Shedding Light on Correlated Electron-Photon States using the Exact Factorization

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Abstract. The Exact Factorization framework is extended and utilized to introduce the electronic-states of correlated electron-photon systems. The formal definitions of an exact scalar potential and an exact vector potential that account for the electron-photon correlation are given. Inclusion of these potentials to the Hamiltonian of the uncoupled electronic system leads to a purely electronic Schrödinger equation that uniquely determines the electronic states of the complete electron-photon system. For a one-dimensional asymmetric double-well potential coupled to a single photon mode with resonance frequency, we investigate the features of the exact scalar potential. In particular, we discuss the significance of the step-and-peak structure of the exact scalar potential in describing the phenomena of photon-assisted delocalization and polaritonic squeezing of the electronic excited-states. In addition, we develop an analytical approximation for the scalar potential and demonstrate how the step-and-peak features of the exact scalar potential are captured by the proposed analytical expression.

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1 Introduction

Rapid progress in the fields of cavity and circuit quantum electrodynamics (QED) has given us a possibility to study how many-electron systems interact with quantum light. The interplay between photons and electrons plays a key role in many fascinating processes in atoms inside optical cavities in cavity-QED [1,2,3], or mesoscopic systems such as superconducting qubits and quantum dots embedded in transmission line resonators in circuit-QED [4,5,6,7,8,9]. Furthermore, in the case of molecules a strong coupling of molecular states to microcavity photons has been achieved experimentally [10,11], and the modification of photo-chemical landscapes, the charge and energy transport by cavity vacuum fields have been reported [12,13,14]. The progress in experiments triggered theoretical activities that address “chemistry-in-cavity” problem. Indeed, the corresponding processes cannot be captured properly within the usual classical approximation for the light as the system now includes new quantum degrees of freedom of photons and the concept of electron-photon correlation comes in as a new player influencing the electronic states of the system. In the last few years, several theoretical approaches have been put forward to describe molecular systems in quantum cavities. These include both mapping to simplified few-level quantum optics models [15,16,17,18], and the cavity-QED generalizations of ab initio electronic structure methods, such as (TD)DFT [19,20,21,22,23,24,25,26], or the Hedin equations framework in the Green functions theory [27].

As long as the light can be treated classically, the electronic many-body states are fully described by the non-relativistic electronic Schrödinger Equation (SÉ), i.e.,

$$\hat{H}_e \phi_j(\mathbf{r}) = E_j \phi_j(\mathbf{r}),$$

(1)

with the Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{V} + \hat{W}_{ee}$$

(2)

where $\hat{T}_e$, $\hat{V}$ and $\hat{W}_{ee}$ are the usual kinetic energy, the external potential, and the Coulomb interaction energies of the electrons, respectively. The Hamiltonian $\hat{H}_e$ acts on the electronic coordinates collectively denoted by $\mathbf{r} \equiv r_1, r_2, \ldots, r_N$. At this level of theory only the electrons are treated quantum mechanically and only the coordinates of electrons appear as arguments of the wavefunction. However, if the electronic system is embedded in a microcavity the presence of quantum electromagnetic degrees of freedom (photons) can modify the electronic
states significantly. The complete description of the quantum states of matter that is now coupled to the photons, in principle, can be provided by the SE of the multi-component system of electrons and photons,

$$\hat{H}_\text{tot} \Psi^j(\mathbf{r}, \mathbf{q}) = E_j \Psi^j(\mathbf{r}, \mathbf{q}),$$  \hspace{1cm} (3)

with the Hamiltonian

$$\hat{H}_\text{tot} = \hat{H}_e + \hat{H}_\text{EM},$$  \hspace{1cm} (4)

which now includes an additional term, $\hat{H}_\text{EM}$, that is resulted from the quantization of the electromagnetic field to properly account for quantum features of the radiation field and the electron-photon correlation. A detailed derivation of $\hat{H}_\text{EM}$ will be presented shortly in the following section. Here, the degrees of freedom of $N_\text{e}$ cavity modes are collectively represented by $\mathbf{q} = q_1, q_2, \ldots, q_{N_\text{e}}$. In the length gauge, the “electromagnetic coordinate” $q_\alpha$ corresponds to the amplitude of electric displacement in the $\alpha$-mode of the cavity (see section 2 for more details).

A numerically exact solution of the complete electron-photon SE, Eq. (3), can only be obtained for small systems, hence, an accurate description of the electronic states of matter in the presence of photons requires an efficient treatment of electronic many-body problem while accounting for the electron-photon correlation. Here, an important question is whether or not the information on the electronic states that are coupled to photons can be obtained from pure electronic states $\Phi^j(\mathbf{r})$ rather than the more complicated electron-photon states $\Psi^j(\mathbf{r}, \mathbf{q})$. And if yes, what Hamiltonian gives such electronic states? How does it differ from the uncoupled electronic Hamiltonian of Eq. (2)?

In this work, we will address these questions and will demonstrate that the answer to the first question is indeed yes. By utilizing the Exact Factorization (EF) framework [28, 29, 30], we will show how pure electronic states, $\Phi^j(\mathbf{r})$, can provide us with important information such as the exact electronic many-body densities and current densities equivalent to those obtained from the complete electron-photon states $\Psi^j(\mathbf{r}, \mathbf{q})$. We furthermore, present the additional purely electronic potentials that are needed to be included in the electronic Hamiltonian in order to account for the electron-photon correlation in a formally exact way. In addition, we derive analytical expressions of these potentials for electronic states of a single electron system in an asymmetric double-well potential that is coupled to a single-photon mode of a cavity with a resonance frequency. Furthermore, we will show how well our analytical expressions match the potential obtained from the numerical solution of the SE. We demonstrate that in the resonance regime the effective electronic potential for excited states demonstrate clear peak and step structures, which are responsible, respectively, for the polaritonic squeezing of the intra-well states and the photon-assisted inter-well tunneling.

Here, we only study the stationary states. However our results have a direct relevance for understanding the dynamics of electron-photon systems and thus for the development of QED-TDDFT [19, 20, 23]. In fact, the step-peak structure of the electronic potential for the stationary excited states should show up in the effective time-dependent potential to account for the charge transfer processes supplemented with the photon emission/absorption.

### 2 Quantization of electromagnetic field: Hamiltonian for cavity QED

The main object of the cavity/circuit QED is a system of non-relativistic electrons interacting with electromagnetic modes of a microcavity. The QED regime assumes that both electrons and the electromagnetic field are treated quantum mechanically. However, to understand better the structure of the quantum theory it is instructive to analyze first the classical dynamics of the system.

