

Relativistic Linear Response in Quantum-Electrodynamical Density Functional Theory

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We present the theoretical derivation and numerical implementation of the linear-response equations for relativistic quantum-electrodynamical density functional theory (QEDFT). In contrast to previous works based on the Pauli-Fierz Hamiltonian, our approach describes electrons interacting with photonic cavity modes at the four-component Dirac-Kohn-Sham level, derived from fully relativistic QED through a series of established approximations. Moreover, we show that a new type of spin-orbit-like (SO) cavity-mediated interaction appears under the relativistic description of the coupling of matter with quantized cavity modes. Benchmark calculations performed for atoms of group 12 elements (Zn, Cd, Hg) demonstrate how a relativistic treatment enables the description of exciton polaritons that arise from the hybridization of formally forbidden singlet-triplet transitions with cavity modes. For atoms in cavities tuned on resonance with a singlet-triplet transition, we discover a significant interplay between SO effects and coupling to an off-resonant intense singlet-singlet transition. This dynamic relationship highlights the crucial role of *ab initio* approaches in understanding cavity quantum electrodynamics. Finally, using the mercury porphyrin complex as an example, we show that relativistic linear-response QEDFT provides computationally feasible first-principles calculations of polaritonic states in large heavy-element-containing molecules of chemical interest.

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I. INTRODUCTION

The strength of light-matter coupling, normally weak when a material interacts with vacuum modes of free space, can be greatly enhanced by placing the material into an optical cavity. If a cavity mode is in resonance with an excitation of the material, new hybrid light-matter states called polaritons emerge [1–4]. Depending on the nature of the excitation, different types of polaritonic states exist, such as exciton polaritons and vibrational polaritons resulting from the coupling of light to electronic and vibrational transitions, respectively. As a result, a new field of cavity quantum-electrodynamical (QED) materials [1,2,5–7] has

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emerged, bringing together various platforms for manipulating and engineering quantum materials with electromagnetic fields. It encompasses a wide spectrum of different fields, including quantum optics [8], polaritonic chemistry [1,2,7,9–13], the generation of light-induced states of matter through classical fields [14,15], or quantum fields emanating from a cavity [16–19]. This rapidly growing field has attracted significant attention from both theorists and experimentalists, leading to the exploration of various effects under strong light-matter coupling. Strong light-matter interaction in a cavity enables the modification of chemical reaction landscapes [20–25] and ground states of matter [26–29], enhances charge and energy transfer [30–35], and allows for selective manipulation of electronic states [35], the modification of electron-phonon coupling and superconductivity [36–39], and controlling of excitons [40–42] while achieving exciton-polariton condensation [43,44]. In recent studies, quantum Hall systems, whether operating in the integer regime [45–49] or the fractional regime [50,51], have exhibited remarkable phenomena when confined within optical cavities. These systems have shown what is known as ultrastrong coupling with the light field, resulting in significant changes in their transport properties [52]. Furthermore, there is a growing interest in exploring the implications of coupling with chiral electromagnetic fields, and this topic is currently being actively investigated [53–56]. This regime of the strong coupling between matter and light can be achieved due to collective effects, when a large number of molecules is placed in a cavity and coherently interact with its modes or for micro- and nanocavities that confine light to very small length scales [1,3,7,57,58].

To describe the interaction of the material with vacuum fluctuations, i.e., cavity modes, the quantum description of light is important, making QED the theory of choice. The standard practical approach is provided by models of cavity QED, which describe a system of photons strongly coupled to a material approximated as a few-level system, e.g., the Jaynes-Cummings [59] and the Dicke [60] model. However, if we want to capture subtle and complex changes of the material inside a cavity, a first-principles description of the matter subsystem becomes necessary [2].

To bridge the worlds of quantum chemistry and quantum optics, new computational methods that simultaneously allow *ab initio* description of matter while treating transverse photons as dynamical variables were developed [2,7,12,61,62]. The first such method was quantum-electrodynamical density functional theory (QEDFT) proposed for time-dependent properties [63–65] and ground state coupled to vacuum [66,67]. In addition to noninteracting auxiliary systems in the Kohn-Sham formulation of QEDFT, also alternative, explicitly correlated approaches were introduced [68]. The first computational implementations of QEDFT were reported by Flick *et al.* for time-dependent situations [5,69], for ground-state

properties [26], and finally as a linear-response theory of a coupled matter-photon system and formulated on a real-space grid [70]. It motivated subsequent implementations based on Gaussian orbitals [71,72], as well as a development of a real-space Sternheimer formalism [73]. Moreover, the work of Yang *et al.* [71] also considered various simplified cases based on the neglect of the dipole self-energy terms and on the Tamm-Dancoff approximation for electrons [74], as well as on an analogous approximation for photons, together with the different combinations of these approximations. In addition to QEDFT, *ab initio* theories combining QED with wave-function-based quantum chemical methods were developed, starting with quantum-electrodynamical Hartree-Fock theory [75–77], ranging to quantum-electrodynamical coupled clusters [76,78] and quantum-electrodynamical configuration interaction singles [79], as well as Green's-function-based approaches [80] and reduced density matrix theories [75,77].

Most of these realizations of QEDFT were based on the nonrelativistic Pauli-Fierz Hamiltonian. However, there exists a plethora of phenomena called relativistic effects that are not covered by the nonrelativistic-, Schrödinger-, or Pauli-equation-based treatment and are described correctly only within relativistic theories based on the Dirac equation [81]. The most prominent examples include the color of gold [82,83], the liquid state of mercury [84], and the voltage of the lead-acid battery [85]. Further manifestations of relativistic effects in atomic, molecular, and solid-state systems involve bound-electron g factor [86,87], electron absorption and x-ray spectra [88–92], NMR [93–96], paramagnetic NMR [97–101], and EPR spectroscopies [101–106], bond lengths, [107] reaction mechanisms [108], phosphorescence and decay pathways [109], properties of superheavy elements [110,111], band structures [112], band gap opening, [113–115], and the stability of structural phases [116]. Relativistic quantum chemistry [117,118] addresses the relativistic effects by describing electrons at the level of the Dirac equation. The gold standard is represented by the four-component (4c) Dirac-Coulomb Hamiltonian that combines the one-electron Dirac equation with the instantaneous Coulomb interaction among electrons and nuclei and electrons with each other [119]. This Hamiltonian contains relativistic kinetic energy as well as one-electron spin-orbit coupling (SOC) and is sometimes extended to include Breit terms [119–122]. Moreover, there is an ongoing research effort focused on including the effects of relativistic QED in quantum chemistry to account for radiative corrections [123–130]. At the same time, researchers are developing approximate two-component Hamiltonians that would capture the most important relativistic effects at a lower computational cost [131–134].

QEDFT with relativistic Dirac-equation-based treatment of electronic structure thus enables the correct description of molecules containing any element across the periodic table

when strongly coupled to cavity modes (under certain stability conditions detailed in Sec. II B). Moreover, the 4c description includes SOC variationally, thus allowing first-principles access to singlet-triplet transitions that are forbidden according to nonrelativistic theories. While spin-orbit coupling can be added perturbatively, usually up to the first order in Z/c^2 (Z being the atomic number and c the speed of light), the fully relativistic treatment accounts for the higher-order effect that can become prominent for high- Z systems [135]. In addition, the linear-response properties, such as the coupling strengths between the singlet and triplet states or the phosphorescence parameters, are correctly obtained from the first-order perturbation theory [136], instead of requiring the more demanding quadratic response as they would with perturbative SOC [137]. Another case for relativistic QEDFT is provided by cavity engineering of the energy ratio between singlet-singlet and singlet-triplet excited states. This was suggested to improve the yields of singlet fission [138] and intersystem crossing [35,139], particularly for heavy-element-containing systems where the rate of these processes is enhanced by the increased spin-orbit coupling [140,141]. Additionally, the inclusion of SOC in QEDFT theory will enable one to compute spin-orbit-related phenomena in complex nanostructures and solids [142,143].

At the same time, relativistic QEDFT calculations close the gap between the stable and nonperturbative low-energy sector of QED described by the Pauli-Fierz quantum field theory [7,144,145] and a fully second-quantized QED formulation in various flavors [146–148]. Even without cavities and their changes in the modes of the electromagnetic field, there are many fundamental questions still to be answered within QED as a general framework to describe on the most fundamental level the interaction between charged particles and light [149].

In this work, we introduce a *relativistic* QEDFT for molecules that combines four-component Dirac-Kohn-Sham

treatment of electrons with quantized description of photonic modes. We first present the theoretical foundation of the developed method, where we derive the relativistic Hamiltonian for the coupled light-matter system in the long-wavelength approximation. We demonstrate the emergence of a novel spin-orbit-like cavity-mediated interaction within the framework of relativistic coupling between matter and quantized cavity modes. Then, in Sec. II D, we formulate a linear-response equation in the framework of QEDFT for its excitation energies that allows the first-principles calculation of polaritonically modified spectra and present its numerical implementation. As an example, we calculate the absorption spectra of Zn, Cd, and Hg atoms, focusing on the singlet-triplet transitions in a cavity. Via careful analysis of the absorption spectra, we show that there is a significant interplay between spin-orbit effects and off-resonant coupling to the intense singlet-singlet transition. This interplay highlights the crucial role of the *ab initio* approach in understanding cavity quantum electrodynamics. Finally, we considered a large heavy-element complex to demonstrate the applicability of our method to systems of chemical interest.

II. THEORY

The Systeme International system of units is used throughout the paper unless specified otherwise. For additional notations and conventions, see Appendix A.

A. Light-matter coupling in fully relativistic limit: Total Hamiltonian of a system

We consider a system of electrons minimally coupled to photons in the presence of external classical fields. The full QED Hamiltonian of such a system in Coulomb gauge is formally given as [64,150]

$$\begin{aligned} \hat{H}_{\text{QED}}(t) = & \int d\mathbf{r} : \hat{\psi}(\mathbf{r}) (-i\hbar c \boldsymbol{\gamma} \cdot \nabla + \alpha^0 m c^2) \hat{\psi}(\mathbf{r}) : + \frac{1}{c} \int d\mathbf{r} : \hat{j}^0(\mathbf{r}) : a_0^{\text{ext}}(\mathbf{r}, t) \\ & + \frac{1}{c^2} \int d\mathbf{r} d\mathbf{r}' \frac{j_0^{\text{ext}}(\mathbf{r}, t) : \hat{j}^0(\mathbf{r}') :}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \frac{1}{2c^2} \int d\mathbf{r} d\mathbf{r}' \frac{\hat{j}_0(\mathbf{r}) \hat{j}_0(\mathbf{r}') :}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \\ & - \frac{1}{c} \int d\mathbf{r} : \hat{\mathbf{j}}(\mathbf{r}) (\mathbf{a}^{\text{ext}}(\mathbf{r}, t) + \hat{\mathbf{A}}(\mathbf{r})) : - \frac{1}{c} \int d\mathbf{r} \mathbf{j}^{\text{ext}}(\mathbf{r}, t) \hat{\mathbf{A}}(\mathbf{r}) \\ & + \frac{\epsilon_0}{2} \int d\mathbf{r} : (\hat{\mathbf{E}}_{\perp}^2(\mathbf{r}) + c^2 \hat{\mathbf{B}}^2(\mathbf{r})) :. \end{aligned} \quad (1)$$

Here c is the speed of the light in free-space vacuum, $\hbar$ is the reduced Planck constant, ϵ_0 is the vacuum permittivity, m is the bare mass of the electron, and $\alpha^\mu = \gamma^0 \gamma^\mu$ are the Dirac matrices in the standard representation (see

Appendix A). Here, all the operators are in the Schrödinger picture and $::$ denotes their normal ordering.

The electron-positron field operator $\hat{\psi}(\mathbf{r})$ is given by [150,151]

$$\hat{\psi}(\mathbf{r}) = \sum_{\mu=\pm\frac{1}{2}} \int d\mathbf{p} \left(\hat{a}_{\mathbf{p}\mu} \psi_{\mathbf{p}\mu}^{(+)}(\mathbf{r}) + \hat{b}_{\mathbf{p}\mu}^{\dagger} \psi_{\mathbf{p}\mu}^{(-)}(\mathbf{r}) \right), \quad (2)$$

where $\hat{a}_{\mathbf{p}\mu}$ is an annihilation operator of the electron with momentum $\mathbf{p} = (p_x, p_y, p_z)$ and helicity μ , and operator $\hat{b}_{\mathbf{p}\mu}^{\dagger}$ is a creation operator for the positron with the same momenta and helicity. Here, $\psi_{\mathbf{p}\mu}^{(+)}(\mathbf{r})$ and $\psi_{\mathbf{p}\mu}^{(-)}(\mathbf{r})$ are the solutions of the free Dirac equation for the electron and positron, respectively. The electron-positron field operator $\hat{\psi}(\mathbf{r})$ formally obeys the usual Heisenberg equation of motion (here we indicate with label H the Heisenberg picture)

$$\frac{d}{dt} \hat{\psi}_H(\mathbf{r}, t) = \frac{i}{\hbar} [\hat{H}_{\text{QED,H}}(t), \hat{\psi}_H(\mathbf{r}, t)]. \quad (3)$$

The Dirac four-current operator $\hat{J}(\mathbf{r})$ is constructed as $\hat{J}(\mathbf{r}) = (\hat{j}_0(\mathbf{r}), \hat{\mathbf{j}}(\mathbf{r}))$ with the components having the following form:

$$\hat{j}_0(\mathbf{r}) = ec : \hat{\psi}(\mathbf{r}) \gamma_0 \hat{\psi}(\mathbf{r}) :, \quad (4)$$

$$\hat{\mathbf{j}}(\mathbf{r}) = ec : \hat{\psi}(\mathbf{r}) \boldsymbol{\gamma} \hat{\psi}(\mathbf{r}) :, \quad (5)$$

where $\hat{\psi}(\mathbf{r}) \equiv \hat{\psi}^{\dagger}(\mathbf{r}) \gamma^0$. The quantized vector potential $\hat{\mathbf{A}}(\mathbf{r})$ in Coulomb gauge is given by [150]

$$\hat{\mathbf{A}}(\mathbf{r}) = \sqrt{\frac{c^2 \hbar}{\epsilon_0 (2\pi)^3}} \int \frac{d\mathbf{k}}{\sqrt{2\omega_{\mathbf{k}}}} \sum_{\lambda=1}^2 [\hat{a}(\mathbf{k}, \lambda) e^{i\mathbf{k} \cdot \mathbf{r}} \boldsymbol{\epsilon}(\mathbf{k}, \lambda) + \hat{a}^{\dagger}(\mathbf{k}, \lambda) e^{-i\mathbf{k} \cdot \mathbf{r}} \boldsymbol{\epsilon}^*(\mathbf{k}, \lambda)]. \quad (6)$$

We note that, in comparison with the usual definition of a vector potential, we here have an extra multiplication by c in order to have the units of A_{μ} in volts. In Eq. (6), $\hat{a}(\mathbf{k}, \lambda)$ and $\hat{a}^{\dagger}(\mathbf{k}, \lambda)$ are the creation and annihilation operators of a photon with momentum $\mathbf{k}$ and helicity λ , respectively; $\omega_{\mathbf{k}} = c|\mathbf{k}|$ is the energy of the photon and $\boldsymbol{\epsilon}(\mathbf{k}, \lambda)$ is the transverse dimensionless polarization vector that obeys [150]

$$\mathbf{k} \cdot \boldsymbol{\epsilon}(\mathbf{k}, \lambda) = \boldsymbol{\epsilon}^*(\mathbf{k}, 1) \cdot \boldsymbol{\epsilon}(\mathbf{k}, 2) = 0. \quad (7)$$

We note that in a Coulomb gauge the field $\hat{\mathbf{A}}(\mathbf{r})$ is fully transverse, i.e., $\nabla \cdot \hat{\mathbf{A}}(\mathbf{r}) = 0$.

The vector potential $\hat{\mathbf{A}}(\mathbf{r})$ formally obeys the following equation of motion:

$$\frac{d}{dt} \hat{\mathbf{A}}_H(\mathbf{r}, t) = \frac{i}{\hbar} [\hat{H}_{\text{QED,H}}(t), \hat{\mathbf{A}}_H(\mathbf{r}, t)]. \quad (8)$$

The last term in Eq. (1) is the free photon Hamiltonian $\hat{H}_{\text{ph,free}}$ which creates and annihilates only transverse photons. Using Eq. (6), one can rewrite it as

$$\begin{aligned} \hat{H}_{\text{ph,free}} &= \frac{\epsilon_0}{2} \int d\mathbf{r} : (\hat{\mathbf{E}}_{\perp}^2(\mathbf{r}) + c^2 \hat{\mathbf{B}}^2(\mathbf{r})) : \\ &= \sum_{\lambda=1}^2 \int d\mathbf{k} \hbar \omega_{\mathbf{k}} \hat{a}^{\dagger}(\mathbf{k}, \lambda) \hat{a}(\mathbf{k}, \lambda). \end{aligned} \quad (9)$$

Here $\hat{\mathbf{E}}_{\perp}(\mathbf{r}) = \{ -[(\partial \hat{\mathbf{A}}_H(\mathbf{r}, t)) / (c \partial t)] \}_S$, with the subindex S denoting the Schrödinger picture, and $\hat{\mathbf{B}}(\mathbf{r}) = (1/c) \nabla \times \hat{\mathbf{A}}(\mathbf{r})$ are quantized transverse electric and magnetic fields, respectively [150], which expressed via photonic creation and annihilation operators assume the form

$$\begin{aligned} \hat{\mathbf{E}}_{\perp}(\mathbf{r}) &= \sqrt{\frac{\hbar}{\epsilon_0 (2\pi)^3}} \int \frac{d\mathbf{k} i \omega_{\mathbf{k}}}{\sqrt{2\omega_{\mathbf{k}}}} \sum_{\lambda=1}^2 [\hat{a}(\mathbf{k}, \lambda) e^{i\mathbf{k} \cdot \mathbf{r}} \boldsymbol{\epsilon}(\mathbf{k}, \lambda) \\ &\quad - \hat{a}^{\dagger}(\mathbf{k}, \lambda) e^{-i\mathbf{k} \cdot \mathbf{r}} \boldsymbol{\epsilon}^*(\mathbf{k}, \lambda)], \end{aligned} \quad (10)$$

$$\begin{aligned} \hat{\mathbf{B}}(\mathbf{r}) &= \sqrt{\frac{\hbar}{\epsilon_0 (2\pi)^3}} \int \frac{d\mathbf{k} i}{\sqrt{2\omega_{\mathbf{k}}}} \sum_{\lambda=1}^2 [\hat{a}(\mathbf{k}, \lambda) e^{i\mathbf{k} \cdot \mathbf{r}} [\mathbf{k} \times \boldsymbol{\epsilon}(\mathbf{k}, \lambda)] \\ &\quad - \hat{a}^{\dagger}(\mathbf{k}, \lambda) e^{-i\mathbf{k} \cdot \mathbf{r}} [\mathbf{k} \times \boldsymbol{\epsilon}^*(\mathbf{k}, \lambda)]]. \end{aligned} \quad (11)$$

In our system, we also introduce external (with respect to the system's electrons plus photons) classical magnetic vector potential $\mathbf{a}^{\text{ext}}(\mathbf{r}, t)$ and scalar potential $a_0^{\text{ext}}(\mathbf{r}, t)$, as well as classical external four-currents $\mathbf{J}^{\text{ext}}(\mathbf{r}, t) = (j_0^{\text{ext}}(\mathbf{r}, t), \mathbf{j}^{\text{ext}}(\mathbf{r}, t))$ with $\rho^{\text{ext}}(\mathbf{r}, t)$ being a charge density. Using Eq. (6) one can rewrite the energy due to coupling to a classical external charge current $\mathbf{j}^{\text{ext}}(\mathbf{r}, t)$ as [66]

$$\begin{aligned} \frac{1}{c} \int d\mathbf{r} \mathbf{j}^{\text{ext}}(\mathbf{r}, t) \cdot \hat{\mathbf{A}}(\mathbf{r}) &= \int d\mathbf{k} \hbar \omega_{\mathbf{k}} (\hat{a}(\mathbf{k}, \lambda) [j^{\text{ext}}]^*(\mathbf{k}, \lambda, t) \\ &\quad + j^{\text{ext}}(\mathbf{k}, \lambda, t) \hat{a}^{\dagger}(\mathbf{k}, \lambda)), \end{aligned} \quad (12)$$

with the expansion coefficients $j^{\text{ext}}(\mathbf{k}, \lambda, t) = [j^{\text{ext}}(-\mathbf{k}, \lambda, t)]^* = (\frac{1}{2} \omega_{\mathbf{k}}^3 \epsilon_0 \hbar (2\pi)^3)^{-1/2} \int d\mathbf{r} \boldsymbol{\epsilon}^*(\mathbf{k}, \lambda) \cdot \mathbf{j}^{\text{ext}}(\mathbf{r}, t) \times e^{-i\mathbf{k} \cdot \mathbf{r}}$. We note that, with these expansion coefficients, one can recover the transverse part of the external current, since $\boldsymbol{\epsilon}(\mathbf{k}, \lambda)$ is a transverse vector,

$$\begin{aligned} \mathbf{j}_{\perp}^{\text{ext}}(\mathbf{r}, t) &= \sqrt{\frac{\hbar \epsilon_0}{(2\pi)^3}} \int \frac{d\mathbf{k} \omega_{\mathbf{k}}^2}{\sqrt{2\omega_{\mathbf{k}}}} \sum_{\lambda=1}^2 [j^{\text{ext}}(\mathbf{k}, \lambda, t) e^{i\mathbf{k} \cdot \mathbf{r}} \boldsymbol{\epsilon}(\mathbf{k}, \lambda) \\ &\quad + [j^{\text{ext}}(\mathbf{k}, \lambda, t)]^* e^{-i\mathbf{k} \cdot \mathbf{r}} \boldsymbol{\epsilon}^*(\mathbf{k}, \lambda)]. \end{aligned} \quad (13)$$

B. Approximations

We note that, so far, we have chosen implicitly circularly polarized vectors $\boldsymbol{\epsilon}(\mathbf{k}, \lambda)$. However, for the quantization of the electromagnetic field, one can choose any pair of polarization vectors obeying Eq. (7), for example, linearly polarized ones. We also note that circular and linear representations are connected by a canonical transformation that preserves the form of the equations. Therefore,

without loss of generality, we restrict ourselves to the case of linear polarization, i.e., real transverse polarization vectors. Then, the coupling term from Eq. (12) reads as

$$\begin{aligned} & \frac{1}{c} \int d\mathbf{r} \mathbf{j}^{\text{ext}}(\mathbf{r}, t) \hat{\mathbf{A}}(\mathbf{r}) \\ &= \int d\mathbf{k} \hbar \omega_{\mathbf{k}} j^{\text{ext}}(\mathbf{k}, \lambda, t) (\hat{a}(\mathbf{k}, \lambda) + \hat{a}^\dagger(\mathbf{k}, \lambda)), \end{aligned} \quad (14)$$

with the real expansion coefficients

$$\begin{aligned} j^{\text{ext}}(\mathbf{k}, \lambda, t) &= [j^{\text{ext}}(\mathbf{k}, \lambda, t)]^* \\ &= \left(\frac{1}{2} \omega_{\mathbf{k}}^3 \epsilon_0 \hbar (2\pi)^3 \right)^{-1/2} \\ &\quad \times \int d\mathbf{r} \boldsymbol{\epsilon}(\mathbf{k}, \lambda) \cdot \mathbf{j}^{\text{ext}}(\mathbf{r}, t) \exp^{-i\mathbf{k} \cdot \mathbf{r}}. \end{aligned} \quad (15)$$

Next, we would like to work with a stable vacuum, i.e., the energy gap between the positive- and negative-energy solutions of the Dirac equation is nonzero. If the intensity of the external fields is small compared to the Schwinger limit, and if one considers the long-wavelength approximation, then no pair production occurs [152–154]. The energy gap then substitutes the boundedness from below (minimal-energy state) of nonrelativistic theories. Since no pair creation is present, in addition to charge conservation, particle-number conservation is satisfied, allowing us to proceed to a first-quantized formulation for electrons. Specifically, due to the long-wavelength approximation, Eq. (6) can be written as

$$\hat{\mathbf{A}} = \sqrt{\frac{\hbar c^2}{\epsilon_0 (2\pi)^3}} \int \frac{d\mathbf{k}}{\sqrt{2\omega_{\mathbf{k}}}} \sum_{\lambda=1}^2 \boldsymbol{\epsilon}(\mathbf{k}, \lambda) [\hat{a}(\mathbf{k}, \lambda) + \hat{a}^\dagger(\mathbf{k}, \lambda)], \quad (16)$$

and then the Hamiltonian of Eq. (1) takes a form

$$\begin{aligned} \hat{H}_{\text{QED}}^{\text{dip}}(t) &\approx \sum_{l=1}^N [-i\hbar c \boldsymbol{\alpha}_l \cdot \nabla_l + \beta_l m c^2 + e a_0^{\text{ext}}(\mathbf{r}_l, t)] \\ &\quad + \frac{e}{c} \sum_{l=1}^N \int d\mathbf{r} \frac{j_0^{\text{ext}}(\mathbf{r}, t)}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}_l|} \\ &\quad + \frac{1}{2} \sum_{l \neq m}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{r}_m|} - e \sum_{l=1}^N (\boldsymbol{\alpha}_l \cdot \mathbf{a}^{\text{ext}}(t) + \boldsymbol{\alpha}_l \cdot \hat{\mathbf{A}}) \\ &\quad + \sum_{\lambda=1}^2 \int d\mathbf{k} \hbar \omega_{\mathbf{k}} [\hat{a}^\dagger(\mathbf{k}, \lambda) \hat{a}(\mathbf{k}, \lambda) \\ &\quad - j^{\text{ext}}(\mathbf{k}, \lambda, t) [\hat{a}(\mathbf{k}, \lambda) + \hat{a}^\dagger(\mathbf{k}, \lambda)]], \end{aligned} \quad (17)$$

where N is the number of electrons in the system. Assume we are dealing with a cavity, in which case the free-space mode expansion Eq. (16) can be converted into the corresponding expansion for the photonic structure, e.g., Fabry-Pérot cavity [155] (see Fig. 1). Since we are working

in a dipole approximation, i.e., no momentum is transferred in a cavity, the actual spatial mode structure and the momentum matching are no longer important. As a result, one can modify free-space frequencies, coupling strength, and polarizations to fit a given cavity structure without breaking fundamental symmetries [7],

$$\hat{\mathbf{A}} = \sqrt{\hbar c^2} \sum_{\alpha}^{M_p} g_{\alpha} \boldsymbol{\epsilon}_{\alpha} \hat{Q}_{\alpha}. \quad (18)$$

