Resolution of Gauge Ambiguities in Molecular Cavity Quantum Electrodynamics

Michael A. D. Taylor,[1,2] Arkajit Mandal,[1] Wanghuai Zhou,[1,3] and Pengfei Huo[1,*]
[1]Department of Chemistry, University of Rochester, Rochester, New York 14627, USA
[2]The Institute of Optics, Hajim School of Engineering, University of Rochester, Rochester, New York 14627, USA
[3]Advanced Functional Material and Photoelectric Technology Research Institution, School of Science, Hubei University of Automotive Technology, Shiyan, Hubei 442002, People's Republic of China

(Received 19 June 2020; accepted 24 August 2020; published 17 September 2020)

This work provides the fundamental theoretical framework for molecular cavity quantum electrodynamics by resolving the gauge ambiguities between the Coulomb gauge and the dipole gauge Hamiltonians under the electronic state truncation. We conjecture that such ambiguity arises because not all operators are consistently constrained in the same truncated electronic subspace for both gauges. We resolve this ambiguity by constructing a unitary transformation operator that properly constrains all light-matter interaction terms in the same subspace. We further derive an equivalent and yet convenient expression for the Coulomb gauge Hamiltonian under the truncated subspace. We finally provide the analytical and numerical results of a model molecular system coupled to the cavity to demonstrate the validity of our theory.

DOI: 10.1103/PhysRevLett.125.123602

Coupling molecules to the quantized radiation field inside an optical cavity creates a set of new photon-matter hybrid excitations, so-called polaritons [1–4]. The rich dynamic interplay among these electronic, photonic, and nuclear degrees of freedom (d.o.f.) has enabled a new paradigm for achieving unique chemical reactivities [5–9]. The nonrelativistic quantum electrodynamics (QED) Hamiltonian that describes such quantum light-matter interactions should obey the gauge principle, i.e., giving rise to the same physical results (physical observables) upon a gauge transformation [10,11]. While the QED Hamiltonian under both the Coulomb gauge and the dipole gauge (length gauge) indeed obeys this principle, these Hamiltonians under a finite electronic state truncation (the few-level approximation) are known to give different results for physical observables [12–20], which is commonly referred to as the gauge ambiguity [14,17–19]. While using a finite level of projection on the dipole gauge Hamiltonian often provides accurate results of the polariton eigenspectrum (when the few-level truncation is a good approximation [18]) compared to the exact simulation, applying the same level of electronic state truncation $\hat{H}'_C$ often leads to different results and, sometimes, a significant error in the ultrastrong light-matter coupling regime [18–20]. In this Letter, we demonstrate that it is possible to resolve it and provide identical polariton eigenspectra from either the Coulomb or the dipole gauge Hamiltonian upon the same level of the electronic state truncation.

We begin by defining the matter Hamiltonian and the corresponding total dipole operator as follows:

$$\hat{H}_M = \hat{\mathbf{T}} + \hat{V}(\hat{\mathbf{x}}) = \sum_j \frac{1}{2m_j}\hat{\mathbf{p}}_j^2 + \hat{V}(\hat{\mathbf{x}}); \quad \hat{\boldsymbol{\mu}} = \sum_j z_j \hat{\mathbf{x}}_j, \tag{1}$$

where j is the index of the jth charged particle (including all electrons and nuclei), with the corresponding mass m_j and charge z_j. In addition, $\hat{\mathbf{x}} \equiv \{\hat{\mathbf{x}}_j\} = \{\hat{\mathbf{R}}, \hat{\mathbf{r}}\}$ with $\hat{\mathbf{R}}$ and $\hat{\mathbf{r}}$ representing the nuclear and electronic coordinates, respectively, $\hat{\mathbf{p}} \equiv \{\hat{\mathbf{p}}_{\mathbf{R}}, \hat{\mathbf{p}}_{\mathbf{r}}\} \equiv \{\hat{\mathbf{p}}_j\}$ is the *mechanical* momentum operator as well as the canonical momentum operator, such that $\hat{\mathbf{p}}_j = -i\hbar\boldsymbol{\nabla}_j$. Further, $\hat{\mathbf{T}} = \hat{\mathbf{T}}_{\mathbf{R}} + \hat{\mathbf{T}}_{\mathbf{r}}$ is the kinetic energy operator, where $\hat{\mathbf{T}}_{\mathbf{R}}$ and $\hat{\mathbf{T}}_{\mathbf{r}}$ represent the kinetic energy operator for nuclei and for electrons, respectively, and $\hat{V}(\hat{\mathbf{x}})$ is the potential operator that describes the Coulombic interactions among electrons and nuclei. The cavity photon field Hamiltonian under the single mode assumption is expressed as $\hat{H}_{\mathrm{ph}} = \hbar\omega_c(\hat{a}^\dagger\hat{a} + \frac{1}{2}) = \frac{1}{2}(\hat{p}_c^2 + \omega_c^2\hat{q}_c^2)$, where ω_c is the frequency of the mode in the cavity, $\hat{a}^\dagger$ and $\hat{a}$ are the photonic creation and annihilation operators, and $\hat{q}_c = \sqrt{\hbar/2\omega_c}(\hat{a}^\dagger + \hat{a})$ and $\hat{p}_c = i\sqrt{\hbar\omega_c/2}(\hat{a}^\dagger - \hat{a})$ are the photonic coordinate and momentum operators, respectively. Choosing the Coulomb gauge, $\boldsymbol{\nabla}\cdot\hat{\mathbf{A}} = 0$, the vector potential becomes purely transverse $\hat{\mathbf{A}} = \hat{\mathbf{A}}_\perp$. Under the long-wavelength approximation, $\hat{\mathbf{A}} = \mathbf{A}_0(\hat{a} + \hat{a}^\dagger) = \mathbf{A}_0\sqrt{2\omega_c/\hbar}\hat{q}_c$, where $\mathbf{A}_0 = \sqrt{\hbar/2\omega_c\varepsilon_0\mathcal{V}}\hat{\mathbf{e}}$, with $\mathcal{V}$ as the quantization volume inside the cavity, ε_0 as the permittivity, and $\hat{\mathbf{e}}$ is the unit vector of the field polarization.

The minimal coupling QED Hamiltonian in the *Coulomb* gauge (the "$p\cdot A$" form) is expressed as

$$\hat{H}_C = \sum_j \frac{1}{2m_j}(\hat{\mathbf{p}}_j - z_j\hat{\mathbf{A}})^2 + \hat{V}(\hat{\mathbf{x}}) + \hat{H}_{\rm ph}, \quad (2)$$

