^i_a + Q^a_i(V_{HF}-U)^i_a + Q^a_i Q^i_a\right]\Delta^a_i + \left[(V_{HF})^a_{\tilde{i}}Q^{\tilde{i}}_a + Q^a_{\tilde{i}}(V_{HF})^{\tilde{i}}_a\right]\Delta^a_{\tilde{i}} - \left[Q^i_{\tilde{i}}Q^{\tilde{i}}_i - U^i_{\tilde{i}}Q^{\tilde{i}}_i - Q^i_{\tilde{i}}U^{\tilde{i}}_i\right]\Delta^{\tilde{i}}_i, \quad (147)$$

where $E^{(2)}_{\mathrm{FS},1}$ arises from the one-body terms of $E^{(2)}(I)$ ($I = 1, \ldots, 12$), while $E^{(2)}_{\mathrm{VS},1}$ from the one-body terms of $E^{(2)}(I)$ ($I = 13, \ldots, 28$). The former agrees with the previous FS result, see Eqs. (54)–(56) of Ref. 16. It can readily be shown that the sum of $E^{(2)}_{\mathrm{FS},1}$ (146) and $E^{(2)}_{\mathrm{VS},1}$ (147) leads to the compact expression shown in Eq. (64). The two-body terms in Eqs. (137), (139), and (140) (i.e., $E^{(2)}(I)$ with $I = 4, 5; 8, \ldots 12$) can be summed up, leading to

$$E^{(2)}_2 = \frac{1}{4}\bar{g}^{ab}_{ij}\bar{g}^{ij}_{ab}\Delta^{ab}_{ij} + \frac{1}{2}\bar{g}^{ab}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{ab}\Delta^{ab}_{i\tilde{j}} - \frac{1}{2}\bar{g}^{ia}_{\tilde{i}\tilde{j}}\bar{g}^{\tilde{i}\tilde{j}}_{ia}\Delta^{ia}_{\tilde{i}\tilde{j}} - \frac{1}{4}\bar{g}^{ij}_{\tilde{i}\tilde{j}}\bar{g}^{\tilde{i}\tilde{j}}_{ij}\Delta^{ij}_{\tilde{i}\tilde{j}}, \quad (148)$$

which agrees with Eq. (66) and also with the FS result (see Eqs. (58)–(61) of Ref. 16).

Compared with the procedure adopted in Sec. II B 1, the above procedure is very lengthy but helpful in identifying various contributions. For instance, the FS/QED energy $E^{(2)}_2$ (148) appears as a sum of both non-radiative and radiative contributions (see Sec. II B 3 (E) for further discussions). More specifically, the former includes $E^{(2)}(4)$ (uncrossed ladder; cf. Fig. 5(4)), $E^{(2)}(5)$ (three-electron two-photon; cf. Fig. 5(5)), as well as $E^{(2)}(12)$ (crossed ladder; cf. Fig. 5(12)), whereas the latter includes $E^{(2)}(8)$ (combined electron and photon self-energy;[51] cf. Fig. 5(8)), $E^{(2)}(9)$ (double vertex correction; cf. Fig. 5(9)), $E^{(2)}(10)$ (single vertex correction; cf. Fig. 5(10)), as well as $E^{(2)}(11)$ (photon self-energy; cf. Fig. 5(11)). In contrast, for the special purpose of exploring correlation-only contributions of NES,[23] only the non-radiative terms $E^{(2)}(4)$, $E^{(2)}(5)$, and $E^{(2)}(12)$ were considered *deliberately* in the previous QED treatments.[16,22] This explains the "apparent discrepancy" between FS and QED observed previously:[16] Different contributions were considered. After all, the time-dependent QED and time-independent MBPT approaches should yield the same results for instantaneous interactions, as long as the same set of diagrams is considered.

It is also interesting to note that the last, positively valued term of $E^{(2)}_2$ (148) arises as a sum of the fourth term of Eq. (137) (actually the last term of $E^{(2)}(4)$ (112)) and the third term of Eq. (139). The former is non-radiative (cf. Fig. 5(4)) and correlating, whereas the latter is radiative (cf. Figs. 5(8) and 5(9)) and anti-correlating. Therefore, if only

TABLE I. The spectrum of relativistic Hamiltonians. SC: Schrödinger-Coulomb; A1C: spin-free part of A2C; A2C: approximate two-component; X1C: spin-free part of X2C; X2C: exact two-component; Q4C: quasi-four-component; DCB: no-pair Dirac-Coulomb-Breit; PI-DCB: potential-independent DCB; eQED: effective (non-retarded) QED.

Interaction	$g(0;1,2)$			$g(\omega;1,2)$
Speed of light	$c=\infty$	$c=137$		
Virtual pairs	0	1[a]	all	
Hamiltonian	SC	A1C, X1C, A2C, X1C+DKH$_n$, X2C, Q4C, DCB	PI-DCB	eQED QED
Methodology	Standard many-body theory			Time-dependent perturbation theory[b]

[a]One-body virtual pairs, see Eq. (150).
[b]For the retarded part of QED.

non-radiative contributions of NES (i.e., Figs. 5(4), 5(5), and 5(12)) are characterized as correlation,[16,22] viz.,

$$E^{(2)}_{2,\mathrm{C}} = \frac{1}{4}\bar{g}^{ab}_{ij}\bar{g}^{ij}_{ab}\Delta^{ab}_{ij} + \frac{1}{4}\bar{g}^{ij}_{\tilde{i}\tilde{j}}\bar{g}^{\tilde{i}\tilde{j}}_{ij}\Delta^{ij}_{\tilde{i}\tilde{j}} + \frac{1}{2}\bar{g}^{kj}_{i\tilde{j}}\bar{g}^{i\tilde{j}}_{kj}\Delta^{kj}_{i\tilde{j}}|_{i\neq j\neq k} - \frac{1}{2}g^{pj}_{i\tilde{j}}g^{i\tilde{j}}_{pj}\Delta^{pj}_{i\tilde{j}}|_{p=i,j,k,a;i\neq j}, \quad (149)$$

the NES would be correlating rather than anti-correlating. Nonetheless, even if all the contributions are included, as should (cf. Sec. II B 3 (E)), the second correlating term of $E^{(2)}_2$ (148) would strongly diminish the last two anti-correlating terms. This is different from CS, where the two terms involving the NES (see Eqs. (24) and (25) of Ref. 16) are both anti-correlating.

The NPA is obtained by neglecting all the terms involving the NES. As shown numerically by Sapirstein,[22] if the last terms of Eqs. (109)–(111) arising from the counter potential $-U$ (cf. Figs. 5(1)–5(3)), viz.,

$$E^{(2)}_{\mathrm{PC}} = (V_{HF})^i_{\tilde{i}}U^{\tilde{i}}_i\Delta^i_{\tilde{i}} + U^i_{\tilde{i}}(V_{HF})^{\tilde{i}}_i\Delta^i_{\tilde{i}} - U^i_{\tilde{i}}U^{\tilde{i}}_i\Delta^i_{\tilde{i}} \quad (150)$$

are retained, the potential dependence of the NPA can be removed to a large extent, thereby leading to a "potential-independent no-pair approximation" (PI-NPA). The corresponding Hamiltonian for Eq. (1) reads

$$H^{\mathrm{PI-DCB}}_{+} = E_{ref} + (f^{\mathrm{DCB}})^q_p\{a^p_q\} + \frac{1}{2}g^{rs}_{pq}\{a^{pq}_{rs}\}, \quad E_{ref} = \langle 0|H^{\mathrm{DCB}}_{+}|0\rangle + E^{(2)}_{\mathrm{PC}}, \quad (151)$$

where all orbital indices refer to PES, except for $E^{(2)}_{\mathrm{PC}}$ (150). At this stage, the whole spectrum of the Hamiltonian axis can be established, see Table I.