Here, we have assumed a discretized continuum of M_p modes labeled by α , with each α corresponding to a different frequency ω_{α} , coupling strength g_{α} , and polarization $\boldsymbol{\epsilon}_{\alpha}$. The modes are given in terms of generalized coordinates $\hat{Q}_{\alpha}$ such as

$$\hat{a}_{\alpha} = \sqrt{\frac{\omega_{\alpha}}{2}} \left(\hat{Q}_{\alpha} + \frac{1}{\omega_{\alpha}} \frac{\partial}{\partial \hat{Q}_{\alpha}} \right), \quad (19)$$

$$\hat{a}_{\alpha}^{\dagger} = \sqrt{\frac{\omega_{\alpha}}{2}} \left(\hat{Q}_{\alpha} - \frac{1}{\omega_{\alpha}} \frac{\partial}{\partial \hat{Q}_{\alpha}} \right), \quad (20)$$

$$\left[\hat{Q}_{\alpha}, -i \frac{\partial}{\partial \hat{Q}_{\alpha'}} \right] = i \delta_{\alpha\alpha'}, \quad (21)$$

$$[\hat{a}_{\alpha}, \hat{a}_{\alpha'}^{\dagger}] = \delta_{\alpha\alpha'}, \quad (22)$$

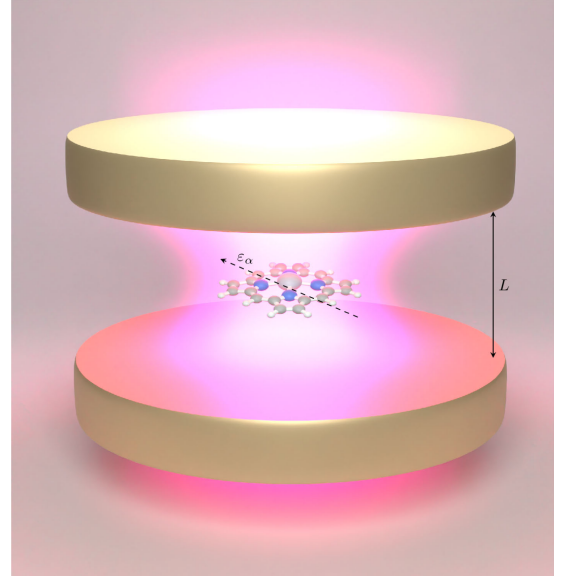


FIG. 1. Schematic representation of a Fabry-Pérot cavity. We assume that a molecule or molecules of interest are localized around a cavity's center, far away from the cavity mirrors. Then one can approximate the main frequency due to the distance between mirrors L by $\omega_n = c(\pi/L)|\mathbf{n}|$ with $\mathbf{n}$ parallel to L . The influence of the continuum free-space modes (perpendicular to L) is incorporated in the observable mass of the particles. The coupling strength $g_{\alpha \equiv (n, \lambda)}$ for the two independent polarization directions λ of the polarization vector $\boldsymbol{\epsilon}_{\alpha \equiv (n, \lambda)}$ increases proportionally to the $\sqrt{1/V}$, where V is an effective volume of a cavity.

where $-i[\partial/(\partial\hat{Q}_\alpha)]$ is conjugate momenta of a generalized coordinate, and $\hat{a}_\alpha$ and $\hat{a}_\alpha^\dagger$ are annihilation and creation of the photon in a mode α , respectively. We note that, in the case of free space with a quantization volume l^3 , the quantities from Eq. (18) correspond to $\mathbf{k}_m = 2\pi\mathbf{m}/l$, $\alpha \equiv (\mathbf{k}_m, \lambda)$, $\omega_\alpha = c|\mathbf{k}_m|$, and $g_\alpha = \sqrt{1/\epsilon_0 l^3}$, where $\mathbf{m} \in \mathbb{Z}^3$. In the case of general photonic structures, the respective quantities can be determined from, e.g., macroscopic QED [156]. Using Eqs. (18)–(22), one can rewrite Eq. (17) as

$$\begin{aligned} \hat{H}_{\text{QED,cavity}}^{\text{dip}}(t) &\cong \sum_{l=1}^N [-i\hbar c \boldsymbol{\alpha}_l \cdot \nabla_l + \beta_l m c^2 + e a_0^{\text{ext}}(\mathbf{r}_l, t)] \\ &+ \frac{1}{2} \sum_{l \neq m}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{r}_m|} - e \sum_{l=1}^N [\boldsymbol{\alpha}_l \cdot \mathbf{a}^{\text{ext}}(t) + \boldsymbol{\alpha}_l \cdot \hat{\mathbf{A}}] \\ &+ \sum_{\alpha=1}^{M_p} \left(-\frac{\hbar}{2} \frac{\partial^2}{\partial \hat{Q}_\alpha^2} + \frac{\hbar \omega_\alpha^2}{2} \hat{Q}_\alpha^2 - \sqrt{2\hbar^2 \omega_\alpha^3} j_\alpha^{\text{ext}}(t) \hat{Q}_\alpha \right), \quad (23) \end{aligned}$$

where

$$j_\alpha^{\text{ext}}(t) = [j_\alpha^{\text{ext}}(t)]^* = \left(\frac{1}{2} \omega_\alpha^3 \hbar \right)^{-1/2} \frac{1}{\epsilon_0 g_\alpha} \boldsymbol{\epsilon}_\alpha \cdot \mathbf{j}^{\text{ext}}(t). \quad (24)$$

Note that we probe our system with an external perturbation $\mathbf{a}^{\text{ext}}(\mathbf{r}_l, t)$ that does not generate longitudinal currents, i.e., $j_0^{\text{ext}}(\mathbf{r}, t) = 0$.

In the dipole approximation, it is possible to eliminate the term $e \sum_{l=1}^N [\boldsymbol{\alpha}_l \cdot \mathbf{a}^{\text{ext}}(t) + \boldsymbol{\alpha}_l \cdot \hat{\mathbf{A}}]$ from Eq. (23) by performing the unitary length-gauge transformation, which is defined as [65,155,157]

$$\hat{H}_L = \hat{U}^\dagger \hat{H} \hat{U} - i\hbar \hat{U}^\dagger (\partial_t \hat{U}), \quad \hat{U} = e^{i\hbar^{-1}[\hat{\mathbf{A}} + \mathbf{a}^{\text{ext}}(t)] \cdot \boldsymbol{\mu}}, \quad (25)$$

where $\boldsymbol{\mu} = \sum_{i=1}^N e \mathbf{r}_i$ is the total dipole operator of the electrons in a system, and index L indicates the length gauge. Using Eq. (25), one can rewrite the Hamiltonian in length gauge as

$$\begin{aligned} \hat{U}^\dagger \hat{H}_{\text{QED,cavity}}^{\text{dip}}(t) \hat{U} &= \hat{H}_L(t) \\ &= \sum_{l=1}^N [-i\hbar c \boldsymbol{\alpha}_l \cdot \nabla_l + \beta_l m c^2 + e a_0^{\text{ext}}(\mathbf{r}_l, t)] + \frac{1}{2} \sum_{l \neq m}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{r}_m|} - \sum_{l=1}^N v^{\text{ext}}(\mathbf{r}_l, t) \\ &+ \sum_{\alpha=1}^{M_p} \left(\frac{\hbar}{2} \left(\omega_\alpha \hat{q}_\alpha - \frac{g_\alpha \boldsymbol{\epsilon}_\alpha \cdot \boldsymbol{\mu}}{\sqrt{\hbar}} \right)^2 - \frac{\hbar}{2} \frac{\partial^2}{\partial \hat{q}_\alpha^2} + i\sqrt{2\hbar^2 \omega_\alpha} j_\alpha^{\text{ext}}(t) \frac{\partial}{\partial \hat{q}_\alpha} \right), \quad (26) \end{aligned}$$

where $v^{\text{ext}}(\mathbf{r}_l, t) = e \mathbf{E}^{\text{ext}}(t) \cdot \mathbf{r}_l$ is the external potential generated by the external electric field $\mathbf{E}^{\text{ext}}(t) = -[\partial/(c\partial t)] \mathbf{a}^{\text{ext}}(t)$. Here, we have performed the additional canonical transformations $-i(\partial/\partial\hat{Q}_\alpha) \mapsto -\omega_\alpha \hat{q}_\alpha$, $\hat{Q}_\alpha \mapsto -i[\partial/(\omega_\alpha \partial \hat{q}_\alpha)]$, which leave the commutation relations unchanged, i.e. $\{\hat{Q}_\alpha, -i[\partial/(\partial\hat{Q}_\alpha)]\} = \{-i[\partial/(\omega_\alpha \partial \hat{q}_\alpha)], -\omega_\alpha \hat{q}_\alpha\} = i\delta_{\alpha\alpha'}$. We want to note that $\hat{q}_\alpha$ does not correspond to a pure photonic quantity when we couple the modes to the electronic system. It is connected to the auxiliary displacement field of the macroscopic Maxwell equations and is usually referred to as a displacement coordinate [155,157].

We are interested in studying the electronic structure properties of molecules and/or atoms coupled to photon modes. Then, $e a_0^{\text{ext}}(\mathbf{r}_l, t) \rightarrow v_{\text{nuc}}(\mathbf{r}_l) = -[1/(4\pi\epsilon_0)] \times \sum_{j=1}^{N_n} [(Z_j e^2)/|\mathbf{r}_l - \mathbf{R}_j|]$ is a Coulomb potential describing the interaction of N_n nuclei with the bound electrons. Yet, we perform another time-dependent unitary transformation

$\hat{U}(t) = e^{i\hbar^{-1} \sum_{\alpha=1}^{M_p} \hat{q}_\alpha \sqrt{2\hbar^2 \omega_\alpha} j_\alpha^{\text{ext}}(t)}$ aiming to eliminate the last term in Eq. (26). Then, the Hamiltonian Eq. (26) takes the final form

$$\begin{aligned} \hat{H}_L(t) &= \sum_{l=1}^N [-i\hbar c \boldsymbol{\alpha}_l \cdot \nabla_l + \beta_l m c^2 + v_{\text{nuc}}(\mathbf{r}_l)] \\ &+ \frac{1}{2} \sum_{m \neq l}^N \sum_{l=1}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{r}_m|} - \sum_{l=1}^N v^{\text{ext}}(\mathbf{r}_l, t) \\ &+ \sum_{\alpha=1}^{M_p} \left(\frac{\hbar}{2} \left(\omega_\alpha \hat{q}_\alpha - \frac{g_\alpha \boldsymbol{\epsilon}_\alpha \cdot \boldsymbol{\mu}}{\sqrt{\hbar}} \right)^2 - \frac{\hbar}{2} \frac{\partial^2}{\partial \hat{q}_\alpha^2} \right. \\ &\left. + \sqrt{2\hbar^2 \omega_\alpha} [\partial_t j_\alpha^{\text{ext}}(t)] \hat{q}_\alpha \right), \quad (27) \end{aligned}$$

where we disregarded the physically irrelevant time-dependent energy or phase shift $-\hbar[j_\alpha^{\text{ext}}(t)]^2$ and we assume in the following that the center of charge of the nuclear

system is at the origin of the Euclidean coordinate system. Otherwise, we will have a linear potential from the total nuclear dipole on the electrons and on the photon modes [157], which we can subsume in a modified external scalar potential and current, respectively.

A particular consequence of the Dirac Hamiltonian is the emergence of the SOC. While SOC can be added *ad hoc* into a nonrelativistic theory based on the Schrödinger equation, it arises naturally only in the Dirac equation

due to its multicomponent structure. The SOC can be made explicit when expressing the Dirac equation in a two-component form or when performing expansion in different orders of the speed of light [117]. There are formally different ways of obtaining such an expansion [158,159]. In our case, the most convenient form is from the relativistic energy correction, such that the potential from the nuclei gives rise to one-electron SOC contributions

$$\Delta E_{1e\text{SOC}} = \frac{1}{4m^2c^2} \left\langle \left(\sum_{l=1}^N \boldsymbol{\sigma}_l \cdot \hat{\mathbf{p}}_l \right) \Psi^L \left| \sum_{m=1}^N v_{\text{nuc}}(\mathbf{r}_m) \left(\sum_{l'=1}^N \boldsymbol{\sigma}_{l'} \cdot \hat{\mathbf{p}}_{l'} \right) \Psi^L \right. \right\rangle, \quad (28)$$

while the electron-electron Coulomb interactions lead to two-electron SOC contributions

$$\Delta E_{2e\text{SOC}} = \frac{1}{4m^2c^2} \left\langle \left(\sum_{l=1}^N \boldsymbol{\sigma}_l \cdot \hat{\mathbf{p}}_l \right) \Psi^L \left| \frac{1}{2} \sum_{m' \neq m}^N \sum_{m=1}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_m - \mathbf{r}_{m'}|} \left(\sum_{l'=1}^N \boldsymbol{\sigma}_{l'} \cdot \hat{\mathbf{p}}_{l'} \right) \Psi^L \right. \right\rangle, \quad (29)$$

where $\hat{\mathbf{p}} = -i\hbar\nabla$ and Ψ^L is the respective “large” component of the Dirac wave function. In the presence of SOC, the spin operator no longer commutes with the Hamiltonian, meaning that the eigenstates of the Hamiltonian are not eigenstates of the spin operator, referred to as “spin no longer being a good quantum number” [117,118]. This results, for example, in nonzero transition amplitudes between states of different spin symmetry. Following the same strategy as done for the standard terms of Eqs. (28) and (29) also for the new cavity-coupling term, we obtain cavity-mediated SOC contributions from the relativistic energy correction as

$$\begin{aligned} \Delta E &= \frac{1}{4m^2c^2} \left\langle \left(\sum_{l=1}^N \boldsymbol{\sigma}_l \cdot \hat{\mathbf{p}}_l \right) \Psi^L \left| \sum_{\alpha=1}^{M_p} \frac{\hbar}{2} \left(-\frac{2\omega_\alpha \hat{q}_\alpha g_\alpha \boldsymbol{\epsilon}_\alpha \cdot \boldsymbol{\mu}}{\sqrt{\hbar}} + \frac{g_\alpha^2 (\boldsymbol{\epsilon}_\alpha \cdot \boldsymbol{\mu})^2}{\hbar} \right) \left(\sum_{l'=1}^N \boldsymbol{\sigma}_{l'} \cdot \hat{\mathbf{p}}_{l'} \right) \Psi^L \right. \right\rangle \\ &= - \left\langle \Psi^L \left| \sum_{l=1}^N \sum_{\alpha=1}^{M_p} \frac{\hat{q}_\alpha \sqrt{\hbar^3} \omega_\alpha g_\alpha e}{8m^2c^2} (\boldsymbol{\epsilon}_\alpha \cdot (\hat{\mathbf{p}}_l \times \boldsymbol{\sigma}_l) + (\hat{\mathbf{p}}_l \times \boldsymbol{\sigma}_l) \cdot \boldsymbol{\epsilon}_\alpha) \right| \Psi^L \right\rangle \\ &\quad + \left\langle \Psi^L \left| \sum_{l=1}^N \sum_{k=1}^N \sum_{\alpha=1}^{M_p} \frac{g_\alpha^2 \hbar e^2}{16m^2c^2} (\boldsymbol{\epsilon}_\alpha \cdot \mathbf{r}_k) [\boldsymbol{\epsilon}_\alpha \cdot (\hat{\mathbf{p}}_l \times \boldsymbol{\sigma}_l) + (\hat{\mathbf{p}}_l \times \boldsymbol{\sigma}_l) \cdot \boldsymbol{\epsilon}_\alpha] \right| \Psi^L \right\rangle + \dots, \end{aligned} \quad (30)$$

where the ellipsis stands for other terms that contain a correction to kinetic energy and a Darwin-like term. Among others, we find a cavity-induced SOC term of the form

$$-\frac{e\hbar}{8m^2c^2} \sum_{l=1}^N \left(\hat{\mathbf{p}}_l \cdot (\boldsymbol{\sigma}_l \times \hat{\mathbf{E}}) + (\boldsymbol{\sigma}_l \times \hat{\mathbf{E}}) \cdot \hat{\mathbf{p}}_l \right), \quad (31)$$

and the electric field operator of the cavity in the length gauge is given by

$$\hat{\mathbf{E}} = \sum_{\alpha=1}^{M_p} \left(\sqrt{\hbar} g_\alpha \omega_\alpha \hat{q}_\alpha - \frac{g_\alpha^2}{2} \boldsymbol{\mu} \cdot \boldsymbol{\epsilon}_\alpha \right) \boldsymbol{\epsilon}_\alpha. \quad (32)$$

The electric dipole moment operator $\boldsymbol{\mu}$ contains a sum over all electrons, and thus it also accounts for collective effects that are defined as the contributions arising from those

electrons in the sum that belong to different atoms and molecules inside the cavity than the ones the field acts on. Here, the first part of the electric field is proportional to the coupling strength g_α and usually dominates for single-molecule situations in the weak- to strong-coupling regime [2,3]. However, for the collective-coupling situation, where it is the response of the total ensemble of molecules, the second term proportional to g_α^2 can become dominant [160–162]. One can therefore imagine that even a collectively coupled ensemble of molecules could show enhanced SOC effects. As a final remark, in a similar way to Eq. (31), the term $v^{\text{ext}}(\mathbf{r}_l, t)$ in Eq. (27) can transiently lead to a light-induced SOC due to external classical fields.

C. Kohn-Sham QEDFT equations of motion

After specifying the Hamiltonian, one can find the time evolution of a system from a given initial state

$\Psi_0(x_1, \dots, x_N; q_1, \dots, q_{M_p})$ by solving the coupled electron-photon equation of motion

$$i\hbar\partial_t\Psi(x_1, \dots, x_N; q_1, \dots, q_{M_p}; t) = \hat{H}_L(t)\Psi(x_1, \dots, x_N; q_1, \dots, q_{M_p}; t), \quad (33)$$

where $x_i \equiv (\mathbf{r}_i, \tau_i)$ denotes spatial coordinate $\mathbf{r}_i$ and the four spin components τ_i of i th Dirac electron. While solutions of Eq. (33) contain all the information about the given system, it becomes numerically intractable for realistic many-electron systems and, therefore, approximate methods have to be employed. In this work, our method of choice is the density functional theory in the form of QEDFT and in notation we follow the formalism outlined in Ref. [70]. The electron-photon system is described by the electronic density $n(\mathbf{r}, t) = N \sum_{\tau, \tau_2, \dots, \tau_N} \int |\Psi(\mathbf{r}, \tau, x_2, \dots, x_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N$ and the expectation value of photonic coordinates $q_\alpha(t)$ as basic variables [64,65,70,73] that uniquely determine its state. We work in the Kohn-Sham (KS) formalism, where we consider an auxiliary system of independent particles that reproduces the density of the real system and is described by molecular spin orbitals $\varphi_j(x, t)$, with index j enumerating the N_{occ} occupied orbitals. The electron density is then calculated as [163]

$$n(\mathbf{r}, t) = \sum_{j=1}^{N_{\text{occ}}} \sum_{\tau=1}^4 |\varphi_j(\mathbf{r}, \tau, t)|^2. \quad (34)$$

Then, the equations of motion for the basic variables in terms of the auxiliary system read as [64,70]

$$i\hbar\partial_t\varphi_j(x, t) = \hat{H}^{\text{KS}}(t)\varphi_j(x, t), \quad (35)$$

$$\left(\frac{\partial^2}{\partial t^2} + \omega_\alpha^2\right)q_\alpha(t) = -\sqrt{2}\partial_t j_{\alpha, \text{KS}}([n, q_\alpha, t]), \quad (36)$$

with the single-particle KS Hamiltonian $\hat{H}^{\text{KS}}(t)$,

$$\hat{H}^{\text{KS}}(t) = -i\hbar\mathbf{c}\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + \beta mc^2 + v_{\text{KS}}([v, n, q]; \mathbf{r}, t), \quad (37)$$

and the Kohn-Sham current $j_{\alpha, \text{KS}}([n, q_\alpha, t])$ defined below in Eq. (44). The Kohn-Sham potential $v_{\text{KS}}([v, n, q]; \mathbf{r}, t)$ in Eq. (37) is defined as

$$v_{\text{KS}}([v, n, q]; \mathbf{r}, t) = v(\mathbf{r}, t) + v_{\text{Mxc}}([n, q]; \mathbf{r}, t). \quad (38)$$

Here, the external potential $v(\mathbf{r}, t)$ according to Eq. (27) is given by

$$v(\mathbf{r}, t) = v_{\text{nuc}}(\mathbf{r}) + v^{\text{ext}}(\mathbf{r}, t), \quad (39)$$

and $v_{\text{Mxc}}([n, q]; \mathbf{r}, t)$ is the mean-field exchange-correlation potential

$$v_{\text{Mxc}}([n, q]; \mathbf{r}, t) = v_{\text{M}}([n, q]; \mathbf{r}, t) + v_{\text{xc}}([n, q]; \mathbf{r}, t). \quad (40)$$

Since we consider a system of electrons coupled to photonic modes, one can split the mean-field potential $v_{\text{M}}([n, q]; \mathbf{r}, t)$ into a contribution that comes solely from the field generated by electrons, the Hartree potential $v_{\text{H}}([n]; \mathbf{r}, t)$, and mean field generated by photons $v_{\text{P}}([n, q]; \mathbf{r}, t)$,

$$v_{\text{M}}([n, q]; \mathbf{r}, t) = v_{\text{H}}([n]; \mathbf{r}, t) + v_{\text{P}}([n, q]; \mathbf{r}, t), \quad (41)$$

where

$$v_{\text{P}}([n, q]; \mathbf{r}, t) = \sum_{\alpha=1}^{M_p} \left(eg_\alpha \int d\mathbf{r}' n(\mathbf{r}', t) \boldsymbol{\epsilon}_\alpha \cdot \mathbf{r}' - \sqrt{\hbar} \omega_\alpha q_\alpha(t) \right) \times eg_\alpha \boldsymbol{\epsilon}_\alpha \cdot \mathbf{r}. \quad (42)$$

Similarly, one can split the exchange-correlation potential $v_{\text{xc}}([n, q]; \mathbf{r}, t)$ into a sum of electron-electron $v_{\text{xc}}^{e-e}([n]; \mathbf{r}, t)$ and photon-electron $v_{\text{xc}}^{e-P}([n, q]; \mathbf{r}, t)$ exchange-correlation potentials,

$$v_{\text{xc}}([n, q]; \mathbf{r}, t) = v_{\text{xc}}^{e-e}([n]; \mathbf{r}, t) + v_{\text{xc}}^{e-P}([n, q]; \mathbf{r}, t), \quad (43)$$

respectively. Note that, in density functional approximations employed in practical calculations, the potentials $v_{\text{xc}}^{e-e}([n]; \mathbf{r}, t)$ and $v_{\text{xc}}^{e-P}([n, q]; \mathbf{r}, t)$ can further depend on the gradient of the density or on spin densities, as well as include an admixture of the exact exchange. Finally, we introduce KS current $j_{\alpha, \text{KS}}([n, q_\alpha, t])$ in Eq. (36),

$$\begin{aligned} \partial_t j_{\alpha, \text{KS}}([n, q_\alpha, \partial_t j_\alpha^{\text{ext}}]; t) &= \partial_t j_{\alpha, \text{Mxc}}([n, q_\alpha]; t) + \partial_t j_\alpha^{\text{ext}}(t) \\ &= \partial_t j_{\alpha, \text{M}}([n]; t) + \partial_t j_{\alpha, \text{xc}}([n, q_\alpha]; t) + \partial_t j_\alpha^{\text{ext}}(t) \\ &= -\frac{\omega_\alpha e}{\sqrt{2}\hbar} \int d\mathbf{r} g_\alpha \boldsymbol{\epsilon}_\alpha \cdot \mathbf{r} n(\mathbf{r}) + \partial_t j_\alpha^{\text{ext}}(t), \end{aligned} \quad (44)$$

where the exchange-correlation current $\partial_t j_{\alpha, \text{xc}}(t)$ is zero in the case of dipole coupling and only the mean-field Kohn-Sham current $\partial_t j_{\alpha, \text{M}}([n]; t)$ contributes [5,70].

D. Linear-response equations for relativistic QEDFT

In the present work, we assume that the external probe potential $v^{\text{ext}}(\mathbf{r}, t)$ and current $j_\alpha^{\text{ext}}(t)$ are sufficiently weak to allow the use of time-dependent perturbation theory for the description of their effect on a molecule coupled to photon modes. Our goal is to develop a solution of Eqs. (35) and (36) to the first order of perturbation theory with the external potential and current acting as the perturbation. Note that we do not assume that the coupling to the cavity modes is weak, only that the external perturbation to the coupled cavity-matter system is small. We will proceed in the spirit of standard time-dependent

(Rayleigh-Schrödinger) perturbation theory following our earlier work [164]. We express the time-dependent spin orbitals as a perturbation series

$$\varphi_i(x, t) = \varphi_i^{(0)}(x, t) + \lambda \varphi_i^{(1)}(x, t) + \lambda^2 \varphi_i^{(2)}(x, t) + \dots, \quad (45)$$

with λ being the perturbation parameter and $\varphi_i^{(k)}(x, t)$ the k th-order correction to the i th molecular spinor. Furthermore, the k th-order corrections are expanded in the basis of ground-state (canonical) molecular spin orbitals,

$$\varphi_i^{(k)}(x, t) = d_{pi}^{(k)}(t) \varphi_p(x) e^{-i\varepsilon_i t}, \quad (46)$$

where $\varphi_p(x)$ are the canonical spin orbitals obtained as the solution of time-independent SCF procedure for $\hat{H}^{\text{KS}}(t)$ from Eq. (37), and $d_{pi}^{(k)}(t)$ are the time-dependent expansion coefficients. The exponential $e^{-i\varepsilon_i t}$ results from the solution for free evolution $\varphi_i(x) e^{-i\varepsilon_i t}$, where the weak perturbation then modifies $\varphi_i(x)$ to $\sum_k d_{pi}^{(k)}(t) \varphi_p(x)$.

Since the Kohn-Sham Hamiltonian $H^{\text{KS}}(t)$ depends on the electron density and, in turn, on the molecular orbitals $\varphi_i(\mathbf{r}, t)$, as well as on the photonic coordinate $q_\alpha(t)$, it is also modified by the perturbation and can be expanded in the orders of λ ,

$$H^{\text{KS}} = H^{\text{KS},(0)} + \lambda H^{\text{KS},(1)} + \lambda^2 H^{\text{KS},(2)} + \dots \quad (47)$$

By inserting the expansion for the Hamiltonian and the molecular orbitals into the time-dependent Kohn-Sham equation, we obtain differential equations for the expansion coefficients of all orders. Similarly, for photons, we consider the perturbation expansion of the displacement coordinate

$$q_\alpha(t) = q_\alpha^{(0)}(t) + \lambda q_\alpha^{(1)}(t) + \lambda^2 q_\alpha^{(2)}(t) + \dots \quad (48)$$

and formulate and solve equations of motion for the different orders in the expansion.

