QED approach to valence-hole excitation in closed-shell systems

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An *ab initio* QED approach to treat a valence-hole excitation in closed-shell systems is developed in the framework of the two-time Green's-function method. The derivation considers a redefinition of the vacuum state and its excitation as a valence-hole pair. The proper two-time Green's function, whose spectral representation confirms the poles at valence-hole excitation energies, is proposed. An contour integral formula which connects the energy corrections and the Green's function is also presented. First-order corrections to the valence-hole excitation energy involving self-energy, vacuum polarization, and one-photon-exchange terms are explicitly derived in the redefined vacuum picture. Reduction to the usual vacuum electron propagators is shown, which agrees in the Breit approximation with the many-body perturbation theory expressions for the valence-hole excitation energy.

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I. INTRODUCTION

Highly charged ions became a field of interest from both the theoretical and experimental sides. It has the great advantage of providing access to strong-field physics [1] and allowing us to probe quantum electrodynamics (QED) corrections up to second order in α (the fine-structure constant) [2,3], although that is a challenging task. Intensive experimental investigations have been carried out over the years in a variety of system, ranging from H-like [4–6], He-like [7–11], Be-like [12,13], and Li-like [14,15] to B-like [16–18] and F-like [19–21] ions. Increasing experimental precision pushes theoretical predictions to their limits and enforces an accurate description of complex electron dynamics. Over the years, many approximated methods have been devised to access higher-order corrections; however, *ab initio* calculations remain the holy grail in the quest for many-electron atoms in the frame of bound-state QED (BSQED).

Dealing with many-electron ions is a difficult task due to the numerical complexity involved as well as the need to derive a formal BSQED expression. That is why *ab initio* calculations have been limited so far to few-electron ions [22–24] and ions with a single valence (or hole) electron [25–28]. To facilitate the derivation of the formal expressions for many-electron systems the redefinition of the vacuum state is widely used in the relativistic many-body perturbation theory (MBPT) [29,30]. However, within BSQED it has not yet been broadly employed. The vacuum redefinition method was employed previously within the BSQED mainly for single-valence-electron states [31–36] and recently for two-valence-electron states [24]. In Ref. [36] we showed that employing the redefined vacuum state allows one to keep track of one-electron gauge-invariant subsets into many-electron Feynman diagrams. Thus, several additional gauge-invariant subsets were identified. Later, we applied it to more sophisticated electron structures generalizing to either N-valence-electron or N-hole cases [37]. As an example, we presented the complete set of formal expressions for BSQED corrections up to second order in α for the single-hole picture [37]. Thus, the situation when both valence electrons and holes are involved in the description of a state has not been considered so far within the vacuum redefinition method.

The aim of this paper is to provide a rigorous *ab initio* derivation of the BSQED perturbation theory for a valence-hole excitation in a closed-shell system with the redefined vacuum approach. The two-time Green's-function (TTGF) formulation of the BSQED theory [31] is employed as a mathematical tool for our derivation. The notion of a redefined vacuum state is used from the very beginning. It is shown that with the appropriate equal-time-choice conditions a Green's function with the proper two-body state normalization in the noninteracting field limit can be constructed. Its spectral representation identifies poles at the valence-hole excitation energies, and the integral formula for the energy correction to the binding energy is obtained. The latter expression is expanded to first order, where one-particle radiative and one-photon exchange corrections are explicitly derived. Section II introduces the basics of BSQED and the redefinition of the vacuum state. The major part of the paper is devoted to the derivation of the TTGF suited for the valence-hole excitation energy, which is presented in Sec. III. Section IV is dedicated to explicit deduction of the first-order corrections. The discussion and conclusion are given in Sec. V. Some calculation details are provided in the Appendix for the zeroth-order TTGF.

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Natural units ($\hbar = c = m_e = 1$) are used throughout this paper; the fine-structure constant is defined as $\alpha = e^2/(4\pi)$, $e < 0$. Unless explicitly stated, all integrals are meant to be on the interval $]-\infty, \infty[$.

II. BOUND-STATE QED

The quantum relativistic description of the bound-state system under consideration relies on the Furry picture [38] of QED, the so-called bound-state QED. In this approach the eigenstates of the Dirac equation

$$h_{\rm D}\phi_j(\mathbf{x}) = [-i\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta + V(\mathbf{x})]\phi_j(\mathbf{x}) = \epsilon_j\phi_j(\mathbf{x}) \tag{1}$$

are solutions in the presence of an external classical Coulomb field arising from the nucleus, $V(\mathbf{x}) = V_{\rm C}(\mathbf{x})$. This means an all-order treatment in αZ, with Z being the nuclear charge, hence going beyond the perturbative regime. The extended Furry picture implies the presence of a screening potential $U(\mathbf{x})$ besides the Coulomb one, $V(\mathbf{x}) = V_{\rm C}(\mathbf{x}) + U(\mathbf{x})$, which partially takes into account the interelectronic interaction. The time-dependent solution is obtained when $\phi_j(\mathbf{x})$ is multiplied by the phase factor $\exp(-i\epsilon_j t)$. α^k and β are Dirac matrices, and j stands for all quantum numbers. The unperturbed normal-ordered Hamiltonian is constructed as [39]

$$H_0 = \int d^3\mathbf{x} : \psi^{(0)\dagger}(t,\mathbf{x}) h_{\rm D}\psi^{(0)}(t,\mathbf{x}) : . \tag{2}$$

A new vacuum state, named the redefined vacuum state, is introduced in such a way that all core orbitals from the closed shell belong to it [29]. It is denoted by $|\alpha\rangle$ notation,

$$|\alpha\rangle = a_a^\dagger a_b^\dagger \cdots |0\rangle . \tag{3}$$

Here and in the following, we employ the MBPT notations of Lindgren and Morisson [29] and Johnson [30]: v designates a valence electron; $a, b, \ldots$ stand for core orbitals; $i, j, \ldots$ correspond to arbitrary states; and h corresponds to a hole. The redefinition of the vacuum state affects the noninteracting fermion field expansion in creation and annihilation operators and the electron propagator as follows:

$$\psi_\alpha^{(0)}(t,\mathbf{x}) = \sum_{\epsilon_j > E_\alpha^F} a_j\phi_j(\mathbf{x})e^{-i\epsilon_j t} + \sum_{\epsilon_j < E_\alpha^F} b_j^\dagger\phi_j(\mathbf{x})e^{-i\epsilon_j t} \tag{4}$$

and

$$\begin{aligned}\langle\alpha|\, T\big[\psi_\alpha^{(0)}(t,\mathbf{x})\bar\psi_\alpha^{(0)}(t',\mathbf{y})\big]\,|\alpha\rangle \\ = \frac{i}{2\pi}\int d\omega \sum_j \frac{\phi_j(\mathbf{x})\bar\phi_j(\mathbf{y})e^{-i(t-t')\omega}}{\omega - \epsilon_j + i\varepsilon\big(\epsilon_j - E_\alpha^F\big)},\end{aligned} \tag{5}$$

respectively. The limit $\varepsilon \to 0$ is implied above, with $\varepsilon > 0$. E_α^F is the Fermi level of the redefined vacuum state lying slightly above the energy of the highest core state.

We refer to Refs. [36,37] for more details on the vacuum redefinition within the BSQED framework and its use in the formula derivation.

