Supplemental Information to Making *ab initio* QED functional(s): Non-perturbative and photon-free effective frameworks for strong light-matter coupling

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I. PHOTON OBSERVABLES IN THE TRUNCATED PHEG BASIS

The Bogoliubov and coherent shift transformations of $\hat{a}_\alpha, \hat{a}_\alpha^\dagger$ mentioned in Sec. 3 (main text) can be combined as

$$\hat{c}_\alpha = \sqrt{\frac{\tilde{\omega}_\alpha}{4\omega_\alpha}}\left(\hat{a}_\alpha^\dagger + \hat{a}_\alpha\right) - \sqrt{\frac{\omega_\alpha}{4\tilde{\omega}_\alpha}}\left(\hat{a}_\alpha^\dagger - \hat{a}_\alpha\right) + \hat{\beta}_\alpha \ ,$$

with the back transformation

$$\hat{a}_\alpha = \frac{1}{2}\left(\sqrt{\frac{\omega_\alpha}{\tilde{\omega}_\alpha}}\left(\hat{c}_\alpha^\dagger + \hat{c}_\alpha\right) - \sqrt{\frac{\tilde{\omega}_\alpha}{\omega_\alpha}}\left(\hat{c}_\alpha^\dagger - \hat{c}_\alpha\right)\right) - \sqrt{\frac{\omega_\alpha}{\tilde{\omega}_\alpha}}\hat{\beta}_\alpha \ .$$

In a photon-free approach that ignores excited states of $\hat{c}_\alpha^\dagger\hat{c}_\alpha$ the photon number operator for mode α is thus found to be $\hat{a}_\alpha^\dagger\hat{a}_\alpha = \frac{\omega_\alpha}{\tilde{\omega}_\alpha}\hat{\beta}_\alpha^2$. In the limits $\omega_\alpha \to 0$ and $\omega_\alpha \to \infty$ this operator goes to zero as expected. The expectation value of the photon number operator for the pHEG ground state with $\beta_\alpha(\mathbf{K}) = 0$ and $n_\alpha = 0$ is found to be $\langle\hat{a}_\alpha^\dagger\hat{a}_\alpha\rangle = (\tilde{\omega}_\alpha - \omega_\alpha)^2/(4\tilde{\omega}_\alpha\omega_\alpha)$ [1] (the factor two in the reference comes from taking two different polarization directions into account).

A benchmark calculation is displayed in Fig. 1 and shows a rapid increase in accuracy including just a few excitation numbers in a truncated pHEG basis. This special feature of the pHEG approximation is further highlighted by plotting the excitation-number distribution, i.e., the probability to find the system in each excitation-number sector, see Fig. 2. For small excitation numbers the pHEG basis shows a much quicker decrease, meaning a higher accuracy if the basis is truncated at low excitation numbers.

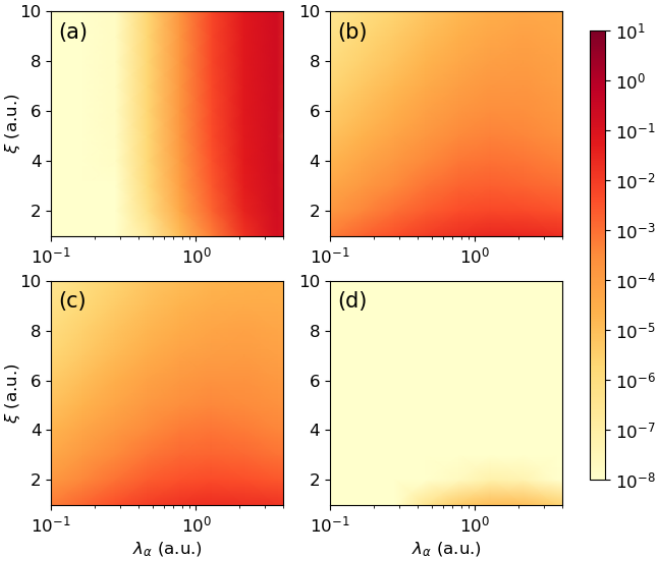

Figure 1: Absolute deviation of the photon number in the ground state compared to a Pauli-Fierz reference solution for a tunable one-dimensional soft-Coulomb hydrogen $v(x) = -1/\sqrt{x^2+\xi^2}$ coupled to a single cavity mode. (a) Pauli-Fierz Hamiltonian with $\max n_\alpha = 4$ excitations, (b) pHEG basis with $\max n_\alpha = 0$ and the original potential v, (c) pHEG basis with $\max n_\alpha = 0$ but mollified potential $v * m_\alpha^{0,0}$, (d) pHEG basis with $\max n_\alpha = 4$. The result is similar to Fig. 4 (main text), just with a lesser benefit from the mollified potential. The electronic dimension has 41 k-points on a periodic grid. The reference solution was obtained using the Pauli-Fierz Hamiltonian with 100 photonic excitations. The displayed parameter area is smaller than in Fig. 4 (main text) in order to limit it to values where the reference solution has converged.

