UNIVERSITY OF THE BASQUE COUNTRY

DOCTORAL THESIS

Quantum Electrodynamical Time-Dependent Density Functional Theory

---

Author:

Camilla PELLEGRINI

Supervisors:

Prof. Angel RUBIO

Prof. Ilya TOKATLY

A thesis submitted in fulfillment of the requirements

for the degree of Doctor of Philosophy

in the

Nano-Bio Spectroscopy Group and ETSF

Department of Materials Physics

June 2, 2017

Contents

List of Figures

List of Abbreviations

CDFT	**C**urrent **D**ensity **F**unctional **T**heory
DFT	**D**ensity **F**unctional **T**heory
SDFT	**S**pin **D**ensity **F**unctional **T**heory
H	**H**artree
HF	**H**artree **F**ock
HK	**H**ohenberg **K**ohn
KS	**K**ohn **S**ham
MF	**M**ean **F**ield
NLSE	**N**on **L**inear **S**chrödinger **E**quation
OEP	**O**ptimized **E**ffective **P**otential
QED	**Q**uantum **E**lectrodynamics
RG	**R**unge **G**ross
TDCDFT	**T**ime **D**ependent **C**urrent **D**ensity **F**unctional **T**heory
TDDFT	**T**ime **D**ependent **D**ensity **F**unctional **T**heory
TDOEP	**T**ime **D**ependent **O**ptimized **E**ffective **P**otential
TDSDFT	**T**ime **D**ependent **S**pin **D**ensity **F**unctional **T**heory
x	**E**xchange
xc	**E**xchange **C**orrelation

Chapter 1

Introduction

Quantum electrodynamics (QED) [92, 93] has established the basic principles of the interaction between electrons as due to the exchange of photons, i.e., the quanta of radiation. As a result, the bare electron is not a good physical picture, and one should think of this particle as surrounded by a photon cloud[1]. The electronic and electromagnetic fields are both quantized and treated on equal footing. However, depending on the problem of interest, approximations for either the electronic or the photonic degrees of freedom are usually employed.

The quantization of the electromagnetic field is needed for the correct description of, e.g., atomic radiation, with application to the laser. The interest in quantum mechanics underlying the laser's principles has brought to the development of quantum optics [48, 94] as a research field into the light, rather than into matter. The interaction of matter with the quantized radiation field is almost always treated in the context of highly simplified models, e.g., with two-level atoms for the laser. Quantum optical studies concern quantum properties of light, such as photon anti-bunching, two-photon interferometry, squeezed and entangled states of light. Remarkable results are the demonstration of quantum entanglement and quantum logic gates.

[1] Mathematically, the matter and the photon field are inextricably linked in the Hilbert space, i.e., this can not be viewed as a simple tensor product of a space for the electrons and a Fock space for the photons.

These are the basis of quantum information theory [95], in which the photons play a major role as carriers of information, interacting with atoms at the single-particle level.

On the other hand, in the description of interacting many-body systems, spanning physics, chemistry and biology, matter and radiation are usually decoupled by approximating the latter classically, i.e., the electromagnetic field is determined independently through solution of the classical Maxwell equations. Molecules, nanostructures and materials are described in first approximation by non-relativistic quantum mechanics for many-electron systems interacting via the Coulomb force. However, this theory ignores corrections of order $(v/c)^2$, i.e., the transverse part of the electron-electron interaction, given by the Breit term [74] in the QED Hamiltonian. This term introduces magnetic coupling (spin-orbit and spin-spin coupling), and retardation effects (orbit-orbit coupling) in the interaction between the electrons. Importantly, vacuum effects, responsible for the Lamb shift [84] and the relaxation of excited states, are also neglected. Despite of the treatment of the radiation field as a classical variable, one encounters the problem of how to deal with the (Coulomb) interaction of a large number of quantum particles. The direct approach to the dynamical properties of the system is solving the (non-relativistic) time-dependent Schrödinger equation for the many-electron wave function $\Psi(\{\boldsymbol{r}\sigma\},t)$

$$i\hbar\frac{\partial\Psi(\{\boldsymbol{r}\sigma\},t)}{\partial t}=\hat{H}(\{\boldsymbol{r}\sigma\},t)\Psi(\{\boldsymbol{r}\sigma\},t), \qquad (\Psi(\{\boldsymbol{r}\sigma\},t_0)\text{ given}) \tag{1.1}$$

where $\hat{H}$ is the Hamiltonian operator of the system and $\{\boldsymbol{r}\sigma\}=\{\boldsymbol{r}_1\sigma_1,\boldsymbol{r}_2\sigma_2,\ldots,\boldsymbol{r}_N\sigma_n\}$ are the spatial and spin coordinates of the N electrons. The interaction of radiation with matter is described by a minimal coupling Hamiltonian of

the following form

$$\hat{H}(t) = \sum_{i=1}^{N} \left\{ \frac{1}{2m} \left[-i\hbar \boldsymbol{\nabla}_i + \frac{e}{c} \boldsymbol{A}_{\text{ext}}(\boldsymbol{r}_i t) \right]^2 + v_{\text{ext}}(\boldsymbol{r}_i t) + \mu_B \boldsymbol{\sigma}_i \cdot \boldsymbol{B}_{\text{ext}}(\boldsymbol{r}_i t) \right\} + \hat{W}. \tag{1.2}$$

Here,

$$\hat{W} = \sum_{i<j=1}^{N} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{1.3}$$

is the (instantaneous and spin-independent) electron-electron interaction, while $v_{\text{ext}}(\boldsymbol{r}t)$ and $\boldsymbol{A}_{\text{ext}}(\boldsymbol{r}, t)$ are, respectively, the external (time-dependent) single-particle scalar and vector potentials associated with the classical electromagnetic fields

$$\boldsymbol{E}_{\text{ext}}(\boldsymbol{r}t) = \frac{1}{e} \boldsymbol{\nabla} v_{\text{ext}}(\boldsymbol{r}t) - \frac{1}{c} \frac{\partial \boldsymbol{A}_{\text{ext}}(\boldsymbol{r}t)}{\partial t}, \tag{1.4}$$

$$\boldsymbol{B}_{\text{ext}}(\boldsymbol{r}t) = \boldsymbol{\nabla} \times \boldsymbol{A}_{\text{ext}}(\boldsymbol{r}t). \tag{1.5}$$

$\mu_B = e\hbar/(2mc)$ is the Bohr magneton, and $\boldsymbol{\sigma}_i$ is the vector of Pauli matrices, which represents the spin operator of the electron i. The Hamiltonian of Eq. (1.2) can be derived from the fully relativistic QED Hamiltonian, either by an expansion in powers of $1/c$, or by a Foldy-Wouthuysen transformation [52] to the lowest order[2].

The resulting time-dependent Schrödinger equation (1.1) is a partial differential equation of $3N$ spatial variables, mutually coupled through the Coulomb interaction, and N spin variables. Even disregarding the spin, if we use M grid points for each coordinate, the effort of computing the wave function at each time step scales exponentially with N as M^{3N}. Thus, apart from very limited applications involving a few interacting electrons in low dimensions, for which one can attempt to solve Eq. (1.1) exactly on a coarse grid, (note that even for a small molecule it is often $N > 100$), approximations are

[2]The non-relativistic limit of the QED Hamiltonian is discussed in details in Sec. 3.3.

unavoidable[3]. This problem has spawned a lot of interest into the question whether one can calculate the observables of many-body systems by solving a closed set of equations for reduced quantities, without the need of calculating Ψ explicitly.

A convenient solution to the many-body problem comes from density functional approaches [12, 33, 58]. Time-dependent density functional theory-(TDDFT) [33, 58] is an exact reformulation of quantum mechanics for electronic systems described by the Hamiltonian above, for the case of time-dependent scalar external potentials (i.e., $\boldsymbol{A}_{\text{ext}}(\boldsymbol{r},t)=0$ in Eq. (1.2)), in terms of the time-dependent one-particle density, instead of the many-body wave function $\Psi(t)$. It is the non-trivial extension of successful ground-state density functional theory (DFT) for stationary systems [12], to the treatment of excited states and time-dependent processes. The central theorem of TDDFT, formulated by Runge and Gross [43], proves that all physical observables of a many-electron system, which evolves from a given initial state, are unique functionals of the one-body time-dependent density alone. Hence, instead of the complex many-body wave function on configuration space, one only needs the simple one-particle density (i.e., a function of three variables), to fully characterize the electronic system. Further, the so-called Kohn-Sham (KS) construction [100] allows one to calculate the density of the interacting many-electron system as the density of an auxiliary system of noninteracting fermions in an effective one-body potential. The complexity of the original many-body problem, i.e., all quantum many-body effects of correlations and interactions, are included in the *unknown* exchange-correlation (xc) part of the KS potential, for which it is essential to find good approximations. This functional of the density determines, in turn, the properties of the electronic

[3]We see that the number of required parameters is $P = M^{3N}$. Call $\tilde{P}$ the maximum value feasible with the best available computer hardware and software, and $\tilde{N}$ the maximum number of electrons. Then, it is $\tilde{N} = \frac{1}{3}\log\tilde{P}/\log M$. Let us optimistically take $\tilde{P} = 10^9$ and $M = 3$. This gives the shocking result $\tilde{N} = 6$ (!). The exponential is indeed a "wall", which severely limits the value of $\tilde{N}$ [96].

system of interest. The KS construction makes (TD)DFT one of the most popular methods for ab-initio calculations. This is because the time to solve numerically the self-consistent KS (single-particle non-interacting Schrödinger) equations only scales as N^3, which allows one to treat, at present, several thousands of atoms [2].

In a two-step process, (TD)DFT has been extended to systems in an external magnetic field. The generalization to (time-dependent) spin density functional theory ((TD)SDFT) [12, 58] allows one to treat spin-polarized systems. Within this approach, the electron coupling to an external (time-dependent) magnetic field is described by a Zeeman term of the form $v^{\sigma}_{ext}(\boldsymbol{r},t) = v_{ext}(\boldsymbol{r},t) \pm \mu_B B_{z,ext}(\boldsymbol{r},t)$. The extension of the formalism is valid for a fixed quantization axis of the spin (collinearity), chosen for simplicity as the z-axis. In addition to the usual single-particle density, SDFT employs the z-component of the ground state magnetization density as a second functional variable. A more general (non-collinear) scheme is available for the description of systems characterized by a local variation of the magnetization density. However, standard implementations of non-collinear SDFT assume the xc magnetic field to be parallel to the magnetization (with no torque exerted on the spin distribution). The best way to treat non-collinear spin configurations such as, e.g., domain walls, is at present an open question [102].

To also account for the Lorentz force exerted on the electrons, Ghosh and Dhara [97] reformulated the theory in terms of the current density, by extending the Runge-Gross proof to vector potentials. The use of the current formulation (TDCDFT) is especially relevant for extended systems, as long range effects can be included into the effective xc vector potential [98]. A density functional description of the general Hamiltonian of Eq. (1.2) is given by the spin-dependent extension of TDCDFT [99]. However, although the different variants of (TD)DFT cover most of the traditional applications in physics and chemistry, by construction these theories can not treat problems involving the

quantum nature of light.

In the last decades, cavity QED [109] has introduced the possibility of coupling quantum light and matter in a controlled fashion, well into the strong coupling regime. Quantum matter here may be, e.g., Rydberg atoms or trapped ions. In a typical cavity QED experiment, the optical cavity is designed in such a way that one mode of the quantized electromagnetic field is almost resonant with the transition frequency of two atomic states. A simplified representation of this situation is given by the Rabi model [108], which describes a two-level system arbitrarily coupled to a single photon mode via the dipole interaction. Although the Rabi model is the simplest quantum model of interacting light and matter, it does not correspond to a simple theoretical problem. Specifically, difficulties arise due to the fact that the radiation mode is, by its nature, a continuous degree of freedom, and the integrability of the model has been proved only recently [7].

In the last few years, remarkable advances have been made towards the realization of condensed-matter physics with light [101]. A solid-state version of cavity QED, which employs superconducting circuits, is a very active field of research, and coupling an ensemble of atoms to quantized photon fields is commonly achieved. First attempts to describe this quantum many-body physics with light have led to Hamiltonians such as the Dicke model of superradiance (cooperative spontaneous emission), where N two-level systems are coupled to a photon mode [107]. However, the validity of such effective Hamiltonians and their properties are questionable [45, 46, 62], due to the difficult realizability in real physical systems. This new regime of light-matter interaction is widely unexplored for, e.g., molecular physics and material science [26], and novel emergent quantum phenomena, either in relation with strong light-matter coupling, or non-equilibrium quantum physics, are expected. Possibilities like altering or strongly influencing the chemical reactions of a molecule by coupling it to cavity modes, or setting the matter

into non-equilibrium states with novel properties, e.g., light-induced superconductivity [72], arise. Further, dissipation and driving effects in matter systems coupled to a continuous spectrum of quantized bosonic modes can be studied by coupling an open cavity to a transmission line, which serves as a photon bath. Placing into the cavity a qubit, (i.e., an artificial quantum two-level system), already results in the rich many-body physics of quantum impurity models, such as the spin-boson Hamiltonian.

In these conditions, an oversimplified description of the matter system is no longer advisable, and an approach that considers both the quantum nature of the radiation field as well as of the electrons, is required. Even though standard TDDFT is a very practical method to handle quantum (electronic) degrees of freedom, the classical treatment of the electromagnetic field prevents the application of the theory to this new class of problems. The motivation of the present work is to generalize TDDFT to the case where the electromagnetic field is treated not as an external field, but as a quantized system with its proper dynamics. We note that since TDDFT is a fully self-consistent method, such generalization would also be applicable to the strong coupling regime between matter and radiation. This nonperturbative theory is thus expected to describe novel, nonlinear phenomena in systems that are traditionally treated by means of phenomenological (mean field) approaches.

In chapter 3, we present the first formulation of the full quantum many-body problem of interacting electrons and photons in terms of a general TDDFT-like framework, that we call quantum electrodynamical time-dependent density functional theory (QED-TDDFT). Previous steps towards a combined electron-photon functional description have been made in Refs. [39, 42] for relativistic condensed-matter systems and in Ref. [55] for atoms and molecules coupled to quantized photon modes. Here, we propose a hierarchy of variants of QED-TDDFT, which covers most possible realizations of

condensed-matter physics with light. We show how, in this general framework, TD(C)DFT for atoms and molecules interacting with cavity photons can be systematically derived from relativistic TDDFT, and reduces in the lowest limit of approximations to the functional description of well-known quantum-optical models. For each version of the theory, we prove the corresponding generalization of the one-to-one mapping theorem, construct the KS system, and suggest possible approximation strategies.

In chapter 4, we construct the first approximation to the xc functional of QED-(TD)DFT, thus making possible ab initio calculations of many-electrons systems coupled to quantized radiation modes. To achieve this goal, we extend the widely used optimized effective potential (OEP) approach in electronic structure methods [104–106] to the photon-mediated electron-electron coupling. In the static limit, our OEP energy functional reduces to the Lamb shift of the ground state energy. The new functional is tested from low to high coupling regime in the Rabi model, through comparison with the exact and mean field solutions. In chapter 5, we propose a way to incorporate magnetic dipole-dipole coupling into SDFT. This functional treatment aims at improving the (mean field) description of inhomogeneous magnetic structures at the nanoscale, e.g., domain walls and skyrmions, which is currently based on the phenomenological theory of micromagnetism. To this end, we treat the (pairwise) spin-spin correction to the Coulomb interaction in the Breit Hamiltonian at the Hartree-Fock level. Here, the Hartree term corresponds to the magnetostatic micromagnetic energy. In addition, we provide quantum corrections by evaluating the exact exchange energy for the ferromagnetic electron gas with dipolar interaction, within the linear response to a noncollinear magnetic field. The relevant theoretical background is summarized in chapter 2.