Our starting point is the Maxwell equations for the transverse part of the electromagnetic field

$$\nabla \times \mathbf{E}_\perp = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{B},$$  \hspace{1cm} (5)

$$\nabla \times \mathbf{B} = \frac{1}{c} \frac{\partial}{\partial t} \mathbf{E}_\perp + \frac{4\pi}{c} \mathbf{j}_\perp,$$  \hspace{1cm} (6)

where $\mathbf{E}_\perp(r,t)$ is the transverse electric field with $\nabla \cdot \mathbf{E}_\perp = 0$, and $\mathbf{j}_\perp(r,t)$ is the transverse part of electron current that enters as a source of the radiation field. In general for $N_\text{e}$ electrons moving along trajectories $\mathbf{r}_j(t)$ the current is defined as follows

$$\mathbf{j}(r,t) = e \sum_{j=1}^{N_\text{e}} \mathbf{r}_j(t) \delta(\mathbf{r} - \mathbf{r}_j(t)).$$  \hspace{1cm} (7)

In a typical cavity QED setup, the motion of electrons is bounded to a region around some point $\mathbf{r}_0$ inside the cavity, which is much smaller than the cavity size and thus much smaller than the characteristic wavelength $\lambda$ of the field. The condition $|\mathbf{r}_j(t) - \mathbf{r}_0| \ll \lambda$ justifies the replacement of $\mathbf{r}_j \mapsto \mathbf{r}_0$ in the arguments of the $\delta$-functions

$$\mathbf{j}(r,t) = e \sum_{j=1}^{N} \mathbf{r}_j(t) \delta(\mathbf{r} - \mathbf{r}_0) = \partial_t \mathbf{P}(r,t),$$  \hspace{1cm} (8)

where we introduced the polarization vector $\mathbf{P}(r,t) = e \mathbf{R}(t) \delta(\mathbf{r} - \mathbf{r}_0)$ with $\mathbf{R} = \sum_{j=1}^{N} \mathbf{r}_j$ being the center-of-mass coordinate of the electrons. This corresponds to the dipole approximation that is fulfilled with a very high accuracy in most of the practical situations. The transverse current entering the Maxwell equations is determined by the transverse projection of the polarization vector

$$\mathbf{P}_\perp(r,t) = e \mathbf{R}(t) \delta^\perp(\mathbf{r} - \mathbf{r}_0) = \frac{e}{4\pi} \nabla \times \left( \nabla \times \frac{\mathbf{R}(t)}{|\mathbf{r} - \mathbf{r}_0|} \right),$$  \hspace{1cm} (9)

where we have used the identity $\delta^\perp(\mathbf{r} - \mathbf{r}_0) = \frac{1}{4\pi} \nabla \times \left( \nabla \times \frac{1}{|\mathbf{r} - \mathbf{r}_0|} \right)$. In a quantum theory, the Maxwell equations (5), (6) should become Heisenberg equations for the
corresponding field operators. The quantum operator algebra can be revealed by representing the classical theory in a Hamiltonian form. To do so, we introduce a new electric variable – the displacement vector
\[ D_⊥ = E_⊥ + 4\pi P_⊥, \]
and rewrite the Maxwell equations (5), (6) as follows
\[ \begin{align*}
\partial_t B &= -\varepsilon \nabla \times (D_⊥ - 4\pi P_⊥), \\
\partial_t D_⊥ &= \varepsilon \nabla \times B.
\end{align*} \]

These equations demonstrate a clear Hamiltonian structure. Indeed, by considering the standard energy of the transverse electromagnetic field
\[
H_{EM} = \frac{1}{8\pi} \int dr \left[ E_⊥^2 + B^2 \right]
\]
\[
= \frac{1}{8\pi} \int dr \left[ (D_⊥ - 4\pi P_⊥)^2 + B^2 \right],
\]
and imposing the following commutation relations
\[
[B_ι(r), D_ι′(r′)] = -i 4\pi e^{i\lambda k} \delta_ι(\mathbf{r} - \mathbf{r}′),
\]
we recover the Maxwell equations from the canonical Heisenberg equations
\[
\begin{align*}
\partial_t B &= i[H_{EM}, D_⊥], \\
\partial_t D_⊥ &= i[H_{EM}, B].
\end{align*}
\]

An important outcome of this analysis is that the proper conjugated Hamiltonian variables for the electromagnetic field are the magnetic field \( B \) and the electric displacement \( D \).

Let us introduce cavity modes as a set of normalized transverse eigenfunctions \( E_α(r) \) of the wave equation inside a metallic cavity \( Ω \)
\[
e^2 \nabla^2 E_α(r) = ω_α^2 E_α(r), \quad r ∈ Ω
\]
\[
(n × E_α)|_{∂Ω} = 0,
\]
where \( n \) is a unit vector normal to the cavity surface \( ∂Ω \).

Now all transverse functions in the Hamiltonian (15) can be expanded in the cavity modes
\[
\begin{align*}
D_⊥(r) &= \sum_α d_α E_α(r), \\
B(r) &= \sum_α b_α \frac{e}{ω_α} \nabla × E_α(r), \\
P_⊥(r) &= e \sum_α (E_α(r_0) × R) E_α(r).
\end{align*}
\]

Here the expansion coefficients \( d_α \) and \( b_α \) are, respectively, the quantum amplitudes of the electric displacement and the magnetic field in the \( α \)-mode. Note that Eq. (15) ensures that the magnetic field satisfies the proper boundary condition \( (B · n)|_{∂Ω} = 0 \). By inserting the above expansions into Eqs. (13) and (14) we obtain the following Hamiltonian
\[
H_{EM} = \frac{1}{8\pi} \sum_α \left[ (d_α - 4\pi e E_α(r_0) · R)^2 + b_α^2 \right],
\]
and the commutation relations for the field amplitudes
\[
[h_α, d_β] = -i4\pi ω_α δ_αβ.
\]

Finally we rescale the electric displacement and the magnetic field amplitudes
\[
d_α = \sqrt{4π} ω_α q_α, \quad b_α = \sqrt{4π} p_α,
\]
so that the new variables \( q_α \) and \( p_α \) satisfy the standard coordinate-momentum commutation relations \([p_α, q_β] = -iδ_αβ\), while the Hamiltonian (20) reduces to that of a set of shifted harmonic oscillators
\[
H_{EM} = \frac{1}{2} \sum_α \left[ p_α^2 + \omega_α^2 \left( q_α - \frac{λ_α}{ω_α} R \right)^2 \right],
\]
where the “coupling constant” \( λ_α \) is related to the electric field of the \( α \)-mode at the location of the electron system
\[
λ_α = 4π e E_α(r_0).
\]

Equation (23) corresponds to the description of quantum electromagnetic field and the electron-photon coupling in a so called Power-Zienau-Woolley (PZW) gauge [30,32,33]. The total Hamiltonian for the combined system of electrons and the field is a sum of \( H_{EM} \) and the standard Hamiltonian of a non-relativistic many-electron system
\[
\hat{H}_{tot} = \hat{H}_e + \hat{H}_{EM},
\]
where \( \hat{H}_e \) is the electronic Hamiltonian of Eq. (6) in the absence of the photon field. This Hamiltonian is commonly used as the starting point in the first-principles approaches to the cavity QED [19,24,21,22,24].