3. The S-matrix approach

The S-matrix formulation[52,53] of QED is well established. Herewith we only recapitulate briefly a few essential points:

(A) In the QED literature, the 4-current operator J^μ is oftentimes written as

$$J^\mu(x) = -|e|\{\phi^\dagger(x)c\alpha^\mu\phi(x)\}, \quad x = \vec{r}t, \quad \alpha^\mu = (c^{-1}, \vec{\alpha}), \quad (152)$$

where the field $\phi(x)$ in the interaction representation is already defined in Eq. (19). The problem resides in that this form of J^μ, viz., normal ordered with respect to $|0;\tilde{0}\rangle$, excludes by construction the electron vacuum polarization represented by a tadpole (i.e., a Fermion loop connected with a single interaction, see Fig. 2(6)). This is correct only for free particles. For bound states, it is the symmetrized form of J^μ that should be adopted, viz.,

$$J^\mu(x) = -\frac{1}{2}|e|[\phi^\dagger(x), c\alpha^\mu\phi(x)] \equiv -\frac{1}{2}|e|c(\alpha^\mu)_{\rho\sigma}(\phi^\dagger_\rho\phi_\sigma - \phi_\sigma\phi^\dagger_\rho), \quad (153)$$

which reduces to Eq. (152) in the special case of free particles. By virtue of the identity for time ordering of Fermion operators

$$T\left[AB\frac{1}{2}(CD - DC)EF\cdots\right] = T[ABCDEF\cdots], \quad (154)$$

J^μ (153) can simply be written as a single product

$$J^\mu(x) = -|e|\phi^\dagger(x)c\alpha^\mu\phi(x) \quad (155)$$

when writing the interaction Hamiltonian density, viz.,

$$\mathcal{H}(x) = -e\phi^\dagger(x)c\alpha^\mu A_\mu(x)\phi(x), \quad A_\mu = (\phi_{ext}, -\vec{A}) \quad (156)$$

$$= \phi^\dagger(x)(V_{ext}(x) + ec\vec{\alpha}\cdot\vec{A}(x))\phi(x). \quad (157)$$

The electron vacuum polarization then arises correctly from the so-called "equal-time contraction" (ETC),[53]

$$\underbrace{A(t)B}(t) = \langle 0;\tilde{0}|T[A(t)B(t)]|0;\tilde{0}\rangle = \langle 0;\tilde{0}|\frac{1}{2}[A(t), B(t)]|0;\tilde{0}\rangle. \quad (158)$$

This is taken into account automatically by the electron propagator (19), viz.,

$$\rho_{vp}(\vec{r}) = |e|iTr[S_F(x_1, x_1)] = -\frac{|e|}{2}(n_-(\vec{r}) - n_+(\vec{r})), \quad (159)$$

where use of the spectral representation of S_F (21) and the half-pole integral $I^-_{10}(0,\epsilon_t)$ (B9) has been made to arrive at the second equality. Equation (159) is obviously the same as

Eq. (49). As such, the previously introduced CCC (36) is just the time-independent equivalent of the above ETC (158). However, the former allows one to generate both the electron vacuum polarization $\tilde{Q}$ (44) and self-energy $\bar{Q}$ (45) due to the Coulomb interaction in a time-independent fashion. Had the ETC been defined as

$$\underbrace{A(t)B(t)} = \lim_{\eta\to 0^+}\langle 0;\tilde{0}|T[A(t)B(t+\eta)]|0;\tilde{0}\rangle, \quad (160)$$

we would obtain

$$\rho_{vp}(\vec{r}) = |e|iTr[S_F(x_1,x_1)] = -|e|n_-(\vec{r}), \quad (161)$$

which corresponds to the contraction (33). This form of ETC holds only in the nonrelativistic limit, where the holes are the occupied PES. It is hence clear that the electron vacuum polarization and self-energy are a direct consequence of the charge conjugation symmetry and are hence intrinsic QED effects.

(B) In the QED literature, the energy relative to the vacuum is oftentimes written as[53]

$$E = \lim_{\gamma\to 0,\lambda\to 1}\frac{i\gamma}{2}\lambda\frac{\frac{\partial}{\partial\lambda}\langle\alpha|S|\alpha\rangle_C}{\langle\alpha|S|\alpha\rangle_C} + \text{constant}, \quad |\alpha\rangle = |N;\tilde{0}\rangle^{(0)}, \quad (162)$$

where the subscript "C" indicates that only connected diagrams are to be included. This should be viewed with caution. It can be demonstrated (vide post) that the disconnected but linked diagrams should also be included to cancel precisely the γ^{-1} type of divergences. That is, the subscript "C" should be replaced with "L" for linked diagrams. The first and second order energies can then be evaluated as

$$E^{(1)} = \lim_{\gamma\to 0}\frac{i\gamma}{2}\left\{\langle\alpha|S^{(1)}|\alpha\rangle_L + \left[2\langle\alpha|S^{(2)}|\alpha\rangle_L - \langle\alpha|S^{(1)}|\alpha\rangle_L^2\right]\right\}, \quad (163)$$

$$E^{(2)} = \lim_{\gamma\to 0}\frac{i\gamma}{2}\{[3\langle\alpha|S^{(3)}|\alpha\rangle_L - 3\langle\alpha|S^{(1)}|\alpha\rangle_L\langle\alpha|S^{(2)}|\alpha\rangle_L] + [4\langle\alpha|S^{(4)}|\alpha\rangle_L - 2\langle\alpha|S^{(2)}|\alpha\rangle_L^2]\}. \quad (164)$$

(C) The nth order S-matrix defined as

$$S^{(n)} = \frac{(-i)^n}{n!}\int dx_1^4\cdots\int dx_n^4 T[\mathcal{H}(x_1)\cdots\mathcal{H}(x_n)]e^{-\gamma(|t_1|+\cdots|t_n|)} \quad (165)$$

can be rewritten in second-quantized form

$$S^{(n)} = \frac{n_d}{n!}(S^{(n)})^{q_1q_2\cdots q_m}_{p_1p_2\cdots p_m}\{a^{p_1p_2\cdots p_m}_{q_1q_2\cdots q_m}\}_n, \quad (166)$$

where $\{p_1,p_2,\ldots,p_m\}$ and $\{q_1,q_2,\ldots,q_m\}$ denote the respective outgoing and incoming free orbital lines of a Feynman diagram (see Figs. 5 and 6), while n_d represents the degeneracy of the diagram. The prefactor $\frac{n_d}{n!}$ for a given diagram can usually be determined by the symmetries of the diagram.[54] However, the use of such rules is sometimes uncertain. Here we provide the following alternative rules for counting the weight factor n_d: Each of the possible assignments of the electron propagators

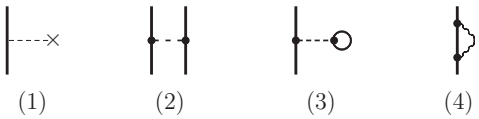

FIG. 6. Non-retarded Feynman diagrams for the first order energy. The retarded diagrams are obtained by replacing the Coulomb photon with a transverse photon.

$$S_F(x_i,x_j) = \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}S_F(\omega;\vec{r}_i,\vec{r}_j)e^{-i\omega(t_i-t_j)}, \quad (167)$$
$$S_F(\omega;\vec{r}_i,\vec{r}_j) = \frac{\varphi_t(\vec{r}_i)\varphi_t^\dagger(\vec{r}_j)}{\omega-\epsilon_t(1-i\eta)}, \quad i\le j$$

contributes a factor of two if $S_F(x_i, x_j)$ $(i < j)$ is not looped by $S_F(x_j, x_i)$, or a factor of one if $S_F(x_i, x_j)$ $(i \le j)$ is looped by $S_F(x_j, x_i)$. The numbers of such electron propagators are denoted as n_{F2} and n_{F1}, respectively. In contrast, each of the possible assignments (n_P) of *all* the photon interactions $I(z;\vec{r}_i,\vec{r}_j)$ contributes a factor of one independently of the ordering of the vertices i and j, i.e., $I(z;\vec{r}_j,\vec{r}_i) = I(z;\vec{r}_i,\vec{r}_j)$. Therefore, $n_d = max(1, n_{F1} + 2n_{F2}) \times max(1, n_P)$. Specific examples are given in Table II.