Chapter 2

Theoretical background

In this chapter we give some useful theoretical basis underlying our work. In Sec. 2.1 we discuss as a starting point the basic ideas of ground-state DFT [12] and introduce the key elements of the formalism, i.e., the Hohenberg-Kohn (HK) theorem [103] and the KS construction [100]. In Sec. 2.2 we consider the extension of the theory to the treatment of excitations and time-dependent processes [33, 58]. Theoretical foundations of TDDFT are the Runge-Gross (RG) theorem [43] and its extension to the KS system by van Leeuwen [28, 59]. The main concepts and proof steps presented here will be used in a more general context in chapter 3 to establish our QED-TDDFT. Moving towards practical applications of the theory, the last section connects TDDFT and many-body perturbation theory in the derivation of the exchange-only TDOEP approximation to the exchange-correlation potential [104–106]. Our extension of this method to the time dependent photon mediated electron-electron interaction is the subject of chapter 4.

2.1 Density functional theory

In quantum mechanics, all information we can possibly have about a given system, is contained in the system's wave function Ψ. Here, we are exclusively concerned with the electronic structure of atoms, molecules and solids.

The nuclei enter the description of the system in the form of an external potential $v_{ext}(\boldsymbol{r})$ acting on the electrons. As a consequence, Ψ depends only on the electronic coordinates[1]. In non-relativistic quantum mechanics the wave function of a system of N electrons is obtained from the Schrödinger equation

$$\left[\sum_{i=1}^{N}\left(\frac{-\hbar^2\boldsymbol{\nabla}_i^2}{2m}+v_{\text{ext}}(\boldsymbol{r}_i)\right)+\sum_{i<j}v_{ee}(\boldsymbol{r}_i,\boldsymbol{r}_j)\right]\Psi(\{\boldsymbol{r}\sigma\})=E\Psi(\{\boldsymbol{r}\sigma\}). \tag{2.1}$$

Here,

$$\hat{T}=-\frac{\hbar^2}{2m}\sum_{i=1}\boldsymbol{\nabla}_i^2 \tag{2.2}$$

is the kinetic energy operator,

$$\hat{W}=\sum_{i<j}v_{ee}(\boldsymbol{r}_i,\boldsymbol{r}_j)=\sum_{i<j}\frac{e^2}{|\boldsymbol{r}_i-\boldsymbol{r}_j|} \tag{2.3}$$

is the electron-electron Coulomb interaction, and

$$\hat{V}=\sum_i v_{ext}(\boldsymbol{r}_i) \tag{2.4}$$

describes the interaction of the electrons with the external sources. While the form of $\hat{T}$ and $\hat{W}$ is universal (i.e., it is the same for any non-relativistic Coulomb system), the external potential actually depends on the system, and specifies it as, e.g., an atom, a molecule or a solid.

The fundamental idea underlying DFT is that for describing the ground-state properties of a quantum many-electron system, the knowledge of the many-body wave function is not required. In fact, the ground-state one-particle density $n_0(\boldsymbol{r})$ already contains all necessary information, and can thus be considered as the basic variable. This was stated by Hohenberg and Kohn [103], who showed that the full many-body ground state $|\Psi_0(\{\boldsymbol{r}\})\rangle$ is a unique functional of the density, i.e., $|\Psi_0\rangle=|\Psi[n_0]\rangle$.

[1] This is the so-called Born-Oppenheimer approximation.

First, we note that the external potential $v_{ext}(\boldsymbol{r})$ defines a unique mapping $v_{ext} \rightarrow n_0$, where n_0 is the corresponding ground-state density obtained from the Schrödinger equation as

$$n_0(\boldsymbol{r}) = N \sum \sigma, \sigma_2, \ldots, \sigma_N \int d^3\boldsymbol{r}_2 \cdots \int d^3\boldsymbol{r}_N |\Psi_0(\boldsymbol{r}\sigma, \boldsymbol{r}_2\sigma_2, ...\boldsymbol{r}_N\sigma_N)|^2. \quad (2.5)$$

The HK theorem [103] states that the mapping from the external potentials to the densities is injective. The proof of this statement makes use of the variational principle to show that the ground states $|\Psi_0\rangle$ and $|\Psi'\rangle$, corresponding to the external potentials $v_{ext}(\boldsymbol{r})$ and $v'_{ext}(\boldsymbol{r})$, cannot give rise to the same density $n_0(\boldsymbol{r})$, if $v_{ext}(\boldsymbol{r})$ and $v'_{ext}(\boldsymbol{r})$ differ by more than a constant. Thus, this defines the inverse mapping $n_0 \rightarrow v_{ext}$, and we can conclude that the external potential is a unique functional of the density.

Since v_{ext} completely determines the Hamiltonian and, in turn, the ground-state wave function, the ground-state expectation value of any observable $\hat{O}$ is also a unique functional of the density, i.e.,

$$O[n_0] = \langle \Psi[n_0] | \hat{O} | \Psi[n_0] \rangle . \quad (2.6)$$

This is of particular interest if one considers the Hamiltonian operator $\hat{H}$. The ground-state energy

$$E[n_0] = \langle \Psi[n_0] | \hat{H} | \Psi[n_0] \rangle \quad (2.7)$$

has the variational property

$$E[n_0] \leq E[n'], \quad (2.8)$$

where n_0 is the ground-state density, which corresponds to the potential v_{ext}, and n' is some other density. Eq. (2.8) states that the energy of the ground state can be obtained by minimizing the total energy of the system $E[n]$ with

respect to the density. The correct density that minimizes the energy is the ground-state density n_0. Due to its importance for practical applications, Eq. (2.8) is often referred to as the second HK theorem [103].

The total energy of the electronic system can then be expressed as

$$E[n] = \int d^3\boldsymbol{r} n(\boldsymbol{r}) v_{ext}(\boldsymbol{r}) + T[n] + W[n], \tag{2.9}$$

where T and W are universal functionals (defined as expectation values of the type 2.6) independent of $v_{ext}(\boldsymbol{r})$. However, the explicit expressions for the energy functionals $T[n]$ and $W[n]$ in terms of the density are not known. A convenient approximation scheme for the kinetic energy functional was proposed by Kohn and Sham [100]. In order to single out many-body effects in Eq. (2.9), these authors re-introduced into the theory a special kind of wave functions (single-particle orbitals). The total energy functional $E[n]$ is then separated as

$$E[n] = \int d^3\boldsymbol{r} n(\boldsymbol{r}) v_{ext}(\boldsymbol{r}) + T_s[\{\phi_i[n]\}] + W_H[n] + E_{xc}[n], \tag{2.10}$$

where

$$T_s[\{\phi_i[n]\}] = -\frac{1}{2}\sum_{i=1}^{N} \int d^3\boldsymbol{r} \phi_i^*(\boldsymbol{r}) \boldsymbol{\nabla}^2 \phi_i(\boldsymbol{r}) \tag{2.11}$$

is the kinetic energy of non-interacting particles with density n, expressed in terms of the orbitals $\phi_i(\boldsymbol{r})$, and

$$W_H[n] = \frac{1}{2} \int d^3\boldsymbol{r} \int d^3\boldsymbol{r}' \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \tag{2.12}$$

is the classical Hartree term representing the electrostatic interaction energy of the charge density n. By construction, the unknown exchange-correlation (xc) energy $E_{xc} = E_x + E_c$ contains the energy differences $T_c = T - T_s$ and $W - W_H$, i.e., all many-body interaction contributions. Here, E_x denotes the

exchange energy (Fock term) due to the Pauli principle, while the index c indicates the correlation term.

In a next step, the problem of minimizing Eq. (2.10) is mapped onto solving the Schrödinger equation for the auxiliary KS system of non-interacting particles

$$\left(-\frac{\nabla^2}{2} + v_s[n](\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r}), \tag{2.13}$$

in the local potential

$$v_s[n](\boldsymbol{r}) = v_{ext}(\boldsymbol{r}) + \frac{\partial W_H[n]}{\partial n(\boldsymbol{r})} + \frac{\partial E_{xc}[n]}{\partial n(\boldsymbol{r})} \tag{2.14}$$

$$= v_{ext}(\boldsymbol{r}) + v_H[n](\boldsymbol{r}) + v_{xc}[n](\boldsymbol{r}), \tag{2.15}$$

where we have introduced the Hartree potential $v_H[n](\boldsymbol{r})$ and the xc potential $v_{xc}[n](\boldsymbol{r})$. The KS potential is defined by the condition that the density of the KS (non-interacting) system equals the density of the real interacting system, i.e.,

$$n(\boldsymbol{r}) = \sum_{i=1}^{N} |\phi_i(\boldsymbol{r})|^2. \tag{2.16}$$

As both the Hartree and xc potentials depend on the density, Eq. (2.13-2.16) have to be solved self-consistently.

The KS scheme assumes that one can always find a local potential $v_S[n](\boldsymbol{r})$ with the property that the orbitals obtained from Eq. (2.13) reproduce the given density of the interacting electron system. However, the validity of this assumption, known as the "non-interacting v-representability", is not obvious, and no general solution in DFT is known[2]. On the other hand, if such a potential exists, by virtue of the HK theorem it is unique, up to a constant.

[2]It is known that in discretized systems each density is ensemble v-representable, i.e., a local potential with a degenerate ground state can always be found.

2.2 Time-dependent density functional theory

In the next step, we assume that the scalar external potential, which acts on the (non-relativistic) many-electron system, is time-dependent. The evolution of the system is described by the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\{\boldsymbol{r}\sigma\},t) = \left[\sum_{i=1}^{N}\left(\frac{-\hbar^2\boldsymbol{\nabla}_i^2}{2m} + v_{\text{ext}}(\boldsymbol{r}_i,t)\right) + \sum_{i<j} v_{ee}(\boldsymbol{r}_i,\boldsymbol{r}_j)\right]\Psi(\{\boldsymbol{r}\sigma,t\}). \tag{2.17}$$

Since the quantum-mechanical treatment of stationary and time-dependent systems differs in many aspects, it is not straightforward to generalize the mathematical framework of DFT to the time-dependent case [33, 58]. In particular, the total energy, which plays a central role in the HK theorem, is not a conserved quantity in the presence of time-dependent external fields, and thus there is no variational principle that can be exploited.

The analogue of the HK theorem for time-dependent systems was formulated by Runge and Gross [43] providing the foundations of TDDFT. The proof is for physical scalar potentials, that are finite everywhere and vary smoothly in time, so that they can be expanded into a Taylor series around the initial time $t = t_0$. Under these restrictions, the RG theorem states that there is a one-to-one correspondence between the external time-dependent potential $v_{ext}(\boldsymbol{r},t)$ and the electronic time-dependent one-body density $n(\boldsymbol{r},t)$ for a many-body system evolving from a given initial state $\Psi_0 = \Psi(t = t_0)$. Of course, for a given external potential $v_{ext}(\boldsymbol{r},t)$ it is always possible, in principle, to solve the time-dependent Schrödinger equation with Ψ_0, and calculate the corresponding density $n(\boldsymbol{r},t)$. What remains to be proved, in order to demonstrate the one-to-one mapping, is that if two potentials $v_{ext}(\boldsymbol{r},t)$ and

$v'_{ext}(\boldsymbol{r},t)$ differ by more than a trivial gauge transformation, i.e.,

$$v_{ext}(\boldsymbol{r},t) - v'_{ext}(\boldsymbol{r},t) \neq c(t), \tag{2.18}$$

then the corresponding densities $n(\boldsymbol{r},t)$ and $n'(\boldsymbol{r},t)$, which evolve from the same initial state Ψ_0, must be distinct. The addition of a purely time-dependent function $c(t)$ is excluded, since it only changes the phase of the wave function, but not the density.

The RG proof consists of two steps. In the first step, by using the equation of motion for the (paramagnetic) current density

$$i\frac{d}{dt}j_p(\boldsymbol{r},t) = \langle\Psi(t)|\left[\hat{j}_p(\boldsymbol{r}),\hat{H}(t)\right]|\Psi(t)\rangle\,, \tag{2.19}$$

it is shown that the potentials $v_{ext}(\boldsymbol{r},t)$ and $v'_{ext}(\boldsymbol{r},t)$ lead to different current densities $j_p(\boldsymbol{r}t)$ and $j'_p(\boldsymbol{r}t)$. In Eq. (2.19) we have used the definition $j_p(\boldsymbol{r},t) = \langle\Psi(t)|\hat{j}_p|\Psi(t)\rangle$, where $\hat{j}_p(\boldsymbol{r},t) = -\frac{i}{2}\sum_{i=1}^{N}[\boldsymbol{\nabla}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i) + \delta(\boldsymbol{r}-\boldsymbol{r}_i)\boldsymbol{\nabla}_i]$. This can be understood on physical grounds by considering that the current density is proportional to the momentum density. Changes in the momentum density are caused by the force density, which is proportional to the gradient of the external potential. Eq. (2.18) implies that the gradients of $v_{ext}(\boldsymbol{r},t)$ and $v'_{ext}(\boldsymbol{r},t)$ differ, thus giving rise to different currents. In the second step, one relates the current to the density through the continuity equation

$$\frac{\partial}{\partial t}n(\boldsymbol{r},t) = -\boldsymbol{\nabla}\cdot j_p(\boldsymbol{r}t), \tag{2.20}$$

which allows one to show that densities associated to distinct currents also differ. We conclude that from the knowledge of the time-dependent density alone, it is possible to uniquely determine the external potential, and hence, (for a given initial state), the many-body wave function. This in turn, determines every observable of the system.

However, the RG theorem gives no prescription about how to actually calculate the density. To overcome this problem, one employs the idea of the KS construction of static DFT. We thus consider an auxiliary KS system of non-interacting electrons moving in an effective time-dependent one-body potential, which is such that the densities of the KS system and of the real interacting system coincide. The main task is then to find good approximations for this a priori unknown effective potential. The KS electrons satisfy the equations

$$i\frac{\partial}{\partial t}\phi_i(\boldsymbol{r},t) = \left(-\frac{\nabla^2}{2} + v_s(\boldsymbol{r},t)\right)\phi_i(\boldsymbol{r},t), \tag{2.21}$$

with the density

$$n(\boldsymbol{r},t) = \sum_{i=1}^{N} |\phi_i(\boldsymbol{r},t)|^2. \tag{2.22}$$

As in ground state DFT, in order to construct useful approximations for the effective KS potential, one employs the separation

$$v_s(\boldsymbol{r},t) = v_{ext}(\boldsymbol{r},t) + v_H(\boldsymbol{r},t) + v_{xc}(\boldsymbol{r},t). \tag{2.23}$$

Here, the first term is the external potential, the second is the classical Hartree potential

$$v_H(\boldsymbol{r},t) = \int d^3\boldsymbol{r}' \frac{n(\boldsymbol{r}',t)}{|\boldsymbol{r}-\boldsymbol{r}'|}, \tag{2.24}$$

and the third is the xc potential, the determination of which is the central problem of TDDFT.

The existence of the KS potential in TDDFT was proved under well-defined conditions by van Leeuwen [28, 59], who extended the RG theorem to different interactions and initial states (the KS system corresponding to the non-interacting case). An important restriction is that the density is assumed to be time-analytic about the initial time, (note that the RG proof only requires the potential to be time-analytic). Then, the non-interacting v-representability

proof shows that an effective local potential with the desired property actually exists if one can find a stationary wave function, which yields the initial density $n(\boldsymbol{r}, t_0)$ and the initial time-derivative of the density, and is the ground state of a non-interacting electron system. The proof has been extended to TDCDFT by Vignale, who showed that currents from an interacting system with some vector potential are also representable by a vector potential in a non-interacting system [61].