In Eqs. (45) and (48), the zeroth order refers to the ground-state solution, i.e., the external probe potential $v^{\text{ext}}(\mathbf{r}, t)$ and current $j_\alpha^{\text{ext}}(t)$ are absent. The stationary solution of Eq. (36) has the form

$$q_\alpha^{(0)} = \frac{e g_\alpha}{\omega_\alpha \sqrt{\hbar}} \int d\mathbf{r} \mathbf{e}_\alpha \cdot \mathbf{r} n(\mathbf{r}), \quad (49)$$

which causes the photonic potential v_p to vanish [as can be verified by direct substitution of Eq. (49) into Eq. (42)]. The coupling to photon modes is still present via the photon-electron exchange-correlation (XC) potential $v_{\text{xc}}^{\text{e-P}}([n, q]; \mathbf{r}_l, t)$, see Eq. (43), which is, however, part of the unperturbed Hamiltonian whose eigenfunctions are the canonical orbitals. Therefore, the zeroth-order electronic equation of motion (EOM) has the usual form

$$i\partial_t d_{pi}^{(0)}(t) = H_{pq}^{\text{KS},(0)} d_{qi}^{(0)}(t), \quad (50)$$

with corresponding solutions

$$d_{pi}^{(0)}(t) = \delta_{pi}. \quad (51)$$

Here, δ_{pi} is the Kronecker delta resulting from the fact that the zeroth-order KS Hamiltonian is diagonal in the basis of ground-state molecular orbitals with molecular orbital energies on the diagonal. Note that, in practical calculations, we employ the photon random-phase approximation (pRPA), which neglects $v_{\text{xc}}^{\text{e-P}}([n, q]; \mathbf{r}_l, t)$ after Eq. (43) and, in addition, starts from the uncoupled ground state. However, the derivation presented in the following text is general and holds also with the full photon-electron exchange-correlation potential included.

In first order, the electronic EOM takes the form

$$\begin{aligned} i\partial_t d_{ai}^{(1)}(t) = & A_{ai,bj}(\omega_{\text{ext}}) d_{bj}^{(1)}(t) + B_{ai,bj}(\omega_{\text{ext}}) d_{bj}^{(1)*}(t) \\ & + \frac{e^2 g_\alpha^2}{2} (\mathbf{r}_{ai} \cdot \mathbf{e}_\alpha) (\mathbf{r}_{jb} \cdot \mathbf{e}_\alpha) d_{bj}^{(1)}(t) \\ & + \frac{e^2 g_\alpha^2}{2} (\mathbf{r}_{ai} \cdot \mathbf{e}_\alpha) (\mathbf{r}_{bj} \cdot \mathbf{e}_\alpha) d_{bj}^{(1)*}(t) \\ & - e g_\alpha \sqrt{\hbar} \omega_\alpha (\mathbf{r}_{ai} \cdot \mathbf{e}_\alpha) q_\alpha^{(1)}(t) \\ & + P_{ai} e^{-i\omega_{\text{ext}} t} + P_{ai}^* e^{i\omega_{\text{ext}} t}, \end{aligned} \quad (52)$$

where the right-hand side contains the electronic kernel, the interaction with the cavity modes, and the interaction with the external field. Specifically, in Eq. (52), the first line on the right-hand side contains the usual Coulomb, exchange, and exchange-correlation coupling matrices

$$A_{ai,bj}(\omega_{\text{ext}}) = (\varepsilon_a - \varepsilon_i) \delta_{ab} \delta_{ij} + K_{\mu\nu\lambda\tau}(\omega_{\text{ext}}) C_{\mu a}^* C_{\nu i} C_{\lambda j}^* C_{\tau b}, \quad (53a)$$

$$B_{ai,bj}(\omega_{\text{ext}}) = K_{\mu\nu\lambda\tau}(\omega_{\text{ext}}) C_{\mu a}^* C_{\nu i} C_{\lambda b}^* C_{\tau j}, \quad (53b)$$

$$K_{\mu\nu\lambda\tau}(\omega_{\text{ext}}) = K_{\mu\nu\lambda\tau}^{\text{HF}}(\xi) + K_{\mu\nu\lambda\tau}^{\text{XC}}(\xi)(\omega_{\text{ext}}) + K_{\mu\nu\lambda\tau}^{\text{e-P}}(\omega_{\text{ext}}), \quad (53c)$$

with molecular orbital energies ε_p ($p = a, i$) and coefficients $C_{\mu p}$ obtained from the solution of the ground-state SCF procedure for the time-independent Dirac-Coulomb equation, and $K_{\mu\nu\lambda\tau}$ being matrix elements of the response kernel with HF, XC, e-P denoting its Hartree-Fock, electron-electron exchange-correlation, and photon-electron parts, respectively, in hybrid functionals mixed with weight ξ . We note that, strictly speaking, in the case of a hybrid auxiliary system, the respective exchange-correlation contributions of the electron-electron and electron-photon parts get modified, but we will not indicate this for notational

simplicity [165]. The XC kernels can be, in general, non-adiabatic, denoted by their dependence on ω_{ext} . The second to the third lines contain terms arising from the mean-field coupling to the photon field, with the dipole self-energy terms in the second and the third line, and in the fourth one the interaction with the displacement field of the cavity modes $q_\alpha^{(1)}(t)$. Finally, the last line contains the coupling to the external classical electromagnetic field representing the probe field used to perform absorption spectroscopy on the molecule, i.e., the perturbation.

For photons, the EOM in the first order reads

$$\left(\frac{\partial^2}{\partial t^2} + \omega_\alpha^2\right) q_\alpha^{(1)}(t) = -\sqrt{2}[(\partial_t j_{\alpha,\text{KS}}^{(1)}([n, q_\alpha, t]) + (\partial_t j^{\text{ext}}(t))), \quad (54)$$

where the first-order contribution to the current comes only from its dependence on the (first-order) electron density in the form

$$\partial_t j_{\alpha,\text{KS}}^{(1)}([n, t]) = -\frac{g_\alpha \omega_\alpha e \int d^3 r n^{(1)}(r, t) (\mathbf{r} \cdot \boldsymbol{\varepsilon}_\alpha)}{\sqrt{2\hbar}}. \quad (55)$$

By expressing the first-order electron density via the canonical molecular orbitals

$$n^{(1)}(r, t) = \varphi_j^\dagger(x) d_{bj}^{(1)}(t) \varphi_b(x) + d_{bj}^{(1)*}(t) \varphi_b^\dagger(x) \varphi_j(x), \quad (56)$$

we obtain the EOM for $q_\alpha^{(1)}(t)$ coupled to electronic coefficients $d_{ai}^{(1)}(t)$ and $d_{ai}^{(1)*}(t)$, which reads

$$\begin{aligned} &\left(\frac{\partial^2}{\partial t^2} + \omega_\alpha^2\right) q_\alpha^{(1)}(t) \\ &= \frac{g_\alpha \omega_\alpha e}{\sqrt{\hbar}} \left[(\mathbf{r}_{jb} \cdot \boldsymbol{\varepsilon}_\alpha) d_{bj}^{(1)}(t) + (\mathbf{r}_{bj} \cdot \boldsymbol{\varepsilon}_\alpha) d_{bj}^{(1)*}(t) \right] \\ &\quad - \sqrt{2} \partial_t j^{\text{ext}}(t). \end{aligned} \quad (57)$$

Equation (57) together with Eq. (52) and its complex conjugate constitute a system of coupled differential equations for variables $q_\alpha^{(1)}(t)$, $d_{ai}^{(1)}(t)$, and $d_{ai}^{(1)*}(t)$. Note that, since $q_\alpha(t)$ is real, we do not need a separate equation for $q_\alpha^{(1)*}(t)$. However, while Eq. (52) is a first-order differential equation, Eq. (57) is a second-order equation. We can transform it to a first-order equation by defining a new variable $p_\alpha^{(1)}(t)$ as

$$p_\alpha^{(1)}(t) = -i \frac{\partial}{\partial t} q_\alpha^{(1)}(t), \quad (58)$$

which obeys a first-order differential equation

$$\begin{aligned} i \frac{\partial}{\partial t} p_\alpha^{(1)}(t) &= -\omega_\alpha^2 q_\alpha^{(1)}(t) + \frac{g_\alpha e \omega_\alpha}{\sqrt{\hbar}} \left[(\mathbf{r}_{jb} \cdot \boldsymbol{\varepsilon}_\alpha) d_{bj}^{(1)}(t) \right. \\ &\quad \left. + (\mathbf{r}_{bj} \cdot \boldsymbol{\varepsilon}_\alpha) d_{bj}^{(1)*}(t) \right] - \sqrt{2} \partial_t j^{\text{ext}}(t). \end{aligned} \quad (59)$$

Thus, we have replaced a second-order differential equation [Eq. (57)] with two first-order differential equations [Eqs. (58) and (59)]. The imaginary unit in Eq. (58) was added for convenience in order to obtain a first-order EOM containing $i\partial_t$ in accord with Eq. (52).

The final complete system of coupled differential equations for first-order corrections to the electronic and photonic degrees of freedom is

$$\begin{aligned} i \partial_t d_{ai}^{(1)}(t) &= (A_{ai,bj} + \Delta_{ai,bj}) d_{bj}^{(1)}(t) \\ &\quad + (B_{ai,bj} + \Delta'_{ai,bj}) d_{bj}^{(1)*}(t) - L_{ai,\alpha} q_\alpha^{(1)}(t) \\ &\quad + P_{ai} e^{-i\omega_{\text{ext}} t} + P_{ai}^* e^{i\omega_{\text{ext}} t}, \end{aligned} \quad (60a)$$

$$\begin{aligned} -i \partial_t d_{ai}^{(1)*}(t) &= (A_{ai,bj}^* + \Delta_{ai,bj}^*) d_{bj}^{(1)*}(t) \\ &\quad + (B_{ai,bj}^* + \Delta'^*_{ai,bj}) d_{bj}^{(1)}(t) - L_{ai,\alpha}^* q_\alpha^{(1)}(t) \\ &\quad + P_{ai}^* e^{i\omega_{\text{ext}} t} + P_{ai} e^{-i\omega_{\text{ext}} t}, \end{aligned} \quad (60b)$$

$$\begin{aligned} i \frac{\partial}{\partial t} p_\alpha^{(1)}(t) &= +Q_{\alpha,bj}^* d_{bj}^{(1)}(t) + Q'_{\alpha,bj} d_{bj}^{(1)*}(t) - \omega_\alpha^2 q_\alpha^{(1)}(t) \\ &\quad - J e^{-i\omega_{\text{ext}} t} - J^* e^{i\omega_{\text{ext}} t}, \end{aligned} \quad (60c)$$

$$-i \frac{\partial}{\partial t} q_\alpha^{(1)}(t) = p_\alpha^{(1)}(t), \quad (60d)$$

where we introduced the notation

$$\Delta_{ai,bj} = \frac{e^2 g_\alpha^2}{2} (\mathbf{r}_{ai} \cdot \boldsymbol{\varepsilon}_\alpha) (\mathbf{r}_{jb} \cdot \boldsymbol{\varepsilon}_\alpha), \quad (61a)$$

$$\Delta'_{ai,bj} = \frac{e^2 g_\alpha^2}{2} (\mathbf{r}_{ai} \cdot \boldsymbol{\varepsilon}_\alpha) (\mathbf{r}_{bj} \cdot \boldsymbol{\varepsilon}_\alpha), \quad (61b)$$

$$L_{ai,\alpha} = -e g_\alpha \sqrt{\hbar} \omega_\alpha (\mathbf{r}_{ai} \cdot \boldsymbol{\varepsilon}_\alpha), \quad (61c)$$

$$Q_{\alpha,bj} = \frac{g_\alpha e \omega_\alpha}{\sqrt{\hbar}} (\mathbf{r}_{jb} \cdot \boldsymbol{\varepsilon}_\alpha), \quad (61d)$$

and where we considered the external current to have a time dependence given by $\sqrt{2} \partial_t j^{\text{ext}}(t) = J e^{-i\omega_{\text{ext}} t} + J^* e^{i\omega_{\text{ext}} t}$. The explicit dependence of coupling matrices on ω_{ext} resulting from such dependence in the exchange-correlation kernel was omitted for brevity. The first-order equations of motion for the coupled electron-photon system, Eqs. (60), can be solved by different approaches, such as the method of undetermined coefficients shown in Appendix B or by the direct solution of the system of equations as a matrix differential equation, followed by a similarity transformation shown in Appendix C. Both of these approaches lead to an algebraic equation corresponding to an eigenvalue problem whose eigenvalues are

excitation energies and eigenvectors are transition vectors of the coupled light-matter system. Alternatively, one can arrive at the final equation for excitation energies by considering a density-density linear-response function as presented at the nonrelativistic level of theory in Ref. [70].

The linear-response QEDFT equation obtained from Eqs. (60) has the form of the Casida equation [163,166,167], of linear-response time-dependent density functional theory (TDDFT) extended by blocks describing photons

$$\begin{pmatrix} \mathbf{A} + \mathbf{\Delta} & \mathbf{B} + \mathbf{\Delta}' & -\mathbf{L} & -\mathbf{L} \\ \mathbf{B}^* + \mathbf{\Delta}'^* & \mathbf{A}^* + \mathbf{\Delta}^* & -\mathbf{L}^* & -\mathbf{L}^* \\ -\mathbf{Q} & -\mathbf{Q}^* & \omega & \mathbf{0} \\ -\mathbf{Q} & -\mathbf{Q}^* & \mathbf{0} & \omega \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \\ \mathbf{M}_n \\ \mathbf{N}_n \end{pmatrix} = \Omega_n \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \\ \mathbf{M}_n \\ \mathbf{N}_n \end{pmatrix}, \quad (62)$$

where the terms $\mathbf{A}$ and $\mathbf{B}$ are the electronic coupling matrices introduced in Eqs. (53), the electron-photon coupling and self-energy terms $\mathbf{L}$, $Q_{jb,\alpha} = [1/(2\omega_\alpha)]Q'_{jb,\alpha} = \frac{1}{2} \frac{q_\alpha e}{\sqrt{\hbar}} (\mathbf{r}_{jb} \cdot \mathbf{e}_\alpha)$, $\mathbf{\Delta}$, and $\mathbf{\Delta}'$ are defined in Eqs. (61). The solutions of Eq. (62) are the eigenvalues Ω_n corresponding to excitation energies of the coupled light-matter system and the eigenvectors that contain the electronic excitation and deexcitation amplitudes $\mathbf{X}_n$ and $\mathbf{Y}_n$ parametrizing $d_{ai}^{(1)}$ and $d_{ai}^{(1)*}$, together with the photonic creation and annihilation amplitudes $\mathbf{M}_n$ and $\mathbf{N}_n$, parametrizing $q_\alpha^{(1)}$ and $p_\alpha^{(1)}$ (for this interpretation, see Appendix C). The linear-response equation, Eq. (62), is formulated in the basis of the ground-state molecular orbitals, where the dimensions of the terms in the equation expressed via the number of occupied orbitals N_{occ} , the number of virtual orbitals N_{vir} , and the number of photon modes N_{ph} are as follows:

- (i) $\mathbf{A}$, $\mathbf{B}$, $\mathbf{\Delta}$, $\mathbf{\Delta}'$: matrices of dimension $N_{\text{vir}}N_{\text{occ}} \times N_{\text{vir}}N_{\text{occ}}$;
- (ii) $\mathbf{L}$, $\mathbf{Q}$: matrices of dimension $N_{\text{vir}}N_{\text{occ}} \times N_{\text{ph}}$;
- (iii) ω : diagonal matrix of dimension $N_{\text{ph}} \times N_{\text{ph}}$;
- (iv) $\mathbf{X}_n$, $\mathbf{Y}_n$: vectors of dimension $N_{\text{vir}}N_{\text{occ}}$;
- (v) $\mathbf{M}_n$, $\mathbf{N}_n$: vectors of dimension N_{ph} .

Note that, while the transition vectors $\mathbf{X}_n$, $\mathbf{Y}_n$ are originally defined as matrices of dimension $N_{\text{vir}} \times N_{\text{occ}}$ (X_{ai} , Y_{ai} where $a \in \text{vir}$, $i \in \text{occ}$), for the purposes of solution and computer implementation of Eq. (62), they are unrolled into one-dimensional vectors (X_κ , Y_κ , where κ runs over all products ai). Similarly, the terms $\mathbf{A}$, $\mathbf{B}$, $\mathbf{\Delta}$, $\mathbf{\Delta}'$ originally defined as rank-four tensors, and the terms $\mathbf{L}$, $\mathbf{Q}$ defined as rank-three tensors, became matrices by considering a virtual-occupied pair ai to label a single dimension. The underlying relativistic theory is manifested in Eq. (62) in the following ways: (i) The ground-state molecular orbitals (MOs), in whose basis the equation is formulated, are necessarily complex, making also the terms in Eq. (62) complex and requiring the presence of several complex conjugations that do not appear in the nonrelativistic version of the equation; (ii) the MO basis set includes all orbitals as opposed to only half, as is common in nonrelativistic implementations where only spin-up orbitals are considered; (iii) the MOs are four-component spinors obtained from a ground-state calculation with a SOC including Hamiltonian, meaning these orbitals are not eigenvectors of the spin operator, resulting in nonzero matrix element coupling orbitals that in nonrelativistic limit correspond to opposite spin states and thus in the presence of spin-flip excited states among the solutions; (iv) the use of noncollinear formulation of the XC kernel $K_{\mu\nu\lambda\tau}^{\text{XC}}$ in the construction of coupling matrices in Eqs. (53).

The matrix on the left-hand side of Eq. (62) is not symmetric, which has consequences for the calculation of spectra as detailed in Sec. II E and Appendix D. Previous works on linear-response QEDFT either transformed Eq. (62) into an equation of half the original dimension, with eigenvalue Ω_n^2 made possible due to real-valued orbitals used in the nonrelativistic theory [70], or worked with a symmetric equation obtained due to approximations made in the electron-photon Hamiltonian [71,72]. In Appendix C, we show that Eq. (62) can be symmetrized by a similarity transformation to a complex version of this symmetric equation, due to equivalent approximations made in the KS potential and current in the practical implementation.

E. Calculation of spectra

The frequency-dependent polarizability [168] that defines the absorption spectrum is given by [compare with Eq. (B8)]

$$\alpha(\omega_{\text{ext}}) = \begin{pmatrix} \mathbf{P}^* & \mathbf{P} & \mathbf{0} & \mathbf{0} \end{pmatrix} \left[\begin{pmatrix} \mathbf{A} + \mathbf{\Delta} & \mathbf{B} + \mathbf{\Delta}' & -\mathbf{L} & -\mathbf{L} \\ \mathbf{B}^* + \mathbf{\Delta}'^* & \mathbf{A}^* + \mathbf{\Delta}^* & -\mathbf{L}^* & -\mathbf{L}^* \\ -\mathbf{Q} & -\mathbf{Q}^* & \omega & \mathbf{0} \\ -\mathbf{Q} & -\mathbf{Q}^* & \mathbf{0} & \omega \end{pmatrix} - \omega_{\text{ext}} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \right]^{-1} \begin{pmatrix} \mathbf{P} \\ \mathbf{P}^* \\ \mathbf{0} \\ \mathbf{0} \end{pmatrix}, \quad (63)$$

where $\mathbf{P}$ is the matrix representation of the electric dipole moment operator. We can replace the matrix $[\dots]^{-1}$ in Eq. (63) by its spectral decomposition from eigenvectors obtained by solving Eq. (62). However, the electron-photon linear-response QEDFT equation, Eq. (62), corresponds to a generalized eigenvalue problem of a non-Hermitian non-symmetric matrix [unlike the electronic linear-response TDDFT equation containing only the Hermitian electron-electron block $(\begin{smallmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{smallmatrix})$]. Therefore, the eigenproblem has different left and right eigenvectors, a fact that has to be taken into account when performing the spectral decomposition. In this case, the expression for the frequency-dependent linear polarizability tensor derived in Appendix D has the form

$$\alpha(\omega) = \sum_n \left[\frac{t_n^{R*} t_n^L}{\Omega_n + \omega + i\gamma} - \frac{t_n^R t_n^{L*}}{\omega - \Omega_n + i\gamma} \right], \quad (64)$$

where index n runs over positive-energy eigenvalues, and the left and right transition dipole moments are

$$t_n^R = \mathbf{P}^\dagger \mathbf{X}_n^R + \mathbf{P} \mathbf{Y}_n^R, \quad (65a)$$

$$t_n^L = \mathbf{P}^\dagger \mathbf{X}_n^L - \mathbf{P} \mathbf{Y}_n^L, \quad (65b)$$

with $\mathbf{X}_n^{R/L}$ and $\mathbf{Y}_n^{R/L}$ corresponding to electronic parts of the right and left n th eigenvector, respectively. An empirical broadening parameter γ has been added to obtain spectra with finite peak widths by replacing ω with $\omega + i\gamma$ in Eq. (64). Note, however, that the empirical broadening parameter is only a convenience used when representing a cavity by a single or few modes. Physical radiative broadening can be described in linear-response QEDFT by considering coupling to a dense spectrum of photon modes [70]. The absorption spectrum of a molecule in a cavity is then calculated using the usual formula for the dipole strength function

$$S(\omega) = \frac{4\pi\omega}{3c} \text{Im Tr}[\alpha(\omega)], \quad (66)$$

where c is the speed of light, Im denotes the imaginary part, and Tr is the trace over the Cartesian components. Note that, while this is the formula used in QEDFT literature, the issue of calculating a proper rotationally averaged spectral function for the molecule-in-cavity setup comparable to experiments is more subtle and requires further work [161,169].

F. Numerical solver

Equation (62) is thus an eigenproblem for a large matrix whose construction and solution comprises the bulk of the computational effort of relativistic linear-response QEDFT. The equation was implemented into the relativistic quantum chemistry density functional theory (DFT) package RESPECT [170] and is built upon an earlier four-component molecular linear-response TDDFT code [171]. The linear-response QEDFT equation, Eq. (62), is solved using an iterative Davidson-Olsen solver [172,173] as is

common in TDDFT implementations, here extended to consider the photon part as well. The solver expresses the solution vector $\mathbf{Z} = (\mathbf{X} \ \mathbf{Y} \ \mathbf{M} \ \mathbf{N})^T$ as a linear combination of so-called trial vectors, i.e., $\mathbf{Z} = \sum_\tau c_\tau \mathbf{t}_\tau$. Moreover, the solvers developed for electronic relativistic linear-response TDDFT employ a paired structure of the trial vectors [171,174,175], where each trial vector $\mathbf{t}_\tau = (\mathbf{t}_\tau^X \ \mathbf{t}_\tau^Y)^T$ and a pair vector $\tilde{\mathbf{t}}_\tau = (\mathbf{t}_\tau^{Y*} \ \mathbf{t}_\tau^{X*})^T$ is considered. However, since the calculation of polarizability requires the left eigenvectors, these also have to be correctly described by the trial basis. To this end, trial vectors with a special internal structure informed by the analytic relationship between the left and right eigenvectors have to be added as well. Such an extension was first suggested by Komorovsky *et al.* [171] for open-shell TDDFT and includes adding a trial vector $\mathbf{t}_\tau^L = (\mathbf{t}_\tau^X - \mathbf{t}_\tau^Y)^T$ for each vector $\mathbf{t}_\tau \equiv \mathbf{t}_\tau^R$, as well as a vector $\tilde{\mathbf{t}}_\tau^L = (\mathbf{t}_\tau^{Y*} - \mathbf{t}_\tau^{X*})^T$ for its pair $\tilde{\mathbf{t}}_\tau \equiv \tilde{\mathbf{t}}_\tau^R$. In the case of linear-response QEDFT describing a coupled electron-photon system, the special structure of paired and left trial vectors is translated to the photon part as well, giving

$$\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \\ \mathbf{M} \\ \mathbf{N} \end{pmatrix} = \sum_\tau c_\tau^R \begin{pmatrix} \mathbf{t}_\tau^X \\ \mathbf{t}_\tau^Y \\ \mathbf{t}_\tau^M \\ \mathbf{t}_\tau^N \end{pmatrix} + \sum_\tau \tilde{c}_\tau^R \begin{pmatrix} \mathbf{t}_\tau^{Y*} \\ \mathbf{t}_\tau^{X*} \\ \mathbf{t}_\tau^{N*} \\ \mathbf{t}_\tau^{M*} \end{pmatrix} + \sum_\tau c_\tau^L \begin{pmatrix} \mathbf{t}_\tau^X \\ -\mathbf{t}_\tau^Y \\ \mathbf{t}_\tau^M \\ -\mathbf{t}_\tau^N \end{pmatrix} + \sum_\tau \tilde{c}_\tau^L \begin{pmatrix} \mathbf{t}_\tau^{Y*} \\ -\mathbf{t}_\tau^{X*} \\ \mathbf{t}_\tau^{N*} \\ -\mathbf{t}_\tau^{M*} \end{pmatrix}, \quad (67)$$

as the ansatz for the solution. The expansion coefficients c_τ and $\tilde{c}_\tau$ are determined by solving Eq. (62) projected onto the subspace defined by the trial vectors. New trial vectors are generated in each iteration by preconditioning the residue vectors, where each desired eigenvalue can contribute up to two trial vectors ($\mathbf{t}$ and its pair $\tilde{\mathbf{t}}$) in each iteration. The subspace is expanded until convergence determined by the norm of the residue vector for the particular frequency is reached. The solutions for the desired number of eigenvalues are sought in a common basis composed of trial vectors contributed by all the eigenvalues. New trial vectors are orthogonalized (i) with respect to the previously added trial vectors using Gram-Schmidt orthogonalization and the Kahan-Partlett “twice is enough” algorithm and (ii) within the $(\mathbf{t}, \tilde{\mathbf{t}})$ pair using an analytic formula. The vectors that are reduced to a length below a set threshold during the orthogonalization are discarded from the trial basis. This protocol achieves robust convergence of the solver across different molecular systems and the number of desired eigenvalues. To cross validate our results, we implemented the symmetrized version of the equation as well and confirmed that these two equations lead to the same spectra. Further discussion

of the numerics can be found in Appendix I. There, we also give details on the computational costs. The bottom line is that a QEDFT calculation is computationally as expensive as a TDDFT calculation.

III. COMPUTATIONAL DETAILS

In the benchmark calculations presented below, we consider the series of group 12 atoms (Zn, Cd, Hg) and a large mercury porphyrin (Hg@porphyrin). The geometry of the Hg porphyrin was taken from Ref. [136] and corresponds to a nonplanar configuration of C_{4v} symmetry (see Table VI in Appendix J).