where $\hat{\mathbf{p}}_j = -i\hbar\boldsymbol{\nabla}_j$ is the *canonical* momentum operator. Upon a gauge transformation $\hat{U}_\chi = \exp[(i/\hbar)\sum_j z_j\boldsymbol{\chi}(\hat{\mathbf{x}}_j)]$, $\hat{H}_\chi = \hat{U}_\chi\hat{H}_C\hat{U}_\chi^\dagger$ remains gauge invariant, because $\hat{H}_\chi = \sum_j(1/2m_j)[\hat{\mathbf{p}}_j - z_j\hat{\mathbf{A}}_\chi(\hat{\mathbf{x}}_j)]^2 + \hat{V}(\hat{\mathbf{x}}) + \hat{H}^\chi_{\rm ph}$, where $\hat{\mathbf{A}}_\chi(\mathbf{x}_j) = \hat{\mathbf{A}} + \boldsymbol{\nabla}_j\chi(\hat{\mathbf{x}}_j)$ is gauge transformed vector potential that provides the same physical field, because $\boldsymbol{\nabla}_j \times \boldsymbol{\nabla}_j\chi(\hat{\mathbf{x}}_j) = 0$. To prove the above equation, we have used $e^{\hat{Y}}\hat{O}(\hat{X})e^{-\hat{Y}} = \hat{O}(e^{\hat{Y}}\hat{X}e^{-\hat{Y}})$ for a unitary operator, as well as $\hat{U}_\chi\hat{\mathbf{p}}_j\hat{U}_\chi^\dagger = \hat{\mathbf{p}}_j - z_j\boldsymbol{\nabla}_j\chi(\hat{\mathbf{x}}_j)$. Further, $\hat{H}^\chi_{\rm ph} = \hat{U}_\chi\hat{H}_{\rm ph}\hat{U}_\chi^\dagger$, $\hat{U}_\chi\hat{V}(\hat{\mathbf{x}})\hat{U}_\chi^\dagger = \hat{V}(\hat{\mathbf{x}})$ because $\hat{V}$ is a local potential operator for the matter, that is, only a function of $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ independent.

We further introduce the Power-Zienau-Woolley (PZW) gauge transformation operator [10,21] as

$$\hat{U} = \exp\left[-\frac{i}{\hbar}\hat{\boldsymbol{\mu}}\cdot\hat{\mathbf{A}}\right] = \exp\left[-\frac{i}{\hbar}\hat{\boldsymbol{\mu}}\cdot\mathbf{A}_0(\hat{a}+\hat{a}^\dagger)\right]. \quad (3)$$

The PZW transformation operator can also be expressed as $\hat{U}=\exp[-(i/\hbar)\sqrt{2\omega_c/\hbar}\hat{\boldsymbol{\mu}}\mathbf{A}_0\hat{q}_c]=\exp[-(i/\hbar)(\sum_j z_j\hat{\mathbf{A}}\mathbf{x}_j)]$. Recall that a momentum boost operator $\hat{U}_p = e^{-(i/\hbar)p_0\hat{q}}$ displaces $\hat{p}$ by the amount of p_0, such that $\hat{U}_p\hat{O}(\hat{p})\hat{U}_p^\dagger = \hat{O}(\hat{p}+p_0)$. Hence, $\hat{U}$ is a boost operator for both the photonic momentum $\hat{p}_c$ by the amount of $\sqrt{2\omega_c/\hbar}\hat{\boldsymbol{\mu}}\mathbf{A}_0$, as well as for the matter momentum $\hat{\mathbf{p}}_j$ by the amount of $z_j\hat{\mathbf{A}}$. The PZW gauge operator [Eq. (3)] is a special case of $\hat{U}_\chi$, such that $\chi = -\hat{\mathbf{x}}_j\cdot\hat{\mathbf{A}}$. Using $\hat{U}^\dagger$ to boost the matter momentum, one can show that

$$\hat{H}_C = \hat{U}^\dagger\hat{H}_M\hat{U} + \hat{H}_{\rm ph}, \quad (4)$$

hence $\hat{H}_C$ can be obtained [19] by a momentum boost with the amount of $-z_j\hat{\mathbf{A}}$ for $\hat{\mathbf{p}}_j$, then adding $\hat{H}_{\rm ph}$.

The QED Hamiltonian under the *dipole* gauge (the "$d\cdot E$" form [21,22]) can be obtained by performing the PZW transformation on $\hat{H}_C$ as follows:

$$\begin{aligned}\hat{H}_D &= \hat{U}\hat{H}_C\hat{U}^\dagger = \hat{U}\hat{U}^\dagger\hat{H}_M\hat{U}\hat{U}^\dagger + \hat{U}\hat{H}_{\rm ph}\hat{U}^\dagger \\ &= \hat{H}_M + \hbar\omega_c\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right) + i\omega_c\hat{\boldsymbol{\mu}}\mathbf{A}_0(\hat{a}^\dagger-\hat{a}) + \frac{\omega_c}{\hbar}(\hat{\boldsymbol{\mu}}\mathbf{A}_0)^2,\end{aligned} \quad (5)$$

where we have used Eq. (4) to express $\hat{H}_C$, and the last three terms of the above equation are the results of $\hat{U}\hat{H}_{\rm ph}\hat{U}^\dagger$. Using $\hat{q}_c$ and $\hat{p}_c$, one can instead show that $\hat{H}_D = \hat{H}_M + \frac{1}{2}\omega_c^2\hat{q}_c^2 + \frac{1}{2}(\hat{p}_c + \sqrt{2\omega_c/\hbar}\hat{\boldsymbol{\mu}}\mathbf{A}_0)^2$, because the PZW operator boosts the photonic momentum $\hat{p}_c$ by $\sqrt{2\omega_c/\hbar}\hat{\boldsymbol{\mu}}\mathbf{A}_0$.

When describing light-matter interactions, it is often necessary to truncate the electronic states for the matter (atoms or molecules), due to the difficulties of obtaining accurate high-lying electronic excited states. The gauge invariance is explicitly enforced between $\hat{H}_C$ [Eq. (2)] and $\hat{H}_D$ [Eq. (5)] through the unitary PZW gauge transformation [Eq. (3)] in the full Hilbert space. However, the gauge invariance could explicitly break down when a truncation of electronic states is applied to both Hamiltonians [18,19,23]. Consider a finite subset of states $\{|\alpha\rangle\}$, where the projection operator $\hat{\mathcal{P}} = \sum_\alpha|\alpha\rangle\langle\alpha|$ defines the truncation of the full electronic Hilbert space $\hat{\mathbb{1}}_r = \hat{\mathcal{P}} + \hat{\mathcal{Q}}$ to the corresponding subspace $\hat{\mathcal{P}}$. This truncation reduces the size of the Hilbert space from originally $\hat{\mathbb{1}}_r \otimes \hat{\mathbb{1}}_R \otimes \hat{\mathbb{1}}_{\rm ph}$ to now $\hat{\mathcal{P}} \otimes \hat{\mathbb{1}}_R \otimes \hat{\mathbb{1}}_{\rm ph}$, where $\hat{\mathbb{1}}_R$ and $\hat{\mathbb{1}}_{\rm ph}$ represent the identity operators of the nuclear and the photonic d.o.f., respectively.