The interacting Hamiltonian takes the form

$$H_{\rm int} = \int d^3\mathbf{x} : \psi^{(0)\dagger}(t,\mathbf{x}) h_{\rm int}\psi^{(0)}(t,\mathbf{x}) :, \tag{6}$$

where $h_{\rm int} = e\alpha^\mu A_\mu(t,\mathbf{x}) - U(\mathbf{x})$ contains the interaction with the quantized electromagnetic field A_μ and the counterpotential term $-U(\mathbf{x})$ when one works within the extended Furry picture. The interaction term is treated within BSQED perturbation theory. For its formulation there are several approaches [31,39–41]. Our derivation presented in the following is based on the TTGF method [31].

III. VALENCE-HOLE GREEN'S FUNCTION

Let us derive the Green's function for the valence-hole excitation in a closed-shell system and show that its spectral representation indeed has poles at valence-hole excitation energies. To begin, we consider the general four-point Green's function

$$G(t_1',\mathbf{x}_1,t_2',\mathbf{x}_2,t_1,\mathbf{y}_1,t_2,\mathbf{y}_2) = \langle 0|\, T[\psi(t_1',\mathbf{x}_1)\psi(t_2',\mathbf{x}_2)\bar\psi(t_2,\mathbf{y}_2)\bar\psi(t_1,\mathbf{y}_1)]\,|0\rangle . \tag{7}$$

This Green's function contains all the information about the two-particle dynamics in the presence of the nuclear Coulomb field. However, it is a difficult task to extract the necessary information. To get the energy levels it is enough to consider a two-time Green's function. In the original work [31], Shabaev proposed considering the equal-time choices $t_1' = t_2' = t'$ and $t_1 = t_2 = t$:

$$G(t',\mathbf{x}_1,t',\mathbf{x}_2,t,\mathbf{y}_1,t,\mathbf{y}_2) = \langle 0|\, T[\psi(t',\mathbf{x}_1)\psi(t',\mathbf{x}_2)\bar\psi(t,\mathbf{y}_2)\bar\psi(t,\mathbf{y}_1)]\,|0\rangle . \tag{8}$$

However, the spectral representation of the Green's function for this particular choice of times unambiguously reveals poles only for pure electron (charge $2e$) or positron (charge $-2e$) states [31]. This is a clear message that such an equal-time Green's function cannot deal with valence-hole excitation. Thus, one has to come up with a different Green's function to describe such a system. Notice that although the choice of times was motivated and justified *a posteriori* when the spectral representation was derived, it is nevertheless an arbitrary choice. *A priori* one can also choose to have equal times such as $t_1' = t_1 = t$ and $t_2' = t_2 = t'$; then the resulting Green's function reads

$$G(t,\mathbf{x}_1,t',\mathbf{x}_2,t,\mathbf{y}_1,t',\mathbf{y}_2) = \langle 0|\, T[\psi(t,\mathbf{x}_1)\psi(t',\mathbf{x}_2)\bar\psi(t',\mathbf{y}_2)\bar\psi(t,\mathbf{y}_1)]\,|0\rangle . \tag{9}$$

Similar Green's functions were studied previously by Logunov and Tavkhelidze [42], Fetter and Walecka [43], Oddershede and Jørgensen [44], and Liegener [45]. In order to achieve the desired structure and for normalization reasons, as can be seen in the Appendix, one has to take into account three extra terms. One might argue that other structures are possible; by virtue of Ockham's razor the one proposed here is, to our view, the simplest one. Hence, the Green's function one has to consider takes

the following form in the redefined vacuum $|\alpha\rangle$:

$$G_\alpha(t_1,t_2;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2) = \langle\alpha|\,T[\psi_\alpha(t_1,\mathbf{x}_1)\psi_\alpha(t_2,\mathbf{x}_2)\bar{\psi}_\alpha(t_2,\mathbf{y}_2)\bar{\psi}_\alpha(t_1,\mathbf{y}_1) - \psi_\alpha(t_1,\mathbf{x}_2)\psi_\alpha(t_2,\mathbf{x}_1)\bar{\psi}_\alpha(t_2,\mathbf{y}_2)\bar{\psi}_\alpha(t_1,\mathbf{y}_1) - \psi_\alpha(t_1,\mathbf{x}_1)\psi_\alpha(t_2,\mathbf{x}_2)\bar{\psi}_\alpha(t_2,\mathbf{y}_1)\bar{\psi}_\alpha(t_1,\mathbf{y}_2) + \psi_\alpha(t_1,\mathbf{x}_2)\psi_\alpha(t_2,\mathbf{x}_1)\bar{\psi}_\alpha(t_2,\mathbf{y}_1)\bar{\psi}_\alpha(t_1,\mathbf{y}_2)]\,|\alpha\rangle\,. \quad (10)$$

To demonstrate that this Green's function has the expected pole structure, one has to consider its spectral representation, which is obtained by taking the Fourier transform of the Green's function. For the sake of clarity, the steps that need to be performed are briefly described. The first one is to rearrange the Dirac spinors to get identical times close to each other, keeping in mind that for equal time the only nonzero anticommutator is $\{\psi_\alpha(t,\mathbf{x}),\psi_\alpha^\dagger(t,\mathbf{y})\} = \delta^{(3)}(\mathbf{x}-\mathbf{y})$. The next step is to proceed with the time ordering. Once that is done, a completeness relation, $\mathbb{1} = \sum_\beta |\beta\rangle\langle\beta|$, is inserted to separate terms with different times within the time-ordered product. Then the Heisenberg representation of the field operator is introduced, $\psi_\alpha(t,\mathbf{x}) = e^{iHt}\psi_\alpha(0,\mathbf{x})e^{-iHt}$, with $H = H_0 + H_{\rm int}$, and the integral representation of the Heaviside function is applied. One ends up with

$$\begin{aligned}\mathcal{G}_\alpha(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\delta(E-E') &= \frac{1}{2\pi i}\frac{1}{2!}\int dt_1dt_2e^{iEt_1-iE't_2}G_\alpha(t_1,t_2;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\\ &= \frac{1}{4\pi^2}\frac{1}{2!}\int dt_1dt_2e^{iEt_1-iE't_2}\int d\omega e^{-i\omega(t_1-t_2)}\left\{\sum_\beta\frac{\mathcal{A}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)}{\omega-E_\beta+i\varepsilon} - \sum_\beta\frac{\mathcal{B}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)}{\omega+E_\beta-i\varepsilon}\right\}\\ &= \frac{\delta(E-E')}{2!}\left\{\sum_\beta\frac{\mathcal{A}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)}{E-E_\beta+i\varepsilon} - \sum_\beta\frac{\mathcal{B}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)}{E+E_\beta-i\varepsilon}\right\},\end{aligned} \quad (11)$$