All spectra were calculated using the relativistic spectroscopy DFT program RESPECT [170]. The reference orbitals for the linear-response calculations were obtained from the ground state uncoupled to photons. The relativistic four-component molecular spin orbitals for electrons were described Gaussian-type orbital (GTO) basis sets where the scalar GTOs were used for the large component and the basis for the small-component basis was generated by imposing the restricted kinetically balanced relation [176]. The selected scalar basis sets were the uncontracted Dyall's valence double-zeta (VDZ) basis sets for metals (Zn, Cd, Hg) [177–180], the uncontracted Dunning's correlation-consistent polarized VDZ basis sets [181] for light elements. The B3LYP XC approximation of the density functional [182–186] was used in all calculations. The numerical integration of the noncollinear exchange-correlation potential and kernel was done with an adaptive molecular grid of medium size (program default). In the 4c calculations, atomic nuclei of finite size were approximated by a Gaussian charge distribution model.

The electron-photon correlation is treated under the pRPA [70,73], which amounts to disregarding the photon-electron exchange-correlation potential $v_{xc}^{e-P}([n, q]; \mathbf{r}_l, t)$ and kernel $K_{\mu\nu\lambda\kappa}^{e-P}$ in Eqs. (43) and (53c), respectively. Moreover, we consider the adiabatic approximation in the construction of the XC kernels, i.e., all dependencies on ω_{ext} in Eqs. (53) are dropped. At present, we restrict ourselves to closed-shell systems for which the adiabatic noncollinear XC kernel has the form given in Eqs. (24)–(26c) in Ref. [164]. The eigenvalue equation was solved iteratively for the first 50 or 100 excitation energies for systems coupled to a single cavity mode. The spectra were subsequently evaluated from the excitation energies and transition moments obtained from the left and right eigenvectors; in the case of coupling to a single cavity mode, empirical Lorentzian broadening was used to obtain finite-width peaks.

IV. RESULTS AND DISCUSSION

A. Atoms with singlet-triplet transitions

First, we consider the case of atoms of group 12 metals (Zn, Cd, and Hg), whose spectra were previously studied at the level of the four-component Dirac-Coulomb

Hamiltonian using linear-response [175,187] and real-time TDDFT [188]. The first two excited states correspond to the triplet state 3P and the singlet state 1P , where the transition from the 1S_0 ground state to the excited triplet state is forbidden in theories neglecting SOC. With SOC considered, the transition to 3P_1 becomes allowed, while the transitions to the other two triplet components ($^3P_0, ^3P_2$) remain forbidden due to the ΔJ selection rule within the dipole approximation. The excitation energies for the allowed $^1S_0 \rightarrow ^3P_1$ and $^1S_0 \rightarrow ^1P_1$ transitions are summarized in Table II in Appendix E, while the calculated values reproduce reference experimental data [189] reasonably well given the functional and basis set size. Both the $^1S_0 \rightarrow ^3P_1$ and $^1S_0 \rightarrow ^1P_1$ transitions are composed of three degenerate spectral lines. In the orbital picture, the highest occupied shell corresponds to ns orbitals and the lowest unoccupied to np , while after SOC is taken into account the p shell splits into $np_{1/2}$ and $np_{3/2}$ levels. There are in total 12 possible single-electron excitations between ns and $np_{1/2}$ and $np_{3/2}$ orbitals and these constitute the dominant contributions to TDDFT transition vectors. However, these 12 simple configurations cannot be straightforwardly identified with the components of the singlet and triplet excited states, as their transition vectors contain more than one significant orbital pair contribution.

To investigate the effect of the strong coupling to photons on these atomic spectra, we solve the linear-response QEDFT equation for a single atom coupled to a single effective cavity mode with the cavity frequency scanning the region around the singlet-triplet (S - T) and singlet-singlet (S - S) transitions. By focusing on a single effective cavity mode, it is implied that the remaining spectrum of modes is accounted for by working with the renormalized (observable) masses of the electrons [7,190].

The results of a series of calculations with different cavity frequencies are excitation energies and corresponding transition moments, from which it is possible to calculate absorption spectra. Such spectra are depicted in Fig. 2, showing both nonrelativistic one-component (1c) and fully relativistic (4c) calculations. The x axis shows the cavity frequency, the y axis corresponds to excitation energy, and the magnitude of the spectral function is depicted as the color gradient in logarithmic ($\log_{10}$) scale to allow comparison between the S - T and S - S transitions of vastly different magnitudes. The spectra were artificially broadened using Lorentzian broadening with broadening parameter $\gamma = 0.00002$ a.u. [see text after Eqs. (65)]. Only excited states with nonzero transition dipole moments are visible as signals in the spectra, i.e., 1P_1 and 3P_1 , while the other components of the triplet state with total angular momentum $J = 0$ and $J = 2$ are dark.

The plots depict a common scenario wherein light-matter mixing increases as the cavity frequency approaches a resonance with an excitation energy. Both the 3P_1 and 1P_1 excited states are originally triply degenerate with the

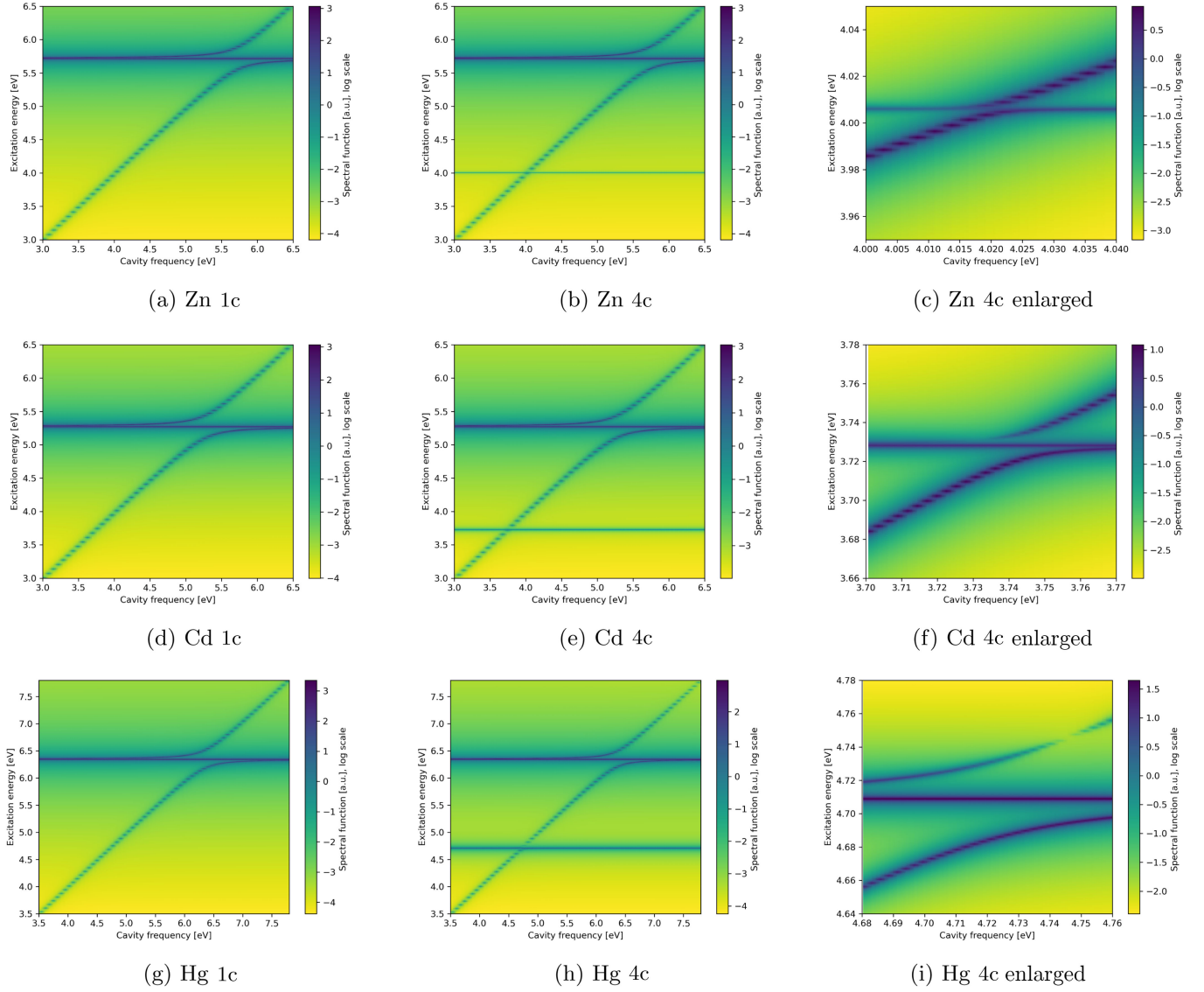


FIG. 2. Absorption spectra of group 12 atoms (Zn, Cd, and Hg) in an optical cavity under strong light-matter coupling (coupling strength $g_\alpha = 0.01$ a.u.). Panels (a), (d), and (g) show nonrelativistic (1c) calculations for Zn, Cd, and Hg, respectively. Panels (b), (e), and (h) present the corresponding relativistic (4c) results. Panels (c), (f), and (i) provide enlarged views of the relativistic spectra from panels (b), (e), and (h), respectively.

degenerate levels having perpendicular transition dipole moments. Therefore, the photon state mixes with only one of the three states—the one with the transition dipole moment parallel with the photon polarization—and the uncoupled excitation energies are still visible due to the two remaining levels of both 3P_1 and 1P_1 . When compared with the nonrelativistic picture, the relativistic description causes a shift in the energy of the excited singlet state—the nonrelativistic spectra were artificially shifted so that the S - S excitation energies would be aligned. The specific shifts were 0.16, 0.43, and 1.57 eV, for Zn, Cd, and Hg, respectively. Furthermore, the inclusion of relativity introduces a transition to the excited triplet state. The intensity of the S - T transition as well as the spectral shifts are more prominent for heavier atoms. As the transition to the excited

triplet state becomes allowed, a mixing with the cavity mode is observed near the resonant frequency. Since the coupling to the cavity mode is proportional to the transition dipole moment, which for the S - T transition increases with atomic number, the Rabi splitting of the polaritons originating from the triplet state is the largest for mercury. From the enlarged insets in the dispersion plots in Fig. 2, we see that the polaritonic states are not centered around the resonance frequency but around a higher frequency. This shift of the resonance frequencies is due to the self-consistent solution of the coupled light-matter system. Physically, it arises mainly due to the change in refractive index inside the cavity when filling it with a polarizable medium [162,191]. While in a simple two-level model, a cavity resonance mixes with matter excitation to form two polaritonic states, the lower

polariton (LP) and the upper polariton (UP), in a many-level electronic system, all matter excitations whose transition moments are not perpendicular to photon polarization, even those that are not in resonance with the photon mode, mix with the light to some degree. This means that now many excitations have a polaritonic character. Still, if the photon frequency is close to the resonance with an electronic excitation, the two-dimensional (2D) spectrum (such as depicted in Fig. 2) resembles the picture known from the two-level model. The difference is that, due to the photon mode being coupled to other states as well, the matter:light content in the LP and UP will not be 50:50 since the photon contribution to all states sums to 1 [defined via the norm of the photon part of the response vectors $\sum_n (|M_n|^2 - |N_n|^2)$]. We can, however, define the effective resonance frequency as that frequency at which the matter-light ratio is the same for the LP and UP, with the caveat that the admixture of matter in both states will be larger than that of the light. Furthermore, the light admixture in the UP and LP will decrease with coupling strength, as stronger coupling will increase the photonic contribution in off-resonant states. For example, in the Hg atom, the matter-light ratio was about 51:49 for the LP and UP at $g_\alpha = 0.01$ a.u., and it was 60:40 at $g_\alpha = 0.08$ a.u.. Finally, let us note that this definition of effective resonance also ensures that $\Omega_n - \omega_{\text{LP}} = \omega_{\text{UP}} - \Omega_n$, where Ω_n is the bare excitation energy of the state with which the cavity frequency is in resonance. The effective resonances for different atoms and coupling strengths are summarized in Table I. The maximum light-matter mixing around the S - S resonance also occurs at a frequency shifted from the resonance by approximately the same amount as around the S - T transition.

We calculated absorption spectra with cavities tuned to these effective resonant frequencies E_{res}^{ST} (listed in Table I). The spectra are depicted in Fig. 3 for $g_\alpha = 0.01$ a.u.. while additional spectra calculated with different values of g_α are available in Appendix F, Figs. 8–10. As discussed above, two S - T transitions with perpendicular transition dipole are still present as excitation energies and visible in the spectra of Cd and Hg as a line with 2/3 of the intensity seen in the uncoupled system (for Zn, the extremely weak line corresponding to the uncoupled S - T transitions is obscured by peak broadening). In the spectral region around the S - T

transition, the spectra contain very intense polaritonic peaks with the increase of the transition moment with respect to the original S - T transition ranging from a striking 50-fold increase for Zn to about 20% for Hg (compared to the intensity of one of the three degenerate states, meaning that the peak composed of two degenerate uncoupled S - T states is more intense than the polaritonic peak in Hg).

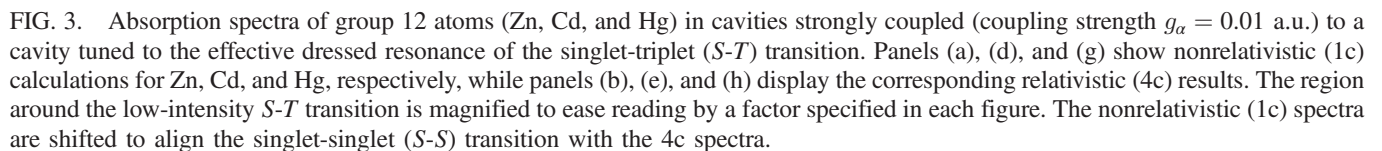
While it is tempting to suggest an interpretation based on cavity enhancement of the S - T transition, it is important to note that the peak appears also in the one-component nonrelativistic (1c) spectra. Since the 1c spectra are evaluated from the nonrelativistic linear-response calculations that do not contain the S - T transition, the peak must correspond to the lower polariton originating from the mixing of cavity mode with S - S exciton. Even if the cavity frequency is far from the resonance with the S - S transition and the polaritonic state is lightlike ($> 90\%$), its intensity is sufficient to be comparable with the S - T transition in the relativistic (4c) calculations. This is in agreement with the 2D spectra in Fig. 2, where the intensity of the lower polaritonic branch in the 1c calculations is more intense (Zn) or comparable (Hg, also Cd) with the S - T transition in the 4c spectra.

In the 4c calculations, the effects of the coupling to the low-intensity S - T transition and the intense but off-resonant S - S transition combine. In addition to the spectral signature in the S - T region discussed above, in the region around the S - S transition, one of the originally three degenerate spectral lines is blueshifted and its response vector contains a small but non-negligible (10^{-3}) photonic contribution. Most of the intensity increase of the polaritonic peaks arising from the S - T transition is accounted for by the corresponding decrease in intensity of the shifted S - S transition. The decrease in intensity of the shifted S - S line is, in fact, larger than the gain of the S - T transition, with the gain being about 80% of the decrease. The Thomas-Reiche-Kuhn sum rule is then preserved by states higher in the spectrum when one state of three degenerate states is also slightly shifted in energy and its intensity is now higher. This repeats for all triply degenerate states at higher energies. The sum of photonic contributions from the lower and upper S - T polariton and the shifted S - S line is 1 with the accuracy of $10^{-4} - 10^{-5}$ and lower for the higher-lying states. Note that, in pRPA QEDFT with a single cavity mode, the total sum of photon contributions should be 1, and only one extra peak can appear in the spectrum of an atom or molecule coupled to the cavity.

These results show the importance of the off-resonant coupling where the photon mode is coupled not only to the resonant S - T exciton but also to the off-resonant yet high-transition-moment S - S exciton as well as *all* higher-lying states. In turn, this demonstrates the importance of an *ab initio* QEDFT treatment, where all states and their mutual interactions are taken into account. In contrast, if we set up a few-state approximation, we need to make *a priori* several severe modeling decisions, which might influence

TABLE I. Singlet-triplet excitation energies E^{ST} of free atoms and resonant frequencies E_{res}^{ST} of dressed atoms in cavities with different coupling strengths g_α (in a.u.) defined as cavity mode frequency at which equal light-matter mixing in the lower and upper polariton occurs.

Atom	E^{ST} (eV)	E_{res}^{ST} (eV)			
		$g_\alpha = 0.01$	$g_\alpha = 0.02$	$g_\alpha = 0.05$	$g_\alpha = 0.08$
Zn	4.0060	4.0205	4.0627	4.3470	4.8327
Cd	3.7282	3.7443	3.7933	4.1144	4.6531
Hg	4.7089	4.7239	4.7674	5.0613	5.5783



linear-response theory and its realization via TDDFT and time-dependent QEDFT so appealing and relevant in practice. In ground-state linear-response theory, we only have access to the exact transition densities $\langle \Psi_n | \hat{n}(\mathbf{r}) | \Psi_0 \rangle$, where Ψ_0 and Ψ_n are the ground and n th excited state,

respectively. We do not have access to transition densities and as a result to transition dipole moment matrix elements *between* excited states. Moreover, we do not have access to the two-body part of the dipole self-interaction terms in Eq. (27). Thus, even from exact linear-response theory, the only straightforward few-level model is a two-level approximation, where also the dipole self-energy term becomes a constant offset [155]. Already, for a three-level approximation, we need to choose and approximate how excited states can couple to each other and what we do with the dipole self-energy term. Within linear-response TDDFT, one can, for instance, set up approximate eigenfunction via the KS orbitals and then approximate transition densities between these excited states and also the dipole self-energy contributions. Moreover, as detailed in Appendix I, calculating the different parameters for, e.g., a three-state model can be computationally more involved than directly performing a QEDFT simulation. In addition to this, the level of coupling needs to be chosen. Here, commonly, the rotating-wave approximation is assumed; hence, for a two-state model, we find the ubiquitous Jaynes-Cummings (JC) model. A simple two-state model built from the corresponding S - T excitation produces two polaritonic states whose intensity sums (wrongly) to the original S - T intensity. Another problem is capturing the shift of the S - T resonance toward higher frequencies

correctly. This becomes more pronounced as the coupling strength increases, as shown in Fig. 4. Here, the results of QEDFT calculations are compared with the JC energies $E_{\pm} = \frac{1}{2}(\hbar\omega_{\alpha} + \hbar\omega_{S-T} \pm \sqrt{\hbar^2(\omega_{\alpha} - \omega_{S-T})^2 + 4|G|^2|\boldsymbol{\mu}_{S-T} \cdot \boldsymbol{\epsilon}|^2})$, where $G = -ig_{\alpha}\sqrt{(\hbar\omega_{\alpha})/2}$ with the S - T excitation energy ω_{S-T} and transition dipole moment $\boldsymbol{\mu}_{S-T} = \langle {}^3P_1 | \boldsymbol{\mu} \cdot \boldsymbol{\epsilon}_{\alpha} | S_0 \rangle$ taken from the respective calculations without a cavity. For additional details of the model and its results see Appendix G and Fig. 11. A three-level model offers an improvement over the JC model by including the higher-lying singlet excited state and the corresponding off-resonant coupling to this state. It achieves qualitative agreement with the QEDFT results and confirms our explanation of the origin of the high intensity of the polaritonic transitions, but fails quantitatively, particularly for higher coupling strengths [see Figs. 12–17 and Table V in Appendix G as well as Figs. 4(d)–4(f)]. Models based on more states might lead to an improvement, but the construction of such models relies on more than just a linear-response TDDFT calculation for parametrization. Thus, the full QEDFT calculation is simpler, more straightforward, and more reliable, particularly for systems with dense spectra such as molecules. The advantages of QEDFT over few-level approximations become even more apparent once we consider chemically relevant real-space resolved

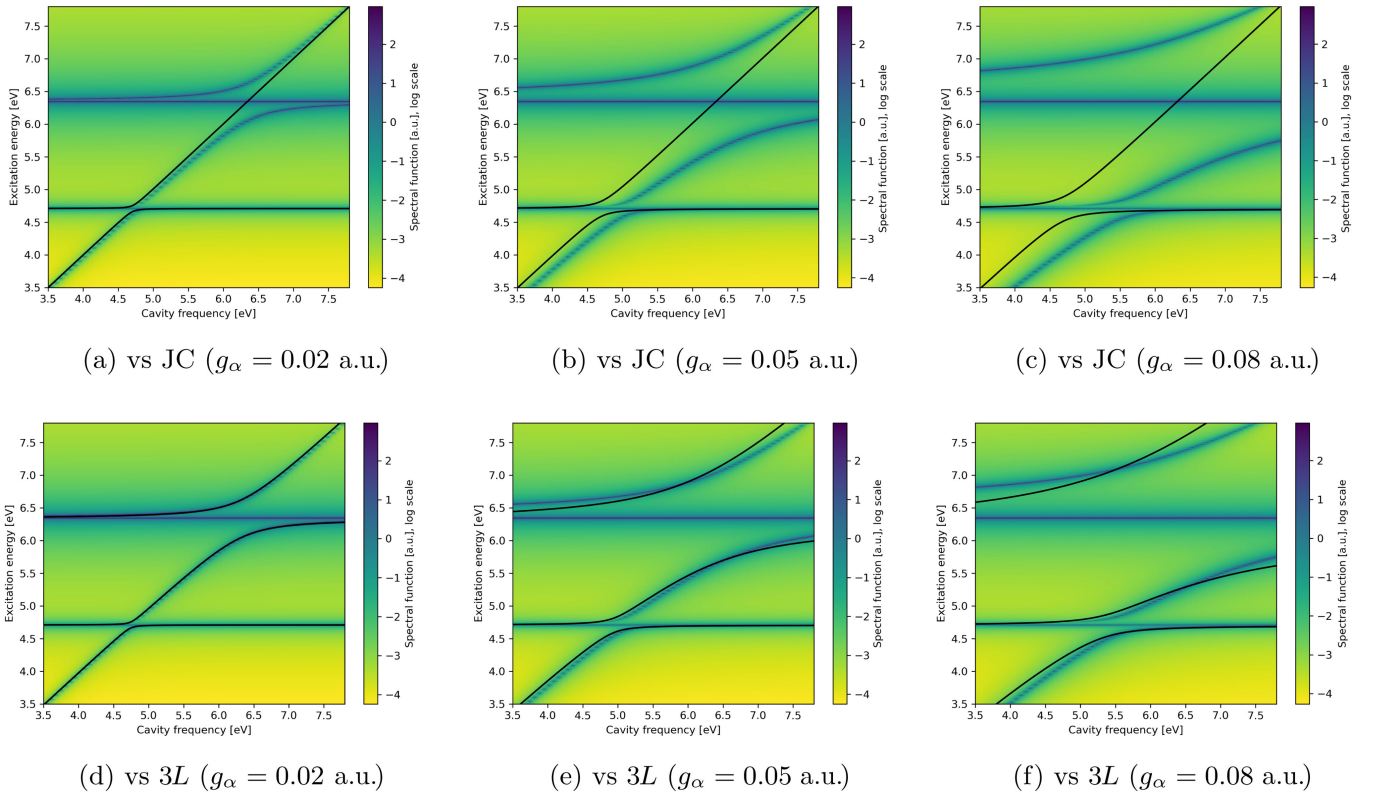


FIG. 4. Absorption spectra of Hg atom in a cavity with different light-matter coupling strengths g_{α} , compared to simplified few-level models (solid black lines). Panels (a)–(c) show the comparison with a two-level Jaynes-Cummings (JC) model considering only the singlet-triplet (S - T) transition. Panels (d)–(f) present the comparison to a three-level model including both the - and singlet-singlet (S - S) transitions.

quantities such as the transition densities (see Sec. IV B). Therefore, *ab initio* calculations are an indispensable tool for qualitative and quantitative predictions of properties of strongly bound light-matter systems, as well as for guiding the development of models. The quest to extend their capabilities to include further effects, such as relativity and spin-orbit coupling, is thus an important direction in polaritonic chemistry.

B. Large molecular metal complex

To demonstrate that our implementation is not restricted to atoms, but applicable also to large molecules containing heavy elements, we calculate the electron absorption spectrum of a mercury porphyrin inside a Fabry-Pérot cavity. Porphyrins are a class of molecules with important biological roles as well as technological applications and there is a large number of both experimental [192] and theoretical [193,194] works devoted to their study, including the modification of their properties in optical cavities [140,195,196]. Moreover, the absorption spectra of porphyrin complexes of group 12 atoms, including the Hg porphyrin considered here, were studied before at the four-component relativistic level of theory by Fransson *et al.* [136]. Note that, unlike Ref. [136], we do not explicitly consider point group symmetry, thus performing all-atom all-electron calculations.

The spectrum of the free Hg-substituted porphyrin is dominated by the strong *B* band at 3.39 eV, while other notable features are the *N* and *L* bands at 3.76 and 4.12 eV, respectively, with the *Q* band being very weak and not visible in this spectrum. All of these spectral lines arise from doubly degenerate excited states with perpendicular transition dipole moments, i.e., *y* and *z* for the molecule oriented such that its C_4 symmetry axis coincides with the *x* axis. In the calculations of polaritonically modified spectra, we consider the Hg porphyrin complex embedded in a Fabry-Pérot cavity with an effective single mode of frequency that is in resonance with the *B*-band excitation energy, with progressively stronger coupling constant g_α . The resulting spectra, together with the spectrum of the uncoupled system, are depicted in Fig. 5. While for the weakest coupling $g_\alpha = 0.005$ a.u. (dark blue line), the dominating modification of the spectrum due to the cavity is the splitting of one of the two degenerate *B* lines into an upper and lower polariton, for the stronger values of the coupling, other lines in the spectrum start to be affected as well. Particularly, for $g_\alpha = 0.02$ a.u., we see breaking of the degeneracy in the form of frequency and intensity shifts of other spectral lines including the *N* and *L* lines. In addition, the lower polariton shows in the spectrum as a more intense line compared to the upper polariton. This is due to the fact that the cavity frequency was tuned to be in resonance with the uncoupled state, while in the coupled system the “true” resonance shifts to a higher frequency. This is consistent with our results for atoms (see Fig. 4). This effect is due to the self-consistent treatment of light

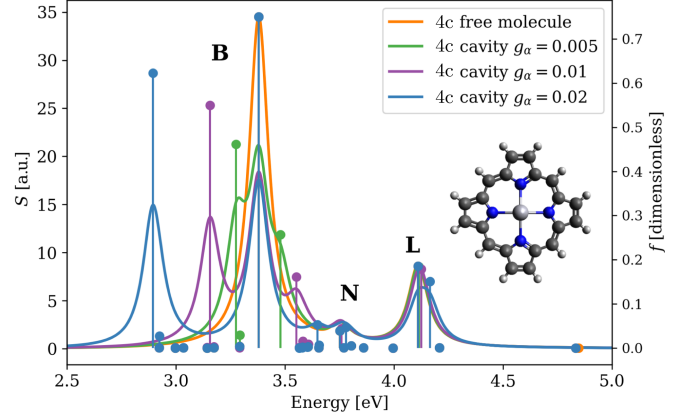


FIG. 5. Comparison of relativistic (4c) electron absorption spectra (band spectra, i.e., spectral function S on the left vertical axis and line spectra as oscillator strength f on the right vertical axis; for the latter, only lines with $f > 10^{-5}$ are plotted.) of Hg porphyrin complex (inset) in free space and in cavity. The spectra are dominated by three lines conventionally called *B*, *N*, and *L*, and the cavities are set to resonance with the porphyrin *B* line with different coupling strengths g_α (a.u.). The Lorentzian spectra were obtained using broadening parameter $\gamma = 0.002$ a.u.. Inset: the structure of the molecule.

and matter and takes into account the change in refractive index due to putting matter inside the cavity [162,191]. Therefore, in addition to demonstrating the readiness of our method for the treatment of chemically relevant molecules, these results again stress the importance of *ab initio* QED methods.