The truncated matter Hamiltonian is $\hat{\mathcal{H}}_M = \hat{\mathcal{P}}\hat{H}_M\hat{\mathcal{P}} = \hat{\mathcal{P}}\hat{\mathbf{T}}\hat{\mathcal{P}} + \hat{\mathcal{P}}\hat{V}(\hat{\mathbf{x}})\hat{\mathcal{P}}$. Throughout this Letter, we use calligraphic symbols (such as $\hat{\mathcal{H}}_M$) to indicate operators in the truncated Hilbert space. Truncating the momentum operator and dipole operator as $\hat{\mathcal{P}}\hat{\mathbf{p}}_j\hat{\mathcal{P}}$ and $\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}}$, the QED Hamiltonians under the truncated subspace are defined [18] as

$$\hat{\mathcal{H}}'_C = \hat{\mathcal{H}}_M + \hat{H}_{\rm ph} + \sum_j\left(-\frac{z_j}{m_j}\hat{\mathcal{P}}\hat{\mathbf{p}}_j\hat{\mathcal{P}}\,\hat{\mathbf{A}} + \frac{z_j^2\hat{\mathbf{A}}^2}{2m_j}\right), \quad (6)$$

$$\begin{aligned}\hat{\mathcal{H}}_D = \hat{\mathcal{H}}_M + \hat{H}_{\rm ph} + i\omega_c\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}}\,\mathbf{A}_0(\hat{a}^\dagger-\hat{a}) \\ + \frac{\omega_c}{\hbar}(\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}}\,\mathbf{A}_0)^2.\end{aligned} \quad (7)$$

Note that $\hat{\mathcal{H}}'_C = \hat{\mathcal{P}}\hat{H}_C\hat{\mathcal{P}} = \hat{\mathcal{P}}\hat{U}^\dagger\hat{H}_M\hat{U}\,\hat{\mathcal{P}} + \hat{H}_{\rm ph}$. However, $\hat{\mathcal{H}}_D \neq \hat{\mathcal{P}}\hat{H}_D\hat{\mathcal{P}}$. The latter requires the dipole self-energy term to be evaluated as $\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}^2\hat{\mathcal{P}} = \hat{\mathcal{P}}\hat{\boldsymbol{\mu}}(\hat{\mathcal{P}}+\mathcal{Q})\hat{\boldsymbol{\mu}}\,\hat{\mathcal{P}}$, requiring the knowledge of electronic states in $\hat{\mathcal{Q}}$ (those higher excited states that are difficult to obtain). Hence, $\hat{\mathcal{H}}_D$ is often defined as Eq. (7) in the literature [18,19,23], and $\hat{\mathcal{P}}\hat{H}_D\hat{\mathcal{P}}$ seems to lead to less accurate results compared to the numerically exact calculations (see Supplemental Material [24], Sec. VII).

It is well known that $\hat{\mathcal{H}}'_C$ and $\hat{\mathcal{H}}_D$ do not generate the same polariton eigenspectrum [18–20,23] under the ultrastrong coupling regime [36]. Since electronic state truncation is often necessary, one would have to choose a particular gauge to describes light-matter interactions, leading to a well-known ambiguity [14,17,18] as to which Hamiltonian, $\hat{\mathcal{H}}'_C$ or $\hat{\mathcal{H}}_D$, is viable to compute physical quantities when applying $\hat{\mathcal{P}}$. This fundamentally different behavior of $\hat{\mathcal{H}}'_C$ and $\hat{\mathcal{H}}_D$ upon states truncation is also attributed to the fundamental asymmetry of the $\hat{\mathbf{p}}$ and $\hat{\boldsymbol{\mu}} = \sum_j z_j\hat{\mathbf{x}}_j$ operators [18]. This ambiguity is attributed [18,25] to the fact that $\hat{\mathcal{H}}'_C$ usually requires a larger subset of the matter states to converge or generate consistent

results with $\hat{\mathcal{H}}_D$, and apparently, under the *complete* basis limit, they should be gauge invariant. It will be theoretically novel to resolve this gauge ambiguity and provide consistent results from both gauges under the *same* level of electronic state truncation.

We conjecture that this gauge ambiguity emerges because the $\hat{\mathcal{P}}\hat{U}^\dagger$ and $\hat{U}\hat{\mathcal{P}}$ in $\hat{\mathcal{H}}'_C$ [Eq. (6)] do not consistently constrain light-matter interaction operators in the same electronic subspace as those corresponding operators in $\hat{\mathcal{H}}_D$. Indeed, all light-matter interaction operators in $\hat{\mathcal{H}}_D$ are completely constrained in the subspace $\hat{\mathcal{P}}$. Meanwhile, for $\hat{\mathcal{H}}'_C$, the corresponding light-matter interaction operators are not properly contained in $\hat{\mathcal{P}}$, such that some of them are entering into the subspace $\hat{\mathcal{Q}} = \hat{\mathbb{1}}_r - \hat{\mathcal{P}}$, and this is indeed the case for $\hat{U}\hat{\mathcal{P}} = (\hat{\mathcal{P}} + \hat{\mathcal{Q}})\hat{U}\hat{\mathcal{P}}$. It is also apparent by examining the diamagnetic term $z_j^2\hat{\mathbf{A}}^2/2m_j$ in $\hat{\mathcal{H}}'_C$, which is effectively evaluated in the full space [18,19] $\hat{\mathbb{1}}_r$ (based on the Thomas-Reiche-Kuhn sum rule), hence is not properly confined in $\hat{\mathcal{P}}$. This diamagnetic term overestimates what it should be in the subspace [18,19], and by confining it inside $\hat{\mathcal{P}}$, the results can be significantly improved [19]. Similarly, using $\hat{\mathcal{P}}\hat{U}\hat{\mathcal{P}}$ [19,23] does not resolve this gauge ambiguity either (see Supplemental Material [24], Sec. II).

Based on the above conjecture, the gauge ambiguity in the truncated electronic subspace will be resolved by defining the following unitary operator:

$$\hat{\mathcal{U}} = \exp\left[-\frac{i}{\hbar}\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}}\cdot\hat{\mathbf{A}}\right] \equiv \exp\left[-\frac{i}{\hbar}\tilde{\boldsymbol{\mu}}(\hat{\mathbf{x}},\hat{\mathbf{p}})\cdot\hat{\mathbf{A}}\right], \quad (8)$$

such that all terms in $\hat{\mathcal{U}} = \sum_{n=0}^{\infty}(1/n!)(-i/\hbar)^n(\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}})^n\hat{\mathbf{A}}^n$ are properly confined within the subspace $\hat{\mathcal{P}}$, and upon gauge transformation, all light-matter interaction operators are now consistently confined in $\hat{\mathcal{P}}$ for both gauges. Here, $\hat{\mathcal{U}}$ is defined analogously to the PZW gauge operator $\hat{U}$ in the full space [Eq. (3)], and $\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}} \equiv \tilde{\boldsymbol{\mu}}(\hat{\mathbf{x}},\hat{\mathbf{p}})$ in principle is a function of both $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$, due to the finite level projection that ruins the locality of $\hat{\mathbf{x}}$ [19,37]. Further, $\hat{\mathcal{U}}$ is a unitary transformation operator in the $\hat{\mathcal{P}}$ subspace and the identity operator in the subspace of $\hat{\mathbb{1}}_r - \hat{\mathcal{P}}$, such that we still have $\hat{\mathcal{U}}\hat{\mathcal{U}}^\dagger = \hat{\mathbb{1}}_r \otimes \hat{\mathbb{1}}_R \otimes \hat{\mathbb{1}}_{\rm ph} = \hat{U}\hat{U}^\dagger$. Using $\hat{\mathcal{U}}$, one can define the following Coulomb gauge Hamiltonian:

$$\hat{\mathcal{H}}_C = \hat{\mathcal{U}}^\dagger\hat{\mathcal{H}}_M\hat{\mathcal{U}} + \hat{H}_{\rm ph}, \quad (9)$$

analogously to $\hat{H}_C$ in Eq. (4) in the full space. One can then formally show that $\hat{\mathcal{H}}_C$ [Eq. (9)] and $\hat{\mathcal{H}}_D$ [Eq. (7)] are related through $\hat{\mathcal{U}}$ [Eq. (8)] as follows $\hat{\mathcal{U}}\hat{\mathcal{H}}_C\hat{\mathcal{U}}^\dagger = \hat{\mathcal{H}}_M + \hat{\mathcal{U}}\hat{H}_{\rm ph}\hat{\mathcal{U}}^\dagger = \hat{\mathcal{H}}_D$. Note that to establish the last equality, we have used the fact that $\hat{\mathcal{U}}\hat{H}_{\rm ph}\hat{\mathcal{U}}^\dagger = \hat{\mathcal{U}}(\frac{1}{2}\omega_c^2\hat{q}_c^2 + \frac{1}{2}\hat{p}_c^2)\hat{\mathcal{U}}^\dagger = \frac{1}{2}\omega_c^2\hat{q}_c^2 + \frac{1}{2}(\hat{p}_c + \sqrt{2\omega_c/\hbar}\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}}\mathbf{A}_0)^2$. Thus, we have formally demonstrated that the gauge ambiguities between the Coulomb and dipole gauge Hamiltonians can be resolved for an arbitrary matter-cavity hybrid system, under the same level of electronic state truncation.