The integral $(S^{(n)})^{q_1q_2\cdots q_m}_{p_1p_2\cdots p_m}$ in Eq. (166) reads

$$\begin{aligned}(S^{(n)})^{q_1q_2\cdots q_m}_{p_1p_2\cdots p_m} &= (-1)^{n_l}\int\frac{dz_1}{2\pi}\int\frac{dz_2}{2\pi}\cdots\int\frac{\omega_1}{2\pi}\int\frac{\omega_2}{2\pi}\cdots\\ &\times\langle p_1p_2\cdots p_m|(-i)I(z_1;\vec{r}_{i_1},\vec{r}_{i_2})(-i)I(z_2;\vec{r}_{i_3},\vec{r}_{i_4})\cdots\\ &\times iS_F(\omega_1;\vec{r}_{j_1},\vec{r}_{j_2})iS_F(\omega_2;\vec{r}_{j_3},\vec{r}_{j_4})\cdots|q_1q_2\cdots q_m\rangle\\ &\times 2\pi\Delta_\gamma(E_1)2\pi\Delta_\gamma(E_2)\cdots 2\pi\Delta_\gamma(E_n). \end{aligned} \quad (168)$$

TABLE II. Degeneracy (n_d) of low-order Feynman diagrams. n_{F2}: number of electron-field contractions between two different vertices enumerated in an ascending order; n_{F1}: number of electron-field contractions within the same vertex; n_P: number of possible assignments of *all* the photon interactions; $n_d = max(1, n_{F1} + 2n_{F2}) \times max(1, n_P)$.

Diagram	n_{F2}	n_{F1}	n_P	n_d	$n_d/n!$
Fig. 5(2)	C_3^2	0	1	6	1
Fig. 5(3)	C_3^2	0	1	6	1
Fig. 5(4)	$\frac{1}{2}C_4^2+\frac{1}{2}C_4^2$	0	1	12	1/2
Fig. 5(5)	C_4^2	0	2	24	1
Fig. 5(6)	C_3^2	0	1	6	1
Fig. 5(7)	0	C_3^2	2	6	1
Fig. 5(11)	0	C_4^2	2	12	1/2
Fig. 5(12)	$\frac{1}{2}C_4^2+\frac{1}{2}C_4^2$	0	1	12	1/2
Fig. 6(2)	0	0	1	1	1/2
Fig. 6(3)	0	C_2^1	1	2	1
Fig. 6(4)	C_2^2	0	1	2	1
Fig. 7(a)	0	0	0	1	1/2
Fig. 7(b)	0	0	C_3^2	3	1/2
Fig. 7(c)	0	0	$\frac{1}{2}C_4^2$	3	1/8

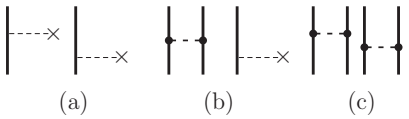

FIG. 7. Disconnected but linked Feynman diagrams: (a), (b), and (c) go with Figs. 5(1), 5(2, 3), and 5(4, 5), respectively.

That is, there is a factor $\int \frac{d\omega}{2\pi} i S_F(\omega; \vec{r}_i, \vec{r}_j)$ for each contracted pair of electron fields and a factor $\int \frac{dz}{2\pi}(-i) I(z; \vec{r}_k, \vec{r}_l)$ for each photon interaction. In the Coulomb gauge, the instantaneous Coulomb/Breit interaction $I(z; \vec{r}_k, \vec{r}_l)$ is simply the standard $g(k, l)$ operator (7). Note that there is no z-integration for the counter potential $-U(\vec{r})$. Furthermore, there is a factor $2\pi\,\Delta_\gamma(E_i)$ for each vertex arising from the time integration (see Eq. (B1)). The argument E_i is just the difference between the incoming and outgoing orbital energies/photon frequencies through the vertex. Finally, there is a global factor $(-1)^{n_l}$, with n_l being the number of loops. These rules of thumb for evaluating the Feynman diagrams have been documented in the recent book by one of the authors.[56] However, they are only complete when combined with the present rules for counting the degeneracy n_d of the diagrams. The integral identities in Appendix B can further be employed to facilitate the evaluation of $(S^{(n)})^{q_1 q_2 \cdots q_m}_{p_1 p_2 \cdots p_m}$ (168).

(D) There exist 4 connected Feynman diagrams for the first order energy (see Fig. 6) and in total 28 connected Feynman diagrams for the second order energy (see Fig. 5). The latter can be obtained by merging the 54 time-ordered Feynman diagrams shown in Fig. 4: Every pair of the time-ordered diagrams corresponds to a time-unordered Feynman diagram, except for diagrams shown in Figs. 4(21) and 4(22), each of which corresponds to a time-unordered Feynman diagram. It is interesting to note that the prefactors of diagrams shown in Figs. 4(21) and 4(22) are both one, whereas the prefactors of the corresponding diagrams shown in Figs. 5(11) and 5(12) are both 1/2. This is due to symmetrization in time. Specifically, the left intermediate state of diagram Fig. 5(11) can either be a PES or NES, while the right intermediate can accordingly be a NES or PES, thereby twice Fig. 4(21). The same occurs also to diagram Figs. 5(12) vs. 4(22).

To illustrate the above rules, we here evaluate the following diagrams: Figs. 5(4), 5(5), 6(2), and 7(c). Although the enumeration of the vertices $x_i = \vec{r}_i t_i$, the "direction" of the virtual photons z_i, as well as the designation of the free orbital lines are completely arbitrary, the following expressions follow the convention that, for a given diagram, the vertices are enumerated in a clockwise and ascending order, the virtual photons are directed from the left to right, while the outgoing (incoming) free orbital lines are denoted as $p, q, \ldots$ $(r, s, \ldots)$ from the left to right. In addition, the frequency ω_i in the electron propagator goes always upwards. These "directions" are necessary just for calculating the arguments $E_i = E_{in} - E_{out}$ of the vertex $2\pi\,\Delta(E_i)$ functions.

Fig. 6(2):

$$S^{(2)} = \frac{1}{2}(S^{(2)})^{rs}_{pq}\left\{a^{pq}_{rs}\right\}_n, \tag{169}$$

$$(S^{(2)})^{rs}_{pq} = \int \frac{dz}{2\pi}\langle pq|(-i)I(z; \vec{r}_2, \vec{r}_1)|rs\rangle \times 2\pi\,\Delta_\gamma(\epsilon_r - \epsilon_p - z)2\pi\,\Delta_\gamma(\epsilon_s - \epsilon_q + z) \tag{170}$$

$$\to -i g^{rs}_{pq} 2\pi\,\Delta_\gamma(\epsilon_r + \epsilon_s - \epsilon_p - \epsilon_q). \tag{171}$$

Note that Eq. (170) holds for both instantaneous and retarded interactions, whereas Eq. (171), as indicated by the arrow, is confined only for the instantaneous interaction. This assumption is adopted hereafter. The expectation value of $S^{(2)}$ over the unperturbed electronic state $|\alpha\rangle$ reads

$$\langle\alpha|S^{(2)}|\alpha\rangle = \frac{\bar{g}^{ij}_{ij}}{2i\gamma}, \tag{172}$$

which contributes to the first order energy (cf. Eq. (163)) as

$$E^{(1)}_{6(2)} = \frac{i\gamma}{2}[2\langle\alpha|S^{(2)}|\alpha\rangle] = \frac{1}{2}(V_{HF})^i_i. \tag{173}$$

Fig. 5(4):

$$S^{(4)} = \frac{1}{2}(S^{(4)})^{rs}_{pq}\left\{a^{pq}_{rs}\right\}_n, \tag{174}$$

$$\begin{aligned}(S^{(4)})^{rs}_{pq} = &\int \frac{dz_1}{2\pi}\int \frac{dz_2}{2\pi}\int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi} \\ &\times \langle pq|(-i)I(z_1; \vec{r}_2, \vec{r}_1)(-i)I(z_2; \vec{r}_3, \\ &\vec{r}_4 i S_F(\omega_1; \vec{r}_1, \vec{r}_4) i S_F(\omega_2; \vec{r}_2, \vec{r}_3)|rs\rangle \\ &\times 2\pi\,\Delta_\gamma(\epsilon_r - z_2 - \omega_1)2\pi\,\Delta_\gamma(z_2 + \epsilon_s - \omega_2) \\ &\times 2\pi\,\Delta_\gamma(\omega_1 - \epsilon_p - z_1)2\pi\,\Delta_\gamma(z_1 + \omega_2 - \epsilon_q)\end{aligned} \tag{175}$$

$$\begin{aligned}\to &\int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi}\langle pq|g(2,1)g(3,4)S_F(\omega_1; \vec{r}_1, \vec{r}_4) \\ &\times S_F(\omega_2; \vec{r}_2, \vec{r}_3)|rs\rangle \\ &\times 2\pi\,\Delta_{2\gamma}(\epsilon_r + \epsilon_s - \omega_1 - \omega_2) \\ &\times 2\pi\,\Delta_{2\gamma}(\epsilon_p + \epsilon_q - \omega_1 - \omega_2)\end{aligned} \tag{176}$$