### 3 Exact factorization of the complete electron-photon wavefunction

The framework of the exact factorization (EF) for static [29,34,28] and time-dependent problems [30,35,36] was originally developed to go beyond the Born-Oppenheimer treatment of multicomponent systems of electrons and nuclei. Consequently, the original presentation of the framework provides an exact separation of the complete electron-nuclear wavefunction as a product of a marginal nuclear wavefunction and a conditional electronic wavefunction that parametrically depends on the nuclear configuration. As there is no approximation involved in developing this framework and the two subsystems are treated on the same footings, in principle, the EF can be extended to
It can be proved [29] that the photonic conditional wavefunction, $\chi_p^j(q)$, satisfies
\[ \hat{H}^{ph,j}_\pm \chi_p^j(q) = V_{e-ph}(r) \chi_p^j(q), \] (28)
with the photonic Hamiltonian
\[ \hat{H}^{ph,j}_\pm = \hat{H}_{EM} + \sum_{k=1}^{N_e} \frac{1}{m} \left( -i \nabla_k - S^j_k(r) \right)^2 + \left( -i \frac{\nabla_k \Phi^j}{\Phi^j} + S^j_k(r) \right) \left( -i \nabla_k - S^j_k(r) \right), \] (29)
while the electronic wavefunction $\Phi^j(r)$ satisfies a Schrödinger-like equation:
\[ \left( \sum_{k=1}^{N_e} \frac{1}{2m} \left( -i \nabla_k + S^j_k(r) \right)^2 + V(r) + \hat{W}_{ee}(r) + V_{e-ph}(r) \right) \Phi^j(r) = E_j \Phi^j(r), \] (30)
where $m$ is the electronic mass. As it can be seen in Eq. (30), as a result of the coupling to the cavity photons, the electronic subsystem contains two additional potentials compared to the independent uncoupled electronic SE (1). The influence of electron-photon correlation on the $j$-th electronic state is formally exactly taken care of by addition of a scalar potential,
\[ V_{e-ph}(r) = \left[ \chi_p^j(q) \right] \hat{H}^{ph,j}_\pm \left[ \chi_p^j(q) \right], \] (31)
and a vector potential,
\[ S^j_k(r) = \left[ \chi_p^j(q) \right] -i \nabla_k \chi_p^j(q), \] (32)
to the uncoupled electronic SE (1). Here, $\langle \cdots \rangle_q$ denotes an inner product over all photonic variables only.

Similar to the other extensions of the EF framework, the marginal electronic wavefunction and the conditional photonic wavefunction and their corresponding equations have the following properties:

- Eqs. (28)-(30) are form-invariant under the following gauge-like transformation,
  $$\chi^j_p(q) \rightarrow \tilde{\chi}^j_p(q) = \exp(i \theta_j(r)) \chi^j_p(q)$$
  $$\Phi^j(r) \rightarrow \tilde{\Phi}^j(r) = \exp(-i \theta_j(r)) \Phi^j(r).$$

- The scalar potential given in Eq. (31) is also gauge invariant under the above-mentioned gauge transformation while the vector potential is transformed as
  $$S^j_k(r) \rightarrow \tilde{S}^j_k(r) = S^j_k(r) + \nabla_k \theta_j(r).$$ (33)
- The wavefunctions $\chi_j^\pm(q)$ and $\Phi_j(r)$ are unique up to this $(r)$-dependent gauge transformation and yield the given solution, $\Psi_j(r, q)$, of Eq. (5).
- The electronic wavefunction, $|\Psi_j(r, q)|^2 = \int |\Psi_j(r, q)|^2 dq$, gives the probability density of finding the electronic configuration $r$ of the $j$-th correlated electron-photon state and the photonic conditional wavefunction, $|\chi_j^\pm(q)|^2 = |\Psi_j(r, q)|^2/|\Phi_j(r)|^2$, provides the conditional probability of finding the displacement amplitudes of the cavity at $q$ for a given electronic configuration $r$.

Furthermore, the exact electronic $N_e$-body current-density can be obtained from $\Im(\hat{V}^\rho - \nabla_k \Phi^\rho) + |\Phi^\rho(r)|^2 S_k^e$. Therefore, $\chi_j^\pm(q)$ and $\Phi_j(r)$ can be interpreted as photonic and electronic wavefunctions.

One of the main results of this work is Eq. (30) that can be regarded as the exact electronic equation for the $j$-th electronic state of the correlated electron-photon system: The Hamiltonian that is formed by adding the scalar potential (Eq. (31)) and the vector potential (Eq. (32)) (which are unique up to within a gauge transformation), to the uncoupled electron Hamiltonian provides us with the $j$-th electronic state, $\Phi_j(r)$, that yields the true electron ($N_e$-body) density and current density of the full electron-photon problem.

The scalar electron-photon ($e$-ph) correlation potential (Eq. 33) can also be written as

$$V_{e-ph}^j(r) = \left< \chi_j^+ \left| \hat{H}_{EM}(q, r) \right| \chi_j^- \right>_q + \frac{1}{2m} \sum_{k=1}^{N_e} \left( \nabla_k \chi_j^+ \nabla_k \chi_j^- - S_k^e(r)^2 \right), \tag{34}$$

which for our purposes here has a more convenient form.