To derive the detailed expression of $\hat{\mathcal{H}}_C$, we notice that $\hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}} \equiv \tilde{\boldsymbol{\mu}}(\hat{\mathbf{x}},\hat{\mathbf{p}})$ is in principle a nonlinear function of both $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$, as opposed to $\hat{\boldsymbol{\mu}}$ [Eq. (1)] which is a pure linear function of $\hat{\mathbf{x}}$. Thus, $\hat{\mathcal{U}}^\dagger$ no longer just boosts the matter momentum by $z_j\hat{\mathbf{A}}$. Using the Baker-Campbell-Hausdorff (BCH) identity, $\hat{\mathcal{U}}^\dagger\hat{\mathbf{p}}_j\hat{\mathcal{U}} = \hat{\mathbf{p}}_j + (i/\hbar)[\tilde{\boldsymbol{\mu}}\hat{\mathbf{A}}, \hat{\mathbf{p}}_j] + \frac{1}{2}(i/\hbar)^2[\tilde{\boldsymbol{\mu}}\hat{\mathbf{A}}, [\tilde{\boldsymbol{\mu}}\hat{\mathbf{A}}, \hat{\mathbf{p}}_j]] + \cdots$, we have $\hat{\mathcal{U}}^\dagger\hat{\mathbf{p}}_j\hat{\mathcal{U}} = \hat{\mathbf{p}}_j - \boldsymbol{\nabla}_j\tilde{\boldsymbol{\mu}}(\hat{\mathbf{x}},\hat{\mathbf{p}})\hat{\mathbf{A}} + \tilde{\mathbf{P}}_j$, where $\tilde{\mathbf{P}}_j \equiv \frac{1}{2}(i/\hbar)^2[\tilde{\boldsymbol{\mu}}\hat{\mathbf{A}}, [\tilde{\boldsymbol{\mu}}\hat{\mathbf{A}}, \hat{\mathbf{p}}_j]] + \cdots$ is the residual momentum that accounts for terms with more than one commutator in the BCH identity. Hence, under the projection, $\hat{\mathcal{U}}^\dagger$ boosts the matter momentum by the amount of $-\boldsymbol{\nabla}_j\tilde{\boldsymbol{\mu}}\hat{\mathbf{A}} + \tilde{\mathbf{P}}_j$. Similarly, $\hat{\mathcal{P}}\hat{V}(\hat{\mathbf{x}})\hat{\mathcal{P}} = \hat{\mathcal{V}}(\hat{\mathbf{x}},\hat{\mathbf{p}})$ is a nonlocal potential [16,19,37]. Hence, $\hat{\mathcal{U}}^\dagger$ also displaces the matter coordinate as well as boost the matter momentum inside $\hat{\mathcal{V}}(\hat{\mathbf{x}},\hat{\mathbf{p}})$, whereas $\hat{\mathcal{U}}^\dagger\hat{\mathcal{V}}\hat{\mathcal{U}}$ can be formally derived through the BCH identity.

Using the above result of $\hat{\mathcal{U}}^\dagger\hat{\mathbf{p}}_j\hat{\mathcal{U}}$, as well as the fact that both $\hat{\mathcal{U}}^\dagger$ and $\hat{\mathcal{U}}$ commute with $\hat{\mathcal{P}}$ such that $\hat{\mathcal{U}}^\dagger\hat{\mathcal{P}}\hat{\mathbf{T}}\hat{\mathcal{P}}\hat{\mathcal{U}} = \hat{\mathcal{P}}\hat{\mathcal{U}}^\dagger\hat{\mathbf{T}}\hat{\mathcal{U}}\hat{\mathcal{P}}$, we can derive $\hat{\mathcal{H}}_C$ [in Eq. (9)] as

$$\begin{aligned}\hat{\mathcal{H}}_C &= \hat{\mathcal{U}}^\dagger\hat{\mathcal{P}}\hat{\mathbf{T}}\hat{\mathcal{P}}\hat{\mathcal{U}} + \hat{\mathcal{U}}^\dagger\hat{\mathcal{P}}\hat{V}(\hat{\mathbf{x}})\hat{\mathcal{P}}\hat{\mathcal{U}} + \hat{H}_{\rm ph} \\ &= \sum_j \frac{1}{2m_j}\hat{\mathcal{P}}(\hat{\mathbf{p}}_j - \boldsymbol{\nabla}_j\tilde{\boldsymbol{\mu}}\hat{\mathbf{A}} + \tilde{\mathbf{P}}_j)^2\hat{\mathcal{P}} + \hat{\mathcal{U}}^\dagger\hat{\mathcal{V}}(\hat{\mathbf{x}},\hat{\mathbf{p}})\hat{\mathcal{U}} + \hat{H}_{\rm ph},\end{aligned} \quad (10)$$

where the sum j includes all charged particles (electrons and nuclei). Note that $\hat{\mathcal{H}}'_C$ [Eq. (6)] as well as $\hat{H}_C$ [Eq. (2)] only contain the vector potential $\hat{\mathbf{A}}$ up to the second order. This is no longer the case for $\hat{\mathcal{H}}_C$ in Eq. (10). In fact, both the $\tilde{\mathbf{P}}_j$ term and the $\hat{\mathcal{U}}^\dagger\hat{\mathcal{V}}(\hat{\mathbf{x}},\hat{\mathbf{p}})\hat{\mathcal{U}}$ term in principle contain infinite orders of $\hat{\mathbf{A}}$. It is also self-evident that $\hat{\mathcal{H}}_C$ [Eq. (10)] will return to $\hat{H}_C$ [Eq. (2)] under the complete electronic states limit, such that $\tilde{\boldsymbol{\mu}} \equiv \hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}} \to \hat{\boldsymbol{\mu}}$, thus $\boldsymbol{\nabla}_j\tilde{\boldsymbol{\mu}} \to \boldsymbol{\nabla}_j\hat{\boldsymbol{\mu}} = z_j$, hence $\tilde{\mathbf{P}}_j \to 0$, as well as $\hat{\mathcal{U}} \to \hat{U}$, hence $\hat{\mathcal{U}}^\dagger\hat{\mathcal{P}}\hat{V}(\hat{\mathbf{x}})\hat{\mathcal{P}}\hat{\mathcal{U}} \to \hat{U}^\dagger\hat{V}(\hat{\mathbf{x}})\hat{U} = \hat{V}(\hat{\mathbf{x}})$. Unfortunately, $\hat{\mathcal{H}}_C$ no longer remains a gauge-invariant form (except when approaching the complete electronic states limit), by only involving charges but not higher multipole moments. Nevertheless, $\hat{\mathcal{H}}_C$ is invariant from $\hat{\mathcal{H}}_D$ through the $\hat{\mathcal{U}}$ transformation, resolving the ambiguity between them. There are scenarios where the Coulomb gauge is more convenient [25,38,39] than the dipole gauge for describing light-matter interactions, such as for a solid state material [25,38] interacting with the radiation field where the wave function satisfies periodic boundary conditions and the expectation value of the dipole operator becomes ill defined [40]. For these scenarios, instead of using $\hat{\mathcal{H}}'_C$, the currently derived $\hat{\mathcal{H}}_C$ should be used to investigate the light-matter interactions. Compared to $\hat{\mathcal{H}}'_C$ which requires many

electronic states to provide a reasonable polariton eigenspectrum [18,25], $\hat{\mathcal{H}}_C$ requires as few electronic state as $\hat{H}_D$ and provides identical results.

