Optimized Effective Potential for Quantum Electrodynamical Time-Dependent Density Functional Theory

Camilla Pellegrini,[1,*] Johannes Flick,[2,†] Ilya V. Tokatly,[1,3,‡] Heiko Appel,[2,4,§] and Angel Rubio[1,2,4,‖]

[1]*Departamento de Fisica de Materiales, Nano-bio Spectroscopy Group and ETSF Scientific Development Centre, Universidad del Pais Vasco UPV/EHU, E-20018 San Sebastian, Spain*
[2]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*
[3]*IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain*
[4]*Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany*

We propose an orbital exchange-correlation functional for applying time-dependent density functional theory to many-electron systems coupled to cavity photons. The time nonlocal equation for the electron-photon optimized effective potential (OEP) is derived. In the static limit our OEP energy functional reduces to the Lamb shift of the ground state energy. We test the new approximation in the Rabi model. It is shown that the OEP (i) reproduces quantitatively the exact ground-state energy from the weak to the deep strong coupling regime and (ii) accurately captures the dynamics entering the ultrastrong coupling regime. The present formalism opens the path to a first-principles description of correlated electron-photon systems, bridging the gap between electronic structure methods and quantum optics for real material applications.

The last two decades have witnessed increasing experimental interest in the study and control of many-electron systems strongly interacting with quantum electromagnetic fields. This includes notable experiments in the areas of cavity [1] and circuit [2] quantum electrodynamics (QED), quantum computing via photon-mediated atom entanglement [3], electromagnetically induced transparency [4], quantum plasmonics [5], quantum simulators [6], and chemistry [7,8]. The description of realistic coupled matter-photon systems requires combining electronic structure methods from materials science with quantum optical models. Recently, a time-dependent density-functional theory (TDDFT) for QED has been developed [9–12], allowing for such a first-principles treatment. However, any application of this theory requires approximations to the electron-photon exchange-correlation (xc) functional, which are currently not available.

In this Letter we construct the first approximation to the xc functional of QED-(TD)DFT. To achieve this goal, we extend the widely used optimized effective potential (OEP) approach in electronic structure methods [13–18] to the photon-mediated electron-electron coupling. The new functional is tested from low to high coupling regime in the Rabi model [19–21], through comparison with the exact and classical solutions. We also address the functional dependence on the initial many-body state, assumed to be either a fully interacting or a factorizable state. In both cases, the electron-photon OEP for the model performs well, providing a promising path to the *ab initio* description of strongly coupled matter-photon systems.

Consider a system with an arbitrarily large number N of electrons at coordinates $\{\mathbf{r}_i\}_{i=1}^N$, e.g., an atom, an ion, or a molecule, interacting with M quantized electromagnetic modes of a microcavity with frequencies ω_α. We denote by $\hat{H}_0 = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$ the Hamiltonian of the electronic system with kinetic energy $\hat{T}$, Coulomb interaction $\hat{V}_{ee}$, and (time-dependent) external potential $\hat{V}_{ext} = \sum_{i=1}^N v_{ext}(\mathbf{r}_i t)$, due to the nuclei and any classical field applied to the system. In the dipole approximation [22] the length-gauge Hamiltonian [9,23,24] of the total electron-photon system can be represented as follows:

$$\hat{H} = \hat{H}_0 + \frac{1}{2}\sum_\alpha \left[\hat{p}_\alpha^2 + \omega_\alpha^2 \left(\hat{q}_\alpha - \frac{\lambda_\alpha}{\omega_\alpha}\hat{\mathbf{R}} \right)^2 \right], \quad (1)$$