### 4 Example: photon-assisted delocalization of the electronic states

In this section, we investigate a particular situation in which the character of the electronic excited states of the system undergoes a fundamental change through electron-photon coupling, i.e. they become delocalized as a result of the coupling to a cavity mode with a resonance frequency. Our study is based on a model system in which we consider a single electron in an Asymmetric Double-Well (ADW) potential

$$V(x) = \frac{1}{2} \omega_e^2 (|x| - a)^2 + E x, \tag{35}$$

with the Hamiltonian

$$\hat{H}_{e}^{ADW} = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + V(x) \tag{36}$$

Here, $\omega_e = 1.6$ (a.u.), $a = 2.35$ (a.u.), the static electric field $E = 0.08$ (a.u.), and the electronic mass $m$ is set to 1.
| $\lambda_e$ | 0.1 | 0.5 | 0.9 |
|------------|-----|-----|-----|
| $\omega_c$ | 0.376/6260 | 0.3945042 | 0.43/42993 |

Table 1. The coupling constants and the corresponding resonance frequencies implemented in this work in atomic units.

Fig. 2. (Left) Schematic representation of the displaced harmonic oscillator basis with the usual eigenstates. Eigenstates with the energy quantum number $N$ on the left are degenerate with the Eigenstates with energy quantum number $N - 1$ on the right. (Right) Schematic representation of the (diabatic) approximation in which the $N$-th state of the displaced oscillator on the left is allowed to mix with the $(N - 1)$-th state of the displaced oscillator on the right (similar to the symmetric case of Irish et al. [57]).

equations need to be solved self-consistently that seems to be somehow more complicated than solving the full SE (3). Therefore, we solve the full SE (3) and similar to our previous studies [30-31,57] extract the numerically exact $e$-$ph$ potential by inverting the full SE. In addition, we derive an approximate analytical expression for the exact $e$-$ph$ correlation potential (31) and show how step and peak features of the $e$-$ph$ correlation potential are captured analytically. These features lead to the polaronic localization of the electronic ground-state and delocalization of the electronic excited-states.

For the one dimensional model (Eq.36), the $e$-$ph$ correlation potential reads

$$V_{e-ph}^j(x) = \langle \chi^+_q | H_{EM} | \chi^+_q \rangle + \frac{1}{2m} \left( \frac{\partial \chi^+_j}{\partial x} \frac{\partial \chi^+_q}{\partial x} \right)_q , \quad (39)$$

while the vector potential can be gauged away [35].

4.1 Combining atomic orbitals and displaced harmonic oscillator basis

In order to work out an accurate analytical approximation for the complete electron-photon wavefunction, $\Psi^j(x, q)$, that is the $j$-th eigenstate of Eq. (37), we first expand it in a basis set. Given the fact that the uncoupled electronic system is practically a two-level system with two localized states, it can be accurately described by localized atomic orbitals (AO) that are the ground states of the harmonic potentials centered at $\pm a$, i.e.,

$$\hat{T}_c + \hat{V}^+_{st} \phi^+(x) = E^+ \phi^+(x) \quad (40)$$

where $\hat{V}^+_{st} = \frac{1}{2} \omega^2 (x \mp a)^2$. To form our basis set we combine these atomic orbitals with the so called displaced harmonic oscillator (DHO) basis. The DHO basis are the eigenstates of two harmonic oscillator Hamiltonians that are centered at $\pm a \omega_c$, i.e.,

$$\hat{H}^\pm_{q} \xi^\pm_N(q) = V_{ad}^N \xi^\pm_N(q) \quad (41)$$

where $\hat{H}^\pm_{q} = \frac{1}{2} \frac{\partial^2}{\partial q^2} + \frac{1}{2} \omega^2 (q \mp \lambda_N a)^2 \pm \Delta$ and $V_{ad}^N = \pm \Delta + (N + \frac{1}{2})\omega_c$. We then choose the localized basis as products of the AO on the left (right) and the DHO states on the left (right), $[\xi^\pm_N(q) \phi^-(x)]([\xi^\pm_N(q) \phi^+(x)]$) and expand the full wavefunction in terms of them, i.e.,

$$\Psi(x, q) = \sum_{N=0}^{\infty} \left[ A_N \xi^\pm_N(q) \phi^-(x) + A_N^* \xi^\pm_N(q) \phi^+(x) \right] , \quad (42)$$

where $A_N^+ (A_N^-)$ are the expansion coefficients of the left (right) states. This is analogous to the expansion of the full molecular wavefunction in terms of a diabatic basis. Our choice of basis was inspired by the work of Irish et al. [57] in which they implemented the DHO to solve the two-level Rabi model. We now plug the expansion (42) into the complete electron-photon SE (3) with the Hamiltonian [37] and project onto $\langle \xi^\pm_M \phi^- \rangle$ and $\langle \xi^\pm_M \phi^+ \rangle$ that
leads to
\[ A^{-}_M \left[ \alpha + V^{-}_M \right] + \sum_{N=0}^{\infty} A^{-}_N \left[ \beta (\xi_M (q) | \xi_N (q) )_q + \hat{V}^{-}_N \right] (\xi_M (q) | \xi_N (q) )_q S \]
\[ = E \left[ A^{-}_M + \sum_{N=0}^{\infty} A^{-}_N (\xi_M (q) | \xi_N (q) )_q S \right], \]
\[ \text{Eq. (43)} \]
\[ \text{where} \]
\[ \alpha = \langle \phi^\pm (x) | \hat{T}_c + \frac{1}{2} \omega_c^2 (|x| - a)^2 \rangle | \phi^\pm (x) \rangle, \]
\[ \beta = \langle \phi^\pm | \hat{T}_c + \frac{1}{2} \omega_c^2 (|x| - a)^2 \rangle | \phi^\mp \rangle, \]
\[ S = \langle \phi^- | \phi^+ \rangle, \]
\[ \text{Eq. (44)} \]
are the typical elements of the LCAO technique. The outcome of the projection onto $\langle \xi^+_N | \phi^- \rangle$ is symmetric with Eq. (43). In Fig. 2, we present the DHO basis schematically.

As it can be seen in the figure, for the resonance frequencies the states of the left DHO with the energy quantum number $N^-$ are degenerate with the states of the right DHO with the energy quantum number $(N-1)^+$. In this work we only allow for the mixing of these states and neglect the coupling to the other states that can be regarded as an adiabatic approximation. We discuss how to go beyond this limit in a different publication [58].

4.1.1 Ground state

The full electronic potential of the EF framework for the ground-state, $V(x) + V^{e-ph}_{\text{add}}(x)$, with the e-ph correlation potential obtained from the numerically exact solution of SE of combined systems [3] has been plotted in Fig. 3 (top-right) for $\lambda_c = 0.1, 0.5, 0.9$. As it can be seen in this plot, for smallest coupling constant $\lambda_c = 0.1$ the full electronic potential only slightly differs from the asymmetric double-well potential of the uncoupled electronic system. By increasing $\lambda_c$, the well on the right side is lifted up and both wells are squeezed leading to a polarization squeezing of the electronic states compared to the electronic states of the uncoupled electronic system as it is clear in the top-left panel of the Fig. 3, hence, the larger the coupling constant, the more squeezed the electronic density.