To further present an equivalent yet convenient $\hat{\mathcal{H}}_C$ for molecular cavity QED, we use the electronic states associated with the electronic Hamiltonian $\hat{H}_{\rm el} = \hat{\mathbf{T}}_{\mathbf{r}} + \hat{V} = \hat{H}_M - \hat{\mathbf{T}}_{\mathbf{R}}$. The *adiabatic* electronic states $|\alpha(\mathbf{R})\rangle$ are the eigenstates of $\hat{H}_{\rm el}$ through $\hat{H}_{\rm el}|\alpha(\mathbf{R})\rangle = (\hat{\mathbf{T}}_{\mathbf{r}} + \hat{V})|\alpha(\mathbf{R})\rangle = E_\alpha(\mathbf{R})|\alpha(\mathbf{R})\rangle$. Using $\hat{\mathcal{P}} = \sum_\alpha |\alpha(\mathbf{R})\rangle\langle\alpha(\mathbf{R})|$, the projected electronic Hamiltonian is $\hat{\mathcal{H}}_{\rm el} = \hat{\mathcal{P}}\hat{H}_{\rm el}\hat{\mathcal{P}} = \sum_\alpha E_\alpha(\mathbf{R})|\alpha\rangle\langle\alpha|$. Alternatively, diabatic electronic states [41–44] $\{|\varphi\rangle, |\phi\rangle\}$ can be obtained by the unitary transform [41–45] from the adiabatic states $|\alpha(\mathbf{R})\rangle$. The character of the diabatic states does not depend on $\mathbf{R}$, such that $\langle\varphi|\boldsymbol{\nabla}_{\mathbf{R}}|\phi\rangle = 0$. With $\hat{\mathcal{P}} = \sum_\varphi |\varphi\rangle\langle\varphi|$, $\hat{\mathcal{H}}_{\rm el} = \hat{\mathcal{P}}\hat{H}_{\rm el}\hat{\mathcal{P}} = \sum_\varphi \mathcal{V}_{\varphi\varphi}(\mathbf{R})|\varphi\rangle\langle\varphi| + \sum_{\varphi\neq\phi}\mathcal{V}_{\varphi\phi}(\mathbf{R})|\varphi\rangle\langle\phi|$, where $\mathcal{V}_{\varphi\phi}(\mathbf{R}) = \langle\varphi|\hat{H}_{\rm el}|\phi\rangle$ is a diabatic matrix element of $\hat{H}_{\rm el}$.

The *central* result of this Letter is reached by splitting the matter Hamiltonian as $\hat{H}_M = \hat{\mathbf{T}}_{\mathbf{R}} + \hat{H}_{\rm el}$, then through a similar derivation procedure to obtain the following:

$$\begin{aligned}\hat{\mathcal{H}}_C &= \hat{\mathcal{U}}^\dagger\hat{\mathcal{P}}\hat{T}_R\hat{\mathcal{P}}\hat{\mathcal{U}} + \hat{\mathcal{U}}^\dagger\hat{\mathcal{P}}\hat{H}_{\rm el}(\hat{\mathbf{p}}_r, \hat{\mathbf{x}})\hat{\mathcal{P}}\hat{\mathcal{U}} + \hat{H}_{\rm ph} \\ &= \sum_{j\in R}\frac{1}{2m_j}\hat{\mathcal{P}}(\hat{\mathbf{p}}_j - \boldsymbol{\nabla}_j\tilde{\boldsymbol{\mu}}\,\hat{\mathbf{A}} + \tilde{\mathbf{P}}_j)^2\hat{\mathcal{P}} + \hat{\mathcal{U}}^\dagger\hat{\mathcal{H}}_{\rm el}\hat{\mathcal{U}} + \hat{H}_{\rm ph},\end{aligned} \tag{11}$$

where the sum over j *only* includes nuclei. In the above expression, we did not specify the choice of $\hat{\mathcal{P}}$, which could be either adiabatic or diabatic. Under the limiting case when $\mathbf{A}_0 = 0$ or $\tilde{\boldsymbol{\mu}}\cdot\hat{\mathbf{A}} = 0$, both the $-\boldsymbol{\nabla}_j\tilde{\boldsymbol{\mu}}\,\hat{\mathbf{A}}$ and $\tilde{\mathbf{P}}_j$ terms become 0, and $\hat{\mathcal{U}}^\dagger = \hat{\mathcal{U}} \to \hat{\mathcal{P}}\otimes\hat{\mathbb{1}}_R\otimes\hat{\mathbb{1}}_{\rm ph}$. Thus, under such a limit, $\hat{\mathcal{H}}_C \to \hat{\mathcal{H}}_M + \hat{H}_{\rm ph}$; hence, the matter and the cavity becomes decoupled. When using adiabatic states for the truncation, one can show that [42,46] $\hat{\mathcal{P}}\hat{\mathbf{p}}_j^2\hat{\mathcal{P}} = (\hat{\mathbf{p}}_j - i\hbar\sum_{\alpha,\beta}\mathbf{d}^j_{\alpha\beta}|\alpha\rangle\langle\beta|)^2$, where $\mathbf{d}^j_{\alpha\beta} \equiv \langle\alpha|\boldsymbol{\nabla}_j|\beta\rangle$ is the well-known derivative couplings. Besides these adiabatic derivative couplings, the light-matter interaction also induced additional "derivative"-type couplings, $-\boldsymbol{\nabla}_j\tilde{\boldsymbol{\mu}}\,\hat{\mathbf{A}}$ and $\tilde{\mathbf{P}}_j$, regardless of the electronic representation used in constructing $\hat{\mathcal{P}}$. When using the Mulliken-Hush diabatic states [43,47] which are the eigenstates of the $\tilde{\boldsymbol{\mu}} \equiv \hat{\mathcal{P}}\hat{\boldsymbol{\mu}}\hat{\mathcal{P}}$ operator, such that $\tilde{\boldsymbol{\mu}} = \sum_\phi \mu_{\phi\phi}|\phi\rangle\langle\phi|$, one can prove that $\tilde{\mathbf{P}}_j = 0$ for all nuclei. This is because that $\boldsymbol{\nabla}_j\tilde{\boldsymbol{\mu}} = \sum_\phi \boldsymbol{\nabla}_j\mu_{\phi\phi}|\phi\rangle\langle\phi|$, thus both $\tilde{\boldsymbol{\mu}}\,\hat{\mathbf{A}}$ and $[\tilde{\boldsymbol{\mu}}\,\hat{\mathbf{A}}, \hat{\mathbf{p}}_j]$ become purely diagonal matrices, hence all of the higher order commutators in $\hat{\mathcal{U}}^\dagger\hat{\mathbf{p}}_j\hat{\mathcal{U}}$ become zero, resulting in $\tilde{\mathbf{P}}_j = 0$ for $j \in \mathbf{R}$.