$$\begin{aligned}= g^{tu}_{pq} g^{rs}_{tu} &\int \frac{d\omega_1}{2\pi}\int \frac{d\omega_2}{2\pi}\frac{1}{\omega_1 - \epsilon_t(1 - i\eta)} \\ &\times \frac{1}{\omega_2 - \epsilon_u(1 - i\eta)} 2\pi\,\Delta_{2\gamma}(\epsilon_r + \epsilon_s - \omega_1 - \omega_2) \\ &\times 2\pi\,\Delta_{2\gamma}(\epsilon_p + \epsilon_q - \omega_1 - \omega_2)\end{aligned} \tag{177}$$

$$= g^{tu}_{pq} g^{rs}_{tu} I^{L--}_{22}(\epsilon_t, \epsilon_u; \epsilon_r + \epsilon_s, \epsilon_p + \epsilon_q, 2\gamma), \tag{178}$$

where the integral I^{L--}_{22} is given in Eq. (B20). From the expectation value

$$\langle\alpha|S^{(4)}|\alpha\rangle = \frac{1}{2} g^{tu}_{ij} \bar{g}^{ij}_{tu} I^{L--}_{22}(\epsilon_t, \epsilon_u; \epsilon_i + \epsilon_j, \epsilon_i + \epsilon_j, 2\gamma) \tag{179}$$

$$= \frac{g_{ij}^{tu}\bar{g}_{tu}^{ij}}{4i\gamma}\left\{\frac{L_{tu}}{\epsilon_i+\epsilon_j-\epsilon_t-\epsilon_u+2i\gamma L_{tu}} + \frac{2i\gamma|L_{tu}|}{[\epsilon_i+\epsilon_j-\epsilon_t-\epsilon_u+2i\gamma L_{tu}]^2}\right\} \quad (180)$$

$$= \frac{g_{ij}^{tu}\bar{g}_{tu}^{ij}}{4i\gamma}\left\{\frac{L_{tu}}{\epsilon_i+\epsilon_j-\epsilon_t-\epsilon_u}\Big|_{\epsilon_i+\epsilon_j\neq\epsilon_t+\epsilon_u} + \frac{1}{i\gamma}\Big|_{\epsilon_i+\epsilon_j=\epsilon_t+\epsilon_u}\right\}, \quad (181)$$

we obtain (cf. Eq. (164)),

$$E^{(2)}_{5(4),\gamma} = \frac{i\gamma}{2}[4\langle\alpha|S^{(4)}|\alpha\rangle] = \frac{1}{4}\frac{\bar{g}_{ij}^{tu}\bar{g}_{tu}^{ij}L_{tu}}{\epsilon_i+\epsilon_j-\epsilon_t-\epsilon_u}\Big|_{\epsilon_i+\epsilon_j\neq\epsilon_t+\epsilon_u} + \frac{\bar{g}_{ij}^{ij}\bar{g}_{ij}^{ij}}{2i\gamma}, \quad (182)$$

where the first term can be written as

$$E^{(2)}_{5(4)} = \frac{1}{4}\bar{g}_{ij}^{ab}\bar{g}_{ab}^{ij}\Delta_{ij}^{ab} + \frac{1}{2}\bar{g}_{ij}^{ak}\bar{g}_{ak}^{ij}\Delta_{ij}^{ak}|_{i\neq j\neq k} + \bar{g}_{ij}^{aj}\bar{g}_{aj}^{ij}\Delta_{ij}^{aj} + \frac{1}{4}\bar{g}_{\tilde{i}\tilde{j}}^{ij}\bar{g}_{ij}^{\tilde{i}\tilde{j}}\Delta_{\tilde{i}\tilde{j}}^{ij}, \quad (183)$$

which is identical with $E^{(2)}(4)$ (112).

Fig. 5(5):

$$S^{(4)} = (S^{(4)})_{pqr}^{ijk}\{a_{ijk}^{pqr}\}_n, \quad i\neq j\neq k, \quad (184)$$

$$\begin{aligned}(S^{(4)})_{pqr}^{ijk} &= \int\frac{dz_1}{2\pi}\int\frac{dz_2}{2\pi}\int\frac{d\omega}{2\pi}\langle pqr|(-i)I(z_1;\vec{r}_2,\vec{r}_1)(-i)\\ &\times I(z_2;\vec{r}_3,\vec{r}_4)iS_F(\omega;\vec{r}_2,\vec{r}_4)|ijk\rangle\\ &\times 2\pi\Delta_\gamma(\epsilon_i-\epsilon_p-z_1)2\pi\Delta_\gamma(\epsilon_j-z_2-\omega)\\ &\times 2\pi\Delta_\gamma(\epsilon_k+z_2-\epsilon_r)2\pi\Delta_\gamma(z_1+\omega-\epsilon_q)\\ &\to -i\int\frac{d\omega}{2\pi}\langle pqr|g(2,1)g(3,4)S_F(\omega;\vec{r}_2,\vec{r}_4)|ijk\rangle\\ &\times 2\pi\Delta_{2\gamma}(\epsilon_i-\epsilon_p-\epsilon_q+\omega)\\ &\times 2\pi\Delta_{2\gamma}(\epsilon_j+\epsilon_k-\epsilon_r-\omega) \quad (185)\end{aligned}$$

$$= -ig_{pq}^{it}g_{rt}^{kj}\int\frac{d\omega}{2\pi}\frac{1}{\omega-\epsilon_t(1-i\eta)} \times 2\pi\Delta_{2\gamma}(\epsilon_p+\epsilon_q-\epsilon_i-\omega) \times 2\pi\Delta_{2\gamma}(\epsilon_j+\epsilon_k-\epsilon_r-\omega) \quad (186)$$

$$= -ig_{pq}^{it}g_{rt}^{kj}I_{12}^{-}(\epsilon_t;\epsilon_p+\epsilon_q-\epsilon_i,\epsilon_j+\epsilon_k-\epsilon_r,2\gamma). \quad (187)$$

From the expectation value (cf. Eq. (108)),

$$\langle\alpha|S^{(4)}|\alpha\rangle = -i\left\{\bar{g}_{ij}^{it}\bar{g}_{kt}^{kj}I_{12}^{-}(\epsilon_t;\epsilon_j,\epsilon_j,2\gamma) - \frac{1}{2}\bar{g}_{kj}^{it}\bar{g}_{it}^{kj}I_{12}^{-}(\epsilon_t;\epsilon_j+\epsilon_k-\epsilon_i,\epsilon_j+\epsilon_k-\epsilon_i,2\gamma)\right\} \quad (188)$$

$$= \frac{\bar{g}_{ij}^{it}\bar{g}_{kt}^{kj}}{2i\gamma}\left[\frac{1}{\epsilon_j-\epsilon_t(1-2i\gamma)} + \frac{2i\gamma\,\mathrm{sgn}(\epsilon_t)}{[\epsilon_j-\epsilon_t(1-2i\gamma)]^2}\right] - \frac{\bar{g}_{kj}^{it}\bar{g}_{it}^{kj}}{4i\gamma}\left[\frac{1}{\epsilon_j+\epsilon_k-\epsilon_i-\epsilon_t(1-2i\gamma)} + \frac{2i\gamma\,\mathrm{sgn}(\epsilon_t)}{[\epsilon_j+\epsilon_k-\epsilon_i-\epsilon_t(1-2i\gamma)]^2}\right], \quad i\neq j\neq k, \quad (189)$$

we obtain (cf. Eq. (164)),

$$E^{(2)}_{5(5),\gamma} = \frac{i\gamma}{2}[4\langle\alpha|S^{(4)}|\alpha\rangle] \quad (190)$$

$$= \left\{\frac{(V_{HF})_i^t(V_{HF})_t^i}{\epsilon_i-\epsilon_t}\Big|_{i\neq t} - \frac{\bar{g}_{ij}^{tj}\bar{g}_{tj}^{ij}}{\epsilon_i-\epsilon_t}\Big|_{i\neq t} - \frac{1}{2}\frac{\bar{g}_{ij}^{kt}\bar{g}_{kt}^{ij}}{\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_t}\Big|_{i\neq j\neq k\neq t}\right\} + \frac{\bar{g}_{ij}^{ij}\bar{g}_{ik}^{ik}}{i\gamma}\Big|_{i\neq j\neq k}, \quad (191)$$