We now turn to our approximate evaluation of the correlated e-ph potential to see whether this effect is reflected in our approximation and if yes how? Due to the asymmetry of the potential in Hamiltonian (56), there is no state from the right side (+) in resonance with the localized state $\Phi^- \xi_0 (q)$ at the left side. Therefore, the conditional photon wavefunction of the ground state can be approximated as $\xi_0 (q)$. The corresponding e-ph correlation potential reads
\[ V^{e-ph}_{\text{add}}(x) = \langle \xi_0 (q) | \hat{H}_{\text{EM}} | \xi_0 (q) \rangle q = \frac{\omega_e}{2} + \frac{\lambda_c^2}{2} (x + a)^2, \]
\[ \text{as the second term in Eq. (39) is zero. The final outcome of Eq. (45)} \]
\[ \text{is obtained by replacing} \hat{H}_{\text{EM}} \text{with} \]
\[ \hat{H}_{\text{q}} + \frac{1}{2} \omega_e^2 \left[ \left( q - \frac{\lambda_c}{\omega_e} x \right)^2 - \left( q + \frac{\lambda_c}{\omega_e} a \right)^2 \right] + \Delta. \]
\[ \text{In Fig. 3 (bottom-right), we present the full electronic potential that is resulted from addition of this analytically approximate e-ph correlation potential (45) to the asymmetric double-well potential of the uncoupled electronic system. Furthermore, we implement these potential to calculate the electronic states from Eq. (39) and show the difference between the electronic densities of the uncoupled electronic system with the approximate electronic densities of coupled electron-photon system in Fig. 3 (bottom-left). It can be seen that the potentials and densities corresponding to the approximate analytical e-ph correlation potentials follow the same trend as the numerically exact results and exhibit the main features, i.e., the right well is elevated while both wells are squeezed. The densities are also squeezed compared to the electronic density of the uncoupled electronic system, following the same trend as the exact electronic densities. Although, in both cases of approximate potentials and electronic densities the squeezing is more exaggerated. The approximate e-ph correlation potential also shifts up the right well fairly above the exact results. However, given the fact that the most simple approximation for the conditional photon wavefunction has been implemented here, the agreement with the exact result is fulfilling.}
We shall now investigate how these features are captured by our approximate analytical treatment. Here we note that while we give general analytical expressions for the e-ph correlation potential, our discussions are only focused on \( N = 1 \). Furthermore, our results are valid as long as the energies of coupled electron-photon system is well bellow the second excited state of the uncoupled electronic system.

As we only allow for the mixing of the states with the same energy in the expansion \( |\psi_N\rangle \), within our approximate treatment, the full electron-photon excited-states that are the eigenstates of Eq. \( (37) \) may be written as

\[
\psi_N(x, q) = \frac{1}{\sqrt{2\nu^N}} \left[ \xi_N\phi^- \pm \xi_{N-1}^+ \phi^+ \right],
\]

with the corresponding excited-state energies

\[
E_N^\pm = N\omega_c + \frac{\alpha \pm \beta \langle \xi_N^\pm | \xi_{N-1}^\pm \rangle q}{\nu^\pm},
\]

where

\[
\nu^\pm = 1 \pm S \langle \xi_N^\pm | \xi_{N-1}^\pm \rangle q.
\]

Here \( \lambda_c \) is an associated Laguerre polynomial. From this electron-photon wavefunctions we can obtain the corresponding electronic wavefunction,

\[
\Psi_N(x) = \frac{1}{\sqrt{2\nu^N}} \left[ |\phi^-|^2 + |\phi^+|^2 \pm 2 \langle \xi_N^\pm | \xi_{N-1}^\pm \rangle q \phi^- \phi^+ \right]^{1/2},
\]

and conditional photonic wavefunction,

\[
\chi_N^\pm(q|x) = \frac{1}{\sqrt{2}} \frac{\xi_N \phi^- \pm \xi_{N-1}^+ \phi^+}{\Phi_N^\pm(x)}. \tag{51}
\]

Then we simply implement the conditional photonic wavefunction to derive the e-ph correlation potential. Here, we first discuss the expression of the second term in [39] that has the following analytical form in our approximation (considering \( m = 1 \)):

\[
\frac{1}{2} \langle \partial_x \chi_N^+ \partial_x \chi_N^- \rangle_q = \frac{a^2 \omega_c^2 |\phi^+|^2 |\phi^-|^2 (1 - \langle \xi_N^\pm | \xi_{N-1}^\pm \rangle^2)}{2 |\Phi_N^\pm|^4}. \tag{52}
\]

In Fig. 5 we plot the expression above for the first (upper panel) and second (lower panel) excited state calculated from the numerically exact results, reproducing the peak feature of the e-ph correlation qualitatively well. Here we can further simplify the expression of the peak for the

\[
\psi_N(x, q) = \frac{1}{\sqrt{2\nu^N}} \left[ \xi_N\phi^- \pm \xi_{N-1}^+ \phi^+ \right],
\]

with the corresponding excited-state energies

\[
E_N^\pm = N\omega_c + \frac{\alpha \pm \beta \langle \xi_N^\pm | \xi_{N-1}^\pm \rangle q}{\nu^\pm},
\]

where

\[
\nu^\pm = 1 \pm S \langle \xi_N^\pm | \xi_{N-1}^\pm \rangle q.
\]

Here \( \lambda_c \) is an associated Laguerre polynomial. From this electron-photon wavefunctions we can obtain the corresponding electronic wavefunction,

\[
\Psi_N(x) = \frac{1}{\sqrt{2\nu^N}} \left[ |\phi^-|^2 + |\phi^+|^2 \pm 2 \langle \xi_N^\pm | \xi_{N-1}^\pm \rangle q \phi^- \phi^+ \right]^{1/2},
\]

and conditional photonic wavefunction,

\[
\chi_N^\pm(q|x) = \frac{1}{\sqrt{2}} \frac{\xi_N \phi^- \pm \xi_{N-1}^+ \phi^+}{\Phi_N^\pm(x)}. \tag{51}
\]