where the $\mathcal{A}$ term is given by

$$\mathcal{A}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2) = \langle\alpha|\,[\psi_\alpha(0,\mathbf{x}_1)\bar{\psi}_\alpha(0,\mathbf{y}_1)\,|\beta\rangle\langle\beta|\,\psi_\alpha(0,\mathbf{x}_2)\bar{\psi}_\alpha(0,\mathbf{y}_2) - \psi_\alpha(0,\mathbf{x}_2)\bar{\psi}_\alpha(0,\mathbf{y}_1)\,|\beta\rangle\langle\beta|\,\psi_\alpha(0,\mathbf{x}_1)\bar{\psi}_\alpha(0,\mathbf{y}_2) - \psi_\alpha(0,\mathbf{x}_1)\bar{\psi}_\alpha(0,\mathbf{y}_2)\,|\beta\rangle\langle\beta|\,\psi_\alpha(0,\mathbf{x}_2)\bar{\psi}_\alpha(0,\mathbf{y}_1) + \psi_\alpha(0,\mathbf{x}_2)\bar{\psi}_\alpha(0,\mathbf{y}_2)\,|\beta\rangle\langle\beta|\,\psi_\alpha(0,\mathbf{x}_1)\bar{\psi}_\alpha(0,\mathbf{y}_1)]\,|\alpha\rangle \quad (12)$$

and the $\mathcal{B}$ one is

$$\mathcal{B}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2) = \langle\alpha|\,[\psi_\alpha(0,\mathbf{x}_2)\bar{\psi}_\alpha(0,\mathbf{y}_2)\,|\beta\rangle\langle\beta|\,\psi_\alpha(0,\mathbf{x}_1)\bar{\psi}_\alpha(0,\mathbf{y}_1) - \psi_\alpha(0,\mathbf{x}_1)\bar{\psi}_\alpha(0,\mathbf{y}_2)\,|\beta\rangle\langle\beta|\,\psi_\alpha(0,\mathbf{x}_2)\bar{\psi}_\alpha(0,\mathbf{y}_1) - \psi_\alpha(0,\mathbf{x}_2)\bar{\psi}_\alpha(0,\mathbf{y}_1)\,|\beta\rangle\langle\beta|\,\psi_\alpha(0,\mathbf{x}_1)\bar{\psi}_\alpha(0,\mathbf{y}_2) + \psi_\alpha(0,\mathbf{x}_1)\bar{\psi}_\alpha(0,\mathbf{y}_1)\,|\beta\rangle\langle\beta|\,\psi_\alpha(0,\mathbf{x}_2)\bar{\psi}_\alpha(0,\mathbf{y}_2)]\,|\alpha\rangle\,. \quad (13)$$

Thus, we derived the spectral representation of expression (10). Under the assumption of noninteracting electron-positron fields and their expansion in creation and annihilation operators, as in Eq. (4), the only consistent zeroth-order $|\beta\rangle$ states are found to be

$$|\beta\rangle = \{|vh\rangle = a_v^\dagger b_h^\dagger\,|\alpha\rangle\,,\ |\alpha\rangle\}. \quad (14)$$

Now that the Green's function spectral representation is obtained as a function of E, one can define its analytic continuation in the complex E plane. Then, one sees the presence of poles at the valence-hole excitation energies E_{vh} and $-E_{vh}$ as well as at the zero (vacuum energy). Some remarks are important here. First, although Eq. (11) looks similar to the equation obtained in Ref. [31], it has poles at essentially different energies. Second, despite the structure of $\mathcal{A}$ and $\mathcal{B}$ looks complicated, in the noninteracting cases it contains neutral charged states corresponding to valence-hole excitations of a closed shell. Third and most important, it leads to normalized two-particle wave functions in the zeroth order, as can be seen in the Appendix. A coordinate integrated Green's function is built out of the spectral representation of the Green's function in the following manner:

$$g_\alpha(E) = \frac{1}{2!}\int d^3\mathbf{x}_1d^3\mathbf{x}_2d^3\mathbf{y}_1d^3\mathbf{y}_2\ :\psi_\alpha^{(0)\dagger}(\mathbf{x}_1)\psi_\alpha^{(0)\dagger}(\mathbf{x}_2)\mathcal{G}_\alpha(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\gamma_1^0\gamma_2^0\psi_\alpha^{(0)}(\mathbf{y}_2)\psi_\alpha^{(0)}(\mathbf{y}_1):\,. \quad (15)$$

Further, we employ the occupation number representation as in the MBPT description provided by Lindgren [46] to construct the two-particle operator. Since our interest lies in the valence-hole state described by [47,48]

$$|(vh)_{JM}\rangle = \sum_{m_v,m_h}\langle j_vm_vj_h-m_h|JM\rangle\,(-1)^{j_h-m_h}a_v^\dagger b_h^\dagger\,|\alpha\rangle \equiv F_{vh}a_v^\dagger b_h^\dagger\,|\alpha\rangle\,, \quad (16)$$

where the jj-coupling scheme is applied to form a state with total angular momentum J and its projection M, we work out and retain only the six terms involving two a and two b operators. After normal ordering we arrive at the

expression

$$g_\alpha(E) \cong \frac{1}{2!}\Bigg\{ \sum_{i,j>E_\alpha^F,k,l<E_\alpha^F} a_i^\dagger a_j^\dagger b_l^\dagger b_k^\dagger - \sum_{k,l>E_\alpha^F,i,j<E_\alpha^F} a_k a_l b_i b_j + \sum_{i,l>E_\alpha^F,j,k<E_\alpha^F} a_i^\dagger a_l b_k^\dagger b_j + \sum_{j,k>E_\alpha^F,i,l<E_\alpha^F} a_j^\dagger a_k b_l^\dagger b_i - \sum_{i,k>E_\alpha^F,j,l<E_\alpha^F} a_i^\dagger a_k b_l^\dagger b_j - \sum_{j,l>E_\alpha^F,i,k<E_\alpha^F} a_j^\dagger a_l b_k^\dagger b_i \Bigg\} g_{\alpha,ijkl}(E), \tag{17}$$

with

$$g_{\alpha,ijkl}(E) = \int d^3\mathbf{x}_1 d^3\mathbf{x}_2 d^3\mathbf{y}_1 d^3\mathbf{y}_2 \phi_i^\dagger(\mathbf{x}_1)\phi_j^\dagger(\mathbf{x}_2)\mathcal{G}_\alpha(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\gamma_1^0\gamma_2^0\phi_k(\mathbf{y}_1)\phi_l(\mathbf{y}_2). \tag{18}$$

Further, we have to evaluate the matrix element of $g_\alpha(E)$ with the valence-hole state defined by Eq. (16). The first two terms in Eq. (17) do not contribute since they cannot be fully contracted with the valence-hole state. Computing the matrix element, we get

$$\langle (vh)_{JM}|\, g_\alpha(E)\,|(vh)_{JM}\rangle = F_{v_1h_1}F_{v_2h_2}[g_{\alpha,v_1h_2h_1v_2}(E) - g_{\alpha,v_1h_2v_2h_1}(E)]. \tag{19}$$

Now all the necessary pieces are available to derive the energy correction formula for the valence-hole binding energy. Applying the integral formalism developed in Ref. [31] and focusing only on the first term with the contour Γ_{vh} surrounding only the pole $E \sim E_{vh}^{(0)}$,

$$E_{vh}^{(0)} = \langle vh|\, H_0\,|vh\rangle = \epsilon_v - \epsilon_h, \tag{20}$$

we end up with the expression

$$E_{vh} = \frac{\frac{1}{2\pi i}\oint_{\Gamma_{vh}} dE\, E\,\langle (vh)_{JM}|\, g_\alpha(E)\,|(vh)_{JM}\rangle}{\frac{1}{2\pi i}\oint_{\Gamma_{vh}} dE\,\langle (vh)_{JM}|\, g_\alpha(E)\,|(vh)_{JM}\rangle}. \tag{21}$$