2.2.1 Time-dependent optimized effective potential

In this section we establish a connection between TDDFT and the nonequilibrium Green's functions formalism (NEGF) due to Keldysh. In particular, we introduce an exact integral equation for the xc potential of TDDFT in terms of the irreducible self-energy, i.e., the time-dependent Sham-Schlüter equation [104]. This equation is then used as a starting point to discuss the TDOEP method in the exchange-only approximation [104–106].

We consider the situation in which the system is driven out of equilibrium at time $t = t_0$ by the external potential $v_{ext}(t)$. One is usually interested in calculating the expectation value of some observable $\hat{O}$ at time t'. This can be expressed in terms of KS quantities as

$$< \hat{O}(t') >= \langle \Phi_0 | \hat{S}(-\infty, t') \hat{O}(t') \hat{S}(t', -\infty) | \Phi_0 \rangle \,, \tag{2.25}$$

where $|\Phi_0\rangle$ is the ground state of the unperturbed KS Hamiltonian H_s at time $t = -\infty$, and $\hat{O}(t) = \hat{U}_s(t_0, t) \hat{O} \hat{U}_s(t, t_0)$ is the KS operator in the Heisenberg representation. Here, $\hat{U}_s(t_2, t_1) = T\text{exp}\left[-i \int_{t_1}^{t_2} \hat{H}_s(t) dt\right]$. Further, $\hat{S}(t_2, t_1) = T\text{exp}\left[-i \int_{t_1}^{t_2} \left(\hat{H} - \hat{H}_s\right)(t) dt\right]$ is the $\hat{S}$-matrix operator which describes the evolution due to the interaction Hamiltonian $\hat{H} - \hat{H}_s$. Note that in Eq. (2.25) we have assumed that the Coulomb interaction is switched on adiabatically in the time interval $(-\infty, t_0)$. This provides an adiabatic connection between

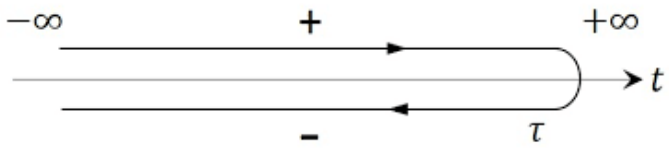

Figure 2.1: The closed time contour $\mathcal{C}$.

the stationary ground state of the non-interacting KS system at $t \to -\infty$, and the wave function Ψ_0 of the true interacting electron system at time $t = t_0$. Under the influence of the external potential, the system evolves to some unpredictable non-stationary state, which depends, in general, on the switching procedure, as well as on the history of the system. In order to apply standard perturbation techniques to Eq. (2.25), we use a method due to Keldysh [51]. The central idea is bypassing the knowledge of the state at time $t = +\infty$ by letting the quantum system evolve first in the forward direction in time, and then backwards to the known initial stationary state. In the corresponding theory, the time evolution takes place along the two-branch Schwinger-Keldysh contour $\mathcal{C}$ in Fig. 2.1. The physical time $t(\tau)$ is parametrized by a pseudotime τ in such a way that while τ runs from $-\infty$ to $+\infty$, t runs from $-\infty$ to t' and back.

All time-dependent functions are defined for time-arguments on the contour. In particular, the one-particle NEGF is a function of two contour variables defined as

$$G(\boldsymbol{r}\tau, \boldsymbol{r}'\tau') \equiv -i < T_C \hat{\psi}_H(\boldsymbol{r}, \tau)\hat{\psi}_H^\dagger(\boldsymbol{r}', \tau') >, \tag{2.26}$$

where T_C is the time ordering operator on the contour, and $\hat{\psi}_H^\dagger$, $\hat{\psi}_H$ are creation and annihilation operators in the Heisenberg picture. Eq. (2.26) can be written in the form

$$G(\tau, \tau') = \theta(\tau - \tau')G^>(\tau, \tau') + \theta(\tau' - \tau)G^<(\tau, \tau'), \tag{2.27}$$

where the function $\theta(\tau - \tau')$ is the theta function on the contour. The density-functional and NEGF formalisms are linked by the requirement that the former has to yield the correct density given by the one-particle Green's function of the latter, both for the interacting system and the KS system, i.e.,

$$n(\boldsymbol{r}, \tau) = -iG(\boldsymbol{r}\tau, \boldsymbol{r}\tau^+) = -iG_s(\boldsymbol{r}\tau, \boldsymbol{r}\tau^+). \tag{2.28}$$

With this condition, from the Dyson-Schwinger equation and the equation of motion for the KS Green's function, one obtains the Sham-Schlüter equation

$$\int d2 \int d3\, G_s(1,2)\Sigma(2,3)G(3,1) = \int d2 G_s(1,2)[v_s(2) - v_{ext}(2)]G_s(2,1), \tag{2.29}$$

where we have used the compact notation $1 = (\mathbf{r}_1 t_1)$. Here, the self-energy $\Sigma = v_H + \Sigma_{xc}$ includes all diagrams, except those involving the external potential difference $v - v_s$. By setting $G = G_s$ and $\Sigma[G] = \Sigma[G_s]$ in Eq. (2.29), this reduces to a linearized integral equation for the xc potential, i.e., the TDOEP equation

$$\int d2 \int d3\, G_s(1,2)\Sigma_{xc}[G_s](2,3)G_s(3,1) = \int d2 G_s(1,2)v_{xc}(2)G_s(2,1). \tag{2.30}$$

In the simplest approximation, Σ_{xc} is given by the exchange-only self-energy of Fig. 2.2,

$$\Sigma_x(1,2) = iG_s^<(1,2)v_{ee}(1,2) = -\sum_j n_j \phi_j(1)\phi_j^*(2)v_{ee}(1,2), \tag{2.31}$$

where n_j is the occupation number and ϕ_j are the KS orbitals. This approximation yields the exchange-only TDOEP equation. Since Σ_x is local in time, only one-time integration has to be performed in Eq. (2.30) (in chapter 4 we extend the method to the case of time-dependent Σ_x). By using the Langreth rules for the convolution and the product of two functions in the Keldysh

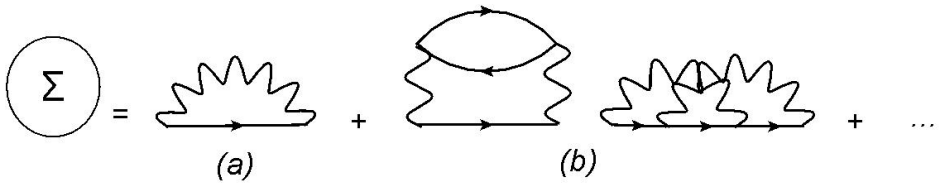

Figure 2.2: Self-energy diagrams: (a) exchange diagram, and (b) second order approximation.

space [51], one obtains from Eq. (2.30)

$$\int_{-\infty}^{t_1} dt_2 \int d^3r_2 \int d^3r_3 \left[G_s^<(1,2)\tilde{\Sigma}(2,3)G_s^>(3,1) - G_s^>(1,2)\tilde{\Sigma}(2,3)G_s^<(3,1)\right] = 0, \tag{2.32}$$

where we have introduced the notation $\tilde{\Sigma}(1,2) = \Sigma_x(\boldsymbol{r}_1 t_1, \boldsymbol{r}_2 t_1) - \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)v_x(\boldsymbol{r}_1 t_1)$. The explicit form of the exchange-only TDOEP equation in terms of the KS orbitals then reads as [104–106]

$$i\sum_j \sum_{k\neq j} n_j \int_{-\infty}^{t_1} dt_2 \int d^3r_2 [v_x(2) - u_{x,j}(2)]\phi_j(1)\phi_j^*(2)\phi_k^*(1)\phi_k(2) + c.c. = 0, \tag{2.33}$$

where

$$u_{x,j}(1) = -\frac{1}{\phi_j^*(1)}\sum_k n_k \int d2\phi_j^*(2)\phi_k(2)\phi_k^*(1)v_{ee}(1,2). \tag{2.34}$$

We note that the integral from $-\infty$ to t_0 in Eq. (2.33) accounts for the equilibrium condition of the system at the initial time $t = t_0$.

The TDOEP can be equivalently derived from the action formalism. Also in this case, the combination of the adiabatic connection with the Keldysh method makes it possible to apply standard perturbation techniques and expand the xc action functional in terms of the KS orbitals and the Coulomb interaction.

Although the computational cost of orbital dependent functionals, such as the TDOEP, is typically much higher than evaluating an explicit parametrization in the density, this approach offers the advantage of sistematically more accurate approximations. In fact, the link between TDDFT and NEGF allows

one to perturbatively construct meaningful approximations to the xc potential by including the description of relevant physical processes in the form of Feynman diagrams.

Chapter 3

Foundations of QED-TDDFT

3.1 Introduction

In this chapter we give a comprehensive derivation of our QED-TDDFT, as a formally exact and numerically feasible approach, that generalizes TDDFT to the electron-photon coupling. The KS construction of QED-TDDFT here introduced provides a practical scheme to perform ab-initio calculations of quantum realistic many-particle systems and radiation, thus bridging the gap between condensed-matter theory and quantum optics. QED-TDDFT for non-relativistic electronic systems coupled to photon modes of mesoscopic cavities was formulated in Ref. [55]. Here, we develop a general framework for the functional description of the electron-photon coupling in most possible systems of interest, ranging from the fully relativistic case, introduced in Refs. [39, 42], to effective quantum-optical Hamiltonians. By ignoring all photonic degrees of freedom, we recover at each step the corresponding standard formulations of TDDFT, which are extensively used by the electronic structure community [33, 58].

In Sec. 3.2 we show how the dynamics of a relativistic electron-photon system is uniquely determined by its initial state and two reduced quantities, i.e., the polarization of the Dirac field and the vector potential of the photon

field. These fundamental observables can be calculated by solving two coupled, nonlinear evolution equations without the need of evaluating the numerically infeasible many-body wave function of the full interacting system. To find reliable approximations to the implicit functionals, we present the appropriate KS construction. In Sec. 3.3 we discuss the non-relativistic limit of QED-TDDFT. This corresponds to the functional reformulation of the Pauli-Fierz Hamiltonian (see e.g., [23, 25], which is based on the electronic current density and the electromagnetic vector potential. By introducing further approximations, i.e., by restricting the number of allowed photonic modes, and performing the dipole approximation, we recover TDDFT for localized many-electron systems interacting with cavity photons [55]. In the limit of only two sites and one mode, we deduce the appropriate effective theory for the Rabi model. In Sec. 3.4 this model system is used to illustrate the basic ideas of a density functional reformulation of QED in great detail, and for it we present the exact KS potential.

3.2 Relativistic QED-TDDFT

Before starting the actual discussion on QED, we introduce the notation used in this chapter. We employ the standard covariant notation $x = (x^\mu) = (ct, \vec{r}) = (ct, r^k)$ with Greek letters indicating four vectors, i.e., $\mu \in \{0, 1, 2, 3\}$, and Roman letters indicating spatial vectors, i.e., $k \in \{1, 2, 3\}$. To lower (or raise) the indices, i.e., going from contravariant to covariant vectors (or vice versa), we adopt the convention

$$g_{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

for the Minkwoski metric. Spatial vectors are denoted by a vector symbol and consist of contravariant components, e.g., $\vec{A} \equiv A^k$. Covariant components differ by a minus sign, i.e., $A_k = -A^k$. Note that this distinction does not apply to the non-relativistic case, where also A_k must be interpreted as contravariant. The four gradient is indicated by $\partial_\mu = \partial/\partial x^\mu = \left(\frac{1}{c}\frac{\partial}{\partial t}, \vec{\nabla}\right)$. With these definitions the divergence can be written as $\partial_k A^k = \vec{\nabla} \cdot \vec{A}$. Further we note that $J_k A^k = -\vec{J} \cdot \vec{A}$. With the help of the Levi-Civita symbol ϵ^{ijk} the curl is expressed as $\epsilon^{ijk}\partial_j A_k \equiv -\vec{\nabla} \times \vec{A}$ and the multiplication of Pauli matrices reads as $\sigma^k \sigma^l = (1/2)(\{\sigma^k, \sigma^l\} + [\sigma^k, \sigma^l]) = -g^{kl} - \mathrm{i}\epsilon^{klm}\sigma_m$.

For ordinary matter relativistic effects are not dominant, but they may be noticeable. In large atoms ($Z \geq 50$) these effects severely change the innermost electrons, inducing noticeable effects on the overall electron density profile. Relativistic atoms, molecules and solids interacting with quantized electromagnetic fields are infinitely-many-body-problems described within the quantum field theory of QED. The canonical quantization of the photon field A_μ requires fixing a gauge. Here, we choose the Coulomb gauge as it reduces the independent components of the photon field to the two transverse physical polarizations, and singles out the classical Coulomb interaction. Since we want to connect our QED-TDDFT to cavity QED, where Coulomb gauge photons are usually employed, and condensed-matter theory, where the Coulomb interaction plays a dominant role, the Coulomb gauge is for the present purpose the natural gauge to work in. The nuclei, along with external magnetic fields used to drive the electronic system, are described by the classical external four potential $a^\mu_{\text{ext}}(x)$, which couples to the matter current. External excitations of the photon field, possibly involved in radiation source problems, are described by the coupling to the classical external four current density $j^\mu_{\text{ext}}(x)$.

In Sec. 3.2.1 we introduce the Coulomb gauge QED Hamiltonian for

the system of interest, briefly discuss the points concerning renormalization, pair production, etc., and formulate the problem in terms of basic functional variables, i.e., the four current density (polarization) of the Dirac field and the electromagnetic four potential. In Sec. 3.2.2 we prove the relativistic Runge-Gross theorem for QED-TDDFT. In Sec. 3.2.3 we construct the KS system, which allows one to calculate the above basic variables by solving self-consistent equations for non-interacting particles. We employ SI units throughout since in Sec. 3.3 we perform the non-relativistic limit, which is most easily done by keeping the physical constants explicit. A detailed discussion of quantizing QED in Coulomb gauge is given in appendix A.