where the second term corresponds to the energy $1/8\pi \int (\hat{\mathbf{B}}^2 + \hat{\mathbf{E}}^2)d\mathbf{r}$ of the transverse radiation field. The magnetic field $\hat{B}_\alpha = \sqrt{4\pi}\hat{p}_\alpha$ in the α mode is proportional to the photon canonical momentum $\hat{p}_\alpha$, while the electric field $\hat{E}_\alpha = \sqrt{4\pi}(\omega_\alpha \hat{q}_\alpha - \lambda_\alpha \hat{\mathbf{R}})$ is related to the canonical coordinate $\hat{q}_\alpha$. The latter is defined via the displacement field $\hat{D}_\alpha = \sqrt{4\pi}\omega_\alpha \hat{q}_\alpha$, which is the proper dynamical variable conjugated to $\hat{B}_\alpha$. Finally, $\boldsymbol{\lambda}_\alpha$ describes the polarization and the amplitude of the normalized D_α mode at the position of the electronic system with dipole moment $\hat{\mathbf{R}} = \sum_{i=1}^N \mathbf{r}_i$ [25]. We define $\hat{q}_\alpha = -(\hat{a}_\alpha + \hat{a}_\alpha^\dagger)/\sqrt{2\omega_\alpha}$ in terms of photon annihilation and creation operators. The photon-induced interaction Hamiltonian in Eq. (1) consists of two terms: (i) the "cross" term $\sim \hat{q}_\alpha \hat{\mathbf{R}}$

$$\hat{V}_{el\text{-}ph} = \sum_\alpha \sqrt{\frac{\omega_\alpha}{2}}(\hat{a}_\alpha + \hat{a}_\alpha^\dagger)\int d^3\mathbf{r}(\boldsymbol{\lambda}_\alpha \mathbf{r})\hat{n}(\mathbf{r}), \quad (2)$$

where $\hat{n}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$ is the electron density operator, describing the dipole-displacement coupling, and (ii) the "squared" term $\sum_\alpha (\lambda_\alpha \hat{\mathbf{R}})^2/2$, representing the polarization energy of the electrons. The coupling to the quantized radiation field then gives rise to an additional, photon-mediated electron-electron interaction

$$W_{ee}(1,2) = \sum_\alpha (\lambda_\alpha \mathbf{r}_1)(\lambda_\alpha \mathbf{r}_2) \mathcal{W}_\alpha(t_1, t_2),$$

$$\mathcal{W}_\alpha(t_1, t_2) = \omega_\alpha^2 \mathcal{D}_\alpha(t_1, t_2) + \delta(t_1 - t_2), \quad (3)$$

where we use the compact notation $1 = (\mathbf{r}_1 t_1)$. Here, the first term is the effective interaction, via the photon displacement D_α propagator $i\mathcal{D}_\alpha(t_1, t_2) \equiv \langle \mathcal{T}\{q_\alpha(t_1) q_\alpha(t_2)\}\rangle$, derived from Eq. (2). The second term, due to the polarization contribution in the Hamiltonian, removes the instantaneous part of the D_α propagator and brings it to the E_α propagator, which describes the full physical interaction mediated by the quantized electric field [26].

Our formulation of QED-(TD)DFT combines one of the most popular exact methods for ground (excited) state electronic calculations [27], with the full quantum treatment of the electromagnetic field. In this theory, the wave function of the total system $\Psi(\{\mathbf{r}_j\}, \{q_\alpha\}, t)$ is a unique functional of the electron density $n(\mathbf{r}t) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$ and the expectation values of the photon coordinates $Q_\alpha(t) = \langle \Psi | \hat{q}_\alpha | \Psi \rangle$ [9]. The former can be calculated for a fictitious Kohn-Sham (KS) system of N noninteracting particles, whose orbitals $\{\phi_j\}$ satisfy the self-consistent equations $i\partial_t \phi_j(\mathbf{r}t) = [-\nabla^2/2 + v_s(\mathbf{r}t)]\phi_j(\mathbf{r}t)$ with the potential $v_s = v_{ext} + v_{Hxc}^{el} + v_{eff}^\alpha$. Here, we assume [9] the separate description of the Coulomb interaction V_{ee} and the photon-mediated interaction W_{ee} by the standard TDDFT Hartree-xc term $v_{Hxc}^{el}[n]$ and the effective potential $v_{eff}^\alpha[n, Q_\alpha]$. The latter is defined as $v_{eff}^\alpha = v_{MF}^\alpha + v_{xc}^\alpha$, where