Then we simply implement the conditional photonic wavefunction to derive the e-ph correlation potential. Here, we first discuss the expression of the second term in [39] that has the following analytical form in our approximation (considering \( m = 1 \)):

\[
\frac{1}{2} \langle \partial_x \chi_N^+ \partial_x \chi_N^- \rangle_q = \frac{a^2 \omega_c^2 |\phi^+|^2 |\phi^-|^2 (1 - \langle \xi_N^\pm | \xi_{N-1}^\pm \rangle^2)}{2 |\Phi_N^\pm|^4}. \tag{52}
\]
Now let us investigate the analytical expression for the first term of Eq. (53) that within our approximation is
\[
\langle \lambda_{x}^{N \pm} | \hat{H}_{\text{EM}} | \chi_{x}^{N \pm} \rangle = N \omega_{c} + \frac{\omega_{c}}{2} \left( \frac{|\phi^{-}|^2 - |\phi^{+}|^2}{|\hat{\Phi}_{N}|^2} \right) + f(\lambda_{c})
\]
where
\[
f(\lambda_{c}) = \frac{\lambda_{c} a x}{2} \left( \frac{|\phi^{-}|^2 - |\phi^{+}|^2}{|\hat{\Phi}_{N}|^2} \right) + \frac{\lambda_{c} a^2}{2} \left( \frac{\omega_{c} x (\xi_{N} |q| \xi_{N-1})_{q} \phi - \phi^{+}}{|\hat{\Phi}_{N}|^2} \right)
\]
While the first term of (54) gives a constant general shift, the second term gives a step-like function with the height equal to \( \omega_{c} \) as it is shown in Fig. 7 and as it can be seen in the figure, the larger the coupling constant \( \lambda_{c} \), the sharper the step around \( x = 0 \). This proves how this approximation can capture yet another essential feature of the exact \( e-ph \) correlation potential that was shown schematically in Fig. 4 and was discussed earlier in this section. Finally, as the concluding result of this work, we present the full electronic potentials \( V(x) + V\text{\textit{e-ph}}(x) \) obtained analytically approximately versus the ones calculated numerically exactly in Fig. 8 for three different \( \lambda_{c} \)'s as indicated in the figure. As it was discussed previously and can also be seen in Fig. 8, the approximate analytical expression for the \( e-ph \) correlation potential captures the essential step and peak features of the exact \( e-ph \) correlation very well. It also captures the squeezing of the wells but overestimates this feature as \( \lambda_{c} \) increases.

5 Summary and Outlook

We have extended the EF framework to study the electronic states of the correlated electron-photon systems and have shown that within this new approach to correlated electron-photon states, the electronic states are uniquely determined by addition of a scalar potential (\( e-ph \) correlation potential) and a vector potential to the uncoupled electronic Hamiltonian. For a one dimensional asymmetric double-well potential coupled to a single photon mode of a cavity with resonance frequencies, we have calculated the exact \( e-ph \) correlation potential numerically exactly and discussed their significant features namely steps, intra-well peaks and squeezing of the wells of the double-well potential. These features of the \( e-ph \) correlation potential are responsible for the polaritonic squeezing of the electronic ground-state and photon-assisted delocalization as well as polaritonic squeezing of the electronic excited-states. Although not directly related, the step-and-peak structure of the \( e-ph \) correlation potential investigated in this work is reminiscent of the step-and-peak structure of the Kohn-Sham potential of density functional theory in the dissociation limit [59][60][61].
We have furthermore derived an approximate analytical expression for the e-ph correlation of the model system studied, by extending the atomic orbitals via combining them with displaced harmonic oscillator states. In the case of the ground electronic state of the coupled electron-photon system, we have shown how our analytical approximation captures the key features of the exact e-ph correlation potential, i.e., squeezing of both wells and the elevation of the right well that leads to the polaritonic squeezing of the electronic states in the left well which is enhanced as the coupling constant increases. In the case of the first two excited states, the analytical approximation reproduces the step and peak features of the exact e-ph correlation potential that are essential to capture the photon-assisted delocalization of the electronic excited-states. In the case of the ground-state and the first two excited state discussed in this work, we have shown that while the analytical approximation captures the polaritonic squeezing of the electronic states that is enhanced as $\lambda$, increases, it overestimates this effect. In our upcoming work we will discuss how to go beyond the approximation presented here. One of the main motivation of these analytical investigations is to set the stage to utilize the time-dependent EF framework for studying the correlated electron-photon dynamics. This approach to coupled electron-photon dynamics is complementary to the recently developed TDDFT approach to cavity QED. Indeed, the e-ph correlation potential which was the heart of our investigation in this work is closely related to the correlation potential of the cavity QED (TD)DFT, therefore, the features of the e-ph correlation potential we discussed in this work together with the analytical approximation of the potential presented here are particularly relevant for developing the cavity QED (TD)DFT exchange-correlation functionals. Another interesting avenue to explore is the connection between the approach proposed here and the Born-Huang expansion for the cavity QED that has been proposed very recently.