So far, we have used the excitation energies and transition vectors to evaluate absorption spectra. However, the eigenvectors can also yield any other one-electron transition property. Here, we calculate and visualize transition densities associated with polaritonic states that offer real-space information about the excitations. The transition density corresponding to the n th excitation is calculated as a trace of the first-order transition density matrix $\mathbf{D}^{(1)}$ evaluated from the eigenvectors of the linear-response QEDFT equation, expressed on a real-space grid and plotted. Figure 6 shows transition densities for the transitions associated with the porphyrin *B* line, namely, the lower polariton [Fig. 6(a)], uncoupled state [Fig. 6(b)], and upper polariton [Fig. 6(c)] for the case of Hg porphyrin coupled to the cavity with the coupling strength $g_\alpha = 0.02$ a.u., as well as the transition densities of the molecule uncoupled to a cavity [Figs. 6(d) and 6(e) show the two degenerate transitions comprising the *B* line]. The cavity mode is polarized in the vertical direction, which is noticeable by the symmetry breaking in the form of vertical distortion of the lower polariton (a stronger signal in the spectrum than the upper polariton) transition density, as well as around the mercury atom: The polaritonic transitions have the density in the vertical direction, while the uncoupled state is in the perpendicular direction. The latter is similar to a pattern observed in a single mercury atom in

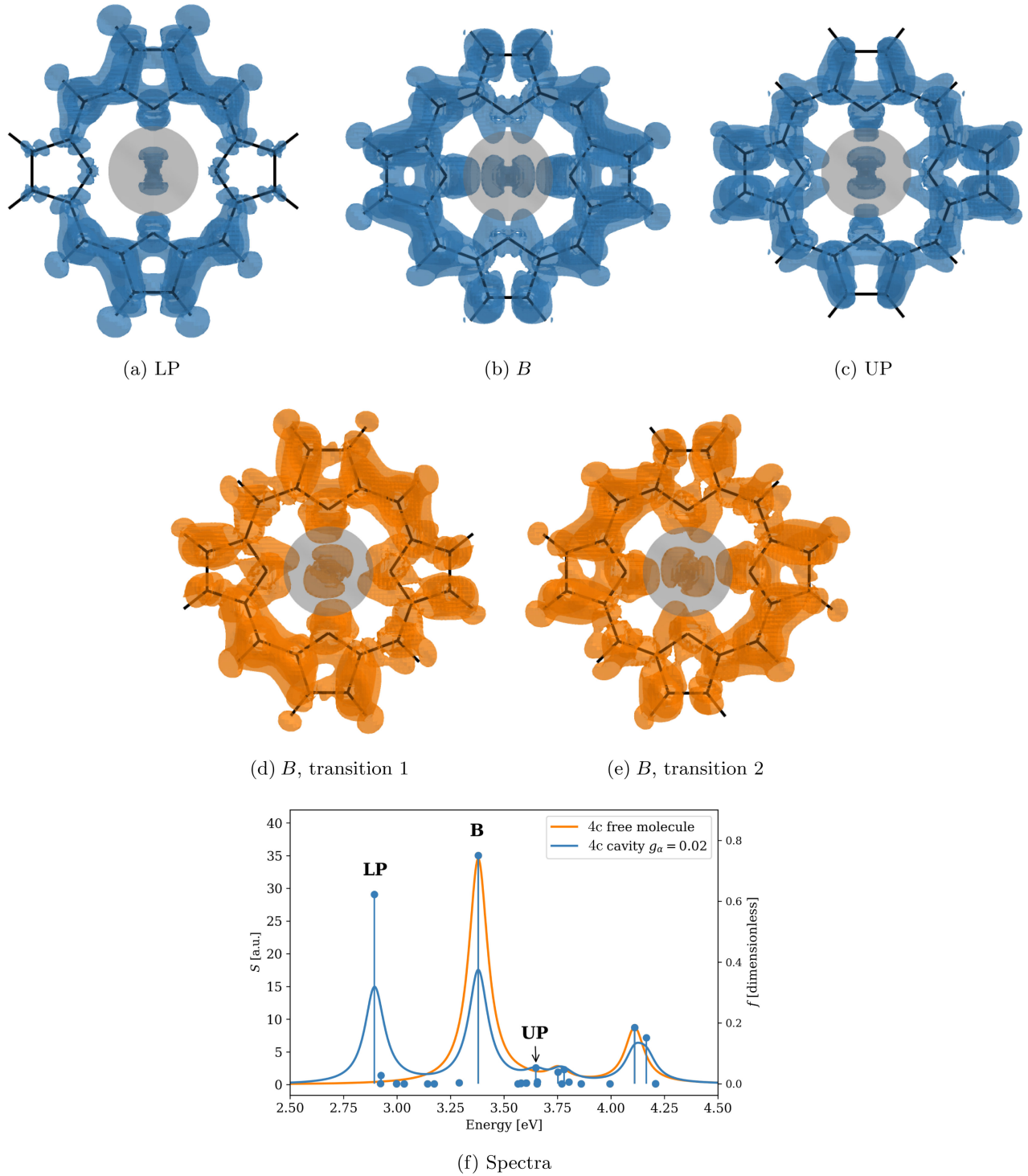


FIG. 6. Transition densities (a)–(e) corresponding to various excitations [uncoupled B line (doubly degenerate for the free molecule), lower polariton (LP), upper polariton (UP)] in the spectra of cavity-embedded and free Hg porphyrin (f). The densities are plotted as isosurfaces of absolute values at 6.0×10^{-4} a.u. and overlaid on porphyrin skeletal structure and the central mercury atom is depicted as a sphere with the size given by mercury’s van der Waals radius. Colors are matched to the spectra.

Fig. 7. The transition densities in Fig. 6 correspond to the coupling to a cavity mode polarized in the z direction (vertical), while the direction of the transition dipole moments of the uncoupled molecule’s transitions pointed to the bridges between the porphyrin’s five-membered rings.

If the cavity mode polarization is exactly aligned with one of the transition dipoles, the transition densities similarly show a disconnected pattern for the lower polariton, while the uncoupled state now exactly corresponds to the other transition of the free molecule (see Fig. 18 in Appendix H).

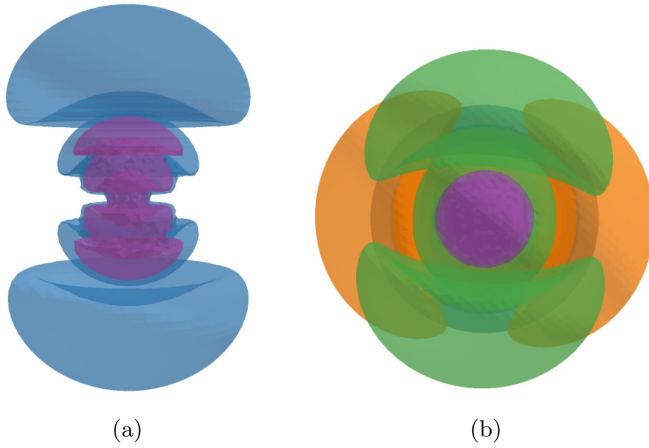


FIG. 7. Transition densities corresponding to different excitations in the spectrum of cavity-embedded Hg atom with the cavity tuned to resonance with the singlet-triplet transition. (a) Lower and upper polaritons. (b) All transitions (perpendicular view). The densities are plotted as isosurfaces at value 6.0×10^{-4} a.u.. Color legend: blue, lower polariton; purple, upper polariton; orange and green, uncoupled (perpendicular) states.

Transition densities give local and spatially resolved information about an excitation that shows where electronic density decreases and increases, which is valuable from a chemical point of view. For instance, such an analysis has allowed the origin of local modifications of chemical systems in collectively coupled ensembles to be uncovered [169] and modifications of electronic densities have been employed to interpret changes in transition temperatures of phonon-driven superconductors inside a cavity [197]. Potential other applications of transition densities are to suggest where a light- or cavity-driven chemical reaction will occur, as the places of increased (decreased) electron density will attract or repel reactants depending on their electrophilic or nucleophilic character. Additionally, an interesting direction where the examination of transition densities can point is a hypothesis that just as a chiral cavity was used to induce currents in a porphyrin complex [196], so a linearly polarized cavity may break aromaticity by disconnecting the delocalized electron density [Fig. 7(a)].

V. CONCLUSIONS

In this article, we presented the first implementation of a relativistic *ab initio* quantum-electrodynamical method, combining relativistic description of electronic structure with the treatment of transverse photons as dynamical variables in the form of linear-response QEDFT based on the four-component Dirac-Kohn-Sham Hamiltonian. We presented a detailed theory derivation of the final electron-photon Hamiltonian starting from relativistic QED, while keeping track of all approximations made on the way. For the linear-response equations, we showed how a spectral function can be calculated from a non-Hermitian Casida-like equation by considering both the left and right

eigenvectors, as well as also showing how this equation can be transformed to the symmetric equation often considered in *ab initio* QEDFT literature.

We applied the developed method to the calculation of polaritonically modified spectra of heavy-element atoms with singlet-triplet transitions and demonstrated that the intensity of the transition can be enhanced by the coupling to the cavity, as well as showing the coupling between the singlet-singlet and singlet-triplet transitions via the cavity modes that results in nonresonant splitting of spectral lines and the transfer of intensity between them. Of specific interest is that the cavity, even in the long-wavelength limit, can influence the SOC due to a fully relativistic (four-component) treatment of the electrons. Our results showing the interplay of off-resonant coupling and spin-orbit-driven transition demonstrate the need for accurate *ab initio* methods such as QEDFT to describe cavity modification of molecular properties, as well as help to guide the formulation of approximate models. In the presented cases, a minimal two-state model would be insufficient to describe the cavity modification of spectra around the singlet-triplet resonance. Moreover, the linear-response QEDFT methodology developed with the primary motivation of describing polaritonic chemistry in cavities allows one to address other situations when electrons are coupled to photons as well. Such an example is the coupling to free-space vacuum modes that presents a way of calculating radiative lifetimes from first principles, thereby resolving one of the shortcomings of electronic-structure linear-response theories that add this variable as an empirical parameter. Finally, by addressing the spectrum of mercury porphyrin in the cavity, we demonstrated that our program is capable of handling even large molecules of chemical interest. The current implementation can treat 100–200 atoms before hitting time and memory restrictions (see also Appendix J). To improve the computational performance and applicability of relativistic QEDFT, we are currently developing a two-component version of the linear-response QEDFT formalism based on the X2C transformation that promises significant computational savings, while preserving accuracy.

Ab initio QED methods have emerged recently as a first-principles approach for the prediction and interpretation of phenomena occurring under strong coupling of electronic and vibrational degrees of freedom of a material to the photonic modes of an optical cavity. In this work, we expanded the toolbox of *ab initio* QED methods further by bringing them into the relativistic domain. Considering the advances in also understanding collective-coupling effects [160,161,169] and the here-presented changes in the SOC, we think that this toolbox can help to design cavity setups such that SOC and other relativistic effects can be enhanced. This also conceptually is very interesting since it highlights that the transverse photons, usually discarded when deriving relativistic quantum chemistry equations from full QED, can be decisive for real atomic and molecular

systems. For instance, taking into account (approximately) the continuum of modes can be used to study nonperturbatively very fundamental effects of quantum field theories, such as mass renormalization of the electrons [7,198]. We also showed how the relativistic description of electrons inside a photonic structure reveals the presence of a new type of spin-orbit interaction mediated by cavity photons. This opens a new avenue in the fields of cavity QED and polaritonic chemistry, with a potential for follow-up works focused on the development of quadratic response theory to access transitions between excited states with applications to singlet-triplet transitions in reverse intersystem crossing systems, the exploration of the new SOC term in solid-state systems, or the development of effective Hamiltonians.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [199].

APPENDIX A: NOTATIONS AND CONVENTIONS

We use the following definitions: x^μ for contravariant four-vector, $x_\mu = g_{\mu\nu}x^\nu$ for covariant four-vector, $g_{\mu\nu}$ is the metric tensor

$$g_{\mu\nu} = g^{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix},$$

and $\alpha^\mu = \gamma^0 \gamma^\mu$ are the Dirac matrices in their standard representation,

$$\alpha^0 = \begin{pmatrix} \mathbb{1}_{2 \times 2} & 0 \\ 0 & \mathbb{1}_{2 \times 2} \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix},$$

$$\gamma^0 \equiv \beta = \begin{pmatrix} \mathbb{1}_{2 \times 2} & 0 \\ 0 & -\mathbb{1}_{2 \times 2} \end{pmatrix}, \quad \boldsymbol{\gamma} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ -\boldsymbol{\sigma} & 0 \end{pmatrix},$$

and the 2×2 Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Here, $\mathbb{1}_{2 \times 2}$ is a unit 2×2 matrix

$$\mathbb{1}_{2 \times 2} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

We use the italic style (r) for scalars, boldface ($\mathbf{r}$) for three-vectors, and Roman style ($\mathbf{r}$) for four-vectors and their components. Four-vectors have the form $\mathbf{p} = (p_0, \mathbf{p})$ and coordinates in four space are also denoted as $\mathbf{r} = (t, \mathbf{r})$. The scalar product of four-vectors is defined as $\mathbf{kp} = k^\mu p_\mu = k^0 p_0 - \mathbf{k} \cdot \mathbf{p}$. The summing over repeated indices is assumed by default. Fock space vectors and matrices are also denoted by Roman boldface, with 1 and 0 denoting the unit and zero matrix, respectively.

APPENDIX B: SOLUTION OF FIRST-ORDER EQUATIONS OF MOTION BY UNDETERMINED COEFFICIENTS

In the method of undetermined coefficients, we use the following ansatz for the electronic equation:

$$d_{ai}^{(1)}(t) = X_{ai} e^{-i\omega_{\text{ext}} t} + Y_{ai}^* e^{i\omega_{\text{ext}} t}, \quad (\text{B1a})$$

$$d_{ai}^{(1)*}(t) = X_{ai}^* e^{i\omega_{\text{ext}} t} + Y_{ai} e^{-i\omega_{\text{ext}} t}, \quad (\text{B1b})$$

motivated by the inhomogeneity in Eq. (52). Similarly, we formulate an ansatz for the photonic displacement coordinate in the form

$$q_\alpha^{(1)}(t) = \tilde{M}_\alpha e^{-i\omega_{\text{ext}} t} + \tilde{M}_\alpha^* e^{i\omega_{\text{ext}} t}, \quad (\text{B2})$$

from which follows

$$p_\alpha^{(1)}(t) = -\omega_{\text{ext}} \tilde{M}_\alpha e^{-i\omega_{\text{ext}} t} + \omega_{\text{ext}} \tilde{M}_\alpha^* e^{i\omega_{\text{ext}} t}, \quad (\text{B3})$$

and where the real nature of $q_\alpha^{(1)}(t)$ was taken into account.

We consider only a single inhomogeneity in the whole system of equations at a time, i.e., the external field or the external current. The ansatz will then contain its respective frequency (i.e., ω_{ext} or ω'_{ext}). By inserting expressions from Eqs. (B1)–(B3) into Eqs. (60) and selecting only the terms with time dependence $\exp(-i\omega_{\text{ext}} t)$, we obtain a set of coupled algebraic equations

$$\omega_{\text{ext}} X_{ai} = (A_{ai,bj} + \Delta_{ai,bj}) X_{bj} + (B_{ai,bj} + \Delta'_{ai,bj}) Y_{bj} - L_{ai,\alpha} \tilde{M}_\alpha + P_{ai}, \quad (\text{B4a})$$

$$-\omega_{\text{ext}} Y_{ai} = (A_{ai,bj}^* + \Delta_{ai,bj}^*) Y_{bj} + (B_{ai,bj}^* + \Delta'_{ai,bj}^*) X_{bj} - L_{ai,\alpha}^* \tilde{M}_\alpha + P_{ai}^*, \quad (\text{B4b})$$

$$(-\omega_{\text{ext}}^2 + \omega_\alpha^2) \tilde{M}_\alpha = Q'_{jb,\alpha} X_{bj} + Q_{jb,\alpha}^* Y_{bj}. \quad (\text{B4c})$$

Unfortunately, the equation for $\tilde{M}_\alpha$ contains ω_{ext}^2 , a recurrence of the second-order differential equation (57) as we would obtain the system of equations (B4) also by considering Eq. (57) instead of Eqs. (58) and (59) for the photonic degrees of freedom. Since we want to get an equation linear in ω_{ext} , we remove the second power by employing the identity

$$\frac{1}{\omega_{\text{ext}}^2 - \omega_\alpha^2} = \frac{1}{2\omega_\alpha} \left(\frac{1}{\omega_{\text{ext}} + \omega_\alpha} - \frac{1}{\omega_{\text{ext}} - \omega_\alpha} \right), \quad (\text{B5})$$

which transforms Eq. (B4c) into

$$\tilde{M}_\alpha = \frac{1}{2\omega_\alpha} \left(\frac{Q'_{jb,\alpha} X_{bj} + Q'^*_{jb,\alpha} Y_{bj}}{\omega_{\text{ext}} + \omega_\alpha} - \frac{Q'_{jb,\alpha} X_{bj} + Q'^*_{jb,\alpha} Y_{bj}}{\omega_{\text{ext}} - \omega_\alpha} \right). \quad (\text{B6})$$

We can now divide $\tilde{M}_\alpha$ into two components $\tilde{M}_\alpha = M_\alpha + N_\alpha$ that satisfy Eq. (B6) term by term,

$$M_\alpha = -\frac{1}{2\omega_\alpha} \frac{Q'_{jb,\alpha} X_{bj} + Q'^*_{jb,\alpha} Y_{bj}}{\omega_{\text{ext}} - \omega_\alpha}, \quad (\text{B7a})$$

$$N_\alpha = \frac{1}{2\omega_\alpha} \frac{Q'_{jb,\alpha} X_{bj} + Q'^*_{jb,\alpha} Y_{bj}}{\omega_{\text{ext}} + \omega_\alpha}, \quad (\text{B7b})$$

and both contain ω_{ext} only in the first power. This way, we can write four coupled algebraic equations linear in ω_{ext} for the variables X_{ai} , Y_{ai} , M_α , and N_α that collected in a matrix give

$$\left[\begin{pmatrix} \mathbf{A} + \mathbf{\Delta} & \mathbf{B} + \mathbf{\Delta}' & -\mathbf{L} & -\mathbf{L} \\ \mathbf{B}^* + \mathbf{\Delta}^* & \mathbf{A}^* + \mathbf{\Delta}'^* & -\mathbf{L}^* & -\mathbf{L}^* \\ -\mathbf{Q} & -\mathbf{Q}^* & \boldsymbol{\omega} & \mathbf{0} \\ -\mathbf{Q} & -\mathbf{Q}^* & \mathbf{0} & \boldsymbol{\omega} \end{pmatrix} - \omega_{\text{ext}} \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & -\mathbf{1} \end{pmatrix} \right] \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \\ \mathbf{M} \\ \mathbf{N} \end{pmatrix} = \begin{pmatrix} \mathbf{P} \\ \mathbf{P}^* \\ \mathbf{0} \\ \mathbf{0} \end{pmatrix}, \quad (\text{B8})$$

where we defined

$$\begin{aligned} Q_{jb,\alpha} &= \frac{1}{2\omega_\alpha} Q'_{jb,\alpha} = \frac{g_\alpha e \omega_\alpha}{\sqrt{\hbar}} \frac{1}{2\omega_\alpha} (\mathbf{r}_{jb} \cdot \boldsymbol{\epsilon}_\alpha) \\ &= \frac{1}{2} \frac{g_\alpha e}{\sqrt{\hbar}} (\mathbf{r}_{jb} \cdot \boldsymbol{\epsilon}_\alpha), \end{aligned} \quad (\text{B9})$$

and $\boldsymbol{\omega}$ is a diagonal matrix with elements ω_α on the diagonal. An analogous equation can be derived for the case of external current with the right-hand side having the form $(\mathbf{0} \mathbf{0} \mathbf{J} \mathbf{J}^*)^T$. This is the Sternheimer equation describing the response of a molecular system in a cavity to an external field of frequency ω_{ext} coupled to the electronic subsystem via operator $\mathbf{P}$. The algebraic form of the homogeneous equation to the system, Eq. (60), can now be obtained from Eq. (B8) by discarding the right-hand side with the frequency of the external field gaining the meaning of a resonance frequency of the system, i.e., n th excitation energy Ω_n , leading to Eq. (62).

APPENDIX C: SOLUTION OF THE MATRIX DIFFERENTIAL EQUATION AND THE INTERPRETATION OF PHOTON TERMS

It is interesting to note that an alternative approach to Eq. (62) exists based on a direct solution of the coupled system of differential equations (60). This system corresponds to a matrix differential equation in the form $i\dot{\mathbf{x}}(t) = \mathcal{M}\mathbf{x}(t) + \mathbf{b}(t)$, where

$$\mathbf{x}(t) = (\mathbf{d}^{(1)}(t), \mathbf{d}^{(1)*}(t), \mathbf{p}^{(1)}(t), \mathbf{q}^{(1)}(t))^T, \quad (\text{C1a})$$

$$\mathcal{M} = \begin{pmatrix} \mathbf{A} + \mathbf{\Delta} & \mathbf{B} + \mathbf{\Delta}' & \mathbf{0} & -\mathbf{L} \\ -\mathbf{B}^* - \mathbf{\Delta}'^* & -\mathbf{A}^* - \mathbf{\Delta}^* & \mathbf{0} & \mathbf{L}^* \\ \mathbf{Q}^* & \mathbf{Q}' & \mathbf{0} & -\boldsymbol{\omega}^2 \\ \mathbf{0} & \mathbf{0} & -\mathbf{1} & \mathbf{0} \end{pmatrix}, \quad (\text{C1b})$$

$$\mathbf{b}(t) = (\mathbf{P}e^{-i\omega_{\text{ext}}t} + \mathbf{P}^*e^{i\omega_{\text{ext}}t}, -\mathbf{P}^*e^{i\omega_{\text{ext}}t} - \mathbf{P}e^{-i\omega_{\text{ext}}t}, \mathbf{J}e^{-i\omega'_{\text{ext}}t} - \mathbf{J}^*e^{i\omega'_{\text{ext}}t}, \mathbf{0})^T. \quad (\text{C1c})$$

The homogeneous equation takes the form $i\dot{\mathbf{x}}(t) = \mathcal{M}\mathbf{x}(t)$ and its general solution is $\mathbf{x}(t) = \sum_n c_n e^{-i\Omega_n t} \mathbf{u}_n$, where $\mathbf{u}_n$ are the eigenvectors of matrix $\mathcal{M}$, Ω_n their corresponding eigenvalues, and c_n constant coefficients. The solution of the homogeneous equation thus boils down to finding the eigenvectors and eigenvalues of the matrix $\mathcal{M}$ defined in Eq. (C1). Since two matrices related by a similarity transformation have the same set of eigenvalues, one can alternatively solve the eigenproblem for its similar matrix $\mathcal{M}' = \mathbf{S}\mathcal{M}\mathbf{S}^{-1}$ with eigenvectors $\mathbf{u}' = \mathbf{S}\mathbf{u}$, if the new matrix has some more favorable properties. For example, matrix $\mathcal{M}$ defined in Eq. (C1) can be transformed into a diagonally dominant matrix by

$$\begin{pmatrix} \mathbf{A} + \Delta & \mathbf{B} + \Delta' & -\mathbf{L} & -\mathbf{L} \\ -\mathbf{B}^* - \Delta'^* & -\mathbf{A}^* - \Delta^* & \mathbf{L}^* & \mathbf{L}^* \\ -\mathbf{Q}^* & -\mathbf{Q} & \omega & 0 \\ \mathbf{Q}^* & \mathbf{Q} & 0 & -\omega \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2\omega} & \frac{1}{2} \\ 0 & 0 & \frac{1}{2\omega} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \mathbf{A} + \Delta & \mathbf{B} + \Delta' & 0 & -\mathbf{L} \\ -\mathbf{B}^* - \Delta'^* & -\mathbf{A}^* - \Delta^* & 0 & \mathbf{L}^* \\ \mathbf{Q}'^* & \mathbf{Q}' & 0 & -\omega^2 \\ 0 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\omega & \omega \\ 0 & 0 & 1 & 1 \end{pmatrix}, \quad (\text{C2})$$

with the same definition of $\mathbf{Q}$ as above and matrices $\pm[\mathbf{1}/(2\omega)]$, $\frac{1}{2}$, and $\pm\omega$ corresponding to diagonal matrices with $\pm[1/(2\omega_\alpha)]$, $\frac{1}{2}$, and $\pm\omega_\alpha$, respectively, on the diagonal. This transformation recovers the matrix in Eq. (62) [after multiplication with the matrix $\text{diag}(\mathbf{1}, -\mathbf{1}, \mathbf{1}, -\mathbf{1})$ on the right-hand side]. Moreover, the similarity transformation also shows a relationship between the new photonic variables M_α and N_α and the old $\mathbf{p}^{(1)}(t)$ and $\mathbf{q}^{(1)}(t)$ in the form

$$M_\alpha = -\frac{1}{2\omega_\alpha} p_\alpha^{(1)} + \frac{1}{2} q_\alpha^{(1)}, \quad (\text{C3a})$$

$$N_\alpha = \frac{1}{2\omega_\alpha} p_\alpha^{(1)} + \frac{1}{2} q_\alpha^{(1)}, \quad (\text{C3b})$$

which is analogous, but not yet identical to the definition of creation and annihilation operators in Eqs. (20) and (19), suggesting an interpretation of M_α as a creation and N_α as an annihilation amplitude, respectively.