$$v_{MF}^\alpha(\mathbf{r}t) = \int d1 \, W_{ee}^R(\mathbf{r}t, \mathbf{r}_1 t_1) n(\mathbf{r}_1 t_1) \quad (4)$$

is the mean-field contribution due to M classical electromagnetic modes, whose expectation values Q_α obey the Ampere-Maxwell equation for the displacement field. All the quantum many-body effects are embedded in the unknown xc potential, which must be approximated. Assuming the treatment of the electronic contribution v_{xc}^{el} by standard TDDFT functionals (e.g., x-only OEP or KLI [13], ALDA, GGA), we generalize the OEP approach to construct approximations to the photonic contribution v_{xc}^α.

We derive the TDOEP equation for the electron-photon system starting from the linearized Sham-Schlüter equation on the Keldysh contour [15]

$$\int d2 \, G_s(1,2) v_{xc}(2) G_s(2,1)$$

$$= \int d2 \int d3 \, G_s(1,2) \Sigma(2,3) G_s(3,1), \quad (5)$$

where the electron self-energy Σ contains the interaction W_{ee} of Eq. (3) and G_s is the Green's function of the time-dependent KS system. Equation (5) allows one to perturbatively construct the local potential v_{xc}, that mimics the effects of the self-energy Σ, to any desired order in the coupling strength λ_α. Analogously to the GW approximation [28,29] for electronic structure methods, we approximate the electron self-energy by the exchangelike diagram

$$\Sigma(1,2) = iG_s(1,2)W_{ee}(2,1), \quad (6)$$

where we assume the photon propagator in W_{ee} to be free. Here, the quantum nature of the electromagnetic field is accounted for by the dynamical part of Σ, related to the first term of Eq. (3). This part describes the processes of emission and absorption of a photon. Neglecting the above dynamical contribution to v_{eff} corresponds to the classical treatment of the electromagnetic field.

Making use of the Langreth rules [30], we rewrite Eq. (5) more explicitly as follows

$$i\int_{-\infty}^{t} dt_1 G_s^R(t, t_1) v_{xc}(t_1) G_s^<(t_1, t) + \text{c.c.}$$

$$= i\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 G_s^R(t, t_1)[\Sigma^>(t_1, t_2) G_s^<(t_2, t)$$

$$- \Sigma^<(t_1, t_2) G_s^>(t_2, t)] + \text{c.c.}, \quad (7)$$

where the superscripts R, $>$ and $<$ stand for retarded, greater, and lesser Keldysh components, respectively, and the integration over the spatial coordinates is implied. For computational convenience we consider Eq. (7) in the low temperature limit $T \to 0$. The electron-photon collision integral on the right-hand side then is responsible for the spontaneous photon emission of the excited electrons and the broadening in the electronic levels. Using Eq. (6) for the self-energy and expressing all G_s in terms of KS orbitals [30], Eq. (7) becomes

$$i\sum_{i,j} \int_{-\infty}^{t} dt_1 [\langle \phi_i(t_1)|v_x(t_1)|\phi_j(t_1)\rangle f_i - S_{ij}(t_1)]\phi_j^*(t)\phi_i(t)$$

$$+ \text{c.c.} = 0, \quad (8)$$

where we define

$$S_{ij}(t_1) = \sum_{k,\alpha} \int_{-\infty}^{t_1} dt_2 \, d_{ik}^\alpha(t_2) d_{kj}^\alpha(t_1)[(1 - f_i)f_k \mathcal{W}^>(t_1, t_2)$$

$$- f_i(1 - f_k)\mathcal{W}^<(t_1, t_2)]$$

with $\mathcal{W}^\gtrless(t_1, t_2) = \omega_\alpha^2(-i/2\omega_\alpha)e^{\pm i\omega_\alpha(t_2 - t_1)} \pm \delta(t_1 - t_2)$. Here, f_i is the fermion occupation number and $d_{ik}^\alpha(t) = \lambda_\alpha \langle \phi_i(t)|\mathbf{r}|\phi_k(t)\rangle$ is the dipole matrix element projected on the coupling constant of the α mode. For definiteness we assume that the external potential v_{ext} does not depend on time for all $t < 0$. Hence the orbitals $\{\phi_j\}$ are solutions of the KS equations with the initial condition $\phi_j(\mathbf{r}t) = \phi_j(\mathbf{r})e^{-i\varepsilon_j t}$ for $-\infty < t \leq 0$. Equation (8) relates the matrix