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References

1. J. M. Raimond, M. Brune, and S. Haroche, “Manipulating quantum entanglement with atoms and photons in a cavity,” Rev. Mod. Phys., vol. 73, pp. 565–582, 2001.
2. H. Mabuchi and A. C. Doherty, “Cavity quantum electrodynamics: Coherence in context,” Science, vol. 298, pp. 1372–1377, 2002.
3. H. Walther, B. T. Varcoe, B.-G. Englert, and T. Becker, “Cavity quantum electrodynamics,” Rep. Prog. Phys., vol. 69, pp. 1325–1382, 2006.
4. A. Wallraff, D. I. Schuster, A. Blais, L. Frunzio, R.-S. Huang, J. Majer, S. Kumar, S. M. Girvin, and R. J. Schoelkopf, “Strong coupling of a single photon to a superconducting qubit using circuit quantum electrodynamics,” Nature, vol. 431, pp. 162–167, 2004.
5. A. Blais, R.-S. Huang, A. Wallraff, S. M. Girvin, and R. J. Schoelkopf, “Cavity quantum electrodynamics for superconducting electrical circuits: An architecture for quantum computation,” Phys. Rev. A, vol. 69, p. 062320, 2004.
6. T. Frey, P. J. Leek, M. Beck, A. Blais, T. Ihn, K. Ensslin, and A. Wallraff, “Dipole coupling of a double quantum dot to a microwave resonator,” Phys. Rev. Lett., vol. 108, p. 046807, 2012.
7. M. R. Delbecq, V. Schmitt, F. D. Parmentier, N. Roch, J. J. Viennot, G. Fève, B. Huard, C. Mora, A. Cottet, and T. Kontos, “Coupling a quantum dot, fermionic leads, and a microwave cavity on a chip,” Phys. Rev. Lett., vol. 107, p. 256804, 2011.
8. K. D. Petersson, L. W. McFaul, M. D. Schroer, M. Jung, J. M. Taylor, A. A. Houck, and J. R. Petta, “Circuit quantum electrodynamics with a spin qubit,” Nature, vol. 490, pp. 380–383, 2012.
9. Y.-Y. Liu, K. D. Petersson, J. Stehlik, J. M. Taylor, and J. R. Petta, “Photon emission from a cavity-coupled double quantum dot,” Phys. Rev. Lett., vol. 113, p. 036801, Jul 2014.
10. T. Schwartz, J. A. Hutchison, C. Genet, and T. W. Ebbesen, “Reversible switching of ultrastrong light-molecule coupling,” Phys. Rev. Lett., vol. 106, p. 196405, 2011.
11. T. W. Ebbesen, “Hybrid light-matter states in a molecular and material science perspective,” Accounts of Chemical Research, vol. 49, no. 11, pp. 2403–2412, 2016. PMID: 27779846.
12. 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., vol. 51, pp. 1592–1596, 2012.
13. E. Orgiu, J. George, J. A. Hutchison, E. Devaux, J. F. Dayen, B. Doudin, F. Stellacci, C. Genet, J. Schachenmayer, C. Genes, G. Pupillo, P. Samori, and T. W. Ebbesen, “Conductivity in organic semiconductors hybridized with the vacuum field,” Nature Materials, no. 14, pp. 1123–1129, 2015. arXiv:1409.1900.
14. X. Zhong, T. Cheryv, L. Zhang, A. Thomas, J. George, C. Genet, J. A. Hutchison, and T. W. Ebbesen, “Energy transfer between spatially separated entangled molecules,” Angewandte Chemie International Edition, vol. 56, no. 31, pp. 9034–9038, 2017.
15. M. Kowalewski, K. Bennett, and S. Mukamel, “Cavity femtochemistry: Manipulating nonadiabatic dynamics at avoided crossings,” The Journal of Physical Chemistry Letters, vol. 7, no. 11, pp. 2050–2054, 2016. PMID: 27186666.
16. J. Galego, F. J. García-Vidal, and J. Feist, “Cavity-induced modifications of molecular structure in the strong-coupling regime,” Phys. Rev. X, vol. 5, p. 041022, Nov 2015.
17. J. Galego, F. J. Garcia-Vidal, and J. Feist, “Suppressing photochemical reactions with quantized light fields,” Nature Comm., vol. 7, p. 13841, 2016.
18. J. Galego, F. J. Garcia-Vidal, and J. Feist, “Many-molecule reaction triggered by a single photon in polaritonic chemistry,” Phys. Rev. Lett., vol. 119, p. 136001, Sep 2017.
19. I. V. Tokatly, “Time-dependent density functional theory for many-electron systems interacting with cavity photons,” Phys. Rev. Lett., vol. 110, p. 233001, 2013.
20. M. Ruggenthaler, J. Flick, C. Pellegrini, H. Appel, I. V. Tokatly, and A. Rubio, “Quantum-electroynamical density-functional theory: Bridging quantum optics and electronic-structure theory,” Phys. Rev. A, vol. 90, p. 012508, Jul 2014.
21. C. Pellegrini, J. Flick, I. V. Tokatly, H. Appel, and A. Rubio, “Optimized effective potential for quantum electrodynamical time-dependent density functional theory,” Phys. Rev. Lett., vol. 115, p. 093001, Aug 2015.
22. M. Ruggenthaler, “Ground-state quantum-electroynamical density-functional theory,” arXiv preprint arXiv:1509.01417, 2015.
23. J. Flick, M. Ruggenthaler, H. Appel, and A. Rubio, “Kohn–sham approach to quantum electrodynamical density-functional theory: Exact time-dependent effective potentials in real space,” PNAS, vol. 112, no. 50, pp. 15285–15290, 2015.
24. J. Flick, M. Ruggenthaler, H. Appel, and A. Rubio, “Atoms and molecules in cavities, from weak to strong coupling in quantum-electroynamics (qed) chemistry,” PNAS, vol. 114, no. 12, pp. 3026–3034, 2017.
25. J. Flick, C. Schafer, M. Ruggenthaler, H. Appel, and A. Rubio, “Ab initio optimized effective potentials for real molecules in optical cavities: Photon contributions to the molecular ground state,” ACS photonics, vol. 5, no. 3, pp. 992–1005, 2018.
26. T. Dimitrov, J. Flick, M. Ruggenthaler, and A. Rubio, “Exact functionals for correlated electron–photon systems,” New Journal of Physics, vol. 19, no. 11, p. 113036, 2017.
27. P. E. Trevisanutto and M. Miletari, “Hedin equations in resonant microcavities,” Phys. Rev. B, vol. 92, p. 235303, Dec 2015.
28. G. Hunter, “Conditional probability amplitudes in wave mechanics,” International Journal of Quantum Chemistry, vol. 9, no. 2, pp. 237–242, 1975.
29. N. I. Gidopoulos and E. K. U. Gross, “Electronic nonadiabatic states: towards a density functional theory beyond the Born-Oppenheimer approximation,” Phil. Trans. R. Soc. A, vol. 372, p. 20130059, 2014.
30. A. Abedi, N. T. Maitra, and E. K. U. Gross, “Exact factorization of the time-dependent electron-nuclear wave function,” Phys. Rev. Lett., vol. 105, no. 12, p. 123002, 2010.
31. E. A. Power and S. Zienau, “Coulomb gauge in nonrelativistic quantum electro-dynamics and the shape of spectral lines,” Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, vol. 251, no. 999, pp. 427–454, 1959.
32. R. G. Woolley, “Molecular quantum electrodynamics,” Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, vol. 321, no. 1547, pp. 557–572, 1971.
33. M. Babiker and R. Loudon, “Derivation of the power-zienau-woolley hamiltonian in quantum electrodynamics by gauge transformation,” Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, vol. 385, no. 1789, pp. 439–460, 1983.
34. L. S. Cederbaum, “The exact molecular wavefunction as a product of an electronic and a nuclear wavefunction,” The Journal of Chemical Physics, vol. 138, no. 22, p. 224110, 2013.
35. A. Abedi, N. T. Maitra, and E. K. U. Gross, “Correlated electron-nuclear dynamics: Exact factorization of the molecular wave-function,” J. Chem. Phys., vol. 137, no. 22, p. 22A530, 2012.
36. A. Abedi, N. T. Maitra, and E. K. U. Gross, “Reply to comment on ‘Correlated electron-nuclear dynamics: Exact factorization of the molecular wave-function’”, J. Chem. Phys., vol. 139, no. 8, p. 087102, 2013.
37. A. Abedi, F. Agostini, Y. Suzuki, and E. K. U. Gross, “Dynamical steps that bridge piecewise adiabatic shapes in the exact time-dependent potential energy surface,” Phys. Rev. Lett., vol. 110, no. 26, p. 263001, 2013.
38. F. Agostini, A. Abedi, Y. Suzuki, and E. K. U. Gross, “Mixed quantum-classical dynamics on the exact time-dependent potential energy surfaces: A novel perspective on nonadiabatic processes,” Mol. Phys., vol. 111, no. 22-23, p. 3625, 2013.
39. A. Abedi, F. Agostini, and E. K. U. Gross, “Mixed quantum-classical dynamics from the exact decomposition of electron-nuclear motion,” Europhys. Lett., vol. 106, no. 3, p. 33001, 2014.
40. F. Agostini, A. Abedi, and E. K. U. Gross, “Classical nuclear motion coupled to electronic non-adiabatic transitions,” J. Chem. Phys., vol. 141, no. 21, p. 214101, 2014.
41. F. Agostini, A. Abedi, Y. Suzuki, S. K. Min, N. T. Maitra, and E. K. U. Gross, “The exact electronic back-reaction on classical nuclei in non-adiabatic charge transfer,” J. Chem. Phys., vol. 142, no. 8, p. 084303, 2015.
42. A. Schild, F. Agostini, and E. K. U. Gross, “A study of the electronic flux density in the born-oppenheimer limit,” To be submitted.
43. F. Agostini, S. K. Min, A. Abedi, and E. K. U. Gross, “Quantum-classical nonadiabatic dynamics: Coupled- vs independent-trajectory methods,” Journal of Chemical Theory and Computation, vol. 12, no. 5, pp. 2127–2143, 2016. PMID: 27030209.
44. B. F. E. Curchod and F. Agostini, “On the dynamics through a conical intersection,” The Journal of Physical Chemistry Letters, vol. 8, no. 4, pp. 831–837, 2017. PMID: 28151670.
45. S. K. Min, F. Agostini, I. Taveneri, and E. K. U. Gross, “Ab initio nonadiabatic dynamics with coupled trajectories: A rigorous approach to quantum (de)coherence,” The Journal of Physical Chemistry Letters, vol. 8, no. 13, pp. 3048–3055, 2017. PMID: 28618782.
46. A. Scherrer, F. Agostini, D. Sebastiani, E. K. U. Gross, and R. Vuilleumier, “On the mass of atoms in molecules: Beyond the born-oppenheimer approximation,” Phys. Rev. X, vol. 7, p. 031035, Aug 2017.
47. J.-K. Ha, I. S. Lee, and S. K. Min, “Surface hopping dynamics beyond nonadiabatic couplings for quantum coherence,” The Journal of Physical Chemistry Letters, vol. 9, no. 5, pp. 1097–1104, 2018. PMID: 29439572.
48. S. K. Min, A. Abedi, K. S. Kim, and E. K. U. Gross, “Is the molecular berry phase an artifact of the born-oppenheimer approximation?”, Phys. Rev. Lett., vol. 113, no. 26, p. 263004, 2014.
49. R. Requist, F. Tandetzky, and E. K. U. Gross, “Molecular geometric phase from the exact electron-nuclear factorization,” Phys. Rev. A, vol. 93, p. 042108, Apr 2016.
50. R. Requist and E. K. U. Gross, “Exact factorization-based density functional theory of electrons and nuclei,” *Phys. Rev. Lett.*, vol. 117, p. 193001, Nov 2016.