Finally, we use the above general principle to derive analytical results for a model system. Without loosing generality, let us consider a molecular system within the diabatic states $\{|0\rangle, |1\rangle\}$, which represents a broad range of chemical systems [48–50]. To simplify our algebra, we will assume there is only one nuclear d.o.f. with the coordinate $\hat{R}$ and momentum $\hat{p}_R$, and $\hat{\boldsymbol{\mu}}$ is always aligned along the polarization direction of $\hat{\mathbf{A}}$ (which is $\hat{\mathbf{e}}$). Under the truncated space, $\hat{\mathcal{P}} = |0\rangle\langle 0| + |1\rangle\langle 1|$, the dipole operator is expressed as $\tilde{\mu} \equiv \hat{\mathcal{P}}\hat{\mu}\hat{\mathcal{P}} = \Delta\mu\hat{\sigma}_z + \bar{\mu}\hat{\mathcal{P}} + \mu_{10}\hat{\sigma}_x$, where $\Delta\mu = \frac{1}{2}(\mu_{00} - \mu_{11})$, $\bar{\mu} = \frac{1}{2}(\mu_{00} + \mu_{11})$, and $\mu_{\varphi\phi}(\hat{R}) = \langle\varphi|\hat{\mu}|\phi\rangle$. Note that these transition and permanent dipoles are functions of $\hat{R}$. The electronic Hamiltonian in this truncated subspace is $\hat{\mathcal{H}}_{\rm el} = \hat{\mathcal{P}}\hat{H}_{\rm el}\hat{\mathcal{P}} = \varepsilon(\hat{R})\hat{\sigma}_z + \bar{\mathcal{V}}(\hat{R})\hat{\mathcal{P}} + \mathcal{V}_{10}(\hat{R})\hat{\sigma}_x$, where $\varepsilon(\hat{R}) = \frac{1}{2}[\mathcal{V}_{00}(\hat{R}) - \mathcal{V}_{11}(\hat{R})]$, $\bar{\mathcal{V}}(\hat{R}) = \frac{1}{2}[\mathcal{V}_{00}(\hat{R}) + \mathcal{V}_{11}(\hat{R})]$, and $\mathcal{V}_{\varphi\phi}(\hat{R}) = \langle\varphi|\hat{H}_{\rm el}|\phi\rangle$ (i.e., they are $\hat{H}_{\rm el}$'s matrix elements). Using the above spin representation for $\tilde{\mu}$ and $\hat{H}_{\rm el}$, as well as the BCH identity, one can analytically show (see Supplemental Material [24], Sec. I) that for the terms in $\hat{\mathcal{H}}_C$ from Eq. (11), we have

$$\begin{aligned}\hat{\mathcal{U}}^\dagger\hat{\mathcal{H}}_{\rm el}\hat{\mathcal{U}} = \hat{\mathcal{H}}_{\rm el} &+ [\varepsilon(\hat{R})\sin\theta - \mathcal{V}_{10}(\hat{R})\cos\theta]\{\sin[\xi\hat{A}]\hat{\sigma}_y \\ &+ \cos\theta(1 - \cos[\xi\hat{A}])\hat{\sigma}_x + \sin\theta(\cos[\xi\hat{A}] - 1)\hat{\sigma}_z\},\end{aligned} \tag{12}$$

$\xi = \sqrt{(\mu_{00} - \mu_{11})^2 + 4\mu_{10}^2}$, $\tan\theta = 2\mu_{01}/(\mu_{00} - \mu_{11})$, and the residual momentum is $\tilde{P}_R = \frac{1}{2}(\boldsymbol{\nabla}_R\tan\theta)\cos^2\theta\{(1 - \cos[\xi\hat{A}])\hat{\sigma}_y + [(\sin\theta)\hat{\sigma}_z - (\cos\theta)\hat{\sigma}_x](\sin[\xi\hat{A}] - \xi\hat{A})\}$. Note that for using adiabatic states projection $\hat{\mathcal{P}} = \sum_\alpha |\alpha(R)\rangle\langle\alpha(R)|$, the $\hat{\mathcal{U}}^\dagger\hat{\mathcal{H}}_{\rm el}\hat{\mathcal{U}}$ expression in Eq. (12) remains the same form with $\hat{\mathcal{V}}_{01} = 0$, and so does the form of $\hat{\mathcal{H}}_C$, except for the detailed expression of $\tilde{P}$. The above result has two interesting limits. The first limit is the Rabi model (two-level atom interacts with a cavity) under the Coulomb gauge [19] that provides the consistent results of the dipole gauge Rabi model (see Supplemental Material [24], Sec. I). The second limit is when these diabatic states are also Mulliken-Hush diabatic states, which means that $\mu_{10} = 0$ and $\tan\theta(R) = 0$, hence $\boldsymbol{\nabla}_R\tan\theta(R) = 0$, and $\tilde{P}_R = 0$, agreeing with our previous analysis of this residual momentum.

Figure 1 demonstrates the validity of our theory with a numerical example of a molecule couple to the cavity [1]. Here, we use the Shin-Metiu model molecular system [26], which contains two fixed ions, one moving electron and proton (whose position is R), all interacting with each other through modified Coulombic potentials. The details of this model, as well as the procedure to obtain the strict diabatic states (not the Mulliken-Hush diabatic representation) are provided in Supplemental Material, Secs. V–VII. Figure 1(a) presents the diabatic potential and the matrix elements of $\tilde{\mu}$. Here, we focus on comparing the polaritonic potential energy surface $\mathcal{E}_k(R)$, which is defined as $\hat{H}^D_{\rm pl}|\Phi_k(R)\rangle = \mathcal{E}_k(R)|\Phi_k(R)\rangle$, where $\hat{H}^D_{\rm pl} = \hat{H}_D - \hat{T}_R$ represents the polariton Hamiltonian under the dipole gauge. In the truncated electronic subspace, $\hat{\mathcal{H}}^D_{\rm pl} = \hat{\mathcal{H}}_{\rm el} + \hat{\mathcal{U}}\hat{H}_{\rm ph}\hat{\mathcal{U}}^\dagger$, $\hat{\mathcal{H}}^C_{\rm pl} = \hat{\mathcal{U}}^\dagger\hat{\mathcal{H}}^D_{\rm pl}\hat{\mathcal{U}} = \hat{\mathcal{U}}^\dagger\hat{\mathcal{H}}_{\rm el}\hat{\mathcal{U}} + \hat{H}_{\rm ph}$, and $\hat{\mathcal{H}}^{C'}_{\rm pl} = \hat{\mathcal{P}}\hat{U}^\dagger\hat{H}^D_{\rm pl}\hat{U}\,\hat{\mathcal{P}}$. Note that the analytical results of $\hat{\mathcal{U}}^\dagger\hat{\mathcal{H}}_{\rm el}\hat{\mathcal{U}}$ is expressed in