II. BENCHMARK FOR A DOUBLE-WELL POTENTIAL

The soft-Coulomb potential represents the simplest imaginable realization of an atomic/molecular system. Potentials with a single charge-center, e.g., periodic cosine and harmonic potentials, provided similar benchmark results. A double-well potential, a common model to describe phase-transitions [2] and molecular reactivity [3], provides an alternative point-of-view for the benchmark as two separate charge centers are present. Using

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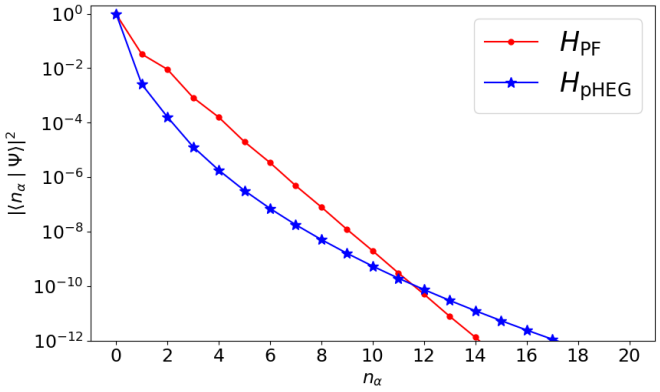

Figure 2: Excitation-number distribution for the ground state with a pHEG basis compared to a Pauli-Fierz reference solution for a one-dimensional soft-Coulomb potential with $\xi = 1$ coupled to a single cavity mode with $\lambda_\alpha = 1$. The electronic dimension has 41 k-points on a periodic grid. The photon filling in the low-number sectors in considerably reduced in the pHEG basis which makes the truncation at low excitation numbers numerically accurate.

the potential $v_{ext}(x) = \frac{1}{20}[-x^2 + \frac{1}{25}x^4]$, Fig. 3-5 illustrates the performance of the various developed approximations. All approximations capture the overall tendency to localize charge in the individual wells, similar to previous investigations [2, 4, 5]. The photon-free construction and the photon-coupled HEG basis provide therefore still very good predictions for this model. While the LDA has the right tendency, it underestimates the influence of the field and stays too strongly delocalized. This is well in line with the failures of ordinary DFT, where also there it is common for the LDA to delocalize density too strongly. The latter aspect is why LDA+U, i.e., adding local strong correlation to specific orbitals, obtained over the past years increasing interest as it targets specifically this short-coming. A similar local correlation could be considered in the presented framework.

III. MINIMAL-COUPLING PHOTON-EXCHANGE APPROXIMATION

The static Pauli-Fierz Hamiltonian in full minimal coupling in SI units takes the form [6, 7]

$$\begin{aligned}\hat{H}(t) =& \sum_{i=1}^{N_e} \frac{1}{2m}\left(-\mathrm{i}\hbar\nabla_i - \frac{q}{c}\hat{\mathbf{A}}(\mathbf{r}_i)\right)^2 + \sum_{i=1}^{N_e} \underbrace{q a_0(\mathbf{r}_i)}_{=v(\mathbf{r}_i)} \\ &- \sum_{i=1}^{N_e} \frac{q}{2mc}\boldsymbol{\sigma}_i \cdot \left(\nabla_i \times \hat{\mathbf{A}}(\mathbf{r}_i)\right) + \frac{1}{4\pi\epsilon_0}\sum_{i<j}^{N_e} \frac{q^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &+ \sum_{s=1}^{2} \int \hbar\omega(\mathbf{k})\hat{a}^\dagger(\mathbf{k}, s)\hat{a}(\mathbf{k}, s)\mathrm{d}\mathbf{k} \ ,\end{aligned}$$

where additionally an external current can be coupled to the photon subsystem to establish the basic mapping the-