Evaluating the zeroth-order Green's function

$$\langle (vh)_{JM}|\, g_\alpha^{(0)}(E)\,|(vh)_{JM}\rangle = \frac{1}{E - E_{vh}^{(0)}} + \text{regular terms at } E \sim E_{vh}^{(0)} \tag{22}$$

(the detailed calculation is presented in the Appendix), we derive also the expression for the energy shift $\Delta E_{vh} = E_{vh} - E_{vh}^{(0)}$:

$$\Delta E_{vh} = \frac{\frac{1}{2\pi i}\oint_{\Gamma_{vh}} dE\big(E - E_{vh}^{(0)}\big)\,\langle (vh)_{JM}|\, \Delta g_\alpha(E)\,|(vh)_{JM}\rangle}{1 + \frac{1}{2\pi i}\oint_{\Gamma_{vh}} dE\,\langle (vh)_{JM}|\, \Delta g_\alpha(E)\,|(vh)_{JM}\rangle}, \tag{23}$$

where $\Delta g_\alpha(E) = g_\alpha(E) - g_\alpha^{(0)}(E)$. Expanding $\Delta g_\alpha(E)$ into a series in α, $\Delta g_\alpha(E) = \Delta g_\alpha^{(1)}(E) + \Delta g_\alpha^{(2)}(E) + \cdots$, and combining the terms of the same order, we easily obtain the BSQED perturbation expansion for the valence-hole energy $\Delta E_{vh} = \Delta E_{vh}^{(1)} + \Delta E_{vh}^{(2)} + \cdots$. Thus, in this section we obtain the two-time Green's function suited to the treatment of valence-hole states and derive the formula expressing the energy corrections as contour integrals of the Green's function. In the next section we apply this formalism to evaluate the first-order corrections to the energy of the valence-hole excitation.

IV. FIRST-ORDER CORRECTIONS

The first-order energy correction, obtained from the expansion of Eq. (23), yields

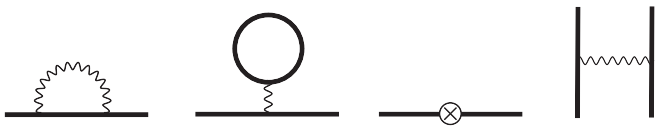
$$\Delta E_{vh}^{(1)} = \frac{1}{2\pi i}F_{v_1h_1}F_{v_2h_2}\oint_{\Gamma_{vh}} dE\big(E - E_{vh}^{(0)}\big)\big[\Delta g_{\alpha,v_1h_2h_1v_2}^{(1)}(E) - \Delta g_{\alpha,v_1h_2v_2h_1}^{(1)}(E)\big]. \tag{24}$$

The energy correction can be split into one-particle ($\Delta E_{vh}^{(1)1}$) and two-particle ($\Delta E_{vh}^{(1)2}$) terms:

$$\Delta E_{vh}^{(1)} = \Delta E_{vh}^{(1)1} + \Delta E_{vh}^{(1)2}. \tag{25}$$

In turn, the one-particle contribution originates from three Feynman diagrams: self-energy (SE), vacuum polarization (VP), and counterpotential (CP), which are depicted in Fig. 1(a) and give rise to the following terms in the Green's function:

$$\Delta g_\alpha^{(1)1}(E) = \Delta g_\alpha^{(1)\mathrm{SE}}(E) + \Delta g_\alpha^{(1)\mathrm{VP}}(E) + \Delta g_\alpha^{(1)\mathrm{CP}}(E). \tag{26}$$



(a) (b)

FIG. 1. (a) The first-order one-particle Feynman diagrams corresponding, from left to right, to the self-energy, vacuum-polarization, and counterpotential contributions and (b) the valence-hole one-photon exchange Feynman diagram. Single solid lines indicate the electron propagators in the redefined vacuum representation. Wavy lines correspond to the photon propagator, and the cross inside the circle represents a counterpotential term, $-U(\mathbf{x})$.

The two-particle contribution corresponds to the Green's function $\Delta g_\alpha^{(1)2}$ and the valence-hole one-photon exchange diagram presented in Fig. 1(b). We start by considering the one-particle diagrams.

A. One-particle contributions

Formally, for single-particle graphs, SE, VP, or CP, a second disconnected line (propagator) is present. However, these diagrams reduce to the single-particle case since the disconnected line can be integrated out, as we will show below. In what follows we consider in detail the SE correction, which can be further divided into two terms, one in which the SE loop is located on the valence electron line $\Delta g_\alpha^{(1)\mathrm{SE}v}$ and one in which it is located on the hole line $\Delta g_\alpha^{(1)\mathrm{SE}h}$. Let us consider the valence SE graph with disconnected hole line first. The Feynman rules, according to [31] but noting that the hole's energy formally flows in the negative t direction while being a positive quantity, provide us with the following expression:

$$\begin{aligned}\Delta g^{(1)\mathrm{SE}v}_{\alpha,v_1h_2v_2h_1}(E)\delta(E-E') &= e^2\Big(\frac{i}{2\pi}\Big)^2\int d^3\mathbf{x}d^3\mathbf{y}dp_1^0dp_2^0d\omega dk^0\delta\big(E-p_1^0+p_2^0\big)\delta\big(E'-p_1^0+p_2^0\big)\delta\big(p_1^0-\omega-k^0\big)\\ &\times\frac{\bar\psi_{v_1}(\mathbf{y})}{p_1^0-\epsilon_v+i\varepsilon}\gamma^\mu\sum_j\frac{\psi_j(\mathbf{y})\bar\psi_j(\mathbf{x})}{k^0-\epsilon_j+i\varepsilon\big(\epsilon_j-E_\alpha^F\big)}D_{\mu\nu}(\omega,\mathbf{y}-\mathbf{x})\gamma^\nu\frac{\psi_{v_2}(\mathbf{x})}{p_1^0-\epsilon_v+i\varepsilon}\frac{\delta_{h_1h_2}}{p_2^0-\epsilon_h-i\varepsilon}\\ &=\Big(\frac{i}{2\pi}\Big)^2\int dp_1^0d\omega\sum_j\frac{I_{v_1jjv_2}(\omega)}{p_1^0-\omega-\epsilon_j+i\varepsilon\big(\epsilon_j-E_\alpha^F\big)}\frac{\delta(E-E')}{\big[p_1^0-\epsilon_v+i\varepsilon\big]^2}\frac{\delta_{h_1h_2}}{p_1^0-E-\epsilon_h-i\varepsilon},\end{aligned}\tag{27}$$

where two momentum integrations have been carried out with the help of δ functions and further simplified due to the orthogonality of the wave functions. We highlight the fact that p_2^0 and $p_2'^0$ are the hole's energy in all calculations and that the δ functions taking care of the energy conservation of the initial and final states are affected, as can be expected from Eq. (20). Notice also that the zeroth-order energy of each particle does not depend on its spin projection, i.e., $\epsilon_{v_1}=\epsilon_{v_2}=\epsilon_v$, $\epsilon_{h_1}=\epsilon_{h_2}=\epsilon_h$. The interelectronic-interaction matrix element $I_{ijkl}(\omega)$ is shorthand notation for

