Relativistic formalism of nonadiabatic electron-nucleus-radiation dynamics in molecules: Path-integral approach

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Many-electron relativistic quantum theories of stationary molecular electronic states have been developed in so-called quantum chemistry, in which nuclear configuration is frozen in space-time under the Born-Oppenheimer approximation. These time-independent methods are concerned with energetics, which are supposed to determine molecular structures and dominate low-energy chemical reactions. Yet, rapid progress in laser technology demands that theoretical chemistry should get prepared for relativistic electron-nucleus coupled dynamics driven by unconventional ultrastrong laser pulses. We therefore generalize our previously developed path-integral formalism of nonadiabatic electron dynamics [Hanasaki and Takatsuka, Phys. Rev. A **81**, 052514 (2010)] to cover the relativistic regime in radiation fields. Starting from a formal relativistic path-integral formulation of electron-nucleus coupled systems interacting with quantum radiation fields, we reduce it to a tractable level of approximations to set a theoretical foundation for future applications.

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I. INTRODUCTION

The Born-Oppenheimer (BO) approximation, having emerged from the large discrepancy between the timescales of the dynamics of electrons and nuclei in molecules, effectively separates the molecular quantum mechanics into two subfields, one mainly treating energetics given by the stationary electronic states at each frozen nuclear configuration and the other for dynamics, which is represented by nuclear wave packets running on thus derived electronic energy hypersurfaces. Within the BO approximation, systematic *ab initio* calculation methods for many-electron stationary states have been developed [1] and have contributed to great successes in understanding static properties of molecules and also in explaining a large number of chemical reactions in which most of the electronic states under study adiabatically stay in the lowest energy level.

On the other hand, the breakdown of the BO approximation in the so-called nonadiabatic reactions has also long been known [2–4]. Such breakdown has become critically important with the advent of femtosecond laser techniques [5], which enabled direct observation and control over dynamical electronic state transitions with a timescale of typical nuclear vibrational motion. The notion of ultrafast electron wave packets undergoing kinematic interactions with moving nuclei is a key to studying those dynamical processes [6–9]. Further progress in laser technology has offered even more powerful tools including free-electron laser sources [10] that generate ultraintense laser pulses of variable wavelengths including x rays [11,12] and attosecond techniques [13,14] that enable direct observation of electron dynamics, including those in relativistic regime.

Electrons accelerated close to the speed of light exhibit relativistic effects [15–17]. In molecular science, relativistic electrons have long been studied in heavy atoms [18–21] and their static properties have been subjects of intensive research. Radiation corrections arising from those electrons have been extensively studied using field-theoretical approaches and have achieved accurate reproduction of experimental observations [20,22]. The roles of those states on the static chemical properties of many-electron atoms and molecules [21] have been studied by chemists using quantum chemical *ab initio* calculations, which include detailed analysis of the relativistic orbitals [23,24] and clarification of characteristic bonding properties of those materials [21,25,26].

Dynamics of those electrons, on the other hand, has not yet been fully investigated, partly because those inner-shell electrons hardly take part in dynamics of typical energy scales in conventional atomic and molecular experiments. However, the advent of intense ultrafast x-ray laser sources [10,12] and development of core-excitation spectroscopic techniques [27] have been removing such limitations. Core electrons as deep as several keV can now be controlled with femtosecond time resolution [12,28]. Indeed, a number of pioneering studies including heavy elements [28–30] lead us to believe that core-hole dynamics with significant relativistic effects can be observed in the near future. Another type of dynamically controlled relativistic electrons is realized in ultraintense infrared optical fields by directly accelerating electrons close to the speed of light [31,32], though the latter type of field-induced dynamics, which requires nonperturbative treatment of strong external optical fields, is not a subject of this paper, but has been discussed in our recent publication [33].

Relativistic dynamics of interacting electrons is described by the quantum electrodynamics (QED), which was

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established in the first half of the twentieth century by a number of researchers including Tomonaga [34], Schwinger [35], and Feynman [36,37]. The framework, including the covariant perturbation theory and renormalization as its core components, was soon applied to bound systems in the pioneering works by Bethe and Salpeter [38] and Gell-Mann and Low [39]. The bound-state QED was then applied to the calculation of static properties of atoms [18–20], including the radiative energy corrections of heavy-element ions as a typical example, and realized accurate reproduction of experimental observations. Study of atomic properties has further been developed and is reviewed in Refs. [18–20,40–42]. More recent progress in these studies include efficient calculation techniques applicable to non-Coulombic potential [43], Coulomb gauge formulation [44–46], and inclusion of many-body perturbation theory (MBPT) techniques [47,48], which should realize more accurate calculation of many-electron systems.

Apart from these works, a number of low-energy effective theories have been invented including the theory of Breit [49] and Pauli [50], which provides low-energy expansions of the Dirac Hamiltonian [51]. These theories provide useful tools for inclusion of relativistic corrections into the nonrelativistic Hamiltonian framework. However, we do not proceed in this direction since the validity of these effective theories is often limited to low-energy physics and their applicability to dynamical processes is not clear.

A more systematic *ab initio* numerical calculation of relativistic electronic states has also been developed by a number of quantum chemists [17,52]. Advantages in their approach include applicability to arbitrary molecular systems, taking account of electron correlation effects and ability to construct relativistic wave functions. Practical calculations of chemical properties of large molecules are often best achieved by two-component theories including the Douglass-Kroll theory [53,54] and the exact two-component (X2C) approaches [55–57] because of the smaller computational cost than that of its four-component counterpart. In this paper, however, we concentrate on the original four-component representation. Such four-component wave functions can then be constructed by a variational approach [58], by relativistic density-functional theory [59,60], or even by exactly solving the Dirac equation [61]. Multiconfiguration calculation procedures to include correlation effects beyond the self-consistent field (SCF) level include the relativistic multiconfigurational self-consistent field [62] and the relativistic configuration interaction [63,64]. On the other hand, those quantum chemical approaches usually rest on the Hamiltonian formalism and the equal-time (i.e., all N_e electrons lies on the same spacelike surface) wave functions. Although such formulation is essential for enabling direct extension of nonrelativistic quantum chemistry, retardation effects, and/or dynamical coupling to the radiation field are usually missing. Here, we note the recent works [65–67] that explore systematic reformulation of relativistic quantum chemistry with direct correspondence to the QED formulation. They succeed in including one-loop QED effects, including the vacuum polarization effects and the electronic self-energy, into the framework of quantum chemistry. At this point, however, it is not clear if such advanced formulation extends to dynamical problems. In this paper, we work on a formulation that explicitly takes account of the radiation field degrees of freedom, which is beyond the framework of quantum chemistry.

We start from the QED Lagrangian or the full Hamiltonian to formulate relativistic dynamics of molecular systems, which is then reduced to a more feasible form. In the latter step, we can take two independent tracks: a path integral approach and a wave-packet approach. These two bear their own distinguished advantages and applicability. We here discuss the path-integral approach, whereas the wave-packet approach has been discussed in our recent paper [33]. The molecular relativistic path integral, to be presented in this paper, is formulated by extending our formerly built nonrelativistic nonadiabatic path integral [68] into the relativistic domain. We use the standard perturbation expansion [15,16] to include electron-radiation couplings. Although such perturbative approach is close in idea to the most standard established approach in QED [15,16], it also limits its application range to perturbative dynamics such as dynamics induced by high-energy x-ray irradiation. We consider that nonperturbative dynamics is better formulated by the wave-packet approach, which has been discussed in our recent publication [33]. In the present molecular studies, nuclear dynamics is treated within the nonrelativistic approximation, taking account of their much heavier masses. Nevertheless, it must be formulated in such a manner that is consistent with relativistic electron-radiation coupled dynamics.

This paper is organized as follows. In Sec. II, we discuss a formal theory of relativistic dynamics of molecules. After formulating fundamental quantities and defining initial and final states, we decouple the nuclear degrees of freedom and construct perturbation expansion to derive a formal path-integral expression of dynamical observables of our interest. We then proceed to practical formulation in Sec. III, which is the main part of this paper. We construct an effective Hamiltonian and reformulate the formal path-integral expression derived in Sec. II to a feasible form in that matrix elements required in practical calculations are within the reach of existing techniques [41,42], which is briefly discussed in Sec. IV. Section V is devoted to summary and discussion.

II. FORMAL THEORY OF ELECTRON-NUCLEUS-RADIATION COUPLED DYNAMICS

A. Fundamental quantities in relativistic dynamics

We first define fundamental quantities required in our discussion. In this paper, we use the sign convention $(1,-1,-1,-1)$, and the metric tensor $\eta^{\mu\nu}$ is a diagonal tensor with $\eta_{00}=1$, $\eta_{11}=\eta_{22}=\eta_{33}=-1$. Symbol q_e represents the electronic charge, which takes a negative value: $q_e=-|e|$. We use the Gauss unit for the electromagnetic field and the fine-structure constant is $e^2/\hbar c\approx 1/137$. Unless specified otherwise, we consider a molecular system with $N_{\rm nuc}$ nucleus and N_e electrons allowing for additional virtual electron-positron pairs arising from the electron-radiation coupling. The nuclear coordinates are denoted by $3N_{\rm nuc}$-dimensional vector $\mathbf{R}$ which collects $N_{\rm nuc}$ three-dimensional vectors $\mathbf{R}\doteq(\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_{N_{\rm nuc}})$. We assume the ath nucleus as a nonrelativistic pointlike particle with mass M_a and charge

Q_a at spatial coordinate $\mathbf{R}_a$. Other notations, which follow the standard convention in QED [16], are described explicitly in the main text.

We first introduce an abstract expression of dynamical observables, which represents the target quantity in dynamical calculations. We consider a transition matrix element of a set of arbitrary observables $\mathcal{O}_A, \mathcal{O}_B, \ldots$ at given space-time points $X_A, X_B, \ldots$, along the time evolution of the system from an electron-nucleus coupled state $|\Omega_i : \mathbf{R}_i\rangle$ at time t_i to $|\Omega_f : \mathbf{R}_f\rangle$ at time t_f to define

$$\mathcal{M}_{fi}(X_A, X_B, \ldots; \mathbf{R}_f, \mathbf{R}_i) = \langle \Omega_f : \mathbf{R}_f | e^{-i\epsilon\mathcal{H}^{\rm tot}/\hbar} \ldots \mathcal{O}_A(X_A) \ldots e^{-i\epsilon\mathcal{H}^{\rm tot}/\hbar} | \Omega_i : \mathbf{R}_i \rangle, \tag{1}$$

where $\mathcal{H}^{\rm tot}$ is the total Hamiltonian in the Heisenberg picture. The Coulomb gauge path-integral expression of the quantity $\mathcal{M}_{fi}$ reads

$$\mathcal{M}_{fi} = \int \prod d\mathbf{R} \int \prod d\mathbf{A}^{tr} \int \prod d\psi^* \int \prod d\psi \times \mathcal{O}(X_A) \ldots \delta(\nabla \cdot \mathbf{A}^{tr}) \langle \Omega_f | \xi_f \rangle \langle \xi_i | \Omega_i \rangle e^{\frac{i}{\hbar}S}, \tag{2}$$

where $\mathbf{R}$, $\mathbf{A}^{tr}$, and ψ represent the nuclear coordinate, transversal radiation field, and electronic field, respectively, whereas S represents the action as a functional of these fields. Symbols $|\xi_i\rangle$ and $|\xi_f\rangle$ represent the initial- and final-state vectors, respectively. The numerical factor $\langle \Omega_f | \xi_f \rangle \langle \xi_i | \Omega_i \rangle$ adds to an infinitesimal imaginary part to the action integral by which the field propagators have the correct boundary conditions [16]. The action integral S reads

$$S = \int dt L^{\rm nuc}(\mathbf{R}, \dot{\mathbf{R}}) + \int d^4x \left\{ \mathcal{L}_F^{\rm tr} + \mathcal{L}_{\rm el} + \mathcal{L}_{\rm Coul} + \mathcal{L}_{\rm int}^{\rm tr} \right\}, \tag{3}$$

with

$$L^{\rm nuc} = -\sum_a M_a c^2 \sqrt{1 - \dot{\mathbf{R}}_a{}^2/c^2} \approx \sum \frac{M_a \dot{\mathbf{R}}^2}{2} + \text{const.}, \tag{4a}$$

$$\mathcal{L}_{\rm rad}^{\rm tr} = \frac{1}{8\pi}\{(\dot{\mathbf{A}}^{\rm tr}/c)^2 - (\nabla \times \mathbf{A}^{\rm tr})^2\}, \tag{4b}$$

$$\mathcal{L}_{\rm el} = \psi^\dagger \left[i\hbar\partial_t - \left(c\boldsymbol{\alpha} \cdot \frac{\hbar}{i}\nabla + \beta m_e c^2 \right) \right] \psi, \tag{4c}$$

$$\mathcal{L}_{\rm Coul} = -\frac{1}{2} \int d^3\mathbf{y} \rho_{\rm mat}(\mathbf{x}, t) \frac{1}{|\mathbf{x} - \mathbf{y}|} \rho_{\rm mat}(\mathbf{y}, t), \tag{4d}$$

$$\mathcal{L}_{\rm int}^{\rm tr} = \mathbf{J}_{\rm mat} \cdot \mathbf{A}^{\rm tr}, \tag{4e}$$

where M_a and m_e indicate the nuclear and electron masses, respectively, and $\rho_{\rm mat}$ ($\mathbf{J}_{\rm mat}$) represents the matter field charge density (current) or the summation of the electronic and nuclear charge densities (currents). Symbols $\boldsymbol{\alpha}$ and β represent the Dirac matrices, and c is the speed of light. Symbol x represents the four-dimensional coordinate of the field operator, whose components are denoted by $x^\mu \doteq (x^0 = ct, \mathbf{x})$. Following the standard convention, those denoted by bold symbols, $\mathbf{x}, \mathbf{y}, \ldots$ represent the (three-dimensional) spatial part of coordinates.

For later convenience, we also write down an equivalent Hamiltonian,

$$\mathcal{H}^{\rm tot} = \sum_a \frac{1}{2M_a} \left\{ \mathbf{P}_a^2 + \left[\frac{Q_a}{c} \mathbf{A}(\mathbf{R}_a) \right]^2 \right\} + \int d^3\mathbf{x} \frac{1}{2} \left[4\pi c^2 \boldsymbol{\Pi}^{\rm tr 2} + \frac{1}{4\pi} (\nabla \times \mathbf{A})^2 \right] + \int d^3\mathbf{x} \psi^\dagger \left(c\boldsymbol{\alpha} \cdot \frac{\hbar}{i}\nabla + \beta m_e c^2 \right) \psi + \frac{1}{2} \int d^3\mathbf{x} \int d^3\mathbf{y} \rho_{\rm mat}(\mathbf{x}, t) \frac{1}{|\mathbf{x} - \mathbf{y}|} \rho_{\rm mat}(\mathbf{y}, t) - \frac{1}{c} \int d^3\mathbf{x} \mathbf{J}_{\rm mat} \cdot \mathbf{A}^{\rm tr}, \tag{5}$$

where $\boldsymbol{\Pi}^{\rm tr} = \dot{\mathbf{A}}^{\rm tr}/(4\pi c^2)$, negative of the transversal part of the electric field, is the canonical conjugate of $\mathbf{A}^{\rm tr}$. We then introduce an electronic mean-field potential $W_{\rm HF}(\mathbf{x}, \mathbf{y}, t)$ to rewrite the electronic Coulombic term as

$$\mathcal{L}_{\rm Coul}(\mathbf{x}, t) = -\psi^\dagger(\mathbf{x}, t) U_{\rm nuc}(\mathbf{x}) \psi(\mathbf{x}, t) - \int d^3\mathbf{y} \psi^\dagger(\mathbf{x}, t) \times W_{\rm HF}(\mathbf{x}, \mathbf{y}, t) \psi(\mathbf{y}, t) + \mathcal{L}_C', \tag{6}$$

where $U_{\rm nuc}$ represents the nuclear Coulombic potential acting on electrons

$$U_{\rm nuc}(\mathbf{x}) \equiv q_e \int d^3\mathbf{y} \frac{1}{|\mathbf{x} - \mathbf{y}|} \sum_a Q_a \mathfrak{f}_a(\mathbf{y}) \tag{7}$$

with $\mathfrak{f}_a(\mathbf{y})$ being the normalized charge distribution of the ath nucleus. An obvious choice of $\mathfrak{f}_a$ is a δ function $\mathfrak{f}_a(\mathbf{y}) = \delta^3(\mathbf{y} - \mathbf{R}_a)$ but we also allow the use of a finite-size distribution function taken from existing nuclear models [69]. Such nontrivial charge distribution is, however, only be used for convenience of electronic wave-function calculations. Otherwise, nuclei are treated as nonrelativistic point charges. The last term in Eq. (6), $\mathcal{L}_C'$, represents the difference between the Coulombic interaction and the mean-field potential defined as

$$\mathcal{L}_C'(\mathbf{x}, t) \equiv -\frac{1}{2} \int d^3\mathbf{y} \rho_{\rm el}(\mathbf{x}, t) \frac{1}{|\mathbf{x} - \mathbf{y}|} \rho_{\rm el}(\mathbf{y}, t) + \int d^3\mathbf{y} \psi^\dagger(\mathbf{x}, t) W_{\rm HF}(\mathbf{x}, \mathbf{y}) \psi(\mathbf{y}, t). \tag{8}$$

We then introduce a Fermionic eigenvalue equation

$$\left[c\boldsymbol{\alpha} \cdot \frac{\hbar}{i}\nabla + \beta m_e c^2 + U_{\rm nuc} \right] \varphi_\ell(\mathbf{x}, t) + \int d^3\mathbf{y} W_{\rm HF}(\mathbf{x}, \mathbf{y}, t) \varphi_\ell(\mathbf{y}, t) = \varepsilon_\ell \varphi_\ell(\mathbf{x}, t), \tag{9}$$

whose eigenfunctions are hereafter referred to as the molecular orbitals (MOs). Here we are interested in the state with a given configuration of N_e positive-energy MOs represented by an index set $\mathcal{I}_{\rm occ}$ (if we are interested in the ground state, for example, the lowest N_e are occupied and occupied orbitals are $\mathcal{I}_{\rm occ} = \{1, 2, \ldots, N_e\}$):

$$\overline{\rho}(\mathbf{x}, t) = \sum_{\ell \in \mathcal{I}_{\rm occ}} \varphi_\ell^\dagger(\mathbf{x}, t) \varphi_\ell(\mathbf{x}, t). \tag{10}$$

The mean-field potential $W_{\rm HF}$ is set in such a manner that makes later calculation easier. The most natural choice should be the Hartree-Fock potential

$$W_{\rm HF}(\mathbf{x},\mathbf{y})_{\mathfrak{ij}} = \delta^3(\mathbf{x}-\mathbf{y})\delta_{\mathfrak{ij}}\int d^3\mathbf{x}'\frac{q_e^2}{|\mathbf{x}-\mathbf{x}'|}\overline{\rho}(\mathbf{x}',t) - \sum_{\ell\in\mathcal{I}_{\rm occ}}\psi^\dagger_{\ell\mathfrak{j}}(\mathbf{y},t)\frac{q_e^2}{|\mathbf{x}-\mathbf{y}|}\psi_{\ell\mathfrak{i}}(\mathbf{x},t), \tag{11}$$

with $\mathfrak{i}$ and $\mathfrak{j}$ representing the spinor indices. However, the nonlocal nature of $W_{\rm HF}$ will later appear to be inconvenient in perturbation expansion, which is discussed in Sec. IV. We therefore replace the original $W_{\rm HF}$ by its local approximation $W_{\rm HF}^{\rm loc}$ obtained by one of existing techniques [70–73]. Our action integral now becomes

$$S = \int dt L^{\rm nuc}(\mathbf{R},\dot{\mathbf{R}};\mathbf{A}^{\rm tr}) + \int d^4x\left(\mathcal{L}_F^{\rm tr} + \mathcal{L}_{\rm mf} + \mathcal{L}_{\rm Coul} + \mathcal{L}_{\rm int}\right), \tag{12}$$

with

$$\mathcal{L}_{\rm mf} = \psi^\dagger(\mathbf{x},t)\left(i\hbar\partial_t - c\boldsymbol{\alpha}\cdot\frac{\hbar}{i}\boldsymbol{\nabla} - U_{\rm nuc}\right)\psi(\mathbf{x},t) - \psi^\dagger(\mathbf{x},t)W_{\rm HF}^{\rm loc}(\mathbf{x},t)\psi(\mathbf{x},t), \tag{13a}$$

$$\mathcal{L}_{\rm int} = \mathcal{L}_{\rm int}^{\rm tr} + \mathcal{L}_C', \tag{13b}$$

$$L^{\rm nuc}(\mathbf{R},\dot{\mathbf{R}}) = \sum_a\left(\frac{1}{2}M_a\dot{\mathbf{R}}_a^2 + \frac{Q_a}{c}\dot{\mathbf{R}}_a\cdot\mathbf{A}^{\rm tr}(\mathbf{R},t)\right) - \sum_{a>b}\frac{Q_aQ_b}{|\mathbf{R}_a-\mathbf{R}_b|}. \tag{13c}$$

Then, the Hamiltonian representation $\mathcal{H}^{\rm tot} = H^{\rm nuc} + H_{\rm mf}^{\rm el} + H_{\rm int}^{\rm el} + H_{\rm rad}$ follows with

$$H^{\rm nuc} = \sum_a\frac{1}{2M_a}\left(\frac{\hbar}{i}\boldsymbol{\nabla}_a - \frac{Q_a}{c}\mathbf{A}\right)^2 + \sum_{a>b}\frac{Q_aQ_b}{|\mathbf{R}_a-\mathbf{R}_b|}, \tag{14a}$$

$$H_{\rm mf}^{\rm el} = \int d^3\mathbf{x}\psi(\mathbf{x},t)^\dagger\left[c\boldsymbol{\alpha}\cdot\frac{\hbar}{i}\boldsymbol{\nabla} + \beta m_ec^2 + U_{\rm nuc}(\mathbf{x},t) + W_{\rm HF}^{\rm loc}(\mathbf{x},t)\right]\psi(\mathbf{x},t), \tag{14b}$$

$$H_{\rm int}^{\rm el} = \frac{q_e^2}{2c^2}\int d^3\mathbf{x}\int d^3\mathbf{y}J_{\rm el}^0(\mathbf{x},t)\frac{1}{|\mathbf{x}-\mathbf{y}|}J_{\rm el}^0(\mathbf{y},t) - \int d^3\mathbf{x}\psi(\mathbf{x},t)^\dagger W_{\rm HF}^{\rm loc}(\mathbf{x},t)\psi(\mathbf{x},t) - \frac{q_e}{c}\int d^3\mathbf{x}\mathbf{J}_{\rm el}\cdot\mathbf{A}^{\rm tr}, \tag{14c}$$

$$H_{\rm rad} = \frac{1}{2}\int d^3\mathbf{x}\left[4\pi c^2\boldsymbol{\Pi}^{\rm tr2} + \frac{1}{4\pi}\left(\boldsymbol{\nabla}\times\mathbf{A}^{\rm tr}\right)^2\right], \tag{14d}$$

where $J_{\rm el}^\mu$ represents the electronic current operator formally defined as [74]

$$J_{\rm el}^\mu(\mathbf{x},t) \equiv \frac{1}{2}\sum_{\mathfrak{i},\mathfrak{j}}[\psi_{\mathfrak{i}}^\dagger(\mathbf{x},t)\psi_{\mathfrak{j}}(\mathbf{x},t) - \psi_{\mathfrak{j}}(\mathbf{x},t)\psi_{\mathfrak{i}}^\dagger(\mathbf{x},t)]c\alpha_{\mathfrak{ij}}^\mu, \tag{15}$$

with $\alpha^\mu \doteq (1,\boldsymbol{\alpha})$. In addition to those internal degrees of freedom, we also allow possible addition of an external field into $H_{\rm mf}^{\rm el}$ in the form

$$H_{\rm ext}(t) = -q_e\int d^3\mathbf{x}\psi^\dagger(\mathbf{x},t)\boldsymbol{\alpha}\psi(\mathbf{x},t)\cdot\mathbf{A}^{\rm ext}(\mathbf{x},t),$$

which is to be added into the mean-field Hamiltonian $H_{\rm mf}^{\rm el}$.