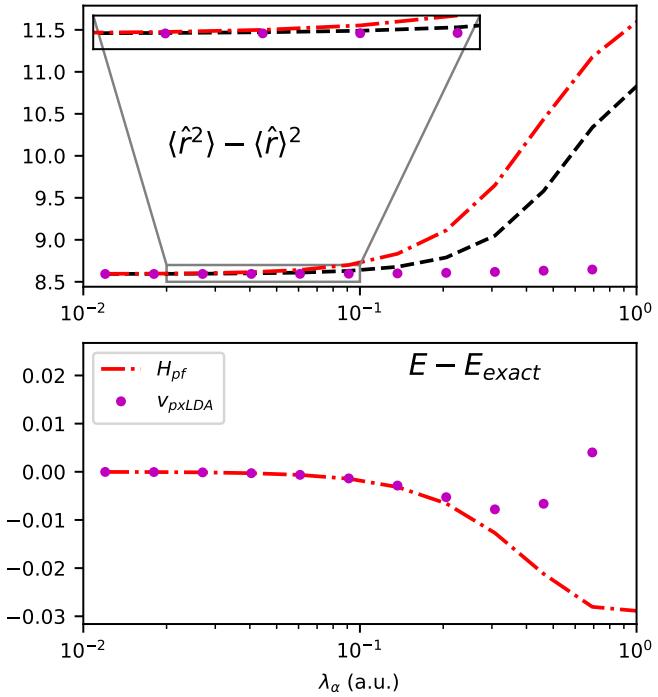

Figure 3: To Fig. 5 (main text) equivalent benchmark using a double-well potential. The ground-state variance and energy difference shows that the photon-free construction provides a qualitatively good description of the accumulation of the charge in each well. We limited the investigation here to a reasonable range up to $\lambda = 1.038$ *a.u.*. For extreme couplings values and depending on the chosen potential, the renormalization can be so drastic, that the electronic density is localized on top of the barrier at $x = 0$ in order to minimize the dipole-fluctuations. This configuration is clearly unstable against any numerical perturbation which impairs the numerical solvers.

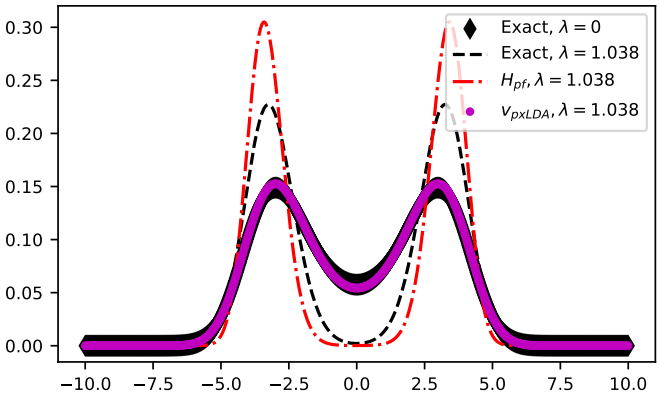

Figure 4: Real-space electronic density for the double-well potential. The local-density approximation is compared to the photon-free and exact solution at $\lambda = 1.038$ *a.u.* and $\lambda = 0$ *a.u.*. While the LDA has the right tendency, it underestimates the influence of the field and stays too strongly delocalized.

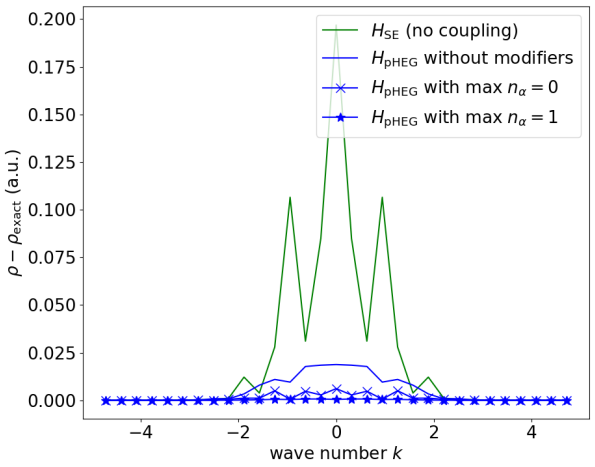

Figure 5: Momentum-space density deviation from the exact result for the double-well potential using different levels of approximation. Already for a cutoff at a single excitation in the pHEG basis we see perfect agreement. Parameters are as before.

orem of ground-state QEDFT [7, 8]. The vector potential operator in Coulomb gauge is given by

$$\hat{\mathbf{A}}(\mathbf{r}) = \sqrt{\frac{\hbar c^2}{\epsilon_0 (2\pi)^3}} \int \frac{\mathrm{d}\mathbf{k}}{\sqrt{2\omega_k}} \sum_{s=1}^{2} \boldsymbol{\epsilon}(\mathbf{k}, s) \left[\hat{a}(\mathbf{k}, s) \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} + \hat{a}^\dagger(\mathbf{k}, s) \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \right].$$

We use the usual definitions for the frequency $\omega(\mathbf{k}) = c|\mathbf{k}|$, the bosonic creation and annihilation field operators $\hat{a}^\dagger(\mathbf{k}, s)$ and $\hat{a}(\mathbf{k}, s)$, as well as for the polarization unit vectors $\boldsymbol{\epsilon}(\mathbf{k}, s)$ for the continuum of free-space modes indicated by their wave vector $\mathbf{k}$ and the two physical polarization directions s. Further, $a^0(\mathbf{r})$ is a scalar external vector potential and $\boldsymbol{\sigma}$ denotes a vector of the 2×2 Pauli matrices in the Stern-Gerlach term. The Pauli-Fierz Hamiltonian can be derived either by taking the non-relativistic limit of the Dirac Hamiltonian [7], where the Stern-Gerlach term appears naturally, or by quantizing the Abraham model of classical radiation-reactions with an *ad hoc* inclusion of the Stern-Gerlach term [6]. In order for the Pauli-Fierz Hamiltonian to be well-defined we need to include an ultra-violet cutoff and we further note that m is the bare mass of the electrons. The main reason for working in SI units in this appendix is to keep track of the difference between bare and physical mass.