where the first term can be written as

$$E^{(2)}_{5(5)} = \left[(V_{HF})_i^a(V_{HF})_a^i\Delta_i^a - \bar{g}_{ij}^{aj}\bar{g}_{aj}^{ij}\Delta_{ij}^{aj} - \frac{1}{2}\bar{g}_{ij}^{ak}\bar{g}_{ak}^{ij}\Delta_{ij}^{ak}|_{i\neq j\neq k}\right] - \left[(V_{HF})_{\tilde{i}}^{i}(V_{HF})_{i}^{\tilde{i}}\Delta_{\tilde{i}}^{i} - \bar{g}_{\tilde{i}j}^{ij}\bar{g}_{ij}^{\tilde{i}j}\Delta_{\tilde{i}j}^{ij} - \frac{1}{2}\bar{g}_{i\tilde{j}}^{kj}\bar{g}_{kj}^{i\tilde{j}}\Delta_{i\tilde{j}}^{kj}|_{i\neq j\neq k}\right], \quad (192)$$

which is identical with $E^{(2)}(5)$ (113).

Fig. 7(c):

$$S^{(4)} = \frac{1}{8}(S^{(4)})_{pqtu}^{rsvw}\{a_{rsvw}^{pqtu}\}_n. \quad (193)$$

A direct evaluation of this diagram according to Eq. (193) is possible but is very lengthy. The evaluation is expedited by observing that transitions between the disconnected parts of a disconnected diagram all vanish in the limit $\gamma\to 0$. That is, the disconnected parts can be treated as if they were infinitely separated in space and time. Therefore, the expectation of $S^{(4)}$ (193) can be factorized as

$$\langle\alpha|S^{(4)}|\alpha\rangle = \frac{1}{8}\big(S_L^{(2)}\big)_{pq}^{rs}\langle\alpha|\{a_{pq}^{rs}\}_n|\alpha\rangle\big(S_R^{(2)}\big)_{tu}^{vw}\langle\alpha|\{a_{tu}^{vw}\}_n|\alpha\rangle \quad (194)$$

$$= \frac{1}{2}\langle\alpha|S_L^{(2)}|\alpha\rangle\langle\alpha|S_R^{(2)}|\alpha\rangle \quad (195)$$

$$= \frac{1}{2}\frac{\bar{g}_{ij}^{ij}}{2i\gamma}\frac{\bar{g}_{kl}^{kl}}{2i\gamma}|_{i\neq j\neq k\neq l}, \quad (196)$$

where use of the expression (172) has been made for both the left ($S_L^{(2)}$) and right ($S_R^{(2)}$) parts of the diagram. We then obtain (cf. Eq. (164)),

$$E^{(2)}_{7(c),\gamma} = \frac{i\gamma}{2}[4\langle\alpha|S^{(4)}|\alpha\rangle] = \frac{\bar{g}_{ij}^{ij}\bar{g}_{kl}^{kl}}{4i\gamma}\Big|_{i\neq j\neq k\neq l}. \quad (197)$$

The second terms of Eqs. (182) and (191) together can only be canceled out by the sum of Eq. (197) and the following term (cf. Eqs. (164) and (172)):

$$\frac{i\gamma}{2}[-2\langle\alpha|S^{(2)}|\alpha\rangle^2] = -\frac{\bar{g}^{ij}_{ij}\bar{g}^{kl}_{kl}}{4i\gamma}\Big|_{i\neq j,k\neq l} = -\frac{\bar{g}^{ij}_{ij}\bar{g}^{ij}_{ij}}{2i\gamma}\Big|_{i\neq j} - \frac{\bar{g}^{ij}_{ij}\bar{g}^{kl}_{kl}}{i\gamma}\Big|_{i\neq j\neq k} - \frac{\bar{g}^{ij}_{ij}\bar{g}^{kl}_{kl}}{4i\gamma}\Big|_{i\neq j\neq k\neq l}. \quad (198)$$

It is therefore clear that the disconnected but linked diagrams are responsible for removing the γ^{-1}-type of divergences from the reducible diagrams (i.e., diagrams without photon crossings, e.g., Figs. 5(1)–5(5); 5(13)–5(20); and 5(25)–5(28)), although they do not contribute to the energy. Note in passing that, at variance with such complete manipulations, the same results can alternatively be obtained by discarding the singular terms from the outset, including the terms with a negative sign in Eqs. (163) and (164), the last terms in the integrals (B6)–(B8) and (B20)–(B27). It is this "shortcut" that is usually employed in the literature.[56] It looks like that this shortcut is equivalent to imposing the intermediate normalization, as done in Sec. II B 2.

All the Feynman diagrams in Figs. 5 and 6 can readily be evaluated by following the above rules and examples. The results agree completely with the previous expressions for $E^{(1)}$ (71) and $E^{(2)}(I)$ ($I = 1, \ldots, 28$) shown in Eqs. (109)–(136). As expected, the results also agree with those by the covariant evolution operator (CEO) approach[55,56] that aims to treat correlation, relativity and full QED on the same footing.

(E) In the QED literature, numerical results are usually reported for individual Feynman diagrams. This should be viewed with caution. For instance, the last two terms of Eqs. (137), (139), and (140) are the so-called EPV (exclusion-principle violating) terms. They can only be canceled out by summing up the corresponding diagrams, viz., Figs. 5(4), 5(5), and 5(8)–5(12). Many diagrams (e.g., Figs. 5(6)–5(24)) even cannot be expressed in terms of anti-symmetrized two-electron integrals (cf. Eqs. (114)–(132)), implying that such diagrams may contain individually unphysical self-interactions (SI) (i.e., $(ip|ii)$). Therefore, the Feynamn diagrams must be combined properly so as to cancel precisely the EPV and SI errors. This raises the question whether the standard partitioning[23] of QED effects into radiative (e.g., Figs. 5(8)–5(11)) and non-radiative effects (e.g., Figs. 5(4), 5(5), and 5(12)) is meaningful at all. In essence, only electron vacuum polarization and self-energy, as well as retardation, are genuine QED effects, whereas photon self-energy (another kind of vacuum polarization) and vertex correction should be regarded as "derived" QED effects[51] or simply correlation/screening effects in the case of instantaneous interactions. This viewpoint is further supported by the fact that photon self-energy and vertex correction also appear in non-relativistic descriptions of correlation/screening effects.

(F) The S-matrix approach discussed so far treats all the occupied PES as particles. To treat the core states (denoted as c and d) as holes, one can modify the electron propagator S_F (21) as follows:[57]

$$S_F^M(x_2, x_1) = S_F(x_2, x_1) + S_F^c(x_2, x_1), \quad (199)$$

where

$$S_F^c(x_2, x_1) = \oint_{R_c} \frac{d\omega}{2\pi} \frac{\varphi_c(\vec{r}_2)\varphi_c^\dagger(\vec{r}_1)}{\omega - \epsilon_c(1 + i\eta)} e^{-i\omega(t_2 - t_1)}. \quad (200)$$