In what follows, our discussion therefore takes account of possible time dependence of $H_{\rm mf}^{\rm el}$.

B. Decoupling of nuclear degrees of freedom

We extend the path-integral formulation we developed in Ref. [68], which closely follows the novel nonadiabatic path-integral formulation established in pioneering work by Pechukas [75]. The Pechukas formalism uses a formal stepwise integration of the fast (electron and radiation field) and slow (nucleus) components of the system. Application of this technique gives our target quantity $\mathcal{M}_{fi}$ the following form:

$$\mathcal{M}_{fi}(X_A,X_B,\ldots;\mathbf{R}_f,\mathbf{R}_i) = \int_{\mathbf{R}_i}^{\mathbf{R}_f}\mathcal{D}\mathbf{R}_t e^{\frac{i}{\hbar}S_{\rm nuc}[\mathbf{R}_t]}\mathcal{M}_{fi}^{\rm el,rad}[\mathbf{R}_t](X_A,X_B,\ldots), \tag{16}$$

where $\int_{\mathbf{R}_i}^{\mathbf{R}_f}\mathcal{D}\mathbf{R}_t$ represents a formal nuclear coordinate path integral connecting the initial ($\mathbf{R}_i$) and final ($\mathbf{R}_f$) nuclear configurations and $\mathcal{M}_{fi}^{\rm el,rad}$ is a functional of nuclear path $\mathbf{R}_t$, defined by the electron-radiation path integral

$$\mathcal{M}_{fi}^{\rm el,rad}[\mathbf{R}_t](X_A,X_B,\ldots) \equiv \langle\Psi_f|e^{-i\epsilon\mathcal{H}_{n-1}^{\rm el,rad}/\hbar}\ldots e^{-i\epsilon\mathcal{H}_{j_a+1}^{\rm el,rad}/\hbar}O_A(X_A)e^{-i\epsilon\mathcal{H}_{j_a}^{\rm el,rad}/\hbar}\ldots|\Psi_i\rangle, \tag{17}$$

where $|\Psi_i\rangle$ and $|\Psi_f\rangle$ are the initial and final electron-radiation coupled state vectors in the Heisenberg representation, respectively, whereas $\mathcal{H}^{\rm el,rad}$ is defined as

$$\mathcal{H}^{\rm el,rad}(\mathbf{R},t) \equiv H^{\rm el,rad}(\mathbf{R},t) - \sum_a\frac{Q_a}{c}\dot{\mathbf{R}}_a\cdot\mathbf{A}^{\rm tr}(\mathbf{R}_a) \tag{18}$$

with electron-radiation part of the Hamiltonian $H^{\rm el,rad}$

$$H^{\rm el,rad}(\mathbf{R},t) \equiv H_{\rm mf}^{\rm el}(\mathbf{R},t) + H_{\rm int}^{\rm el} + H_{\rm rad}, \tag{19}$$

where possible explicit time dependence of $H_{\rm mf}^{\rm el}$ arises from external fields. In Eq. (17), we have discretized the time in the interval $[t_i,t_f]$ into n infinitesimal slices of width $\epsilon \equiv (t_f-t_i)/n$ and each step point is denoted by $t_n \equiv t_i + n\epsilon$. We assume that time points $X_A^0, X_B^0, \ldots$ are approximated by the step points $j_a, j_b, j_c, \ldots$. In such discretized time representation, for notational simplicity, we use shorthand notations such as $\mathbf{R}_j \equiv \mathbf{R}(t_j)$ and $\mathcal{H}_j^{\rm el,rad} \equiv \mathcal{H}^{\rm el,rad}(\mathbf{R}_j,t_j)$. We also drop the explicit reference to the nuclear coordinate when obvious, for example, $|\Psi_f:\mathbf{R}_f\rangle \to |\Psi_f\rangle$. No approximation, except for nonrelativistic approximation on the nuclear dynamics, is formally involved in Eq. (16), provided that one can perform the nuclear coordinate path integration exactly. In practice, however, there is no established general way of performing such path integration but the stationary phase approximation. Nevertheless, we can formally treat $\mathbf{R}_t$ as a given function

of time in the evaluation of electron-radiation path integral, Eq. (17), and thereby formally decouple the nuclear dynamics.

C. Formal perturbation expansion

We next formulate a perturbation expansion of the electron-radiation part $\mathcal{M}_{fi}^{\mathrm{el,rad}}$, defined as Eq. (17). Since we have decoupled the nuclear degrees of freedom, we can treat the nuclear coordinates as a given function of time, $\mathbf{R}_t$. We first set the zeroth-order Hamiltonian to the mean-field Hamiltonian, that is,

$$H_0 = H_{\mathrm{mf}}^{\mathrm{el}}(\mathbf{R}_t, t) + H_{\mathrm{rad}}, \tag{20}$$

which has an explicit dependence on the nuclear configuration $\mathbf{R}_t$ and additional explicit time dependence arising from possible external field. We then introduce an interaction representation for an arbitrary operator O by

$$\check{O}(t) \equiv e^{-i\int_t^0 H_0 d\tau/\hbar}\mathcal{O}(t=0)e^{-i\int_0^t H_0 d\tau/\hbar}, \tag{21}$$

where $\mathcal{O}(t)$ represents the Heisenberg operator, and we also introduced time-evolution operator

$$\begin{aligned} e^{-i\int_b^a A d\tau} \equiv \lim_{M\to\infty} & e^{-i\frac{a-b}{M}A(b+(n-1)\frac{a-b}{M})} \\ & \times e^{-i\frac{a-b}{M}A(b+(n-2)\frac{a-b}{M})}\cdots e^{-i\frac{a-b}{M}A(b)} \end{aligned} \tag{22}$$

or alternatively, using the time-ordering ($\mathcal{T}$) and anti-time-ordering ($\widetilde{\mathcal{T}}$) operators, we may compactly write

$$e^{-i\int_b^a A d\tau} \equiv \begin{cases} \mathcal{T}\exp\left[-i\int_b^a A(\tau)d\tau\right] & \text{for } a \geqslant b \\ \widetilde{\mathcal{T}}\exp\left[i\int_a^b A(\tau)d\tau\right] & \text{for } b > a \end{cases}. \tag{23}$$

The right-hand side (RHS) of Eq. (21) can further be rewritten as

$$\check{O}(t) = \check{u}(t,0)\mathcal{O}(t)\check{u}(0,t) \tag{24}$$

with time-evolution operator $\check{u}$, defined as

$$\check{u}(t,t') \equiv e^{-i\int_t^0 H_0 d\tau/\hbar}e^{-i\int_{t'}^t H d\tau/\hbar}e^{-i\int_0^{t'} H_0 d\tau/\hbar}. \tag{25}$$

Since this time evolution operator satisfies the following differential equation,

$$i\hbar\frac{\partial}{\partial t}\check{u}(t,t') = \left[e^{-i\int_t^0 H_0 d\tau/\hbar}H_{\mathrm{int}}^{\mathrm{el}}(\mathbf{R}_t,t)e^{-i\int_0^t H_0 d\tau/\hbar}\right]\check{u}(t,t'), \tag{26}$$

with the boundary condition $\check{u}(t,t)=1$, a formal solution can be obtained as

$$\check{u}(t,t') = \mathcal{T}\exp\left[\frac{1}{i\hbar}\int_{t'}^t ds\check{H}_{\mathrm{int}}^{\mathrm{el}}(\mathbf{R}_s,s)\right]. \tag{27}$$

Without loss of generality, we can assume the initial and final states of the dynamics to be the adiabatic states, or the energy eigenstates of the electron-radiation coupled system with a fixed nuclear configuration. We can also assume the "adiabatic connectivity" between the zeroth-order eigenstates of $H_0(\mathbf{R})$ and the radiation-corrected eigenstate of $H(\mathbf{R})$. The initial state of the dynamics should then be obtained by a formal infinite time integral

$$|\Psi_\alpha:\mathbf{R}\rangle = \frac{1}{\mathcal{N}_\alpha^{\mp}}\lim_{\eta\to 0}\frac{U_\eta(0,\mp\infty:\mathbf{R})|\Phi_\alpha:\mathbf{R}\rangle}{\langle\Phi_\alpha:\mathbf{R}|U_\eta(0,\mp\infty:\mathbf{R})|\Phi_\alpha:\mathbf{R}\rangle}, \tag{28}$$

where $\mathcal{N}_\alpha^{\mp}$ represents an appropriate normalization factor, $|\Phi_\alpha:\mathbf{R}\rangle$ is the eigenstate of $H_0(\mathbf{R})$, and $|\Psi_\alpha:\mathbf{R}\rangle$ is its radiation-corrected counterpart. The adiabatic wave operator $U_\eta(0,\mp\infty:\mathbf{R})$ is defined as

$$U_\eta(0,\mp\infty:\mathbf{R}) = (\mathcal{T}/\widetilde{\mathcal{T}})\exp\left[\frac{1}{i\hbar}\int_{\mp\infty}^0 ds e^{-\eta|s|}\check{H}_{\mathrm{int}}^{\mathrm{el}}(\mathbf{R},s)\right], \tag{29}$$

with η being a small damping factor and $\check{H}_{\mathrm{int}}^{\mathrm{el}}(\mathbf{R})$ being the electronic interaction Hamiltonian for a fixed nuclear configuration $\mathbf{R}$. In Eq. (29), $\mathcal{T}(\widetilde{\mathcal{T}})$ should be taken in case of $-\infty(+\infty)$.

We can thus define a formal perturbation expansion of our target quantity for a given nuclear trajectory $\mathbf{R}_\tau$

$$\mathcal{M}_{fi}^{\mathrm{el,rad}}[\mathbf{R}_\tau] = \lim_{\eta\to+0}\frac{\langle\Phi_f:\mathbf{R}_f|\mathcal{T}\check{U}(\infty,-\infty;\widetilde{\mathbf{R}}_\tau)\check{O}_A(X_A)\ldots|\Phi_i:\mathbf{R}_i\rangle}{\mathcal{N}_f^{+*}\mathcal{N}_i^{-}\langle\Phi_f:\mathbf{R}_f|\check{U}(\infty,0)|\Phi_f:\mathbf{R}_f\rangle\langle\Phi_i:\mathbf{R}_i|\check{U}(0:-\infty)|\Phi_i:\mathbf{R}_i\rangle}, \tag{30}$$

where the nuclear trajectory is extended to an infinite time domain,

$$\widetilde{\mathbf{R}}_\tau = \begin{cases} \mathbf{R}_{t_i} & \text{for } t \leqslant t_i \\ \mathbf{R}_t & \text{for } t_i \leqslant t \leqslant t_f \\ \mathbf{R}_{t_f} & \text{for } t \geqslant t_f \end{cases}, \tag{31}$$

and the initial and final states in Eq. (30), $|\Phi_i:\mathbf{R}_i\rangle$ and $|\Phi_f:\mathbf{R}_f\rangle$, are the eigenstates of H_0 corresponding, in the sense of Eq. (29), to $|\Psi_i:\mathbf{R}_i\rangle$ and $|\Psi_f:\mathbf{R}_f\rangle$, respectively. In what follows, we drop the tilde over $\mathbf{R}$ for the sake of simplicity.

D. Lagrangian formulation of nuclear dynamics

Having thus formulated the Lagrangian and Hamiltonian as well as the initial and final adiabatic states, we now proceed to the study of electron-nucleus coupled dynamics. We first consider a direct relativistic extension of the Pechukas formulation.

We first introduce a path-integral expression of the transition amplitude $\mathcal{K}_{fi}$ and its associated electron-radiation path integral $\mathcal{K}_{fi}^{\mathrm{el,rad}}$ by removing operators O_A, O_B, etc. such that

$$\mathcal{K}_{fi} = \int_{\mathbf{R}_i}^{\mathbf{R}_f}\mathcal{D}\mathbf{R}_t e^{\frac{i}{\hbar}S_{\mathrm{nuc}}[\mathbf{R}_t]}\mathcal{K}_{fi}^{\mathrm{el,rad}}[\mathbf{R}_t]. \tag{32}$$

The stationary phase condition for the nuclear trajectory $\mathbf{R}_a(t)$ gives a Newtonian classical equations of motion

$$M_a\ddot{\mathbf{R}}_a = \mathbf{F}_a(t) \tag{33}$$

but with a nonclassical force derived by a functional differentiation of the effective action $S_{\rm nuc} + \hbar \ln \mathcal{K}_{fi}/i$ as

$$\mathbf{F}_a(t) = \mathrm{Re}\frac{\delta}{\delta \mathbf{R}_a(t)}\left(S_{\rm nuc}[\mathbf{R}_t] + \frac{\hbar}{i}\ln \mathcal{K}_{fi}[\mathbf{R}_t]\right), \tag{34}$$

where the real part projection has been introduced, following Pechukas [75], in order to obtain a real-valued force. Applying the same idea, our path integral leads to the following nuclear equation of motion:

$$\begin{aligned} M_a\ddot{\mathbf{R}}_a(t_k) = \mathrm{Re}\Bigg[&\langle \Psi_f | e^{-i\epsilon \mathcal{H}_{n-1}^{\rm el,rad}/\hbar} \cdots e^{-i\epsilon \mathcal{H}_{k}^{\rm el,rad}/\hbar} \left(\frac{-\partial U_{\rm nuc}}{\partial \mathbf{R}_a} + \frac{Q_a}{c}\left\{ -\frac{\partial}{\partial t}\mathbf{A}^{\rm tr}(\mathbf{R}_a) + \dot{\mathbf{R}}_a \times [\nabla_a \times \mathbf{A}^{\rm tr}(\mathbf{R}_a)] \right\}\right) \\ &\times e^{-i\epsilon \mathcal{H}_{k-1}^{\rm el,rad}/\hbar} \cdots e^{-i\epsilon \mathcal{H}_{0}^{\rm el,rad}/\hbar} |\Psi_i\rangle / \langle \Psi_f | e^{-i\epsilon \mathcal{H}_{n-1}^{\rm el,rad}/\hbar} \cdots e^{-i\epsilon \mathcal{H}_{0}^{\rm el,rad}/\hbar} |\Psi_i\rangle \Bigg], \end{aligned} \tag{35}$$

where the operators in the curly bracket represent the Coulomb and Lorentz force acting on the nucleus. While the Coulombic term, $-\partial U_{\rm nuc}/\partial \mathbf{R}_a$, is essentially the same as what we find in the nonrelativistic theory [68], the rest arises from interaction with the radiation field. In actual calculations, the radiation field is a summation of possible external field $\mathbf{A}^{\rm ext}$ plus the internal fields arising from the electronic current evaluated by a perturbation expansion, the latter formally leading to the following expression:

$$\begin{aligned} \overline{A}_j^{\rm tr}(\mathbf{x}, t) &\approx \langle \Phi_f | \frac{q_e}{i\hbar c} \int d^4y \mathcal{T}\left\{ \overline{\psi}(y)\gamma^\ell \psi(y) A_\ell^{\rm tr}(y) A_j^{\rm tr}(\mathbf{x}, t)\right\} |\Phi_i\rangle / \langle \Phi_f | \breve{U}_\eta(\infty, -\infty)|\Phi_i\rangle \\ &= \frac{1}{c}\int d^4y D_{j\ell}^{\rm tr}(\mathbf{x}, t; y)\overline{J}_{\rm el}^{\ell}(y), \end{aligned} \tag{36}$$

with $D_{j\ell}^{\rm tr}$ representing the transversal photon propagator and $\overline{J}_{\rm el}^{\ell}(y)$ representing the expectation value of the electronic current. For classical nuclear dynamics, however, one should replace $D_{j\ell}^{\rm tr}(\mathbf{x}, t; \xi)$ with the retarded Green's function in order to get a physically clearer picture. Such expressions recover the retardation effects and electronic current effects missing in the Coulombic interaction.

In the nonrelativistic regime, the force given by Eq. (35) is sometimes referred to as the *Pechukas force* and the corresponding dynamics, formally represented by a pair of self-consistent equations (33) and (35), is referred to as the *Pechukas dynamics* [note that the Pechukas force expression Eq. (35) implicitly depends on the nuclear trajectory, and hence the Pechukas dynamics requires self-consistency of the solution]. Although it is one of the most accurate formal expressions of the mixed quantum-classical nonadiabatic dynamics, the Pechukas dynamics has a severe problem: There is no established scheme [76] to solve these self-consistent equations. A more practical approach is then to replace it by the equal-time expectation value of the force operator,

$$\mathbf{F}_a(t_k) = \langle \Psi_i | e^{i\epsilon \mathcal{H}_0^{\rm el,rad}/\hbar} \cdots e^{i\epsilon \mathcal{H}_{k-1}^{\rm el,rad}/\hbar} \left[\frac{-\partial U}{\partial \mathbf{R}_a} + \frac{Q_a}{c}\left\{ -\frac{\partial}{\partial t}\mathbf{A}^{\rm tr}(\mathbf{R}_a, t_k) + \dot{\mathbf{R}}_a \times [\nabla_a \times \mathbf{A}^{\rm tr}(\mathbf{R}_a, t_k)]\right\}\right) e^{-i\epsilon \mathcal{H}_k^{\rm el,rad}/\hbar} \cdots e^{-i\epsilon \mathcal{H}_0^{\rm el,rad}/\hbar} |\Psi_i\rangle, \tag{37}$$

which can be evaluated by a perturbation expansion of the form

$$\begin{aligned} \mathbf{F}_a(t_k) = \langle \Phi_i | \breve{U}_\eta(-\infty, t_i) \mathcal{T}_c \breve{u}(t_i, T, t_i) \Bigg[&\frac{-\partial U}{\partial \mathbf{R}_a} + \frac{Q_a}{c}\left\{ -\frac{\partial}{\partial t}\mathbf{A}^{\rm tr}(\mathbf{R}_a, t_n) + \dot{\mathbf{R}}_a \times [\nabla_a \times \mathbf{A}^{\rm tr}(\mathbf{R}_a, t_k)]\right\}\Bigg) \\ &\times \breve{U}_\eta(t_i, -\infty)|\Phi_i\rangle / \langle \Phi_i | \breve{U}_\eta(-\infty, t_i)\mathcal{T}_c \breve{u}(t_i, T, t_i)\breve{U}_\eta(t_i, -\infty)|\Phi_i\rangle, \end{aligned} \tag{38}$$

with $|\Phi_i\rangle$ ($|\Phi_f\rangle$) being the initial (final) zeroth-order state vector corresponding to $|\Psi_i\rangle$ ($|\Psi_f\rangle$), the symbol $\mathcal{T}_c$ representing the ordering of operators along a folded timelike contour represented by (t_i, T, t_i), which starts from t_i and increases to some far future time $T > t_k$ and then decreases back to t_i. Here the nuclear configuration in the time range $t > t_k$ can be fixed as $\mathbf{R}_{t_k}$, since all the contributions from the time range $t > t_k$ cancels out. In nonrelativistic theory, the force represented by an equal-time expectation value of the gradient of the electronic Hamiltonian is referred to as the *Ehrenfest force* and the corresponding dynamics is the Ehrenfest dynamics. Equation (37) is a relativistic extension of the Ehrenfest force [68,77]. The Ehrenfest dynamics, which is a combination of Eqs. (33) and (38), can be solved in an explicit manner since Eq. (38) does not depend on the future trajectory, R_t, with $t > t_k$. A well-known deficiency of the Ehrenfest dynamics is that a system evolves into a fictitious superposition of multiple adiabatic states with nuclei moving in an averaged force field. Such problem is, however, avoidable by additional modifications, including those proposed in Refs. [78,79]. For simplicity of the discussion, we hereafter assume validity of Eq. (38).

III. PRACTICAL FORMULATION OF ELECTRON-RADIATION COUPLED DYNAMICS

Evaluation of the matrix elements represented by Eq. (30), which contains time-dependent H_0, requires real-time

integrations, whose numerical implementation should require large computational cost if not impossible. In order to get a tractable expression, we propose an alternative formulation. Below we construct an effective Hamiltonian that includes radiation corrections.

A. Construction of an effective Hamiltonian

We first consider a d-dimensional subspace of the Fock space, $\mathscr{H}_0$, which we require to be invariant with respect to the operation of H_0,

$$\forall|\phi\rangle \in \mathscr{H}_0, \quad H_0|\phi\rangle \in \mathscr{H}_0. \tag{39}$$

We also introduce a projection operator $\mathcal{P}$ which projects an arbitrary state vector to $\mathscr{H}_0$. As is discussed in Refs. [80,81] (also see Appendix A), one can construct a wave operator Ω having the following properties:

$$H^{\mathrm{el,rad}}\Omega\mathcal{P} = \Omega\mathcal{P}H^{\mathrm{el,rad}}\Omega\mathcal{P}, \tag{40a}$$

$$\mathcal{P}\Omega = \mathcal{P}; \tag{40b}$$

i.e., the image of the linear map Ω, which is hereafter denoted by $\Omega\mathscr{H}_0$, is a d-dimensional space and is invariant by the operation of the full electron-radiation Hamiltonian $H^{\mathrm{el,rad}}$. An explicit expression of Ω is given as (see Appendix A)

$$\Omega = \lim_{\eta\to+0} U_\eta(0,-\infty)\frac{1}{\mathcal{P}U_\eta(0,-\infty)\mathcal{P}}, \tag{41}$$

with U_η being the perturbative time evolution operator with a damping factor η, given in Eq. (29). It follows that $\Omega\mathscr{H}_0$ is spanned by a set of eigenvectors of the full Hamiltonian, $\{|\Psi_\alpha\rangle : \alpha = 1, 2, \ldots, d\}$, such that

$$H^{\mathrm{el,rad}}|\Psi_\alpha\rangle = \mathcal{E}_\alpha|\Psi_\alpha\rangle, \tag{42}$$

with $\mathcal{E}_\alpha$ being the αth energy eigenvalue. We also introduce a set of projected eigenvectors $\{|F_\alpha\rangle \equiv \mathcal{P}|\Psi_\alpha\rangle : \alpha = 1, 2, \ldots, d\}$, which are also the preimages of the eigenvector in the sense $|\Psi_\alpha\rangle = \Omega|F_\alpha\rangle$ by virtue of Eq. (40b). The mapping operator Ω can then be expanded as

$$\Omega = \sum_\alpha |\Psi_\alpha\rangle\langle\widetilde{F}_\alpha| \tag{43}$$

with $\{|\widetilde{F}_\alpha\rangle : \alpha = 1, 2, \ldots, d\}$ being the set of conjugate vectors to the preimages in the sense

$$\langle\widetilde{F}_\alpha|F_\beta\rangle = \delta_{\alpha\beta}. \tag{44}$$

In order for the conjugate set of vectors to be well defined, we here require the overlap matrix $S_{\alpha\beta} \equiv \langle F_\alpha|F_\beta\rangle$, which is by construction Hermitian, to be positive definite. It then follows that S is invertible and one can construct the conjugate vector by $\langle\widetilde{F}_\alpha| = \sum_{\beta,I}(S^{-1})_{\alpha\beta}F_\beta^{I*}\langle I|$.