3.2.1 Description of the system

The Coulomb gauge QED Hamiltonian of the system takes in the Heisenberg picture the following form

$$\hat{H}(t) = \hat{H}_{\mathrm{M}} + \hat{H}_{\mathrm{E}} + \hat{H}_{\mathrm{C}}(t) + \hat{H}_{\mathrm{int}} + \hat{H}_{\mathrm{ext}}(t), \tag{3.1}$$

where we indicate by t the explicit time dependence due to the external fields. Here, the mass term is given by the free Dirac Hamiltonian

$$\hat{H}_{\mathrm{M}} = \int \mathrm{d}^3x : \hat{\bar{\psi}}(x) \left(-\mathrm{i}\hbar c\, \vec{\gamma} \cdot \vec{\nabla} + mc^2 \right) \hat{\psi}(x) :, \tag{3.2}$$

where $\hat{\psi}^\dagger(x) = \left(\hat{\phi}^\dagger(x), \hat{\chi}^\dagger(x) \right)$ denotes the fermion field operator, and we use the Dirac representation for the vector of γ^k matrices (see appendix A). The energy of the free photon field is expressed as

$$\hat{H}_{\mathrm{E}} = \frac{\epsilon_0}{2} \int \mathrm{d}^3x \, : \left(\hat{\vec{E}}^2(x) + c^2 \hat{\vec{B}}^2(x) \right) :, \tag{3.3}$$

where $\hat{\vec{E}}$ and $\hat{\vec{B}}$ are the transverse electric and magnetic field operators defined as in appendix A in terms of the vector potential $\hat{\vec{A}}$. We point out that, due to the Coulomb gauge condition $\vec{\nabla} \cdot \vec{A} = 0$, only the spatial components of the Maxwell field $\hat{A}^k$ are dynamical variables subject to quantization. The time component A^0 corresponds to the classical Coulomb potential generated by the total charge density. The associated Coulomb energy can be written as

$$\hat{H}_{\mathrm{C}}(t) = \frac{1}{2c^2} \int \frac{\mathrm{d}^3x\, \mathrm{d}^3x'}{4\pi\epsilon_0 |\vec{x} - \vec{x}'|} \left(j^0_{\mathrm{ext}}(x') \hat{J}_0(x) + : \hat{J}^0(x) \hat{J}_0(x') : \right), \tag{3.4}$$

where j^0_{ext} is the charge density of the external current source, and $\hat{J}^0$ is the charge density of the Dirac field, i.e., the time component of the fermionic four current

$$\hat{J}^\mu(x) = ec : \hat{\bar{\psi}}(x) \gamma^\mu \hat{\psi}(x) : . \tag{3.5}$$

The coupling to the external sources is described by the term

$$\hat{H}_{\mathrm{ext}}(t) = \frac{1}{c} \int \mathrm{d}^3x \, \left(\hat{J}_\mu(x) \hat{a}^\mu_{\mathrm{ext}}(x) + \hat{A}_\mu(x) \hat{j}^\mu_{\mathrm{ext}}(x) \right). \tag{3.6}$$

Finally, the interaction between the quantized Dirac and Maxwell fields in Coulomb gauge reads as

$$\hat{H}_{\mathrm{int}} = -\frac{1}{c} \int \mathrm{d}^3x \, \hat{\vec{J}}(x) \cdot \hat{\vec{A}}(x). \tag{3.7}$$

Divergent vacuum contributions of the homogeneous QED Hamiltonian (i.e., the interacting QED Hamiltonian without external fields) have been removed by normal ordering (:...:) of the field operators. However, without further refinements, the above QED Hamiltonian is not well-defined since it gives rise

to UV-divergences. These divergences occur in three subdiagrams of the perturbation expansion [22, 44, 63]: the fermion self-energy, the vacuum polarization (the photon self-energy) and the vertex correction. Suitable regularization procedures allow one to remove these infinities to each order in the fine structure constant, e.g., by introducing frequency cutoffs in the plane-wave expansions for the fermionic as well as the bosonic field operators, or by dimensional regularization [44]. Since we are interested exclusively in condensed-matter systems, a physical highest cutoff would be at energies that allow for pair creation. In this work we thus restrict our considerations to the case of a stable vacuum [12, 39, 42]. Such regularization procedures make the Hamiltonian operator self-adjoint [53], but introduce a dependence on the cutoff parameters which changes the theory at smallest and largest length scales. In order to get rid of this dependence, renormalization schemes are employed perturbatively, e.g., with the addition of counterterms to cancel the singularities introduced in the subdiagrams by the cutoffs. All counterterms are defined by expectation values in the vacuum of the homogeneous Hamiltonian [12, 44]. This allows one to compare Hamiltonians with different external potentials and currents. The effect of these counterterms is a renormalization of the electron mass and field operator (from the fermion self-energy), of the photon field operator (from the vacuum polarization) and of the charge (from the vertex graph). The Ward-Takahashi identities [44] ensure that the QED Hamiltonian is renormalizable to all orders in perturbation theory. In the following we thus interpret Eq. (3.1) as the bare Hamiltonian expressed in terms of the renormalized quantities[1].

The renormalized Hamiltonian of Eq. (3.1) is uniquely defined by the choice of the external fields, which we denote by $\hat{H}(t) = \hat{H}([a^{\mu}_{\mathrm{ext}}, j^{\mu}_{\mathrm{ext}}]; t)$.

[1] Note that an exhaustive discussion of renormalization is beyond the scope of the present work. Nevertheless, the description of relativistic electron-photon systems requires a general field-theoretical approach. If one wants to avoid the difficulties of renormalization, the cutoffs must be kept.

Given an initial state $|\Psi_0\rangle$, the time evolution of the coupled matter-photon system is governed by the equation

$$\mathrm{i}\hbar c\partial_0 |\Psi(t)\rangle = \hat{H}([a^\mu_{\mathrm{ext}}, j^\mu_{\mathrm{ext}}]; t) |\Psi(t)\rangle \,. \tag{3.8}$$

This equation determines the electron-photon wave function $|\Psi(t)\rangle$ as a functional of the initial state $|\Psi_0\rangle$ and the pair of external variables $(a^\mu_{\mathrm{ext}}, j^\mu_{\mathrm{ext}})$, i.e., $|\Psi(t)\rangle = |\Psi([\Psi_0, a^\mu_{\mathrm{ext}}, j^\mu_{\mathrm{ext}}]; t)\rangle$. Accordingly, the expectation value of any arbitrary operator $\hat{O}$ is also a functional of the same variables, i.e., $\langle\Psi(t)|\hat{O}\,|\Psi(t)\rangle = O([\Psi_0, a^\mu_{\mathrm{ext}}, j^\mu_{\mathrm{ext}}]; t)$. However, for any but the simplest systems, the numerically exact solution of Eq. (3.8) is not feasible. On the other hand, even decoupling the electron and photon fields by employing the lowest order approximation for the photon-mediated electron-electron interaction, the resulting problem is far from trivial. As discussed in the previous chapters, the starting point of any DFT-like approach is to identify a small set of basic observables that also uniquely characterize the many-body wave function, and for which one can write a closed set of equations, that do not involve the wave function explicitly. An obvious choice are the equations of motion for the new variables. These equations can at the same time be used to prove that the wave function is a unique functional of the initial state and the functional variables.

In the next step, we determine possible functional variables for the electron-photon wave function $|\Psi([\Psi_0, a^\mu_{\mathrm{ext}}, j^\mu_{\mathrm{ext}}]; t)\rangle$, which obeys Eq. (3.8), and derive their equations of motions. A change of functional variables requires a bijective mapping from the allowed set $(a^\mu_{\mathrm{ext}}, j^\mu_{\mathrm{ext}})$ to some other set of variables, for a fixed initial state $|\Psi_0\rangle$. This new set is usually identified by employing arguments based on the Legendre transformation [59], and the new functional variables are often called conjugate variables. We apply this method

to the QED action integral [39, 42]. This is readily evaluated from the Lagrangian of Eq. (A.1) as

$$\begin{aligned}\tilde{\mathcal{A}}[\Psi_0, a_\mu^{\text{ext}}, j_\mu^{\text{ext}}] &= -\int d^4x\, \mathcal{L}_{\text{QED}} \\ &= -\mathcal{B} + \frac{1}{c}\int d^4x\ (j^\mu_{\text{ext}} A_\mu + J_\mu a^\mu_{\text{ext}})\,. \end{aligned} \tag{3.9}$$

Here, we have used the notation $\int d^4x \equiv \int_0^T \mathrm{d}t \int \mathrm{d}^3r$, where T is an arbitrary time, and defined the internal action

$$\mathcal{B} = \int_0^T \mathrm{d}t \langle \Psi(t)| \mathrm{i}\hbar c\partial_0 - \hat{H}_{\text{M}} - \hat{H}_{\text{E}} - \hat{H}_{\text{int}}(t) - \hat{H}_{\text{C}}(t)|\Psi(t)\rangle.$$

Apparently, for a fixed initial state, Eq. (3.9) is a Legendre transformation from the pair of variables $(a^\mu_{\text{ext}}, j^\mu_{\text{ext}})$ to the conjugate pair (J_μ, A_μ)[2]. One might note that if these were indeed conjugate variables connected via a standard Legendre transformation, differentiating Eq. (3.9) with respect to a^μ_{ext} (j^μ_{ext}) should give J_μ (A_μ). However, evaluating these functional derivatives as in [60], we obtain the following results

$$\frac{\delta\tilde{\mathcal{A}}}{\delta a^\mu_{\text{ext}}(x)} + \mathrm{i}\hbar c\langle\Psi(T)|\frac{\delta\Psi(T)}{\delta a^\mu_{\text{ext}}(x)}\rangle = \frac{1}{c}J_\mu(x) \tag{3.10}$$

$$\frac{\delta\tilde{\mathcal{A}}}{\delta j^\mu_{\text{ext}}(x)} + \mathrm{i}\hbar c\langle\Psi(T)|\frac{\delta\Psi(T)}{\delta j^\mu_{\text{ext}}(x)}\rangle = \frac{1}{c}A_\mu(x), \tag{3.11}$$

which include non-trivial additional terms. These terms appear due to the fact that variations of the external fields produce non-zero variations of the wave function at the arbitrary upper boundary T (in contrast to direct variations of the wave function which obey $\delta\Psi(T) = 0$) [59]. In other terms, these boundary terms are required to guarantee the causality of J_μ and A_μ [60]. Eqs. (3.10) and (3.11) thus show that a straightforward approach based

[2] One should not confuse these conjugate variables with the conjugate momenta that are used in field theory to quantize the system. In Coulomb-gauge QED the pairs of conjugate momenta are $(\vec{A}, \psi)$ and $(\epsilon_0\vec{E}, \mathrm{i}\hbar c\psi^\dagger)$ [22]

on the Legendre transformation to demonstrate a one-to-one correspondence between $(a^{\mu}_{\text{ext}}, j^{\mu}_{\text{ext}})$ and (J_{μ}, A_{μ}) becomes problematic [42].

We observe that choosing the charge-current density J_{μ} as a functional variable may also lead to difficulties, since its internal structure involves both electronic and positronic degrees of freedom. J_{μ} in fact describes the net-charge flow of negatively charged electrons and positively charged positrons [22]. Therefore, the expectation value of the four current operator does not differ between the current of, e.g., $(N+1)$ electrons and N positrons, and of N electrons and $(N-1)$ positrons.

However, for the moment we follow the above identification scheme and derive the equations of motion for $\hat{J}_{\mu}$ and $\hat{A}_{\mu}$. Since $\int \mathrm{d}^3 r' \, [\hat{J}_{\mu}(\vec{r}), \hat{J}_0(\vec{r}')] f(\vec{r}') = 0$, where $f(\vec{r}')$ is any test function, $\hat{J}_{\mu}$ commutes with the Coulomb interaction Hamiltonian of Eq. (3.4), and the equation of motion is the same as in the Lorentz gauge [42]:

$$\partial_0 \hat{J}^k(x) = \hat{q}^k_{\text{kin}}(x) + \hat{q}^k_{\text{int}}(x) + \hat{n}^{kl}(x)\hat{a}^{\text{ext}}_l(x), \tag{3.12}$$

where

$$\begin{aligned}\hat{q}^k_{\text{kin}}(x) = &- ec\hat{\bar{\psi}}(x)\Big[\gamma^k\gamma^0\Big(\vec{\gamma}\cdot\vec{\nabla}\Big)+\Big(\vec{\gamma}\cdot\overleftarrow{\nabla}\Big)\gamma^0\gamma^k\Big]\hat{\psi}(x) \\ &+ \mathrm{i}\,\frac{e}{\hbar}mc^2\hat{\bar{\psi}}(x)\left[\gamma^0\gamma^k - \gamma^k\gamma^0\right]\hat{\psi}(x),\end{aligned}$$

$$\hat{n}^{kl}(x) = -\frac{2e^2}{\hbar}\epsilon^{klj}\hat{\psi}^{\dagger}(x)\Sigma_j\hat{\psi}(x),$$

$$\hat{q}^k_{\text{int}}(x) = \hat{n}^{kl}(x)\hat{A}_l(x).$$

Here, ϵ^{klj} is the Levi-Civita tensor and

$$\Sigma^k = \begin{pmatrix} \sigma^k & 0 \\ 0 & \sigma^k \end{pmatrix}.$$

The time component is given by $\partial_0 \hat{J}^0 = -\vec{\nabla} \cdot \hat{\vec{J}}$, i.e., the current obeys the charge conservation. A different equation for the four current operator is obtained by the Gordon decomposition [12], in the form of the evolution equation for the polarization

$$\hat{P}^\mu(x) = ec : \hat{\psi}^\dagger(x)\gamma^\mu\hat{\psi}(x) : .$$

This reads as

$$\partial_0 \hat{P}^k(x) = \hat{Q}^k_{\text{kin}}(x) + \hat{Q}^k_{\text{int}}(x) + \frac{2emc}{\mathrm{i}\hbar}\hat{J}^k(x) + \frac{2e}{\mathrm{i}\hbar c}\hat{P}_0(x)\hat{a}^k_{\text{ext}}(x), \tag{3.13}$$

where we have used the definitions

$$\hat{Q}^k_{\text{kin}}(x) = ec\hat{\bar{\psi}}(x)\left(\vec{\partial}^k - \overleftarrow{\partial}^k\right)\hat{\psi}(x) + \mathrm{i}ec\epsilon^{klj}\partial_l\left(\hat{\bar{\psi}}(x)\Sigma_j\hat{\psi}(x)\right),$$

$$\hat{Q}^k_{\text{int}}(x) = \frac{2e}{\mathrm{i}\hbar c}\hat{P}_0(x)\hat{A}^k(x).$$

We note that the current and the polarization are the real and imaginary part of the same operator, i.e.,

$$\hat{J}^k(x) = 2\Re\left\{ec : \hat{\phi}^\dagger(x)\sigma^k\hat{\chi}(x) :\right\},$$
$$\hat{P}^k(x) = 2\Im\left\{ec : \hat{\phi}^\dagger(x)\sigma^k\hat{\chi}(x) :\right\},$$

where $\hat{\phi}$ and $\hat{\chi}$ are the bigger and smaller components of the Dirac four spinor.

The Heisenberg equation of motion for the photon field operator is obtained as

$$\partial_0 \hat{A}^k(x) = -\hat{E}^k(x). \tag{3.14}$$

Evaluating the second derivative with respect to time gives

$$\begin{aligned} \Box \hat{A}^k(x) - \partial^k \partial_0 \left(\frac{1}{c} \int \mathrm{d}^3 r' \frac{j^0_{\mathrm{ext}}(x') + \hat{J}^0(x')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \right) \\ = \mu_0 c \left(j^k_{\mathrm{ext}}(x) + \hat{J}^k(x) \right), \end{aligned} \tag{3.15}$$

which is indeed the quantized version of the inhomogeneous Maxwell equations in Coulomb gauge.

3.2.2 One-to-one mapping

In this section, we show that the polarization is better suited as a fundamental variable for the matter part, and prove the one-to-one correspondence between the external (time-dependent) fields $(a^\mu_{\mathrm{ext}}, j^\mu_{\mathrm{ext}})$ and the internal variables (P_μ, A_μ) for the coupled matter-photon system evolving from a given initial state $|\Psi_0\rangle$. However, already here we point out that both the approaches (based on the current or on the polarization) lead to the same functional theory in the non-relativistic limit.

A first restriction that we need to impose is fixing a specific gauge for the external potential a^μ_{ext}. Since by construction external potentials that differ by a gauge transformation, i.e., $\tilde{a}^\mu_{\mathrm{ext}} = a^\mu_{\mathrm{ext}} + \partial^\mu \Lambda$, lead to the same current density J_μ (and polarization P_μ)[3], the desired one-to-one correspondence holds

[3]This can be seen by considering the commutator $[\hat{J}^\mu; \int \hat{J}_\nu \partial^\nu \Lambda]$, which determines the effect of a gauge transformation on the equation for $\hat{J}_\mu$ (Eq. (3.12)). By partial integration, application of the continuity equation and the fact that $[\hat{J}^\mu; \hat{J}^0] \equiv 0$, this term becomes zero and therefore has no effect on the current. The same reasoning shows that also $\hat{P}_\mu$ is gauge independent.

only modulo this transformation. In principle we thus consider a bijective mapping between equivalence classes, and by fixing a gauge we choose a unique representative of each class. As we have seen (Eq. (2.18)), the same type of non-uniqueness is also found in standard TDDFT [43], where the mapping between densities and scalar external potentials is unique up to a purely time-dependent function $\Lambda(t)$. For simplicity, here we impose the temporal gauge condition [61]

$$a^0_{\text{ext}}(x) = 0. \tag{3.16}$$

In the following, any other gauge that keeps the initial state unchanged, i.e., for which the gauge function obeys $\Lambda(0, \vec{r}) = 0$, is also allowed [61].