$$I_{ijkl}(\omega)=\int d^3\mathbf{x}d^3\mathbf{y}\psi_i^\dagger(\mathbf{x})\psi_j^\dagger(\mathbf{y})I(\mathbf{x}-\mathbf{y};\omega)\psi_k(\mathbf{x})\psi_l(\mathbf{y})\tag{28}$$

and satisfies the transposition symmetry property $I_{ijkl}(\omega)=I_{jilk}(\omega)$. The interelectronic-interaction operator $I(\mathbf{x}-\mathbf{y};\omega)$ is defined as $I(\mathbf{x}-\mathbf{y};\omega)=e^2\alpha^\mu\alpha^\nu D_{\mu\nu}(\mathbf{x}-\mathbf{y};\omega)$, where $\alpha^\mu=(1,\boldsymbol{\alpha})$, $D_{\mu\nu}(\mathbf{x}-\mathbf{y};\omega)$ is the photon propagator, and ω is the photon's energy. Since the integration over energy E is the next step, the singularities in $E-E_{vh}^{(0)}$ should be analyzed. Notice that

$$\frac{1}{\big[p_1^0-\epsilon_v+i\varepsilon\big]^2}\frac{1}{p_1^0-E-\epsilon_h-i\varepsilon}=\frac{1}{\big(E-E_{vh}^{(0)}\big)^2}\left[\frac{1}{p_1^0-E-\epsilon_h-i\varepsilon}-\frac{1}{p_1^0-\epsilon_v+i\varepsilon}\right]-\frac{1}{E-E_{vh}^{(0)}}\frac{1}{\big[p_1^0-\epsilon_v+i\varepsilon\big]^2}.\tag{29}$$

Only the most singular part is retained. It leads to

$$\begin{aligned}\Delta E_{vh}^{(1)\mathrm{SE}v} &= -\frac{1}{2\pi i}F_{v_1h_1}F_{v_2h_2}\oint_{\Gamma_{vh}}dE\big(E-E_{vh}^{(0)}\big)\Delta g^{(1)\mathrm{SE}v}_{\alpha,v_1h_2v_2h_1}(E)\\ &=\frac{i}{2\pi}F_{v_1h_1}F_{v_2h_2}\int d\omega\sum_j\frac{I_{v_1jjv_2}(\omega)\delta_{h_1h_2}}{\epsilon_v-\omega-\epsilon_j+i\varepsilon\big(\epsilon_j-E_\alpha^F\big)}\equiv F_{v_1h_1}F_{v_2h_2}\delta_{h_1h_2}\langle v_1|\,\Sigma_\alpha(\epsilon_v)\,|v_2\rangle\,,\end{aligned}\tag{30}$$

where Σ_α stands for the SE operator in the redefined vacuum framework and the identity

$$\delta(x)=\frac{i}{2\pi}\left(\frac{1}{x+i\varepsilon}+\frac{1}{-x+i\varepsilon}\right)\tag{31}$$

was utilized. Since the investigated graph is the SE matrix element for a single valence electron, there is no need to distinguish between the initial state v_1 and the final state v_2 because the SE operator preserves the spin projection, which was the sole

difference between them. Hence, we can write $\delta_{v_1v_2}$, and the previous prefactor is then $F_{v_1h_1}F_{v_2h_2}\delta_{v_1v_2}\delta_{h_1h_2} = 1$ [47]. The same calculation is performed for the SE graph located on the hole line, and the electron line is integrated out this time:

$$\Delta g^{(1)\mathrm{SE}h}_{\alpha,v_1h_2v_2h_1}(E) = \left(\frac{i}{2\pi}\right)^2 \int dp_2^0 d\omega \sum_j \frac{I_{h_2jjh_1}(\omega)}{p_2^0 - \omega - \epsilon_j + i\varepsilon\left(\epsilon_j - E_\alpha^F\right)} \frac{1}{\left[p_2^0 - \epsilon_h - i\varepsilon\right]^2} \frac{\delta_{v_1v_2}}{E + p_2^0 - \epsilon_v + i\varepsilon}. \tag{32}$$

As before, we isolate the most singular part,

$$\frac{1}{\left[p_2^0 - \epsilon_h - i\varepsilon\right]^2} \frac{1}{E + p_2^0 - \epsilon_v + i\varepsilon} = \frac{1}{E - E_{vh}^{(0)}} \frac{1}{\left[p_2^0 - \epsilon_h - i\varepsilon\right]^2} - \frac{1}{\left(E - E_{vh}^{(0)}\right)^2}\left[\frac{1}{p_2^0 - \epsilon_h - i\varepsilon} - \frac{1}{E + p_2^0 - \epsilon_v + i\varepsilon}\right]. \tag{33}$$

Thus, we get

$$\begin{aligned}\Delta E_{vh}^{(1)\mathrm{SE}h} &= -\frac{1}{2\pi i} F_{v_1h_1}F_{v_2h_2} \oint_{\Gamma_{vh}} dE\left(E - E_{vh}^{(0)}\right)\Delta g^{(1)\mathrm{SE}h}_{\alpha,v_1h_2v_2h_1}(E) \\ &= -\frac{i}{2\pi} F_{v_1h_1}F_{v_2h_2} \int d\omega \sum_j \frac{I_{h_2jjh_1}(\omega)\delta_{v_1v_2}}{\epsilon_h - \omega - \epsilon_j + i\varepsilon\left(\epsilon_j - E_\alpha^F\right)} \equiv -F_{v_1h_1}F_{v_2h_2}\delta_{v_1v_2}\left\langle h_2\right|\Sigma_\alpha(\epsilon_h)\left|h_1\right\rangle. \end{aligned} \tag{34}$$

As before, the SE contribution to a single-hole state is considered; thus, $\delta_{h_1h_2}$ and the prefactor reduces to 1. The one-particle result is recovered in both cases. Such calculations can be extended to the VP graph under the modification $\langle v_1|\,\Sigma_\alpha(\epsilon_v)\,|v_2\rangle$ to

$$\begin{aligned}\left\langle v_1\right|\Upsilon_\alpha\left|v_2\right\rangle &= -\frac{ie^2}{2\pi}\int d^3\mathbf{x}d^3\mathbf{y}\psi^\dagger_{v_1}(\mathbf{y})\alpha^\mu D_{\mu\nu}(0,\mathbf{y}-\mathbf{x})\int d\omega \mathrm{Tr}\left[\sum_j \frac{\psi_j(\mathbf{x})\psi_j^\dagger(\mathbf{x})}{\omega - \epsilon_j + i\varepsilon\left(\epsilon_j - E_\alpha^F\right)}\alpha^\nu\right]\psi_{v_2}(\mathbf{y}) \\ &\equiv -\frac{i}{2\pi}\int d\omega \sum_j \frac{I_{v_1jv_2j}(0)}{\omega - \epsilon_j + i\varepsilon\left(\epsilon_j - E_\alpha^F\right)}, \end{aligned} \tag{35}$$

and accordingly for the hole case: $\langle h_2|\,\Sigma_\alpha(\epsilon_h)\,|h_1\rangle$ to $\langle h_2|\,\Upsilon_\alpha\,|h_1\rangle$. Hence, the one-particle graph contributions in the redefined vacuum framework are given by

$$\begin{aligned}\Delta E_{vh}^{(1)1} &= F_{v_1h_1}F_{v_2h_2}\delta_{v_1v_2}\delta_{h_1h_2}[\langle v_1|\,\Sigma_\alpha(\epsilon_v)\,|v_2\rangle + \langle v_1|\,\Upsilon_\alpha\,|v_2\rangle - U_{v_1v_2} - \langle h_2|\,\Sigma_\alpha(\epsilon_h)\,|h_1\rangle - \langle h_2|\,\Upsilon_\alpha\,|h_1\rangle + U_{h_2h_1}] \\ &= \langle v|\,\Sigma_\alpha(\epsilon_v)\,|v\rangle + \langle v|\,\Upsilon_\alpha\,|v\rangle - U_{vv} - \langle h|\,\Sigma_\alpha(\epsilon_h)\,|h\rangle - \langle h|\,\Upsilon_\alpha\,|h\rangle + U_{hh}. \end{aligned} \tag{36}$$

Two counterpotential terms $U_{ij} = \langle i|\,U\,|j\rangle$ are added to the formula above to accommodate for the extended Furry picture. Their treatment is straightforward and does not need to be given in detail.

