Reduced Density-Matrix Approach to Strong Matter-Photon Interaction

F. Buchholz\textsuperscript{1}, I. Theophilou\textsuperscript{1}, S. E. B. Nielsen\textsuperscript{1}, M. Ruggenthaler\textsuperscript{1}, and A. Rubio\textsuperscript{1,2*}

\textsuperscript{1}Theory Department, Max Planck Institute for the Structure and Dynamics of Matter - Luruper Chaussee 149, 22761 Hamburg, Germany
\textsuperscript{2}Center for Computational Quantum Physics (CCQ), Flatiron Institute, 162 Fifth Avenue, New York NY 10010, USA

E-mail: florian.buchholz@mpsd.mpg.de

Abstract

In this work, we present a first-principles approach to electronic many-body systems strongly coupled to cavity modes in terms of matter-photon reduced density matrices. The theory is fundamentally non-perturbative and thus captures not only the effects of correlated electronic systems but accounts also for strong interactions between matter and photon degrees of freedom. We do so by introducing a higher-dimensional auxiliary system that maps the coupled fermion-boson system to a purely fermionic problem as proposed recently in the context of density-functional theory.\textsuperscript{1} This reformulation allows us to overcome many fundamental challenges of density-matrix theory in the context of coupled fermion-boson systems and we can employ conventional reduced density-matrix functional theory developed for purely fermionic systems. We provide results for model systems in real space and show that simple density-matrix approximations are accurate from the weak to the deep-strong coupling regime.
1 Introduction

Experiments performed in the last decades (see, e.g., Refs. [2,3]) have made accessible the strong interaction regime between matter degrees of freedom and the quantized modes of optical cavities, which allows for the study of many new phenomena including modification of chemical reaction rates,[4,5] interacting photons in quantum non-linear media,[6] or superradiance of atoms in a photonic trap.[7] At the same time it creates opportunities such as the modification of energy-transfer pathways within photosynthetic organisms,[8] an increase of conductivity in organic semiconductors hybridized with the vacuum field[9] or the generation of long-distance molecular interactions that, for example, allow for energy transfer way beyond the short-range dipole-dipole mediated transfer (Förster theory).[10] All these phenomena are related by the emergence of hybrid light-matter quasi-particle states, called polaritons, that determine the properties of the respective coupled electron-photon system. When it comes to theoretical understanding of these exotic states there is still a need for new theoretical tools that treat matter and photons at the same level of theory.[11,12] Up to now, standard theoretical modeling treats in detail either the photons or the matter, which becomes insufficient when the matter and photon degrees of freedom are equally important.[12] For example, it is quite common to use simplified model systems of Dicke-type, meaning several few-level systems coupled to some photon modes.[13,14] On the other hand, it is common, e.g., in quantum chemistry or solid-state physics, to treat the matter system quantum mechanically in detail but consider the photons as classical external electromagnetic fields, not taking into account the back-reaction of the matter system to the photons and their quantum fluctuations. The ongoing research on the theoretical understanding of super-radiance provides an example for the necessity of a description of the coupled light-matter system on the same footing (a good summary can be found in Ref. [17]). However, the full quantum-mechanical description of just the electronic degrees of freedom is already computationally very challenging due to the exponential scaling of the wave function. Instead, reformulations of the many-body problem in terms of reduced quantities like the electron density[18,19] or
the Green’s function$^{20,21}$ have been shown to provide accurate results for relatively low computational costs. Thus, working with reduced quantities seems to be a natural choice also for the coupled light-matter system. Recently, quantum-electrodynamical density-functional theory (QEDFT) was introduced as an extension to pure electronic density-functional theory (DFT)$^{22,25}$ First calculations showed the feasibility of QEDFT$^{20,24}$ leading to the possibility to perform full first-principles calculations of real molecules coupled to cavity modes$^{25,29}$ However, standard approximations in DFT (usually based on a non-interacting auxiliary Kohn-Sham system) become inaccurate if applied to strongly-correlated systems. This is very well studied in terms of the strong-correlation regime in electronic systems$^{30}$ and also observed for the existing QEDFT functionals that approximate the electron-photon interaction$^{28}$. Consequently, to study novel effects arising in the ultra-strong$^{31}$ or deep-strong coupling regime$^{32}$ of light and matter from first principles, i.e., without the resort to simplified few-level systems, it is worth to explore methods that go beyond the standard DFT setting.

Reduced density-matrix functional theory (RDMFT) is such a method. RDMFT is based on the electronic one-body reduced density matrix (1RDM) instead of the electronic density (like in DFT) as its basic functional variable$^{33}$. Similarly to DFT, approximations are necessary in RDMFT as it is not known how to express explicitly all expectation values of operators in terms of the 1RDM. Simple approximations within this approach$^{34}$ have proven very efficient in dealing with long lasting problems within many DFT functional approximations like the correct qualitative description of a dissociating molecule$^{35}$ or the prediction of the Mott-insulating phase of certain strongly-correlated solids$^{36}$. Having proved itself efficient for describing systems of (strongly) interacting electrons, RDMFT seems to be a natural candidate for describing also the strong interaction between molecular systems and cavity modes.

In this work we will discuss the properties of coupled light-matter systems in a setting that resembles typical cavity experiments. It turns out that transferring RDMFT to such
systems involves overcoming additional difficulties in contrast to the DFT framework. The reason behind this are the conditions under which the corresponding reduced density matrices (RDMs) (which will be purely electronic, purely photonic and coupled) connect to the original wave function, which is crucial to construct a well-defined reduced density-matrix framework. Already for the purely electronic system the conditions under which such a connection exists (known as N-representability conditions) are not trivial. For RDMs in matter-photon systems these conditions are entirely unexplored. Nevertheless, we manage to overcome this difficulty by mapping the original system to a higher-dimensional auxiliary system that allows for an effective description of the problem only by fermions. Hence, the corresponding RDMs connect to the auxiliary wave functions under N-representability conditions of fermionic systems. Despite being fermions, the newly introduced quasi-particles will depend on electronic and bosonic degrees of freedom. This construction was recently introduced by Nielsen et al. and used to construct a DFT scheme specifically for the strong-coupling regime of light-matter systems. In the auxiliary system, the Hamiltonian consists of only 1- and 2-body terms for the new quasi-particles, thus it has the same structure as the conventional electronic Hamiltonian for molecular systems, which allows us to apply electronic RDMFT theory without major modifications. We will present some results for model systems with the simplest known RDMFT functional, the Müller functional, and show how this dressed RDMFT (dRDMFT) is accurate from the weak to the strong-coupling regime. Finally we comment on some open issues and challenges for future applications.

This article is structured as follows. First we explain the physical setting of an electronic system in a cavity in section 2. In section 3 we discuss the RDMs that appear in the ground-state energy expression of the coupled light-matter system. We will explain the difficulties that are introduced by the coupling between fermions and bosons and having non-particle-conserving terms. In section 4 we introduce the higher-dimensional auxiliary system which will allow us to avoid most of the aforementioned difficulties. We show how to construct a proper RDMFT framework in this system in section 5 explain our numerical
implementation in section 6 and present first numerical results in section 7. We finish with discussing possibilities as well as challenges of dRDMFT in section 8.

2 Physical Setting

To describe strong matter-photon interaction, it is necessary to go beyond typical quantum-chemistry or solid-state physics theories that describe electrons in a local potential interacting via Coulomb interaction and perturbed by a classical external electromagnetic field. Instead, we need to treat explicitly the quantum nature of light and the back-reaction between electrons and electromagnetic field excitations (photons). Therefore the framework that needs to be employed is quantum electrodynamics (QED). However, we do not want to treat QED in its full complexity but will apply some well-established approximations. First, we apply the Born-Oppenheimer approximation and treat the nuclei as fixed. Second, we work in the non-relativistic limit, which for the typical energy scales of molecules and their low-energy excitations is usually sufficient. Third, we assume that the wavelength $\lambda$ of the relevant electromagnetic modes is much larger than the spatial extension $d$ of the electronic system ($\lambda \gg d$) such that the dipole approximation (here in the Coulomb gauge) is valid. In the case of the dipole approximation, where every photon mode couples to all Fourier components of the charge current of the electronic subsystem, an effective description with only a few modes is usually sufficient. The continuum of modes (openness of the cavity) is then effectively taken into account by using instead of the bare mass the physical mass of the electrons. Since we focus on equilibrium situations, this approximation is known to be highly accurate.

Therefore, the basic Hamiltonian that we use to describe strongly-coupled light-matter

\footnote{The extension to also include the nuclei as quantum particles is in principle straightforward by following, e.g., similar strategies like discussed in Refs. 12, 27}
systems reads (we use atomic units throughout)

\[
\hat{H} = \sum_{k=1}^{N} \left[ -\frac{1}{2} \nabla_{r_k}^2 + v(r_k) \right] + \frac{1}{2} \sum_{k \neq l} w(r_k, r_l) \\
+ \frac{1}{2} \sum_{\alpha=1}^{M} \left[ -\frac{\partial^2}{\partial p_\alpha^2} + \left( \omega_\alpha p_\alpha - \lambda_\alpha \cdot \sum_{k=1}^{N} r_k \right)^2 \right].
\]  

(1)

Here the first two sums on the right-hand side correspond to the usual electronic many-body Hamiltonian \( \hat{H}_e = \hat{T} + \hat{V} + \hat{W} \) used to describe the uncoupled matter system consisting of \( N \) electrons in an external potential \( v(r) \) interacting via the Coulomb repulsion \( w(r, r') \). The third sum describes \( M \) photon modes with frequency \( \omega_\alpha \) and polarization vectors \( \lambda_\alpha \) that include already the effective coupling strength, which couple to the total dipole \( \mathbf{D} = \sum_{k=1}^{N} \mathbf{r}_k \) of the electronic system. It can be decomposed in a purely photonic part \( \hat{H}_{ph} = \sum_{\alpha=1}^{M} \left( -\frac{1}{2} \frac{\partial^2}{\partial p_\alpha^2} + \frac{\omega_\alpha^2}{2} p_\alpha^2 \right) \), the dipole self-interaction \( \hat{H}_d = \sum_{\alpha=1}^{M} \frac{1}{2} (\lambda_\alpha \cdot \mathbf{D})^2 \), which we split again for later convenience in its one-body \( \hat{H}^{(1)}_d = \sum_{\alpha=1}^{M} \sum_{k=1}^{N} \frac{1}{2} (\lambda_\alpha \cdot r_k)^2 \) and two-body part \( \hat{H}^{(2)}_d = \sum_{\alpha=1}^{M} \sum_{k \neq l} \frac{1}{2} (\lambda_\alpha \cdot r_k)(\lambda_\alpha \cdot r_l) \), and the bilinear interaction \( \hat{H}_I = -\sum_{\alpha=1}^{M} \omega_\alpha p_\alpha \lambda_\alpha \cdot \mathbf{D} \).