elements of v_x to the matrix elements S_{ij} of the self-energy Σ, and thus to the physical processes of excitation (annihilation) of electron-hole pairs by photon absorption (emission). Alternatively, Eq. (8) can be derived via variational principle from the Keldysh action functional, with the exchange part given by

$$A_x = \sum_{i,k,\alpha} \int dz_1 \int dz_2 d_{ik}^\alpha(z_2) d_{ki}^\alpha(z_1)(1 - f_i)f_k$$
$$\times \theta(z_1 - z_2)\left[\omega_\alpha^2\left(\frac{-i}{2\omega_\alpha}\right)e^{i\omega_\alpha(z_2 - z_1)} + \delta(z_1 - z_2)\right],$$

where z denotes the contour variable. Furthermore, the time-dependent mean-field potential is evaluated from Eq. (4) as

$$v_{MF}(\mathbf{r}t) = -\sum_\alpha \omega_\alpha(\boldsymbol{\lambda}_\alpha\mathbf{r})\int_0^t dt_1 \sin\left[\omega_\alpha(t - t_1)\right][\boldsymbol{\lambda}_\alpha\mathbf{R}(t_1)]$$
$$- \sum_\alpha(\boldsymbol{\lambda}_\alpha\mathbf{r})\{[\boldsymbol{\lambda}_\alpha\mathbf{R}(0)]\cos(\omega_\alpha t) - [\boldsymbol{\lambda}_\alpha\mathbf{R}(t)]\},$$
(9)

where $\mathbf{R}(t) = \int d^3\mathbf{r}\,\mathbf{r}n(\mathbf{r}t)$ is the expectation value of the dipole moment operator of the electronic system.

In the case of time independent external potential, Eq. (8) reduces to the stationary OEP equation for the equilibrium electron-photon system

$$\sum_{i,j}\left[\frac{\langle\phi_i|v_x|\phi_j\rangle}{\varepsilon_i - \varepsilon_j - i\eta}f_i - S_{ij}\right]\phi_j^*(\mathbf{r})\phi_i(\mathbf{r}) + c.c. = 0, \quad (10)$$

where

$$S_{ij} = \sum_{k,\alpha}\frac{d_{ik}^\alpha d_{kj}^\alpha(\varepsilon_i - \varepsilon_k - i\eta)}{2(\varepsilon_i - \varepsilon_j - i\eta)}\left[\frac{f_i(1 - f_k)}{\varepsilon_i - \varepsilon_k - \omega_\alpha - i\eta}\right.$$
$$\left. + \frac{(1 - f_i)f_k}{\varepsilon_i - \varepsilon_k + \omega_\alpha - i\eta}\right].$$
(11)

Here, we assume the limit $\eta \to 0$. Apparently, Eq. (11) describes virtual processes of excitation of electron-hole pairs, supplemented by the emission of photons. Variationally Eq. (10) can be derived employing the second-order correction to the ground-state energy

$$E_x = -\frac{1}{2}\sum_{i,k,\alpha}|d_{ik}^\alpha|^2\left\{\omega_\alpha\frac{(1 - f_i)f_k}{\varepsilon_i - \varepsilon_k + \omega_\alpha} - (1 - f_i)f_k\right\},$$
(12)

which is the Lamb shift due to the virtual emission of photons [31]. The second term in Eq. (12) comes from the term $\sum_\alpha(\boldsymbol{\lambda}_\alpha\mathbf{R})^2/2$ in the Hamiltonian, and accounts for the free electron behavior in the high photon energy limit $\omega_\alpha \to \infty$.