Following the discussion in the main text we will use two basic equations of motion to establish the minimal-coupling px approximation. The first one is the operator form of the Maxwell's equation in the Heisenberg picture [7, 8]

$$\left(\frac{1}{c^2} \frac{\mathrm{d}}{\mathrm{d}t} - \nabla^2 \right) \hat{\mathbf{A}}_{\mathrm{H}}(\mathbf{r}, t) = \mu_0 c q \, \hat{\mathbf{j}}_{\perp,\mathrm{H}}(\mathbf{r}, t), \qquad (1)$$

where the physical-current-density operator in the Schrödinger picture is

$$\hat{\mathbf{j}}(\mathbf{r}) = \hat{\mathbf{j}}_{\mathrm{p}}(\mathbf{r}) + \hat{\mathbf{j}}_{\mathrm{d}}(\mathbf{r}) + \hat{\mathbf{j}}_{\mathrm{m}}(\mathbf{r}).$$

The additional $\perp$ indicates that we only consider the divergence-free part due to the Coulomb gauge [7, 8] and the first term in the total current density is the paramagnetic current density

$$\hat{\mathbf{j}}_{\mathrm{p}}(\mathbf{r}) = \frac{\hbar}{2m\mathrm{i}} \sum_{i=1}^{N_e} \left(\delta(\mathbf{r} - \mathbf{r}_i) \overrightarrow{\nabla}_i - \overleftarrow{\nabla}_i \delta(\mathbf{r} - \mathbf{r}_i) \right) ,$$

the second term is the diamagnetic current density

$$\hat{\mathbf{j}}_{\mathrm{d}}(\mathbf{r}) = -\frac{q}{mc} \sum_{i=1}^{N_e} \delta(\mathbf{r} - \mathbf{r}_i) \hat{\mathbf{A}}(\mathbf{r}) ,$$

and the last one is the magnetization current due to the Stern-Gerlach term

$$\hat{\mathbf{j}}_{\mathrm{m}}(\mathbf{r}) = \sum_{i=1}^{N_e} \frac{\hbar}{2m} \left(\delta(\mathbf{r} - \mathbf{r}_i) \overrightarrow{\nabla}_i \times \boldsymbol{\sigma}_i + \overleftarrow{\nabla}_i \times \boldsymbol{\sigma}_i \delta(\mathbf{r} - \mathbf{r}_i) \right) .$$

The second equation of motion, which will be enough to investigate the static case in analogy to the main text, is the (component wise) paramagnetic equation of motion [7, 8]

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \hat{j}^k_{\mathrm{p,H}}(\mathbf{r}, t) &= \hat{F}^k_{T,\mathrm{H}}(\mathbf{r}, t) + \hat{F}^k_{W,\mathrm{H}}(\mathbf{r}, t) \qquad (2) \\ &+ \frac{q}{mc} \sum_{l=1}^{3} \left[\hat{A}^l_{\mathrm{H}}(\mathbf{r}, t) \partial_l \hat{j}^k_{\mathrm{p,H}}(\mathbf{r}, t) + \left(\partial_k \hat{A}^l_{\mathrm{H}}(\mathbf{r}, t) \right) \hat{j}^l_{\mathrm{p,H}}(\mathbf{r}, t) \right] \\ &- \frac{1}{m} \left[\partial_k \left(\frac{q^2}{2mc^2} \hat{\mathbf{A}}_{\mathrm{H}}(\mathbf{r}, t)^2 + v(\mathbf{r}) \right) \right] \hat{\rho}_{\mathrm{H}}(\mathbf{r}, t) \\ &+ \frac{q}{mc} \sum_{l,m,n=1}^{3} \left(\partial_k \partial_l \hat{A}^m_{\mathrm{H}}(\mathbf{r}, t) \right) \epsilon^{lmn} \hat{\mu}^n_{\mathrm{H}}(\mathbf{r}, t) , \end{aligned}$$

where ϵ^{lmn} is the anti-symmetric Levi-Civita symbol and

$$\begin{aligned} \hat{\mathbf{F}}_T(\mathbf{r}) &= \frac{\mathrm{i}\hbar^2}{2m} \left[\hat{\mathbf{j}}_{\mathrm{p}}(\mathbf{r}), \sum_i \nabla_i^2 \right] , \\ \hat{\mathbf{F}}_W(\mathbf{r}) &= -\frac{\mathrm{i}}{4\pi\epsilon_0} \left[\hat{\mathbf{j}}_{\mathrm{p}}(\mathbf{r}), \sum_{i<j}^{N_e} \frac{q^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] , \\ \hat{\boldsymbol{\mu}}(\mathbf{r}) &= \frac{\hbar}{2m} \sum_i \boldsymbol{\sigma}_i \delta(\mathbf{r} - \mathbf{r}_i) . \end{aligned}$$