We can identify $\mathcal{P}H^{\mathrm{el,rad}}\Omega$ appearing in Eq. (40a) as an effective Hamiltonian $H_{\mathrm{eff}}^{\mathrm{el,rad}}$:

$$H_{\mathrm{eff}}^{\mathrm{el,rad}} \equiv \mathcal{P}H^{\mathrm{el,rad}}\Omega\mathcal{P}. \tag{45}$$

Although not being Hermitian in general, $H_{\mathrm{eff}}^{\mathrm{el,rad}}$ maps $\mathscr{H}_0$ to itself and decomposes as

$$H_{\mathrm{eff}}^{\mathrm{el,rad}} = \sum_{\alpha=1}^{d} |F_\alpha\rangle\mathcal{E}_\alpha\langle\widetilde{F}_\alpha|, \tag{46}$$

which shows that the (right) eigenvalues are the true adiabatic energies.

In practical application, we calculate $H_{\mathrm{eff}}^{\mathrm{el,rad}}$ by a (finite-order) perturbation expansion using a set of orthonormal basis set $\{|I\rangle : I = 1, 2, 3, \ldots, d\}$. We then calculate right eigenvectors of the matrix representation of $H_{\mathrm{eff}}^{\mathrm{el,rad}}$ as

$$\sum_J \langle I|H_{\mathrm{eff}}^{\mathrm{el,rad}}|J\rangle F_\alpha^J = \mathcal{E}_\alpha F_\alpha^I \tag{47}$$

to obtain each eigenvalue $\mathcal{E}_\alpha$ and the associated preimage vector $|F_\alpha\rangle = \sum_I |I\rangle F_\alpha^I$.

We can also switch to a Hermitian expression of $H_{\mathrm{eff}}^{\mathrm{el,rad}}$ by a transformation

$$\widetilde{H}_{\mathrm{eff}}^{\mathrm{el,rad}} \equiv S^{-1/2}H_{\mathrm{eff}}^{\mathrm{el,rad}}S^{1/2}, \tag{48}$$

together with an associated transformation on the state vector, from $|\chi\rangle$ to $|\widetilde{\chi}\rangle \equiv S^{-1/2}|\chi\rangle$. Note that matrices $S^{\pm1/2}$ are both well defined under the assumption of positive definiteness of the overlap matrix S. Such symmetrization can potentially be useful in numerical calculation, however, we here keep the original non-Hermitian $H_{\mathrm{eff}}^{\mathrm{el,rad}}$ for simplicity of the discussion.

Up to this point, the requirements on the choice of $\mathscr{H}_0$ are the invariance with respect to H_0 and the additionally introduced positive definiteness of the overlap matrix S. We may then expect that $\mathscr{H}_0$ can include an arbitrarily large number of eigenvectors of H_0. Reference [80], for example, discusses an infinite dimensional $\mathscr{H}_0$ that consists of the whole set of two-particle states, though their analysis is based on a model different from ours. On the other hand, as we discuss in Appendix A, at least in our present model with Coulombic bound states as the main target, there can be further restrictions on $\mathscr{H}_0$ in order for the perturbative expression Eq. (41) to be meaningful. We will later come back to this problem.

B. Effective time-evolution operator and derivative couplings

We now formulate the molecular time evolution. Hereafter, the nuclear coordinate dependence of the operators and vectors discussed above is written down explicitly. We first consider the exact dynamics of the state vector starting from a given superposition of adiabatic states $|\Psi_{t_0}\rangle = \sum_\alpha |\Psi_\alpha : \mathbf{R}_0\rangle C_\alpha(t_0)$ at time t_0 and evolving in time to t_f. By discretizing the time in the interval $[t_0, t_f]$ into small slices

$\epsilon \equiv (t_f - t_0)/n$, the time evolution can be described as

$$
\begin{aligned}
|\Psi_{t_f}\rangle &= e^{-i\epsilon H_{n-1}^{\mathrm{el,rad}}/\hbar} \cdots e^{-i\epsilon H_0^{\mathrm{el,rad}}/\hbar} \left[\sum_\alpha |\Psi_\alpha : \mathbf{R}_0\rangle C_\alpha(t_0) \right] \\
&= e^{-i\epsilon H_{n-1}^{\mathrm{el,rad}}/\hbar} \cdots e^{-i\epsilon H_1^{\mathrm{el,rad}}/\hbar} \left[\sum_{\alpha,\beta} |\Psi_\alpha : \mathbf{R}_0\rangle \left(e^{-i\epsilon H_0^{\mathrm{el,rad}}/\hbar}\right)_{\alpha\beta} C_\beta(t_0) \right] \\
&= e^{-i\epsilon H_{n-1}^{\mathrm{el,rad}}/\hbar} \cdots e^{-i\epsilon H_1^{\mathrm{el,rad}}/\hbar} \left[\sum_{\alpha,\beta,\gamma} |\Psi_\alpha : \mathbf{R}_1\rangle (e^{-\epsilon \dot{\mathbf{R}}_0 \cdot \mathbf{X}(\mathbf{R}_0)})_{\alpha\beta} \left(e^{-i\epsilon H_0^{\mathrm{el,rad}}/\hbar}\right)_{\beta\gamma} C_\gamma(t_0) \right] \\
&\vdots \\
&= \sum_{\alpha_n,\cdots,\alpha_0,\beta_{n-1},\cdots,\beta_0} |\Psi_{\alpha_n} : \mathbf{R}_n\rangle \left[\prod_{k=0}^{n-1} (e^{-\epsilon \dot{\mathbf{R}}_k \cdot \mathbf{X}(\mathbf{R}_k)})_{\alpha_{k+1}\beta_k} \left(e^{-i\epsilon H_k^{\mathrm{el,rad}}/\hbar}\right)_{\beta_k\alpha_k} \right] C_{\alpha_0}(t_0),
\end{aligned}
\tag{49}
$$

where quantities at the jth time slice are denoted as $t_j \equiv t_0 + j\epsilon$, $\mathbf{R}_j \equiv \mathbf{R}(t_j)$, and $H_j^{\mathrm{el,rad}} \equiv H^{\mathrm{el,rad}}(\mathbf{R}_j, t_j)$, etc. The symbol $\mathbf{X}$ represents the derivative coupling of the true adiabatic states

$$
\mathbf{X}_{\alpha\beta} = \langle \Psi_\alpha : \mathbf{R}| \frac{\partial}{\partial \mathbf{R}} |\Psi_\beta : \mathbf{R}\rangle. \tag{50}
$$

We then define a corresponding effective time evolution operator by

$$
U_{\mathrm{eff}}^{(n)}(t_f, t_0) \equiv e^{-i\epsilon H_{\mathrm{eff}\ n-1}^{\mathrm{el,rad}}/\hbar} \cdots e^{-i\epsilon H_{\mathrm{eff}\ 0}^{\mathrm{el,rad}}/\hbar} \tag{51}
$$

with $H_{\mathrm{eff}\ j}^{\mathrm{el,rad}} \equiv H_{\mathrm{eff}}^{\mathrm{el,rad}}(\mathbf{R}_j, t_j)$. The superscript (n) in the left-hand side (LHS) of Eq. (51) represents the number of time slices, which should be sufficiently large. It acts on the projected initial state vector $|\mathcal{F}(t_0)\rangle \equiv \mathcal{P}|\Psi_{t_0}\rangle = \sum |F_\alpha : \mathbf{R}_0\rangle C_\alpha(t_0)$ as

$$
\begin{aligned}
U_{\mathrm{eff}}^{(n)}(t_f, t_0)|\mathcal{F}(t_0)\rangle &= e^{-i\epsilon H_{\mathrm{eff}\ n-1}^{\mathrm{el,rad}}/\hbar} \cdots e^{-i\epsilon H_{\mathrm{eff}\ 0}^{\mathrm{el,rad}}/\hbar} \left[\sum_\alpha |F_\alpha : \mathbf{R}_0\rangle C_\alpha(t_0) \right] \\
&= e^{-i\epsilon H_{\mathrm{eff}\ n-1}^{\mathrm{el,rad}}/\hbar} \cdots e^{-i\epsilon H_{\mathrm{eff}\ 1}^{\mathrm{el,rad}}/\hbar} \left[\sum_{\alpha,\beta} |F_\alpha : \mathbf{R}_0\rangle \left(e^{-i\epsilon H_0^{\mathrm{el,rad}}/\hbar}\right)_{\alpha\beta} C_\beta(t_0) \right] \\
&= e^{-i\epsilon H_{\mathrm{eff}\ n-1}^{\mathrm{el,rad}}/\hbar} \cdots e^{-i\epsilon H_{\mathrm{eff}\ 1}^{\mathrm{el,rad}}/\hbar} \left[\sum_{\alpha,\beta,\delta} |F_\alpha : \mathbf{R}_1\rangle \left(e^{-\epsilon \dot{\mathbf{R}}_0 \cdot \mathbf{X}^{\mathrm{eff}}(\mathbf{R}_0)}\right)_{\alpha\beta} \left(e^{-i\epsilon H_0^{\mathrm{el,rad}}/\hbar}\right)_{\beta\gamma} C_\gamma(t_0) \right] \\
&\vdots \\
&= \sum_{\alpha_n,\ldots,\alpha_0,\beta_{n-1},\ldots,\beta_0} |F_{\alpha_n} : \mathbf{R}_n\rangle \prod_{k=0}^{n-1} \left[\left(e^{-\epsilon \dot{\mathbf{R}}_k \cdot \mathbf{X}^{\mathrm{eff}}(\mathbf{R}_k)}\right)_{\alpha_{k+1}\beta_k} \left(e^{-i\epsilon H_k^{\mathrm{el,rad}}/\hbar}\right)_{\beta_k\alpha_k} \right] C_{\alpha_0}(t_0).
\end{aligned}
\tag{52}
$$

In Eq. (52), $\mathbf{X}^{\mathrm{eff}}$ defines an approximate derivative coupling associated with the projected adiabatic states

$$
\mathbf{X}_{\alpha\beta}^{\mathrm{eff}} = \langle \widetilde{F}_\alpha : \mathbf{R}| \frac{\partial}{\partial \mathbf{R}} |F_\beta : \mathbf{R}\rangle, \tag{53}
$$

which is related to the true adiabatic derivative coupling $\mathbf{X}_{\alpha\beta}$ by (see Appendix B)

$$
\mathbf{X}_{\alpha\beta}^{\mathrm{eff}} = \mathbf{X}_{\alpha\beta} + \left\langle \frac{\partial}{\partial \mathbf{R}} \widetilde{F}_\alpha \right| (1 - \mathcal{P}) |\Psi_\beta : \mathbf{R}\rangle, \tag{54}
$$

and the difference between $\mathbf{X}_{\alpha\beta}^{\mathrm{eff}}$ and $\mathbf{X}_{\alpha\beta}$, represented by the second term, is negligible or at least can be reasonably truncated [82]. If we neglect differences between the derivative couplings, Eq. (52) describes the same time evolution of the coefficient $c_a(t)$ as that of the true dynamics, Eq. (49). We therefore propose Eq. (51) as an approximate time evolution operator.

One can in principle calculate the true derivative couplings between two adiabatic state vectors using the formula

$$
\mathbf{X}_{\alpha\beta}(\mathbf{R}) = \frac{1}{\mathcal{E}_\beta - \mathcal{E}_\alpha} \langle \Psi_\alpha : \mathbf{R}| \frac{\partial H^{\mathrm{el,rad}}(\mathbf{R})}{\partial \mathbf{R}} |\Psi_\beta : \mathbf{R}\rangle \tag{55}
$$

where the matrix elements in the RHS are to be evaluated by perturbation expansions. Nevertheless, Eq. (52), which requires that we should neglect the small difference between $\mathbf{X}$ and $\mathbf{X}^{\mathrm{eff}}$, is practically important since it allows basis set

transformation in the projected space $\mathscr{H}_0$. It is well known in (nonrelativistic) nonadiabatic dynamics that numerical calculation can be much easier and more stable by avoiding the adiabatic basis set and using quasidiabatic basis set with smaller derivative couplings [83]. We can indeed switch to an arbitrary orthonormal basis set $\mathscr{B} \equiv \{|I:\mathbf{R}\rangle : I = 1, 2, ..., d\}$, which has nonsingular dependence on the nuclear configuration, and start our calculation from $|\mathcal{F}(t_0)\rangle = \sum_{\alpha,I} |I:\mathbf{R}_0\rangle F^I_\alpha(\mathbf{R}_0) C^\alpha_0$, thus deriving

$$|\mathcal{F}_{t_f}\rangle = \sum_{I_n,\cdots,I_0,J_{n-1},\cdots,J_0} |I_n:\mathbf{R}_n\rangle \Bigg[\prod_{k=0}^{n-1} \left(e^{-\epsilon \dot{\mathbf{R}}_k \cdot \mathbf{X}^{\mathscr{B}}_{\rm eff}(\mathbf{R}_k)}\right)_{I_{k+1}J_k} \times \left(e^{-i\epsilon H^{\mathscr{B}}_{\rm eff}(\mathbf{R}_k,t_k)/\hbar}\right)_{J_k I_k}\Bigg] \sum_\alpha F^{I_0}_\alpha(\mathbf{R}_0) C^\alpha_0, \tag{56}$$

where $H^{\mathscr{B}}_{\rm eff}(\mathbf{R})$ is expanded by the basis set $\mathscr{B}$ and the derivative coupling is defined by $[\mathbf{X}^{\mathscr{B}}_{\rm eff}(\mathbf{R})]_{IJ} = \langle I:\mathbf{R}|\partial/\partial\mathbf{R}|J:\mathbf{R}\rangle$. One can indeed show that Eq. (56) is equivalent to Eq. (52) [but not directly equivalent to Eq. (49)] within the basis set expansion.

C. Path-integral expression using the effective Hamiltonian

We have thus rewritten the electron-radiation coupled time evolution into a more managable form, Eq. (51). In order to obtain the corresponding practical approximation for the electron-radiation path integral in Eq. (17), we reintroduce the radiation-nucleus coupling part $\sum_a Q_a \dot{\mathbf{R}}_a \cdot \mathbf{A}(\mathbf{R}_a, t)/c$, where $\mathbf{A}(\mathbf{R}_a, t)$ represents a combination of the transversal radiation field $\mathbf{A}^{\rm tr}$ plus possible external field. Because of the factor $|\dot{\mathbf{R}}_a|/c$, which is small for nonrelativistic nuclear motion, we can assume that its effect on the radiation-field dynamics is negligible. We therefore treat it within the first-order approximation in the following sense: (i) We use $H^{\rm el,rad}$, which neglects the nucleus-radiation coupling, in evaluation of the wave operator Ω and the effective Hamiltonian $H^{\rm el,rad}_{\rm eff}$, etc. (ii) In evaluation of the path integral, $\sum_a Q_a \dot{\mathbf{R}}_a \cdot \mathbf{A}(\mathbf{R}_a, t)/c$ is included in the action integral as a small external perturbation that virtually does not affect the time evolution of the system. (iii) In the calculation of the nuclear dynamics, for example, by solving Eqs. (33) and Eq. (37), we apply the perturbative expression, Eq. (36), to evaluate the transversal fields at the space-time points $(\mathbf{R}_a, t)$. We also reintroduce the operators $\mathcal{O}_A$ appearing in Eq. (17) with an analogous manner to Eq. (45) as

$$\mathcal{O}^{\rm eff}_A \equiv \mathcal{P}\mathcal{O}_A\Omega\mathcal{P}, \tag{57}$$

with $\mathbf{R}_{t_A}$ being the nuclear coordinate at time t_A. The meaning of Eq. (57) should be clear from the following expansion:

$$\begin{aligned}\langle\widetilde{F}_\alpha|\mathcal{O}^{\rm eff}_A|F_\beta\rangle &= \langle\widetilde{F}_\alpha|\mathcal{P}\mathcal{O}_A\left(\sum_c |\Psi_c\rangle\langle\widetilde{F}_c|\right)|F_\beta\rangle \\ &= \langle\widetilde{F}_\alpha|\mathcal{P}\sum_{c,d}|\Psi_d\rangle\langle\Psi_d|\mathcal{O}_A|\Psi_c\rangle\langle\widetilde{F}_c|F_\beta\rangle \\ &= \langle\Psi_\alpha|\mathcal{O}_A|\Psi_\beta\rangle,\end{aligned} \tag{58}$$

where the last side represents the matrix element of $\mathcal{O}$ evaluated between the exact energy eigenstates. We can then formulate our approximation on $\mathcal{M}^{\rm el,rad}_{fi}$ as

$$\begin{aligned}\mathcal{M}^{\rm el,rad}_{fi}[\mathbf{R}_\tau] \approx \langle\widetilde{\mathcal{F}}_f|e^{-\frac{i}{\hbar}\epsilon\{H^{\rm el,rad}_{{\rm eff}\,N-1} - \sum_a \dot{\mathbf{R}}_a\cdot[\frac{Q_a}{c}\mathbf{A}_{aN-1} + i\hbar\mathbf{X}^{\rm eff}_a(\mathbf{R}_{N-1})]\}} e^{-\frac{i}{\hbar}\epsilon\{H^{\rm el,rad}_{{\rm eff}\,N-2} - \sum_a \dot{\mathbf{R}}_a\cdot[\frac{Q_a}{c}\mathbf{A}_{aN-2} + i\hbar\mathbf{X}^{\rm eff}_a(\mathbf{R}_{N-2})]\}} \\ \cdots \mathcal{O}^{\rm eff}(t_A) \cdots e^{-\frac{i}{\hbar}\epsilon\{H^{\rm el,rad}_{{\rm eff}\,0} - \sum_a \dot{\mathbf{R}}_a\cdot[\frac{Q_a}{c}\mathbf{A}^{\rm tr} + i\hbar\mathbf{X}^{\rm eff}_a(\mathbf{R}_0)]\}}|\mathcal{F}_i\rangle\end{aligned} \tag{59}$$

with $\mathbf{A}_{aj}$ being a shorthand notation for $\mathbf{A}(\mathbf{R}_a, t_j)$, and $[\mathbf{X}^{\rm eff}_a(\mathbf{R})]_{\alpha\beta} \equiv \langle\widetilde{F}_\alpha:\mathbf{R}|\partial/\partial\mathbf{R}_a|F_\beta:\mathbf{R}\rangle$ being the effective derivative coupling with respect to the ath nucleus. In Eq. (59), we have included the derivative coupling $\mathbf{X}^{\rm eff}$ in an explicit manner. We see that it appears together with the vector field in the form $\exp\{i\sum_a \dot{\mathbf{R}}_a \cdot [i\hbar\mathbf{X}^{\rm eff}_a + \frac{Q_a}{c}\mathbf{A}(\mathbf{R}_a, t)]/\hbar\}$, which is an expected behavior by the (generalized) gauge symmetry and partly supports the appropriateness of our first-order treatment of the vector field. We also note that, in Eq. (59), in contrast to Eq. (17), both the initial and final states belong to the model space, the initial state being the model state projection of the adiabatic state, $|\mathcal{F}_i\rangle = \mathcal{P}|\Psi_i:\mathbf{R}_i\rangle$, whereas the final state $\langle\widetilde{\mathcal{F}}_f|$ is the conjugate [in the sense Eq. (44)] of the projected adiabatic state $|F_f:\mathbf{R}_f\rangle = \mathcal{P}|\Psi_f:\mathbf{R}_f\rangle$. In practice, those vectors are computed from the right eigenvectors of $H_{\rm eff}$ at the initial and final nuclear configurations.