51. Y. Suzuki, A. Abedi, N. T. Maitra, K. Yamashita, and E. K. U. Gross, “Electronic Schrödinger equation with nonclassical nuclei,” *Phys. Rev. A*, vol. 89, no. 4, p. 040501(R), 2014.

52. Y. Suzuki, A. Abedi, N. T. Maitra, and E. K. U. Gross, “Laser-induced electron localization in H\(_2^+\): Mixed quantum-classical dynamics based on the exact time-dependent potential energy surface,” *Phys. Chem. Chem. Phys.*, vol. 17, pp. 29271–29280, 2015.

53. E. Khosravi, A. Abedi, and N. T. Maitra, “Exact potential driving the electron dynamics in enhanced ionization of h\(_2^+\),” *Physical review letters*, vol. 115, no. 26, p. 263002, 2015.

54. E. Khosravi, A. Abedi, A. Rubio, and N. T. Maitra, “Electronic non-adiabatic dynamics in enhanced ionization of isotopologues of hydrogen molecular ions from the exact factorization perspective,” *Physical Chemistry Chemical Physics*, vol. 19, no. 12, pp. 8269–8281, 2017.

55. A. Schild and E. K. U. Gross, “Exact single-electron approach to the dynamics of molecules in strong laser fields,” *Phys. Rev. Lett.*, vol. 118, p. 163202, Apr 2017.

56. N. M. Hoffmann, H. Appel, A. Rubio, and N. T. Maitra, “Light-matter interactions via the exact factorization approach,” *arXiv preprint arXiv:1803.02020*, 2018.

57. E. Irish, J. Gea-Banacloche, I. Martin, and K. Schwab, “Dynamics of a two-level system strongly coupled to a high-frequency quantum oscillator,” *Physical Review B*, vol. 72, no. 19, p. 195410, 2005.

58. A. Abedi, E. Khosravi, and I. Tokatly *In preparation*, 2018.

59. N. Helbig, I. Tokatly, and A. Rubio, “Exact kohn–sham potential of strongly correlated finite systems,” *The Journal of chemical physics*, vol. 131, no. 22, p. 224105, 2009.

60. O. V. Gritsenko and E. J. Baerends, “Electron correlation effects on the shape of the kohn–sham molecular orbital,” *Theoretical Chemistry Accounts*, vol. 96, pp. 44–50, Apr 1997.

61. D. G. Tempel, T. J. Martinez, and N. T. Maitra, “Revisiting molecular dissociation in density functional theory: a simple model,” *Journal of chemical theory and computation*, vol. 5, no. 4, pp. 770–780, 2009.

62. A. Abedi, E. Khosravi, and I. Tokatly *In preparation*, 2018.

63. C. Schafer, M. Ruggenthaler, and A. Rubio, “Insights from ab-initio non-relativistic quantum electrodynamics: Bridging quantum chemistry and quantum optics,” *arXiv preprint arXiv:1804.00923*, 2018.