The ground-state wave function of Eq. (1) is a function of \( 4N + M \) coordinates

\[
\Psi(r_1 \sigma_1, ..., r_N \sigma_N; p_1, ..., p_M),
\]  

(2)

where \( \sigma_k \) are the electronic spin degrees of freedom. The wave function \( \Psi \) is as usual anti-symmetric with respect to the exchange of any two electron coordinates \( r_j \sigma_j \leftrightarrow r_k \sigma_k \), and also depends on \( M \) photon-mode displacement coordinates \( p_\alpha \).

At this point, we want to remind the reader that there is no fundamental symmetry with respect to the exchange of two displacement coordinates \( p_\alpha \leftrightarrow p_\beta \). The bosonic symmetry instead refers to the exchange of mode excitations, which are interpreted as photons in the number-state representation. To see this we first use the ladder operators \( \hat{a}_\alpha = \sqrt{\frac{\omega_\alpha}{2}} (p_\alpha - \text{if symmetric} \),
\[ \hat{\alpha} = \sqrt{\frac{\omega \alpha}{2}} (p_{\alpha} + \frac{1}{\omega \alpha} \frac{\partial}{\partial p_{\alpha}}) \]

and

\[ \hat{\alpha}^+ = \frac{1}{\sqrt{2\omega}} \left( p_{\alpha} + \frac{1}{\omega \alpha} \frac{\partial}{\partial p_{\alpha}} \right) \]

to represent the sum of harmonic Hamiltonians, i.e.,

\[ \hat{H}_{ph} = \sum_{\alpha=1}^{M} \omega_{\alpha} \left( \hat{\alpha}^+ \hat{\alpha}_{\alpha} + \frac{1}{2} \right). \] (3)

Eigenstates of the individual \( \hat{\alpha}^+ \hat{\alpha}_{\alpha} \) in the above representation are then given by multiple application of creation operators to the vacuum state \( |0\rangle \), i.e.,

\[ |\varphi_{\alpha}^{n}\rangle = (\hat{\alpha}^+)^n |0\rangle \]

These eigenstates are connected to the displacement representation by

\[ |\phi_{n1,...,n_M}(p_1,...,p_M)\rangle = \langle p_1...p_M | (\hat{\alpha}^+)^{n_1}... (\hat{\alpha}^+_{M})^{n_M} |0\rangle. \]

In this form it becomes clear that a multi-mode eigenstate \( |\phi_{n1,...,n_M}\rangle \) can be considered to consist of \( N_b = n_1 + ... + n_M \) photons (mode excitations). We can then associate each such multi-mode eigenstate with a specific photon-number sector, i.e., the zero-photon sector is merely one-dimensional and corresponds to \( |\phi_{0,...,0}\rangle \equiv |0\rangle \), the single-photon sector is \( M \)-dimensional and corresponds to the span of \( \hat{\alpha}^+ |0\rangle \equiv |\alpha\rangle \) for all \( \alpha \) and so on. For the multi-photon sectors we see due to the commutation relations of the ladder operators the bosonic exchange symmetry appearing, e.g.,

\[ \hat{\alpha}^+_{\alpha_1} \hat{\alpha}^+_{\alpha_2} |0\rangle = \hat{\alpha}^+_{\alpha_2} \hat{\alpha}^+_{\alpha_1} |0\rangle \equiv |\alpha_1,\alpha_2\rangle \]

for \( \alpha_1,\alpha_2 \in \{1,...,M\} \). It is no accident that the bosonic symmetry becomes explicit in this representation since the different modes \( \alpha \) determine how the photon wave functions looks like in real space.\[21,22\] A general photon state, which is given by

\[ |\Phi\rangle = \sum_{n_1,...,n_M=1}^{\infty} \Phi(n_1,...,n_M) |\phi_{n_1,...,n_M}\rangle, \]

can therefore also be represented by a sum over all photon-number sectors as

\[ |\Phi\rangle = \sum_{n=0}^{\infty} \left( \sum_{\alpha_1,...,\alpha_n=1}^{M} \Phi(\alpha_1,...,\alpha_n) |\alpha_1,...,\alpha_n\rangle \right). \]

For more details see appendix A.

3 Reduced Density Matrices for coupled light-matter systems

Having introduced our system of interest, we now want to discuss how to find its ground state. A ground state (if it exists) is defined as the state (possibly degenerate) that has the
lowest energy expectation value

\[ E_0[\Psi] = \inf_\Psi \langle \Psi | \hat{H} | \Psi \rangle. \quad (4) \]

This is the classical formulation of the variational principle due to Ritz and is well-defined for every Hamiltonian that is bounded from below. While well-known, Eq. (4) has the disadvantage that in practice the minimization has to be performed over an enormous configuration space that is spanned by all possible many-body wave functions. A possible reduction of computational complexity presents itself by the fact that the full wave function is usually not necessary to compute the energy expectation value but typically only reduced quantities are sufficient. Varying instead over the space of reduced objects makes the minimization simpler. A standard example is DFT, where it is only the space of physical densities that needs to be explored instead of correlated wave functions over the configuration space. For instance, in the case of an electronic many-body state \( \psi(r_1, \sigma_1, ... , r_N, \sigma_N) \) of \( N \) electrons, the expectation value of a general (non-local) \( q \)-body operator \( \hat{O}(r_1, ... , r_q, r'_1, ... , r'_q) \), which is given by \( O = \langle \psi | \hat{O} | \psi \rangle \), can be determined via the electronic (spin-summed) \( q \)-body RDM (qRDM):\(^2\)

\[
\Gamma_e^{(q)}(r_1, ... , r_q, r'_1, ... , r'_q) = \frac{N!}{(N-q)!} \sum_{\sigma_1, ... , \sigma_N} \int d^3(N-q) \Gamma_e(r_1, ... , r_q, r'_1, ... , r'_q). \quad (5)
\]

A prominent example of such a higher-order operator in the electronic case is the two-body Coulomb interaction among the \( N \) electrons. The electronic 1RDM, which is enough to calculate all electronic single-particle observables such as the kinetic energy, we denote by \( \gamma_e(r, r') = \Gamma_e^{(1)}(r, r') \). In the chosen normalization, it integrates to the particle number \( \int d^3 r \gamma_e(r, r) = N \). The higher-order RDMs meet similar sum rules (the 2RDM integrates

\(^2\)We define here only the spin-summed version of the qRDM, because in this work, we do not consider explicitly spin-dependent quantities. For instance, if we included magnetic fields in the Hamiltonian, the situation would change.
to two times the number of pairs) and they are connected to the lower-order RDMs via
\[ \Gamma_e^{(q)}(r_1, \ldots, r_q; r'_1, \ldots, r'_q) = \frac{1}{N-q} \int d^3r \Gamma_e^{(q+1)}(r_1, \ldots, r_{q+1}; r'_1, \ldots, r'_{q+1}) \]. For bosons the same construction is possible. In our case, where we have a discrete set of possible single-boson states, a \( N_b \) boson state in the (symmetrized) mode-representation \( \phi(\alpha_1, \ldots, \alpha_{N_b}) \) (see appendix A for more details) leads to the corresponding bosonic \( q \)RDM,

\[ \Gamma_b^{(q)}(\alpha_1, \ldots, \alpha_q; \alpha'_1, \ldots, \alpha'_q) = \frac{N_b!}{(N_b-q)!} \sum_{\alpha_{q+1}, \ldots, \alpha_{N_b}=1}^M \phi^*(\alpha'_1, \ldots, \alpha'_q, \alpha_{q+1}, \ldots, \alpha_{N_b}) \phi(\alpha_1, \ldots, \alpha_q, \alpha_{q+1}, \ldots, \alpha_{N_b}). \] (6)

Accordingly to the electronic case we denote the 1RDM by \( \gamma_b(\alpha, \beta) = \Gamma_b^{(1)}(\alpha; \beta) \). However, in the specific bosonic case of photons, where the number of particles is indetermined and we work with Fock-space wave functions \( |\Phi\rangle \), we need to consider a Fock-space 1RDM of the form

\[ \gamma_b(\alpha, \beta) = \langle \phi| \hat{a}^+_\beta \hat{a}_\alpha \phi \rangle = \sum_{n=0}^\infty n \left( \sum_{\alpha_2, \ldots, \alpha_n=1}^M \phi^*(\beta, \alpha_2, \ldots, \alpha_n) \phi(\alpha, \alpha_2, \ldots, \alpha_n) \right). \]

In an according manner one can define a bosonic Fock-space \( q \)RDM via

\[ \langle \Phi| \hat{a}^+_\alpha_1 \cdots \hat{a}^+_\alpha_q \hat{a}_{\alpha'_q} \cdots \hat{a}_{\alpha'_1} \Phi \rangle. \]

The fermionic and bosonic RDMs can be extended to the coupled fermion-boson case in a straightforward manner by just integrating/summing out the other degrees of freedom. That is, if we have a general electron-boson state of the form of Eq. (2) we can accordingly define

\[ \Gamma_e^{(q)}(\alpha_1, \ldots, \alpha_q; \alpha'_1, \ldots, \alpha'_q) = \langle \Psi| \hat{a}^+_\alpha_1 \cdots \hat{a}^+_\alpha_q \hat{a}_{\alpha'_q} \cdots \hat{a}_{\alpha'_1} \Psi \rangle. \]