There are yet more advantages in this approach relevant to solving nuclear dynamics. From Eq. (59), we find that the path-integral expression using the effective Hamiltonian has the same form as that of the nonrelativistic electron-nucleus coupled dynamics. It can therefore be mapped onto a Schrödinger dynamics [68]. To see this more clearly, we first recall that the full time evolution of the system is described by Eq. (32). Applying the time evolution operator Eq. (51) for electron-radiation coupled time evolution, we obtain

$$\begin{aligned}\mathcal{K}_{fi} &= \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathcal{D}\mathbf{R}_t e^{\frac{i}{\hbar}S_{\rm nuc}[\mathbf{R}_t]} \langle\widetilde{F}_f:\mathbf{R}_f|e^{-\frac{i}{\hbar}\epsilon\{H^{\rm el,rad}_{{\rm eff}\,n-1} - \sum_a \dot{\mathbf{R}}_a\cdot[\frac{Q_a}{c}\mathbf{A}^{\rm tr} + i\hbar\mathbf{X}^{\rm eff}_a(\mathbf{R}_{n-1})]\}} \\ &\quad \times e^{-\frac{i}{\hbar}\epsilon\{H^{\rm el,rad}_{{\rm eff}\,n-2} - \sum_a \dot{\mathbf{R}}_a\cdot[\frac{Q_a}{c}\mathbf{A}^{\rm tr} + i\hbar\mathbf{X}^{\rm eff}_a(\mathbf{R}_{n-2})]\}} \cdots e^{-\frac{i}{\hbar}\epsilon\{H^{\rm el,rad}_{{\rm eff}\,0} - \sum_a \dot{\mathbf{R}}_a\cdot[\frac{Q_a}{c}\mathbf{A}^{\rm tr} + i\hbar\mathbf{X}^{\rm eff}_a(\mathbf{R}_0)]\}}|F_i:\mathbf{R}_i\rangle \\ &= \int \prod_{j=1}^{n-1} d\mathbf{R}_j \sum_{\alpha_{n-1}} \cdots \sum_{\alpha_1} \prod \langle\mathbf{R}_{j+1}|\langle\widetilde{F}_{\alpha_{j+1}}:\mathbf{R}_{j+1}|e^{\frac{i}{\hbar}\epsilon\sum_a M_a(\frac{\mathbf{R}^{(a)}_{j+1} - \mathbf{R}^{(a)}_j}{\epsilon})^2} e^{-\frac{i}{\hbar}\epsilon\{H^{\rm el,rad}_{{\rm eff}\,j} - \sum_a \frac{\mathbf{R}^{(a)}_{j+1} - \mathbf{R}^{(a)}_j}{\epsilon}\cdot[\frac{Q_a}{c}\mathbf{A}^{\rm tr} + i\hbar\mathbf{X}^{\rm eff}_a(\mathbf{R}_j)]\}}|F_{\alpha_j}:\mathbf{R}_j\rangle|\mathbf{R}_j\rangle\end{aligned}$$

$$
\begin{aligned}
&= \int \prod_{j=1}^{n-1} d\mathbf{R}_j \int \prod_{j=1}^{n-1} d\mathbf{P}_j \sum_{\alpha_{n-1}} \cdots \sum_{\alpha_1} \prod \langle \mathbf{R}_{j+1} | \langle \widetilde{F}_{\alpha_{j+1}} : \mathbf{R}_{j+1} | e^{-\frac{i}{\hbar}\epsilon \sum_a \frac{1}{2M_a}[\mathbf{P}_j^{(a)} - \frac{Q_a}{c}\mathbf{A}^{\mathrm{tr}} - i\hbar \mathbf{X}_a(\mathbf{R}_j)]^2} \\
&\quad \times e^{\frac{i}{\hbar}\mathbf{P}_j \cdot (\mathbf{R}_{j+1} - \mathbf{R}_j)} e^{-\frac{i}{\hbar}\epsilon H_{\mathrm{eff}\,j}^{\mathrm{el,rad}}} | F_{\alpha_j} : \mathbf{R}_j \rangle | \mathbf{R}_j \rangle \\
&= \int \prod_{j=1}^{n-1} d\mathbf{R}_j \int \prod_{j=1}^{n-1} d\mathbf{P}_j \sum_{\alpha_{n-1}} \cdots \sum_{\alpha_1} \prod \langle \mathbf{R}_{j+1} | \langle \widetilde{F}_{\alpha_{j+1}} : \mathbf{R}_{j+1} | v e^{-\frac{i}{\hbar}\epsilon \sum_a \frac{1}{2M_a}[\frac{\hbar}{i}\frac{\partial}{\partial \mathbf{R}_j^{(a)}} - \frac{Q_a}{c}\mathbf{A}^{\mathrm{tr}} - i\hbar \mathbf{X}_a(\mathbf{R}_j)]^2} \\
&\quad \times | \mathbf{P}_j \rangle \langle \mathbf{P}_j | e^{-\frac{i}{\hbar}\epsilon H_{\mathrm{eff}\,j}^{\mathrm{el,rad}}} | F_{\alpha_j} : \mathbf{R}_j \rangle | \mathbf{R}_j \rangle, \qquad (60)
\end{aligned}
$$

where $|\mathbf{P}_j\rangle$ represents a momentum eigenstate, the boundary terms, $j = 0$ and $j = n$ are fixed by the initial and final conditions in a such manner that $|\mathbf{R}_0\rangle \equiv |\mathbf{R}_i\rangle$, $|\mathbf{R}_n\rangle \equiv |\mathbf{R}_f\rangle$, $|F_{\alpha_0}\rangle = |F_i\rangle$, $|F_{\alpha_n}\rangle = |F_f\rangle$, etc. In Eq. (60), we have also slightly rearranged subscripts and superscripts for notational clarity; either $\mathbf{R}_j^{(a)}$ ($\mathbf{P}_j^{(a)}$) represents the ath component of $\mathbf{R}$ ($\mathbf{P}$) at the jth time slice, etc. From Eq. (60), one can extract an operator expression of the full time propagation of the system. Switching from the path-integral picture to the wave-packet picture, we expand the time-dependent electron-nucleus coupled state as

$$
|\Omega_t\rangle = \int d\mathbf{R} |\mathbf{R}\rangle \sum_I |\Phi_I : \mathbf{R}\rangle \chi_I(\mathbf{R}, t), \qquad (61)
$$

where $\sum_I |\Phi_I : \mathbf{R}\rangle \chi_I$ is an expansion of the electron-radiation state vector at time t using a given orthonormal basis set $\{|I : \mathbf{R}\rangle : I = 1, \ldots, d\}$ which expands the model space $\mathscr{H}_0$ associated with the nuclear configuration $\mathbf{R}$. The initial condition on the state vector should be set so that $\sum_I |\Phi_I : \mathbf{R}\rangle \chi_I(\mathbf{R}, 0)$ equals the projection of the initial adiabatic state

$$
\sum_I |\Phi_I : \mathbf{R}_i\rangle \chi_I(\mathbf{R}_i, 0) = |F_{\alpha_i} : \mathbf{R}_i\rangle \chi_0(\mathbf{R}_i), \qquad (62)
$$

where α_i is the index of the initial adiabatic state and $\chi_0(\mathbf{R})$ is the initial nuclear wave function. The time evolution of the wave packet is then represented by the Schrödinger equation

$$
\begin{aligned}
i\hbar \dot{\chi}_I(\mathbf{R}, t) = \sum_J \Bigg[\sum_a \frac{1}{2M_a} \left(\frac{\hbar}{i} \nabla_a - i\hbar \mathbf{X}_a^{\mathrm{eff}} - \frac{Q_a}{c} \overline{\mathbf{A}} \right)^2 \\
+ H_{\mathrm{eff}}^{\mathrm{el,rad}}(\mathbf{R}, t) \Bigg]_{IJ} \chi_J(\mathbf{R}, t), \qquad (63)
\end{aligned}
$$

where, since we are treating the nucleus-radiation coupling by the first-order approximation, $\overline{\mathbf{A}}$ is not a dynamical degrees of freedom but a summation of possible external field plus an expectation value of the dynamical radiation field evaluated in a similar manner as Eq. (36). Depending on the strength of the induced current in the target system, the latter can even be completely neglected. The Schrödinger equation Eq. (63) then enables application of almost all the types of existing nonadiabatic calculation tools. In particular, besides the effective Newtonian-like equation of motion of Eq. (35), it allows for larger number of choices of nuclear dynamics implementation, including quantum-mechanical wave-packet approaches (see Ref. [84–86] for just a few examples) or various semiclassical wave-packet approaches developed for nonadiabatic dynamics [87–89].

D. Discussion

We here discuss the validity and limitations of our present approach. Our effective Hamiltonian $H_{\mathrm{eff}}^{\mathrm{el,rad}}$ includes radiation corrections through the wave operator Ω which is rewritten as a perturbation series as shown in Eq. (41). Unlike the formal perturbative expression given in Eq. (30), the perturbation series Eq. (41) is evaluated at a fixed nuclear position, and thus it allows application of the standard techniques in QED. In Sec. IV, we calculate the lowest few order terms in the perturbation series.

Another implicit advantage of the present approach is that our working equations, Eqs. (60) or (63), formally reduce back to the corresponding equations for the conventional radiation-free nonadiabatic dynamics for vanishing electron-radiation coupling. This aspect is important since we empirically know that such conventional radiation-free approximation has successfully been applied to numerous nonrelativistic dynamics of molecules.

Yet we also need to take care of the limitations in the present approach. First, the size of the Hilbert space $\mathscr{H}_0$ (or $\Omega\mathscr{H}_0$) is limited to a d-dimensional linear space. Unlike in the nonrelativistic dynamics, there are certain restrictions on the choice of $\mathscr{H}_0$ as we discuss in Appendix A, though we are at this point not certain about maximal extensibility of $\mathscr{H}_0$.

Second, a considerable part of radiational excited states are missing. While our effective Hamiltonian reflects radiation field excitations that are coupled to the electronic states, other types of excitations, for example, excited states of a pure radiational character, are missing. Such missing effects should only be recoverable by explicitly taking summation over all possible radiational excited states in all the intermediate time steps (see Ref. [90] for path-integral expressions connecting different excitation levels of the radiation field). In this paper, we assumed that those missing effects to be negligible but it certainly illustrates formal deficiency of our present scheme that expands the electron-radiation dynamics with a purely electronic (photon free) basis set.

Third, we clearly need another formulation if there are short-lived excited states with the radiative decay processes within the timescale of the target dynamics. We discuss such dynamics separately in Appendix C.

IV. EVALUATION OF THE RADIATION CORRECTIONS

Here we discuss explicit expressions of the effective Hamiltonian $H_{\rm eff}^{\rm el,rad}$ [Eq. (45)] and the effective operator for a given observable $\mathcal{O}_A^{\rm eff}$ [Eq. (57)].

A. General strategy

Below we consider an N_e electron molecule with a fixed nuclear configuration and we assume that the solutions of the set of electronic mean-field equations, Eqs. (9), (10), and (11), are already at our hands. We also assume that the exchange terms are localized by application of one of existing techniques [70–73]. To our knowledge, such locality is prerequisite for performing QED calculation using established techniques [20,40,43], though there are attempts to lift this restriction as discussed in Ref. [66]. We set the zeroth-order Hamiltonian as Eq. (20) and consider perturbative corrections by $H_{\rm int}^{\rm el} = H^{\rm el,rad} - H_0$. The full expression of $H_{\rm int}^{\rm el}$, given as Eq. (14c), is, however, not convenient for a systematic perturbation expansion because of its complexity arising from the Coulombic and mean-field subtraction terms. Instead of the full expression of $H_{\rm int}^{\rm el}$, we start with much simplified one,

$$H_{\rm int}^{\rm el\ tr}(t) = -\frac{1}{c}\int d^3\mathbf{x} J_{\rm el}^{\mu}(\mathbf{x},t) A_{\mu}^{\rm tr}(\mathbf{x},t), \tag{64}$$

to construct the diagrammatic expression of the perturbation series. The remaining part, $H_{\rm int}^{\rm el\ '} \equiv H_{\rm int}^{\rm el} - H_{\rm int}^{\rm el\ tr}$, can be reintroduced afterward by exploiting the one-to-one correspondence between the Coulombic interactions and the transversal photon exchange interactions (i.e., one should accompany the other in order for the final expression to be gauge invariant). We "reinterpret" the (transversal) photon lines in the obtained diagram to include the Coulombic effects according to the following scheme: (i) All transversal photon lines of the self-interaction type, i.e., those emitted and reabsorbed by an identical electron lime, are reinterpreted as the summation of the Coulombic and transversal photon exchange interactions,

$$-D_{\mu\nu}^{\lambda}(x-y) = -\int \frac{d^4k}{(2\pi)^4}\frac{4\pi}{k^2+i\epsilon} e^{-ik(x-y)}\Theta_{\mu\nu}^{\lambda}, \tag{65}$$

where ϵ represents an infinitesimal positive constant, whereas the symbol λ, representing the gauge choice, takes either the Coulomb gauge ($\lambda = C$) or the Feynman gauge ($\lambda = F$) with corresponding factor $\Theta_{\mu\nu}^{\lambda}$ given as

$$\Theta_{\mu\nu}^{C} = -\delta_{\mu}^{0}\delta_{\nu}^{0}\frac{k^2}{\mathbf{k}^2} - \left(1-\delta_{\mu}^{0}\right)\left(1-\delta_{\nu}^{0}\right)\left(\delta_{\mu\nu} - \frac{k_{\mu}k_{\nu}}{\mathbf{k}^2}\right), \tag{66a}$$

$$\Theta_{\mu\nu}^{F} = \eta_{\mu\nu}. \tag{66b}$$

(ii) All transversal photon lines of the other type, i.e., those connecting distinct two photon lines are to be reinterpreted as the summation of $-D^C$ or $-D^F$ plus the mean-field subtraction term

$$-\mathcal{D}_{\mu\nu}^{\lambda}(x-y) = -D_{\mu\nu}^{\lambda}(x-y) - \delta(x^0-y^0)\delta_{\mu}^{0}\delta_{\nu}^{0} \times \frac{W_{\rm HF}^{\rm loc}(\mathbf{x}) + W_{\rm HF}^{\rm loc}(\mathbf{y})}{2}. \tag{67}$$

Hereafter, we use the Feynman gauge for its simplicity, whereas we also note on the recent progress in the Coulomb gauge formalism [44–46], which indicates that the Coulomb gauge is also be applicable in practical calculations and it can be even more suitable choice [91] for molecular systems with strong electron-electron correlation effects.

B. Radiation corrections to the total energy

We first consider the relativistic radiation corrections to the total energy. For this purpose, there are a number of advanced techniques available including the S-matrix approach [92,93], the two-time Green's function technique [42], and the covariant time-evolution method [41]. A detailed comparison among those three was given in Ref. [41] where they argued that the latter two are more flexible in that they are applicable to (quasi)degenerate multidimensional model spaces which we discussed in Subsec. III A. We here adopt the two-time Green's function technique [42,94] for its clarity and broad applicability.

Following Ref. [42], we introduce an N_e electron Green's function defined as

$$\begin{aligned} &G_{TT}^{N_e}(\mathbf{x}_1,\ldots;t;\mathbf{x}_1',\ldots;t') \\ &\quad\equiv \langle\Omega_0|\frac{1}{i\hbar}\mathcal{T}\big(\mathbf{\Psi}(\mathbf{x}_1,t)\mathbf{\Psi}(\mathbf{x}_2,t)\ldots\overline{\mathbf{\Psi}}\big(\mathbf{x}_{N_e}',t'\big) \\ &\qquad\times\overline{\mathbf{\Psi}}\big(\mathbf{x}_{N_e-1}',t'\big)\ldots\big)|\Omega_0\rangle, \end{aligned} \tag{68}$$

with Ω_0 representing the vacuum and $\mathbf{\Psi}$ being the electronic annihilation operator in the Heisenberg representation, and its Fourier transformation,

$$\begin{aligned} &G_{TT}^{N_e}(\mathbf{x}_1,\ldots;\mathbf{x}_1',\ldots;\omega)2\pi\delta(\omega-\omega') \\ &\quad\equiv\int dt\int dt' e^{i\omega t - i\omega' t'} G_{TT}^{N_e}(\mathbf{x}_1,\ldots;t;\mathbf{x}_1',\ldots;t'), \end{aligned} \tag{69}$$

which is then expanded in the basis functions of the model space, $\{\Phi_I : I = 1,2,\ldots,d\}$ as

$$\begin{aligned} \mathcal{G}_{IJ}(z) \equiv &\int\prod d^3\mathbf{x}_j\int\prod d^3\mathbf{x}_j'\Phi_I^{\dagger}(\mathbf{x}_1,\ldots,\mathbf{x}_N) \\ &\times G_{TT}^{N_e}(\mathbf{x}_1,\ldots;\mathbf{x}_1',\ldots;z)\gamma_{(N_e)}^{0}\gamma_{(N_e-1)}^{0}\cdots\gamma_{(1)}^{0} \\ &\times\Phi_J(\mathbf{x}_1',\ldots,\mathbf{x}_N'). \end{aligned} \tag{70}$$

We then consider its integration along the complex contour Γ, which is supposed to enclose all the (true) eigenvalues of H of the target states but not other poles of $G_{TT}^{N_e}$, whereas in reality, poles of finite-order expansion of $G_{TT}^{N_e}$ arises from the eigenvalues of H_0 [94]. We then define the following two matrices,

$$\mathcal{S}_{IJ} \equiv \oint_{\Gamma}\frac{dz}{2\pi i}\mathcal{G}_{IJ}(z), \tag{71a}$$

$$\mathcal{K}_{IJ} \equiv \oint_{\Gamma}\frac{dz}{2\pi i}z\mathcal{G}_{IJ}(z), \tag{71b}$$

together with their operator forms, $\mathcal{S} \equiv \sum_{I,J=1}^{d}|\Phi_I\rangle\mathcal{S}_{IJ}\langle\Phi_J|$ and $\mathcal{K} \equiv \sum_{I,J=1}^{d}|\Phi_I\rangle\mathcal{K}_{IJ}\langle\Phi_J|$. The effective Hamiltonian is then constructed as

$$H_{\rm eff} = \mathcal{K}\mathcal{S}^{-1}, \tag{72}$$

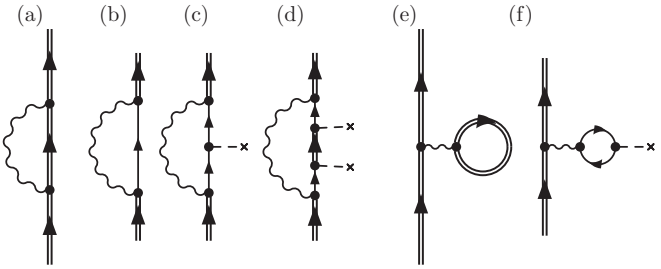

FIG. 1. The lowest order single-electron radiation corrections. Panel (a) represents the one-loop electronic self-energy correction to the Hartree-Fock propagator, which is decomposed into the free-electron self-energy (b) and one- (c) and two-potential (d) terms, whereas panel (e) represents the vacuum polarization effect, which can be approximated by the Uehling potential (f). Single and double arrows represent the free-particle and Hartree-Fock electronic propagators, respectively, the wavy lines represent photon propagators and the dashed lines emitted from crosses represent the mean-field potential field $W_{\rm HF}^{\rm loc}$.

which expands as

$$H_{\rm eff}^{(1)} = \mathcal{K}^{(1)} - \mathcal{K}^{(0)}\mathcal{S}^{(1)}, \tag{73a}$$

$$H_{\rm eff}^{(2)} = \mathcal{K}^{(2)} - \mathcal{K}^{(0)}\mathcal{S}^{(2)} - (\mathcal{K}^{(1)} - \mathcal{K}^{(0)}\mathcal{S}^{(1)})\mathcal{S}^{(0)} \cdots . \tag{73b}$$

Below, we show the outline of our scheme, which follows the Green's function approach described in Refs. [41,42,94]. Details are summarized in Appendix D.

We first evaluate diagrams arising from a single-electron interaction with the radiation field. The contribution of the one-loop self-energy [Fig. 1(a)] to the effective Hamiltonian is

$$H_{\rm eff}^{(1,SE)}{}_{ri} = (\mathcal{K}^{(1)} - \mathcal{K}^{(0)}\mathcal{S}^{(1)})_{ri} = \langle r|\Sigma(\varepsilon_i)|i\rangle, \tag{74}$$

and hence we only need the MO matrix elements of the self-energy operator Σ at energy ε_i.

Following Ref. [93], the self-energy of the Hartree-Fock propagator, Fig. 1(a) is decomposed into Figs. 1(b) to 1(d). Using the free-electron one-loop self-energy Σ_{1L} and the vertex correction [16,40] Γ_{1L}^{μ}, the summation of Figs. 1(b) and 1(c) is evaluated as

$$\langle r|\Sigma(\varepsilon_i)|i\rangle^{(b,c)} = \iint d^3\mathbf{x}d^3\mathbf{x}'\overline{\varphi}_r(\mathbf{x})\Bigg(\int \frac{d^3\mathbf{p}}{(2\pi)^3}e^{i\mathbf{p}\cdot(\mathbf{x}-\mathbf{x}')}\{\Sigma_{1L}(\mathbf{p},\varepsilon_i) - \delta m_e c^2 - (Z_2-1)[(\varepsilon_i\gamma^0 - c\mathbf{p}\cdot\boldsymbol{\gamma}) - m_e c^2]\} + \iint \frac{d^3\mathbf{p}}{(2\pi)^3}\frac{d^3\mathbf{p}'}{(2\pi)^3}e^{i\mathbf{p}'\cdot\mathbf{x}-i\mathbf{p}\cdot\mathbf{y}'}\big[\Gamma_{1L}^0(\mathbf{p}',\varepsilon_i;\mathbf{p},\varepsilon_i) - (Z_1-1)\gamma^0\big]W_{\rm HF}^{\rm loc}(\mathbf{p}'-\mathbf{p})\Bigg)\varphi_i(\mathbf{x}'), \tag{75}$$

with $\delta m_e c^2 = \Sigma_{1L}(p)|_{p=(m_e c,\mathbf{0})}$, $Z_2 - 1$ and $Z_1 - 1$ being the mass, wave function, and vertex renormalization, respectively, where $Z_2 = Z_1$ follows from the Ward identity [95,96]. Since the MOs satisfy the mean-field Dirac equation, divergent contributions proportional to $Z_2 - 1$ and $Z_1 - 1$ cancel and the remaining divergence is only $\delta m_e c^2$. Both Σ_{1L} and Γ_{1L}^{μ} have analytical expressions [40]. The remaining one, Fig. 1(d), is finite but requires numerical evaluation of the following integral:

$$\langle r|\Sigma(\varepsilon_i)|i\rangle^{(d)} = \iint d^3\mathbf{x}d^3\mathbf{x}'\iint d^3\mathbf{y}_1 d^3\mathbf{y}_2\overline{\varphi}_r(\mathbf{x})\int c\frac{dk_0}{2\pi}\gamma^{\mu}S_0^F(\mathbf{x},\mathbf{y}_1;\varepsilon_i - ck^0)\gamma^0 W_{\rm HF}^{\rm loc}(\mathbf{y}_1) \times S^F(\mathbf{y}_1,\mathbf{y}_2;\varepsilon_i - ck^0)\gamma^0 W_{\rm HF}^{\rm loc}(\mathbf{y}_2)S_0^F(\mathbf{y}_2,\mathbf{x}';\varepsilon_i - ck^0)\gamma^{\nu}\varphi_i(\mathbf{x}')D_{\mu\nu}^F(\mathbf{x},\mathbf{x}';ck^0), \tag{76}$$

with S_0^F and S^F being the free-particle and Hartree-Fock electronic Feynman propagators, respectively. Since the expression in Eq. (76) is finite, coordinate integrations can be performed numerically using the real-space expansion of those propagators, and the remaining k_0 integral is to be performed along the imaginary axis, as is established in Refs. [43].

We also consider the vacuum polarization effects, represented by Fig. 1(e). Within the first-order correction to the free-electron result, it is approximated as Fig. 1(f) and evaluated as

$$\langle r|\Sigma(\varepsilon_i)|i\rangle^{(f)} = \iint d^3\mathbf{x}d^3\mathbf{x}'\overline{\varphi}_r(\mathbf{x})\Sigma^{vp,1}(\mathbf{x},\mathbf{x}';\omega)\varphi_i(\mathbf{x}'), \tag{77}$$

where $\Sigma^{vp,1}$ is defined as

$$\Sigma^{vp,1}(\mathbf{x},\mathbf{x}';\omega) \equiv \int \frac{d^3\mathbf{q}}{(2\pi)^3}e^{i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')}\gamma^{\mu}D_{\mu\nu}^F(\mathbf{q},0) \times \Pi_{1L}^{v0}(\mathbf{q},0)W_{\rm HF}^{\rm loc}(\mathbf{q}), \tag{78}$$

with $\Pi_{1L}^{\mu\nu}$ being the one-loop vacuum polarization function [16] calculated using the free-electron propagators. This integral is then evaluated by using the integral representation of

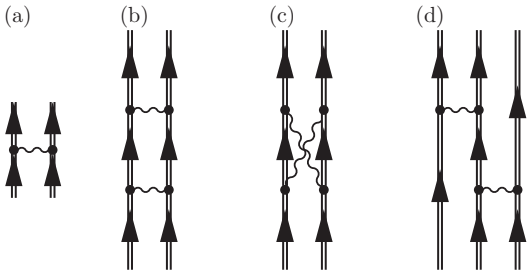

FIG. 2. Electron-electron interaction diagrams. Notations are the same as those in Fig. 1. Each panel is referred to as (a) single-photon exchange, (b) ladder, (c) crossed ladder, and (d) three-electron ladder, respectively. As stated in the main text, each photon line in these diagrams is evaluated with the mean-field subtraction term as Eq. (67).