Also with respect to j^μ_{ext} one has to choose a unique representative of an equivalence class of external currents. This freedom corresponds to the gauge freedom of the internal photon field A_μ. Since we employ the Coulomb gauge for A_μ, only the transverse component of the external current $j^k_{\text{ext}} = \partial^k v_{\text{ext}} - \epsilon^{klj}\partial_l \Upsilon^{\text{ext}}_j$ couples to the quantized photon field, as it can be seen from Eq. (3.15). Therefore, external currents which differ in their longitudinal components lead to the same transverse electromagnetic field A_k. By fixing j^0_{ext} for all further considerations, we also choose a unique longitudinal component v_{ext} of j^k_{ext} by the continuity equation $\partial_0 j^0_{\text{ext}} = \Delta v_{\text{ext}}$. Note that as a consequence, we also fix the classical Coulomb potential A_0 by Eq. (A.4).

In order to prove the one-to-one correspondence

$$(a^k_{\text{ext}}, j^k_{\text{ext}}) \overset{1:1}{\leftrightarrow} (J_k, A_k), \tag{3.17}$$

we need to show that if $(a^k_{\text{ext}}, j^k_{\text{ext}}) \neq (\tilde{a}_{\text{ext}}, \tilde{j}_{\text{ext}})$, then necessarily $(J_k, A_k) \neq (\tilde{J}_k, \tilde{A}_k)$ for a fixed initial state $|\Psi_0\rangle$. To do so we first note that each expectation value in Eqs. (3.12) and (3.15) is by construction a functional of $(a^k_{\text{ext}}, j^k_{\text{ext}})$

for a fixed initial state:

$$\partial_0 J^k([a^m_{\rm ext}, j^m_{\rm ext}]; x) = q^k_{\rm kin}([a^m_{\rm ext}, j^m_{\rm ext}]; x) + q^k_{\rm int}([a^m_{\rm ext}, j^m_{\rm ext}]; x) + n^{kl}([a^m_{\rm ext}, j^m_{\rm ext}]; x) a^{\rm ext}_l(x), \tag{3.18}$$

$$\Box A^k([a^m_{\rm ext}, j^m_{\rm ext}]; x) + \partial^k \left(\frac{1}{c} \int {\rm d}^3 r' \frac{\vec{\nabla}' \cdot \vec{j}_{\rm ext}(x') + \vec{\nabla}' \cdot \vec{J}([a^m_{\rm ext}, j^m_{\rm ext}]; x')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \right) = \mu_0 c \left(j^k_{\rm ext}(x) + J^k([a^m_{\rm ext}, j^m_{\rm ext}]; x) \right). \tag{3.19}$$

Suppose now that in the above equations we fix (J_k, A_k)[4], i.e., we do not regard them as functionals, but rather as functional variables. Then Eqs. (3.18) and (3.19) read as equations of motions for the external variables $(a^k_{\rm ext}, j^k_{\rm ext})$, which produce the given internal pair (J_k, A_k) via propagation of the initial state $|\Psi_0\rangle$:

$$\partial_0 J^k(x) = q^k_{\rm kin}([a^m_{\rm ext}, j^m_{\rm ext}]; x) + q^k_{\rm int}([a^m_{\rm ext}, j^m_{\rm ext}]; x) + n^{kl}([a^m_{\rm ext}, j^m_{\rm ext}]; x) a^{\rm ext}_l(x), \tag{3.20}$$

$$\Box A^k(x) + \partial^k \left(\frac{1}{c} \int {\rm d}^3 r' \frac{\vec{\nabla}' \cdot \vec{j}_{\rm ext}(x') + \vec{\nabla}' \cdot \vec{J}(x')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \right) = \mu_0 c \left(j^k_{\rm ext}(x) + J^k(x) \right). \tag{3.21}$$

Here, (J_k, A_k) satisfy the initial conditions

$$J^{(0)}_k = \langle \Psi_0 | \hat{J}_k | \Psi_0 \rangle, \tag{3.22}$$

$$A^{(0)}_k = \langle \Psi_0 | \hat{A}_k | \Psi_0 \rangle, \ A^{(1)} = -\langle \Psi_0 | \hat{E}_k | \Psi_0 \rangle, \tag{3.23}$$

[4]Note that the freedom of the internal variable J_k is constrained since J_0 is fixed by the initial state, and the continuity equation holds for all times. As a consequence, the freedom of the corresponding external variable $a^k_{\rm ext}$ is also restricted. Analogously, the freedom of the external current $j^k_{\rm ext}$ corresponds to the freedom of the internal field A_k as previously explained.

where we have used the definition

$$O^{(\alpha)} = \partial_0^\alpha O(t)|_{t=0}\,. \tag{3.24}$$

Therefore, the mapping (3.17) is bijective if Eqs. (3.20) and (3.21) allow for one and only one solution $(a^k_{\rm ext}, j^k_{\rm ext})$.

We first note that for a given pair (J_k, A_k), Eq. (3.21) uniquely determines the external current $j^k_{\rm ext}$. In fact, by defining the vector field

$$\zeta^k(x) = \Box A^k(x) + \partial^k\left(\frac{1}{c}\int \mathrm{d}^3r' \frac{\vec{\nabla}'\cdot\vec{J}(x')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}\right) - \mu_0 c J^k(x),$$

and using the Helmholtz decompositions for $\vec{\zeta} = \vec{\nabla}\times\vec{\Xi}$ and $\vec{j}_{\rm ext} = -\vec{\nabla}v_{\rm ext} + \vec{\nabla}\times\vec{\Upsilon}_{\rm ext}$, (where $v_{\rm ext}$ is gauge-fixed[5]), it follows that

$$\vec{\Upsilon}_{\rm ext}(x) = \frac{1}{\mu_0 c}\vec{\Xi}(x). \tag{3.25}$$

Thus, the original problem reduces to showing whether Eq. (3.20) determines $a^k_{\rm ext}$ uniquely. The most general approach to answer this question rely on a fixed-point scheme similar to [41]. Here, we follow the standard TD(C)DFT proof based on the assumption of time-analyticity of the external potential [43]. Assuming that $a^k_{\rm ext}(t)$ is time-analytic around the initial time $t = 0$, we represent it by the Taylor series

$$a^k_{\rm ext}(t) = \sum_{\alpha=0}^{\infty} \frac{a^{k\,(\alpha)}_{\rm ext}}{\alpha!}(ct)^\alpha. \tag{3.26}$$

[5]Note that instead of fixing $j^0_{\rm ext}$ one can equivalently choose A_0 for all times to select a unique $j^k_{\rm ext}$ by the zero-component of the internal current J_0 and Eq. (A.3).

From Eq. (3.20) we then obtain the Taylor coefficients of the corresponding current density as

$$J_k^{(\alpha+1)}(\vec{r}) = q_{\mathrm{kin},k}^{(\alpha)}(\vec{r}) + q_{\mathrm{int},k}^{(\alpha)}(\vec{r}) + \sum_{\beta=0}^{\alpha} \binom{\alpha}{\beta} \left(a_{\mathrm{ext}}^{l\,(\beta)}(\vec{r})\right) \left(n_{kl}^{(\alpha-\beta)}(\vec{r})\right), \tag{3.27}$$

where $q_{\mathrm{int},k}^{(\alpha)}(\vec{r}) = \langle\Psi_0|\hat{n}^{kl}(\vec{r})\hat{A}_l(\vec{r})\,|\Psi_0\rangle^{(\alpha)}$ and $n^{kl(\alpha)}$ are given by the respective Heisenberg equations evaluated at $t = 0$. Now, suppose that we have two different external potentials $a^k(t)_{\mathrm{ext}} \neq \tilde{a}^k(t)_{\mathrm{ext}}$. This implies that there is a lowest order α for which

$$a_{\mathrm{ext}}^{(\alpha)} \neq \tilde{a}_{\mathrm{ext}}^{(\alpha)}. \tag{3.28}$$

For all orders $\beta < \alpha$ the expansion coefficients of the corresponding current densities satisfy

$$J^{(\beta+2)} - \tilde{J}^{(\beta+2)} = 0. \tag{3.29}$$

However, for $\beta = \alpha$ we find that

$$\vec{J}^{(\alpha+1)}(\vec{r}) - \vec{\tilde{J}}^{(\alpha+1)}(\vec{r}) = \vec{n}^{(0)}(\vec{r}) \times \left(\vec{a}_{\mathrm{ext}}^{(\alpha)}(\vec{r}) - \vec{\tilde{a}}_{\mathrm{ext}}^{(\alpha)}(\vec{r})\right), \tag{3.30}$$

where

$$\vec{n}^{(0)}(\vec{r}) = \frac{2e^2}{\hbar}\langle\Psi_0|\hat{\psi}^\dagger(\vec{r})\vec{\Sigma}\hat{\psi}(\vec{r})|\Psi_0\rangle.$$

If there was no curl operator on the r.h.s. of Eq. (3.30) we could conclude that infinitesimally later than $t = 0$ the difference between the two current densities $\vec{J}(x)$ and $\vec{\tilde{J}}(x)$ becomes non-zero (provided that $\vec{n}^{(0)} \neq 0$), and that

we have a one-to-one correspondence. On the contrary, we need to restrict the set of allowed external potentials $\{\vec{a}_{\rm ext}\}$ to those that are perpendicular to $\vec{n}^{(0)}$. This aspect was not taken into account in previous works [39, 42], where the proof of the theorem is effectively restricted to a smaller set of potentials and currents.

In order to avoid the problems with the current, in the following we consider the polarization P_k as the basic variable for the relativistic condensed-matter system. While the current describes the flow of the total charge of the system, (which is conserved), the polarization depends on the actual number of particles and anti-particles, (which is not conserved). Therefore, unlike J_k, the polarization differs between a local current produced by, e.g., N electrons and $N-1$ positrons, and by $N+1$ electrons and N positrons. To prove that for a given initial state $|\Psi_0\rangle$ the one-to-one mapping

$$(a^k_{\rm ext}, j^k_{\rm ext}) \overset{1:1}{\leftrightarrow} (P_k, A_k) \tag{3.31}$$

actually holds, we need to show that for a given pair (P_k, A_k) the two coupled equations

$$\begin{aligned} \partial_0 \vec{P}(x) &= \vec{Q}_{\rm kin}([a^k_{\rm ext}, j^k_{\rm ext}]; x) + \vec{Q}_{\rm int}([a^k_{\rm ext}, j^k_{\rm ext}]; x) \\ &\quad + \frac{2emc}{\mathrm{i}\hbar}\vec{J}([a^k_{\rm ext}, j^k_{\rm ext}]; x) + \frac{2e}{\mathrm{i}\hbar c}P_0([a^k_{\rm ext}, j^k_{\rm ext}]; x)\vec{a}_{\rm ext}(x), \end{aligned} \tag{3.32}$$

$$\begin{aligned} &\Box\vec{A}(x) - \mu_0 c\left(\vec{j}_{\rm ext}(x) + \vec{J}([a^k_{\rm ext}, j^k_{\rm ext}]; x)\right) \\ &\quad = \vec{\nabla}\left(\frac{1}{c}\int \mathrm{d}^3r' \frac{\vec{\nabla}'\cdot\vec{j}_{\rm ext}(x') + \vec{\nabla}'\cdot\vec{J}([a^k_{\rm ext}, j^k_{\rm ext}]; x')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}\right), \end{aligned} \tag{3.33}$$

allow for a unique solution $(a^k_{\rm ext}, j^k_{\rm ext})$. Here, (P_k, A_k) obey the initial conditions

$$P^{(0)}_k(\vec{r}) = \langle\Psi_0|\hat{P}_k(\vec{r})|\Psi_0\rangle, \tag{3.34}$$

$$A^{(0)}_k(\vec{r}) = \langle\Psi_0|\hat{A}_k(\vec{r})|\Psi_0\rangle,\ A^{(1)}_k(\vec{r}) = -\langle\Psi_0|\hat{E}_k(\vec{r})|\Psi_0\rangle. \tag{3.35}$$

Assuming that both the external fields $a^k_{\rm ext}$ and $j^k_{\rm ext}$ are Taylor-expandable around $t = 0$, we find for the lowest order α on the one hand

$$\vec{P}^{(\alpha+1)}(\vec{r}) - \vec{\tilde{P}}^{(\alpha+1)}(\vec{r}) = \frac{2e}{\mathrm{i}\hbar c} P^{(0)}_0(\vec{r}) \left(\vec{a}^{(\alpha)}_{\rm ext}(\vec{r}) - \vec{\tilde{a}}^{(\alpha)}_{\rm ext}(\vec{r})\right) \neq 0, \tag{3.36}$$

provided that $P^{(0)}_0(\vec{r}) = \langle\Psi_0|\hat{P}_0(\vec{r})|\Psi_0\rangle \neq 0$, i.e., (the local) total number of particles and anti-particles is non-zero. On the other hand, we also have

$$\begin{aligned} &\vec{A}^{(\alpha+2)}(\vec{r}) - \vec{\tilde{A}}^{(\alpha+2)}(\vec{r}) \\ &\quad = \mu_0 c \left(\vec{\nabla} \times \vec{\Upsilon}^{(\alpha)}_{\rm ext}(\vec{r}) - \vec{\nabla} \times \vec{\tilde{\Upsilon}}^{(\alpha)}_{\rm ext}(\vec{r})\right) \neq 0, \end{aligned} \tag{3.37}$$

since all external currents have the same longitudinal component. Thus, the mapping (3.31) is bijective, at least for time-analytic external sources $(a^k_{\rm ext}, j^k_{\rm ext})$. It follows that, instead of solving the (numerically infeasible) interacting QED problem for the wave function $|\Psi(t)\rangle$, one can in principle determine the exact functional variables (P_k, A_k) from the coupled nonlinear equations

$$\begin{aligned} \partial_0 \vec{P}(x) &= \vec{Q}_{\rm kin}([P_k, A_k]; x) + \vec{Q}_{\rm int}([P_k, A_k]; x) \\ &\quad + \frac{2emc}{\mathrm{i}\hbar} \vec{J}([P_k, A_k]; x) + \frac{2e}{\mathrm{i}\hbar c} P_0([P_k, A_k]; x) \vec{a}_{\rm ext}(x), \end{aligned} \tag{3.38}$$

$$\begin{aligned} &\Box \vec{A}(x) - \vec{\nabla} \left(\frac{1}{c} \int \mathrm{d}^3 r' \frac{\vec{\nabla}' \cdot \vec{j}_{\rm ext}(x') + \vec{\nabla}' \cdot \vec{J}([P_k, A_k]; x')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \right) \\ &\quad = \mu_0 c \left(\vec{j}_{\rm ext}(x) + \vec{J}([P_k, A_k]; x)\right), \end{aligned} \tag{3.39}$$

with the initial conditions (3.34) and (3.35). However, solving in practice these equations requires approximations for the unknown functionals.