Here, R_c is the counter-clockwise integration contour closing all the core states. This amounts to shifting the Fermi level to the top edge of the core states. The above rules as well as the integral identities in Appendix B can still be employed. For instance, we can readily obtain the following results for the diagrams in Fig. 6:

$$E^{(1)}_{6(1)} = -U^v_v, \quad (201)$$

$$E^{(1)}_{6(2)} = \frac{1}{2}\bar{g}^{uv}_{uv}, \quad (202)$$

$$E^{(1)}_{6(3)} = -\frac{1}{2}g^{v\omega}_{v\omega}\mathrm{sgn}(\epsilon_\omega) + g^{vc}_{vc}, \quad (203)$$

$$E^{(1)}_{6(4)} = \frac{1}{2}g^{\omega v}_{v\omega}\mathrm{sgn}(\epsilon_\omega) - g^{cv}_{vc}, \quad (204)$$

where u and v refer to the valence states. Use of Eq. (B28) has been made to arrive at Eqs. (203) and (204). The sum of these terms can be rewritten as

$$E^{(1)}_c = \sum_{i=1}^{4} E^{(1)}_{6(i)} = E^{(1)} - \left(\frac{1}{2}\bar{g}^{cd}_{cd} + Q^c_c - U^c_c\right), \quad (205)$$

where $E^{(1)}$ (71) is the first order energy by treating all the occupied NES as particles. That is, the two treatments differ only by a constant, which does not affect valence excitation energies. This holds also for higher order terms. However, the situation would be different if the relevant diagrams are not all considered simultaneously. For instance, if only diagram shown in Fig. 5(2) is considered, its valence energy $E^{(1)}_{6(2)}$ (202) differs from the all-particle energy $\frac{1}{2}\bar{g}^{ij}_{ij}$ by $-\bar{g}^{vc}_{vc} - \frac{1}{2}\bar{g}^{cd}_{cd}$, the first term of which is not a constant and hence does affect valence excitation energies. Again, this shows that numerical results should not be reported only for individual Feynman diagrams. Note also that, although both are treated as holes, the core states and the NES are still different: They interact differently with the valence states, as can be seen from Eqs. (203) to (204). If all the occupied PES are treated as holes, the result $E^{(1)}_c$ (205) is simply zero. This is a direct consequence of the fact that the modified electron propagator (199) excludes by construction the interaction between the positive- and negative-energy holes. In other words, unlike the approach presented in Sec. II B 1, the S-matrix formulation of QED is a valence approach and cannot treat all the occupied PES as holes.

III. CONCLUSIONS AND OUTLOOK

The exponible as how to go beyond the no-pair relativistic quantum chemistry has been addressed critically. While

the configuration space approach is plainly wrong, the previous Fock space approach also has to be extended. This has been achieved by introducing the charge-conjugated contraction of Fermion operators, which gives rise naturally to an effective one-body potential Q (43) responsible for electron vacuum polarization and self-energy. The resulting many-body Hamiltonian (46), constructed in a bottom-up fashion rather than derived from QED in a top-down manner, can account for all kinds of virtual-pair effects due to non-retarded interactions. In particular, it is fully compatible with the standard methodologies of electronic structure. After adding in the contribution from the exchange of a transverse photon, the Q potential can be regularized/renormalized and then fitted into a semi-local all-electron model potential, such that electron vacuum polarization and self-energy together can be treated variationally at the mean-field level, just like the nuclear attraction. The subsequent treatments of correlation and properties are then simplified greatly, e.g., diagrams shown in Figs. 5(13)–5(28) are no longer needed. In practice, the following ansatz[16] may be pursued for high precision calculations of many-electron systems

$$E = E^{\mathrm{HL}}_{\mathrm{NPP},++}(\mathrm{valence}) + E^{(2)}_{\mathrm{EQED},+-}(\mathrm{core}') + E^{\mathrm{R}}_{\mathrm{FQED}}. \quad (206)$$

Here, the first term stands for a high-level treatment of valence electrons within the PES manifold, combined favorably with explicitly correlated functions.[26] If the electron vacuum polarization and self-energy are included variationally at the mean-field level, the interplay between them and no-pair correlation is already accounted for at this stage. The second term of Eq. (206) stands for the second order treatment of core-core and core-valence interactions within both the PES and NES manifolds (see Eqs. (64) and (66)), whereas the third term stands for further corrections due to retardation, finite nuclear mass, and quantization of the electromagnetic field. It is the second term that will eliminate the often mentioned intrinsic uncertainty of order $(Z\alpha)^3$ in the eigenenergies of the no-pair DC or DCB equation.

Finally, it deserves to be mentioned that the Hamiltonians discussed so far (see Table I) are defined in the laboratory frame of reference. For molecular spectroscopies involving nuclear vibrations and/or rotations, it is the body-fixed molecular Hamiltonians that should be used. A general body-fixed no-pair relativistic molecular Hamiltonian, including nuclear mass-polarization and recoil, is just proposed,[58] the extension of which to the present effective QED Hamiltonian is straightforward.

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APPENDIX A: USEFUL RELATIONS FOR OPERATOR CONTRACTIONS

There exist two kinds of contractions between V (77) and $\Omega^{(1)}$ (72): (1) The $a^{\tilde{p}}$ operators of V and the $a_{\tilde{q}}$ operators of $\Omega^{(1)}$ must all be contracted. (2) The a_p operators of V and the a^q operators of $\Omega^{(1)}$ should also be contracted. However, neither zero nor full contractions are allowed. With these rules we have

$$\{a^p_q\}_n\{a^t_u\}_n = \delta^t_q\{a^p_u\}_n, \quad (A1)$$

$$\{a^{\tilde{p}}_q\}_n\{a^t_{\tilde{u}}\}_n = -\delta^{\tilde{p}}_{\tilde{u}}\{a^t_q\}_n, \quad (A2)$$

$$\{a^p_q\}_n\{a^{tu}_{vw}\}_n = \delta^t_q\{a^{pu}_{vw}\}_n + \delta^u_q\{a^{tp}_{vw}\}_n, \quad (A3)$$

$$\{a^{\tilde{p}}_q\}_n\{a^{tu}_{v\tilde{w}}\}_n = -\delta^{\tilde{p}}_{\tilde{w}}\{a^{tu}_{vq} + \delta^t_q a^u_v - \delta^u_q a^t_v\}_n, \quad (A4)$$

$$\{a^{pq}_{rs}\}_n\{a^t_u\}_n = \delta^t_r\{a^{pq}_{us}\}_n + \delta^t_s\{a^{pq}_{rs}\}_n, \quad (A5)$$

$$\{a^{p\tilde{q}}_{rs}\}_n\{a^t_{\tilde{u}}\}_n = -\delta^{\tilde{q}}_{\tilde{u}}\{a^{pt}_{rs} + \delta^t_r a^p_s - \delta^t_s a^p_r\}_n, \quad (A6)$$

$$\{a^{pq}_{rs}\}_n\{a^{tu}_{vw}\}_n = \delta^t_r\{a^{pqu}_{vsw}\}_n + \delta^t_s\{a^{pqu}_{rvw}\}_n + \delta^u_r\{a^{pqt}_{wsv}\}_n + \delta^u_s\{a^{pqt}_{rwv}\}_n + (\delta^t_r\delta^u_s - \delta^t_s\delta^u_r)\{a^{pq}_{vw}\}_n, \quad (A7)$$

$$\{a^{p\tilde{q}}_{rs}\}_n\{a^{tu}_{v\tilde{w}}\}_n = -\delta^{\tilde{q}}_{\tilde{w}}\{a^{put}_{rsv} - (\delta^t_r a^{pu}_{sv} - \delta^t_s a^{pu}_{rv} + \delta^u_s a^{pt}_{rv} - \delta^u_r a^{pt}_{sv}) - (\delta^t_r\delta^u_s - \delta^t_s\delta^u_r)a^p_v\}_n, \quad (A8)$$

$$\{a^{\tilde{p}\tilde{q}}_{rs}\}_n\{a^{tu}_{\tilde{v}\tilde{w}}\}_n = (\delta^{\tilde{p}}_{\tilde{v}}\delta^{\tilde{q}}_{\tilde{w}} - \delta^{\tilde{p}}_{\tilde{w}}\delta^{\tilde{q}}_{\tilde{v}})\{a^{tu}_{rs} - \delta^t_r a^u_s + \delta^t_s a^u_r - \delta^u_s a^t_r + \delta^u_r a^t_s\}_n. \quad (A9)$$

APPENDIX B: USEFUL INTEGRALS

We first define[56]

$$\int_{-\infty}^{+\infty} dt e^{i\omega t} e^{-\gamma|t|} = \frac{2\gamma}{\omega^2 + \gamma^2} = 2\pi\,\Delta_\gamma(\omega), \quad (B1)$$

where $\Delta_\gamma(\omega)$ is an even function of ω and has the following properties:

$$\lim_{\gamma\to 0}\Delta_\gamma(\omega) = \delta(\omega), \quad (B2)$$

$$\lim_{\gamma\to 0}\pi\gamma\,\Delta_\gamma(\omega) = \delta^\omega_0, \quad (B3)$$

$$\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}2\pi\,\Delta_\alpha(a-\omega)2\pi\,\Delta_\beta(b+\omega) = 2\pi\,\Delta_{\alpha+\beta}(a+b). \quad (B4)$$