In a next step, we see whether these standard ingredients of RDMFT are sufficient to express the energy expectation value of the coupled Hamiltonian of Eq. (1). For the purely electronic part the different contributions can be expressed either explicitly by the electronic 1RDM or by the electronic 2RDM. The single-particle operators of \( \hat{H}_e \) and the single-particle
part of the dipole self-energy \( \hat{H}^{(1)}_d \) are given in terms of the 1RDM by

\[
(T + V) [\gamma_e] = \int d^3r \left[ -\frac{1}{2} \nabla_r^2 + v(r) \right] \gamma_e(r; r') |_{r' = r},
\]

\[
H^{(1)}_d [\gamma_e] = \int d^3r \left[ \sum_{\alpha=1}^{M} \frac{1}{2} (\lambda_{\alpha} \cdot r)^2 \right] \gamma_e(r; r).
\]

Here we have denoted on the left-hand side the explicit dependence of the expectation value on the 1RDM and the subscript \( |_{r' = r} \) indicates that \( r' \) is set to \( r \) after the application of the semi-local single-particle operator \((-\frac{1}{2} \nabla_r^2 + v(r))\). The expectation value of the electronic interaction energy \( \hat{W} \) and the two-body part of the dipole self-energy \( \hat{H}^{(2)}_d \) are given in terms of the (diagonal) of the 2RDM by

\[
W[\Gamma^{(2)}_e] = \frac{1}{2} \int d^3r d^3r' w(r, r') \Gamma^{(2)}_e(r, r'; r, r'),
\]

\[
H^{(2)}_d [\Gamma^{(2)}_e] = \frac{1}{2} \int d^3r d^3r' \left[ \sum_{\alpha=1}^{M} (\lambda_{\alpha} \cdot r) (\lambda_{\alpha} \cdot r') \right] \Gamma^{(2)}_e(r, r'; r, r').
\]

Hence, for the electronic operator expectation values little changes in comparison to a purely fermionic problem, except that we have a coupled electron-boson wave function and the extra contributions of the dipole self-energy. For the purely bosonic part of the coupled Hamiltonian we find

\[
H_{ph}[\gamma_b] = \sum_{\sigma_1, \ldots, \sigma_N} \int d^3r d^M p \Psi^* (r_1 \sigma_1, \ldots, p_M) \left\{ \sum_{\alpha=1}^{M} \left[ -\frac{1}{2} \frac{\partial^2}{\partial p^2_{\alpha}} + \frac{\omega_{\alpha}^2}{2} p^2_{\alpha} \right] \right\} \Psi (r_1 \sigma_1, \ldots, p_M)
\]

\[
= \sum_{\alpha=1}^{M} \left( \omega_{\alpha} + \frac{1}{2} \right) \gamma_b(\alpha, \alpha).
\]
However, the bilinear coupling term is not given in a simple RDM form but becomes

\[
H_{I}[\Gamma_{e,b}^{(3/2)}] = \sum_{\sigma_1,\ldots,\sigma_N} \int d^3N_r \, d^M p \Psi^*(r_1\sigma_1,\ldots,p_M) \left[ \sum_{\alpha=1}^{M} -\omega_{\alpha} p_{\alpha} \lambda_{\alpha} \cdot \hat{D} \right] \Psi(r_1\sigma_1,\ldots,p_M)
\]

\[
= \sum_{\alpha=1}^{M} -\omega_{\alpha} \langle \Psi | \left[ \sqrt{2} \omega_{\alpha} (\hat{a}_{\alpha}^+ + \hat{a}_{\alpha}) \lambda_{\alpha} \cdot \hat{D} \right] \Psi \rangle.
\]

A new reduced quantity appears that mixes light and matter degrees of freedom and can be interpreted as a 3/2-body operator \( \Gamma_{e,b}^{(3/2)}(\alpha; r, r') \). The bilinear interaction term therefore creates/annihilates bosons by interacting with the electronic subsystem. The 3/2-body RDM has in general no simple connection to any qRDM, even if we extend the definitions to include combined matter-boson qRDMs. One obvious reason is that qRDMs conserve particle numbers, while half-body RDMs do not. Take, for instance, the Fock-space \( \gamma_{b}(\alpha, \beta) = \langle \Phi | \hat{a}_{\beta}^+ \hat{a}_{\alpha} \Phi \rangle \). In the special case that \( |\Phi\rangle \) consists only of coherent states for each mode (which essentially means that we have treated the photons in mean field) and since the coherent states are eigenfunctions to the annihilation operators, we find \( \gamma_{b}(\alpha, \beta) = d_{\beta}^* d_{\alpha} \), where \( d_{\alpha} \) is the total displacement of the coherent state of mode \( \alpha \). In this case we also know \( \langle \Phi | \hat{a}_{\beta}^+ \Phi \rangle = d_{\beta}^* \). If we now assume all but one mode, say mode 1, having zero displacement, then we only know \( \gamma_{b}(1, 1) = |d_1|^2 \) from the bosonic 1RDM. We do, however, in general not know what \( d_1^* \) is. For other states, such a connection is even less explicit.

Putting the interrelations among the different RDMs aside for the moment, the mini-

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3To see this in a simple manner we also lift the continuous fermionic problem into its own Fock space and introduce genuine field operators \( \hat{\psi}^\dagger(r\sigma) \) and \( \hat{\psi}(r\sigma) \) with the usual anti-commutation relations. The electronic RDMs can then be written, similar to the discussed bosonic case, in terms of strings of creation and annihilation field operators. We can then re-express \( \langle \Psi | \left[ (\hat{a}_{\alpha}^+ + \hat{a}_{\alpha}) \lambda_{\alpha} \cdot \hat{D} \right] \Psi \rangle = \sum_{\sigma} \int d^3r \langle \Psi | \left[ (\hat{a}_{\alpha}^+ + \hat{a}_{\alpha}) \hat{\psi}^\dagger(r\sigma) \hat{\psi}(r\sigma) (\lambda_{\alpha} \cdot r) \right] \Psi \rangle \). If we then define \( \Gamma_{e,b}^{(3/2)}(\alpha; r, r') = \sum_{\sigma} \langle \Psi | \left[ (\hat{a}_{\alpha}^+ + \hat{a}_{\alpha}) \hat{\psi}^\dagger(r\sigma) \hat{\psi}(r'\sigma) \right] \Psi \rangle \) we can re-write \( \langle \Psi | \left[ (\hat{a}_{\alpha}^+ + \hat{a}_{\alpha}) \lambda_{\alpha} \cdot \hat{D} \right] \Psi \rangle = \int d^3r \, (\lambda_{\alpha} \cdot r) \Gamma_{e,b}^{(3/2)}(\alpha; r, r) \)

4Using the field-operator formulation the usual qRDMs consist of strings of particle-number-conserving combinations of electron and boson operators. Integrating/summing out a number-non-conserving part of it does not lead to a simple relation to half-body RDMs in general.
mization for the coupled matter-boson problem can be reformulated by

\[
E_0 = \inf_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \inf_{\{\gamma_e, \Gamma_e^{(2)}, \gamma_b, \Gamma_{e,b}^{(3/2)}\} \rightarrow \Psi} \left\{ \left( \hat{T} + \hat{V} \right) [\gamma_e] + \left( \hat{W} + \hat{H}_d \right) [\Gamma_e^{(2)}] + \hat{H}_{ph}[\gamma_b] + \hat{H}_{I}[\Gamma_{e,b}^{(3/2)}] \right\}.
\]

(7)

So in principle, we could replace the variation over all wave functions \( \Psi \) by their respective set of RDMs needed to define the energy expectation values. We could make the search space even more compact by expressing the lower-order RDMs by higher-order RDMs. Irrespective thereof, we see that instead of varying over the full configuration space \((r_1\sigma_1, ..., p_M)\), the above reformulation seems to indicate that we can replace this by varying over \((r, r')\) for the diagonal of \(\Gamma_e^{(2)}\) and also for the 1RDM \(\gamma_e\) together with a variation over \((\alpha, \beta)\) for \(\gamma_b\) and over \((\alpha, r)\) for \(\Gamma_{e,b}^{(3/2)}\). Such a reformulation is the basis of any RDMFT, and for electronic systems the properties of RDMs have been studied for more than 50 years. However, this seeming reduction of complexity is deceptive. In order to find physically sensible results we cannot vary arbitrarily over the above RDMs but need to ensure that they are consistent among each other and that they are all connected to a physical wave function. This is indicated in Eq. (7), where \(\{\gamma_e, \Gamma_e^{(2)}, \gamma_b, \Gamma_{e,b}^{(3/2)}\} \rightarrow \Psi\) highlights that the RDMs are contractions of a common wave function. For systems with fixed particle numbers it is in principle known how to restrict the set of trial RDMs to physical ones. The corresponding restrictions are called N-representability conditions. However, only for the 1RDM of ensembles (fermionic or bosonic) the conditions are simple. In this case, by diagonalizing the 1RDM in its eigenbasis \(\gamma_{e/b} = \sum n_i^{e/b} (\phi_{e/b}^i)^* \phi_{e/b}^i\) where the \(\phi_{e/b}^i\) are called the natural orbitals and the \(n_i^{e/b}\) the natural occupation numbers, the conditions are

\[
0 \leq n_i^e \leq 1,
0 \leq n_i^b,
\]

(8)
for fermions and bosons, respectively. If, the particle number \(N_{e/b}\) of one species of the system is conserved, the respective sum-rule

\[
\sum_{i=1}^{\infty} n_i^{e/b} = N_{e/b} \tag{9}
\]

becomes a second part of the N-representability conditions. Consequently, to define a proper RDM framework for coupled electron-boson problems, one would need to know the corresponding constraints that connect the wave function with all the necessary RDMs. A glance at the history of an important example, the search for the N-representability conditions of the electronic 2RDM, suggests that finding similar conditions for the novel half-body RDMs together with connections between the fermionic and bosonic qRDMs is a very challenging task. The electronic-2RDM problem was proposed in 1960 and it took until 2012, to understand how to make the conditions explicit. In 1995, the National Research Council of the USA designated the N-representability problem for fermions as one of ten most prominent research challenges in quantum chemistry.