Using now a Pauli-Kohn-Sham system with the exact $\mathbf{A}(\mathbf{r}) = \langle \hat{\mathbf{A}}(\mathbf{r}) \rangle$ from the Maxwell-Kohn-Sham equation [8] we get the same Eq. (2), where instead of $\hat{\mathbf{A}}(\mathbf{r})$ we just use the expectation value (mean-field) $\mathbf{A}(\mathbf{r})$ and replace $v(\mathbf{r})$ by $v_{\mathrm{s}}(\mathbf{r})$. Using now that $v_{\mathrm{Mxc}}(\mathbf{r}) = v_{\mathrm{s}}(\mathbf{r}) - v(\mathbf{r})$ we find (suppressing the $\mathbf{r}$ dependency)

$$\nabla^2 v_{\rm Mxc} = m\sum_{k=1}^{3}\partial_k\frac{1}{\rho}\Big[F_T^k[\Phi]-F_T^k[\Psi]-F_W^k[\Psi]-\frac{q}{mc}\sum_{l=1}^{3}\Big(\langle\hat{A}^l\partial_l\hat{j}_{\rm p}^k\rangle-A^l\partial_l j_{\rm p}^k[\Phi]+\Big\langle\Big(\partial_k\hat{A}^l\Big)\,\hat{j}_{\rm p}^l\Big\rangle-\big(\partial_k A^l\big)\,j_{\rm p}^l[\Phi]\Big)$$
$$+\frac{1}{m}\left(\left\langle\left(\partial_k\frac{q^2}{2mc^2}\hat{\mathbf{A}}^2\right)\hat{\rho}\right\rangle-\left(\partial_k\frac{q^2}{2mc^2}\mathbf{A}^2\right)\rho\right)-\frac{q}{mc}\sum_{l,m,n=1}^{3}\Big(\Big\langle\Big(\partial_k\partial_l\hat{A}^m\Big)\,\epsilon^{lmn}\hat{\mu}^n\Big\rangle-\left(\partial_k\partial_l A^m\right)\epsilon^{lmn}\mu^n[\Phi]\Big)\Big]\ . \tag{3}$$

Again, the major issue is to find a reasonable approximation for the explicit light-matter coupling terms. Following the discussion in the main text we solve Eq. (1) formally, consider the fluctuations about the mean-field $\Delta\hat{\mathbf{A}}(\mathbf{r})$ and replace

$$\Delta\hat{\mathbf{A}}(\mathbf{r})\to\frac{q}{4\pi\epsilon_0 c}\int\frac{\Delta\hat{\mathbf{j}}_\perp(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' \tag{4}$$

in Eq. (3) (in a symmetrized manner as discussed in the main text) and use $\Psi\to\Phi$ throughout. In this way, we have defined the corresponding minimal-coupling px approximation, where the usual quantum-mechanical Hx part is defined by Eq. (14) (main text).

Assuming now that the induced fields have wavelengths that are much larger than the extension of the matter subsystem of interest, we can make the long-wavelength approximation for the px potential. Considering Eq. (3), the only term that is not strongly suppressed in this case is

$$\frac{q}{mc}\sum_{l=1}^{3}\Big(\Big\langle\hat{A}^l\partial_l\hat{j}_{\rm p}^k\Big\rangle-A^l\partial_l j_{\rm p}^k[\Phi]\Big)$$
$$\longrightarrow\frac{q}{mc}\Big(\Big\langle\big(\hat{\mathbf{A}}\cdot\nabla\big)\hat{\mathbf{j}}_{\rm p}\Big\rangle-(\mathbf{A}\cdot\nabla)\mathbf{j}_{\rm p}[\Phi]\Big)\ .$$

Since in the long-wavelength limit also the Stern-Gerlach term vanishes, the physical current is just $\hat{\mathbf{j}}(\mathbf{r})=\hat{\mathbf{j}}_{\rm p}(\mathbf{r})+\hat{\mathbf{j}}_{\rm d}(\mathbf{r})$. Furthermore, replacing the Green's function of the free-space Laplacian by its periodic finite-volume counterpart

$$\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}\to\sum_{\boldsymbol{n}\in\mathbb{Z}^3}\frac{1}{V\mathbf{k}_{\boldsymbol{n}}^2}\mathrm{e}^{\mathrm{i}\mathbf{k}_{\boldsymbol{n}}\cdot(\mathbf{r}-\mathbf{r}')}\ , \tag{5}$$

where $\mathbf{k}_{\boldsymbol{n}}=\frac{2\pi}{L}\boldsymbol{n}$ and $V=L^3$, we can express Eq. (4) explicitly by

$$\Delta\hat{\mathbf{A}}(\mathbf{r})=\frac{q}{\epsilon_0 c}\sum_{\boldsymbol{n},s}\frac{\boldsymbol{\epsilon}_{\boldsymbol{n},s}}{V\mathbf{k}_{\boldsymbol{n}}^2}\int\mathrm{e}^{\mathrm{i}\mathbf{k}_{\boldsymbol{n}}\cdot(\mathbf{r}-\mathbf{r}')}\boldsymbol{\epsilon}_{\boldsymbol{n},s}\cdot\Delta\hat{\mathbf{j}}(\mathbf{r}')\mathrm{d}\mathbf{r}'\ .$$