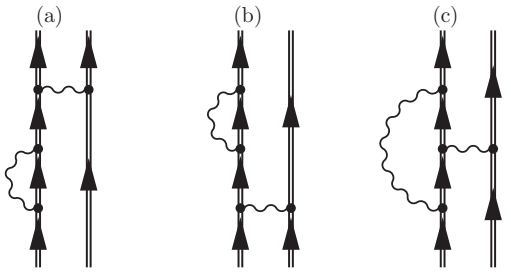

FIG. 3. Diagrams arising from combination of single-electron and electron-electron interaction terms, referred to as the screened self-energies. Notations are the same as those in Fig. 1. In these figures, the photon lines connecting the two distinct electron lines accompany the mean-field subtraction term.

the Uehling potential [20], which results in

$$\Sigma^{vp,1}(\mathbf{x},\mathbf{y};\omega)=\delta(\mathbf{x}-\mathbf{y})\int\frac{d^3\mathbf{q}}{(2\pi)^3}e^{i\mathbf{q}\cdot\mathbf{x}}\frac{-e^2}{\pi}\int_1^\infty ds\sqrt{s^2-1}\times\left(\frac{2}{3s^2}+\frac{1}{3s^4}\right)\frac{\mathbf{q}^2}{\mathbf{q}^2+4s^2\kappa_C^2}W_{\rm HF}^{\rm loc}(\mathbf{q}),\quad(79)$$

where $\kappa_C\equiv m_ec/\hbar$ represents the inverse of the (reduced) electronic Compton wavelength. The total self-energy, in our present scheme, is thus given by

$$\Sigma=\Sigma^{(b)}_{fin.}+\Sigma^{(c)}_{fin.}+\Sigma^{(d)}+\Sigma^{vp,1},\qquad(80)$$

where the subscript $fin.$ stands for the finite part.

We next consider the lowest two orders of the electron-electron interaction terms, which are represented by the four diagrams in Fig. 2. The corresponding explicit expressions are shown in Appendix D.

We also consider the second-order diagrams arising from a combination of single-electron and two-electron terms. In the present level of calculation, such combination takes the same form as the screened self-energy, which is discussed extensively in Refs. [46,97–99]. We therefore follow the discussions in Refs. [46,98] and consider the three diagrams in Fig. 3, whose explicit expressions are also given in Appendix D. We have thus shown a perturbative calculation scheme of $H_{\rm eff}^{\rm el,rad}$.

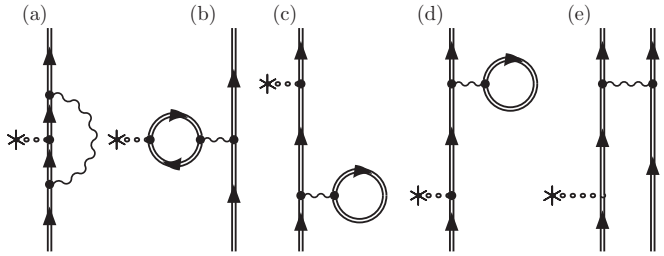

FIG. 4. Diagrams representing the second-order expansion of $\mathcal{O}_{\rm eff}$. Hexacrosses represent the operation of $\mathcal{O}$, whereas other notations are the same as those of Fig. 1.

C. Radiation corrections to general observables

We next discuss evaluation of general matrix of the form Eq. (57), which represents a radiation-corrected operator for a given observable $\mathcal{O}$ [hereafter, we drop subscript A in Eq. (57)]. We use the perturbative expression of Ω given in Eq. (41), to derive an order-by-order expansion of $\mathcal{O}_{\rm eff}$

$$\mathcal{O}^{{\rm eff}\,(0)}=\mathcal{P}\mathcal{O}\mathcal{P},\qquad(81a)$$

$$\mathcal{O}^{{\rm eff}\,(1)}=\mathcal{P}\mathcal{O}U_\eta^{(1)}\mathcal{P},\qquad(81b)$$

$$\mathcal{O}^{{\rm eff}\,(2)}=\mathcal{P}\mathcal{O}U_\eta^{(2)}\mathcal{P}-\mathcal{P}\mathcal{O}U_\eta^{(1)}\mathcal{P}\mathscr{S}^{(1)}\mathcal{P}-\mathcal{P}\mathcal{O}\mathcal{P}\mathscr{S}^{(2)}\mathcal{P},$$
$$\cdots\qquad(81c)$$

with $\mathscr{S}^{(r)}\equiv\mathcal{P}U_\eta^{(r)}\mathcal{P}$. All η appearing in Eq. (81) are to be understood as a sufficiently small positive number, which is to be taken the limit $\eta\to+0$ in the end.

We take an example in the single-particle potential-type operator $\mathcal{O}=\int d^3\mathbf{x}\overline{\psi}(\mathbf{x})\gamma^0o(\mathbf{x})\psi(\mathbf{x})$, where $o(\mathbf{x})$ is an arbitrary given potential function. Again, we construct perturbation series by $H_{\rm int}^{\rm el\ tr}$. Since $H_{\rm int}^{\rm el\ tr}$ is odd in the photon number while potential type operator $\mathcal{O}$ is not, the lowest order nontrivial contribution therefore arises from the second order,

$$\mathcal{O}^{(2)}_{\rm eff}=\mathcal{P}\mathcal{O}U_\eta^{(2)}\mathcal{P}-\mathcal{P}\mathcal{O}\mathcal{P}\mathscr{S}^{(2)}\mathcal{P}.\qquad(82)$$

The diagrammatic expression of the corresponding perturbation series are shown in Fig. 4. Among those diagrams, we first evaluate the one-particle irreducible ones, shown as Figs. 4(a) and 4(b), the sum of which reads

$$\mathcal{O}^{(a,b)}_{{\rm eff}\ ri}=i\hbar e^2\int d^3\mathbf{x}\iint d^3\mathbf{y}_1d^3\mathbf{y}_2\iint_{-\infty}^0 d\tau_1d\tau_2\overline{\varphi}_r(\mathbf{y}_1)\gamma^\mu S^F(\xi_1,\tau_1;\mathbf{x},0)\gamma^0o(\mathbf{x})S^F(\mathbf{x},0;\mathbf{y}_2,\tau_2)\gamma^\nu$$
$$\times\varphi_i(\mathbf{y}_2)e^{i(\xi_r\tau_1-\xi_i\tau_2)}D_{\mu\nu}(\mathbf{y}_1,\tau_1;\mathbf{y}_2,\tau_2)+i\hbar e^2\int d^3\mathbf{x}\iint d^3\mathbf{y}_1d^3\mathbf{y}_2\iint_{-\infty}^0 d\tau_1d\tau_2{\rm Tr}[\gamma^0S^F(\mathbf{x},0;\mathbf{y}_1,\tau_1)\gamma^\mu$$
$$\times S^F(\mathbf{y}_1,\tau_1;\mathbf{x},0)]\,\overline{\varphi}_r(\mathbf{y}_2)\gamma^\nu\varphi_i(\mathbf{y}_2)e^{i(\xi_r-\xi_i)\tau_2}D_{\mu\nu}(\mathbf{y}_1,\tau_1;\mathbf{y}_2,\tau_2),\qquad(83)$$

with ξ_ℓ being the reduced molecular orbital energy $\xi_\ell\equiv\varepsilon_\ell/\hbar$. In Eq. (83), the photon propagator $D_{\mu\nu}$ is the transversal photon propagator $D^{\rm tr}_{\mu\nu}$, but it is to be replaced to $D^F_{\mu\nu}$ when we reintroduce the Coulombic interactions. Equation (83) can then be further rewritten as

$$\mathcal{O}^{(a,b)}_{{\rm eff}\ ri}=\iiint d^3\mathbf{x}d^3\mathbf{y}_1d^3\mathbf{y}_2\iint_{-\infty}^0 d\tau_1d\tau_2\overline{\varphi}_r(\mathbf{y}_1)\Gamma^0_{1L}(\mathbf{y}_1,\tau_1;\mathbf{y}_2,\tau_2;\mathbf{x},0)\varphi_i(\mathbf{y}_2)o(\mathbf{x})e^{i(\xi_r\tau_1-\xi_i\tau_2)}$$
$$+\iiint d^3\mathbf{x}d^3\mathbf{y}_1d^3\mathbf{y}_2\iint_{-\infty}^0 d\tau_1d\tau_2o(\mathbf{x})\Pi^{0\mu}_{1L}(\mathbf{x},0;\mathbf{y}_1,\tau_1)D_{\mu\nu}(\mathbf{y}_1,\tau_1;\mathbf{y}_2,\tau_2)\overline{\varphi}_r(\mathbf{y}_2,\tau_2)\gamma^\nu\varphi_i(\mathbf{y}_2)e^{i(\xi_r-\xi_i)\tau_2}\qquad(84)$$

with Γ_{1L} and Π_{1L} representing the one-photon vertex function and the vacuum polarization function, respectively. With use of the established techniques for removing divergences from these functions [16,40], we can set Eq. (84) free of divergences.

We next consider the one-particle reducible diagrams, Figs. 4(c) and 4(d). We first consider the part $\mathcal{POU}^{(2)}\mathcal{P}$ whereas the "subtraction term," $\mathcal{POP}\mathscr{S}^{(2)}\mathcal{P}$, will be taken into account later. The diagram Fig. 4(c) reads

$$\begin{aligned}\mathcal{O}^{(c)}_{\mathrm{eff}\,ri} &= \int\!\!\int_{-\infty}^{0} d\tau_1 d\tau_2 \iiint d^3\mathbf{x} d^3\mathbf{y}_1 d^3\mathbf{y}_2 \overline{\varphi}_r(\mathbf{x})\gamma^0 o(\mathbf{x}) S^F(\mathbf{x},0;\mathbf{y}_1,\tau_1)\gamma^\mu \varphi_i(\mathbf{y}_1) e^{-i\xi_i\tau_1} \\ &\quad \times e^2 D_{\mu\nu}(\mathbf{y}_1,\tau_1;\mathbf{y}_2,\tau_2)\mathrm{Tr}\big[-i\hbar\gamma^\mu S^F(\mathbf{y}_2,\tau_2-0;\mathbf{y}_2,\tau_2)\big] - \text{subtraction term} \\ &= i\hbar\int\frac{d\omega}{2\pi}\int\frac{d^3\mathbf{k}}{(2\pi)^3}\sum_\lambda \frac{1}{\hbar(\omega-\xi_i-i\eta)}\frac{1}{\hbar[\omega-\xi_\lambda(1-i\epsilon)]}\frac{4\pi e^2\eta_{\mu\nu}}{\mathbf{k}^2}\varrho^\nu_{\mathbf{k}}\langle\overline{\varphi}_\lambda|\gamma^\mu_{\mathbf{k}}|\varphi_i\rangle\langle\overline{\varphi}_r|\gamma^0 o|\varphi_\lambda\rangle - \text{subtraction term}. \end{aligned} \tag{85}$$

Matrices newly introduced in Eq. (85) are defined as $\langle\overline{\varphi}_a|\gamma^\mu_{\mathbf{k}}|\varphi_b\rangle \equiv \int d^3\mathbf{x}\overline{\varphi}_a(\mathbf{x})\gamma^\mu e^{-i\mathbf{k}\cdot\mathbf{x}}\varphi_b(\mathbf{x})$ and $\varrho^\nu_{\mathbf{k}} \equiv \int d^3\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}}\mathrm{Tr}[-i\hbar S^F(\mathbf{r},-\epsilon;\mathbf{r},0)\gamma^\nu]$. The subtraction term has the same form of expression as described above with λ limited to $\mathscr{H}_0$. We thus obtain

$$\mathcal{O}^{(c)}_{\mathrm{eff}\,ri} = i\hbar\int\frac{d\omega}{2\pi}\int\frac{d^3\mathbf{k}}{(2\pi)^3}\sum_{\lambda\notin\mathscr{H}_0}\frac{1}{\hbar(\omega-\xi_i-i\eta)}\frac{1}{\hbar[\omega-\xi_\lambda(1-i\epsilon)]}\frac{4\pi e^2\eta_{\mu\nu}}{\mathbf{k}^2}\varrho^\nu_{\mathbf{k}}\langle\overline{\varphi}_\lambda|\gamma^\mu_{\mathbf{k}}|\varphi_i\rangle\langle\overline{\varphi}_r|\gamma^0 o|\varphi_\lambda\rangle \tag{86}$$

We can also evaluate Fig. 4(d) as

$$\mathcal{O}^{(d)}_{\mathrm{eff}\,ri} = i\hbar\int\frac{d\omega}{2\pi}\int\frac{d^3\mathbf{k}}{(2\pi)^3}\sum_{\lambda\notin\mathscr{H}_0}\frac{1}{\hbar(\xi_r-\omega-i\eta)}\frac{1}{\hbar[\omega-\xi_\lambda(1-i\epsilon)]}\frac{4\pi e^2\eta_{\mu\nu}}{\mathbf{k}^2}\varrho^\nu_{\mathbf{k}}\langle\overline{\varphi}_r|\gamma^\mu_{\mathbf{k}}|\varphi_\lambda\rangle\langle\overline{\varphi}_\lambda|\gamma^0 o|\varphi_i\rangle \tag{87}$$

For the diagonal element, where $\mathcal{O}^{(d)}_{\mathrm{eff}\,ii}$ should take a real value, Eqs. (86) and (87) sums up as

$$\mathcal{O}^{(c,d)}_{\mathrm{eff}\,ii} = \int\frac{d^3\mathbf{k}}{(2\pi)^3}\sum_{\lambda\notin\mathscr{H}_0}\frac{1}{\hbar[\xi_i-\xi_\lambda(1-i\epsilon)]}\frac{4\pi e^2\eta_{\mu\nu}}{\mathbf{k}^2}\varrho^\nu_{\mathbf{k}}\langle\overline{\varphi}_i|\gamma^\mu_{\mathbf{k}}|\varphi_\lambda\rangle\langle\overline{\varphi}_\lambda|\gamma^0 o|\varphi_i\rangle. \tag{88}$$

Much less convenient expressions in the general cases, as Eqs. (86) and (87), result from the upper limit in the time integration. We will discuss this problem in Appendix D. Nevertheless, we have shown a formal expression of radiation corrections to a typical potential-type operator.

V. SUMMARY AND DISCUSSIONS

In this paper, we have discussed a general framework for relativistic electron-nucleus coupled dynamics of molecules, which has been recently realized by progress in experimental techniques. Starting from the exact QED formulation of the system, we derived a formal expression of our target dynamical observable as Eqs. (16) and (17), with the latter represented, using a formal perturbation expansion given as Eq. (30). Although being unfeasible for numerical implementation, we consider these expressions potentially useful to get an overview of the correlated dynamics of the electron, nucleus, and radiation field.

We then have rearranged the perturbation expansion as represented by Eqs. (41) and (45) in order to obtain a more tractable expression. Under several restrictions, we derived Eq. (59), as a practical expression, potentially feasible for numerical implementation. Indeed, calculation of the effective Hamiltonian Eq. (45) and effective observable, Eq. (57), for a given nuclear configuration should be within the reach of existing techniques as we examined in Sec. IV. Moreover, inclusion of the radiation corrections into the form of an effective Hamiltonian realizes smooth connection to the Schrödinger dynamics of nuclei. We have shown that the dynamics represented by the path-integral expression with effective Hamiltonian, Eq. (59), is essentially equivalent to the Schrödinger dynamics represented by Eq. (63), whose numerical integration should be achievable by many of existing techniques.

We have also carefully examined the limitations of Eq. (59) and/or restrictions intrinsic to this formulation, which include limited size of the basis set and absence of radiative excitations. The formulation given here should also be insufficient for dynamics with rapidly decaying states. Although we presented possible extension in Appendix C, details are left to future study.

In this paper, electron-radiation couplings are treated in a perturbation-theoretic manner. Yet it should be applicable to experimental dynamics induced by high-energy photons such as x rays, in which smallness of the vector field amplitude allows perturbation theory analysis [28]. On the other hand, it should be hardly applicable to systems of nonperturbative strength of electron-radiation coupling, such as dynamics induced by ultrastrong infrared laser fields. Nonperturbative formulation has been discussed separately in our recent publication, which proposes a wave-packet approach to relativistic dynamics [33].

Another advantage of our approach is its close tie to the established static QED calculation schemes, which should work favorably in extending and combining the present theory with the other developing sophisticated theories such as MBPT [48] and Coulomb gauge formalism [44–46]. Although we have shown, in Sec. IV, explicit expressions of radiation correction, we further need to find a way to obtain high-quality correlated wave functions in order to obtain accurate numerical values in calculations, as was suggested in Ref. [41]. For this purpose, we conceive that we can make use of tools developed in relativistic quantum chemistry since our

effective Hamiltonian at each step is built on a fixed-nuclei model. Assets in the quantum chemistry, including efficient basis sets [100], variational techniques [58], and computation techniques [101,102], should be exploited in future numerical calculations.

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APPENDIX A: THE GENERALIZED GELL-MANN-LOW THEOREM

We here discuss a multidimensional extension of the Gell-Mann-Low theorem, represented by Eqs. (40a) and (40b), which was formulated in Refs. [80,81]. In order to clarify the details including underlying assumptions, we briefly show the derivation, closely following Ref. [81]. A similar theorem was also discussed in Ref. [41] but with different assumptions.

We assume that the total Hamiltonian H is decomposed into the zeroth-order Hamiltonian H_0 and the interaction part $H_{\rm int}$. We introduce a projection operator $\mathcal{P}$ which projects state vectors in the total Hilbert space $\mathscr{H}$ onto a d-dimensional subspace $\mathscr{H}_0$. We require that the subspace $\mathscr{H}_0$ should be invariant with respect to the operation of H_0 [Eq. (39)].

We then switch to the interaction representation and introduce a perturbative time-evolution operator with a damping factor $\eta > 0$

$$U_\eta(0,\mp\infty) \equiv \sum_r \frac{1}{r!}\left(\frac{1}{i\hbar}\right)^r \int_{\mp\infty}^{0} \prod dt_j (\mathcal{T}/\widetilde{\mathcal{T}}) g^r \times H_{\rm int}(t_1)\dots H_{\rm int}(t_r) e^{-\eta\sum_j |t_j|}, \tag{A1}$$

with g being a dimensionless constant that scales $H_{\rm int}$, which takes a fixed value $g=1$ and is to be neglected in the final results. As was shown in the original derivation [39], $U_\eta(0,\mp\infty)$ satisfies the following equation:

$$[H_0, U_\eta(0,\mp\infty)] = -H_{\rm int}(0)U_\eta(0,\mp\infty) \pm i\hbar\eta g\frac{\partial}{\partial g}U_\eta(0,\mp\infty), \tag{A2}$$

or, equivalently,

$$HU_\eta(0,\mp\infty) = U_\eta(0,\mp\infty)H_0 \pm i\hbar\eta g\frac{\partial}{\partial g}U_\eta(0,\mp\infty). \tag{A3}$$

We then introduce a mapping operator $U_\eta(0,\mp\infty)\frac{1}{\mathcal{P}U_\eta(0,\mp\infty)\mathcal{P}}$, where $\frac{1}{\mathcal{P}U_\eta(0,\mp\infty)\mathcal{P}}$ is to be understood as $\mathcal{P}\frac{1}{\mathcal{P}U_\eta(0,\mp\infty)\mathcal{P}}\mathcal{P}$. Using Eq. (A3), we obtain

$$\left[H \mp i\hbar\eta g\frac{\partial}{\partial g}\right]U_\eta^{(\mp)}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}} = U_\eta^{(\mp)}H_0\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}} \pm U_\eta^{(\mp)}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}i\hbar\eta g\frac{\partial U_\eta^{(\mp)}}{\partial g}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}, \tag{A4}$$

with a shorthand notation $U_\eta^{(\mp)} \equiv U_\eta(0,\mp\infty)$. Recalling the assumption that $\mathscr{H}_0$ is closed with respect to the operation of H_0, we have

$$\begin{aligned} U_\eta^{(\mp)}H_0\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}} &= U_\eta^{(\mp)}\mathcal{P}H_0\mathcal{P}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}\mathcal{P} \\ &= U_\eta^{(\mp)}\mathcal{P}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}\mathcal{P}U_\eta^{(\mp)}H_0\mathcal{P}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}\mathcal{P}. \end{aligned} \tag{A5}$$

Substituting Eq. (A5) into Eq. (A4), and also making use of Eq. (A3), we obtain

$$\begin{aligned} \left[H \mp i\hbar\eta g\frac{\partial}{\partial g}\right]U_\eta^{(\mp)}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}} &= U_\eta^{(\mp)}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}\left(\mathcal{P}U_\eta^{(\mp)}H_0\mathcal{P}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}\mathcal{P} \pm i\hbar\eta g\frac{\partial U_\eta^{(\mp)}}{\partial g}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}\right) \\ &= U_\eta^{(\mp)}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}\left(\mathcal{P}HU_\eta^{(\mp)}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}\right). \end{aligned} \tag{A6}$$

Assuming the existence of the limit $\eta \to +0$ and also assuming finiteness of $g\frac{\partial}{\partial g}U_\eta^{(\mp)}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}$ [so that the second term in the LHS of Eq. (A6), $i\hbar\eta g\frac{\partial}{\partial g}U_\eta^{(\mp)}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}}$ vanishes as $\eta \to +0$], we finally obtain

$$H\Omega^{(\mp)}\mathcal{P} = \Omega\{\mathcal{P}H\Omega^{(\mp)}\mathcal{P}\} \tag{A7}$$

with

$$\Omega^{(\mp)} \equiv \lim_{\eta\to+0} U_\eta(0,\mp\infty)\frac{1}{\mathcal{P}U_\eta(0,\mp\infty)\mathcal{P}}, \tag{A8}$$

which is a linear operator acting on $\mathscr{H}_0$. This proves the main part of the generalized Gell-Mann-Low theorem, Eq. (40a) in the main text. Using Eq. (A8), we can also show

$$\mathcal{P}\Omega^{(\mp)} = \lim_{\eta\to+0}\mathcal{P}U_\eta^{(\mp)}\mathcal{P}\frac{1}{\mathcal{P}U_\eta^{(\mp)}\mathcal{P}} = \mathcal{P}, \tag{A9}$$

which proves the supplemental relation Eq. (40b). As we have shown that either expression of Ω [Eq. (A8)] satisfies Eqs. (40a) and (40b), we can drop superscript $(\mp)$ in the subsequent discussion, which does not depend on the choice of sign.

As we discussed in the main text, $H^{\rm eff} \equiv \mathcal{P}H\Omega\mathcal{P}$ works as an effective Hamiltonian in $\mathscr{H}_0$. Expanding $\mathscr{H}_0$ with a d-dimensional orthonormal basis set $\{|I\rangle; I = 1, 2, \dots, d\}$, we

obtain

$$H\Omega|I\rangle = \sum_{J=1}^{d} \Omega|J\rangle H^{\rm eff}_{JI} \tag{A10}$$

and the right eigenvector of $H^{\rm eff}$ works as a preimage of the true eigenvector

$$\sum_{K=1}^{d} H^{\rm eff}_{JK} F^K_\alpha = \mathcal{E}_\alpha F^J_\alpha, \tag{A11a}$$

$$\Omega \sum_{K=1}^{d} |K\rangle F^K_\alpha = |\Psi_\alpha\rangle. \tag{A11b}$$

These preimage vectors are in general not necessarily eigenvectors of H_0, which is in contrast to the remark related to an another variant of the generalized Gell-Mann-Low theorem (or the generalized Gell-Mann-Low relation) in p. 183 of Ref. [41]. The starting assumption here is invariance of $\mathscr{H}_0$ with respect to the operation of H_0. It is a natural multidimensional extension of its one-dimensional counterpart [39], which requires the preimage vector to be an eigenvector of H_0.