Although the connection of the different RDMs in coupled fermion-boson systems are a very interesting subject, and recent results for a grand-canonical formulation of fermions or bosons suggest that also a combined formulation is feasible, we will follow an alternative route in this work. We want to reformulate the problem in such a way that we “fermionize” the coupled fermion-boson problem and we can apply the known conditions of the fermionic problem.

4 The “fermionization” of matter-photon systems

To “fermionize” the coupled fermion-boson problem, we follow a recent work by Nielsen et al. The exact “fermionization” of the problem is done in three steps. First, we introduce for each mode auxiliary extra dimensions \((p_{\alpha,2}, ..., p_{\alpha,N})\), where the number of these extra dimensions depends on the number of electrons \(N\). We therefore embed the physical config-
uration space in a higher-dimensional space, i.e., we now consider wave functions depending on \((r_1, r_2, ..., r_N, p_1, ..., p_M, p_{1,2}, ..., p_{1,N}, ..., p_{M,2}, ..., p_{M,N})\). Second, we add for every mode \(\alpha\) a linear operator

\[
\hat{\Pi}_\alpha(p_{\alpha,1}, ..., p_{\alpha,N}) = \sum_{i=2}^{N} \left( -\frac{1}{2} \frac{\partial^2}{\partial p_{\alpha,i}^2} + \frac{\omega^2_{\alpha}}{2} p_{\alpha,i}^2 \right)
\]

(10)

to the physical Hamiltonian of Eq. (1). This auxiliary Hamiltonian is a sum of quantum harmonic oscillators with respect to the auxiliary coordinates. The resulting Hamiltonian in the extended configuration space is \(\hat{H}' = \hat{H} + \sum_{\alpha=1}^{M} \hat{\Pi}_\alpha\). Here we see that the auxiliary degrees of freedom do not mix with the physical ones. This will allow in a very simple manner to embed but also to reconstruct the physical wave function. In the third step, we perform an orthogonal variable transformation of the photonic plus auxiliary coordinates to new coordinates \((q_{\alpha,1}, ..., q_{\alpha,N})\) such that we can express the displacement \(p_{\alpha}\) as

\[
p_{\alpha} = \frac{1}{\sqrt{N}} (q_{\alpha,1} + ... + q_{\alpha,N}),
\]

(11)

and it holds that \(\sum_{i=1}^{N} \left( -\frac{1}{2} \frac{\partial^2}{\partial q_{\alpha,i}^2} + \frac{\omega^2_{\alpha}}{2} q_{\alpha,i}^2 \right) = -\frac{1}{2} \frac{\partial^2}{\partial p_{\alpha}^2} + \hat{\Pi}_\alpha(p_{\alpha,2}, ..., p_{\alpha,N}).\) This whole procedure can be viewed as the inverse of a center-of-mass coordinate transformation. In total, we find the auxiliary Hamiltonian in the higher-dimensional configuration space given as

\[
\hat{H}' = \hat{H} + \sum_{\alpha} \hat{\Pi}_\alpha(p_{\alpha,2}, ..., p_{\alpha,N})
\]

(12)

\[
= \sum_{k=1}^{N} \left\{ -\frac{1}{2} \nabla_{r_k}^2 + v(r_k) + \sum_{\alpha=1}^{M} \left[ -\frac{1}{2} \frac{\partial^2}{\partial q_{\alpha,k}^2} + \frac{1}{2} \omega^2_{\alpha} q_{\alpha,k}^2 - \frac{\omega^2_{\alpha}}{2\sqrt{N}} q_{\alpha,k} (\lambda_{\alpha} \cdot r_k) + \frac{1}{2} (\lambda_{\alpha} \cdot r_k)^2 \right] \right\} \\
+ \frac{1}{2} \sum_{k \neq l} \left[ w(r_k, r_l) + \sum_{\alpha=1}^{M} \left( -\frac{\omega^2_{\alpha}}{2\sqrt{N}} q_{\alpha,k} \lambda_{\alpha} \cdot r_l - \frac{\omega^2_{\alpha}}{2\sqrt{N}} q_{\alpha,l} \lambda_{\alpha} \cdot r_k + \lambda_{\alpha} \cdot r_k \lambda_{\alpha} \cdot r_l \right) \right].
\]

Introducing then a \((3 + M)\)-dimensional polaritonic vector of space and auxiliary photon coordinates \(z = (r, q_1, ..., q_M)\) and the corresponding Laplacian \(\Delta = \sum_{i=1}^{3} \frac{\partial^2}{\partial r_i^2} + \sum_{\alpha=1}^{M} \frac{\partial^2}{\partial q_{\alpha}^2}\)
we can rewrite the above Hamiltonian as

$$\hat{H}'(t) = \sum_{k=1}^{N} \left[ -\frac{1}{2} \Delta_k + v'(z_k) \right] + \frac{1}{2} \sum_{k \neq l} w'(z_k, z_l)$$

\[ (13) \]

$$= \hat{T}' + \hat{V}' + \hat{W}' ,$$

where $v'$ and $w'$ are defined via the remaining terms in Eq. (12).

Note that the choice of the linear auxiliary operator and the coordinate transformation have some arbitrariness. The operator of Eq. (10) must not contain physical coordinates, but besides that other options seem possible. We decided for the harmonic-oscillator operator, because it simplifies the new Hamiltonian in comparison to other choices due to cancellations in the two-body potential. The coordinate transformation needs to adhere to Eq. (11) such that the electron-photon coupling term gives rise to new 1- and 2-body terms, as shown in Eq. (12). The rest of the transformation only acts on the auxiliary coordinates $p_{\alpha,i}$ for $i = 2, \ldots, M$ and hence leaves the physical part of the extended configuration space unchanged. This is the reason why the normalized physical solution $\Psi'$ of the auxiliary Hamiltonian $\hat{H}'$ in a very simple manner, i.e.,

$$\Psi' (r_1, \ldots, p_{M,N}) = \Psi (r_1, \ldots, r_N, p_1, \ldots, p_M) \chi(p_{1,2}, \ldots, p_{M,N}).$$

Here the normalized solution $\Psi'$ of the auxiliary Schrödinger equation $E_0' \Psi' = \hat{H}' \Psi'$ is found with $\chi$ being the ground state of $\sum_{\alpha} \hat{\Pi}_{\alpha}$. The ground state $\chi$ is merely a tensor product of individual harmonic-oscillator ground states and therefore exchanging $p_{\alpha,i}$ with $p_{\alpha,j}$ does not change the total wave function $\Psi'$. If we rewrite this wave function in the new coordinates

$$\Psi' (r_1, \ldots, r_N, q_1, \ldots, q_{M,N}) = \Psi' (z_1, \ldots, z_N),$$

and due to the fact that we constructed $\chi$ to be symmetric with respect to the exchange
of $q_{\alpha,k}$ and $q_{\alpha,l}$, we realize that $\Psi'$ is anti-symmetric with respect to the exchange of $(z_k \sigma_k)$ and $(z_l \sigma_l)$. Thus $\Psi'$ is fermionic with respect to the polaritonic coordinates $(z \sigma)$ and can be represented by a sum of Slater determinants of $(3 + M)$-dimensional polaritonic orbitals $\varphi(z \sigma)$. This makes the application of usual fermionic many-body methods possible and we can rely on fermionic $N$-representability conditions. However, besides the extra dimensions and the new fermionic exchange symmetry, the physical wave functions also have a further new $q_{\alpha,k} \leftrightarrow q_{\alpha,l}$ exchange symmetry. Simple approximations based on single polaritonic Slater determinants will violate this extra condition. We will remark on such violations a little later. To further see that indeed the constructed $\Psi'$ is a minimal-energy state in the extended space with the appropriate symmetries, we first point out that for any trial wave function

$$\Phi'(z_1 \sigma_1, ... z_N \sigma_N) \equiv \Phi'(r_1 \sigma_1, ..., p_M; p_1, 2, ..., p_{M,N})$$

the $q$-exchange symmetry implies that the fermionic symmetry is in the $(r \sigma)$ coordinates. Then it holds since $\hat{H}$ only acts on $(r_1, ..., p_M)$ and $\sum_{\alpha=1}^{M} \hat{\Pi}_{\alpha}$ only acts on $p_1, 2, ..., p_{M,N}$ that

$$\inf_{\Phi'} \langle \Phi' | \hat{H}' \Phi' \rangle \geq \inf_{\Phi'} \langle \Phi' | \hat{H} \Phi' \rangle + \inf_{\Phi'} \langle \Phi' | \sum_{\alpha=1}^{M} \hat{\Pi}_{\alpha} \Phi' \rangle = \langle \Psi | \hat{H} \Psi \rangle + \langle \chi | \sum_{\alpha=1}^{M} \hat{\Pi}_{\alpha} \chi \rangle,$$

which is the energy of $\Psi'$.

5 Dressed Reduced Density-Matrix Functional Theory

From the observations of the previous chapter we can conclude that every electronic many-body theory can be applied to this auxiliary problem. In Ref. 1 this is done for time-dependent DFT and it is compared to the standard Kohn-Sham formulation of QEDFT. It is shown that a simple dressed Kohn-Sham approximation can capture matter-photon correlations that are hard to capture with standard approximations of Kohn-Sham QEDFT.
But from the experience with purely electronic DFT we expect that for ultra-strong and deep-strong coupling situations the simple dressed approximations also become less reliable. Instead of developing more advanced approximations for a dressed Kohn-Sham approach we here propose to follow another route. Similar to electronic-structure theory, where RDMFT becomes a reasonable alternative to DFT methods when strong correlations become important, we here develop a dRDMFT approach.