B. Two-particle contributions

The only two-particle correction found at this order is the valence-hole one-photon exchange, with the exchange part $\Delta E_{vh}^{(1)2\mathrm{exc}}$ minus the direct part $\Delta E_{vh}^{(1)2\mathrm{dir}}$ according to Eq. (24):

$$\Delta E_{vh}^{(1)2\mathrm{exc}} = \frac{1}{2\pi i} F_{v_1h_1}F_{v_2h_2} \oint_{\Gamma_{vh}} dE(E - E_{vh}^{(0)})\Delta g^{(1)2\mathrm{exc}}_{\alpha,v_1h_2h_1v_2}(E), \tag{37}$$

$$\Delta E_{vh}^{(1)2\mathrm{dir}} = -\frac{1}{2\pi i} F_{v_1h_1}F_{v_2h_2} \oint_{\Gamma_{vh}} dE(E - E_{vh}^{(0)})\Delta g^{(1)2\mathrm{dir}}_{\alpha,v_1h_2v_2h_1}(E). \tag{38}$$

Let us tackle first the direct graph, keeping in mind that the hole's energies are flowing backward in time. Similar to previous calculations, trivial steps are already performed, and the expression is given by

$$\begin{aligned}\Delta g^{(1)\mathrm{dir}}_{\alpha,v_1h_2v_2h_1}(E)\delta(E - E') &= e^2\left(\frac{i}{2\pi}\right)^2 \int d^3\mathbf{x}d^3\mathbf{y}dp_1^0dp_1'^0dp_2^0dp_2'^0d\omega\delta\left(E - p_1^0 + p_2^0\right)\delta\left(E' - p_1'^0 + p_2'^0\right)\delta\left(p_1^0 - \omega - p_1'^0\right) \\ &\quad\times \delta\left(p_2'^0 + \omega - p_2^0\right)\frac{\bar\psi_{v_1}(\mathbf{x})}{p_1'^0 - \epsilon_v + i\varepsilon}\frac{\bar\psi_{h_2}(\mathbf{y})}{p_2'^0 - \epsilon_h - i\varepsilon}\gamma^\mu\gamma^\nu D_{\mu\nu}(\omega,\mathbf{x}-\mathbf{y})\frac{\psi_{v_2}(\mathbf{x})}{p_1^0 - \epsilon_v + i\varepsilon}\frac{\psi_{h_1}(\mathbf{y})}{p_2^0 - \epsilon_h - i\varepsilon} \\ &= \left(\frac{i}{2\pi}\right)^2 \int dp_2^0dp_2'^0 \frac{I_{v_1h_2v_2h_1}\left(p_2^0 - p_2'^0\right)}{E + p_2'^0 - \epsilon_v + i\varepsilon}\frac{1}{p_2'^0 - \epsilon_h - i\varepsilon}\frac{\delta(E - E')}{E + p_2^0 - \epsilon_v + i\varepsilon}\frac{1}{p_2^0 - \epsilon_h - i\varepsilon}. \end{aligned} \tag{39}$$

Rewriting the denominators to pull out the singular part as

$$\begin{aligned}\frac{1}{E + p_2'^0 - \epsilon_v + i\varepsilon}\frac{1}{p_2'^0 - \epsilon_h - i\varepsilon} &= \frac{1}{E - E_{vh}^{(0)}}\left(\frac{1}{p_2'^0 - \epsilon_h - i\varepsilon} - \frac{1}{E + p_2'^0 - \epsilon_v + i\varepsilon}\right), \\ \frac{1}{E + p_2^0 - \epsilon_v + i\varepsilon}\frac{1}{p_2^0 - \epsilon_h - i\varepsilon} &= \frac{1}{E - E_{vh}^{(0)}}\left(\frac{1}{p_2^0 - \epsilon_h - i\varepsilon} - \frac{1}{E + p_2^0 - \epsilon_v + i\varepsilon}\right), \end{aligned} \tag{40}$$

we get

$$\Delta E^{(1)2\mathrm{dir}}_{vh} = -F_{v_1h_1}F_{v_2h_2}I_{v_1h_2v_2h_1}(0). \tag{41}$$

Last, but not least, is the exchange graph. The partially simplified expression is found to be

$$\begin{aligned}\Delta g^{(1)2\mathrm{exc}}_{\alpha,v_1h_2h_1v_2}(E)\delta(E-E') &= e^2\Big(\frac{i}{2\pi}\Big)^2\int d^3\mathbf{x}d^3\mathbf{y}dp_1^0dp_1'^0dp_2^0dp_2'^0d\omega\delta\big(E-p_1^0+p_2^0\big)\delta\big(E'-p_1'^0+p_2'^0\big)\delta\big(p_2^0-\omega-p_1'^0\big)\\ &\times\delta\big(p_2'^0+\omega-p_1^0\big)\frac{\bar\psi_{v_1}(\mathbf{x})}{p_1'^0-\epsilon_v+i\varepsilon}\frac{\bar\psi_{h_2}(\mathbf{y})}{p_2'^0-\epsilon_h-i\varepsilon}\gamma^\mu\gamma^\nu D_{\mu\nu}(\omega,\mathbf{x}-\mathbf{y})\frac{\psi_{h_1}(\mathbf{x})}{p_2^0-\epsilon_h-i\varepsilon}\frac{\psi_{v_2}(\mathbf{y})}{p_1^0-\epsilon_v+i\varepsilon}\\ &=\Big(\frac{i}{2\pi}\Big)^2\int dp_1^0dp_2'^0\frac{I_{v_1h_2h_1v_2}\big(p_2'^0-p_1^0\big)}{E+p_2'^0-\epsilon_v+i\varepsilon}\frac{1}{p_2'^0-\epsilon_h-i\varepsilon}\frac{\delta(E-E')}{p_1^0-E-\epsilon_h-i\varepsilon}\frac{1}{p_1^0-\epsilon_v+i\varepsilon}.\end{aligned} \tag{42}$$

As before, the singular part of the denominators is separated. Hence, the energy integration gives

$$\Delta E^{(1)2\mathrm{exc}}_{vh} = F_{v_1h_1}F_{v_2h_2}I_{v_1h_2h_1v_2}(\Delta_{hv}), \tag{43}$$

where we introduced $\Delta_{hv}=\epsilon_h-\epsilon_v$, and the total two-particle contribution is

$$\Delta E^{(1)2}_{vh} = F_{v_1h_1}F_{v_2h_2}[I_{v_1h_2h_1v_2}(\Delta_{hv})-I_{v_1h_2v_2h_1}(0)]. \tag{44}$$