In the above discussion, there appears no explicit restriction on the choice of $\mathscr{H}_0$ except that it should be invariant with respect to the operation of H_0. In the application to bound-state QED models, however, we have to take account of radiative decays of excited states when we construct a perturbation expansion of U_η. One of the most sophisticated formulations of quasidegenerate models of bound-state QED, given in Refs. [42,94], suggests that one should introduce photon mass μ, which is much larger than any of energy differences among states in $\mathscr{H}_0$ but much smaller than any energy differences between an energy eigenstate in $\mathscr{H}_0$ and one that does not belong to $\mathscr{H}_0$. Such treatment should certainly remove possible radiative decay among $\mathscr{H}_0$, whereas it also means that the largest energy separation among $\mathscr{H}_0$ should be much smaller than the smallest energy separation between states in and outside of $\mathscr{H}_0$.

APPENDIX B: PROOFS OF SEVERAL EQUATIONS RELATED TO THE DERIVATIVE COUPLINGS

We here prove several equations related to the derivative couplings we encountered in Subsec. III A. We first derive Eq. (54). We start from evaluation of derivative coupling between two distinct preimage vectors

$$\langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}|F_\beta\rangle = \frac{1}{\mathcal{E}_\beta - \mathcal{E}_\alpha}\langle\widetilde{F}_\alpha|\frac{\partial H^{\rm el,rad}_{\rm eff}}{\partial\mathbf{R}}|F_\beta\rangle, \tag{B1}$$

and by differentiation of Eq. (45), $\partial H^{\rm el,rad}_{\rm eff}/\partial\mathbf{R}$ expands as

$$\begin{aligned}\frac{\partial}{\partial\mathbf{R}}H^{\rm el,rad}_{\rm eff} = {}& \left(\frac{\partial}{\partial\mathbf{R}}\mathcal{P}\right)H^{\rm el,rad}\Omega\mathcal{P} + \mathcal{P}\left(\frac{\partial}{\partial\mathbf{R}}H^{\rm el,rad}\right)\Omega\mathcal{P} \\ & + \mathcal{P}H^{\rm el,rad}\left(\frac{\partial}{\partial\mathbf{R}}\Omega\right)\mathcal{P} + \mathcal{P}H^{\rm el,rad}\Omega\left(\frac{\partial}{\partial\mathbf{R}}\mathcal{P}\right).\end{aligned} \tag{B2}$$

We then consider the derivative of $\mathcal{P}$. Using an arbitrary orthonormal basis set $\{|I\rangle : I = 1, 2, ..., d\}$, which expands $\mathscr{H}_0$ and also extends outside of $\mathscr{H}_0$, as $\{|I\rangle : I = d+1, d+2, ...\}$, $\frac{\partial}{\partial\mathbf{R}}\mathcal{P}$ expands as

$$\begin{aligned}\frac{\partial}{\partial\mathbf{R}}\mathcal{P} = {}& \sum_{A\notin\mathscr{H}_0, I\in\mathscr{H}_0} |A\rangle\langle A|\frac{\partial}{\partial\mathbf{R}}|I\rangle\langle I| \\ & - \sum_{A\notin\mathscr{H}_0, I\in\mathscr{H}_0} |I\rangle\langle I|\frac{\partial}{\partial\mathbf{R}}|A\rangle\langle A|,\end{aligned} \tag{B3}$$

which does not include block-diagonal projection to $\mathscr{H}_0$, i.e., $\mathcal{P}(\frac{\partial}{\partial\mathbf{R}}\mathcal{P})\mathcal{P} = 0$. Turning to a specific representation, $\mathcal{P} = \sum_{a=1}^{d}|F_\alpha\rangle\langle\widetilde{F}_\alpha|$, we can derive

$$\frac{\partial}{\partial\mathbf{R}}\mathcal{P} = (1-\mathcal{P})\sum_{\alpha=1}^{d}\left|\frac{\partial}{\partial\mathbf{R}}F_\alpha\right\rangle\langle\widetilde{F}_\alpha| + \sum_{\alpha=1}^{d}|F_\alpha\rangle\left\langle\frac{\partial}{\partial\mathbf{R}}\widetilde{F}_\alpha\right|(1-\mathcal{P}). \tag{B4}$$

The remaining parts can also be expanded using Eq. (43). Since we are only interested in the matrix element in Eq. (B1), we only need a part of Eq. (B3), projected as $\mathcal{P}(\partial H^{\rm el,rad}_{\rm eff}/\partial\mathbf{R})\mathcal{P}$, which is expanded as

$$\begin{aligned}\mathcal{P}\left(\frac{\partial}{\partial\mathbf{R}}H^{\rm el,rad}_{\rm eff}\right)\mathcal{P} = {}& \sum_{\alpha,\beta=1}^{d}|F_\alpha\rangle\langle\Psi_\alpha|\frac{\partial H^{\rm el,rad}}{\partial\mathbf{R}}|\Psi_\beta\rangle\langle\widetilde{F}_\beta| + \sum_{\alpha,\beta=1}^{d}|F_\alpha\rangle\mathcal{E}_\alpha\langle\Psi_\alpha|\frac{\partial}{\partial\mathbf{R}}|\Psi_\beta\rangle\langle\widetilde{F}_\beta| \\ & + \sum_{\alpha,\beta=1}^{d}|F_\alpha\rangle\mathcal{E}_\alpha\left\langle\frac{\partial}{\partial\mathbf{R}}\widetilde{F}_\alpha\right| + \mathcal{P}\left(\frac{\partial}{\partial\mathbf{R}}\mathcal{P}\right)H^{\rm el,rad}\Omega\mathcal{P} + \mathcal{P}H^{\rm el,rad}\Omega\left(\frac{\partial}{\partial\mathbf{R}}\mathcal{P}\right)\mathcal{P} \\ = {}& \sum_{\alpha,\beta=1}^{d}|F_\alpha\rangle(\mathcal{E}_\beta - \mathcal{E}_\alpha)\langle\Psi_\alpha|\frac{\partial}{\partial\mathbf{R}}|\Psi_\beta\rangle\langle\widetilde{F}_\beta| + \sum_{\alpha,\beta=1}^{d}|F_\alpha\rangle\mathcal{E}_\alpha\left(\langle\Psi_\alpha|\frac{\partial}{\partial\mathbf{R}}|\Psi_\beta\rangle - \langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}|F_\beta\rangle\right)\langle\widetilde{F}_\beta| \\ & + \sum_{\alpha,\beta=1}^{d}|F_\alpha\rangle\left(\langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}\mathcal{P}|\Psi_\beta\rangle\mathcal{E}_\beta + \mathcal{E}_\alpha\langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}\mathcal{P}|F_\beta\rangle\right)\langle\widetilde{F}_\beta|,\end{aligned} \tag{B5}$$

where in the last side, $\langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}\mathcal{P}|F_\beta\rangle$ vanishes because of $\mathcal{P}(\frac{\partial}{\partial\mathbf{R}}\mathcal{P})\mathcal{P} = 0$. We therefore obtain

$$\langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}|F_\beta\rangle = \langle\Psi_\alpha|\frac{\partial}{\partial\mathbf{R}}|\Psi_\beta\rangle + \frac{\mathcal{E}_\alpha}{\mathcal{E}_\beta - \mathcal{E}_\alpha}\left(\langle\Psi_\alpha|\frac{\partial}{\partial\mathbf{R}}|\Psi_\beta\rangle - \langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}|F_\beta\rangle\right) + \frac{1}{\mathcal{E}_\beta - \mathcal{E}_\alpha}\left(\langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}\mathcal{P}|\Psi_\beta\rangle\mathcal{E}_\beta\right). \tag{B6}$$

Moving $\langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}|F_\beta\rangle$ in the RHS to LHS and applying Eq. (B4), we finally obtain

$$\langle\widetilde{F}_\alpha|\frac{\partial}{\partial\mathbf{R}}|F_\beta\rangle = \langle\Psi_\alpha|\frac{\partial}{\partial\mathbf{R}}|\Psi_\beta\rangle + \langle\frac{\partial}{\partial\mathbf{R}}\widetilde{F}_\alpha|(1-\mathcal{P})|\Psi_\beta\rangle, \quad \text{(B7)}$$

which proves Eq. (54).

We next show equivalence of Eqs. (52) and (56). It is enough to show the equivalence of a single-step time evolution, which reads, for each representation,

$$\begin{aligned} &e^{-i\epsilon H_{\rm eff}/\hbar}\sum_\beta |F_\beta:\mathbf{R}_0\rangle c_0^\beta \\ &\quad=\sum_{\gamma\beta\alpha}|F_\gamma:\mathbf{R}_1\rangle(e^{-\epsilon\dot{\mathbf{R}}\cdot\mathbf{X}^{\rm eff}})_{\gamma\beta}(e^{-i\epsilon H_{\rm eff}/\hbar})_{\beta\alpha}c_0^\alpha \\ &\quad=\sum_{J\gamma\beta\alpha}|J:\mathbf{R}_1\rangle F_\gamma^J(\mathbf{R}_1)(e^{-\epsilon\dot{\mathbf{R}}\cdot\mathbf{X}^{\rm eff}})_{\gamma\beta}(e^{-i\epsilon H_{\rm eff}/\hbar})_{\beta\alpha}c_0^\alpha \quad \text{(B8)} \end{aligned}$$

and

$$\begin{aligned} &e^{-i\epsilon H_{\rm eff}^{\mathscr{B}}/\hbar}\sum_{I,\beta}|I:\mathbf{R}_0\rangle F_\beta^I(\mathbf{R}_0)c_0^\beta \\ &\quad=|J:\mathbf{R}_1\rangle\left(e^{-\epsilon\dot{\mathbf{R}}\cdot\mathbf{X}_{\rm eff}^{\mathscr{B}}}\right)_{JK}\left(e^{-i\epsilon H_{\rm eff}^{\mathscr{B}}/\hbar}\right)_{KL}F_a^L(\mathbf{R}_0)c_0^\alpha \\ &\quad=|J:\mathbf{R}_1\rangle(e^{-\epsilon\dot{\mathbf{R}}\cdot\mathbf{X}_{\rm eff}^{\mathscr{B}}})_{JK}F_\beta^K(\mathbf{R}_0)\left(e^{-i\epsilon H_{\rm eff}^{\mathscr{B}}/\hbar}\right)_{\beta\alpha}c_0^\alpha, \quad \text{(B9)} \end{aligned}$$

respectively. Our task thus reduces to prove

$$\sum_\gamma F_\gamma^J(\mathbf{R}_1)(e^{-\epsilon\dot{\mathbf{R}}\cdot\mathbf{X}^{\rm eff}})_{\gamma\beta} = \sum_K\left(e^{-\epsilon\dot{\mathbf{R}}\cdot\mathbf{X}_{\rm eff}^{\mathscr{B}}}\right)_{JK}F_\beta^K(\mathbf{R}_0). \quad \text{(B10)}$$

To prove Eq. (B10), we consider an overlap $\langle J:\mathbf{R}_1|F_\beta:\mathbf{R}_0\rangle$, which can be evaluated either by forward propagating the ket vector or backward propagating the bra vector as

$$\begin{aligned} &\langle J:\mathbf{R}_1|F_\beta:\mathbf{R}_0\rangle \\ &\quad=\langle J:\mathbf{R}_1|\left[\sum_\gamma|F_\gamma:\mathbf{R}_1\rangle(e^{-\epsilon\dot{\mathbf{R}}\cdot\mathbf{X}^{\rm eff}})_{\gamma\beta}\right] \\ &\quad=\left[\sum_K\left(e^{-\epsilon\dot{\mathbf{R}}\cdot\mathbf{X}_{\rm eff}^{\mathscr{B}}}\right)_{JK}\langle K:\mathbf{R}_0|\right]|F_\beta:\mathbf{R}_0\rangle, \quad \text{(B11)} \end{aligned}$$

which proves Eq. (B10). Extending the above observation to multiple steps, we can show equivalence of Eqs. (52) and (56).

APPENDIX C: DECAYING STATES

Short-time and/or high-energy dynamics naturally includes excited states, which are, in general, subject to radiative decay processes. Such decay processes may restrict the validity of the standard wave operator formulation which is based on a formal long-time limit of perturbative time propagation.

Here we consider a possible alternative formulation that takes account of radiative decays in an explicit manner. We assume unstable states with relatively large radiative decay widths whose corresponding life time being comparable in order to the typical timescale of the target dynamics. We then consider the Laplace-Fourier transformation method introduced in the classic textbook by Heitler [103] with a slight extension.

1. Basic formulation

We assume that the total Hamiltonian H is decomposed into the zeroth-order Hamiltonian H_0 and the interaction part V. We expand the states with a set of states $\{|\Phi_X\rangle\}$ which are eigenstates of H_0, $H_0|\Phi_X\rangle = E_X|\Phi_X\rangle$. We consider a d-dimensional subspace $\mathscr{H}_0$ and its associated projection operator $\mathcal{P}$ and its complement $\mathcal{Q}=1-\mathcal{P}$. States in $\mathscr{H}_0$ and its complement space, denoted by $\mathscr{H}^{\complement}$, are labeled by indices I, J, K, ... and A, B, C, ..., respectively, whereas states of general type are labeled by indices X, Y, Z, ... States with distinct labels are, for simplicity of discussion, assumed to be orthonormal. We also use a symbol $\mathcal{I}_0$ to indicate the set of state labels in $\mathscr{H}_0$.

Time-dependent state of the system is represented as $|\Psi_t\rangle=\sum_X|\Phi_X\rangle c_X(t)$, which starts as $|\Psi_0\rangle=\sum_{I\in\mathcal{I}_0}|\Phi_I\rangle c_I^{\rm ini}$ at $t=0$. With such an initial condition, we solve the time evolution equation

$$i\hbar\partial_t|\Psi_t\rangle = (H_0+V)|\Psi_t\rangle. \quad \text{(C1)}$$

We then apply the Laplace-Fourier transformation to the coefficients

$$C_X(\omega)=\frac{1}{i\hbar}\int_0^\infty dt e^{i\omega t}c_X(t). \quad \text{(C2)}$$

It then follows that

$$[\hbar\omega-E_X+i\hbar\eta]C_X(\omega)=\sum_Y V_{XY}C_Y+c_X^{\rm ini}, \quad \text{(C3)}$$

where η is an infinitesimal positive number. We then introduce a matrix T_{AI}

$$C_A(\omega)=\sum_{I\in\mathcal{I}_0}T_{AI}(\omega)C_I(\omega) \quad \text{(C4)}$$

and rewrite

$$\begin{aligned} [\hbar\omega-E_I]C_I(\omega) &= \sum_J V_{IJ}^{\mathcal{P}\mathcal{P}}C_J(\omega)+\sum_{A,J}V_{IA}^{\mathcal{P}\mathcal{Q}} \\ &\quad\times T_{AJ}(\omega)C_J(\omega)+c_I^{\rm ini}, \quad \text{(C5a)} \\ [\hbar\omega-E_A]T_{AI}(\omega) &= V_{AI}^{\mathcal{Q}\mathcal{P}}+\sum_B V_{AB}^{\mathcal{Q}\mathcal{Q}}T_{BI}(\omega), \quad \text{(C5b)} \end{aligned}$$

which can formally be solved as

$$\begin{aligned} T_{AI}(\omega) &= ([\hbar\omega-H_0-V^{\mathcal{Q}\mathcal{Q}}]^{-1}V^{\mathcal{Q}\mathcal{P}})_{AI}, \quad \text{(C6a)} \\ C_I(\omega) &= \sum_J([\hbar\omega-H_0-V^{\mathcal{P}\mathcal{P}}-\Sigma(\omega)]^{-1})_{IJ}c_J^{\rm ini}, \quad \text{(C6b)} \end{aligned}$$

with the self-energy operator $\Sigma(\omega)$ defined as

$$\Sigma(\omega)=V^{\mathcal{P}\mathcal{Q}}[\hbar\omega-H_0-V^{\mathcal{Q}\mathcal{Q}}]^{-1}V^{\mathcal{Q}\mathcal{P}}. \quad \text{(C7)}$$

For later convenience, we also write down the first few orders of expansion

$$\begin{aligned} [\hbar\omega-E_I]C_I^{(0)}(\omega) &= c_I^{\rm ini}, \quad \text{(C8a)} \\ [\hbar\omega-E_I]C_I^{(1)}(\omega) &= \sum_J V_{IJ}^{\mathcal{P}\mathcal{P}}C_J^{(0)}(\omega), \quad \text{(C8b)} \end{aligned}$$

$$[\hbar\omega - E_I]C_I^{(2)}(\omega) = \sum_J V_{IJ}^{\mathcal{PP}} C_J^{(1)}(\omega) + \sum_{A,J} V_{IA}^{\mathcal{PQ}} \times T_{AJ}^{(1)}(\omega) C_J^{(0)}(\omega), \tag{C8c}$$

and

$$[\hbar\omega - E_A]T_{AI}^{(1)}(\omega) = V_{AI}^{\mathcal{QP}}, \tag{C9a}$$

$$[\hbar\omega - E_A]T_{AI}^{(2)}(\omega) = \sum_B V_{AB}^{\mathcal{QQ}} T_{BI}^{(1)}(\omega). \tag{C9b}$$

2. Fixed nuclei QED model

We now apply the formulation we developed in the previous subsection to the electron-radiation coupled dynamics. For simplicity, we assume that the decay lifetime is so much shorter than the timescale of the nuclear dynamics that we can apply a fixed nuclei model. Following the discussion in the main text, we decompose the total electron-radiation Hamiltonian $H^{\mathrm{el,rad}}$ into the zeroth-order Hamiltonian $H_0 = H_{\mathrm{mf}}^{\mathrm{el}} + H_{\mathrm{rad}}$ [Eq. (20)] and the interaction part $V = H_{\mathrm{int}}^{\mathrm{el}}$. The d-dimensional space $\mathscr{H}_0$ is constructed from N_e electron bound states without photons or antiparticles requiring that it contains the initial state vector $|\Psi_0\rangle \in \mathscr{H}_0$, which we assume to be a stable excited bound state under H_0. It then follows that $V^{\mathcal{PP}}$ describes the Coulombic mean-field correction term, whereas $V^{\mathcal{QP}}$ describe electron-radiation coupling terms, through which the initial excited states decay.

Concentrating on the lowest order expansion, we consider a single-photon emission-absorption. We then need two types of states in $\mathscr{H}^{\mathfrak{C}}$,

$$\left|I_j^r; \mathbf{k}\lambda\right\rangle \equiv \hat{a}_{\mathbf{k}\lambda}^\dagger \hat{c}_r^\dagger \hat{c}_{I_j} |I\rangle, \tag{C10a}$$

$$|I; \overline{a}, r; \mathbf{k}\lambda\rangle \equiv \hat{a}_{\mathbf{k}\lambda}^\dagger \hat{c}_r^\dagger \hat{b}_{\overline{a}}^\dagger |I\rangle, \tag{C10b}$$

where $\hat{a}$, $\hat{c}$, and $\hat{b}$ represent the annihilators of photon, electron, and positron, respectively. Symbols $\mathbf{k}$ and λ represent the photon wave vector and polarization, respectively, where modes are formally discretized in system a volume $\mathscr{V}$, which is later taken the limit $\mathscr{V} \to \infty$. Lowercase indices r and $\overline{a}$ represents positive- and negative-energy MO indices. The uppercase index $I \doteq \{I_1, I_2, \ldots, I_{N_e}\}$ represents a set of MO indices that characterizes an N_e electron Slater determinant, whereas I_j^r is defined as $I_j^r \doteq \{I_1, I_2, \ldots, I_{j-1}, \overset{j}{\underset{\vee}{r}}, I_{j+1}, \ldots, I_{N_e}\}$. All N_e electron states that derives from the initial state via a "real" photon emission is represented as a linear combination of states of the form Eq. (C10a), which is orthogonal to $\mathscr{H}_0$. Our treatment here is thus closely related to the Tamm-Dancoff (TD) expansion [104,105], with which we have recently formulated a wave-packet representation of relativistic electron-nucleus coupled dynamics [33].