Let us therefore analyze the structure of $\hat{H}'$ given in Eq. (13). It consists of only (polaritonic) one-body terms $\hat{h}^{(1)}(z) = -\frac{1}{2}\Delta + v'(z)$, and two-body terms $\hat{h}^{(2)}(z, z') = w'(z, z')$. It commutes with the polaritonic particle-number operator $\hat{N}' = \int d^{3+M} z \hat{n}(z)$, where we used the definition of the polaritonic local density operator $\hat{n}(z) = \sum_{\sigma=1}^{N} \delta^{3+M}(z - z_i)$. This means that the auxiliary system has a constant polaritonic particle number $N$. Additionally, the physical wave function of the dressed system $\Psi'(z_1\sigma_1, \ldots, z_N\sigma_N)$ is per construction anti-symmetric. This allows for the definition of a polaritonic (spin-summed) 1RDM

$$\gamma(z, z') = N \sum_{\sigma_1, \ldots, \sigma_N} \int d^{(3+M)(N-1)} z$$

$$\Psi'^*(z'\sigma_1, z_2\sigma_2, \ldots, z_N\sigma_N) \Psi'(z_1\sigma_1, z_2\sigma_2, \ldots, z_N\sigma_N),$$

in accordance to Eq. (5). By construction this auxiliary density matrix reduces to the physical electron density matrix via $\gamma_e(r, r') = \int d^M q \gamma(r, q_1, \ldots, q_M; r', q_1, \ldots, q_M)$. Furthermore we introduce the (spin-summed) dressed 2RDM $\Gamma^{(2)}(z_1, z_2; z'_1, z'_2) = N(N-1) \sum_{\sigma_1, \ldots, \sigma_N} \int d^{(3+M)(N-2)} z$ $\Psi'^*(z'_1\sigma_1, z'_2\sigma_2, z_3\sigma_3, \ldots, z_N\sigma_N) \Psi'(z_1\sigma_1, z_2\sigma_2, z_3\sigma_3, \ldots, z_N\sigma_N)$. These dressed RDMs allow now to express the energy expectation value of the dressed system by

$$E'_0 = \langle \Psi' | \hat{H}' | \Psi' \rangle = \langle \Psi' | \sum_{k=1}^{N} \hat{h}^{(1)}(z_k) + \frac{1}{2} \sum_{k \neq l} \hat{h}^{(2)}(z_k, z_l) | \Psi' \rangle$$

$$= \int d^{3+M} z \hat{h}^{(1)}(z) \gamma(z, z') |_{z'=z} + \frac{1}{2} \int d^{3+M} z d^{3+M} z' \hat{h}^{(2)}(z, z') \Gamma^{(2)}(z, z', z, z'),$$

With these definitions we can define the variational principle for the ground state only with
respect to reduced quantities as

\[ E'_0 = \inf_{\{\gamma, \Gamma^{(2)}\} \to \Psi'} E[\gamma, \Gamma^{(2)}], \tag{15} \]

To perform this minimization, we would need to constrain the configuration space to the physical dressed RDMs that connect to an anti-symmetric wave function with the extra \( q \)-exchange symmetry by testing the appropriate \( N \)-representability conditions of the dressed 2RDM and the dressed 1RDM. Besides the by now well-known conditions for the fermionic 2RDM and the fermionic 1RDM, we would in principle get further conditions to ensure the extra exchange symmetry. However, already for the usual electronic 2RDM the number of conditions grows exponentially with the number of particles, and it is out of the scope of this work to discuss possible approximations. The interested reader is referred to, e.g., Ref.\[ 49. \]

Instead, we want to stick to the dressed 1RDM \( \gamma \) and approximate the 2-body part as a functional of the dressed 1RDM. The mathematical justification of RDMFT is given by Gilbert’s theorem, which is a generalization of the Hohenberg-Kohn theorem of DFT. More specifically, Gilbert proves that the ground state energy of any system with maximum 2-body terms is a unique functional of its 1RDM. Following this idea we will express the ground-state energy of the dressed system as a partly unknown functional \( F' \) of only the system’s dressed 1RDM

\[ E'_0 = \inf_{\gamma} F'[\gamma] = \inf_{\gamma} \left\{ \int d^{3+M}z \hat{h}^{(1)}(z)\gamma(z, z')|_{z'=z} + \frac{1}{2} \int d^{3+M}z d^{3+M}z' \hat{\Gamma}^{(2)}(z, z') |_{z', z, z, z'} \right\} = W'[\gamma]. \tag{16} \]

What we need here, is a functional of the diagonal of the dressed 2RDM in terms of the dressed 1RDM as well as adhering to all dressed \( N \)-representability conditions when varying over \( \gamma \). We also see now the advantage of the dRDMFT approach, which avoids the original variation over all wave functions as well as a variation over many different RDMs as shown
in Eq. (7). Instead, we only need the dressed 1RDM, which has a comparatively simple connection to fermionic wave functions (at least when we vary over ensembles, i.e., Eq.s (8,9)).

The price we pay for this is twofold: First, we have a new symmetry that will most likely lead to extra $N$-representability conditions. Second, we need to increase the dimension of the natural orbitals by one for every photon mode. However, to capture the main physics of usual cavity experiments, often one effective mode is enough. Computations with four-dimensional dressed orbitals are numerically feasible.

It is specifically such settings where we envision a dRDMFT to be a reasonable alternative to dressed Kohn-Sham or standard QEDFT calculations for matter-photon systems. To see whether our approach is practical and accurate, we want to perform first simple calculations for coupled matter-photon systems. We will make the following pragmatic approximations:

We only enforce the fermionic ensemble $N$-representability conditions and ignore presently the extra exchange symmetry, and we employ simple approximations to the unknown part $W'[\gamma]$ that have been developed for the electronic case. To do so we further, similar to the electronic case, decompose $W'[\gamma] = E_{H}[\gamma] + E_{xc}[\gamma]$ into a classical Hartree part $E_{H}[\gamma] = \frac{1}{2} \int \int d^{3+M}zd^{3+M}z' \gamma(z,z')\gamma(z',z')w'(z,z')$ and an unknown exchange-correlation part $E_{xc}[\gamma]$. Almost all known functionals $E_{xc}[\gamma]$ are expressed in terms of the eigenbasis and eigenvalues of the 1RDM. In our case the dressed natural orbitals $\phi_{i}(z)$ and occupation numbers $n_{i}$ are found by solving $\int \gamma(z,z')\phi_{i}(z')d^{3+M}z' = n_{i}\phi_{i}(z)$. The simplest approximation is to only retain the fermionic exchange symmetry and employ the Hartree-Fock functional

$$E_{HF}[\gamma] = -\frac{1}{2} \sum_{i,j} n_{i}n_{j} \int \int d^{3+M}zd^{3+M}z' \phi_{i}^{*}(z)\phi_{j}^{*}(z')w'(z,z')\phi_{i}(z')\phi_{j}(z),$$

where the occupation numbers only take the values $n_{i} = 0, 1$ and we end up with a single Slater determinant of dressed orbitals. This approximation, which we call dressed Hartree-

\[5\] This approximation is similarly employed in electronic RDMFT. For details we refer to, e.g., Ref. [51].
Fock (dHF), therefore generally violates the extra exchange symmetry. We can go beyond the single Slater determinant in dRDMFT if we instead of the dHF approximation employ the Müller functional\(^\text{34}\)

\[
E_M = -\frac{1}{2} \sum_{i,j} \sqrt{n_in_j} \int \int d^{3+M}zd^{3+M}z' \phi_i^*(z)\phi_j^*(z') w(z,z')\phi_i(z)\phi_j(z),
\]

which has been re-derived by Bjuise and Baerends.\(^\text{52}\) The Müller functional has been studied for many physical systems\(^\text{35,52}\) and gives a qualitatively reasonable description of the electronic ground states. Additionally, it has many advantageous mathematical properties.\(^\text{34,53}\) A thorough discussion of different functionals goes beyond the scope of this work, and we only want to remark that a variety of functionals were proposed since 1984 and it is likely to have even better agreement with the exact solution by choosing more elaborate functionals.

6 Numerical Implementation

For numerical convenience we first rewrite the approximated energy functional in the natural orbital basis as

\[
E[\gamma] = -\sum_{i=0}^\infty n_i \int d^{3+M}z \phi_i^*(z) \left[-\frac{1}{2} \Delta + v(z)\right] \phi_i(z) + \\
\frac{1}{2} \sum_{i,j} n_in_j \int \int d^{3+M}zd^{3+M}z' \left|\phi_i(z)\right|^2 \left|\phi_j^*(z')\right|^2 w(z,z') + E_M[\gamma]
\]

We use this form to minimize the energy functional by adopting the natural orbitals as well as the natural occupation numbers. To impose fermionic ensemble \(N\)-representability, we first represent the occupation numbers as angles \(0 \leq n_i = \sin^2(\alpha_i) \leq 1\) to satisfy Eq. (8). The second part of the conditions (Eq. (9)), i.e., \(\sum_{i=1}^N n_i = N\), as well as the orthonormality of the polaritonic natural orbitals, i.e., \(\int d^{3+M}z\phi_i^*(z)\phi_j(z) = \delta_{ij}\), are imposed via Lagrange
multipliers as, e.g., explained in Ref. [54]. We use the orbital-optimization method introduced by Piris et al. in Ref. [55]. That is, we choose a basis over which we optimize the form of the natural orbitals. To construct such a basis we solve the single-polariton equation

\[ \left( -\frac{1}{2} \Delta + v'(z) \right) \varphi_k(z) = \epsilon_k \varphi_k(z), \]

and take the lowest \( N + S \) orbitals, where \( N \) is the polariton number and \( S \) a specific number of extra states (for the test calculations with two polaritons, presented in the following section, we chose \( S = 70 \) to get a very high precision). At this point, we want to mention a practical problem in the calculations due to the orbital optimization method. For certain parameters we encounter convergence issues even for a very large number of basis states. The reason is that either the electronic or the photonic degrees of freedom are not represented well enough by the basis of the independent-polariton calculation. This can happen if the energy scales of the electronic, i.e., the eigenenergies of the uncoupled electronic system, and the photonic degrees of freedom, i.e., the photon energies \( \omega_\alpha \), are very different. For instance, consider the zero-coupling case and let \( \Delta E \) be the electronic transition frequency between the ground and the first excited state. If we choose the frequency of the photon field as \( \omega = \Delta E/10 \), then the first 9 excited polariton states will just be products of the electronic ground state with the corresponding photonic excited states. If our basis consists of mainly such states, the electronic part of the polaritonic natural orbitals are not flexible enough to perform a reasonable dRDMFT minimization. However, for the following examples, we have made sure that this issue does not occur and it can generally be avoided by choosing a well-balanced basis (enough electronic as well as photonic freedom) or by changing the orbital optimization technique to, for example, a conjugated gradient algorithm over a complete basis set in our polaritonic space.