As a proof of principles, we apply these results to a simple, yet nontrivial quantum optical model that can be solved exactly, i.e., the tight-binding model for the H_2^+ molecule coupled to one photon mode. The one electron choice here prevents from introducing the extra error in approximating the standard TDDFT potential v_{xc}^{el}, thus allowing us to assess the accuracy of our approximation to the electron-photon potential v_{xc}. The electron coordinate can only take two values, given by the atomic site indexes (1,2). The electron density reduces to the on-site occupation number $n_{1,2}$. By projecting the Hamiltonian in Eq. (1) onto the two-site space, the electronic kinetic energy gives the tunneling amplitude between the sites. As the total occupation is fixed, the external and photon fields couple to the on-site occupation difference $\Delta n = n_1 - n_2$. This plays the role of the TDDFT density variable for the model. In terms of Pauli matrices $\sigma_{x,z}$ [$\hat{T} \to -T\hat{\sigma}_x$ and $\Delta\hat{n} \to \hat{\sigma}_z$], the projected Hamiltonian

$$\hat{H} = -T\hat{\sigma}_x + \left[\sqrt{\frac{\omega}{2}}\lambda(\hat{a} + \hat{a}^\dagger) + v_{ext}(t)\right]\hat{\sigma}_z$$
$$+ \omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) + \frac{\lambda^2}{2}$$
(13)

reads isomorphic to the Rabi Hamiltonian with external potential $v_{ext}(t)$ and coupling strength $\sqrt{\omega/2}\lambda$.

We consider first the system in equilibrium. The summation in Eq. (10) runs over the ground (g) and excited (e) KS states with the corresponding orbitals, $\phi_g^\dagger = (\bar{v}, \bar{u})$ and $\phi_e^\dagger = (\bar{u}, -\bar{v})$, and eigenvalues, $\varepsilon_g = -W$ and $\varepsilon_e = W$. Here, $\bar{u}, \bar{v} = \sqrt{(1 \pm v_s/W)/2}$ and $W = \sqrt{v_s^2 + T^2}$. Explicitly, Eq. (10) gives

$$v_x = -\lambda^2\frac{v_s}{W}\left[\frac{\omega(\omega + 3W)}{(\omega + 2W)^2} - 1\right],$$
(14)

where the second term corresponds to the classical contribution associated with the first interaction term in Eq. (3). The total energy functional takes the form

$$E[v_s] = -T\langle\sigma_x\rangle + v_{ext}\Delta n + E_x[v_s] + \frac{1}{2}\omega,$$
(15)

where $\Delta n = -v_s/W$ and Eq. (12) reduces to

$$E_x = \frac{\lambda^2 T^2}{W(\omega + 2W)}.$$
(16)

The Lamb shift of Eq. (16) vanishes in the classical limit of coupling $\lambda \to \infty$, as expected.

In Fig. 1 we show the calculated OEP density difference Δn and total energy E as functions of the coupling strength λ, compared to the results from the exact and classical treatment of the electromagnetic field. It is worth noting that $0.1 \lesssim \lambda \lesssim 1.4$ and $\lambda \gtrsim 1.4$ corresponds, respectively, to
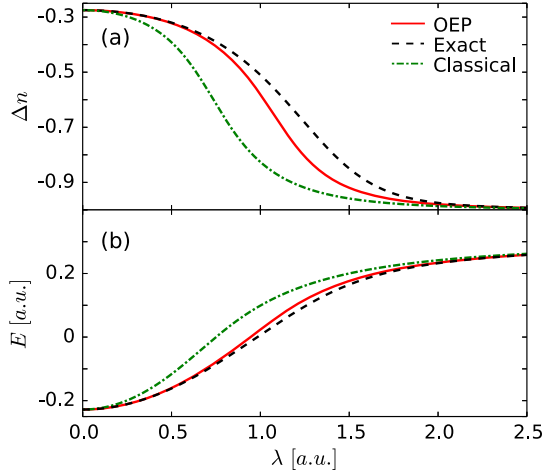
FIG. 1 (color online). Comparison of the OEP (red), exact
(black), and classical (green) (a) density difference Δn and
(b) energy E versus the coupling parameter λ in a.u. Other
parameters: $\omega = 1$, $v_{\text{ext}} = 0.2$, $T = 0.7$.