In what follows, the orbital energy of the rth MO is denoted by ε_r, and the total zeroth-order energy of N-electron state $|I\rangle$ is denoted by $E_I^{(N)} \equiv \sum_k \varepsilon_{I_k}$. We also introduce notation $E_{I\setminus j}^{(N-1)} \equiv E_I^{(N)} - \varepsilon_{I_j}$. We then obtain the lowest order of $T(\omega)$ as

$$\langle I; \mathbf{k}\lambda|T^{(1)}(\omega)|J\rangle = \frac{1}{\hbar\omega - \left(E_I^{(N)} + \hbar\omega_{\mathbf{k}}\right) + i\hbar\eta} \sum_j (\mathscr{E}_{\mathbf{k}\lambda}^*)_{I_j,r} \langle I_j^r|J\rangle, \tag{C11a}$$

$$\langle I; \overline{a}, r; \mathbf{k}\lambda|T^{(1)}(\omega)|J\rangle = \frac{1}{\hbar\omega - \left(E_I^{(N)} + |\varepsilon_a| + \varepsilon_r + \hbar\omega_{\mathbf{k}}\right) + i\hbar\eta} (\mathscr{E}_{\mathbf{k}\lambda}^*)_{s,a} \langle I|\hat{c}_r \hat{c}_s^\dagger|J\rangle, \tag{C11b}$$

with $(\mathscr{E}_{\mathbf{k}\lambda}^*)_{\ell m} \equiv q_e \int d^3\mathbf{r} \overline{\chi}_\ell(\mathbf{r}) \gamma_\mu e_{\mathbf{k}\lambda}^{\mu\ *} e^{-i\mathbf{k}\cdot\mathbf{r}} \chi_m(\mathbf{r}) \sqrt{4\pi c^2 \hbar/(2\omega_{\mathbf{k}}\mathscr{V})}$ representing an effective electron-radiation coupling to the transversal photon mode $\mathbf{k}\lambda$ with polarization vector $\mathbf{e}_{\mathbf{k}\lambda}$. By expanding the transversal part of H_{int}, the zeroth- and second-order terms of C_I reads

$$C_I^{(0)}(\omega) = \frac{1}{\hbar\omega - E_I^{(N)} + i\hbar\eta} c_I^{\mathrm{ini}}, \tag{C12a}$$

$$C_I^{(2)}(\omega) = \frac{1}{\hbar\omega - E_I^{(N)} + i\hbar\eta} \sum_{\mathbf{k}\lambda} \sum_j (\mathscr{E}_{\mathbf{k}\lambda})_{I_j,r} \frac{1}{\hbar\omega - \left(E_{I\setminus j}^{(N-1)} + \varepsilon_r + \hbar\omega_{\mathbf{k}}\right) + i\hbar\eta} \left((\mathscr{E}_{\mathbf{k}\lambda}^*)_{r,s} c_{I_j^s}^{\mathrm{ini}} + \sum_{\ell\neq j} (\mathscr{E}_{\mathbf{k}\lambda}^*)_{I_\ell,s} c_{I_{j\ell}^{rs}}^{\mathrm{ini}} \right) - \frac{1}{\hbar\omega - E_I^{(N)} + i\hbar\eta} \sum_{\mathbf{k}\lambda} \sum_j (\mathscr{E}_{\mathbf{k}\lambda})_{a,r} \frac{1}{\hbar\omega - \left(E_I^{(N)} + |\varepsilon_{\overline{a}}| + \varepsilon_r + \hbar\omega_{\mathbf{k}}\right) + i\hbar\eta} (\mathscr{E}_{\mathbf{k}\lambda}^*)_{I_j,a} c_{I_j^r}^{\mathrm{ini}}. \tag{C12b}$$

Taking account of the Coulombic term, we obtain the final result,

$$C_I^{(0,2)}(\omega) = \frac{1}{\hbar\omega - E_I^{(N)} + i\hbar\eta} \left\{ c_I^{\mathrm{ini}} - \sum_{j\neq\ell} i\hbar c \int \frac{dk_0}{2\pi} \frac{1}{\hbar\omega - \left(E_{I\setminus j}^{(N-1)} + \varepsilon_r + c\hbar k_0\right) + i\hbar\eta} \langle I_j, I_\ell|\mathscr{I}(ck_0)|rs\rangle c_{I_{j\ell}^{rs}}^{\mathrm{ini}} + \sum_j \sum_{s\notin I} \left[\langle I_j|\Sigma_>^{\mathrm{fin.}}\left(\hbar\omega - E_{I\setminus j}^{(N-1)}\right)|s\rangle + \langle I_j|\Sigma_<^{\mathrm{fin.}}\left(E_I^{(N)} + \varepsilon_s - \hbar\omega\right)|s\rangle \right] c_{I_j^s}^{\mathrm{ini}} \right\} \tag{C13}$$

with the four-electron matrix defined as

$$\langle rs|\mathscr{I}(ck_0)|ij\rangle \equiv -e^2 \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)} \overline{\chi}_r(\mathbf{r}_1)\gamma^\mu \chi_i(\mathbf{r}_1)\overline{\chi}_s(\mathbf{r}_2)\gamma^\nu \chi_j(\mathbf{r}_2) e^{i\mathbf{k}(\mathbf{r}_1-\mathbf{r}_2)} D_{\mu\nu}(k) - \frac{1}{2}\int d^3\mathbf{r}\big(\delta_{sj}\overline{\chi}_r(\mathbf{r})\gamma^0 W_{\rm HF}^{\rm loc}(\mathbf{r})\chi_i(\mathbf{r}) + \delta_{ri}\overline{\chi}_s(\mathbf{r})\gamma^0 W_{\rm HF}^{\rm loc}(\mathbf{r})\chi_j(\mathbf{r})\big) \tag{C14}$$

with

$$D_{\mu\nu}(k) \equiv \frac{4\pi e^2}{k^2 + i\epsilon}\Theta_{\mu\nu}(\mathbf{k}), \tag{C15}$$

where ϵ is an infinitesimal positive constant, whereas the factor $\Theta_{\mu\nu}(\mathbf{k})$ in the Coulomb gauge reads $\Theta^C_{\mu\nu} = -(1-\delta^0_\mu)(1-\delta^0_\nu)\{\delta_{\mu\nu} - k_\mu k_\nu/\mathbf{k}^2\} - \delta^0_\mu\delta^0_\nu k^2/\mathbf{k}^2$. For simplicity of the discussion, however, by assuming the gauge invariance of the final results, we replace $\Theta_{\mu\nu}(\mathbf{k})$ in Eq. (C15) by its Feynman gauge expression $\Theta^F_{\mu\nu}(\mathbf{k}) = \eta_{\mu\nu}$. The self-energy operators $\Sigma^{\rm fin.\cdots}_{\gtrless}$ appearing in Eq. (C13) are the finite part of the one-loop electronic self-energies, defined as

$$\Sigma_\zeta(\mathbf{r}_1,\mathbf{r}_2;\omega) \equiv i\hbar e^2 \int_{-\infty}^{\infty} dt e^{i\omega t}\overline{\chi}_r(\mathbf{r}_1)\gamma^\mu S^\zeta(\mathbf{r}_1,t;\mathbf{r}_2,0) \times \gamma^\nu \chi_i(\mathbf{r}_2) D_{\mu\nu}(\mathbf{r}_1,t;\mathbf{r}_2,0), \tag{C16}$$

where ζ represents $>$, $<$, or F, depending on the type of the electronic propagator appearing in the RHS, which can be one of the following;

$$S^F(\mathbf{x},t;\mathbf{x}',t') = \langle 0|\frac{1}{i\hbar}\mathcal{T}\psi(\mathbf{x},t)\overline{\psi}(\mathbf{x}',t')|0\rangle, \tag{C17a}$$

$$S^{\gtrless}(\mathbf{x},t;\mathbf{x}',t') = \theta(\pm(t-t'))S^F(\mathbf{x},t;\mathbf{x}',t'). \tag{C17b}$$

The finite part of the standard one-loop self-energy, $\Sigma_F(\mathbf{r}_1,\mathbf{r}_2;\omega)$ is well-defined based on the renormalization theory and is also numerically available using established calculation techniques [20]. Using such a finite part expression $\Sigma^{\rm fin.}_F$, the finite parts of other types are obtained as

$$\Sigma^{\rm fin.\cdots}_{\gtrless}(\mathbf{x},\mathbf{x}';\omega) = \mp\int \frac{d\omega'}{2\pi i}\frac{1}{\omega-\omega'\pm i\eta}\Sigma^{\rm fin.\cdots}_F(\mathbf{x},\mathbf{x}';\omega'). \tag{C18}$$

3. Resummation of $V^{\mathcal{PP}}$

We go back to Eq. (C5) and, assuming that we can solve the eigenvalue problem of the projected Hamiltonian $H^{\mathcal{PP}} = H_0 + V^{\mathcal{PP}}$ as

$$\sum_J \big(E_I\delta_{IJ} + V^{\mathcal{PP}}_{IJ}\big)R_{J\lambda} = R_{I\lambda}E_\lambda, \tag{C19}$$

we consider a linear transformation of expansion basis as

$$C_I = \sum_\lambda R_{I\lambda}\mathcal{C}_\lambda. \tag{C20}$$

We then obtain

$$[\hbar\omega - \mathcal{E}_\lambda]\mathcal{C}_\lambda(\omega) = \sum_{A,J}(\mathcal{R}^\dagger V^{\mathcal{PQ}})_{\lambda A}(T\mathcal{R})_{A\kappa}(\omega)C_\kappa(\omega) + \tilde{c}^{\rm ini}_\lambda, \tag{C21a}$$

$$[\hbar\omega - E_A](T\mathcal{R})_{A\lambda}(\omega) = (V^{\mathcal{QP}}\mathcal{R})_{A\lambda} + \sum_B V^{\mathcal{QQ}}_{AB}(T\mathcal{R})_{B\lambda}(\omega). \tag{C21b}$$

We then find that we can apply new expansion basis for $\mathscr{H}_0$ but keep those for $\mathscr{H}^{\complement}$.

In the molecular application, we may apply such techniques to diagonalize the Coulombic interaction in the sense of the configuration-interaction (CI) theory. In such reformulation, the electron-electron interaction term $\langle rs|I(ck_0)|ij\rangle$ in Eq. (C13) should be replaced by the transversal interaction, whereas one does not have to change the self-energy expression, since the Coulombic terms included in the resummation here are the interelectron Coulombic interactions and do not include the Coulombic self-interaction appearing in the self-energy expression.

4. Inclusion of nuclear dynamics

In the previous subsection, we assumed that the lifetime of the initial electronic state is short enough to apply a fixed-nuclei approximation. Such an assumption is, however, not always applicable in models with rapid nuclear motion such as molecular decay models including Coulomb explosions [28]. In such cases, we may be able to switch to the Tamm-Dancoff theory of electron-nucleus-radiation coupled dynamics, developed in Ref. [33], which includes nuclear dynamics, though we can no longer use the Fourier transformed expressions like Eq. (C13), which gives better insight to decaying dynamics than real-time expression does.

APPENDIX D: DETAILS OF PERTURBATION EXPANSION

1. Energy corrections

Here, we derive explicit analytic expressions corresponding to the diagrams shown in Figs. 1, 2, and 3, which were discussed in Sec. IV. We follow the approach given in Refs. [41,42] to derive those expressions. In the following discussions, orbitals in the initial and final states, labeled by i, j, r, and s are all positive-energy MOs, since our model space consists of N_e-electron (no positron) states. We use the symbol ξ_ℓ to describe the ℓth reduced orbital energy, $\xi_\ell \equiv \varepsilon_\ell/\hbar$, and $\xi_{\ell m}$ to describe the difference, $\xi_{\ell m} \equiv \xi_\ell - \xi_m$. The symbol ϵ represents an infinitesimal positive number. Following Ref. [42], we also introduce "photon mass" $\hbar\mu/c$, which is to be taken the limit $\mu \to +0$ after all calculations. The frequency of a photon with wave vector $\mathbf{k}$ therefore becomes $\omega_{|\mathbf{k}|} = c\sqrt{|\mathbf{k}|^2+\mu^2}$.

a. Single-electron terms

We start with the self-energy contribution to the effective Hamiltonian $\mathcal{H}_{\rm eff}$, shown in Figs. 1(a) and 1(f), and given as Eq. (80). We first evaluate $\mathcal{K}$ [Eq. (71b)] as

$$\begin{aligned}\mathcal{K}^{(1)}_{ri} &= \left[\oint_{\varepsilon_i} + \oint_{\varepsilon_r}\right]\frac{dz}{2\pi i}\langle\varphi_r|zG^{SE}_{TT}(z)|\varphi_i\rangle \\ &= \frac{\xi_i}{\xi_{ir}}\Sigma(\xi_i) + \frac{\xi_r}{\xi_{ri}}\Sigma(\xi_r), \end{aligned} \tag{D1}$$

where $\oint_\varepsilon dz/2\pi i$ represents complex contour integral that encircles the (discrete) zeroth-order energy pole $z = \varepsilon$. Taking account of a similar expression for $\mathcal{S}$, we obtain

$$\mathcal{H}_{\rm eff}{}^{(1,SE)}{}_{ri} = (\mathcal{K}^{(1)} - \mathcal{K}^{(0)}\mathcal{S}^{(1)})_{ri} = \langle r|\Sigma(\xi_i)|i\rangle, \tag{D2}$$

where evaluation of $\Sigma(\omega)$, the self-energy operator of the Hartree-Fock propagator, is discussed in the main text.

b. Electron-electron interaction terms

Following Ref. [41], we introduce a two-body integral

$$\begin{aligned}\langle rs|I^\lambda(\omega)|ij\rangle &\equiv -e^2\iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \overline{\chi}_r(\mathbf{r}_1)\gamma^\mu\varphi_i(\mathbf{r}_1)\overline{\chi}_s(\mathbf{r}_2)\gamma^\nu\varphi_j(\mathbf{r}_2)D^\lambda_{\mu\nu}(\mathbf{r}_1,\mathbf{r}_2;\omega) \\ &= \int\frac{d^3\mathbf{k}}{(2\pi)^3}\iint d^3\mathbf{r}_1 d^3\mathbf{r}_2\overline{\chi}_r(\mathbf{r}_1)\gamma^\mu\varphi_i(\mathbf{r}_1)\overline{\chi}_s(\mathbf{r}_2)\gamma^\nu\varphi_j(\mathbf{r}_2)\frac{4\pi e^2}{\mathbf{k}^2+\mu^2-(\omega/c)^2-i\epsilon}e^{i\mathbf{k}(\mathbf{r}_1-\mathbf{r}_2)}\Theta^\lambda_{\mu\nu}(\mathbf{k}) \\ &= \int_0^\infty dk\langle rs|f^\lambda(k)|ij\rangle\left[\frac{c}{\omega-\omega_k+i\epsilon}-\frac{c}{\omega+\omega_k-i\epsilon}\right], \end{aligned} \tag{D3}$$

where λ represents the gauge choice, either C or F, whose corresponding coupling $\Theta_{\mu\nu}$ given as Eq. (66), whereas $f^\lambda(k)$ in the last side is defined as

$$\langle rs|f^\lambda(k)|ij\rangle \equiv \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2\overline{\chi}_r(\mathbf{r}_1)\gamma^\mu\varphi_i(\mathbf{r}_1)\overline{\chi}_s(\mathbf{r}_2)\gamma^\nu\varphi_j(\mathbf{r}_2)\frac{-e^2}{\pi r_{12}}\sin(kr_{12})\frac{ck}{\omega_k}\Theta^\lambda_{\mu\nu}(\mathbf{k}). \tag{D4}$$

It then follows that

$$\int\frac{d\omega}{2\pi}\langle rs|I^\lambda(\omega)|ij\rangle\left[\frac{1}{\omega-\xi_a(1-i\epsilon)}-\frac{1}{\omega+\xi_b(1-i\epsilon)}\right] = i\int_0^\infty cdk\langle rs|f^\lambda(k)|ij\rangle\left[\frac{1}{\theta_a(\omega_k-i0)+\xi_a}+\frac{1}{\theta_b(\omega_k-i0)+\xi_b}\right], \tag{D5}$$

where $\theta_a = \pm 1$ for $\xi_a \gtrless 0$. In our model, we further need to include the mean-field subtraction terms in the effective interelectron interactions

$$\langle rs|\mathscr{I}^\lambda(\omega)|ij\rangle \equiv \langle rs|I^\lambda(\omega)|ij\rangle - \frac{1}{2}\int d^3\mathbf{r}\left(\delta_{sj}\overline{\chi}_r(\mathbf{r})\gamma^0 W^{\rm loc}_{\rm HF}(\mathbf{r})\chi_i(\mathbf{r}) + \delta_{ri}\overline{\chi}_s(\mathbf{r})\gamma^0 W^{\rm loc}_{\rm HF}(\mathbf{r})\chi_j(\mathbf{r})\right), \tag{D6}$$

which is a slight extension of Eq. (C14). We also introduce an expression $\langle rs|V^\lambda(\xi_a,\xi_b)|ij\rangle$ by [41]

$$\langle rs|V^\lambda(\xi_a,\xi_b)|ij\rangle \equiv \int\frac{d\omega}{2\pi i}\langle rs|\mathscr{I}^\lambda(\omega)|ij\rangle\left[\frac{1}{\omega-\xi_a(1-i\epsilon)}-\frac{1}{\omega+\xi_b(1-i\epsilon)}\right]. \tag{D7}$$

Hereafter, we use the Feynman gauge and drop λ in the superscript.

The single-photon electron-electron interaction (ee1) diagram shown in Fig. 2(a) is evaluated as

$$\begin{aligned}H^{(ee1)rs}_{{\rm eff}\ ij} &= \mathcal{K}^{(1)} - \mathcal{K}^{(0)}\mathcal{S}^{(1)} \\ &= \int\frac{d\omega_1}{2\pi i}\left[\frac{1}{\omega_1-\xi_r(1-i\epsilon)}+\frac{1}{E_I/\hbar-\omega_1-\xi_s(1-i\epsilon)}\right]\langle rs|\mathscr{I}(\omega-\xi_i)|ij\rangle = \langle rs|V(\xi_{ri},\xi_{sj})|ij\rangle, \end{aligned} \tag{D8}$$

with E_I being the incident energy, $E_I \equiv \varepsilon_i + \varepsilon_j$. The two photon electron-electron ladder (ee2L) diagram shown in Fig. 2(b) is evaluated as

$$\begin{aligned}H^{(ee2L)rs}_{{\rm eff}\ ij} = &-\sum_{t,u}\iint\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\left(\frac{1}{\omega_1+\omega_2-\xi_{ri}+i\epsilon_r}-\frac{1}{\omega_1+\omega_2+\xi_{sj}-i\epsilon_s}\right)\left(\frac{1}{\omega_2-\xi_{ti}+i\epsilon_t}-\frac{1}{\omega_2+\xi_{uj}-i\epsilon_u}\right) \\ &\times\frac{1}{E_{IM}}\langle rs|\mathscr{I}(\omega_1)|tu\rangle\langle tu|\mathscr{I}(\omega_2)|ij\rangle - \sum_{t,u\in\mathscr{H}_0}\langle rs|V(\xi_{rt},\xi_{su})|tu\rangle\frac{1}{E_{IM}}\langle tu|V(\xi_{ti},\xi_{uj})|ij\rangle, \end{aligned} \tag{D9}$$

where ϵ_r is a shorthand notation for $\epsilon\xi_r$, either an infinitesimal positive or negative number depending on the sign of the associated orbital energy ξ_r. The denominator in the first term can be further decomposed as

$$-\Delta_1^{-1}\Delta_{1+3}^{-1}\Delta_2^{-1}\Delta_{2+4}^{-1}\Delta_{1234} = -\{\Delta_1^{-1}\Delta_2^{-1}(\Delta_{1+2+3}^{-1}+\Delta_{1+2+4}^{-1})\} - \{\Delta_1^{-1}\Delta_{13}^{-1}\Delta_{123}^{-1}+\Delta_2^{-1}\Delta_{24}^{-1}\Delta_{124}^{-1}\}, \tag{D10}$$

where Δ_i^{-1} represents an energy denominator associated to the ith transition whereas combined ones are denoted as $\Delta_{ijk\cdots}^{-1} \equiv (\Delta_i+\Delta_j+\Delta_k+\cdots)^{-1}$. In the ladder diagram in our current discussion, $\Delta_1 = \xi_{ti}-\omega_2$, $\Delta_2 = \xi_{uj}+\omega_2$, $\Delta_3 = \xi_{rt}-\omega_1$, and $\Delta_4 = \xi_{su}+\omega_1$. Two curly brackets in the RHS of Eq. (D10) represent the separable and nonseparable components, respectively. We now rewrite Eq. (D9) as

$$\begin{aligned}
H_{\text{eff}}^{(ee2L)rs}{}_{ij} &= \iint \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\Bigg[\sum_{t,u\notin\mathscr{H}_0}(\Delta_1^{-1}\Delta_{1+3}^{-1}\Delta_2^{-1}\Delta_{2+4}^{-1}\Delta_{1234})\langle rs|\mathscr{I}(\omega_1)|tu\rangle\langle tu|\mathscr{I}(\omega_2)|ij\rangle \\
&\quad + \sum_{t,u\in\mathscr{H}_0}\{\Delta_1^{-1}\Delta_{13}^{-1}\Delta_{123}^{-1}+\Delta_2^{-1}\Delta_{24}^{-1}\Delta_{124}^{-1}\}\langle rs|\mathscr{I}(\omega_1)|tu\rangle\langle tu|\mathscr{I}(\omega_2)|ij\rangle \\
&\quad + \sum_{t,u\in\mathscr{H}_0}\{\Delta_1^{-1}\Delta_2^{-1}(\Delta_{1+2+3}^{-1}+\Delta_{1+2+4}^{-1})\}\langle rs|\mathscr{I}(\omega_1)|tu\rangle\langle tu|\mathscr{I}(\omega_2)|ij\rangle\Bigg] \\
&\quad - \sum_{t,u\in\mathscr{H}_0}\langle rs|V(\xi_{rt},\xi_{su})|tu\rangle\frac{1}{E_{IM}}\langle tu|V(\xi_{ti},\xi_{ij})|ij\rangle \\
&= \iint \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\Bigg[\sum_{t,u\notin\mathscr{H}_0}(\Delta_1^{-1}\Delta_{1+3}^{-1}\Delta_2^{-1}\Delta_{2+4}^{-1}\Delta_{1234})\langle rs|\mathscr{I}(\omega_1)|tu\rangle\langle tu|\mathscr{I}(\omega_2)|ij\rangle \\
&\quad + \sum_{t,u\in\mathscr{H}_0}\{\Delta_1^{-1}\Delta_{13}^{-1}\Delta_{123}^{-1}+\Delta_2^{-1}\Delta_{24}^{-1}\Delta_{124}^{-1}\}\langle rs|\mathscr{I}(\omega_1)|tu\rangle\langle tu|\mathscr{I}(\omega_2)|ij\rangle\Bigg] \\
&\quad + \sum_{t,u\in\mathscr{H}_0}\left\{\frac{\langle rs|V(\xi_{rt}+\frac{E_{MI}}{\hbar},\xi_{su}+\frac{E_{MI}}{\hbar})|tu\rangle - \langle rs|V(\xi_{rt},\xi_{su})|tu\rangle}{E_{IM}}\right\}\langle tu|V(\xi_{ti},\xi_{uj}+\Delta)|ij\rangle.
\end{aligned} \tag{D11}$$

Performing ω integration, we obtain

$$\begin{aligned}
H_{\text{eff}}^{(ee2L)rs}{}_{ij} &= \sum_{(t,u)\notin\mathscr{H}_0}\frac{1}{E_{IM}}\iint_0^\infty c^2 dk_1 dk_2\langle rs|f(k_1)|tu\rangle\langle tu|f(k_2)|ij\rangle \\
&\quad\times\Bigg[\theta_t\left\{\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{ri}}\times\frac{1}{\omega_{k_2}+\xi_{ti}}+\frac{1}{\omega_{k_1}+\xi_{ti}+\xi_{sj}}\left(\frac{1}{\omega_{k_2}+\xi_{ti}}+\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{sj}}\right)\right\} \\
&\quad+(1-\theta_t)\left\{-\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{sj}}\times\frac{1}{\omega_{k_2}-\xi_{ti}}-\frac{1}{\omega_{k_1}+\xi_{rt}}\left(\frac{1}{\omega_{k_2}-\xi_{ti}}+\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{ri}}\right)\right\} \\
&\quad\times\theta_u\left\{\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{sj}}\times\frac{1}{\omega_{k_2}+\xi_{uj}}+\frac{1}{\omega_{k_1}+\xi_{uj}+\xi_{ri}}\left(\frac{1}{\omega_{k_2}+\xi_{uj}}+\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{ri}}\right)\right\} \\
&\quad+(1-\theta_u)\left\{-\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{ri}}\times\frac{1}{\omega_{k_2}-\xi_{uj}}-\frac{1}{\omega_{k_1}+\xi_{su}}\left(\frac{1}{\omega_{k_2}-\xi_{uj}}+\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{sj}}\right)\right\}\Bigg] \\
&\quad+\sum_{(t,u)\in\mathscr{H}_0}c^2\iint_0^\infty dk_1 dk_2\langle rs|f(k_1)|tu\rangle\langle tu|f(k_2)|ij\rangle\Bigg(\frac{1}{(\omega_{k_1}+\xi_{ri}+\xi_{uj})(\omega_{k_1}+\omega_{k_2}+\xi_{ri})(\omega_{k_2}+\xi_{ti})} \\
&\quad+\frac{1}{(\omega_{k_1}+\xi_{ti}+\xi_{sj})(\omega_{k_1}+\omega_{k_2}+\xi_{sj})(\omega_{k_2}+\xi_{uj})}\Bigg) \\
&\quad+\sum_{(t,u)\in\mathscr{H}_0}\frac{\langle rs|V(\xi_{tr}+E_{IM}/\hbar,\xi_{us}+E_{IM}/\hbar)|tu\rangle-\langle rs|V(\xi_{tr},\xi_{us})|tu\rangle}{E_{IM}/\hbar}\langle tu|V(\xi_{it},\xi_{ju})|ij\rangle,
\end{aligned} \tag{D12}$$

where the symbol θ_t takes 1 if $\xi_t > 0$ or 0 otherwise, and the energy difference between the initial and intermediate state, E_{IM}, here indicates $E_{IM} = \varepsilon_i+\varepsilon_j-\varepsilon_r-\varepsilon_s$.