Besides the fact that we can re-use many ideas from electronic RDMFT, a further advantage of the dressed reformulation is that we can also re-use most numerical techniques
developed for quantum chemistry. For instance, to determine the polaritonic orbitals we merely need to be able to solve higher-dimensional static Schrödinger-type equations. We only have to change the usual electronic potential \( v \) to its polaritonic counter part \( v' \). This, together with a change of the electronic Coulomb interaction \( w \) to it polaritonic counter part \( w' \), already allows to perform dHF calculations. If the code is furthermore able to perform RDMFT minimizations, it is straightforward to extend the implementation to also solve coupled electron-photon problems via dRDMFT from first principles.

We have done so with the electronic-structure code Octopus. Since the Octopus code in principle allows to solve Schrödinger-type equations of arbitrary dimensions (in practice 6 dimensions are feasible with current technology) we could still solve the case of two (one-dimensional) electrons interacting with one photon mode exactly as a reference. To check the consistency of our implementation, we furthermore compared to several standard implementations in the \( \lambda = 0 \) limit. We made sure that dRDMFT finds the same ground-state densities like the already implemented RDMFT and we compared dHF to the usual HF for electrons only as well as to the exact-exchange approximation in DFT that for two particles is equivalent to HF. We also extensively tested our implementation for \( \lambda > 0 \) by comparing our results to results obtained with the code that was used in Ref. The latter uses a Lanczos algorithm to find the full interacting ground state of small dressed systems but can also calculate the ground-state of the exact-exchange approximation in dressed DFT. For two-particle systems, the exact solutions of both codes were compared and the dHF routine of Octopus was validated with the dressed exact-exchange routine of the other code.

7 Numerical Results

In the following we consider systems of two-electrons in one spatial dimension coupled to one photon mode. We transfer the systems in the dressed basis, where the explicit coordinate transformation of type \( (11) \) reads \( p = \frac{1}{\sqrt{2}}(q_1 + q_2) \) and \( p_2 = \frac{1}{\sqrt{2}}(q_1 - q_2) \). This leads to a
dressed local potential \( v'(r, q) = v(r) + \frac{1}{2}(\lambda \cdot r)^2 + \frac{\omega^2}{2} q^2 - \frac{\omega}{\sqrt{2}} q(\lambda \cdot r) \).

As test systems we consider a one-dimensional model of a helium atom (He), i.e., \( v_{He}(r) = -\frac{2}{\sqrt{x^2+1}} \), and a one-dimensional model of a hydrogen molecule \((H_2)\) at its equilibrium position \( d = 1.628 \) a.u., i.e., \( v_{H_2}(r) = -\frac{1}{\sqrt{(x-d)^2+1}} - \frac{1}{\sqrt{(x+d)^2+1}} \). We use the soft Coulomb interaction \( w(x, x') = 1/\sqrt{|x - x'|^2 + 1} \) and determine the ground and first excited state of the exact “bare” systems, so outside of the cavity, to find the corresponding excitation frequencies \( \omega_{He} = 0.5535 \) a.u. and \( \omega_{H_2} = 0.4194 \) a.u.. All the following results are calculated with the photon frequency in resonance with these transitions. However, it should be noted that resonance is not an important feature for ground state calculations, in contrast to the excited states and the ensuing Rabi splitting. In this setting the polaritonic auxiliary system is 4-dimensional, which is still small enough to be solved exactly in a 4-dimensional discretised simulation box, so that we can compare dRDMFT (with the Müller functional of Eq. [18]), dHF (see Eq. [17]) and the exact solutions. We used 2-dimensional boxes with a length of 14 a.u. and a spacing of 0.14 a.u. to model the dressed orbitals. To make sure that the results were converged, we used 71 natural orbitals for all calculations.
Figure 1: Differences of dHF and dRDMFT from the exact ground state energies (in Hartree) as a function of the coupling constant \( \lambda \) for the He atom (left) and \( \text{H}_2 \) molecule (right) in the dressed orbital description. dRDMFT improves considerably upon dHF. For both systems, the energy of dRDMFT remains close to the exact one, the error of dHF instead increases with the coupling strength.

We first show (see Fig. 1) the deviations of the ground state energies for dRMDFT and dHF from the exact dressed calculation as a function of the coupling strength \( \lambda \) of He and \( \text{H}_2 \), respectively. We thereby go from weak to deep-strong coupling with \( \lambda = 1 \). While dHF deviates strongly for large couplings, the dRDMFT approximation stays very accurate over the whole range. Still, a more severe test of the accuracy of our method is if we compare spatially resolved quantities instead of merely energies. In Fig. 2, we consider exemplarily the deviations of the approximate ground-state densities from the exact one in the ultrastrong-coupling regime \( \lambda = 0.1 \) for both systems. For a better visibility, we separated the electronic and photonic parts of the two-dimensional densities by integration, i.e., \( n(x) = \int dq n(x, q) \) and \( n(q) = \int dx n(x, q) \). For dRDMFT the deviations are for both systems considerably smaller with respect to both the electronic and photonic coordinate, which is consistent with the deviations in the energies. This holds for all the considered coupling strengths. Looking at the electronic densities, we can observe a feature that the
ground state energy does not reveal. In some cases the effects of the two approximations are contrary to each other as we can see in the He case, where the dRDMFT electron density is more localized around the center of mass than the exact reference and the electron density of dHF less. In other cases instead, both theories over-localize the density (here visible for $H_2$). An even more stringent test of the accuracy of the dRDMFT approach is to compare the dressed 1RDMs. The essential ingredients of the dressed 1RDMs are their natural orbitals $\phi_i(x,q)$. Again, we separated electronic and photonic contributions and show their reduced electronic density $\rho_i(x) = \int dq |\phi_i(x,q)|^2$. Fig. 3 depicts the first three dressed natural orbital densities of dRDMFT in comparison with the exact ones for both test systems. While it holds that for both systems, the lowest natural orbital density of the dRDMFT approximation is almost the same as the exact one, and the second natural orbital densities are only slightly different, the third natural orbital densities of $H_2$ differ even qualitatively. For He, similar strong deviations are visible for the fourth natural orbital. However, as long as such strong deviations only occur for natural orbitals with small natural occupation numbers, like in these cases ($H_2: n_1 = 1.878, n_2 = 0.102, n_3 = 0.015$, He: $n_1 = 1.978, n_2 = 0.020, n_3 = 0.001$), their (inaccurate) contribution to the density and total energy remains small. We do not show the photonic orbital densities, but want to mention that the dRDMFT orbitals agree all qualitatively with the exact ones.
Figure 2: Deviations of dHF and dRDMFT ground state densities from the exact solution (depicted in the insets) for the He atom (top) and the $H_2$ molecule (bottom) with coupling $\lambda = 0.1$. We separated the electronic ($x$, left) and photonic ($q$, right) coordinates as explained in the text. For both coordinates for both systems, dRDMFT finds a considerably better ground-state density than dHF, which is consistent with the better result in energy (see Fig. 1). We also see that the deviations of dHF and dRDMFT from the exact density can be qualitatively similar like in the $H_2$ case. For the spatial density of He instead, the deviations are contrary in the sense that dRDMFT localizes but dHF expands it too much.
Figure 3: The first three natural orbital densities $\rho_{ex/dR}(x)$ of the exact (ex) and dRDMFT (dR) calculations are depicted for the He atom (top) and the $H_2$ molecule (bottom) with coupling $\lambda = 0.1$. We see in both cases that $\rho_{ex}^1(x)$ is almost exactly reproduced by dRDMFT, but $\rho_{dR}^2(x)$ deviates already visibly from $\rho_{ex}^2(x)$ (left). However, it is in both cases qualitatively correct. This changes for $\rho_{dR}^3(x)$ of $H_2$, which has one node more than $\rho_{ex}^3(x)$. Nevertheless, $\rho_{dR}^3(x)$ of He, is reproduced correctly (right).
8 Conclusion

In this work, we presented, to the best of our knowledge, the first RDMFT formalism for coupled matter-photon systems. This formalism is capable to account for the full quantum-mechanical degrees of freedom of the coupled fermion-boson problem. We discussed that extending the standard formulation of electronic RDMFT to systems with coupled fermionic and bosonic degrees of freedom is not straightforward. Then we presented an alternative approach which overcomes most of the intricate representability issues by embedding the coupled matter-photon system in a higher-dimensional auxiliary space. Specifically, we introduced for a problem with $N$ electrons coupled to $M$ photon modes, $(N-1)M$ auxiliary coordinates, which allowed us to “fermionize” the coupled problem with respect to new polaritonic coordinates. The resulting dressed fermionic particles are governed by a Hamiltonian with only 1-body and 2-body terms and thus one can apply any standard electronic-structure method. The extension is constructed in such a way that the auxiliary dimensions do not modify the original physical system and the physical observables are easy to recover. We used this framework to develop and implement dRDMFT in the electronic-structure code Octopus\textsuperscript{54} and tested it with the Hartree-Fock and Müller functional. For simple one-dimensional models of atoms and molecules the obtained approximate results were in good agreement with the exact results from the weak to the deep-strong coupling regime.