The integral $I^{\pm}_{11}$ with one electron propagator and one Δ function reads

$$I^{\pm}_{11}(\epsilon_t; a, \gamma) = \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{1}{\omega - \epsilon_t(1 \pm i\eta)}2\pi\,\Delta_\gamma(a-\omega) = \frac{1}{a - \epsilon_t(1 \pm i\gamma)}, \quad (B5)$$

where η is an infinitesimally positive number, whereas γ is a small but finite positive number (i.e., $\eta + \gamma \approx \gamma$). The integral $I_{12}^{\pm}$ with one electron propagator and two Δ functions reads

$$\begin{aligned} I_{12}^{\pm}(\epsilon_t; a, b, \gamma) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{\omega - \epsilon_t(1 \pm i\eta)} 2\pi\,\Delta_{\gamma}(a-\omega) 2\pi\,\Delta_{\gamma}(b-\omega) \\ &= 2\pi\,\Delta_{2\gamma}(a-b) \Bigg\{ \frac{1}{2[a - \epsilon_t(1 \pm i\gamma)]} + \frac{1}{2[b - \epsilon_t(1 \pm i\gamma)]} \\ &\quad \pm \frac{\gamma\,\mathrm{sgn}(\epsilon_t)}{i[a - \epsilon_t(1 \pm i\gamma)][b - \epsilon_t(1 \pm i\gamma)]} \Bigg\}, \end{aligned} \tag{B6}$$

which reduces to

$$I_{12}^{\pm}(\epsilon_t; a, a, \gamma) = \frac{1}{\gamma[a - \epsilon_t(1 \pm i\gamma)]} \pm \frac{\mathrm{sgn}(\epsilon_t)}{i[a - \epsilon_t(1 \pm i\gamma)]^2} \tag{B7}$$

in the case of $a = b$. Likewise,

$$\begin{aligned} J_{12}^{\pm}(\epsilon_t; a, a, \gamma) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{\omega - \epsilon_t(1 \pm i\eta)} 2\pi\,\Delta_{\gamma}(a-\omega) 2\pi\,\Delta_{2\gamma}(a-\omega) \\ &= \frac{2}{3\gamma} \left\{ \frac{2}{a - \epsilon_t(1 \pm i\gamma)} - \frac{1}{a - \epsilon_t(1 \pm 2i\gamma)} \right\} \\ &= \begin{cases} \dfrac{2}{3\gamma} \dfrac{1}{a - \epsilon_t}, & \text{if } a \neq \epsilon_t, \\ \dfrac{\pm i\,\mathrm{sgn}(\epsilon_t)}{\gamma^2}, & \text{if } a = \epsilon_t \end{cases} \end{aligned} \tag{B8}$$

Further in view of the identities

$$\begin{aligned} I_{10}^{\pm}(a, \epsilon_t) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{a + \omega - \epsilon_t(1 \pm i\eta)} \\ &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{a - \omega - \epsilon_t(1 \pm i\eta)} \\ &= \pm \frac{i}{2} \mathrm{sgn}(\epsilon_t), \end{aligned} \tag{B9}$$

$$\begin{aligned} I_{20}^{L--}(a, \epsilon_t, b, \epsilon_u; n) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{a \pm \omega - \epsilon_t(1 - i\eta)} \frac{1}{[b \mp \omega - \epsilon_u(1 - i\delta)]^n} \\ &= \frac{-i\,L_{tu}}{\{a + b - \epsilon_u - \epsilon_t + i(\eta + \delta) L_{tu}\}^n}, \end{aligned} \tag{B10}$$

$$\begin{aligned} I_{20}^{L++}(a, \epsilon_t, b, \epsilon_u; n) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{a \pm \omega - \epsilon_t(1 + i\eta)} \frac{1}{[b \mp \omega - \epsilon_u(1 + i\delta)]^n} \\ &= \frac{i\,L_{tu}}{\{a + b - \epsilon_u - \epsilon_t - i(\eta + \delta) L_{tu}\}^n}, \end{aligned} \tag{B11}$$

$$\begin{aligned} I_{20}^{L+-}(a, \epsilon_t, b, \epsilon_u; n) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{a \pm \omega - \epsilon_t(1 + i\eta)} \frac{1}{[b \mp \omega - \epsilon_u(1 - i\delta)]^n} \\ &= \frac{i\,X_{tu}}{\{a + b - \epsilon_u - \epsilon_t - i(\eta + \delta) X_{tu}\}^n}, \end{aligned} \tag{B12}$$

$$\begin{aligned} I_{20}^{L-+}(a, \epsilon_t, b, \epsilon_u; n) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{a \pm \omega - \epsilon_t(1 - i\eta)} \frac{1}{[b \mp \omega - \epsilon_u(1 + i\delta)]^n} \\ &= \frac{-i\,X_{tu}}{\{a + b - \epsilon_u - \epsilon_t + i(\eta + \delta) X_{tu}\}^n}, \end{aligned} \tag{B13}$$

$$\begin{aligned} I_{20}^{X--}(a, \epsilon_t, b, \epsilon_u; n) &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{a \pm \omega - \epsilon_t(1 - i\eta)} \frac{1}{[b \pm \omega - \epsilon_u(1 - i\delta)]^n} \\ &= \frac{-i\,X_{tu}(-1)^n}{\{a - b + \epsilon_u - \epsilon_t + i(\eta + \delta) X_{tu}\}^n}, \end{aligned} \tag{B14}$$

$$I_{20}^{X++}(a,\epsilon_t,b,\epsilon_u;n) = \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{1}{a\pm\omega-\epsilon_t(1+i\eta)}\frac{1}{[b\pm\omega-\epsilon_u(1+i\delta)]^n}$$
$$= \frac{iX_{tu}(-1)^n}{\{a-b+\epsilon_u-\epsilon_t-i(\eta+\delta)X_{tu}\}^n}, \tag{B15}$$

$$I_{20}^{X+-}(a,\epsilon_t,b,\epsilon_u;n) = \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{1}{a\pm\omega-\epsilon_t(1+i\eta)}\frac{1}{[b\pm\omega-\epsilon_u(1-i\delta)]^n}$$
$$= \frac{iL_{tu}(-1)^n}{\{a-b+\epsilon_u-\epsilon_t-i(\eta+\delta)L_{tu}\}^n}, \tag{B16}$$

$$I_{20}^{X-+}(a,\epsilon_t,b,\epsilon_u;n) = \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{1}{a\pm\omega-\epsilon_t(1-i\eta)}\frac{1}{[b\pm\omega-\epsilon_u(1+i\delta)]^n}$$
$$= \frac{-iL_{tu}(-1)^n}{\{a-b+\epsilon_u-\epsilon_t+i(\eta+\delta)L_{tu}\}^n}, \tag{B17}$$

where

$$L_{tu} = L_{++} = -L_{--} = 1, \quad L_{tu} = L_{+-} = L_{-+} = 0, \tag{B18}$$

$$X_{tu} = X_{++} = X_{--} = 0, \quad X_{tu} = X_{+-} = -X_{-+} = 1, \tag{B19}$$

the integrals I_{22}^{Abc} ($A = L, X$; $b, c = +, -$) with two electron propagators and two Δ functions can readily be evaluated as

$$I_{22}^{L--}(\epsilon_t,\epsilon_u;a,b,\gamma) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\epsilon_t(1-i\eta)}\frac{1}{\omega_2-\epsilon_u(1-i\eta)}$$
$$\times 2\pi\,\Delta_\gamma(a-\omega_1-\omega_2)2\pi\,\Delta_\gamma(b-\omega_1-\omega_2)$$
$$= 2\pi\,\Delta_{2\gamma}(a-b)\left\{\frac{-iL_{tu}}{2[a-\epsilon_t-\epsilon_u+i\gamma L_{tu}]}\right.$$
$$+\frac{-iL_{tu}}{2[b-\epsilon_t-\epsilon_u+i\gamma L_{tu}]}$$
$$\left.+\frac{\gamma|L_{tu}|}{[a-\epsilon_t-\epsilon_u+i\gamma L_{tu}][b-\epsilon_t-\epsilon_u+i\gamma L_{tu}]}\right\}, \tag{B20}$$