We next evaluate the two-photon crossed electron-electron ladder (ee2xL) diagram shown in Fig. 2(c), which has no reducible contribution and is evaluated as

$$
\begin{aligned}
H_{\mathrm{eff}}{}^{(ee2xL)^{rs}}_{ij} &= \mathcal{K}^{(1)} - \mathcal{K}^{(0)}\mathcal{S}^{(1)} \\
&= \sum_{t,u} \frac{-1}{E_{IM}} \iint \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\left[\frac{1}{\omega_1 - \xi_r(1-i\epsilon)} + \frac{1}{E_I/\hbar - \omega_1 - \xi_s(1-i\epsilon)}\right] \\
&\quad \times \left[\frac{1}{\omega_2 - \xi_t(1-i\epsilon)} + \frac{1}{E_I/\hbar - \omega_2 - \xi_u(1-i\epsilon)}\right] \langle ru|\mathscr{I}(\omega_{12})|tj\rangle\langle ts|\mathscr{I}(\omega_2 - \xi_i)|iu\rangle \\
&= \sum_{(t,u)} \frac{1}{E_{IM}} c^2 \iint_0^\infty dk_1 dk_2 \langle ru|f(k_1)|tj\rangle\langle ts|f(k_2)|iu\rangle \\
&\quad \times \left[\theta_t\left\{\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{ri}} \times \frac{1}{\omega_{k_2}+\xi_{ti}} + \frac{1}{\omega_{k_1}+\xi_{ti}+\xi_{sj}}\left(\frac{1}{\omega_{k_2}+\xi_{ti}} + \frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{sj}}\right)\right\}\right. \\
&\quad + (1-\theta_t)\left\{-\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{sj}} \times \frac{1}{\omega_{k_2}-\xi_{ti}} - \frac{1}{\omega_{k_1}+\xi_{rt}}\left(\frac{1}{\omega_{k_2}-\xi_{ti}} + \frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{ri}}\right)\right\} \\
&\quad + \theta_u\left\{\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{sj}} \times \frac{1}{\omega_{k_2}+\xi_{uj}} + \frac{1}{\omega_{k_1}+\xi_{uj}+\xi_{ri}}\left(\frac{1}{\omega_{k_2}+\xi_{uj}} + \frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{ri}}\right)\right\} \\
&\quad \left. + (1-\theta_u)\left\{-\frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{ri}} \times \frac{1}{\omega_{k_2}-\xi_{uj}} - \frac{1}{\omega_{k_1}+\xi_{su}}\left(\frac{1}{\omega_{k_2}-\xi_{uj}} + \frac{1}{\omega_{k_1}+\omega_{k_2}+\xi_{sj}}\right)\right\}\right].
\end{aligned}
\tag{D13}
$$

The lowest order three-electron term (ee3), shown in Fig. 2(d), is

$$
\begin{aligned}
H_{\mathrm{eff}}{}^{(ee3)^{rst}}_{ijk} &= \mathcal{K}^{(2)} - \mathcal{K}^{(0)}\mathcal{S}^{(2)} - \big(\mathcal{K}^{(1)} - \mathcal{K}^{(0)}\mathcal{S}^{(1)}\big)\mathcal{S}^{(1)} \\
&= \frac{-1}{\hbar}\sum_u \iint \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\left[\frac{1}{\omega_1 - \xi_{uj} + i\epsilon_u}\left(\frac{1}{\omega_2 - \xi_{ri} + i\epsilon_r} + \frac{1}{\omega_1 - \omega_2 - \xi_{sj} + i\epsilon_s}\right)\right. \\
&\quad \left.\times\left(\frac{1}{\omega_1 - \xi_{ri} - \xi_{sj} + i\epsilon_r} - \frac{1}{\omega_1 + \xi_{tk} - i\epsilon_t}\right)\langle rs|\mathscr{I}(\omega_2)|iu\rangle\langle ut|\mathscr{I}(\omega_1)|jk\rangle\right] \\
&\quad - \langle rs|V(\xi_{ri},\xi_{su})|iu\rangle\langle rs|V(\xi_{ri},\xi_{su})|iu\rangle\frac{1}{\varepsilon_{ju}+\varepsilon_{kt}}.
\end{aligned}
\tag{D14}
$$

The denominator can be decomposed as

$$
\begin{aligned}
\Delta_1^{-1}\big(\Delta_4^{-1} + \Delta_{12}^{-1}\big)\big(\Delta_{124}^{-1} + \Delta_3^{-1}\big) &= \Delta_1^{-1}\Delta_{12}^{-1}\Delta_3^{-1}\Delta_4^{-1}\Delta_{1234} = \Delta_1^{-1}\Delta_{12}^{-1}\Delta_3^{-1}\Delta_{34}^{-1}\Delta_{1234} + \Delta_1^{-1}\Delta_{12}^{-1}\Delta_4^{-1}\Delta_{34}^{-1}\Delta_{1234} \\
&= \big\{\Delta_1^{-1}\Delta_3^{-1}\big(\Delta_{123}^{-1} + \Delta_{134}^{-1}\big)\big\} + \big\{\big(\Delta_1^{-1}\Delta_{12}^{-1}\Delta_{123}^{-1} + \Delta_3^{-1}\Delta_{34}^{-1}\Delta_{134}^{-1}\big)\big\} + \big\{\Delta_1^{-1}\Delta_{12}^{-1}\Delta_4^{-1}\Delta_{34}^{-1}\Delta_{1234}\big\}
\end{aligned}
\tag{D15}
$$

with $\Delta_1 = \xi_{uj} - \omega_1 - i\epsilon_u \Delta_2 = \xi_{su} + \omega_2 - i\epsilon_s \Delta_3 = \xi_{tk} + \omega_1 - i\epsilon_t \Delta_4 = \xi_{ri} - \omega_2 - i\epsilon_r$. The three round brackets in the last side of Eq. (D15) indicate perturbation processes, where two photon lines (i) do not overlap, (ii) overlap, and (iii) cross in time, respectively, and hence only the first one, (i), is separable. We therefore rewrite Eq. (D14) as

$$
\begin{aligned}
H_{\mathrm{eff}}{}^{(ee3)^{rst}}_{ijk} &= \frac{-1}{\hbar}\sum_{u\notin\mathscr{H}_0} \iint \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1 - \xi_{uj} + i\epsilon_u}\left(\frac{1}{\omega_2 - \xi_{ri} + i\epsilon_r} + \frac{1}{\omega_1 - \omega_2 - \xi_{sj} + i\epsilon_s}\right) \\
&\quad \times\left(\frac{1}{\omega_1 - \xi_{ri} - \xi_{sj} + i\epsilon_r} - \frac{1}{\omega_1 + \xi_{tk} - i\epsilon_t}\right)\langle rs|\mathscr{I}(\omega_2)|iu\rangle\langle ut|\mathscr{I}(\omega_1)|jk\rangle \\
&\quad - \frac{1}{\hbar}\sum_{u\in\mathscr{H}_0} \iint \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\big\{\big(\Delta_1^{-1}\Delta_{12}^{-1}\Delta_{123}^{-1} + \Delta_3^{-1}\Delta_{34}^{-1}\Delta_{134}^{-1}\big) + \Delta_1^{-1}\Delta_{12}^{-1}\Delta_4^{-1}\Delta_{34}^{-1}\Delta_{1234}\big\}\langle rs|\mathscr{I}(\omega_2)|iu\rangle\langle ut|\mathscr{I}(\omega_1)|jk\rangle \\
&\quad - \langle rs|V(\xi_{ri},\xi_{su})|iu\rangle\frac{\langle rs|V(\xi_{ri}+\Delta',\xi_{su}+\Delta')|iu\rangle - \langle rs|V(\xi_{ri},\xi_{su})|iu\rangle}{\hbar\Delta'}
\end{aligned}
\tag{D16}
$$

with $\Delta' \equiv \xi_{uj} + \xi_{tk}$.

c. Mixed terms

Here, we evaluate screened the self-energy (sSE) diagrams shown in Fig. 3. Figure 3(a) gives

$$H_{\rm eff}^{(sSE-a)rs}{}_{ij} = \sum_{t\notin\mathscr{H}_0}\langle rs|V(\xi_{ri},\xi_{tj})|tj\rangle\frac{\langle t|\Sigma(\xi_i)|i\rangle}{\varepsilon_{it}} + \sum_{t\in\mathscr{H}_0}\langle rs|\frac{V(\xi_{ri},\xi_{tj})-V(\xi_{ri}+\xi_{it},\xi_{tj})}{\hbar\xi_{it}}|tj\rangle\langle t|\Sigma(\xi_i)|i\rangle, \tag{D17}$$

whereas Fig. 3(b) reads

$$\begin{aligned}H_{\rm eff}^{(sSE-a)rs}{}_{ij} = \frac{-1}{\hbar}\sum_t\iint\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\Bigg[&\frac{1}{\omega_1-\omega_2-\xi_{ui}+i\epsilon_u}\times\frac{1}{\omega_1-\xi_{ti}+i\epsilon_t}\times\frac{1}{\omega_1-\xi_{ri}+i\epsilon_r}\\ &\times\frac{1}{\omega_1+\xi_{sj}+i\epsilon_s}\big(\xi_{sj}+\xi_{ri}\big)\langle ru|I(\omega_2)|ut\rangle\langle ts|I(\omega_1)|ij\rangle\Bigg] - \sum_{t\in\mathscr{H}_0}\langle r|\Sigma(\xi_t)|t\rangle\langle ts|V(\xi_{ti},\xi_{sj})|sj\rangle\frac{1}{\varepsilon_{it}+\varepsilon_{js}},\end{aligned} \tag{D18}$$

where the denominator in the RHS decomposes as

$$\Delta_{123}^{-1}\Delta_4^{-1}\Delta_1^{-1}\Delta_{12}^{-1} = \big\{\Delta_1^{-1}\Delta_4^{-1}\Delta_{124}^{-1}\Delta_{1234}^{-1}\big\} + \big\{\Delta_1^{-1}\Delta_{12}^{-1}\big(\Delta_{123}^{-1}+\Delta_{124}^{-1}\big)\Delta_{1234}^{-1}\big\} \tag{D19}$$

with $\Delta_1 = \xi_{ti}-\omega_1-i\epsilon_t$, $\Delta_2 = \xi_{ut}+\omega_2-i\epsilon_u$, $\Delta_3 = \xi_{ru}-\omega_2+i\epsilon_u$, and $\Delta_4 = \xi_{sj}+\omega_1-i\epsilon_s$. Two curly brackets in the RHS of Eq. (D19) are identified as the separable and nonseparable parts, respectively. The separable contribution sums up as

$$\begin{aligned}H_{\rm eff}^{(sSE-b)rs({\rm sep})}{}_{ij} &= \sum_{t,u}\iint\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\left(\frac{1}{\omega_1-\xi_{ti}+i\epsilon_t}-\frac{1}{\omega_1+\xi_{sj}-i\epsilon_s}\right)\frac{1}{\hbar(\xi_{sj}+\xi_{ti})}\frac{1}{\xi_i+\xi_{js}-\omega_2-\xi_u}\langle ru|I(\omega_2)|ut\rangle\langle ts|I(\omega_1)|ij\rangle\\ &= -\sum_t\frac{\langle r|\Sigma(\xi_i+\xi_{js})|t\rangle}{\hbar(\xi_{sj}+\xi_{ti})}\langle ts|V(\xi_{ti},\xi_{sj})|ij\rangle,\end{aligned} \tag{D20}$$

and the first part of nonseparable sums up as

$$\begin{aligned}H_{\rm eff}^{(sSE-b)rs({\rm non-sep}),1}{}_{ij} &= -\frac{1}{\hbar}\sum_t\iint\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\sum_u\frac{1}{\omega_1-\xi_{ti}+i\epsilon_t}\times\frac{1}{\xi_i+\omega_1-\omega_2-\xi_u+i\epsilon_u}\\ &\quad\times\frac{1}{\omega_1-\xi_{ri}+i\epsilon_r}\langle ru|I(\omega_2)|ut\rangle\langle ts|I(\omega_1)|ij\rangle\\ &= -\frac{i}{\hbar}\sum_t\int\frac{d\omega_1}{2\pi}\langle r|\Sigma(\xi_i+\omega_1)|t\rangle\frac{1}{\omega_1-\xi_{ti}+i\epsilon_t}\times\frac{1}{\omega_1-\xi_{ri}+i\epsilon_r}\langle ts|I(\omega_1)|ij\rangle.\end{aligned} \tag{D21}$$

We therefore have

$$\begin{aligned}H_{\rm eff}^{(sSE-b)rs}{}_{ij} =& -\sum_{t\in\mathscr{H}_0}\frac{\langle r|\Sigma(\xi_i+\xi_{js})-\Sigma(\xi_t)|t\rangle}{\hbar(\xi_{sj}+\xi_{ti})}\langle ts|V(\xi_{ti},\xi_{sj})|ij\rangle - \sum_{t\notin\mathscr{H}_0}\frac{\langle r|\Sigma(\xi_i+\xi_{js})|t\rangle}{\hbar(\xi_{sj}+\xi_{ti})}\langle ts|V(\xi_{ti},\xi_{sj})|ij\rangle\\ &-\frac{i}{\hbar}\sum_t\int\frac{d\omega_1}{2\pi}\langle r|\Sigma(\xi_i+\omega_1)|t\rangle\frac{1}{\omega_1-\xi_{ti}+i\epsilon_t}\times\frac{1}{\omega_1-\xi_{ri}+i\epsilon_r}\langle ts|I(\omega_1)|ij\rangle\\ &+\frac{1}{\hbar}\sum_t\iint\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{1}{\omega_1-\xi_{ti}+i\epsilon_t}\times\frac{1}{\omega_1-\omega_2-\xi_{ui}+i\epsilon_u}\frac{1}{\omega_2+\xi_{ui}+\xi_{sj}+i\epsilon_s}\langle ru|I(\omega_2)|ut\rangle\langle ts|I(\omega_1)|ij\rangle.\end{aligned} \tag{D22}$$

The third diagram, Fig. 3(c), which accompanies no counterterm, is evaluated as

$$\begin{aligned}H_{\rm eff}^{(sSE-c)rs}{}_{ij} = \frac{-1}{\hbar}\sum_{t,u}\iint\frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}&\left(\frac{1}{\omega_1-\xi_{ri}+i\epsilon_r}-\frac{1}{\omega_1+\xi_{sj}-i\epsilon_s}\right)\frac{1}{\omega_1-\omega_2-\xi_{ti}+i\epsilon_t}\\ &\times\frac{1}{\xi_i-\omega_2-\xi_u+i\epsilon_u}\langle ru|I(\omega_2)|ti\rangle\langle ts|\mathscr{I}(\omega_1)|uj\rangle.\end{aligned} \tag{D23}$$

Integration over ω_1, ω_2 gives

$$\begin{aligned}H_{\rm eff}^{(sSE-c)rs}{}_{ij} = \frac{1}{\hbar}\sum_{t,u}c^2\iint dk_1dk_2\langle ru|f(k_2)|ti\rangle\langle ts|f(k_1)|uj\rangle\\ \times\Bigg[\left(\frac{1}{\mathsf{s}_t\omega_{k_1}-\xi_{sj}}-\frac{1}{\mathsf{s}_t\omega_{k_1}+\xi_{ri}}\right)\frac{1}{\mathsf{s}_t\omega_{k_1}+\mathsf{s}_t\omega_{k_2}+\xi_{ti}}\times\frac{1}{\mathsf{s}_t\omega_{k_2}+\xi_{ui}}\end{aligned}$$

$$+\theta_t\left\{\frac{1}{\xi_{sj}+\omega_{k_2}+\xi_{ti}}\times\frac{1}{\omega_{k_2}+\xi_{ui}}\times\frac{2\omega_{k_1}}{\xi_{sj}^2-\omega_{k_1}^2}\right\}+(1-\theta_t)\left\{\frac{1}{-\xi_{ri}-\omega_{k_2}+\xi_{ti}}\times\frac{1}{-\omega_{k_2}+\xi_{ui}}\times\frac{2\omega_{k_1}}{\xi_{ri}^2-\omega_{k_1}^2}\right\}$$
$$-\theta_t(1-\theta_u)\left\{\left(\frac{1}{\omega_{k_1}-\xi_{sj}}-\frac{1}{\omega_{k_1}+\xi_{ri}}\right)\frac{1}{\omega_{k_1}+\xi_{tu}}\times\frac{2\omega_{k_2}}{\xi_{ui}^2-\omega_{k_2}^2}+\frac{1}{\xi_{sj}+\xi_{tu}}\frac{2\omega_{k_2}}{\xi_{ui}^2-\omega_{k_2}^2}\times\frac{2\omega_{k_1}}{\xi_{sj}^2-\omega_{k_1}^2}\right\}$$
$$+(1-\theta_t)\theta_u\left\{\left(\frac{1}{-\omega_{k_1}-\xi_{sj}}-\frac{1}{-\omega_{k_1}+\xi_{ri}}\right)\frac{1}{\omega_{k_1}+\xi_{tu}}\times\frac{2\omega_{k_2}}{\xi_{ui}^2-\omega_{k_2}^2}+\frac{1}{\xi_{tr}-\xi_{ui}}\frac{2\omega_{k_2}}{\xi_{ui}^2-\omega_{k_2}^2}\times\frac{2\omega_{k_1}}{\xi_{sj}^2-\omega_{k_1}^2}\right\}\Bigg]$$
$$-\frac{1}{\hbar}\delta_{sj}\int cdk\frac{1}{\mathsf{s}_t\omega_k+\xi_{ti}-i\epsilon_t}\left(W_{\mathrm{HF}}^{\mathrm{loc}}\right)_{tu}\frac{1}{\mathsf{s}_t\omega_k+\xi_{ui}-i\epsilon_u}\langle ru|f(k)|ti\rangle$$
$$-\frac{1-\mathsf{s}_t\mathsf{s}_u}{2}\mathsf{s}_t\frac{1}{\hbar}\int cdk\frac{1}{\xi_{tu}}\left(W_{\mathrm{HF}}^{\mathrm{loc}}\right)_{tu}\frac{2\omega_k}{\xi_{ui}^2-\omega_k^2}\langle ru|f(k)|ti\rangle+\left(\frac{1}{\xi_{ir}+i\epsilon_r}+\frac{1}{\xi_{js}+i\epsilon_s}\right)\Sigma(\xi_i)\left(W_{\mathrm{HF}}^{\mathrm{loc}}\right)_{sj},\tag{D24}$$

where s_i takes 1 or -1 for $\xi_i>0$ or $\xi_i<0$, whereas $\theta_i=(1+\mathsf{s}_i)/2$ takes 1 or 0 for $\xi_i>0$ or $\xi_i<0$, respectively.

2. General matrices

Here, we discuss possible simplification of the perturbative evaluation of general matrix elements. We consider a slight generalization of Eq. (41) as (see also Appendix A)

$$\Omega^{(\mp)}=\lim_{\eta\to+0}U_\eta(0,\mp\infty)\frac{1}{\mathcal{P}U_\eta(0,\mp\infty)\mathcal{P}}.\tag{D25}$$

The corresponding effective Hamiltonian can also be written as

$$H_{\mathrm{eff}}^{(\mp)}=\mathcal{P}H\Omega^{(\mp)}.\tag{D26}$$

Here, we note that the effective Hamiltonian in principle should not depend on the choice of sign in Eq. (D26). Assuming the absence of degeneracy, the αth energy $\mathcal{E}_\alpha$ and the eigenvector $|\Psi_\alpha\rangle$, together with its projection $|F_\alpha\rangle=\mathcal{P}|\Psi_\alpha\rangle$ and its conjugate $|\widetilde{F}_\alpha\rangle$, are all uniquely defined. It follows that, in the limit of infinite order perturbation, the effective Hamiltonian, $H_{\mathrm{eff}}=\sum_{\alpha=1}^d|F_\alpha\rangle\mathcal{E}_\alpha\langle\widetilde{F}_\alpha|$, is uniquely defined. Nevertheless, we here keep distinction $+$ or $-$ in Eqs. (D25) and (D26) since the discussion above does not apply to a finite-order perturbation results.

We then redefine the effective operator $\mathcal{O}^{\mathrm{eff}}$ as

$$\mathscr{O}^{\mathrm{eff}}=\Omega^{(+)^\dagger}\mathcal{O}\Omega^{(-)},\tag{D27}$$

which is expanded as

$$\mathscr{O}^{\mathrm{eff}}=\sum_{\alpha=1}^d|\widetilde{F}_\alpha^{(+)}\rangle\langle\Psi_\alpha|\mathcal{O}|\Psi_\beta\rangle\langle\widetilde{F}_\beta^{(-)}|,\tag{D28}$$

where $|F_\alpha^{\mp}\rangle$ and $|\widetilde{F}_\alpha^{\mp}\rangle$ represents the αth right eigenvector of $H_{\mathrm{eff}}^{(\mp)}$ and its conjugate. The quantity $\mathscr{O}^{\mathrm{eff}}$ is different from the matrix of our interest, $\mathcal{O}^{\mathrm{eff}}$, defined as Eq. (57), but it is easy to transform into the desired form as $\mathcal{O}^{\mathrm{eff}}=\sum_{\alpha=1}^d|F_\alpha^{(-)}\rangle\langle F_\alpha^{(+)}|\mathscr{O}^{\mathrm{eff}}$.

By virtue of definition, Eq. (D27), $\mathscr{O}^{\mathrm{eff}}$ is expanded as

$$\mathscr{O}^{\mathrm{eff}}=\left(\lim_{\eta_1\to0}\frac{1}{\mathcal{P}U_{\eta_1}(\infty,0)\mathcal{P}}U_{\eta_1}(\infty,0)\right)$$
$$\times\mathcal{O}\left(\lim_{\eta_2\to0}U_{\eta_2}(0,-\infty)\frac{1}{\mathcal{P}U_{\eta_2}(0,-\infty)\mathcal{P}}\right).\tag{D29}$$

We can safely assume that the two limiting operations $(\eta_1,\eta_2)\to(0,0)$ can be deformed into $(\eta,\eta)\to(0,0)$ [92], and therefore we obtain

$$\mathscr{O}^{\mathrm{eff}}=\lim_{\eta\to0}\frac{1}{\mathcal{P}U_\eta(\infty,0)\mathcal{P}}\mathcal{T}(U_\eta(\infty,-\infty)$$
$$\times\mathcal{O}(0))\frac{1}{\mathcal{P}U_\eta(0,-\infty)\mathcal{P}},\tag{D30}$$

where the calculation of $\mathcal{T}(U_\eta(\infty,-\infty)\mathcal{O}(0))$ should be easier than $\mathcal{O}U_\eta(0,-\infty)$ because of the absence of the upper limit in the time integration.

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