If we now denote $\alpha\equiv(\boldsymbol{n},s)$, $S_\alpha(\mathbf{r})=\exp(\mathrm{i}\mathbf{k}_{\boldsymbol{n}}\cdot\mathbf{r})/\sqrt{V}$, $\lambda_\alpha(\mathbf{r})=S_\alpha(\mathbf{r})\sqrt{1/\epsilon_0}$ and $\omega_{\rm d}^2=q^2N/(m\epsilon_0 V)$ this becomes in the long-wavelength limit

$$\Delta\hat{\mathbf{A}}=\frac{c}{qN}\sum_\alpha\boldsymbol{\epsilon}_\alpha\frac{\omega_{\rm d}^2}{\omega_\alpha^2}\boldsymbol{\epsilon}_\alpha\cdot\Big(\Delta\hat{\mathbf{J}}_{\rm p}-\Delta\hat{\mathbf{J}}_{\rm d}\Big)\,, \tag{6}$$

where $\hat{\mathbf{J}}_{\rm p}=-\mathrm{i}\hbar\sum_i\nabla_i$ and $\hat{\mathbf{J}}_{\rm d}=\frac{q}{c}N_e\hat{\mathbf{A}}$. Eq. 6 can then be solved for $\hat{\mathbf{A}}$ by the Bogoliubov transformation introduced in Materials and Methods which leads to the new frequencies $\tilde{\omega}_\alpha$ and polarization vectors $\tilde{\boldsymbol{\epsilon}}_\alpha$. If we further allow to take into account a cavity in the long-wavelength limit by changing the λ_α and $\boldsymbol{\epsilon}_\alpha$, only keep a few effective modes, subsume the rest of the modes in the physical mass of the electrons $m\to m_{\rm e}$ and use atomic units ($\hbar=|e|=m_{\rm e}=1/(4\pi\epsilon_0)=1$), we recover exactly the case of the main text. We note that for the sake of consistency, if we change the local form of the modes by hand, also the longitudinal modes will change as can be seen from Eq. (5). We therefore use a generic $w(\mathbf{r},\mathbf{r}')$ in the main text to accommodate also this eventuality.

This connection to the long-wavelength limit also directly shows that if we go beyond the dipole approximation, in lowest order we can just re-substitute $\lambda_\alpha\to\lambda_\alpha(\mathbf{r})$ and $\boldsymbol{\epsilon}_\alpha\to\boldsymbol{\epsilon}_\alpha(\mathbf{r})$.

IV. TIME-DEPENDENT PHOTON-EXCHANGE APPROXIMATION

In the time-dependent case the simple idea that the interacting and the auxiliary system have both the same (zero) paramagnetic currents does no longer hold. Various choices for the basic variables of QEDFT are possible [7, 9]. The one that is most consistent with our static discussion is to make the physical currents the same in both systems. This is then a more general setting for the long-wavelength situation than the usual density-based QEDFT [7, 9].

We therefore use the orbital equations (here again in atomic units)

$$\mathrm{i}\partial_t\varphi_i(\mathbf{r},t)=\left[\frac{1}{2}\left(-\mathrm{i}\nabla+\frac{1}{c}\mathbf{A}_s(\mathbf{r},t)\right)^2+v_s(\mathbf{r},t)\right]\varphi_i(\mathbf{r},t)\ , \tag{7}$$

for the Kohn-Sham system, whereas in the static case we only had the spatially independent $\mathbf{A}_s=\mathbf{A}$. In the static case this homogeneous effective field can be discarded without loss of generality. It corresponds to a trivial global gauge transformation. For the interacting system the basic equation of motion for the matter is [7, 8]

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{j}(\mathbf{r},t)=\mathbf{F}_T([\Psi],\mathbf{r},t)+\mathbf{F}_W([\Psi],\mathbf{r},t) \tag{8}$$
$$-\frac{1}{c}\Big\langle\big(\hat{\mathbf{A}}_{\rm H}(t)\cdot\nabla\big)\hat{\mathbf{j}}_{\rm p,H}(\mathbf{r},t)\Big\rangle-\rho(\mathbf{r},t)\nabla v(\mathbf{r},t)$$
$$-\frac{1}{c}\Big\langle\hat{\mathbf{A}}_{\rm H}(t)\big(\nabla\cdot\hat{\mathbf{j}}_{\rm H}(\mathbf{r},t)\big)\Big\rangle-\Big\langle\hat{\mathbf{E}}_{\rm H}(t)\hat{\rho}_{\rm H}(\mathbf{r},t)\Big\rangle\,,$$

where the physical current in the Schrödinger picture is $\hat{\mathbf{j}}(\mathbf{r}) = \hat{\mathbf{j}}_\mathrm{p}(\mathbf{r}) + \frac{N_e}{c}\hat{\mathbf{A}}$ and $-\frac{1}{c}\partial_t \hat{\mathbf{A}}_\mathrm{H}(t) = \hat{\mathbf{E}}_\mathrm{H}(t)$. Here $\langle\cdot\rangle$ indicates to evaluate the expectation value with a fixed initial state of the coupled light-matter system Ψ, which will usually be the ground state of the Pauli-Fierz Hamiltonian Eq. (1) (main text). The corresponding equation of motion for the Kohn-Sham system is then (see also discussion in SI Sec. III, while the Stern-Gerlach part is now omitted in accordance with Eq. (7))