$$I_{22}^{L++}(\epsilon_t,\epsilon_u;a,b,\gamma) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\epsilon_t(1+i\eta)}\frac{1}{\omega_2-\epsilon_u(1+i\eta)}$$
$$\times 2\pi\,\Delta_\gamma(a-\omega_1-\omega_2)2\pi\,\Delta_\gamma(b-\omega_1-\omega_2)$$
$$= 2\pi\,\Delta_{2\gamma}(a-b)\left\{\frac{iL_{tu}}{2[a-\epsilon_t-\epsilon_u-i\gamma L_{tu}]}\right.$$
$$+\frac{iL_{tu}}{2[b-\epsilon_t-\epsilon_u-i\gamma L_{tu}]}$$
$$\left.+\frac{\gamma|L_{tu}|}{[a-\epsilon_t-\epsilon_u-i\gamma L_{tu}][b-\epsilon_t-\epsilon_u-i\gamma L_{tu}]}\right\}, \tag{B21}$$

$$I_{22}^{L+-}(\epsilon_t,\epsilon_u;a,b,\gamma) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\epsilon_t(1+i\eta)}\frac{1}{\omega_2-\epsilon_u(1-i\eta)}$$
$$\times 2\pi\,\Delta_\gamma(a-\omega_1-\omega_2)2\pi\,\Delta_\gamma(b-\omega_1-\omega_2)$$
$$= 2\pi\,\Delta_{2\gamma}(a-b)\left\{\frac{iX_{tu}}{2[a-\epsilon_t-\epsilon_u-i\gamma X_{tu}]}\right.$$
$$+\frac{iX_{tu}}{2[b-\epsilon_t-\epsilon_u-i\gamma X_{tu}]}$$
$$\left.+\frac{\gamma|X_{tu}|}{[a-\epsilon_t-\epsilon_u-i\gamma X_{tu}][b-\epsilon_t-\epsilon_u-i\gamma X_{tu}]}\right\}, \tag{B22}$$

$$
\begin{aligned}
I_{22}^{L--}(\epsilon_t,\epsilon_u;a,b,\gamma) &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\epsilon_t(1-i\eta)}\frac{1}{\omega_2-\epsilon_u(1+i\eta)} \\
&\quad\times 2\pi\,\Delta_\gamma(a-\omega_1-\omega_2)2\pi\,\Delta_\gamma(b-\omega_1-\omega_2) \\
&= 2\pi\,\Delta_{2\gamma}(a-b)\left\{\frac{-iX_{tu}}{2[a-\epsilon_t-\epsilon_u+i\gamma X_{tu}]}\right. \\
&\quad+\frac{-iX_{tu}}{2[b-\epsilon_t-\epsilon_u+i\gamma X_{tu}]} \\
&\quad\left.+\frac{\gamma|X_{tu}|}{[a-\epsilon_t-\epsilon_u+i\gamma X_{tu}][b-\epsilon_t-\epsilon_u+i\gamma X_{tu}]}\right\}, \qquad \text{(B23)} \\
I_{22}^{X--}(\epsilon_t,\epsilon_u;a,b,\gamma) &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\epsilon_t(1-i\eta)}\frac{1}{\omega_2-\epsilon_u(1-i\eta)} \\
&\quad\times 2\pi\,\Delta_\gamma(a+\omega_1-\omega_2)2\pi\,\Delta_\gamma(b+\omega_1-\omega_2) \\
&= 2\pi\,\Delta_{2\gamma}(a-b)\left\{\frac{-iX_{tu}}{2[a+\epsilon_t-\epsilon_u-i\gamma X_{tu}]}\right. \\
&\quad+\frac{-iX_{tu}}{2[b+\epsilon_t-\epsilon_u-i\gamma X_{tu}]} \\
&\quad\left.-\frac{\gamma|X_{tu}|}{[a+\epsilon_t-\epsilon_u-i\gamma X_{tu}][b+\epsilon_t-\epsilon_u-i\gamma X_{tu}]}\right\}, \qquad \text{(B24)} \\
I_{22}^{X++}(\epsilon_t,\epsilon_u;a,b,\gamma) &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\epsilon_t(1+i\eta)}\frac{1}{\omega_2-\epsilon_u(1+i\eta)} \\
&\quad\times 2\pi\,\Delta_\gamma(a+\omega_1-\omega_2)2\pi\,\Delta_\gamma(b+\omega_1-\omega_2) \\
&= 2\pi\,\Delta_{2\gamma}(a-b)\left\{\frac{iX_{tu}}{2[a+\epsilon_t-\epsilon_u+i\gamma X_{tu}]}\right. \\
&\quad+\frac{iX_{tu}}{2[b+\epsilon_t-\epsilon_u+i\gamma X_{tu}]} \\
&\quad\left.-\frac{\gamma|X_{tu}|}{[a+\epsilon_t-\epsilon_u+i\gamma X_{tu}][b+\epsilon_t-\epsilon_u+i\gamma X_{tu}]}\right\}, \qquad \text{(B25)} \\
I_{22}^{X+-}(\epsilon_t,\epsilon_u;a,b,\gamma) &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\epsilon_t(1+i\eta)}\frac{1}{\omega_2-\epsilon_u(1-i\eta)} \\
&\quad\times 2\pi\,\Delta_\gamma(a+\omega_1-\omega_2)2\pi\,\Delta_\gamma(b+\omega_1-\omega_2) \\
&= 2\pi\,\Delta_{2\gamma}(a-b)\left\{\frac{iL_{tu}}{2[a+\epsilon_t-\epsilon_u+i\gamma L_{tu}]}\right. \\
&\quad+\frac{iL_{tu}}{2[b+\epsilon_t-\epsilon_u+i\gamma L_{tu}]} \\
&\quad\left.-\frac{\gamma|L_{tu}|}{[a+\epsilon_t-\epsilon_u+i\gamma L_{tu}][b+\epsilon_t-\epsilon_u+i\gamma L_{tu}]}\right\}, \qquad \text{(B26)} \\
I_{22}^{X-+}(\epsilon_t,\epsilon_u;a,b,\gamma) &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\epsilon_t(1-i\eta)}\frac{1}{\omega_2-\epsilon_u(1+i\eta)} \\
&\quad\times 2\pi\,\Delta_\gamma(a+\omega_1-\omega_2)2\pi\,\Delta_\gamma(b+\omega_1-\omega_2) \\
&= 2\pi\,\Delta_{2\gamma}(a-b)\left\{\frac{-iL_{tu}}{2[a+\epsilon_t-\epsilon_u-i\gamma L_{tu}]}\right. \\
&\quad+\frac{-iL_{tu}}{2[b+\epsilon_t-\epsilon_u-i\gamma L_{tu}]} \\
&\quad\left.-\frac{\gamma|L_{tu}|}{[a+\epsilon_t-\epsilon_u-i\gamma L_{tu}][b+\epsilon_t-\epsilon_u-i\gamma L_{tu}]}\right\}. \qquad \text{(B27)}
\end{aligned}
$$

At variance with the half-pole integral (B9), the following integral is a full-pole integral:

$$I^{\pm}_{R_c}(a,\epsilon_c) = \oint_{R_c} \frac{d\omega}{2\pi} \frac{1}{a+\omega-\epsilon_c(1\pm i\eta)} = \oint_{R_c} \frac{d\omega}{2\pi} \frac{1}{a-\omega-\epsilon_c(1\pm i\eta)} = i\,\mathrm{sgn}(\epsilon_c), \tag{B28}$$

where R_c is the counter-clockwise integration contour closing the c state.

[1]The generic acronym "X2C" (pronounced as "ecstacy") for exact two-component Hamiltonians resulted from intensive discussions among H. J. Aa. Jensen, W. Kutzelnigg, W. Liu, T. Saue, and L. Visscher during the 12th International Conference on the Applications of Density Functional Theory (DFT-2007), Amsterdam, August 26–30, 2007. Note that the "exact" here means only that all the solutions of the Dirac-based Hamiltonian can be reproduced up to machine accuracy. It is particularly meaningful when compared with finite order quasirelativistic theories.

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[23]The so-called QED effects are usually defined as anything beyond the no-pair approximation of the instantaneous interactions. They are further characterized as *non-radiative* (virtual pairs and retardation) and *radiative* (self-energy, vacuum polarization, and vertex correction) effects. The virtual pairs here may arise from both one- and two-body interactions. It is the virtual pairs created by the non-retarded fluctuation potential that are under concern here. In the parlance of relativistic quantum chemistry, these are precisely the correlation contribution of negative energy states. See Ref. 51 for further discussions.

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