Although the presented method is practical only for a few photon modes, since the number of photon modes determines the dimension of the involved dressed orbitals, it is exactly these cases that are the most relevant in cavity and circuit QED experiments. Since dRDMFT is non-perturbative and seems to be accurate over a wide range of couplings, it is a promising tool to investigate long-standing problems of quantum optics, such as the quest for a super-radiant phase in the ground state of strongly-coupled matter-photon systems.\textsuperscript{[17]} But it also is a very promising tool to investigate changes in the ground-state due to matter-photon coupling that can modify chemical reactions.\textsuperscript{[6]} Besides such interesting applications and fundamental questions of light matter-interactions, there are many open questions to
answer also in the presented theory itself. For instance, how strong is the influence of the
hitherto negelected $q$-exchange symmetry? First calculations for many particles indicate that
it will become important to enforce this extra symmetry to stay accurate when going from
weak to the deep-strong coupling regime. Furthermore, it might become beneficial to avoid
the “fermionization” that we employed and then very interesting mathematical questions
about $N$-representability for coupled fermion-boson systems need to be addressed. Here the
understanding how to enforce the $q$-exchange symmetries in the dressed formulation could
be very useful. Alternatively, based on recent results for fermionic or bosonic systems,[46] a
grand-canonical formulation seems most promising to develop RDMFT for coupled fermion-
bozon systems in the physical configuration space avoiding many representability issues.

**Acknowledgements**

F.B. wants to thank Nicole Helbig, Klaas Giesbertz, Micael Oliveira, and Christian Schäfer
for stimulating and useful discussions. We acknowledge financial support from the European
Research Council (ERC-2015-AdG-694097).
A The bosonic symmetry of the photon wave function

In this appendix we want to go into a little more detail and show how the mode-representation, which makes the bosonic symmetry explicit, arises and introduce in this setting the usual bosonic density matrices.\(^{10}\) Instead of starting with the displacement representation we start with the definition of the single-particle Hilbert space and its Hamiltonian. We choose the single-particle Hilbert space \(\mathcal{H}_1\) to consist of \(M\) orthogonal states \(|\alpha\rangle\). These states are defined by the eigenstates of the Laplacian with fixed boundary conditions and geometry and correspond to the Fourier modes of the electromagnetic field.\(^{24,58}\) Since we work directly in the dipole approximation we do not go through all the steps of the usual quantization procedure of QED but from the start assume that we have chosen a few of these modes \(|\alpha\rangle\) (with a certain frequency and polarization) in Coulomb gauge.\(^{24}\) The single-particle Hamiltonian in this representation is then given by

\[
\hat{h}_{ph}' = \sum_{\alpha=1}^{M} \omega_{\alpha} |\alpha\rangle \langle \alpha|.
\]

Since a total shift of energy does not change the physics and for later reference we can equivalently use \(\hat{h}_{ph} = \sum_{\alpha=1}^{M} (\omega_{\alpha} + \frac{1}{2}) |\alpha\rangle \langle \alpha|\). Therefore the energy of a single-photon wave function \(|\phi\rangle = \sum_{\alpha=1}^{M} \phi(\alpha) |\alpha\rangle\) (corresponding to the classical Maxwell field in Coulomb gauge\(^{59}\)) is given by

\[
E[\phi] = \sum_{\alpha,\beta=1}^{M} \phi^*(\beta) \langle \beta | \hat{h}_{ph} | \alpha \rangle \phi(\alpha) = \sum_{\alpha,\beta} \hat{h}_{ph}(\beta, \alpha) \gamma_{\beta}(\alpha, \beta) = \sum_{\alpha} \left( \omega_{\alpha} + \frac{1}{2} \right) \gamma_{\beta}(\alpha, \alpha) |\phi(\alpha)\rangle^2.
\]

Here we have introduced the single-particle photonic 1RDM \(\gamma_{\beta}(\alpha, \beta) = \phi^*(\beta) \phi(\alpha)\). We can then extend the single-particle space and introduce photonic many-body spaces \(\mathcal{H}_{N_b}\) which...
are the span of all symmetric tensor products of single-particle states of the form:

\[ |\alpha_1, ..., \alpha_{N_b}\rangle = \frac{1}{\sqrt{N_b!}} \sum_{\wp} |\wp(\alpha_1)\rangle \cdots |\wp(\alpha_{N_b})\rangle, \]

where \( \wp \) goes over all permutations of \( \alpha_1, ..., \alpha_{N_b} \). An \( N_b \)-particle Hamiltonian is then given by a sum of individual single-particle Hamiltonians (interactions among the photons will only come about due to the coupling with the electrons). Introducing then for a general \( N_b \) photon state \( |\tilde{\phi}\rangle = \sum_{\alpha_1, ..., \alpha_{N_b}} \tilde{\phi}(\alpha_1, ..., \alpha_{N_b}) |\alpha_1, ..., \alpha_{N_b}\rangle \) the corresponding 1RDM according to Eq. (6) as \( \gamma_b(\alpha, \beta) = N_b \sum_{\alpha_2, ..., \alpha_{N_b}} \tilde{\phi}^*(\beta, \alpha_2, ..., \alpha_{N_b}) \tilde{\phi}(\alpha, \alpha_2, ..., \alpha_{N_b}) \) (where we have assumed that the wave function \( \tilde{\phi}(\alpha, \alpha_2, ..., \alpha_{N_b}) \) is properly symmetrized with respect to the exchange of coordinates), the energy of that state is given by

\[ E[\tilde{\phi}] = \sum_{\alpha, \beta=1}^M \hat{h}_{ph}(\beta, \alpha) \gamma_b(\alpha, \beta) = \sum_{\alpha=1}^M \left( \omega_\alpha + \frac{1}{2} \right) \gamma_b(\alpha, \alpha). \]

Such a state can be constructed, for instance, as a permanent of \( N_b \) single-photon states \( \phi(\alpha) \). Note further that the 1RDM of an \( N_b \) photon state obeys \( N_b = \sum_\alpha \gamma_b(\alpha, \alpha) \).

Finally, since we want to have a simplified form of a field theory without fixed number of photons, we make a last step and represent the problem on a Hilbert space with indetermined number of particles, i.e., a Fock space. By defining the vacuum state \( |0\rangle \), which spans the one-dimensional zero-photon space, the Fock space is defined by a direct sum of \( N_b \)-photon spaces \( F = \bigoplus_{N_b=0}^\infty \mathcal{H}_{N_b} \). Introducing the ladder operators between the different photon-number sectors of \( F \) by

\[ \hat{a}_\alpha^+ |\alpha_1, ..., \alpha_{N_b}\rangle = |\alpha_1, ..., \alpha_{N_b+1}, \alpha\rangle \]
\[ \hat{a}_\alpha |\alpha_1, ..., \alpha_{N_b}\rangle = \sum_{k=1}^{N_b} \delta_{\alpha_k, \alpha} |\alpha_1, ..., \alpha_{k-1}, \alpha_{k+1}, ..., \alpha_{N_b}\rangle \]

with the usual commutation relations, we can then lift the single-particle Hamiltonian to the full Fock space and arrive at Eq. (3). The Fock space 1RDM for a general Fock space wave
function $|\Phi\rangle$ can then be expressed as

$$\gamma_b(\alpha, \beta) = \langle \Phi| \hat{a}^+_\beta \hat{a}_\alpha \Phi \rangle,$$

and $\sum_{\alpha=1}^M \gamma_b(\alpha, \alpha) = N_b$ now corresponds to the average number of photons. And finally, since we know that Eq. (3) is equivalent to $\hat{H}_{ph} = \sum_{\alpha=1}^M \left( -\frac{1}{2} \frac{\partial^2}{\partial p_\alpha^2} + \frac{\omega_\alpha^2}{2} p_\alpha^2 \right)$, we also see that the Fock space $\mathcal{F}$ is isomorphic to $L^2(\mathbb{R}^M)$, which closes our small detour.
References

(1) Nielsen, S. E.; Schäfer, C.; Ruggenthaler, M.; Rubio, A. Dressed Kohn-Sham Scheme for Cavity Quantum Electrodynamics and Beyond. arXiv preprint arXiv:1812.00388 2018.

(2) Ebbesen, T. W. Hybrid Light–Matter States in a Molecular and Material Science Perspective. Accounts of Chemical Research 2016, 49, 2403–2412.

(3) Sukharev, M.; Nitzan, A. Optics of exciton-plasmon nanomaterials. Journal of Physics: Condensed Matter 2017, 29, 443003.

(4) Hutchison, J. A.; Schwartz, T.; Genet, C.; Devaux, E.; Ebbesen, T. W. Modifying chemical landscapes by coupling to vacuum fields. Angew. Chemie - Int. Ed. 2012, 51, 1592–1596.

(5) Thomas, A.; George, J.; Shalabney, A.; Dryzhakov, M.; Varma, S. J.; Moran, J.; Chervy, T.; Zhong, X.; Devaux, E.; Genet, C. Ground-State Chemical Reactivity under Vibrational Coupling to the Vacuum Electromagnetic Field. Angewandte Chemie 2016, 128, 11634–11638.

(6) Firstenberg, O.; Peyronel, T.; Liang, Q. Y.; Gorshkov, A. V.; Lukin, M. D.; Vuletić, V. Attractive photons in a quantum nonlinear medium. Nature 2013, 502, 71–75.

(7) Goban, A.; Hung, C. L.; Hood, J. D.; Yu, S. P.; Muniz, J. A.; Painter, O.; Kimble, H. J. Superradiance for Atoms Trapped along a Photonic Crystal Waveguide. Phys. Rev. Lett. 2015, 115.

(8) Coles, D. M.; Yang, Y.; Wang, Y.; Grant, R. T.; Taylor, R. A.; Saikin, S. K.; Aspuru-Guzik, A.; Lidzey, D. G.; Tang, J. K.-H.; Smith, J. M. Strong coupling between chlorosomes of photosynthetic bacteria and a confined optical cavity mode. Nature communications 2014, 5.
(9) Orgiu, E.; George, J.; Hutchison, J. A.; Devaux, E.; Dayen, J. F.; Doudin, B.; Stellacci, F.; Genet, C.; Schachenmayer, J.; Genes, C.; Pupillo, G.; Samorì, P.; Ebbesen, T. W. Conductivity in organic semiconductors hybridized with the vacuum field. Nat. Mater. 2015, 14, 1123–1129.