Furthermore, we can perform yet another similarity transformation to symmetrize the matrix $\mathcal{M}'$ defined in Eq. (C2),

$$\begin{pmatrix} \mathbf{A} + \Delta & \mathbf{B} + \Delta' & -\Gamma & -\Gamma \\ -\mathbf{B}^* - \Delta'^* & -\mathbf{A}^* - \Delta^* & \Gamma^* & \Gamma^* \\ -\Gamma'^* & -\Gamma' & \omega & 0 \\ \Gamma'^* & \Gamma' & 0 & -\omega \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \sqrt{2\omega} & 0 \\ 0 & 0 & 0 & \sqrt{2\omega} \end{pmatrix} \begin{pmatrix} \mathbf{A} + \Delta & \mathbf{B} + \Delta' & -\mathbf{L} & -\mathbf{L} \\ -\mathbf{B}^* - \Delta'^* & -\mathbf{A}^* - \Delta^* & \mathbf{L}^* & \mathbf{L}^* \\ -\mathbf{Q}^* & -\mathbf{Q} & \omega & 0 \\ \mathbf{Q}^* & \mathbf{Q} & 0 & -\omega \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{2\omega}} & 0 \\ 0 & 0 & 0 & \frac{1}{\sqrt{2\omega}} \end{pmatrix}, \quad (\text{C4})$$

where the photon-electron and the electron-photon coupling has the form

$$\Gamma_{ai,\alpha} = \Gamma'_{\alpha,ai} = \sqrt{\frac{\hbar\omega_\alpha}{2}} g_{a\mathbf{d}} \boldsymbol{\mu}_{ai} \cdot \boldsymbol{\varepsilon}_\alpha, \quad (\text{C5})$$

and matrices $\sqrt{2\omega}$ and $\mathbf{1}/\sqrt{2\omega}$ are diagonal matrices with $\sqrt{2\omega_\alpha}$ and $1/\sqrt{2\omega_\alpha}$, respectively, on the diagonal. Symmetrization in Eq. (C4) recovered the matrix appearing in the linear-response QEDFT equation solved in earlier (nonrelativistic) works [71,72]. Furthermore, the symmetrizing similarity transform gives

$$M_\alpha = \sqrt{\frac{\omega_\alpha}{2}} \left(-\frac{1}{\omega_\alpha} p_\alpha^{(1)} + q_\alpha^{(1)} \right), \quad (\text{C6a})$$

$$N_\alpha = \sqrt{\frac{\omega_\alpha}{2}} \left(\frac{1}{\omega_\alpha} p_\alpha^{(1)} + q_\alpha^{(1)} \right), \quad (\text{C6b})$$

which exactly corresponds to the definition of the creation and annihilation operators in Eqs. (20) and (19), giving M_α and N_α the meaning of creation and annihilation amplitudes, respectively.

APPENDIX D: DERIVATION OF THE EXPRESSION FOR POLARIZABILITY USING LEFT AND RIGHT EIGENVECTORS

To compactify the following discussion, let us adopt the notation common in quantum chemistry where the Sternheimer equation (B8) is written term by term as $[\mathbf{E}^{[2]} - \omega_{\text{ext}} \mathbf{S}^{[2]}] \mathbf{Z} = \mathbf{G}$ and Eq. (63) takes the form $\boldsymbol{\alpha}(\omega_{\text{ext}}) = -\mathbf{G}^\dagger [\mathbf{E}^{[2]} - \omega_{\text{ext}} \mathbf{S}^{[2]}]^{-1} \mathbf{G}$. The right and left eigenvectors are defined as

$$\mathbf{S}^{[2]} \mathbf{E}^{[2]} \mathbf{Z}^{\text{R}} = \mathbf{Z}^{\text{R}} \boldsymbol{\Omega}, \quad (\text{D1a})$$

$$\mathbf{Z}^{\text{L}\dagger} \mathbf{S}^{[2]} \mathbf{E}^{[2]} = \boldsymbol{\Omega} \mathbf{Z}^{\text{L}\dagger}, \quad (\text{D1b})$$

where matrix $\boldsymbol{\Omega}$ is a diagonal matrix containing all the eigenvalues and the columns of matrices $\mathbf{Z}^{\text{R}}$ and $\mathbf{Z}^{\text{L}}$ contain all the right and left eigenvectors, respectively. Moreover, we made use of the fact that $\mathbf{S}^{[2],-1} = \mathbf{S}^{[2]}$. Left and right eigenvectors corresponding to different eigenvalues are orthogonal and can be transformed to be so for degenerate subspaces, meaning that their matrices satisfy $\mathbf{Z}^{\text{L}\dagger} \mathbf{Z}^{\text{R}} = \mathbf{1}$. Let us note that the definition of $\mathbf{Z}^{\text{L}\dagger}$ as a left eigenvector of matrix $\mathbf{S}^{[2]} \mathbf{E}^{[2]}$ is due to the computer implementation that

solves the eigenproblem for matrix $\mathbf{S}^{[2]}\mathbf{E}^{[2]}$ instead of the generalized eigenproblem. The alternative formulation of left eigenvectors stemming from the generalized eigenproblem $\tilde{\mathbf{Z}}^{\text{L}\dagger}\mathbf{E}^{[2]} = \mathbf{\Omega}\tilde{\mathbf{Z}}^{\text{L}\dagger}\mathbf{S}^{[2]}$ is related to ours via $\tilde{\mathbf{Z}}^{\text{L}\dagger}\mathbf{S}^{[2]} = \mathbf{Z}^{\text{L}\dagger}$ and the eigenvectors satisfy the condition $\tilde{\mathbf{Z}}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{Z}^{\text{R}} = \mathbf{1}$. From Eqs. (D1), it also follows that $\mathbf{Z}^{\text{L}\dagger}\mathbf{E}^{[2]}\mathbf{Z}^{\text{R}} = \mathbf{Z}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{Z}^{\text{R}}\mathbf{\Omega}$.

The expression for the polarizability can be worked out as

$$\begin{aligned}\alpha(\omega) &= -\mathbf{G}^\dagger[\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]}]^{-1}\mathbf{G} \\ &= -\mathbf{G}^\dagger\mathbf{Z}^{\text{R}}\mathbf{Z}^{\text{L}\dagger}[\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]}]^{-1}\mathbf{Z}^{\text{R}}\mathbf{Z}^{\text{L}\dagger}\mathbf{G} \\ &= -(\mathbf{G}^\dagger\mathbf{Z}^{\text{R}})(\mathbf{Z}^{\text{L}\dagger}[\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]}]^{-1}\mathbf{Z}^{\text{R}})(\mathbf{Z}^{\text{L}\dagger}\mathbf{G}) \\ &= -(\mathbf{G}^\dagger\mathbf{Z}^{\text{R}})(\mathbf{Z}^{\text{R},-1}[\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]}]\mathbf{Z}^{\text{L}\dagger,-1})^{-1}(\mathbf{Z}^{\text{L}\dagger}\mathbf{G}) \\ &= -(\mathbf{G}^\dagger\mathbf{Z}^{\text{R}})(\mathbf{Z}^{\text{L}\dagger}[\mathbf{E}^{[2]} - \omega\mathbf{S}^{[2]}]\mathbf{Z}^{\text{R}})^{-1}(\mathbf{Z}^{\text{L}\dagger}\mathbf{G}) \\ &= -(\mathbf{G}^\dagger\mathbf{Z}^{\text{R}})(\mathbf{Z}^{\text{L}\dagger}\mathbf{E}^{[2]}\mathbf{Z}^{\text{R}} - \omega\mathbf{Z}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{Z}^{\text{R}})^{-1}(\mathbf{Z}^{\text{L}\dagger}\mathbf{G}) \\ &= -(\mathbf{G}^\dagger\mathbf{Z}^{\text{R}})(\mathbf{Z}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{Z}^{\text{R}}\mathbf{\Omega} - \mathbf{Z}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{Z}^{\text{R}}\omega)^{-1}(\mathbf{Z}^{\text{L}\dagger}\mathbf{G}) \\ &= -(\mathbf{G}^\dagger\mathbf{Z}^{\text{R}})(\mathbf{Z}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{Z}^{\text{R}}[\mathbf{\Omega} - \omega\mathbf{1}])^{-1}(\mathbf{Z}^{\text{L}\dagger}\mathbf{G}) \\ &= -(\mathbf{G}^\dagger\mathbf{Z}^{\text{R}})([\mathbf{\Omega} - \omega\mathbf{1}]^{-1}\mathbf{Z}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{Z}^{\text{R}})(\mathbf{Z}^{\text{L}\dagger}\mathbf{G}) \\ &= -(\mathbf{G}^\dagger\mathbf{Z}^{\text{R}})[\mathbf{\Omega} - \omega\mathbf{1}]^{-1}(\mathbf{Z}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{G}),\end{aligned}\quad (\text{D2})$$

where we renamed ω_{ext} to ω both for clarity as well as to indicate its meaning as the frequency at which the frequency-dependent polarizability is evaluated. The matrix $\mathbf{\Omega} - \omega\mathbf{1}$ is diagonal and can be easily inverted. However, the formula can be further simplified by taking into account the fact that the eigenvalues come in positive-negative pairs, i.e., the matrix $\mathbf{\Omega}$ has the structure

$$\mathbf{\Omega} = \begin{pmatrix} \mathbf{\Omega}^+ & \mathbf{0} \\ \mathbf{0} & -\mathbf{\Omega}^+ \end{pmatrix}, \quad (\text{D3})$$

where $\mathbf{\Omega}^+$ is a diagonal matrix of the positive eigenvalues labeled from 1 to n . Therefore, the expression for the polarizability tensor becomes

$$\alpha(\omega) = -\sum_n \left[\frac{t_n^{\text{R}} t_n^{\text{L}*}}{\mathbf{\Omega}_n - \omega} - \frac{t_{-n}^{\text{R}} t_{-n}^{\text{L}*}}{-\mathbf{\Omega}_n - \omega} \right], \quad (\text{D4})$$

where variables labeled by n and $-n$ belong to excitation energies $\mathbf{\Omega}_n$ and $-\mathbf{\Omega}_n$, respectively, and the right and left transition dipole moments are defined as

$$t_n^{\text{R}} = \mathbf{G}^\dagger\mathbf{Z}^{\text{R}} = \mathbf{P}^\dagger\mathbf{X}_n^{\text{R}} + \mathbf{P}\mathbf{Y}_n^{\text{R}}, \quad (\text{D5a})$$

$$t_n^{\text{L}} = \mathbf{Z}^{\text{L}\dagger}\mathbf{S}^{[2]}\mathbf{G} = \mathbf{P}^\dagger\mathbf{X}_n^{\text{R}} - \mathbf{P}\mathbf{Y}_n^{\text{R}}. \quad (\text{D5b})$$

The fact that only the electronic parts $\mathbf{X}_n^{\text{R/L}}$ and $\mathbf{Y}_n^{\text{R/L}}$ of the transition vector $\mathbf{Z}_n^{\text{R/L}} = (\mathbf{X}_n^{\text{R/L}}, \mathbf{Y}_n^{\text{R/L}}, \mathbf{M}_n^{\text{R/L}}, \mathbf{N}_n^{\text{R/L}})^{\text{T}}$ are used to calculate the transition dipole moment in Eqs. (65) is the consequence of the fact that the electric dipole moment is an electron-only property described by $\mathbf{G} = (\mathbf{P}, \mathbf{P}^*, \mathbf{0}, \mathbf{0})^{\text{T}}$. The eigenvector corresponding to an eigenvalue with the opposite sign has $\mathbf{X}_{-n}^{\text{R/L}} = \mathbf{Y}_n^{\text{R/L}*}$ and $\mathbf{Y}_{-n}^{\text{R/L}} = \mathbf{X}_n^{\text{R/L}*}$, therefore $t_{-n}^{\text{R}} = t_n^{\text{R}*}$ and $t_{-n}^{\text{L}} = t_n^{\text{L}*}$. After inserting these expressions into Eq. (D4), we obtain the final expression for the frequency-dependent polarizability calculated from the distinct right and left eigenvectors,

$$\alpha(\omega) = \sum_n \left[\frac{t_n^{\text{R}*} t_n^{\text{L}}}{\mathbf{\Omega}_n + \omega} - \frac{t_n^{\text{R}} t_n^{\text{L}*}}{\omega - \mathbf{\Omega}_n} \right]. \quad (\text{D6})$$

APPENDIX E: RESULTS WITHOUT CAVITIES

TABLE II. Excitation energies (E in a.u. and eV) and oscillator strengths (f , dimensionless) of group 12 atoms (Dyall's DZ basis, B3LYP functional) for the allowed $^1S_0 \rightarrow ^3P_1$ (S - T) and $^1S_0 \rightarrow ^1P_1$ (S - S) transitions compared to experimental data.

Atom	From	To	E (a.u.)	E (eV)	f	E_{exp} (eV) ^a	f_{exp} ^a
Zn	1S_0	3P_0	0.1463	3.9815	0.0	4.01	0.0
	1S_0	3P_1	0.1472	4.0060	0.000 068 8	4.03	0.000 053
	1S_0	3P_2	0.1491	4.0562	0.0	4.08	0.0
	1S_0	1P_1	0.2101	5.7163	0.493	5.80	0.4895
Cd	1S_0	3P_0	0.1345	3.6594	0.0	3.73	0.0
	1S_0	3P_1	0.1370	3.7282	0.000 792	3.80	...
	1S_0	3P_2	0.1425	3.8772	0.0	3.95	0.0
	1S_0	1P_1	0.1937	5.2713	0.493	5.42	0.4159
Hg	1S_0	3P_0	0.1652	4.4944	0.0	4.67	0.0
	1S_0	3P_1	0.1731	4.7089	0.009 74	4.89	0.0077
	1S_0	3P_2	0.1943	5.2877	0.0	5.46	0.0
	1S_0	1P_1	0.2332	6.3457	0.376	6.70	0.3825

^aReference [189].

APPENDIX F: ADDITIONAL SPECTRA

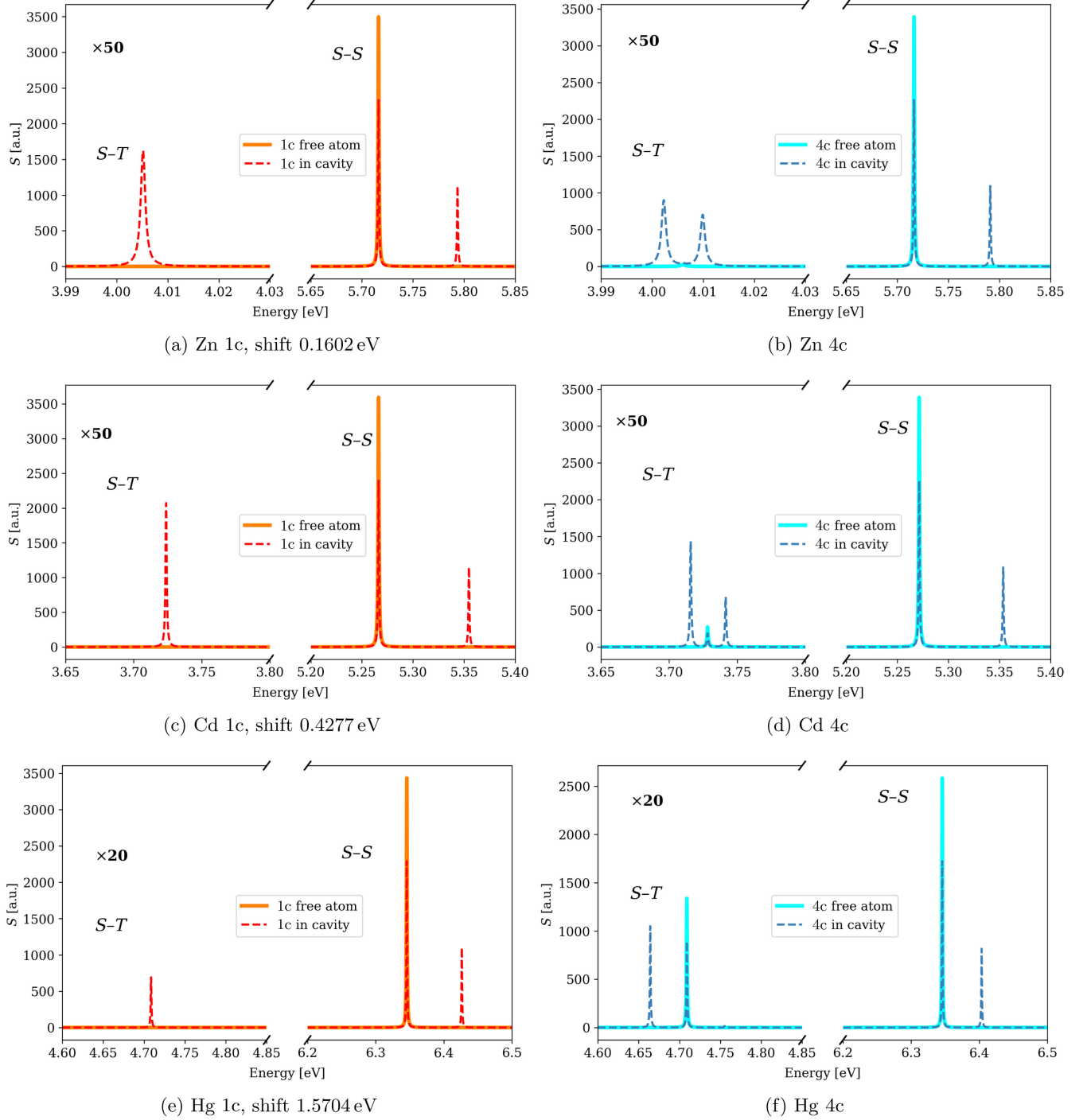


FIG. 8. Absorption spectra of group 12 atoms (Zn, Cd, and Hg) in cavities strongly coupled (coupling strength $g_a = 0.02$ a.u.) to a cavity tuned to the effective dressed resonance of the singlet-triplet (S - T) transition. Panels (a), (d), and (g) show nonrelativistic (1c) calculations for Zn, Cd, and Hg, respectively, while panels (b), (e), and (h) display the corresponding relativistic (4c) results. The region around the low-intensity S - T transition is magnified to ease reading by a factor specified in each figure. The nonrelativistic (1c) spectra are shifted to align the singlet-singlet (S - S) transition with the 4c spectra.

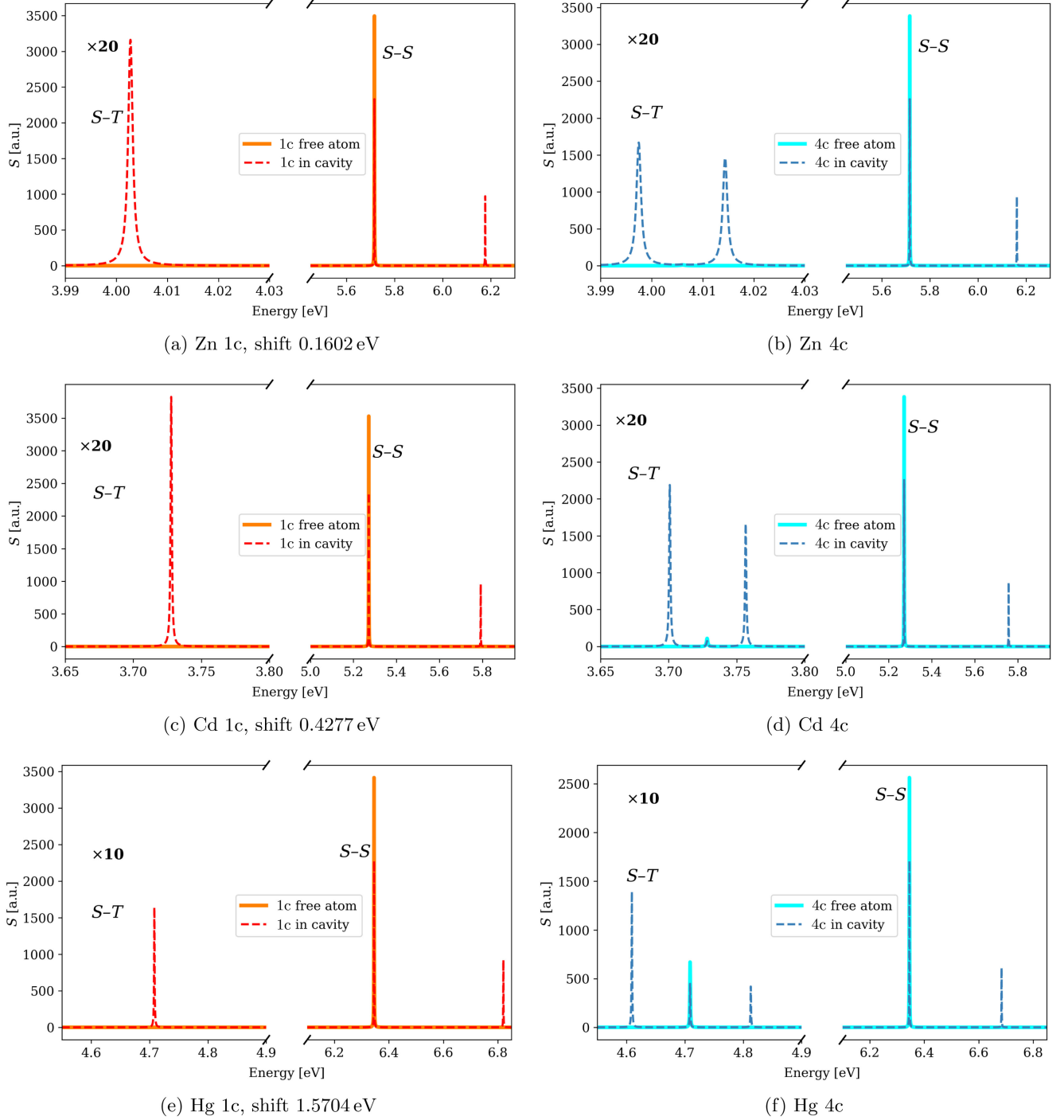


FIG. 9. Absorption spectra of group 12 atoms (Zn, Cd, and Hg) in cavities strongly coupled (coupling strength $g_a = 0.05$ a.u.) to a cavity tuned to the effective dressed resonance of the singlet-triplet (S - T) transition. Panels (a), (d), and (g) show nonrelativistic (1c) calculations for Zn, Cd, and Hg, respectively, while panels (b), (e), and (h) display the corresponding relativistic (4c) results. The region around the low-intensity S - T transition is magnified to ease reading by a factor specified in each figure. The nonrelativistic (1c) spectra are shifted to align the singlet-singlet (S - S) transition with the 4c spectra.

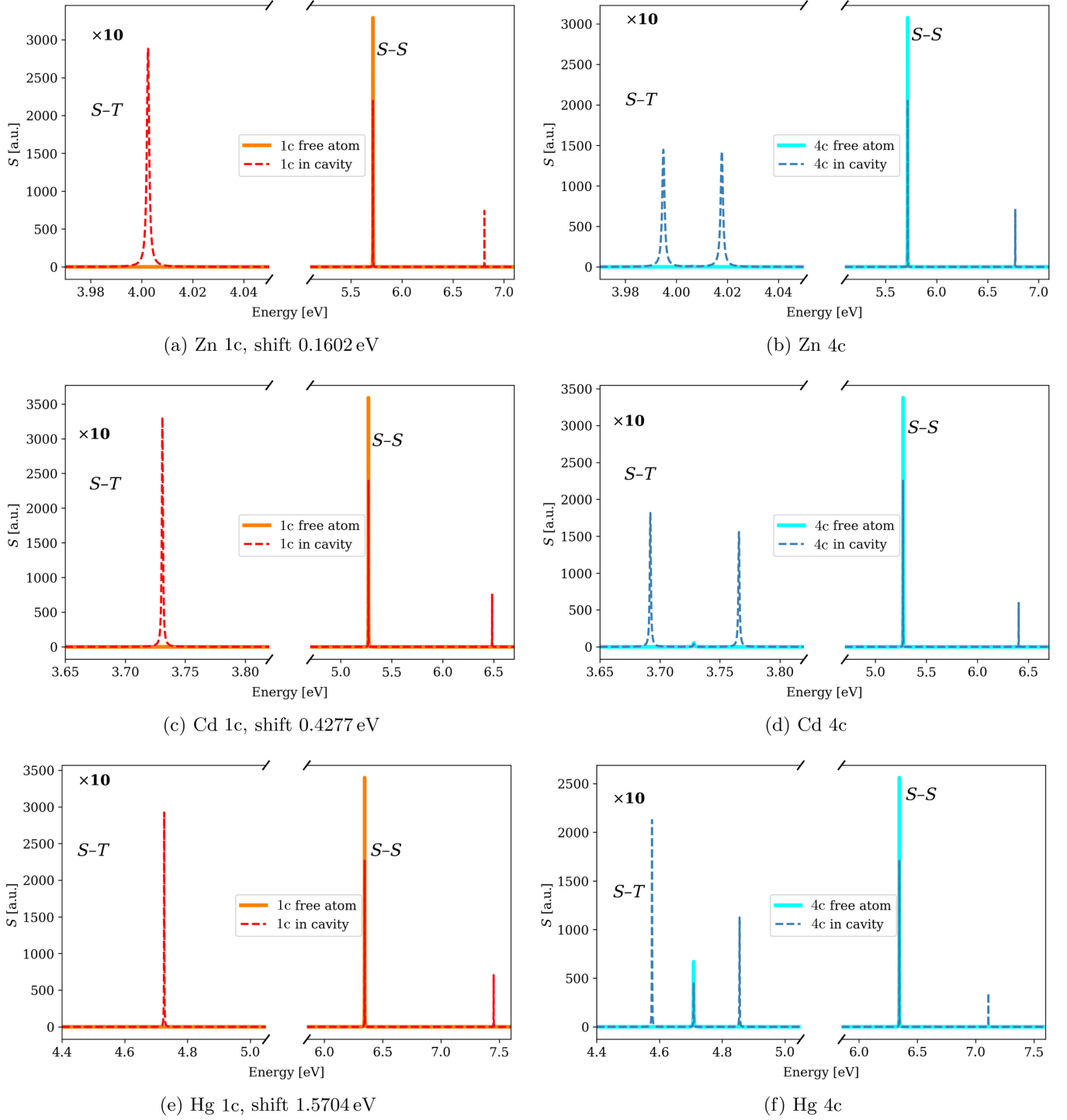


FIG. 10. Absorption spectra of group 12 atoms (Zn, Cd, and Hg) in cavities strongly coupled (coupling strength $g_a = 0.08$ a.u.) to a cavity tuned to the effective dressed resonance of the singlet-triplet (S - T) transition. Panels (a), (d), and (g) show nonrelativistic (1c) calculations for Zn, Cd, and Hg, respectively, while panels (b), (e), and (h) display the corresponding relativistic (4c) results. The region around the low-intensity S - T transition is magnified to ease reading by a factor specified in each figure. The nonrelativistic (1c) spectra are shifted to align the singlet-singlet (S - S) transition with the 4c spectra.