We point out that our QED-TDDFT in Coulomb gauge, which treats explicitly the electrostatic longitudinal interaction between charged fermions, describes as well all retardation effects due to the photon exchange. For instance, we can identify the low frequency Breit contribution [74] to the photon field due to the transverse Dirac current as

$$\hat{A}^k_{\rm Breit}(x) = \frac{1}{c}\int \mathrm{d}^3r' \, \frac{\hat{J}^k(\vec{r}')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|} - \frac{1}{c}\int \mathrm{d}^3r' \frac{(r^k - r'^k)}{4\pi|\vec{r}-\vec{r}'|^3}\int \mathrm{d}^3r'' \frac{\hat{J}^l(\vec{r}'')(r'_l - r''_l)}{4\pi\epsilon_0|\vec{r}'-\vec{r}''|^3}.$$

This is derived by approximating the photon mediated interaction between the electrons by the Green's function of the D'Alambert operator $\Box$, where the retardation is assumed to be negligible. If we express the total photon field as the sum of the Breit term and a remainder, i.e., $\hat{A}^k = \hat{A}^k_{\rm Breit} + \hat{A}^k_{\rm diff}$, we can explicitly identify the contributions due to the Breit interaction in the basic QED-TDDFT Eqs. (3.12), (3.13) and (3.15). By assuming $\vec{A}_{\rm diff} \approx 0$ and $\partial_0 \vec{A}_{\rm Breit} \approx 0$, the usual Breit Hamiltonian, (which also includes the current-current interaction),[6] is then obtained as [74]

$$\hat{H}_{\rm Breit} = \frac{1}{4c^2}\int \mathrm{d}^3r\mathrm{d}^3r' \left[\frac{\hat{J}_k(\vec{r})\hat{J}^k(\vec{r}')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|} - \frac{\hat{J}^k(\vec{r})(r_k - r'_k)\hat{J}^l(\vec{r}')(r_l - r'_l)}{4\pi\epsilon_0|\vec{r}-\vec{r}'|^3}\right]. \tag{3.40}$$

In the non-relativistic limit discussed in Sec. 3.3, the above Breit Hamiltonian would give rise to orbit-orbit, spin-orbit and spin-spin two-electron interactions. However, since we treat the transverse photon field as a whole, these

[6] Here, we assume for simplicity that we do not have a transverse external current $j^k_{\rm ext}$. The inclusion of general external currents is straightforward with the replacement $\hat{J}^k \to \hat{J}^k + j^k_{\rm ext}$.

terms are implicitly included into the coupled matter-photon Hamiltonian.

3.2.3 Time-Dependent Kohn-Sham Equations

In the previous section, we have shown that the wave function of the relativistic electron-photon system is a unique functional of the Dirac polarization P_k and the electromagnetic vector potential A_k. However, the coupled equations for these variables contain implicit functionals that need to be approximated. As discussed, a practical scheme for constructing approximations is considering an auxiliary KS system of non-interacting particles, which exactly reproduces the polarization and vector potential of the true interacting system. The initial (factorized) KS state

$$|\Phi_0\rangle = |\mathrm{M}_0\rangle \otimes |\mathrm{EM}_0\rangle$$

must obey the same initial conditions as the coupled QED problem (Eqs. (3.34) and (3.35)). We also observe that the equations of motion (3.32) and (3.33) for this non-interacting system subject to the effective external fields $(a^k_{\mathrm{eff}}, j^k_{\mathrm{eff}})$ read as

$$\begin{aligned}\partial_0 \vec{P}(x) &= \vec{Q}_{\mathrm{kin}}([a^k_{\mathrm{eff}}, j^k_{\mathrm{eff}}]; x) + \frac{2emc}{\mathrm{i}\hbar}\vec{J}([a^k_{\mathrm{eff}}, j^k_{\mathrm{eff}}]; x) \\ &\quad + \frac{2e}{\mathrm{i}\hbar c} P_0([a^k_{\mathrm{eff}}, j^k_{\mathrm{eff}}]; x)\vec{a}_{\mathrm{eff}}(x) \qquad (3.41)\\ \Box\vec{A}(x) - \vec{\nabla}&\left(\frac{1}{c}\int \mathrm{d}^3 r' \frac{\vec{\nabla}' \cdot \vec{j}_{\mathrm{eff}}(x')}{4\pi\epsilon_0|\vec{r} - \vec{r}'|}\right) \\ &= \mu_0 c\vec{j}_{\mathrm{eff}}(x). \qquad (3.42)\end{aligned}$$

The one-to-one correspondence established in Sec. (3.2.2) also applies to the KS system, thus implying the uniqueness of the pair $(a^k_{\mathrm{eff}}, j^k_{\mathrm{eff}})$. However, the non-interacting v-representability of the observables (P_k, A_k) must be proven. That is, we need to show that a solution $(a^k_{\mathrm{eff}}, j^k_{\mathrm{eff}})$ of Eqs. (3.41)

and (3.42) for a given pair (P_k, A_k) and initial state $|\Phi_0\rangle$ actually exists. The construction of the unique external current j^k_{eff} relies on Eq. (3.25), since its derivation is also valid for the case of a non-interacting system. Again, a general approach to demonstrate the existence of a solution to Eq. (3.41) would employ a fixed-point procedure [41]. Here, we assume for simplicity the Taylor expandability in time of P^k around $t = 0$ [28, 42, 61], and construct the Taylor coefficients of the effective potential a^k_{eff} from Eq. (3.41), as follows

$$P_0^{(0)}(\vec{r})\vec{a}^{(\alpha)}_{\text{eff}}(\vec{r}) = \frac{\mathrm{i}\hbar c}{2e}\left(\vec{P}^{(\alpha+1)}(\vec{r}) - \vec{Q}^{(\alpha)}_{\text{kin}}(\vec{r}) - \frac{2emc}{\mathrm{i}\hbar}\vec{J}^{(\alpha)}(\vec{r})\right) - \sum_{\beta=0}^{\alpha-1}\binom{\alpha}{\beta}\left(\vec{a}^{(\beta)}_{\text{eff}}(\vec{r})\right)\left(P_0^{(\alpha-\beta)}(\vec{r})\right).$$

Further, assuming that this series converges [28, 60], we have constructed the pair of effective fields

$$(a^k_{\text{eff}}[\Phi_0, P_k, A_k], j^k_{\text{eff}}[A_k]),$$

that reproduces in the KS system the functional variables (P_k, A_k) for a given initial state $|\Phi_0\rangle$.

The above construction proves the existence of the mapping

$$(P_k, A_k) \overset{|\Phi_0\rangle}{\mapsto} \left(a^k_{\text{eff}}, j^k_{\text{eff}}\right)$$

for a given pair (P_k, A_k). In order to actually *predict* these physical observables via the KS system, (and thus solve Eqs. (3.38) and (3.39)), the auxiliary system has to be connected to the true interacting system. We then consider the composite mapping

$$\left(a^k_{\text{ext}}, j^k_{\text{ext}}\right) \overset{|\Psi_0\rangle}{\mapsto} (P_k, A_k) \overset{|\Phi_0\rangle}{\mapsto} \left(a^k_{\text{eff}}, j^k_{\text{eff}}\right),$$

i.e., we use the fact that (P_k, A_k) are unique functionals of the initial state $|\Psi_0\rangle$

and external fields $(a^k_{\rm ext}, j^k_{\rm ext})$ of the coupled QED system. The resulting expressions for the KS potential and current are found by matching Eqs. (3.38) and (3.39) for the true interacting system, with Eqs. (3.41) and (3.42) for the uncoupled auxiliary system. This leads to [42, 55]

$$\begin{aligned} P_0([\Phi_0, P_k, A_k]; x)\vec{a}_{\rm KS}(x) = \frac{\mathrm{i}\hbar c}{2e}\Big(&\vec{Q}_{\rm kin}([\Psi_0, P_k, A_k]; x) \\ &-\vec{Q}_{\rm kin}([\Phi_0, P_k, A_k]; x) + \vec{Q}_{\rm int}([\Psi_0, P_k, A_k]; x)\Big) \\ &+ mc^2\Big(\vec{J}([\Psi_0, P_k, A_k]; x) - \vec{J}([\Phi_0, P_k, A_k]; x)\Big) \\ &+ P_0([\Psi_0, P_k, A_k]; x)\vec{a}_{\rm ext}(x) \end{aligned} \tag{3.43}$$

$$\vec{j}_{\rm KS}(x) = \vec{j}_{\rm ext}(x) + \vec{J}([\Psi_0, P_k, A_k]; x). \tag{3.44}$$

Solving the interacting QED problem for the initial state $|\Psi_0\rangle$ and external fields $(a^k_{\rm ext}, j^k_{\rm ext})$, is thus formally equivalent to solving the non-interacting, yet non-linear problem for the initial state $|\Phi_0\rangle$ and effective KS fields $(a^k_{\rm KS}, j^k_{\rm KS})$.

We point out [42] that in order to decouple the matter part from the photon field, the initial state of the KS system should be of product form, i.e., $|\Phi_0\rangle = |\mathrm{M}_0\rangle \otimes |\mathrm{EM}_0\rangle$. If we further choose $|\mathrm{M}_0\rangle$ to be a single Slater determinant of single particle spin-orbitals, we can actually map the whole problem to solving effective Dirac and Maxwell equations with the above KS potential $a^k_{\rm KS}$ and current $j^k_{\rm KS}$. The mean field description of the interacting QED system is obtained by using the following approximations for the KS fields

$$\vec{a}_{\rm MF}(x) = \vec{a}_{\rm ext}(x) + \vec{A}(x), \tag{3.45}$$

$$\vec{j}_{\rm MF}(x) = \vec{j}_{\rm ext}(x) + \vec{J}(x). \tag{3.46}$$

Since for simplicity we have adopted the temporal gauge $a^0_{ext} = 0$ for the external potential, while imposing the Coulomb gauge condition on the photon field, a gauge transformation is required in order to specify the mean field potential $a^\mu_{\rm MF}$ in either one or the other gauge. A similar caveat holds for the

external current. The mean field approximation corresponds to a Maxwell-Schrödinger description of the system, where the photon field is assumed to behave essentially classically.

3.3 Non-relativistic QED-TDDFT

While for the sake of generality we have discussed in the previous section the full relativistic QED problem, for the majority of applications in condensed-matter physics appears reasonable to consider approximations in the low energy regime, in particular below the electron-positron production threshold. Still, we want to investigate the matter coupling to quantized radiation fields. Most prominently these requirements are met in the context of cavity QED. Here, boundary conditions for the quantized Maxwell field at the walls of the cavity have to be taken into account. These additional constraints restrict the available photonic modes, which couple to the electronic system. The starting point for the description of these quantum-optical situations are models of non-relativistic particles interacting with quantized electromagnetic fields, such as the Pauli-Fierz Hamiltonian [23, 25]. In the lowest order of approximations we find the simplest model system of coupled matter and photons, i.e., the tight binding model for the H_2^+ molecule coupled to one photon mode. This model, which will be discussed in Sec. 3.4, also corresponds to the prime non-trivial example of quantum-optical problem, i.e., the Rabi model.

We realize at this point, that all conditions we had to impose in order to make our starting QED Hamiltonian well-defined, are naturally met in all the situations we aim at investigating. Actually, we do not even need to adopt a field-theoretical treatment for the particles in the first place. Such non-relativistic approach thus avoids a lot of unpleasant problems in connection with regularization and renormalization of QED. However, infinities arise

from the mistreatment of (relativistic) virtual photon states, which couple to the non-relativistic electronic states of interest. One way to deal with this problem is removing perturbatively all relativistic states from the theory by cutting off all momentum integrations at $p \sim mc$, where m is the mass of the electron (and keep this physical cutoff). Depending on the application, perturbative relativistic correction terms can then be added to the Hamiltonian to compensate for the effects of the cutoff. However, one would then need to introduce a new QED-TDDFT approach for every type of non-relativistic matter-photon Hamiltonian. In this section we assume non-relativistic QED to be renormalizable, (i.e., we remove the cutoff as usually done by taking the limit to infinity), and demonstrate how naturally all lower lying QED-TDDFT reformulations are just approximations to the full relativistic QED-TDDFT presented in the previous section.

3.3.1 Equations of motion in the non-relativistic limit

In this section we derive the exact non-relativistic limit of the equations of motion for the basic functional variables of QED-TDDFT. We start with the Heisenberg equation of motion for the Dirac field operator, which is given by

$$\begin{aligned}
&\mathrm{i}\hbar c\partial_0\hat{\psi}(x) \\
&= \left[\alpha^k\left(-\mathrm{i}\hbar c\partial_k + e\hat{A}^{\mathrm{tot}}_k(x)\right) + \gamma^0 mc^2 + eA^{\mathrm{tot}}_0(x)\right]\hat{\psi}(x) \\
&\quad + e^2\int \mathrm{d}^3r' \frac{:\hat{\psi}^\dagger(x')\hat{\psi}(x'):}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}\hat{\psi}(x),
\end{aligned} \tag{3.47}$$

where we have used the compact notation

$$\begin{aligned}
\hat{A}^k_{\mathrm{tot}}(x) &= \hat{A}^k(x) + a^k_{\mathrm{ext}}(x), \\
A^0_{\mathrm{tot}}(x) &= a^0_{\mathrm{ext}}(x) + \frac{1}{c}\int \mathrm{d}^3r' \frac{j^0_{\mathrm{ext}}(x')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|},
\end{aligned}$$

and $\alpha^k = \gamma^0\gamma^k$. In Eq. (3.47) the electronic component $\hat{\phi}$ of the Dirac spinor is mixed with the positronic component $\hat{\chi}$. Of course, at small energies only the electronic part of the Dirac field is relevant, and thus we would like to find an equation based solely on $\hat{\phi}$. Hence, we naturally aim at decoupling $\hat{\phi}$ from $\hat{\chi}$. A possible way is finding a unitary transformation of the Dirac Hamiltonian that does this, at least perturbatively. Since in non-relativistic processes the rest mass energy of the electrons is the dominant term, (compared to their kinetic energy or the photon energy), a possible expansion parameter for such a perturbative transformation may be $1/(mc^2)$. mc^2 also represents the spectral gap between the electronic and positronic degrees of freedom, which effectively decouples the dynamics of particles and anti-particles at small enough energies. The required unitary transformation is known as the Foldy-Wouthuysen transformation [52], and is routinely used to generate the non-relativistic limit of the Dirac equation to any desired order. Here, we employ an equivalent but simpler procedure. We first rewrite Eq. (3.47) as a function of $\hat{\phi}$ and $\hat{\chi}$, i.e.,

$$\left(\hat{D}(x) - mc^2\right)\hat{\phi}(x) = \vec{\sigma}\cdot\left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}_{\mathrm{tot}}(x)\right)\hat{\chi}(x), \tag{3.48}$$

$$\left(\hat{D}(x) + mc^2\right)\hat{\chi}(x) = \vec{\sigma}\cdot\left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}_{\mathrm{tot}}(x)\right)\hat{\phi}(x), \tag{3.49}$$

where we have defined the operator

$$\hat{D}(x) = \left(\mathrm{i}\hbar c\partial_0 - eA_0^{\mathrm{tot}}(x) - e^2\int \mathrm{d}^3x' \frac{:\hat{\phi}^\dagger(x')\hat{\phi}(x') + \hat{\chi}^\dagger(x')\hat{\chi}(x'):}{4\pi\epsilon_0|\vec{x}-\vec{x}'|}\right). \tag{3.50}$$

As already stated, for non-relativistic energies the main contribution to the energy of the system stems from mc^2. We can then substitute for the time derivative in Eq. (3.50) $\mathrm{i}\hbar c\partial_0 \approx mc^2$. Furthermore, since c is large, terms of order c^0 and lower can be ignored. Accordingly, we find for the operator in

Eq. (3.49) $\left(\hat{D}(x) + mc^2\right) \approx 2mc^2$, which implies

$$\hat{\chi}(x) \approx \frac{\vec{\sigma}}{2mc^2} \cdot \left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}_{\mathrm{tot}}(x)\right) \hat{\phi}(x). \tag{3.51}$$