C. Usual vacuum description

So far the formulas for the first-order corrections obtained in the previous sections,

$$\Delta E^{(1)}_{vh} = F_{v_1h_1}F_{v_2h_2}[I_{v_1h_2h_1v_2}(\Delta_{hv})-I_{v_1h_2v_2h_1}(0)]+\langle v|\,\Sigma_\alpha(\epsilon_v)\,|v\rangle+\langle v|\,\Upsilon_\alpha\,|v\rangle-U_{vv}-\langle h|\,\Sigma_\alpha(\epsilon_h)\,|h\rangle-\langle h|\,\Upsilon_\alpha\,|h\rangle+U_{hh}, \tag{45}$$

have been written for the case when the redefined vacuum state is employed in the electron propagator [see Eq. (5)]. We also use the subscript α in the Σ_α and Υ_α operators to emphasize this fact. In Eq. (45) the first term in square brackets corresponds to the interelectronic interaction between valence and hole particles taken with a minus sign; the next two blocks of three terms are the one-electron corrections (self-energy, vacuum polarization, and counterterm) for the valence and hole particles, respectively. It is clear that excitation of an electron from state h to v leads to the subtraction of one-electron hole energy and the addition of one-electron valence energy [see Eq. (20)]. As we can see, the interelectronic interaction between the valence (hole) particle and core electrons is not explicitly recognizable in Eq. (45). In fact, the SE and VP terms with the redefined vacuum propagator also contain the interelectronic interaction with the core electrons. As an example we show how the redefined vacuum expressions are linked to the usual ones for the valence SE and VP contributions. We have the following relationship [36]:

$$\begin{aligned}\langle v|\,\Sigma_\alpha(\epsilon_v)\,|v\rangle &= \langle v|\,\Sigma(\epsilon_v)\,|v\rangle-\sum_a I_{vaav}(\Delta_{va}),\\ \langle v|\,\Upsilon_\alpha\,|v\rangle &= \langle v|\,\Upsilon\,|v\rangle+\sum_a I_{vava}(0),\end{aligned} \tag{46}$$

where the Σ and Υ operators differ from the corresponding operators with the subscript α just by setting in Eqs. (30) and (35) $E^F_\alpha=0$. In other words, to extract the interelectronic interactions arising from the one-particle graphs in the redefined vacuum equation (36), we have to subtract the identical graph in the standard vacuum, as inferred from the above equations. Obviously, the two-particle contribution (44) is not affected by such manipulations. The resulting first-order energy correction in the usual vacuum can be written as

$$\begin{aligned}\Delta E^{(1)}_{vh} &= \sum_a[I_{vava}(0)-I_{vaav}(\Delta_{va})]-\sum_a[I_{haha}(0)-I_{haah}(\Delta_{ha})]\\ &+F_{v_1h_1}F_{v_2h_2}[I_{v_1h_2h_1v_2}(\Delta_{hv})-I_{v_1h_2v_2h_1}(0)]+\langle v|\,\Sigma(\epsilon_v)\,|v\rangle+\langle v|\,\Upsilon\,|v\rangle-U_{vv}\\ &-\langle h|\,\Sigma(\epsilon_h)\,|h\rangle-\langle h|\,\Upsilon\,|h\rangle+U_{hh}.\end{aligned} \tag{47}$$

Now, the interaction between valence and hole particles with core electrons appears in the first line of Eq. (47), respectively. Furthermore, the interelectronic interaction obtained [the three terms involving square brackets in Eq. (47)] is in perfect agreement, when the Breit approximation is applied in the Coulomb gauge, with the one found in Ref. [48], where MBPT corrections to the valence-hole state up to second order were derived. The other contributions (the second part of line two and line three) found are the SE and VP corrections to each particle, as expected.

Last, but not least, employing a vacuum redefinition allows us to identify gauge-invariant subsets in the usual vacuum. Following the logic and proofs presented in Ref. [36], the contributions involving square brackets in Eq. (47) are independently gauge invariant. Moreover, each term in the second part of line two and line three is also separately gauge invariant.

V. DISCUSSION AND CONCLUSION

The formalism and expressions presented in this work are ready to be applied to a closed-shell atom or ion, such as Be- and Ne-like ions. Be-like ions having the smallest number of electrons were already treated within the complete BSQED description. In particular, the ground-state and ionization energies were evaluated in Refs. [49,50], respectively, while the transition energies between low-lying levels were just recently addressed in Ref. [24]. In the last case [24], the formal expressions were derived with the TTGF method employing the redefined vacuum prescription, where the $1s^2$ shell was considered to belong to the vacuum and the other two electrons were treated as the valence electrons. For Ne-like ions such decomposition is rather complicated since one has to consider eight electrons to be the valence ones.

The energy levels in Ne-like ions have been investigated for a long time using the MBPT approach [47,48,51,52]. The discrepancies between theory and experiment for different transitions and ions, in absolute value, were less than 2 eV in the earliest work, which shrunk down to less than 1 eV in a more recent one [53]. In the case of Ne-like Ge a recent study [54] report remarkable agreement up to 10^{-4} relative uncertainty between MBPT calculations and measured values. The QED effects have been incorporated at the first order via the model Lamb-shift-operator approach [55,56], and the interelectronic interaction has been captured with the Breit interaction treated in the vanishing frequency limit. Results have been compared with previous computations performed by Safronova *et al.* [53] for Ne-like Mo and showed a difference of less than 0.25 eV, in absolute value, except in one case. Another recent measurement campaign on Ne-like Eu [57] showed agreement, in absolute value, of the order of 1 eV between MBPT predictions and experimental values. Overall, these results show that MBPT treatment reliably captures the essence of the energy difference in Ne-like ions. Nevertheless, a rigorous BSQED treatment of valence-hole excitation in a closed-shell system has been lacking so far. BSQED contributions could fill the energy gap by rigorously including all first-order corrections in α. It could help to achieve outstanding agreement among theory and experiment, which could be especially interesting in view of possible applications as optical atomic clocks with valence-hole transitions in B^+, Al^+, In^+, and Tl^+ ions [58]. An additional application might be seen in searching for an explanation for the disagreement in the oscillator-strength ratio in Ne-like Fe [59,60].

To conclude, in the present paper we derived the two-time Green's function suited for a valence-hole excitation in a closed-shell system within the rigorous BSQED framework. The derivation was carried out in the redefined vacuum framework, which allow us to focus only on the particles which make a difference between the configurations. The complete first-order corrections were considered, the explicit formulas were derived, and the gauge-invariant subsets were identified. Our results can readily be applied for rigorous BSQED calculations of the transition energies in a closed-shell system.