ultrastrong [32] and deep strong coupling [33] values. The
eigenvalue problem for the static Rabi Hamiltonian in
Eq. (13) is solved by employing the exact diagonalization
technique [34,35], after proper truncation of the Fock
space. We observe that both the OEP and classical
approximations reproduce qualitatively the electron's con-
finement on the excited level, as the shift in the energy
levels increases with the coupling strength, and recover the
exact result in the limit $\lambda \to \infty$. In addition, our OEP
scheme is by construction exact in the weak coupling
regime. For the density difference Δn shown in (a), we see
excellent agreement between the OEP and the exact results
up to $\lambda = 0.7$ and above $\lambda = 2$. On the contrary, the
classical result is only asymptotically accurate and largely
underestimating in between. Regarding the energies E
shown in (b), the OEP energy is close to the exact values
in the whole coupling range, with only small deviations
around $\lambda = 1.3$. In contrast, the classical approximation
performs reliably only in the limits of very small or very
high interaction strength.

The TDOEP Eq. (8) for the Rabi model simplifies to

$$i \int_{-\infty}^{t} dt_1 \tilde{v}_x(t_1) d_{ge}(t_1) d_{eg}(t) + \text{c.c.}$$
$$= \lambda^2 \omega \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 c(t, t_1) d_{eg}(t_2) e^{i\omega(t_2 - t_1)} + \text{c.c.}, \tag{17}$$

where $\tilde{v}_x = v_x(t) + \lambda^2 \Delta n(t)$, $d_{ge}(t) = \langle \phi_g(t) | \hat{\sigma}_z | \phi_e(t) \rangle$,
and $c(t, t_1) = d_{ge}(t) \Delta n(t_1) - d_{ge}(t_1) \Delta n(t)$. Moreover, the
mean-field potential of Eq. (9) explicitly reads as

$$v_{\text{MF}}(t) = -\lambda^2 \omega \int_{0}^{t} dt_1 \sin[\omega(t - t_1)] \Delta n(t_1)$$
$$- \lambda^2 \Delta n \cos(\omega t) + \lambda^2 \Delta n(t).$$

Employing the numerical algorithm presented in Ref. [36],
we solve Eq. (17) self-consistently for $t > 0$, together with
the time-dependent KS equation. The former, which is a
Volterra integral equation of the first kind, is evaluated
using a midpoint integration scheme combined with the
trapezoidal rule [37]. The latter is propagated with a
predictor-corrector scheme using an exponential midpoint
propagator [38]. In Fig. 2 we compare the time evolution of
the calculated OEP density difference Δn and effective
potential v_{eff} with the exact and classical results, approach-
ing the ultrastrong coupling regime in two different setups.
In the first setting, we assume that the electron-photon
system, interacting with coupling constant $\lambda = 0.1$, is
driven out of equilibrium at $t = 0$ by a sudden switch in
the external perturbation $v_{\text{ext}}(t) = -0.2\text{sgn}(t)$. In the
second configuration, we choose a noninteracting initial
state with $v_{\text{ext}}(t) = 0$, while switching on at later times
the electron-photon coupling $\lambda(t) = 0.1\theta(t)$. Here, we
use as the initial state for the propagation $|\Psi\rangle =
(1/2|1\rangle + \sqrt{3}/2|2\rangle) \otimes |0\rangle$, where $|1\rangle$ and $|2\rangle$ are the basis
vectors of the electron system, and $|0\rangle$ is the photon vacuum
field. For the chosen parameters, the various density
differences in the two setups undergo off-resonant Rabi
oscillations with nearly identical relative behavior. The
errors $\delta \Delta n$ in the OEP and classical density difference are
shown in (a) for the sudden-switch example. The first is
remarkably low in the entire coupling range. The second
is about 10% at $t = 20$ a.u. and increases up to 20% at
$t = 40$ a.u. The quantum contribution to the OEP is given
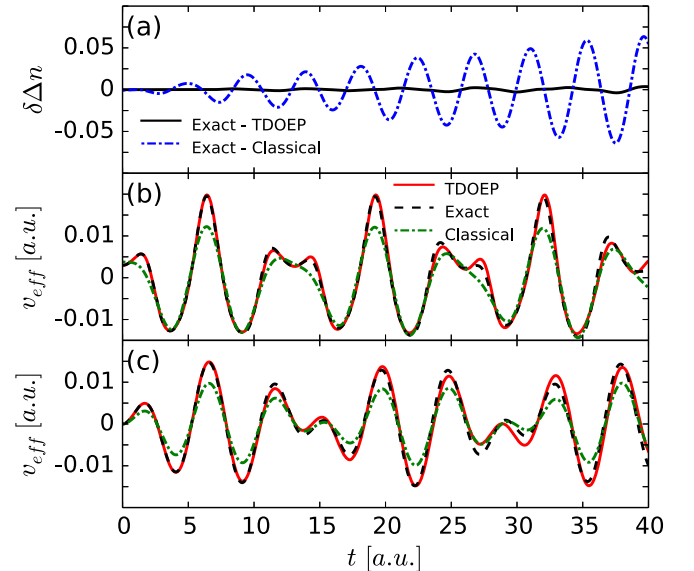by the right-hand side of Eq. (17) and its role in the Rabi