The above equation indicates that $\hat{\chi}$ is of order v/c times $\hat{\phi}$, thus actually being the smaller component of the Dirac field. Using this expression to eliminate $\hat{\chi}$ from Eq. (3.48), we obtain the equation of motion for the Pauli spinor operator $\hat{\phi}$, which describes the dynamics of non-relativistic electrons in a quantized electromagnetic field. This equation is generated by the Pauli-Fierz Hamiltonian

$$\begin{aligned}\hat{H}(t) = \hat{H}_{\mathrm{M}} + \hat{H}_{\mathrm{EM}} + \hat{H}_{\mathrm{C}} - \frac{1}{c}\int \mathrm{d}^3x\ \hat{\vec{J}}(x) \cdot \hat{\vec{A}}(\vec{x}) \\ + \frac{1}{c}\int \mathrm{d}^3x \hat{J}_0(\vec{x}) \left(A^0_{\mathrm{tot}}(x) - \frac{e}{2mc^2}\hat{\vec{A}}^2_{\mathrm{tot}}(\vec{x})\right) \\ - \frac{1}{c}\int \mathrm{d}^3r \left(\hat{\vec{J}}(x) \cdot \vec{a}_{\mathrm{ext}}(x) + \hat{\vec{A}}(\vec{x}) \cdot \vec{j}_{\mathrm{ext}}(x)\right),\end{aligned} \tag{3.52}$$

where $\hat{H}_{\mathrm{M}}$ is the non-relativistic kinetic energy of the electrons,

$$\hat{H}_{\mathrm{M}} = \int \mathrm{d}^3x \hat{\phi}^\dagger(\vec{x}) \left(-\frac{1}{2m}\vec{\nabla}^2\right) \hat{\phi}(\vec{x}),$$

$\hat{H}_{\mathrm{EM}}$ corresponds to the energy of the electromagnetic field (expressed as before, but with a UV regulator), $\hat{H}_{\mathrm{C}}$ represents the electron-electron Coulomb interaction

$$\hat{H}_{\mathrm{C}} = \frac{e^2}{2}\int \mathrm{d}^3x' \frac{\hat{\phi}^\dagger(\vec{x})\hat{\phi}^\dagger(\vec{x}')\hat{\phi}(\vec{x}')\hat{\phi}(\vec{x})}{4\pi\epsilon_0|\vec{x} - \vec{x}'|},$$

and $\hat{J}^k$ denotes the non-relativistic current operator

$$\begin{aligned}\hat{J}^k(x) &= 2ec\Re\left\{\hat{\phi}^\dagger(\vec{x})\frac{\vec{\sigma}}{2mc^2} \cdot \left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}(x)\right) \hat{\phi}(\vec{x})\right\} \\ &= \hat{J}^k_{\mathrm{p}}(\vec{x}) - \epsilon^{klj}\partial_l\hat{M}_j(\vec{x}) - \frac{e}{mc^2}\hat{J}_0(\vec{x})\hat{A}^k_{\mathrm{tot}}(x).\end{aligned} \tag{3.53}$$

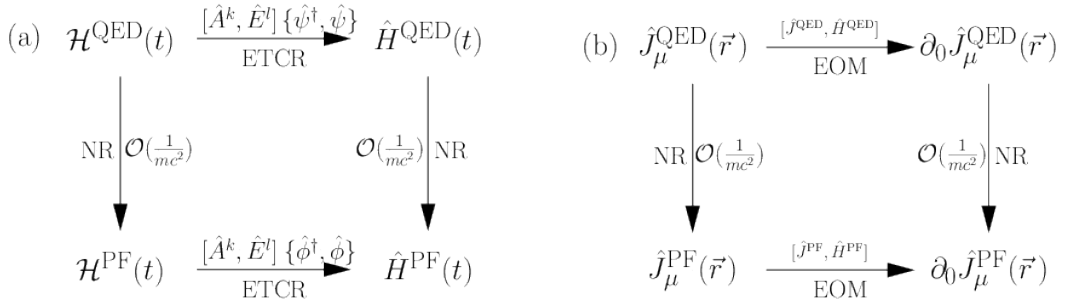

Figure 3.1: The non-relativistic (NR) limits do not depend on the order of the operations. (a) First taking the NR limit of the classical QED Hamiltonian, and then quantizing imposing the equal-time (anti)commutation relations (ETCR), leads to the same (Pauli-Fierz) Hamiltonian as the opposite ordering. (b) First taking the NR limit of the Dirac current, and then calculating the equation of motion (EOM), leads to the same result as taking directly the limit of the relativistic EOM.

This is defined in terms of the paramagnetic current

$$\hat{J}^k_{\mathrm{p}}(\vec{r}) = \frac{e\hbar}{2m\mathrm{i}}\left[\left(\partial^k\hat{\phi}^\dagger(\vec{r})\right)\hat{\phi}(\vec{r}) - \hat{\phi}^\dagger(\vec{r})\partial^k\hat{\phi}(\vec{r})\right],$$

the magnetization density

$$\hat{M}^k(\vec{r}) = \frac{e\hbar}{2m}\hat{\phi}^\dagger(\vec{r})\sigma^k\hat{\phi}(\vec{r}),$$

and the charge density

$$\hat{J}_0(\vec{r}) = ec\hat{\phi}^\dagger(\vec{r})\hat{\phi}(\vec{r}).$$

We note that, due to the non-relativistic limit, the current given by Eq. (3.53) becomes explicitly time-dependent [51]. By construction this current obeys the continuity equation $\partial_0\hat{J}_0(x) = -\vec{\nabla}\cdot\hat{\vec{J}}(x)$. Further, we point out that the result of the above formal derivation can be equivalently obtained by first taking the non-relativistic limit of the classical Hamiltonian $\mathcal{H}^{\mathrm{QED}}(t)$, (constructed from the classical Lagrangian density of Eq. (A.1)), and then canonically quantizing the Pauli field, as shown in Fig. 3.1 (a).

The non-relativistic QED Hamiltonian commutes with the particle-number

operator $\hat{N} = \int \mathrm{d}^3 r \hat{\phi}^\dagger(\vec{r})\hat{\phi}(\vec{r})$, as can be seen directly from the continuity equation. Accordingly, one does not need to employ a field-theoretical description for the electrons, and all matter operators can be expressed in first-quantized notation, while still being a many-particle problem. Nevertheless, infinities arise due to the interaction of the non-relativistic particles with the quantized Maxwell field [23, 25]. The electric charge is not renormalized, since vacuum polarization corrections to the photon propagator involve virtual electron-positron states, that are excluded from the non-relativistic theory (there is no vacuum polarization). However, the divergence in the electron self-energy needs to be treated [23]. To first order in the coupling, the ground-state energy (for $\vec{a}_{\mathrm{ext}} = \vec{j}_{\mathrm{ext}} = 0$) diverges as

$$E_0 \sim \frac{2e}{\pi} \left(\Lambda - \ln(1+\Lambda)\right),$$

where Λ is the UV cutoff for the photon modes (this is the characteristic logarithmic dependence on Λ in Bethe's formula for the Lamb shift [84]). By subtracting the infinite self-energy of the ground-state, which amounts to introducing a renormalized mass, the Pauli-Fierz Hamiltonian can be renormalized perturbatively. In the following we assume that it can be renormalized to each order in the fine structure constant, and interpret Eq. (3.52) as the bare Hamiltonian expressed in terms of the renormalized mass.

The equation of motion for the current $\hat{J}_k$ can be either found by direct calculation with the Pauli-Fierz Hamiltonian, or by taking the non-relativistic limit of Eq. (3.12) (see appendix (B)). We have explicitly checked both ways, as schematically indicated in Fig. 3.1 (b). After some calculations we find

$$\mathrm{i}\partial_0 \hat{J}_k(x) = \hat{q}^k_p(x) + \hat{q}^k_M(x) + \hat{q}^k_0(x), \tag{3.54}$$

where (omitting spatial and temporal dependences)

$$\begin{aligned}\hat{q}_p^k =& -\mathrm{i}\left\{\partial^l \hat{T}_{kl} - \hat{W}_k - \frac{e}{mc^2}\partial_l \hat{A}^l_{\mathrm{tot}} \hat{J}^{\mathrm{p}}_k - \frac{e}{mc^2}\left(\partial_k \hat{A}^l_{\mathrm{tot}}\right)\hat{J}^{\mathrm{p}}_k + \frac{e}{mc^2}\left(\partial_k \partial_l \hat{A}^{\mathrm{tot}}_m\right)\epsilon^{lmn}\hat{M}_n \right.\\ & \left. -\frac{e}{mc^2}\left[\partial_k\left(\frac{1}{2mc^2}\hat{A}^2_{\mathrm{tot}} + A^{\mathrm{tot}}_0\right)\right]\hat{J}_0\right\},\end{aligned}$$

$$\begin{aligned}\hat{q}_M^k =& -\epsilon_{klj}\partial^l\left\{-\frac{e\hbar^3}{4m^2}\hat{\phi}^\dagger\left(\overleftarrow{\partial}^n\overleftarrow{\partial}_n\sigma^j - \sigma^j\partial^n\partial_n\right)\hat{\phi} + \frac{ie}{mc^2}\partial_n\hat{A}^n_{\mathrm{tot}}\hat{M}^j \right.\\ & \left. -\frac{ie}{2mc^2}\left[\left(\partial^j\hat{A}^{\mathrm{tot}}_n\right) - \left(\partial_n j\hat{A}^j_{\mathrm{tot}}\right)\right]\hat{M}^n\right\},\end{aligned}$$

$$\hat{q}_0^k = -\frac{1}{mc^2}\left\{\left(\mathrm{i}\partial_0\hat{A}^{\mathrm{tot}}_k\right)\hat{J}_0 + \hat{A}^{\mathrm{tot}}_k\left(\frac{\mathrm{i}e}{mc^2}\partial_l\hat{A}^l_{\mathrm{tot}}\hat{J}_0 - \mathrm{i}\partial^l\hat{J}^{\mathrm{p}}_l\right)\right\}.$$

Here,

$$\hat{T}_{kl} = \frac{e\hbar^2}{2m^2c}\left[\left(\partial_k\hat{\phi}^\dagger\right)\partial_l\hat{\phi} + \left(\partial_l\hat{\phi}^\dagger\right)\partial_k\hat{\phi} - \frac{1}{2}\partial_k\partial_l\hat{\phi}^\dagger\hat{\phi}\right]$$

is the usual momentum-stress tensor and

$$\hat{W}_k(\vec{r}) = \frac{e^3}{mc}\int \mathrm{d}^3r'\,\hat{\phi}^\dagger(\vec{r})\left(\partial_k\frac{\hat{\phi}^\dagger(\vec{r}')\hat{\phi}(\vec{r}')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}\right)\hat{\phi}(\vec{r})$$

is the interaction-stress force (i.e., the divergence of the interaction-stress tensor) [51, 57, 58]. Starting with an uncoupled problem, we would find a similar equation with the replacements $\hat{\vec{A}}_{\mathrm{tot}} \to \vec{a}_{\mathrm{ext}}$ and $\hat{W}_k \to 0$. Further, the equation for the electromagnetic field does not change, except for the fact that now one has to employ the non-relativistic current (see appendix B).

In the last step, we take the non-relativistic limit of the equation of motion for the polarization, i.e., Eq. (3.13). We find to order $1/mc^2$

$$\begin{aligned} &\mathrm{i}\partial_0 \hat{P}^k \\ &\approx \frac{2emc}{\hbar}\hat{J}^k - \frac{2emc}{\hbar}\left(\hat{J}^k_{\mathrm{p}} - \epsilon^{klj}\partial_l \hat{M}_j - \frac{e}{mc^2}\hat{J}_0\hat{A}^k_{\mathrm{tot}}\right) \\ &= 0, \end{aligned} \tag{3.55}$$

which indicates that at this level of approximation the polarization does not change in time.

3.3.2 QED-TDDFT for the Pauli-Fierz Hamiltonian

In this section we discuss the basics of non-relativistic QED-TDDFT for the Pauli-Fierz Hamiltonian. We show how the non-relativistic limit of the equation of motion for the polarization P_k (in turn, of the Gordon decomposition), makes the electronic current J_k a unique functional of $(a^k_{\mathrm{ext}}, j^k_{\mathrm{ext}})$, and thus this becomes the basic variable for the matter part in this limit. Further, we demonstrate how the KS construction for the Pauli-Fierz Hamiltonian can be derived as the non-relativistic limit of the above KS construction for the QED Hamiltonian.

We start by noting that since the non-relativistic polarization is a constant of motion, the non-relativistic limit of Eq. (3.36) is zero, irrespective of the difference between $\vec{a}_{\mathrm{ext}}$ and $\vec{\tilde{a}}_{\mathrm{ext}}$ (as in Sec. 3.2.2, we work in the temporal gauge $a^0_{\mathrm{ext}} = 0$ for the external potential). However, by using Eq. (3.55), this limit can be expressed in terms of the non-relativistic current as

$$\vec{J}^{(\alpha)}(\vec{r}) - \vec{\tilde{J}}^{(\alpha)}(\vec{r}) = -\frac{J^{(0)}_0(\vec{r})}{mc^2}\left(\vec{a}^{(\alpha)}_{\mathrm{ext}}(\vec{r}) - \vec{\tilde{a}}^{(\alpha)}_{\mathrm{ext}}(\vec{r})\right) \neq 0, \tag{3.56}$$

which is non-zero, provided that the density obeys $J_0^{(0)} \neq 0$. Since the form of Eq. (3.37) does not change, we have proved the one-to-one mapping

$$(a^k_{\mathrm{ext}}, j^k_{\mathrm{ext}}) \overset{1:1}{\leftrightarrow} (J_k, A_k). \tag{3.57}$$

Accordingly, all wave functions of the non-relativistic QED system can be labelled by the internal pair (J_k, A_k). We observe in this regard that J_k has no longer positronic degrees of freedom. Hence, the above conjugate variables can be actually identified by applying the Legendre-transformation arguments of Sec. 3.2.1 to the Pauli-Fierz Lagrangian. Indeed, these arguments hold true for all further non-relativistic approximations.

Now in principle we can, instead of solving the Schrödinger equation for the many-body (electron-photon) wave function, solve the coupled equations for the functional variables (J_k, A_k)

$$\begin{aligned} \mathrm{i}\partial_0 \vec{J}(x) &= \vec{q}_{\mathrm{p}}([J_k, A_k, a^k_{\mathrm{ext}}]; x) + \vec{q}_{\mathrm{M}}([J_k, A_k, a^k_{\mathrm{ext}}]; x) \\ &\quad + \vec{q}_0([J_k, A_k, a^k_{\mathrm{ext}}]; x), \end{aligned} \tag{3.58}$$

$$\begin{aligned} \Box \vec{A}(x) - \vec{\nabla}\left(\frac{1}{c}\int \mathrm{d}^3 r' \frac{\vec{\nabla}' \cdot \vec{j}_{\mathrm{ext}}(x') + \vec{\nabla}' \cdot \vec{J}(x')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}\right) \\ = \mu_0 c \left(\vec{j}_{\mathrm{ext}}(x) + \vec{J}(x)\right), \end{aligned} \tag{3.59}$$

for a given initial state $|\Psi_0\rangle$ and external fields $(a^k_{\mathrm{ext}}, j^k_{\mathrm{ext}})$. The explicit functional dependence on the external potential in the equation of motion for the current is a consequence of the non-relativistic limit. The main advantage of this limit is that in the Maxwell equation there are no longer functionals that need to be approximated.