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APPENDIX: ZEROTH-ORDER GREEN'S FUNCTION

Here, the zeroth-order Green's function in Eq. (22) is calculated explicitly. The reason for the previously added terms and the role of prefactors will become clearer. Let us start by expressing the matrix element of the zeroth-order Green's function as

$$\langle (vh)_{JM}|\, g_\alpha^{(0)}(E)\,|(vh)_{JM}\rangle = F_{vh}F_{vh}\,\langle\alpha|\, b_h a_v\left[\frac{1}{2!}\int d^3\mathbf{x}_1 d^3\mathbf{x}_2 d^3\mathbf{y}_1 d^3\mathbf{y}_2 \mathcal{S}(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\right] a_v^\dagger b_h^\dagger\,|\alpha\rangle\,, \tag{A1}$$

where

$$\begin{aligned}\mathcal{S}(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2) = &\sum_{i,l>E_\alpha^F,j,k<E_\alpha^F} a_i^\dagger a_l b_k^\dagger b_j\left[\phi_i^\dagger(\mathbf{x}_1)\phi_j^\dagger(\mathbf{x}_2)\mathcal{G}_\alpha^{(0)}(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\gamma_1^0\gamma_2^0\phi_k(\mathbf{y}_1)\phi_l(\mathbf{y}_2)\right]\\ &+\sum_{j,k>E_\alpha^F,i,l<E_\alpha^F} a_j^\dagger a_k b_l^\dagger b_i\left[\phi_i^\dagger(\mathbf{x}_1)\phi_j^\dagger(\mathbf{x}_2)\mathcal{G}_\alpha^{(0)}(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\gamma_1^0\gamma_2^0\phi_k(\mathbf{y}_1)\phi_l(\mathbf{y}_2)\right]\\ &-\sum_{i,k>E_\alpha^F,j,l<E_\alpha^F} a_i^\dagger a_k b_l^\dagger b_j\left[\phi_i^\dagger(\mathbf{x}_1)\phi_j^\dagger(\mathbf{x}_2)\mathcal{G}_\alpha^{(0)}(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\gamma_1^0\gamma_2^0\phi_k(\mathbf{y}_1)\phi_l(\mathbf{y}_2)\right]\\ &-\sum_{j,l>E_\alpha^F,i,k<E_\alpha^F} a_j^\dagger a_l b_k^\dagger b_i\left[\phi_i^\dagger(\mathbf{x}_1)\phi_j^\dagger(\mathbf{x}_2)\mathcal{G}_\alpha^{(0)}(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)\gamma_1^0\gamma_2^0\phi_k(\mathbf{y}_1)\phi_l(\mathbf{y}_2)\right].\end{aligned} \tag{A2}$$

The zeroth-order spectral representation of the Green's function is given by

$$\mathcal{G}_\alpha^{(0)}(E;\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2) = \frac{1}{2!}\frac{\mathcal{A}_{vh}^{(0)}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)}{E-E_{vh}^{(0)}+i\varepsilon} + \text{regular terms at } E\sim E_{vh}^{(0)}, \tag{A3}$$

with

$$\begin{aligned}\mathcal{A}^{(0)}_{vh}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2) = \langle\alpha|\big[&\psi^{(0)}_\alpha(0,\mathbf{x}_1)\bar{\psi}^{(0)}_\alpha(0,\mathbf{y}_1)\,|(vh)_{JM}\rangle\,\langle(vh)_{JM}|\,\psi^{(0)}_\alpha(0,\mathbf{x}_2)\bar{\psi}^{(0)}_\alpha(0,\mathbf{y}_2)\\ &-\psi^{(0)}_\alpha(0,\mathbf{x}_2)\bar{\psi}^{(0)}_\alpha(0,\mathbf{y}_1)\,|(vh)_{JM}\rangle\,\langle(vh)_{JM}|\,\psi^{(0)}_\alpha(0,\mathbf{x}_1)\bar{\psi}^{(0)}_\alpha(0,\mathbf{y}_2)\\ &-\psi^{(0)}_\alpha(0,\mathbf{x}_1)\bar{\psi}^{(0)}_\alpha(0,\mathbf{y}_2)\,|(vh)_{JM}\rangle\,\langle(vh)_{JM}|\,\psi^{(0)}_\alpha(0,\mathbf{x}_2)\bar{\psi}^{(0)}_\alpha(0,\mathbf{y}_1)\\ &+\psi^{(0)}_\alpha(0,\mathbf{x}_2)\bar{\psi}^{(0)}_\alpha(0,\mathbf{y}_2)\,|(vh)_{JM}\rangle\,\langle(vh)_{JM}|\,\psi^{(0)}_\alpha(0,\mathbf{x}_1)\bar{\psi}^{(0)}_\alpha(0,\mathbf{y}_1)\big]\,|\alpha\rangle\,. \end{aligned} \tag{A4}$$

As a first step the previous expression, $\mathcal{A}^{(0)}_{vh}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2)$, can be further evaluated. Recalling that $a_i\,|\alpha\rangle = 0$, $b_j\,|\alpha\rangle = 0$, $\bar{\psi} = \psi^\dagger\gamma^0$, and $F_{vh}F_{vh} = 1$, we easily get

$$\mathcal{A}^{(0)}_{vh}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{y}_1,\mathbf{y}_2) = [\phi_v(\mathbf{x}_1)\phi_h(\mathbf{x}_2) - \phi_h(\mathbf{x}_1)\phi_v(\mathbf{x}_2)][\bar{\phi}_h(\mathbf{y}_1)\bar{\phi}_v(\mathbf{y}_2) - \bar{\phi}_v(\mathbf{y}_1)\bar{\phi}_h(\mathbf{y}_2)]. \tag{A5}$$

Two comments should be made at this point. If one were to consider Eq. (9), only the first term from the above expanded expression would be found. Furthermore, in Eq. (15), a $\frac{1}{2!}$ was introduced. The reason is to get a proper normalized two-body wave function in the noninteracting case, as will be seen in the following. Using Eq. (17), we contract the operators to obtain

$$\langle(vh)_{JM}|\,g^{(0)}_\alpha(E)\,|(vh)_{JM}\rangle = \tfrac{1}{2!}\big[g^{(0)}_{\alpha,v_1h_2h_1v_2}(E) - g^{(0)}_{\alpha,v_1h_2v_2h_1}(E) + g^{(0)}_{\alpha,h_2v_1v_2h_1}(E) - g^{(0)}_{\alpha,h_2v_1h_1v_2}(E)\big], \tag{A6}$$

which can be rewritten according to Eq. (18) as

$$\begin{aligned}\langle(vh)_{JM}|\,g^{(0)}_\alpha(E)\,|(vh)_{JM}\rangle &= \frac{1}{E - E^{(0)}_{vh} + i\varepsilon}\\ &\times\int d^3\mathbf{x}_1 d^3\mathbf{x}_2\frac{1}{2!}[\phi^\dagger_v(\mathbf{x}_1)\phi^\dagger_h(\mathbf{x}_2) - \phi^\dagger_h(\mathbf{x}_1)\phi^\dagger_v(\mathbf{x}_2)][\phi_v(\mathbf{x}_1)\phi_h(\mathbf{x}_2) - \phi_h(\mathbf{x}_1)\phi_v(\mathbf{x}_2)]\\ &\times\int d^3\mathbf{y}_1 d^3\mathbf{y}_2\frac{1}{2!}[\phi^\dagger_h(\mathbf{y}_1)\phi^\dagger_v(\mathbf{y}_2) - \phi^\dagger_v(\mathbf{y}_1)\phi^\dagger_h(\mathbf{y}_2)][\phi_h(\mathbf{y}_1)\phi_v(\mathbf{y}_2) - \phi_v(\mathbf{y}_1)\phi_h(\mathbf{y}_2)]\\ &= \frac{1}{E - E^0_{vh} + i\varepsilon}. \end{aligned} \tag{A7}$$

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