FIG. 2 (color online). Comparison of the (a) errors $\delta \Delta n$ in the
TDOEP (black) and classical (blue) density difference Δn and
(b),(c) TDOEP (red), exact (black), and classical (green) effective
potential v_{eff} versus time t in a.u. for the configurations: (a),(b)
$v_{\text{ext}} = -0.2\text{sgn}(t)$, $\lambda = 0.1$ and (c) $v_{\text{ext}} = 0$, $\lambda = 0.1\theta(t)$. Other
parameters: $\omega = 1$, $T = 0.7$.

oscillations is essentially quantified by the error in the classical density difference. Significant is also the improvement of the OEP approach against the classical approximation in the effective potential. It should be noted that, unlike the density difference, this doesn't correspond to a physical observable. As we can see in (b) for the sudden-switch case, and in (c) for the noninteracting initial configuration, the TDOEP result is very accurate up to $t = 20$ a.u. At later times, small deviations appear, especially in (c), where the potential shows a more complex dynamics. Nevertheless, the improvement with respect to the classical result is still evident.

In conclusion, a first-principles approach for describing the quantum dynamics of realistic many-electron systems interacting with photons is proposed. For methodological purposes we have considered here its application to the off-resonant Rabi model. It has been shown that already the lowest order (TD)OEP for the model gives accurate stationary and dynamical properties far beyond the weak-coupling regime, clearly improving over the classical treatment of the electromagnetic field. Future developments include simplifying the QED-TDOEP scheme along the lines of the TDKLI approximation [13,39]. This work opens the path to a simplified numerical description of novel phenomena at the interface between condensed matter physics and quantum optics.

[*] camilla.pellegrini@ehu.es
[†] flick@fhi-berlin.mpg.de
[‡] ilya.tokatly@ehu.es
[§] appel@fhi-berlin.mpg.de
[‖] angel.rubio@ehu.es

[1] J. P. Reithmaier, G. Sęk, A. Löffler, C. Hofmann, S. Kuhn, S. Reitzenstein, L. V. Keldysh, V. D. Kulakovskii, T. L. Reinecke, and A. Forchel, Nature (London) **432**, 197 (2004).

[2] A. A. Houck, H. E. Türeci, and J. Koch, Nat. Phys. **8**, 292 (2012).

[3] A. F. van Loo, A. Fedorov, K. Lalumière, B. C. Sanders, A. Blais, and A. Wallraff, Science **342**, 1494 (2013).

[4] K.-J. Boller, A. Imamoglu, and S. E. Harris, Phys. Rev. Lett. **66**, 2593 (1991).

[5] M. S. Tame, K. R. McEnery, Ş. K. Özdemir, J. Lee, S. A. Maier, and M. S. Kim, Nat. Phys. **9**, 329 (2013).