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t} j^k(\mathbf{r},t) = F_T^k([\Phi],\mathbf{r},t) \\
&- \frac{1}{c}\sum_{l=1}^{3}\left[A_\mathrm{s}^l(\mathbf{r},t)\partial_l j_\mathrm{p}^k([\Phi],\mathbf{r},t) + \left(\partial_k A_\mathrm{s}^l(\mathbf{r},t)\right) j_\mathrm{p}^l([\Phi],\mathbf{r},t)\right] \\
&- \left[\partial_k\left(\frac{1}{2c^2}\mathbf{A}_\mathrm{s}(\mathbf{r},t)^2 + v_s(\mathbf{r},t)\right)\right]\rho(\mathbf{r},t) \\
&+ \frac{1}{c}\left(\partial_t A_\mathrm{s}^k(\mathbf{r},t)\right)\rho(\mathbf{r},t) - \frac{1}{c}A_\mathrm{s}^k(\mathbf{r},t)\nabla\cdot\mathbf{j}(\mathbf{r},t)\ ,
\end{aligned}$$

where we have already used that it generates the same density and current density as the interacting reference system. In general, we would also have contributions due to an external vector potential in Coulomb gauge $\mathbf{A}_\mathrm{ext}(\mathbf{r},t)$ in Eq. (8), which is then used to derive the basic mapping theorems [7, 9]. But since we are only interested in the case where $\mathbf{A}_\mathrm{ext} \equiv 0$ here, we have skipped this possibility from the start for notational simplicity.

We can then define the Mxc potentials via

$$\begin{aligned}
\partial_k v_\mathrm{Mxc} - \frac{1}{c}\partial_t A_\mathrm{Mxc}^k = \frac{1}{\rho}\Bigg[&F_T^k[\Phi] - F_T^k[\Psi] - F_W^k[\Psi] \\
&- \frac{1}{c}\sum_{l=1}^{3}\left(A_\mathrm{Mxc}^l\partial_l j_\mathrm{p}^k[\Phi] + \left(\partial_k A_\mathrm{Mxc}^l\right) j^l\right) \\
&- \frac{1}{c}\sum_{l=1}^{3} A_\mathrm{Mxc}^k\partial_l j^l + \frac{1}{c}\sum_{l=1}^{3}\left\langle \hat{A}_\mathrm{H}^l\partial_l\hat{j}_\mathrm{p,H}^k\right\rangle \\
&+ \frac{1}{c}\sum_{l=1}^{3}\left\langle \hat{A}_\mathrm{H}^k\partial_l\hat{j}_\mathrm{H}^l\right\rangle + \left\langle \hat{E}_\mathrm{H}^k\hat{\rho}_\mathrm{H}\right\rangle\Bigg]\ ,
\end{aligned} \tag{9}$$

where we used $v_\mathrm{Mxc} = v_s - v$ and $\mathbf{A}_\mathrm{Mxc} = \mathbf{A}_\mathrm{s} - \mathbf{A}_\mathrm{ext}$. Now, denoting the right-hand side of Eq. (9) by $Q^k[\Phi,\Psi]$, we can use the Helmholtz decomposition to find in accordance with the main text the (longitudinal) scalar Mxc potential

$$\nabla^2 v_\mathrm{Mxc}(\mathbf{r},t) = \nabla\cdot\boldsymbol{Q}([\Phi,\Psi],\mathbf{r},t) \tag{10}$$

and the (transverse) vector Mxc potential

$$-\partial_t\mathbf{A}_\mathrm{Mxc}(\mathbf{r},t) = c\boldsymbol{Q}_\perp([\Phi,\Psi],\mathbf{r},t)\ .$$

In the static case, where the paramagnetic and diamagnetic contributions are individually zero, all the diamagnetic parts cancel and $\mathbf{A}_\mathrm{Mxc} \equiv 0$ and we are left with Eq. (10) only.