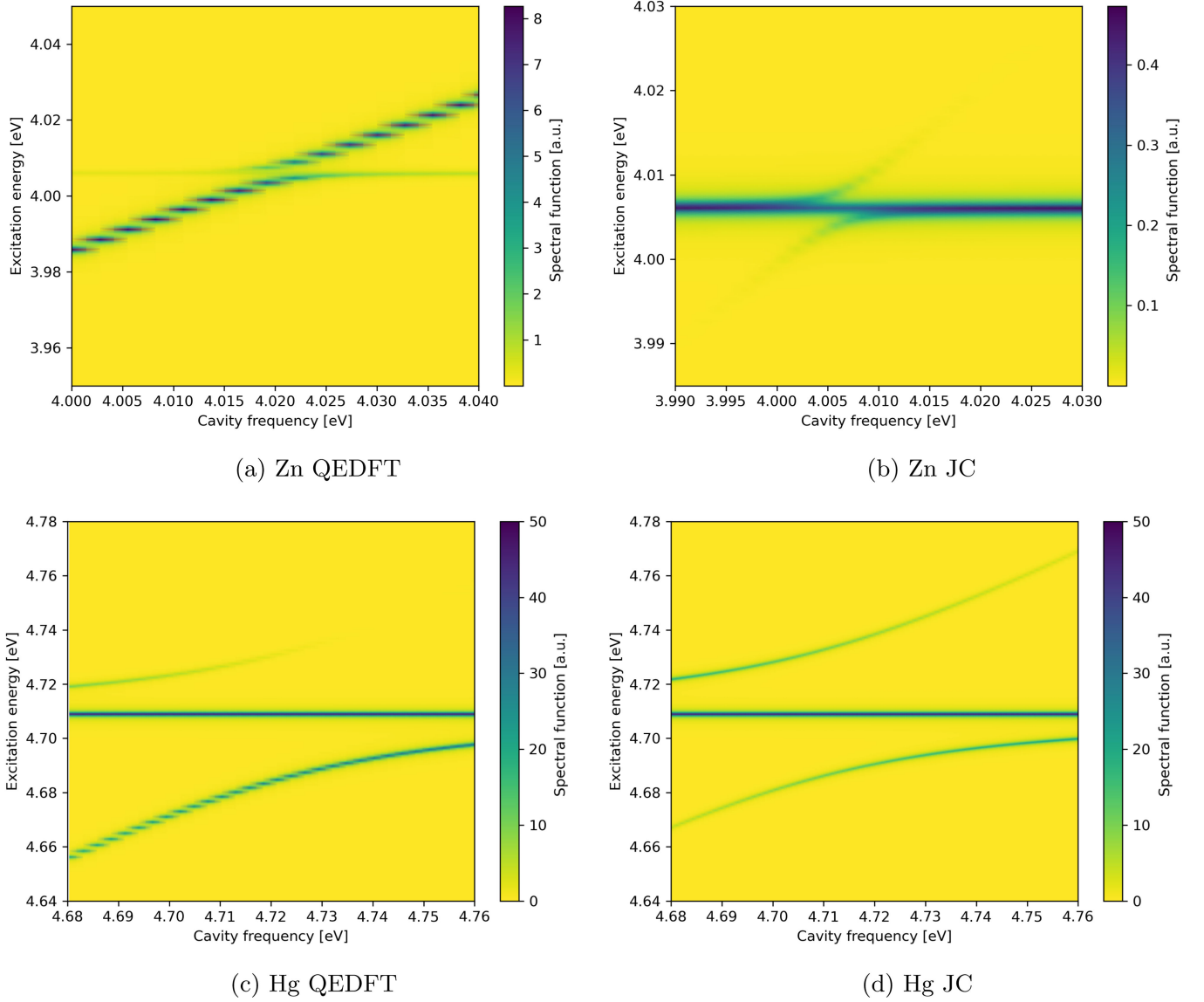


FIG. 11. Absorption spectra of Zn and Hg atoms strongly coupled (coupling strength $g_\alpha = 0.01$ a.u.) to a cavity, computed using the QEDFT formalism and compared to the predictions of the Jaynes-Cummings (JC) model parametrized by relativistic (4c) TDDFT results. Panels (a) and (b) correspond to Zn, while panels (c) and (d) correspond to Hg. Note the different scales used for the Zn spectra in QEDFT and JC, due to discrepancies in the spectral function obtained from the two approaches. For the JC model, spectral lines corresponding to uncoupled states were added according to Eq. (G16).

APPENDIX G: FEW-LEVEL MODELS

1. Two-level Jaynes-Cummings model

The Hamiltonian describing a two-level system coupled to a single cavity mode in length gauge is

$$\hat{H}^{2L} = \hbar\omega_{ge}|e\rangle\langle e| \otimes \mathbb{1}_\gamma + \mathbb{1}_A \otimes \hbar\omega_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha - \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}}, \quad (\text{G1})$$

where $\hat{\mathbf{E}}$ is quantized electromagnetic field

$$\hat{\mathbf{E}} = ig_\alpha \sqrt{\frac{\hbar\omega_\alpha}{2}} (\hat{a}_\alpha - \hat{a}_\alpha^\dagger) \boldsymbol{\epsilon}_\alpha, \quad (\text{G2})$$

and $\hat{\boldsymbol{\mu}}$ is a dipole moment operator

$$\hat{\boldsymbol{\mu}} = \boldsymbol{\mu}_{eg}|e\rangle\langle g| + \boldsymbol{\mu}_{ge}|g\rangle\langle e|. \quad (\text{G3})$$

Here, $|g\rangle$ and $|e\rangle$ are ground and excited states, respectively, ω_{ge} is a frequency of the $g \rightarrow e$ transition, and $\boldsymbol{\mu}_{eg} = -\langle e|\mathbf{e}\mathbf{r} \cdot \boldsymbol{\epsilon}_\alpha|g\rangle$. After performing the rotating-wave approximation (RWA), $\hat{H}^{2L}$ takes a form

$$\hat{H}^{2L,\text{RWA}} = \hbar\omega_{ge}|e\rangle\langle e| \otimes \mathbb{1}_\gamma + \hbar\omega_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha \otimes \mathbb{1}_A + G(\boldsymbol{\mu}_{eg} \cdot \boldsymbol{\epsilon}_\alpha \hat{a}_\alpha |e\rangle\langle g| - \boldsymbol{\mu}_{ge} \cdot \boldsymbol{\epsilon}_\alpha \hat{a}_\alpha^\dagger |g\rangle\langle e|), \quad (\text{G4})$$

where

$$G = -ig_\alpha \sqrt{\frac{\hbar\omega_\alpha}{2}}. \quad (\text{G5})$$

The matrix form of $\hat{H}^{2\text{L,RWA}}$ is

$$\begin{array}{c|ccccc} & |g, 0\rangle & |e, 0\rangle & |g, 1\rangle & |e, 1\rangle & |g, 2\rangle \\ \hline \langle g, 0| & H_0^{2\text{L,RWA}} & 0 & 0 & 0 & 0 \\ \langle e, 0| & 0 & H_{1,(1,1)}^{2\text{L,RWA}} & H_{1,(2,1)}^{2\text{L,RWA}} & 0 & 0 \\ \langle g, 1| & 0 & H_{1,(2,1)}^{2\text{L,RWA}} & H_{1,(2,2)}^{2\text{L,RWA}} & 0 & 0 \\ \langle e, 1| & 0 & 0 & 0 & H_{2,(1,1)}^{2\text{L,RWA}} & H_{2,(1,2)}^{2\text{L,RWA}} \\ \langle g, 2| & 0 & 0 & 0 & H_{2,(2,1)}^{2\text{L,RWA}} & H_{2,(2,2)}^{2\text{L,RWA}} \end{array}, \quad (\text{G6})$$

where

$$H_0^{2\text{L,RWA}} = \langle g, 0 | \hat{H}^{2\text{L,RWA}} | g, 0 \rangle = \hbar\omega_\alpha \quad (\text{G7})$$

and

$$\begin{aligned} \mathbf{H}_n^{2\text{L,RWA}} &= \begin{bmatrix} \hbar\omega_\alpha(n-1) + \hbar\omega_{ge} & \langle e, n-1 | \hat{H}^{2\text{L,RWA}} | g, n \rangle \\ \langle g, n | \hat{H}^{2\text{L,RWA}} | e, n-1 \rangle & n\hbar\omega_\alpha \end{bmatrix} \\ &= \begin{bmatrix} \hbar\omega_\alpha(n-1) + \hbar\omega_{ge} & \sqrt{n}G\boldsymbol{\mu}_{eg} \cdot \boldsymbol{\epsilon}_\alpha \\ -\sqrt{n}G\boldsymbol{\mu}_{ge} \cdot \boldsymbol{\epsilon}_\alpha & n\hbar\omega_\alpha \end{bmatrix}. \end{aligned} \quad (\text{G8})$$

Because of its block-diagonal structure, it is possible to work only with individual 2×2 blocks. We will further consider only the first 2×2 block, as we are interested in the case when transitions occur from the ground state $|g, 0\rangle$, thus obtaining the Jaynes-Cummings Hamiltonian

$$\mathbf{H}^{\text{JC}} = \begin{bmatrix} \hbar\omega_{ge} & G\boldsymbol{\mu}_{eg} \cdot \boldsymbol{\epsilon}_\alpha \\ -G\boldsymbol{\mu}_{ge} \cdot \boldsymbol{\epsilon}_\alpha & \hbar\omega_\alpha \end{bmatrix}. \quad (\text{G9})$$

We can diagonalize this Hamiltonian analytically and get eigenvalues and eigenvectors corresponding to polaritonic states (with + and - labeling the upper and lower polariton, respectively)

$$E_\pm = \frac{1}{2} \left(\hbar\omega_\alpha + \hbar\omega_{ge} \pm \sqrt{\hbar^2(\omega_\alpha - \omega_{ge})^2 + 4|G|^2|\boldsymbol{\mu}_{eg} \cdot \boldsymbol{\epsilon}_\alpha|^2} \right), \quad (\text{G10})$$

and

$$|+\rangle = C_1(A|e, 0\rangle + |g, 1\rangle), \quad (\text{G11})$$

$$|-\rangle = C_2(B|e, 0\rangle + |g, 1\rangle), \quad (\text{G12})$$

where

$$A = \frac{\hbar(\omega_\alpha - \omega_{ge}) - \sqrt{\hbar^2(\omega_\alpha - \omega_{ge})^2 + 4|G|^2|\boldsymbol{\mu}_{eg} \cdot \boldsymbol{\epsilon}_\alpha|^2}}{2G\boldsymbol{\mu}_{eg} \cdot \boldsymbol{\epsilon}_\alpha}, \quad (\text{G13})$$

$$B = \frac{\hbar(\omega_\alpha - \omega_{ge}) + \sqrt{\hbar^2(\omega_\alpha - \omega_{ge})^2 + 4|G|^2|\boldsymbol{\mu}_{eg} \cdot \boldsymbol{\epsilon}_\alpha|^2}}{2\boldsymbol{\mu}_{eg} \cdot \boldsymbol{\epsilon}_\alpha}, \quad (\text{G14})$$

and $C_1 = (1/\sqrt{|A|^2 + 1})$ and $C_2 = (1/\sqrt{|B|^2 + 1})$ are normalization constants. The eigenvectors are then used to evaluate the transition dipole moments from the uncoupled ground state $|g, 0\rangle$ to the polaritonic states, $\langle g, 0 | \boldsymbol{\mu} | + \rangle$ and $\langle g, 0 | \boldsymbol{\mu} | - \rangle$ and subsequently the absorption spectrum [i.e., spectral function $S_\pm(\omega)$] as

$$\begin{aligned} S_\pm(\omega) &= \frac{4\pi\omega}{3c} \text{Im} \left[\frac{|\langle g, 0 | \boldsymbol{\mu} | + \rangle|^2}{E_+ + \omega + i\gamma} - \frac{|\langle g, 0 | \boldsymbol{\mu} | + \rangle|^2}{\omega - E_+ + i\gamma} \right. \\ &\quad \left. + \frac{|\langle g, 0 | \boldsymbol{\mu} | - \rangle|^2}{E_- + \omega + i\gamma} - \frac{|\langle g, 0 | \boldsymbol{\mu} | - \rangle|^2}{\omega - E_- + i\gamma} \right]. \end{aligned} \quad (\text{G15})$$

In addition, we may add the signal resulting from the two triplet states not coupled to the cavity (due to their transition dipole moment being in perpendicular directions to the cavity mode polarization) in order to obtain a final spectrum that is similar to the QEDFT result,

$$S(\omega) = S_\pm(\omega) + 2 \frac{4\pi\omega}{3c} \text{Im} \left[\frac{|\langle e | \boldsymbol{\mu} | g \rangle|^2}{\omega_{eg} + \omega + i\gamma} - \frac{|\langle e | \boldsymbol{\mu} | g \rangle|^2}{\omega - \omega_{eg} + i\gamma} \right], \quad (\text{G16})$$

where the additional factor 2 is for the double degeneracy of the uncoupled states.

When building the JC model for group 12 atoms, we use parametrization based on the results of TDDFT calculations (see Appendix E and Table II) with settings mirroring those used in QEDFT calculations. The particular values of JC parameters are summarized in Table III. The resulting spectra for Zn and Hg are presented in Fig. 11.

2. Three-level model

We consider a three-level atom with states $|e_1\rangle$, $|e_2\rangle$, and $|g\rangle$, which when applied to group 12 atoms represent the excited state triplet (T_1 , i.e., 3P_1), excited singlet

TABLE III. Values of Jaynes-Cummings (JC) model parameters (in a.u.) obtained from TDDFT calculations.

Atom	ω_{eg}	$\langle e \boldsymbol{\mu} g \rangle$
Zn	0.147 219 61	0.026 481
Hg	0.173 050 60	0.290 59

(S_1 , i.e., 1P_1), and ground-state singlet (S_0 , i.e., 1S_0), respectively. The excitation energies and transition dipole moments are summarized in Table IV, while we also assume no transitions between the excited states (i.e., $\langle S_1 | \mu | T_1 \rangle = 0$).

A Hamiltonian describing a three-level matter system consisting of ground state $|g\rangle$, first excited state $|e_1\rangle$ (excitation frequency ω_{ge_1}), and second excited state $|e_2\rangle$ (excitation frequency ω_{ge_2}) interacting with a single cavity mode with frequency ω_α and polarization ϵ_α has the form

$$H^{3L} = H^m \otimes \mathcal{I}^p + \mathcal{I}^m \otimes H^p - g_\alpha \omega_\alpha D^m \otimes q^p, \quad (G17)$$

where the matter Hamiltonian is $H^m = \text{diag}(0, \omega_{ge_1}, \omega_{ge_2})$, the photon Hamiltonian is $H^p = \hbar \omega_\alpha \text{diag}(1, 2, \dots, n_p)$ (n_p being the photon space of dimension), the dipole matrix D^m is a 3×3 matrix containing transition dipole moments (only elements $D_{1,2}^m$, $D_{1,3}^m$, $D_{2,1}^m$, and $D_{3,1}^m$ are nonzero), and the photon coordinate matrix is $q^p = \sqrt{[\hbar/(2\omega_\alpha)](a + a^\dagger)}$, where the matrix representation of the creation and annihilation operators satisfy $a_{k,k+1} = \sqrt{k}$ and $a_{k,k-1}^\dagger = \sqrt{k}$ with the rest of their elements being zero. A solution of this model available in the LIBQED package was used to produce the results presented below.

TABLE IV. Values of three-level model parameters (in a.u.) obtained from TDDFT calculations.

Atom	$\omega_{S_0 T_1}$	$\langle T_1 \mu S_0 \rangle$	$\omega_{S_0 S_1}$	$\langle S_1 \mu S_0 \rangle$
Zn (1c)	...	0.0	0.204 181 42	1.932 62
Zn (4c)	0.147 219 61	0.026481	0.210 070 05	1.876 24
Cd (1c)	...	0.0	0.177 999 07	2.098 30
Cd (4c)	0.137 009 67	0.093103	0.193 718 48	1.953 72
Hg (4c)	...	0.0	0.175 486 90	2.066 55
Hg (4c)	0.173 050 60	0.29059	0.233 198 22	1.554 57

Furthermore, by applying the rotating-wave approximation, we obtain a simplified three-level Hamiltonian

$$\begin{aligned} \hat{H}^{3L,RWA} = & \hbar \omega_{ge_1} |e_1\rangle \langle e_1| \otimes \mathbb{1}_\gamma + \hbar \omega_{ge_2} |e_2\rangle \langle e_2| \otimes \mathbb{1}_\gamma \\ & + \hbar \omega_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha \otimes \mathbb{1}_A \\ & + G(\mu_{e_1 g} \cdot \epsilon_\alpha \hat{a}_\alpha |e_1\rangle \langle g| - \mu_{ge_1} \cdot \epsilon_\alpha \hat{a}_\alpha^\dagger |g\rangle \langle e_1|) \\ & + G(\mu_{e_2 g} \cdot \epsilon_\alpha \hat{a}_\alpha |e_2\rangle \langle g| - \mu_{ge_2} \cdot \epsilon_\alpha \hat{a}_\alpha^\dagger |g\rangle \langle e_2|). \end{aligned} \quad (G18)$$

As seen from the matrix structure, the excitations involving a different number of photons are now decoupled,

$$\begin{array}{cccccccc} & |g, 0\rangle & |e_1, 0\rangle & |e_2, 0\rangle & |g, 1\rangle & |e_1, 1\rangle & |e_2, 1\rangle & |g, 2\rangle \\ \langle g, 0| & H_0^{3L,RWA} & 0 & 0 & 0 & 0 & 0 & 0 \\ \langle e_1, 0| & 0 & H_{1,(1,1)}^{3L,RWA} & H_{1,(1,2)}^{3L,RWA} & H_{1,(1,3)}^{3L,RWA} & 0 & 0 & 0 \\ \langle e_2, 0| & 0 & H_{1,(2,1)}^{3L,RWA} & H_{1,(2,2)}^{3L,RWA} & H_{1,(2,3)}^{3L,RWA} & 0 & 0 & 0 \\ \langle g, 1| & 0 & H_{1,(3,1)}^{3L,RWA} & H_{1,(3,2)}^{3L,RWA} & H_{1,(3,3)}^{3L,RWA} & 0 & 0 & 0 \\ \langle e_1, 1| & 0 & 0 & 0 & 0 & H_{2,(1,1)}^{3L,RWA} & H_{2,(1,2)}^{3L,RWA} & H_{2,(1,3)}^{3L,RWA} \\ \langle e_2, 1| & 0 & 0 & 0 & 0 & H_{2,(2,1)}^{3L,RWA} & H_{2,(2,2)}^{3L,RWA} & H_{2,(2,3)}^{3L,RWA} \\ \langle g, 2| & 0 & 0 & 0 & 0 & H_{2,(3,1)}^{3L,RWA} & H_{2,(3,2)}^{3L,RWA} & H_{2,(3,3)}^{3L,RWA} \end{array}, \quad (G19)$$

allowing us to work only with a 3×3 matrix,

$$\mathbf{H}_n^{3L,RWA} = \begin{pmatrix} \hbar \omega_\alpha (n-1) + \hbar \omega_{ge_1} & 0 & \sqrt{n} G \mu_{e_1 g} \cdot \epsilon_\alpha \\ 0 & \hbar \omega_\alpha (n-1) + \hbar \omega_{ge_2} & \sqrt{n} G \mu_{e_2 g} \cdot \epsilon_\alpha \\ -\sqrt{n} G \mu_{ge_1} \cdot \epsilon_\alpha & -\sqrt{n} G \mu_{ge_2} \cdot \epsilon_\alpha & n \hbar \omega_\alpha \end{pmatrix}, \quad (G20)$$

TABLE V. Singlet-triplet excitation energies E^{ST} of free atoms and resonant frequencies E_{res}^{ST} of dressed atoms described by the three-level model in cavities with different coupling strengths g_α (in a.u.) defined as cavity mode frequency at which maximum light-matter mixing occurs. Compare with Table I.

Atom	E^{ST} (eV)	E_{res}^{ST} (eV)			
		$g_\alpha = 0.01$	$g_\alpha = 0.02$	$g_\alpha = 0.05$	$g_\alpha = 0.08$
Zn	4.0060	4.0205	4.0681	4.4146	5.2137
Cd	3.7282	3.7443	3.7960	4.1933	5.1402
Hg	4.7089	4.7212	4.7593	5.0395	5.6572

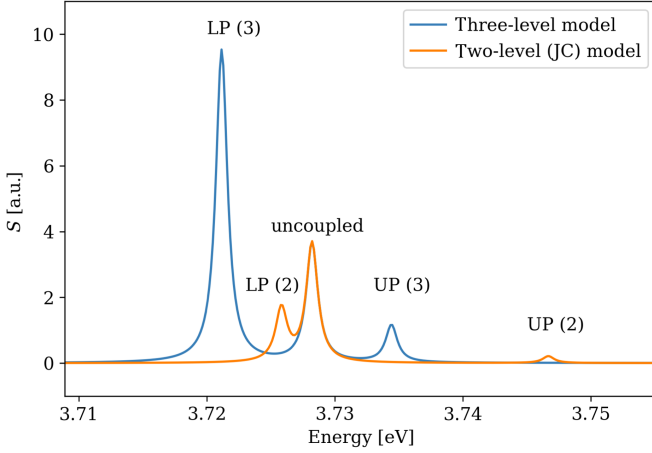


FIG. 12. Singlet-triplet region of the spectrum of a Cd atom strongly coupled to a cavity (coupling strength $g_\alpha = 0.08$ a.u., cavity mode frequency $\omega_\alpha = 0.1376$ a.u.) modeled as a two-level Jaynes-Cummings (JC) model and a three-level model parametrized by relativistic (4c) TDDFT results. Signals LP and UP correspond to lower and upper polaritons, respectively, with (2) and (3) denoting the two- and three-level models. Spectral lines corresponding to uncoupled states were added according to Eq. (G16). No magnification was applied.

where n is the number of photons (in further calculations, we assume $n = 1$).

The three-level model offers significant improvement over the two-level model by including the coupling to off-resonant states and thus explains the strangely intense polaritonic peaks in the singlet-triplet region. See, for example, the case of the Cd atom in Fig. 12 [compare with Fig. 3(d) in the main article], where due to the lack of the higher-energy excited states, the two-level model importantly underestimates the intensities of the polaritonic peaks (some intensity is transferred from the singlet-singlet excitation) as well as, in general, does not qualitatively describe the Rabi splitting and relative intensities of the polaritonic peaks. The difference between the two- and the three-level models thus confirms our explanation for the observed behavior in the singlet-triplet spectral region, where the high intensity of the polaritonic peaks is due to a combination of resonant coupling to the weak S - T (S_0 - T_1) excitation and the nonresonant coupling to the strong S - S (S_0 - S_1) excitation. However, as the following results from the three-level model (Figs. 14, 15, and 17) show, while the three-level model reasonably reproduces the QEDFT results for weak coupling, it deviates from QEDFT for higher coupling strengths. The results were calculated using the LIBQED program that calculates the eigenvalues and eigenvectors of H_{3L} with the size of the photon space set to $n_p = 20$. We then use these solutions to evaluate the dipole strength function according to Eq. (64) from the main text. The contribution of the degenerate states whose transition dipole moment is perpendicular to the states coupled with the cavity modes can be added into the spectrum as in the case of the two-level Jaynes-Cummings model [see Eq. (G16)].

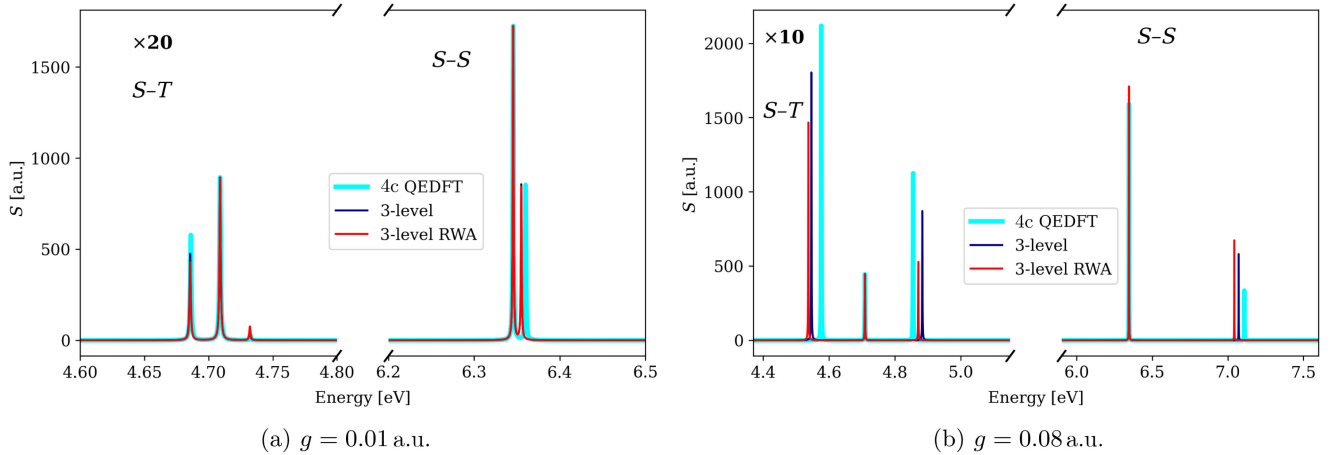


FIG. 13. Comparison of absorption spectra for the Hg atom obtained from three different models: a three-level model beyond the rotating-wave approximation (3-level), a three-level model within the rotating-wave approximation (3-level RWA), and relativistic QEDFT calculations (4c QEDFT). The models describe atom strongly coupled to a cavity with coupling strength $g_\alpha = 0.01$ a.u. (panel (a)) and $g_\alpha = 0.08$ a.u. (panel (b)). The three-level models are parametrized using 4c TDDFT results for the Hg atom.