[6] J. T. Barreiro, M. Müller, P. Schindler, D. Nigg, T. Monz, M. Chwalla, M. Hennrich, C. F. Roos, P. Zoller, and R. Blatt, Nature (London) **470**, 486 (2011).

[7] A. Fontcuberta i Morral and F. Stellacci, Nat. Mater. **11**, 272 (2012).

[8] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, and T. W. Ebbesen, Angew. Chem., Int. Ed. **51**, 1592 (2012).

[9] I. V. Tokatly, Phys. Rev. Lett. **110**, 233001 (2013).

[10] M. Ruggenthaler, J. Flick, C. Pellegrini, H. Appel, I. V. Tokatly, and A. Rubio, Phys. Rev. A **90**, 012508 (2014).

[11] M. Farzanehpour and I. V. Tokatly, Phys. Rev. B **90**, 195149 (2014).

[12] M. Ruggenthaler, F. Mackenroth, and D. Bauer, Phys. Rev. A **84**, 042107 (2011).

[13] C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **74**, 872 (1995).

[14] C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, Ber. Bunsenges. Phys. Chem. **99**, 488 (1995).

[15] R. van Leeuwen, Phys. Rev. Lett. **76**, 3610 (1996).

[16] A. Görling, Phys. Rev. A **55**, 2630 (1997).

[17] S. Kümmel and J. P. Perdew, Phys. Rev. Lett. **90**, 043004 (2003).

[18] S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).

[19] B. W. Shore and P. L. Knight, J. Mod. Opt. **40**, 1195 (1993).

[20] D. Braak, Phys. Rev. Lett. **107**, 100401 (2011).

[21] F. A. Wolf, F. Vallone, G. Romero, M. Kollar, E. Solano, and D. Braak, Phys. Rev. A **87**, 023835 (2013).

[22] The derivation can be generalized to the case of atom-field coupling beyond the dipole approximation in a straightforward manner.

[23] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom-Photon Interactions* (Wiley-VCH, Weinheim, 2004).

[24] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic Press, London, 1984).

[25] We use atomic units (a.u.) throughout the Letter.

[26] In the frequency domain the effective interaction of Eq. (3) reads $\mathcal{W}_\alpha(\omega) = \omega_\alpha^2/(\omega^2 - \omega_\alpha^2) + 1 = \omega^2/(\omega^2 - \omega_\alpha^2) \sim \langle E_\alpha; E_\alpha \rangle_\omega$. As it should be, the total physical interaction is proportional to ω^2 because only accelerated electrons can emit electromagnetic radiation.

[27] M. A. L. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross, *Time-Dependent Density-Functional Theory*, 706 (Springer, Berlin, 2010).

[28] L. Hedin, Phys. Rev. **139**, A796 (1965).

[29] L. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[30] G. Stefanucci and R. van Leeuwen, *Nonequilibrium Many-Body Theory of Quantum Systems* (Cambridge University Press, Cambridge, England, 2013).

[31] A. N. Mitra, Resonance **10**, 33 (2005).

[32] T. Niemczyk, F. Deppe, H. Huebl, E. P. Menzel, F. Hocke, M. J. Schwarz, J. J. Garcia-Ripoli, D. Zueco, T. Hümmer, E. Solano et al., Nat. Phys. **6**, 772 (2010).

[33] A. Crespi, S. Longhi, and R. Osellame, Phys. Rev. Lett. **108**, 163601 (2012).

[34] A. I. Streltsov, O. E. Alon, and L. S. Cederbaum, Phys. Rev. A **81**, 022124 (2010).

[35] J. Flick, H. Appel, and A. Rubio, J. Chem. Theory Comput. **10**, 1665 (2014).

[36] H. O. Wijewardane and C. A. Ullrich, Phys. Rev. Lett. **100**, 056404 (2008).

[37] P. Linz, Computer Journal **12**, 393 (1969).

[38] A. Castro, M. A. L. Marques, and A. Rubio, J. Chem. Phys. **121**, 3425 (2004).

[39] C. Schäfer, H. Appel, J. Flick, C. Pellegrini, I. V. Tokatly, and A. Rubio (unpublished).