Again, we need to find an approximation to the photonic part in terms of Kohn-Sham quantities. As a first step we rewrite $\mathbf{A}_\mathrm{Mxc}(\mathbf{r},t) = \mathbf{A}(t) + \mathbf{A}_\mathrm{xc}(\mathbf{r},t)$ such that we can shift $\mathbf{A}(t)$ to form the fluctuation operator $\Delta\hat{\mathbf{A}}$ in Eq. (9). Then we follow the strategy of the static case and employ the mode-resolved inhomogeneous Maxwell's equation for $\hat{A}^k = \sum_\alpha \hat{A}_\alpha\tilde{\epsilon}_\alpha^k$, which becomes

$$\left(\partial_t^2 + \tilde{\omega}_\alpha^2\right)\hat{A}_{\alpha,\mathrm{H}}(t) = -\frac{c\omega_{\alpha,\mathrm{d}}^2}{N}\hat{\mathbf{J}}_\mathrm{p,H}(t)\cdot\tilde{\boldsymbol{\epsilon}}_\alpha\ .$$

This can be solved formally by

$$\begin{aligned}
\hat{A}_{\alpha,\mathrm{H}}(t) = &-\frac{c\omega_{\alpha,\mathrm{d}}^2}{N}\int_0^t \mathrm{d}t'\ \frac{\sin(\tilde{\omega}_\alpha(t-t'))}{\tilde{\omega}_\alpha}\hat{\mathbf{J}}_\mathrm{p,H}(t')\cdot\tilde{\boldsymbol{\epsilon}}_\alpha \\
&+ \hat{A}_\alpha\cos(\tilde{\omega}_\alpha t) + \frac{\partial_t\hat{A}_{\alpha,\mathrm{H}}(0)}{\tilde{\omega}_\alpha}\sin(\tilde{\omega}_\alpha t)\ .
\end{aligned}$$

We then define the px approximation by using $\hat{A}_{\alpha,\mathrm{H}}(t) = A_\alpha(t) + \Delta\hat{A}_{\alpha,\mathrm{H}}(t)$ and replacing

$$\begin{aligned}
&\Delta\hat{A}_\alpha \to -c\omega_{\mathrm{d},\alpha}^2/(N_e\tilde{\omega}_\alpha^2)\tilde{\boldsymbol{\epsilon}}_\alpha\cdot\Delta\hat{\mathbf{J}}_\mathrm{p}\ , \\
&\Delta\partial_t\hat{A}_{\alpha,\mathrm{H}}(0) \to -c\omega_{\mathrm{d},\alpha}^2/(N_e\tilde{\omega}_\alpha^2)\tilde{\boldsymbol{\epsilon}}_\alpha\cdot\Delta\partial_t\hat{\mathbf{J}}_\mathrm{p,H}(0)\ , \quad \text{and} \\
&\Delta\hat{\mathbf{J}}_\mathrm{p,H}(t) \to \Delta\hat{\mathbf{J}}_{\mathrm{p,H_s}}(t)\ ,
\end{aligned}$$

where H_s indicates that we use now the Kohn-Sham system Heisenberg picture. Further, we use a symmetrized form of the photonic expressions as discussed in Sec. 4 (main text), evaluate all expectation values with the auxiliary Kohn-Sham wave function, and denote the resulting part of the Mxc vector potential as $\mathbf{A}_\mathrm{px}(\mathbf{r},t) = \mathbf{A}(t) + \mathbf{A}_\mathrm{x}(\mathbf{r},t)$. This way we find several further terms in the non-adiabatic px approximation. In the static case only the cosine term survives and we recover exactly Eq. (16) of the main text.

[1] V. Rokaj, M. Ruggenthaler, F. G. Eich, and A. Rubio, The free electron gas in cavity quantum electrodynamics, arXiv e-prints (2020), arXiv:2006.09236 [quant-ph].

[2] S. Latini, D. Shin, S. A. Sato, C. Schäfer, U. De Giovannini, H. Hübener, and A. Rubio, The ferroelectric photo ground state of srtio3: Cavity materials engineering, Proceedings of the National Academy of Sciences **118**, 10.1073/pnas.2105618118 (2021), https://www.pnas.org/content/118/31/e2105618118.full.pdf.

[3] S. Shin and H. Metiu, Multiple time scale quantum wavepacket propagation: Electron-nuclear dynamics, J. Phys. Chem. **100**, 7867 (1996),

http://dx.doi.org/10.1021/jp952498a.

[4] 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).

[5] Y. Ashida, A. İmamoğlu, and E. Demler, Cavity quantum electrodynamics at arbitrary light-matter coupling strengths, Physical Review Letters **126**, 153603 (2021).

[6] H. Spohn, *Dynamics of Charged Particles and Their Radiation Field* (Cambridge University Press, 2004).

[7] M. Ruggenthaler, J. Flick, C. Pellegrini, H. Appel, I. V. Tokatly, and A. Rubio, Quantum-electrodynamical density-functional theory: Bridging quantum optics and electronic-structure theory, Phys. Rev. A **90**, 012508 (2014).

[8] R. Jestädt, M. Ruggenthaler, M. J. Oliveira, A. Rubio, and H. Appel, Light-matter interactions within the ehrenfest–maxwell–pauli–kohn–sham framework: fundamentals, implementation, and nano-optical applications, Adv. Phys. **68**, 225 (2019).

[9] I. V. Tokatly, Time-dependent density functional theory for many-electron systems interacting with cavity photons, Phys. Rev. Lett. **110**, 233001 (2013).