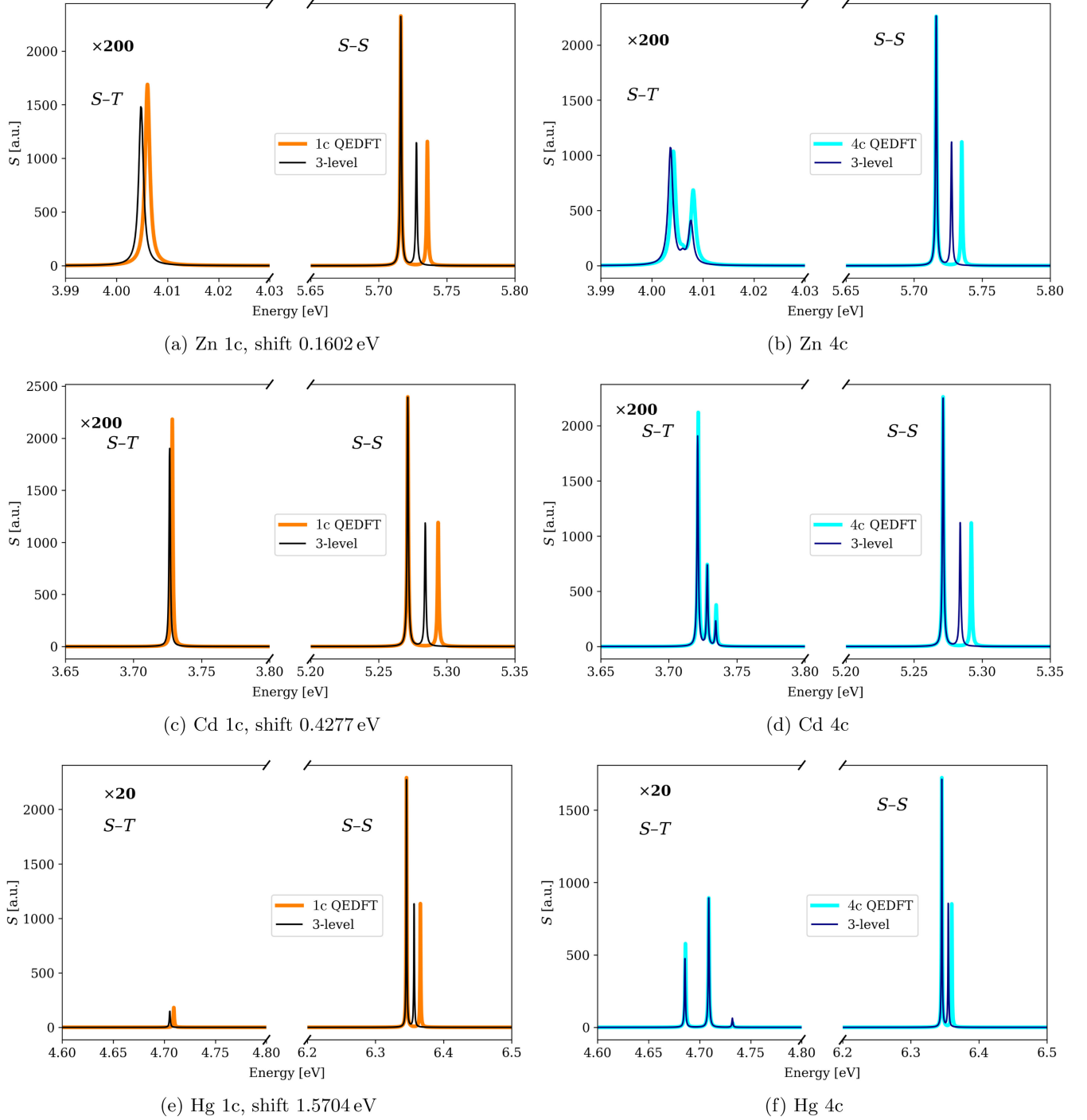


FIG. 14. Absorption spectra of group 12 atoms (Zn, Cd, and Hg) in cavities strongly coupled (coupling strength $g_a = 0.01$ a.u.) to a cavity tuned to the effective dressed resonance of the singlet-triplet (S - T) transition. The region around the weak S - T transition is magnified by a factor indicated in each panel to improve visibility. A comparison is shown between QEDFT calculations and a three-level model, in both nonrelativistic (1c) and relativistic (4c) formalisms. Panels (a), (c), and (e) display 1c results, while panels (b), (d), and (f) show the corresponding 4c results. The nonrelativistic (1c) spectra are shifted to align the singlet-singlet (S - S) transition with the relativistic (4c) spectra. For the three-level model, spectral lines corresponding to uncoupled states were added according to Eq. (G16).

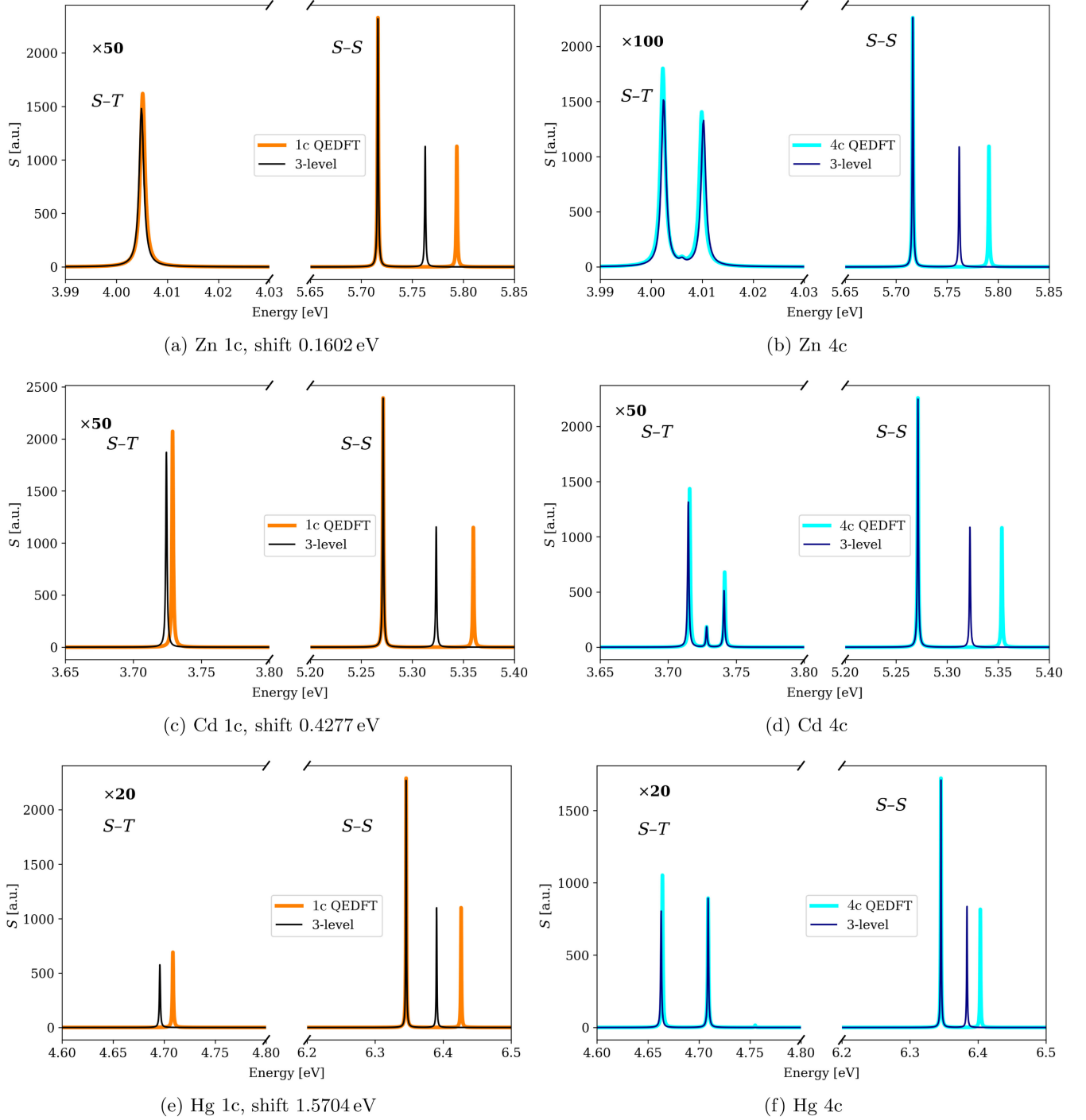


FIG. 15. Absorption spectra of group 12 atoms (Zn, Cd, and Hg) in cavities strongly coupled (coupling strength $g_a = 0.02$ a.u.) to a cavity tuned to the effective dressed resonance of the singlet-triplet (S - T) transition. The region around the weak S - T transition is magnified by a factor indicated in each panel to improve visibility. A comparison is shown between QEDFT calculations and a three-level model, in both nonrelativistic (1c) and relativistic (4c) formalisms. Panels (a), (c), and (e) display 1c results, while panels (b), (d), and (f) show the corresponding 4c results. The nonrelativistic (1c) spectra are shifted to align the singlet-singlet (S - S) transition with the relativistic (4c) spectra. For the three-level model, spectral lines corresponding to uncoupled states were added according to Eq. (G16).

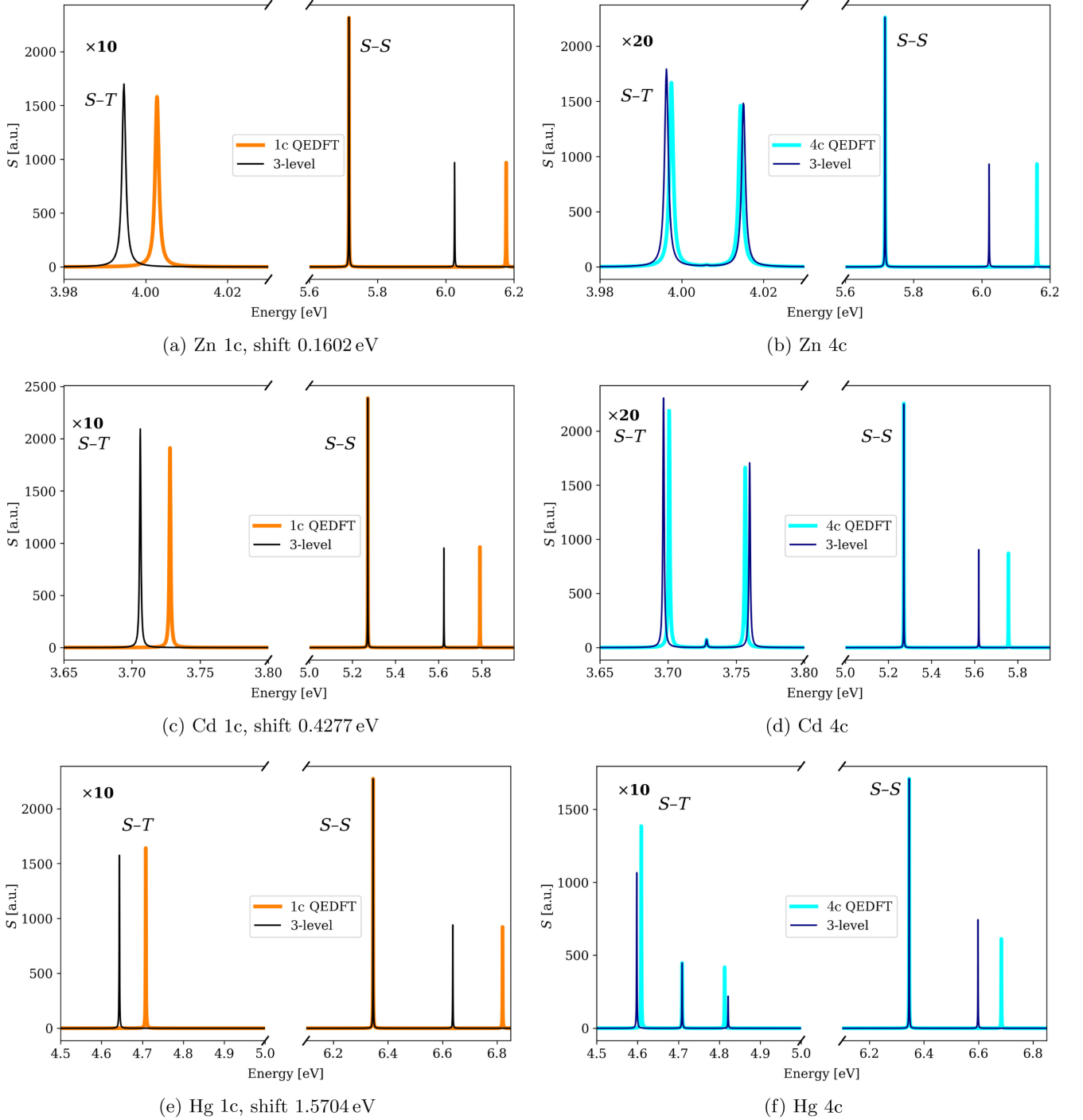


FIG. 16. Absorption spectra of group 12 atoms (Zn, Cd, and Hg) in cavities strongly coupled (coupling strength $g_a = 0.05$ a.u.) to a cavity tuned to the effective dressed resonance of the singlet-triplet (S - T) transition. The region around the weak S - T transition is magnified by a factor indicated in each panel to improve visibility. A comparison is shown between QEDFT calculations and a three-level model, in both nonrelativistic (1c) and relativistic (4c) formalisms. Panels (a), (c), and (e) display 1c results, while panels (b), (d), and (f) show the corresponding 4c results. The nonrelativistic (1c) spectra are shifted to align the singlet-singlet (S - S) transition with the relativistic (4c) spectra. For the three-level model, spectral lines corresponding to uncoupled states were added according to Eq. (G16).

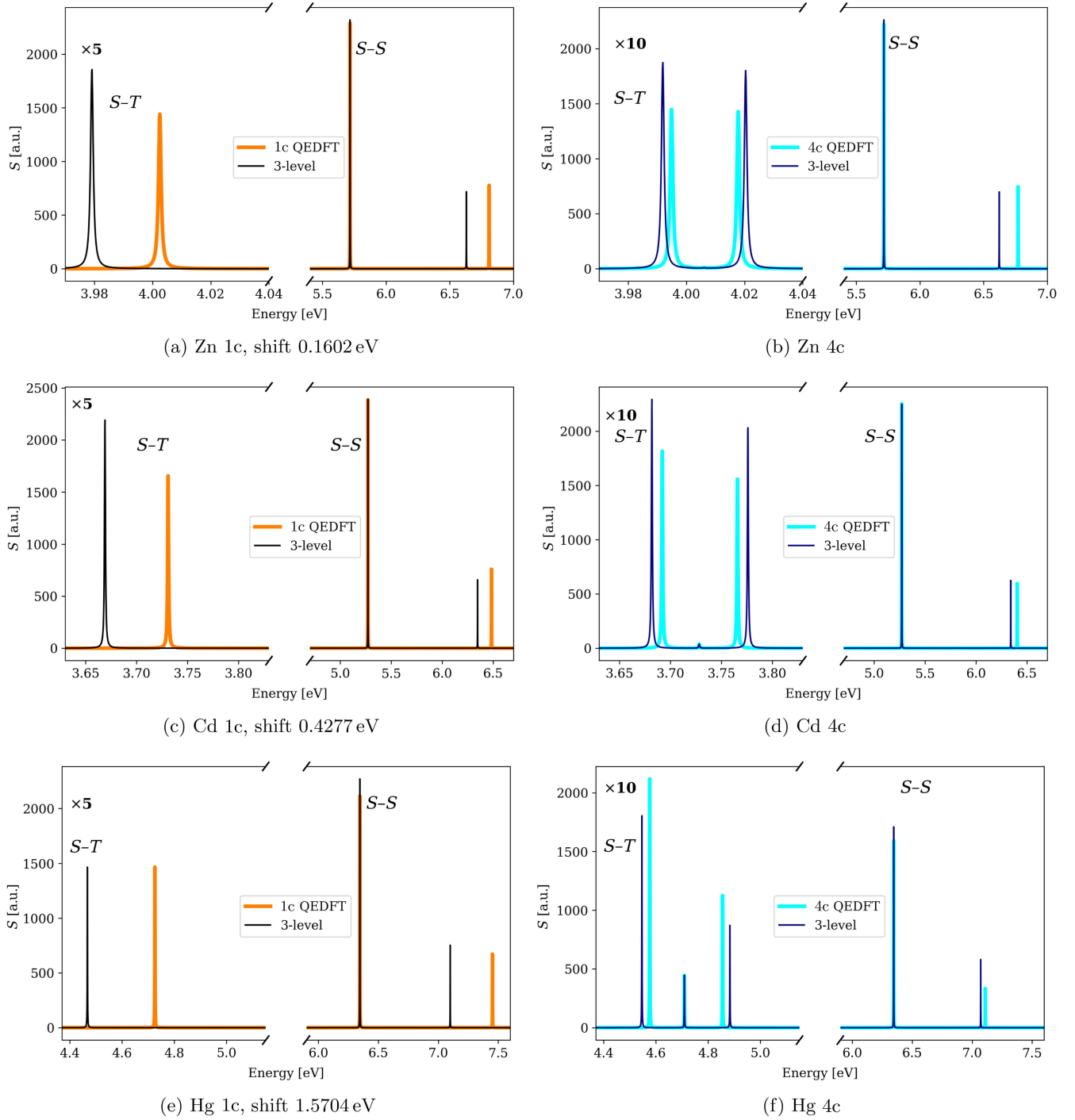


FIG. 17. Absorption spectra of group 12 atoms (Zn, Cd, and Hg) in cavities strongly coupled (coupling strength $g_a = 0.08$ a.u.) to a cavity tuned to the effective dressed resonance of the singlet-triplet (S - T) transition. The region around the weak S - T transition is magnified by a factor indicated in each panel to improve visibility. A comparison is shown between QEDFT calculations and a three-level model, in both nonrelativistic (1c) and relativistic (4c) formalisms. Panels (a), (c), and (e) display 1c results, while panels (b), (d), and (f) show the corresponding 4c results. The nonrelativistic (1c) spectra are shifted to align the singlet-singlet (S - S) transition with the relativistic (4c) spectra. For the three-level model, spectral lines corresponding to uncoupled states were added according to Eq. (G16).

APPENDIX H: ADDITIONAL TRANSITION DENSITY VISUALIZATION

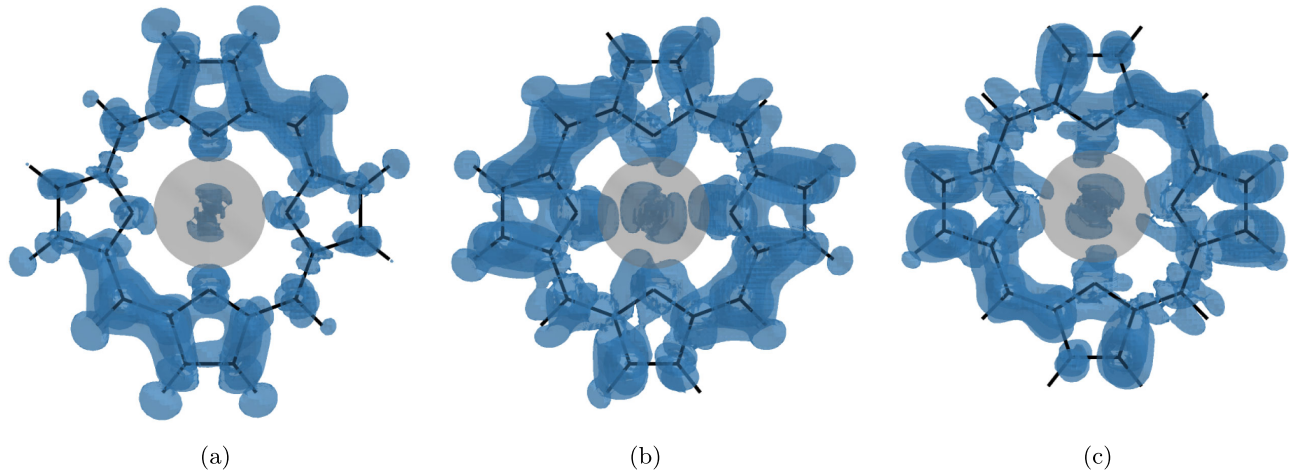


FIG. 18. Transition densities (absolute value) corresponding to different excitations in the spectra of cavity-embedded Hg porphyrin with coupling constant $g_a = 0.02$ a.u. and cavity mode polarization in the direction of the transition moment of the first of the two degenerate transitions comprising the B line. (a) Lower polariton. (b) Uncoupled B transition. (c) Upper polariton. The densities are plotted as isosurfaces at value 6.0×10^{-4} a.u.. Shown is also the porphyrin skeletal structure and the central mercury atom as a sphere with of the size given by mercury’s van der Waals radius.

APPENDIX I: COMPUTATIONAL CONSIDERATIONS

Let us also address some practical aspects of performing a QEDFT calculation, including the computational cost. Relativistic quantum chemical calculations of large molecules such as heavy metal complexes, particularly in the four-component regime, have long been considered computationally expensive. However, recent developments of efficient algorithms and acceleration techniques [170,200–202] are challenging this dogma and allowing fully relativistic all-electron calculations of molecular properties of systems containing up to 100 atoms.

From a practical point of view, a linear-response QEDFT calculation proceeds analogously to a linear-response TDDFT calculation [171,175] with similar scaling behavior. The relevant parameters affecting computational performance are (i) the convergence threshold for the residuum, (ii) the desired number of eigenvalues, and (iii) the system size (the number of virtual and occupied orbitals). The latter two can be connected, as systems with more electrons typically have denser absorption spectra and therefore require more eigenvalues to cover the same frequency range. For example, in the systems included in the computational study in this work, the transitions of interest lie within the first 15 excited states of single atoms, while 100 eigenvalues were required for the porphyrin complex. Unique to the linear-response QEDFT equation are the self-energy term and additional rows and columns of the coupling matrix corresponding to the photon-photon, photon-electron, and electron-photon elements that are not

present in linear-response TDDFT. However, while the self-energy is a two-electron term, it does not require recalculating overlap integrals and is thus significantly cheaper than Coulomb and exchange terms. Moreover, the additional rows and columns represent only an insignificant matrix size increase as long as only a few photon modes are considered. Therefore, linear-response QEDFT calculations are computationally comparable to linear-response TDDFT calculations. Note that the listed factors affect the total computational scaling and cost in different ways: (i) tightening the convergence threshold increases the total number of iterations of the Davidson-Olsen solver; (ii) the desired number of eigenvalues is connected to the number of trial vectors generated per single iteration; (iii) the system size defines the size of the coupling matrix (i.e., matrix representation of the response kernel) and the associated evaluation of Coulomb, exchange, and exchange-correlation terms that are due to memory constraints recalculated for each trial vector (or a small batch of trial vectors) when projecting the linear-response QEDFT equation onto the subspace of trial vectors.

The RESPECT program is designed to run on CPU-based commodity clusters utilizing shared memory parallelization (OPENMP) and message passing (MPI) as well as a hybrid parallel mode combining these techniques [170]. Systems such as heavy atoms, small molecules, and large complexes with up to 200 atoms can be treated on one to few compute nodes equipped with a few tens of CPUs. For example, for the calculations reported in this work, a single Hg atom (243 scalar Cartesian GTOs corresponding to 972 4c basis

spinors), the calculation of 50 excitation energies with convergence threshold 10^{-3} performed on a machine equipped with an Intel Xeon-Gold 6138 2.0 GHz processor with 40 CPU cores took about 50 min with the final subspace containing 193 trial vectors (the total dimension of the subspace matrix being 386×386 due to the paired vectors for whom the calculation of electron repulsion integrals and XC kernel—the most time-consuming part is not performed, as they are related by symmetry to their paired partners), while a calculation of 25 eigenvectors took about 30 min. Increasing the size of the system by adding additional atoms separated by 10 Å (so that their only interaction is mediated by the cavity) leads to an increase in computer time to about 4 h for Hg_2 and 14 h for Hg_3 , respectively. The Hg porphyrin complex consists of 37 atoms and was described by 975 scalar Cartesian GTOs (corresponding to 3900 4c basis spinors) with significantly more overlap and delocalization due to the proximity of the atoms inside the complex. The calculations were performed on four computer nodes each equipped with AMD Epyc 7742 2.25 GHz processors with 128 CPU cores in a hybrid parallel regime with 1 MPI process and 128 OPENMP threads per node. First, a TDDFT calculation was performed to obtain 100 excitation energies (convergence threshold 10^{-3}) that took about 36 h and required 490

trial vectors. We stress that such a calculation (linear-response TDDFT) would be needed to parametrize a few-level QED model for this system as well. Specifically, if we also want to include the dipole self-energy and the transitions between excited states, then we would need further simulations. However, such simulations are not available in standard TDDFT implementations. This makes QEDFT calculations faster than setting up and then calculating the few-states system. Subsequently, QEDFT calculations for the complex inside a cavity whose mode frequency was tuned to one of the excitation energies were performed using the TDDFT results as an initial guess for the eigenvalues and electronic parts of the eigenvectors. These calculations took from 5 (coupling strength $g_\alpha = 0.005$ a.u.) to 6 h ($g_\alpha = 0.02$ a.u.) requiring 111 to 125 trial vectors. While the computational cost of these calculations is standard for relativistic four-component DFT, it can be considered high if one is interested in 2D spectra of larger molecules or in collective effects. This motivates the development of relativistic QEDFT based on efficient yet accurate approximate relativistic two-component methods, a direction we are currently pursuing in our laboratory. The four-component methodology introduced in this work serves as an important benchmark for this development.

APPENDIX J: GEOMETRY OF MERCURY PORPHYRIN

TABLE VI. Molecular geometry of Hg@porphyrin (in Å).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
N	−0.011 132	0.000 000	2.169 275	H	−0.445 739	−5.174 990	1.344 482
N	−0.011 132	2.169 275	0.000 000	N	−0.011 132	0.000 000	−2.169 275
C	−0.164 467	2.451 269	2.451 269	C	−0.164 467	2.451 269	−2.451 269
C	−0.313 340	0.686 057	4.317 622	C	−0.313 340	0.686 057	−4.317 622
C	−0.135 961	1.122 057	2.938 936	C	−0.135 961	1.122 057	−2.938 936
C	−0.135 961	2.938 936	1.122 057	C	−0.135 961	2.938 936	−1.122 057
C	−0.313 340	4.317 622	0.686 057	C	−0.313 340	4.317 622	−0.686 057
H	−0.280 223	3.219 998	3.219 998	H	−0.280 223	3.219 998	−3.219 998
H	−0.445 739	1.344 482	5.174 990	H	−0.445 739	1.344 482	−5.174 990
H	−0.445 739	5.174 990	1.344 482	H	−0.445 739	5.174 990	−1.344 482
Hg	0.381 402	0.000 000	0.000 000	C	−0.164 467	−2.451 269	−2.451 269
N	−0.011 132	−2.169 275	0.000 000	C	−0.313 340	−0.686 057	−4.317 622
C	−0.164 467	−2.451 269	2.451 269	C	−0.135 961	−1.122 057	−2.938 936
C	−0.313 340	−0.686 057	4.317 622	C	−0.135 961	−2.938 936	−1.122 057
C	−0.135 961	−1.122 057	2.938 936	C	−0.313 340	−4.317 622	−0.686 057
C	−0.135 961	−2.938 936	1.122 057	H	−0.280 223	−3.219 998	−3.219 998
C	−0.313 340	−4.317 622	0.686 057	H	−0.445 739	−1.344 482	−5.174 990
H	−0.280 223	−3.219 998	3.219 998	H	−0.445 739	−5.174 990	−1.344 482
H	−0.445 739	−1.344 482	5.174 990				

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