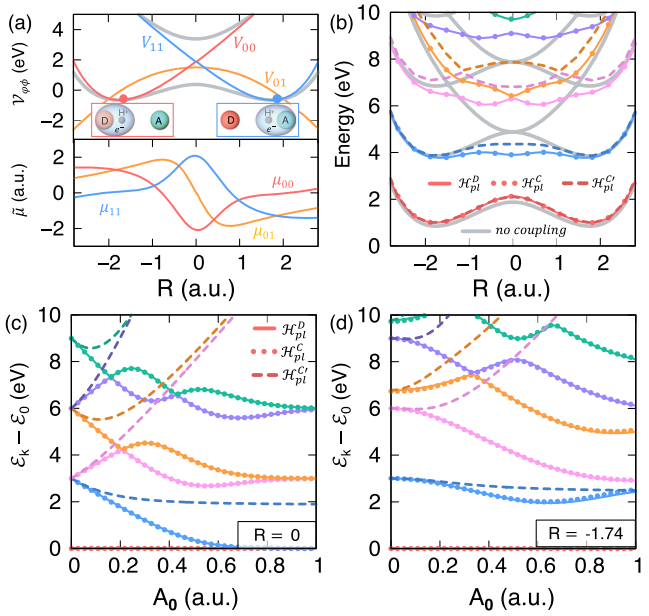

FIG. 1. Shin-Metiu model (transferring proton and electron between two fixed ions) coupled to an optical cavity. (a) Diabatic potentials $\mathcal{V}_{\varphi\phi}(R)$ (upper panel) and dipole $\tilde{\mu}$ (lower panel), with the inset describes characters of the diabatic states. (b) Polariton potential energy surface $\mathcal{E}_k$ for the molecule-cavity hybrid system at $A_0 = 0.2$ and $\hbar\omega_c = 3$ eV, from $\hat{\mathcal{H}}^D_{\rm pl}$ (solid), $\hat{\mathcal{H}}^C_{\rm pl}$ (dotted), and $\hat{\mathcal{H}}^{C'}_{\rm pl}$ (dashed). The polariton eigenenergies as a function of A_0 are depicted at (c) $R = 0$ and (d) $R = -1.74$ a.u..

Eq. (12), whereas the details of other expressions are provided in Supplemental Material [24], Sec. VIII. The matrix elements of these Hamiltonians are evaluated with the two electronic diabatic states and a large number of Fock states, and diagonalizing this matrix gives $\mathcal{E}_k(R)$. Figure 1(b) presents $\mathcal{E}_k(R)$ with $A_0 = 0.2$ a.u. and $\hbar\omega_c = 3$ eV (such that the light and matter excitations are in resonance at $R = 0$). While the $\hat{\mathcal{H}}^D_{\rm pl}$ (solid) and $\hat{\mathcal{H}}^C_{\rm pl}$ (dotted) give identical results throughout all range of R, $\hat{\mathcal{H}}^{C'}_{\rm pl}$ (dashed) gives inconsistent results and breakdown gauge invariance. Figures 1(c)–1(d) present $\mathcal{E}_k - \mathcal{E}_0$ at $\hbar\omega_c = 3$ eV as a function of the field strength A_0, at $R = 0$ (resonance condition) and $R = -1.74$ a.u. (detuned), respectively. Again, the results from the Coulomb gauge and dipole gauge agree with each other exactly throughout the entire range of the field strength, whereas simple state truncation on the Coulomb gauge QED Hamiltonian breaks the gauge invariance, especially in the ultrastrong coupling regime [19,36]. Interestingly, $\hat{\mathcal{H}}_C$ requires much fewer vacuum's Fock states to converge the polariton eigenspectrum [25] compared to $\hat{\mathcal{H}}_D$, as shown in the SI. Hence, using $\hat{\mathcal{H}}_C$ for ultrastrong light-matter interactions provides a numerical advantage of using a much fewer Fock states to converge the polariton eigenspectrum, while uses as few matter states as required in $\hat{\mathcal{H}}_D$ (as opposed to $\hat{\mathcal{H}}'_C$ which requires many electronic states [18,25]).

In conclusion, we lay out the fundamental theoretical framework for the molecular cavity QED by presenting the general procedure to obtain the Coulomb gauge Hamiltonian that provide the consistent results from the dipole gauge Hamiltonian, under the same level of electronic state truncation. While using a finite level of projection on $\hat{H}_D$ often provides accurate results of the polariton eigenspectrum, $\hat{H}'_C$ often introduce the gauge ambiguity (especially in the ultrastrong coupling regime). Instead, $\hat{\mathcal{H}}_C$ in Eq. (11) resolves such gauge ambiguity by proving consistent results as $\hat{\mathcal{H}}_D$. Investigations based upon the Coulomb gauge [25,38,39] should consider using $\hat{\mathcal{H}}_C$.

This work was supported by the National Science Foundation "Enabling Quantum Leap in Chemistry" program under the Grant No. CHE-1836546, as well as by a Cottrell Scholar Award (a program by of Research Corporation for Science Advancement). M. A. D. T. would like to thank Professor Jim Zavislan and the Institute of Optics for supporting this research as a part of his senior thesis. A. M. appreciates the support from his Elon Huntington Hooker Fellowship. W. Z. appreciates the support from the China Scholarship Council. We appreciate valuable discussions with Professor Ahsan Nazir and Professor Peter Milonni.

M. A. D. T. and A. M. contributed equally to this work.

*pengfei.huo@rochester.edu

[1] J. Flick, M. Ruggenthaler, H. Appel, and A. Rubio, Atoms and molecules in cavities, from weak to strong coupling in quantum-electrodynamics (QED) chemistry, Proc. Natl. Acad. Sci. U.S.A. **114**, 3026 (2017).
[2] T. W. Ebbesen, Hybrid light-matter states in a molecular and material science perspective, Acc. Chem. Res. **49**, 2403 (2016).
[3] J. Feist, J. Galego, and F. J. Garcia-Vidal, Polaritonic chemistry with organic molecules, ACS Photonics **5**, 205 (2018).
[4] R. F. Ribeiro, L. A. Martnez-Martnez, M. Du, J. Campos-Gonzalez-Angulo, and J. Yuen-Zhou, Polariton chemistry: Controlling molecular dynamics with optical cavities, Chem. Sci. **9**, 6325 (2018).
[5] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, and T. W. Ebbesen, Modifying chemical landscapes by coupling to vacuum fields, Angew. Chem. Int. Ed. **51**, 1592 (2012).
[6] M. Kowalewski, K. Bennett, and S. Mukamel, Non-adiabatic dynamics of molecules in optical cavities, J. Chem. Phys. **144**, 054309 (2016).
[7] J. Galego, F. J. Garcia-Vidal, and J. Feist, Suppressing photochemical reactions with quantized light fields, Nat. Commun. **7**, 13841 (2016).
[8] A. Mandal and P. Huo, Investigating new reactivities enabled by polariton photochemistry, J. Phys. Chem. Lett. **10**, 5519 (2019).
[9] A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Chervy, A. Shalabney, E. Devaux,