(10) Andrew, P.; Barnes, W. L. Energy transfer across a metal film mediated by surface plasmon polaritons. Science 2004, 306, 1002–1005.

(11) Ruggenthaler, M.; Tancogne-Dejean, N.; Flick, J.; Appel, H.; Rubio, A. From a quantum-electrodynamical light–matter description to novel spectroscopies. Nat. Rev. Chem. 2018, 2, 0118.

(12) Schäfer, C.; Ruggenthaler, M.; Rubio, A. Ab initio nonrelativistic quantum electrodynamics: Bridging quantum chemistry and quantum optics from weak to strong coupling. Physical Review A 2018, 98, 043801.

(13) Feist, J.; Garcia-Vidal, F. J. Extraordinary exciton conductance induced by strong coupling. Phys. Rev. Lett. 2015, 114, 1–5.

(14) Michetti, P.; Mazza, L.; La Rocca, G. C. In Organic Nanophotonics: Fundamentals and Applications; Zhao, Y. S., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2015; pp 39–68.

(15) Galego, J.; Garcia-Vidal, F. J.; Feist, J. Suppressing photochemical reactions with quantized light fields. Nat. Commun. 2016, 7, 1–6.

(16) Kockum, A. F.; Miranowicz, A.; De Liberato, S.; Savasta, S.; Nori, F. Ultrastrong coupling between light and matter. arXiv preprint arXiv:1807.11636 2018, 1–26.

(17) De Bernardis, D.; Pilar, P.; Jaako, T.; De Liberato, S.; Rabl, P. Breakdown of gauge invariance in ultrastrong-coupling cavity QED. arXiv preprint arXiv:1805.05339 2018,
(18) R. Dreizler, E. G. *Density Functional Theory- An Approach to the Quantum Many-Body Problem*; Springer Berlin Heidelberg, 1990.

(19) Dreizler, R. M.; Engel, E. *Density Functional Theory: An Advanced Course*; Springer, 2011.

(20) Fetter, A.; Walecka, J. *Quantum Theory of Many-Particle Systems*; Dover, Mineola, New York, 2003.

(21) Stefanucci, G.; Van Leeuwen, R. *Nonequilibrium many-body theory of quantum systems: a modern introduction*; Cambridge University Press, 2013.

(22) Ruggenthaler, M.; Mackenroth, F.; Bauer, D. Time-dependent Kohn-Sham approach to quantum electrodynamics. *Physical Review A* **2011**, *84*, 042107.

(23) Tokatly, I. V. Time-dependent density functional theory for many-electron systems interacting with cavity photons. *Phys. Rev. Lett.* **2013**, *110*, 1–5.

(24) Ruggenthaler, M.; Flick, J.; Pellegrini, C.; Appel, H.; Tokatly, I. V.; Rubio, A. Quantum-electrodynamical density-functional theory: Bridging quantum optics and electronic-structure theory. *Phys. Rev. A* **2014**, *90*, 1–26.

(25) Ruggenthaler, M. Ground-State Quantum-Electrodynamical Density-Functional Theory. *arXiv Preprint* **2015**, *arXiv:1509*, 1–6.

(26) Flick, J.; Ruggenthaler, M.; Appel, H.; Rubio, A. Kohn–Sham approach to quantum electrodynamical density-functional theory: Exact time-dependent effective potentials in real space. *Proc. Natl. Acad. Sci.* **2015**, *112*, 15285–15290.

(27) Flick, J.; Ruggenthaler, M.; Appel, H.; Rubio, A. Atoms and molecules in cavities, from weak to strong coupling in quantum-electrodynamics (QED) chemistry. *Proc. Natl. Acad. Sci.* **2017**, *114*, 3026–3034.
(28) Flick, J.; Schäfer, C.; Ruggenthaler, M.; Appel, H.; Rubio, A. Ab Initio Optimized Effective Potentials for Real Molecules in Optical Cavities: Photon Contributions to the Molecular Ground State. *ACS Photonics* **2018**, *5*, 992–1005.

(29) Flick, J.; Welakuh, D. M.; Ruggenthaler, M.; Appel, H.; Rubio, A. Light-Matter Response Functions in Quantum-Electrodynamical Density-Functional Theory: Modifications of Spectra and of the Maxwell Equations. *arXiv Preprint arXiv:1803.02519* **2018**, 1–27.

(30) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Challenges for Density Functional Theory. *Chemical Reviews* **2012**, *112*, 289–320, PMID: 22191548.

(31) Niemczyk, T.; Deppe, F.; Huebl, H.; Menzel, E. P.; Hocke, F.; Schwarz, M. J.; Zueco, D.; Hümmert, T.; Solano, E.; Marx, A.; Gross, R. Circuit quantum electrodynamics in the ultrastrong-coupling regime. *Nat. Phys.* **2010**, *6*, 772–776.

(32) Bayer, A.; Pozimski, M.; Schambeck, S.; Schuh, D.; Huber, R.; Bougeard, D.; Lange, C. Terahertz Light-Matter Interaction beyond Unity Coupling Strength. *Nano Lett.* **2017**, *17*, 6340–6344.

(33) Gilbert, T. L. Hohenberg-Kohn theorem for nonlocal external potentials. *Phys. Rev. B* **1975**, *12*, 2111–2120.

(34) Müller, A. M. K. Explicit approximate relation between reduced two- and one-particle density matrices. *Phys. Lett.* **1984**, *105*, 446.

(35) Goedecker, S.; Umrigar, C. J. Natural orbital functional for the many-electron problem. *Phys. Rev. Lett.* **1998**, *81*, 866–869.

(36) Sharma, S.; Dewhurst, J. K.; Shallcross, S.; Gross, E. K. U. Spectral density and metal-insulator phase transition in mott insulators within reduced density matrix functional theory. *Phys. Rev. Lett.* **2013**, *110*, 1–5.
(37) Coleman, A. J. Structure of Fermion Density Matrices. Rev. Mod. Phys. 1963, 35, 668–686.

(38) Klyachko, A. A. Quantum marginal problem and N-representability. Journal of Physics: Conference Series 2006, 36, 72.

(39) Mazziotti, D. A. Structure of Fermionic Density Matrices: Complete N-Representability Conditions. Phys. Rev. Lett. 2012, 108, 263002.

(40) Grynberg, G.; Aspect, A.; Fabre, C. Introduction to quantum optics: from the semiclassical approach to quantized light; Cambridge University Press, 2010.

(41) Rokaj, V.; Welakuh, D. M.; Ruggenthaler, M.; Rubio, A. Light–matter interaction in the long-wavelength limit: no ground-state without dipole self-energy. Journal of Physics B: Atomic, Molecular and Optical Physics 2018, 51, 034005.

(42) Bonitz, M. Quantum Kinetic Theory, 2nd ed.; Springer: Berlin, 2016.

(43) van Leeuwen, R.; Stefanucci, G. Nonequilibrium Many-Body Theory of Quantum Systems; Cambridge University Press, 2013.

(44) Coleman, A. J.; Yukalov, V. I. Reduced density matrices: Coulson’s challenge; Springer Science & Business Media, 2000; Vol. 72.

(45) Coulson, C. Present State of Molecular Structure Calculations. Rev. Mod. Phys. 1960, 32, 170–177.

(46) Giesbertz, K. J.; Ruggenthaler, M. One-body reduced density-matrix functional theory in finite basis sets at elevated temperatures. arXiv preprint arXiv:1710.08805 2017,

(47) Watson, J. K. Simplification of the molecular vibration-rotation Hamiltonian. Molecular Physics 1968, 15, 479–490.

(48) Piris, M. Global Method for Electron Correlation. Phys. Rev. Lett. 2017, 119, 1–5.
(49) Mazziotti, D. A. Two-electron reduced density matrix as the basic variable in many-electron quantum chemistry and physics. *Chem. Rev.* **2012**, *112*, 244–262.

(50) Hohenberg, P.; Kohn, W. Inhomogeneous electron gas. *Physical review* **1964**, *136*, B864.

(51) Theophilou, I.; Lathiotakis, N. N.; Marques, M. A.; Helbig, N. Generalized Pauli constraints in reduced density matrix functional theory. *The Journal of chemical physics* **2015**, *142*, 154108.

(52) Buijse, M. A.; Baerends, E. J. An approximate exchange-correlation hole density as a functional of the natural orbitals. *Mol. Phys.* **2002**, *100*, 401–421.

(53) Frank, R. L.; Lieb, E. H.; Seiringer, R.; Siedentop, H. Müller’s exchange-correlation energy in density-matrix-functional theory. *Phys. Rev. A* **2007**, *76*, 1–16.

(54) Andrade, X. et al. Real-space grids and the Octopus code as tools for the development of new simulation approaches for electronic systems. *Phys. Chem. Chem. Phys.* **2015**, *17*, 31371–31396.

(55) J. M. Ugalde, M. P. Iterative Diagonalization for Orbital Optimization in Natural Orbital Functional Theory. *J. Comput. Chem.* **2008**, *30*, 1545–1614.

(56) Ruggenthaler, M.; Bauer, D. Rabi oscillations and few-level approximations in time-dependent density functional theory. *Phys. Rev. Lett.* **2009**, *102*, 2–5.

(57) Fuks, J. I.; Helbig, N.; Tokatly, I. V.; Rubio, A. Nonlinear phenomena in time-dependent density-functional theory: What Rabi oscillations can teach us. *Phys. Rev. B* **2011**, *84*.

(58) Greiner, W.; Reinhardt, J. *Field quantization*; Springer Science & Business Media, 2013.
(59) Keller, O. *Quantum theory of near-field electrodynamics*; Springer Science & Business Media, 2012.