C. Genet, J. Moran, and T. W. Ebbesen, Tilting a ground-state reactivity landscape by vibrational strong coupling, Science **363**, 615 (2019).
[10] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms: Introduction to Quantum Electrodynamics* (John Wiley & Sons, Inc., Hoboken, NJ, 1989).
[11] G. Grynberg, A. Aspect, and C. Fabre, *Introduction to Quantum Optics: From the Semi-Classical Approach to Quantized Light* (Cambridge University Press, Cambridge, England, 2010).
[12] W. E. Lamb, Fine structure of the hydrogen atom. III., Phys. Rev. **85**, 259 (1952).
[13] Y. Aharonov and C. Au, The question of gauge dependence of transition probabilities in quantum mechanics: Facts, myths and misunderstandings, Phys. Lett. **86A**, 269 (1981).
[14] W. E. Lamb, R. R. Schlicher, and M. O. Scully, Matter-field interaction in atomic physics and quantum optics, Phys. Rev. A **36**, 2763 (1987).
[15] P. W. Milonni, R. J. Cook, and J. R. Ackerhalt, Natural line shape, Phys. Rev. A **40**, 3764 (1989).
[16] A. F. Starace, Length and velocity formulas in approximate oscillator-strength calculations, Phys. Rev. A **3**, 1242 (1971).
[17] K. Rzazewski and R. Boyd, Equivalence of interaction Hamiltonians in the electric dipole approximation, J. Mod. Opt. **51**, 1137 (2004).
[18] D. De Bernardis, P. Pilar, T. Jaako, S. De Liberato, and P. Rabl, Breakdown of gauge invariance in ultrastrong-coupling cavity QED, Phys. Rev. A **98**, 053819 (2018).
[19] O. D. Stefano, A. Settineri, V. Macri, L. Garziano, R. Stassi, S. Savasta, and F. Nori, Resolution of gauge ambiguities in ultrastrong-coupling cavity quantum electrodynamics, Nat. Phys. **15**, 803 (2019).
[20] A. Stokes and A. Nazir, Gauge ambiguities imply Jaynes-Cummings physics remains valid in ultrastrong coupling QED, Nat. Commun. **10**, 499 (2019).
[21] E. A. Power and S. Zienau, Coulomb gauge in non-relativistic quantum electro-dynamics and the shape of spectral lines, Phil. Trans. R. Soc. A **251**, 427 (1959).
[22] M. Göppert-Mayer, Elementary processes with two quantum transitions, Ann. Phys. (Berlin) **18**, 466 (2009).
[23] A. Stokes and A. Nazir, Gauge non-invariance due to material truncation in ultrastrong-coupling QED, arXiv:2005.06499v1.
[24] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.125.123602 for details of the derivations shown in the main-text, Pauli-Fierz Hamiltonian, diabatization scheme and other computational details, which includes Refs. [1,6,19,20,23,25–35].
[25] J. Li, D. Golez, G. Mazza, A. J. Millis, A. Georges, and M. Eckstein, Electromagnetic coupling in tight-binding models for strongly correlated light and matter, Phys. Rev. B **101**, 205140 (2020).
[26] S. Shin and H. Metiu, Nonadiabatic effects on the charge transfer rate constant: A numerical study of a simple model system, J. Chem. Phys. **102**, 9285 (1995).
[27] C. C. Marston and G. G. B. Kurti, The fourier grid hamiltonian method for bound state eigenvalues and eigenfunctions, J. Chem. Phys. **91**, 3571 (1989).
[28] D. Tannor, *Introduction to Quantum Mechanics: A Time-Dependent Perspective* (University Science Books, Mill Valley, CA, 2007).
[29] V. Rokaj, D. M. Welakuh, M. Ruggenthaler, and A. Rubio, Lightmatter interaction in the longwavelength limit: No ground-state without dipole self-energy, J. Phys. B **51**, 034005 (2018).
[30] C. Schäfer, M. Ruggenthaler, and A. Rubio, *Ab initio* nonrelativistic quantum electrodynamics: Bridging quantum chemistry and quantum optics from weak to strong coupling, Phys. Rev. A **98**, 043801 (2018).
[31] N. M. Hoffmann, C. Schfer, N. Skkinen, A. Rubio, H. Appel, and A. Kelly, Benchmarking semiclassical and perturbative methods for real-time simulations of cavity-bound emission and interference, J. Chem. Phys. **151**, 244113 (2019).
[32] E. Jaynes and F. Cummings, Comparison of quantum and semiclassical radiation theories with application to the beam maser, Proc. IEEE **51**, 89 (1963).
[33] K. Bennett, M. Kowalewski, and S. Mukamel, Novel photochemistry of molecular polaritons in optical cavities, Faraday Discuss. **194**, 259 (2016).
[34] A. M. Mebel, M. Baer, and S. H. Lin, Probing the nature of surface intersection by ab initio calculations of the non-adiabatic coupling matrix elements: A conical intersection due to bending motion in C2H, J. Chem. Phys. **112**, 10703 (2000).
[35] E. S. Kryachko and D. R. Yarkony, Diabatic bases and molecular properties, Int. J. Quantum Chem. **76**, 235 (2000).
[36] A. F. Kockum, A. Miranowicz, S. De Liberato, S. Savasta, and F. Nori, Ultrastrong coupling between light and matter, Nat. Rev. Phys. **1**, 19 (2019).
[37] L. Garziano, A. Settineri, O. D. Stefano, S. Savasta, and F. Nori, Gauge invariance of the Dicke and Hopfeld models, arXiv:2002.04241v1 [Phys. Rev. A (to be published)].
[38] S. Latini, E. Ronca, U. D. Giovannini, H. Hübene, and A. Rubio, Cavity control of excitons in two-dimensional materials, Nano Lett. **19**, 3473 (2019).
[39] N. Rivera, J. Flick, and P. Narang, Variational Theory of Nonrelativistic Quantum Electrodynamics, Phys. Rev. Lett. **122**, 193603 (2019).
[40] R. Resta, Quantum-Mechanical Position Operator in Extended Systems, Phys. Rev. Lett. **80**, 1800 (1998).
[41] C. A. Mead and D. G. Truhlar, Conditions for the definition of a strictly diabatic electronic basis for molecular systems, J. Chem. Phys. **77**, 6090 (1982).
[42] T. Pacher, C. A. Mead, L. S. Cederbaum, and H. Koppel, Gauge theory and quasidiabatic states in molecular physics, J. Chem. Phys. **91**, 7057 (1989).
[43] R. J. Cave and M. D. Newton, Generalization of the Mulliken-Hush treatment for the calculation of electron transfer matrix elements, Chem. Phys. Lett. **249**, 15 (1996).
[44] H. Guo and D. R. Yarkony, Accurate nonadiabatic dynamics, Phys. Chem. Chem. Phys. **18**, 26335 (2016).
[45] J. E. Subotnik, E. C. Alguire, Q. Ou, B. R. Landry, and S. Fatehi, The requisite electronic structure theory to describe photoexcited nonadiabatic dynamics: Nonadiabatic derivative couplings and diabatic electronic couplings, Acc. Chem. Res. **48**, 1340 (2015).

[46] G. Worth and L. Cederbaum, Beyond Born-Oppenheimer: Molecular dynamics through a conical intersection, Annu. Rev. Phys. Chem. **55**, 127 (2004).

[47] R. J. Cave and M. D. Newton, Calculation of electronic coupling matrix elements for ground and excited state electron transfer reactions: Comparison of the generalized Mulliken-Hush and block diagonalization methods, J. Chem. Phys. **106**, 9213 (1997).

[48] A. Semenov and A. Nitzan, Electron transfer in confined electromagnetic fields, J. Chem. Phys. **150**, 174122 (2019).

[49] J. F. Triana, D. Peláez, and J. L. Sanz-Vicario, Entangled photonic-nuclear molecular dynamics of LiF in quantum optical cavities, J. Phys. Chem. A **122**, 2266 (2018).

[50] J. F. Triana and J. L. Sanz-Vicario, Revealing the Presence of Potential Crossings in Diatomics Induced by Quantum Cavity Radiation, Phys. Rev. Lett. **122**, 063603 (2019).