In the next step we take the non-relativistic limit of the KS scheme of Eqs. (3.43) and (3.44), which leads to

$$
\begin{aligned}
&J_0([\Phi_0, J_n, A_n]; x) a^k_{\mathrm{KS}}(x) \\
&= J_0([\Psi_0, J_n, A_n]; x) a^k_{\mathrm{ext}}(x) + \langle \hat{A}^k \hat{J}_0 \rangle([\Psi_0, J_n, A_n]; x) \\
&+ \frac{mc}{e} \left(J^k_{\mathrm{p}}([\Phi_0, J_n, A_n]; x) - J^k_{\mathrm{p}}([\Psi_0, J_n, A_n]; x) \right) \\
&+ \frac{mc}{e} \epsilon^{klj} \partial_l \left(M_j([\Psi_0, J_n, A_n]; x) - M_j([\Phi_0, J_n, A_n]; x) \right) \\
&j^k_{\mathrm{KS}}(x) = j^k_{\mathrm{ext}}(x) + J^k(x).
\end{aligned}
$$

Further, by imposing that the initial interacting and KS states fulfill

$$
\langle \Psi_0 | \hat{J}_0(\vec{r}) | \Psi_0 \rangle = \langle \Phi_0 | \hat{J}_0(\vec{r}) | \Phi_0 \rangle,
$$

(due to the continuity equations the physical and KS densities coincide also at later times), we can define the Hxc potential as

$$
\vec{a}_{\mathrm{KS}}[\Psi_0, \Phi_0, J_k, A_k, a^k_{\mathrm{ext}}] = \vec{a}_{\mathrm{ext}} + \vec{a}_{\mathrm{Hxc}}[\Psi_0, \Phi_0, J_k, A_k],
$$

where

$$
\begin{aligned}
a^k_{\mathrm{Hxc}}(x) = \frac{1}{J_0(x)} \Big[&\langle \hat{A}^k \hat{J}_0 \rangle([\Psi_0, J_n, A_n]; x) \\
&+ \frac{mc}{e} \left(J^k_{\mathrm{p}}([\Phi_0, J_n, A_n]; x) - J^k_{\mathrm{p}}([\Psi_0, J_n, A_n]; x) \right) \\
&+ \frac{mc}{e} \epsilon^{klj} \partial_l \left(M_j([\Psi_0, J_n, A_n]; x) - M_j([\Phi_0, J_n, A_n]; x) \right) \Big].
\end{aligned}
$$

Thus, given an initial state of the form $|\Phi_0\rangle = |\mathrm{M}_0\rangle \otimes |\mathrm{EM}_0\rangle$, which is characterized by the same current, potential and electric field (i.e., first time-derivative of the potential) as $|\Psi_0\rangle$, the problem reduces to solving the KS

equations

$$\mathrm{i}\hbar c\partial_0 \left|\mathrm{M}(t)\right\rangle = \Bigg[\hat{H}_{\mathrm{M}} - \frac{1}{c}\int \mathrm{d}^3 r \hat{\vec{J}}(x)\cdot\vec{a}_{\mathrm{KS}}(x) - \frac{e}{2mc^3}\int \mathrm{d}^3 r \hat{J}_0(\vec{r})\vec{a}^2_{\mathrm{KS}}(x)\Bigg]\left|\mathrm{M}(t)\right\rangle , \tag{3.60}$$

$$\Box A^k(x) + \partial^k\left(\frac{1}{c}\int \mathrm{d}^3 r' \frac{\vec{\nabla}'\cdot\vec{j}_{\mathrm{ext}}(x') + \vec{\nabla}'\cdot\vec{J}(x')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}\right) = \mu_0 c\left(j^k_{\mathrm{ext}}(x) + J^k(x)\right). \tag{3.61}$$

If we further assume that the initial state of the matter system $|\mathrm{M}_0\rangle$ is given in the form of a Slater determinant of single-particle orbitals $\varphi(\vec{r})$, we only need to solve single-orbital KS equations. The simplest approximate Hxc potential corresponds to the non-relativistic limit of the mean field approximation of Eq. (3.45), i.e.

$$\vec{a}_{\mathrm{Hxc}}(x) = \vec{A}(x).$$

Note that, again, without a further gauge transformation, also a scalar potential enters the KS Hamiltonian due to A_0.

We point out that one could alternatively use Eq. (3.54) to show the one-to-one correspondence between the external fields $(a^k_{\mathrm{ext}}, j^k_{\mathrm{ext}})$ and the non-relativistic internal variables (J_k, A_k) [61]. However, besides being more involved, also the connection to relativistic QED-TDDFT becomes less clear. Nevertheless, for constructing approximations to the KS potential, Eq. (3.54) seems better suited, since it is a more explicit equation.

3.3.3 QED-TDDFT for approximate non-relativistic theories

In this section we show how, by introducing further approximations for the matter part or the photon field, we find a family of non-relativistic QED-TDDFTs, which in the lowest-order approximation reduces to the functional

description of the Rabi model discussed in Sec. 3.4.

As already pointed out, in the non-relativistic case the initial guess for the conjugate variables can be based on a Legendre transformation in the Lagrangian of the problem. Thus, we can now derive all sorts of approximate QED-TDDFTs by considering different conserved currents and restrictions to the photonic degrees of freedom. This holds since, e.g., approximating the conserved current J_k implies approximating the Hamiltonian in Eq. (3.52) accordingly. Thus by assuming, e.g., a negligible magnetic density $M_l(x) \approx 0$, so that

$$\hat{J}_k(x) = \hat{J}_k^{\mathrm{p}}(\vec{r}) - \frac{1}{mc^2}\hat{J}_0(\vec{r})\hat{A}_k^{\mathrm{tot}}(x),$$

the corresponding Hamiltonian, as well as the basic Eqs. (3.54) and (3.55), change. Specifically, the terms $\hat{M}_l$ and $\hat{q}_l^{\mathrm{M}}$ vanish. Since Eq. (3.56) is still valid, the one-to-one correspondence holds

$$(a_{\mathrm{ext}}^k, j_{\mathrm{ext}}^k) \overset{1:1}{\leftrightarrow} (J_k, A_k), \tag{3.62}$$

and we can consider the coupled Eqs. (3.58) and (3.59). The KS current becomes accordingly $j_{\mathrm{KS}}^k = j_{\mathrm{ext}}^k + J^k$, and the Hxc potential in this limit reduces to

$$\begin{aligned} J_0(x)a_{\mathrm{Hxc}}^k(x) = &\langle \hat{A}^k \hat{J}_0\rangle([\Psi_0, J_k, A_k]; x) \\ &+ \frac{mc}{e}\left(J_{\mathrm{p}}^k([\Phi_0, J_k, A_k]; x) - J_{\mathrm{p}}^k([\Psi_0, J_k, A_k]; x)\right). \end{aligned}$$

On the other hand, we can also restrict the allowed photonic modes. For instance, we can assume a perfect cubic cavity (zero-boundary conditions) of length L[7]. Then, given the allowed wave vectors $\vec{k}_{\vec{n}} = \vec{n}(\pi/L)$, and the

[7] Actually also other boundaries are possible, but then the expansion in the eigenfunctions of the Laplacian, in accordance with the Coulomb-gauge condition, becomes more involved.

corresponding dimensionless creation and annihilation operators, $\hat{a}^\dagger_{\vec{n},\lambda}$ and $\hat{a}_{\vec{n},\lambda}$, we find

$$\hat{A}_k(\vec{r}) = \sqrt{\frac{\hbar c^2}{\epsilon_0}} \sum_{\vec{n},\lambda} \frac{\epsilon_k(\vec{n},\lambda)}{\sqrt{2\omega_n}} \left[\hat{a}_{\vec{n},\lambda} + \hat{a}^\dagger_{\vec{n},\lambda}\right] \mathcal{S}(\vec{n}\cdot\vec{r}),$$

where the mode function $\mathcal{S}$ is given in Eq. (C.1). If we further restrict the modes by introducing a square-summable regularization function $f_{\mathrm{EM}}(\vec{n})$[8], e.g., $f_{\mathrm{EM}} = 1$ for $|\vec{n}| < mcL/(2\pi\hbar)$ (energies smaller than rest-mass energy) and 0 otherwise, the resulting regularized field

$$\hat{A}_k(\vec{r}) = \sqrt{\frac{\hbar c^2}{\epsilon_0}} \sum_{\vec{n},\lambda} f_{\mathrm{EM}}(\vec{n}) \frac{\epsilon_k(\vec{n},\lambda)}{\sqrt{2\omega_n}} \left[\hat{a}_{\vec{n},\lambda} + \hat{a}^\dagger_{\vec{n},\lambda}\right] \mathcal{S}(\vec{n}\cdot\vec{r}) \tag{3.63}$$

makes the coupled Pauli-Fierz Hamiltonian self-adjoint, without the need of any further renormalization procedure [25]. In the following, we assume such a restriction. This approximation is then directly reflected in the Hamiltonian and the derived equations of motion. While Eq. (3.55) does not change, and thus J_k is the basic matter-variable, the equation of motion for the potential A_k is affected by the restriction to specific modes. By multiplying Eq. (3.59) from the left by

$$\epsilon_k(\vec{n},\lambda)\mathcal{S}(\vec{n}\cdot\vec{r})$$

and integrating, we find the mode expansion

$$\begin{aligned}\sqrt{\frac{\hbar c^2}{\epsilon_0}} f_{\mathrm{EM}}(\vec{n}) \left(\partial_0^2 + \vec{k}_{\vec{n}}^2\right) q_{\vec{n},\lambda}(t) \\ = \mu_0 c \left(j^{\mathrm{ext}}_{\vec{n},\lambda}(t) + J_{\vec{n},\lambda}(t)\right),\end{aligned} \tag{3.64}$$

[8] In the case of continuous frequencies one accordingly uses a square-integrable function.

where we have used the definitions $\hat{q}_{\vec{n},\lambda} = (a_{\vec{n},\lambda} + \hat{a}^\dagger_{\vec{n},\lambda})/(\sqrt{2\omega_n})$ and

$$j^{\text{ext}}_{\vec{n},\lambda}(t) = \int \mathrm{d}^3 r \; \vec{\epsilon}(\vec{n},\lambda) \cdot \vec{j}_{\text{ext}}(x)\, \mathcal{S}(\vec{n}\cdot\vec{r}).$$

The Coulomb contribution vanishes since we employ a partial integration and the fact that $\vec{\epsilon}(\vec{n},\lambda)\cdot\vec{n} = 0$. Of course, one finds the same equations by a straightforward calculation of the Heisenberg equation of motion for the Maxwell-field (3.63) with the corresponding Pauli-Fierz Hamiltonian (3.52). Due to the restriction to specific modes, the field A_k is restricted in its spatial form, and therefore the photonic variable changes from A_k to the set of mode expectation values

$$A_k(x) \to \{A_{\vec{n},\lambda}(t)\}\,.$$

This change in the basic variable is also reflected in the conjugate external variable, which is given from Eq. (3.64) by

$$j^{\text{ext}}_{\vec{n},\lambda}(t) = \frac{f_{\text{EM}}(\vec{n})\epsilon_0}{\sqrt{\hbar}} \left(\partial_0^2 + \vec{k}^2_{\vec{n}}\right) q_{\vec{n},\lambda}(t) - J_{\vec{n},\lambda}(t).$$

Thus, we accordingly find

$$j^k_{\text{ext}}(x) \to \left\{j^{\text{ext}}_{\vec{n},\lambda}(t)\right\},$$

and the pairs of conjugate variables become

$$(a^k_{\text{ext}}, \{j^{\text{ext}}_{\vec{n},\lambda}\}) \overset{1:1}{\leftrightarrow} (J_k, \{A_{\vec{n},\lambda}\}).$$

Hence, we need to solve the mode Eq. (3.64) together with the associated equation of motion for the current. Correspondingly, also the KS scheme and the mean field approximation for $\vec{a}_{\text{Hxc}}$ change to their mode equivalents.

If we then also employ the dipole-approximation $e^{\pm \mathrm{i}\vec{k}_n \cdot \vec{r}} \approx 1$, i.e., we assume that the spatial extension of our matter system is small compared to the wavelengths of the allowed photonic modes[9], we have

$$\hat{A}_k = \sqrt{\frac{\hbar c^2}{L^3 \epsilon_0}} \sum_{\vec{n},\lambda} f_{\mathrm{EM}}(\vec{n}) \frac{\epsilon_k(\vec{n},\lambda)}{\sqrt{2\omega_n}} \left[\hat{a}_{\vec{n},\lambda} + \hat{a}^\dagger_{\vec{n},\lambda}\right]. \tag{3.65}$$

This only changes the definition of the effective current that couples to the modes, i.e.,

$$j^{\mathrm{ext}}_{\vec{n},\lambda}(t) = \int \frac{\mathrm{d}^3 r}{L^{3/2}}\, \vec{\epsilon}(\vec{n},\lambda) \cdot \vec{j}_{\mathrm{ext}}(x),$$

but leaves the structure of the QED-TDDFT reformulation otherwise unchanged. If we assume the magnetization density M_l to be negligible, we recover from first principles QED-TDCDFT for many-electron systems coupled to cavity photons presented in [55]. In this work, the situation of only scalar external potentials, i.e., $\vec{a}_{\mathrm{ext}} = 0$ and $a^0_{\mathrm{ext}} \neq 0$, is considered as a further case. In such situation, the gauge freedom is only up to a spatial constant, which is usually fixed by choosing $a^0_{\mathrm{ext}} \to 0$ for $|\vec{r}| \to \infty$. Since a^0_{ext} couples to the zero component of the current, i.e., the density $\hat{J}_0$, the conjugate pairs become

$$(a^0_{\mathrm{ext}}, \{j^{\mathrm{ext}}_{\vec{n},\lambda}\}) \overset{1:1}{\leftrightarrow} (J_0, \{A_{\vec{n},\lambda}\}).$$

To demonstrate this mapping, considering the first time derivative of $\hat{J}_0$ is obviously not enough. Since this amounts to the continuity equation, no direct connection between the two conjugate variables for the matter part of the quantum system is found. Therefore, one has to evaluate the second time derivative of $\hat{J}_0$ [55]. The derivation of the model Hamiltonian, which correspond to this simplified physical situation, is presented in the next section.

[9] This is, e.g., the case of atoms and molecules whose spatial dimensions are of the order of a few Bohr radii.

3.4 QED-TDDFT of the Rabi model

In the following, we present a detailed derivation of the length-gauge Hamiltonian employed in [55] for the formulation of the electron-photon TDDFT. For simplicity, we restrict our derivation to the case of one mode and one particle. The case of several modes and particles works analogously and leads to the Hamiltonian (13) of Ref. [55].

In terms of the photon coordinate q, the single-mode vector potential is given by Eq. (3.65) as

$$\hat{\vec{A}} = \mathcal{C} q \vec{\epsilon}, \tag{3.66}$$

where we have used the definition

$$\mathcal{C} = \left(\frac{\hbar c^2}{\epsilon_0 L^3} \right)^{1/2},$$

and assumed $f_{\mathrm{EM}} = 1$. The resulting Hamiltonian in first quantized notation reads as

$$\begin{aligned} \hat{H}(t) = \frac{1}{2m} \left(\mathrm{i}\hbar \vec{\nabla} + \frac{e}{c} \hat{\vec{A}} \right)^2 - \frac{\hbar}{2} \frac{\mathrm{d}^2}{\mathrm{d}q^2} + \frac{\hbar \omega^2}{2} q^2 \\ + e a^0_{\mathrm{ext}}(x) - \frac{1}{c} \vec{j}_{\mathrm{ext}}(t) \cdot \hat{\vec{A}}, \end{aligned} \tag{3.67}$$

since at this level of approximation $\vec{\nabla} \cdot \vec{j}_{\mathrm{ext}} = 0$, due to the expansion in Coulomb-gauged eigenmodes. In Eq. (3.67) we have introduced the notation

$$\vec{j}_{\mathrm{ext}}(t) = \int \frac{\mathrm{d}^3 r}{L^{3/2}} \vec{j}_{\mathrm{ext}}(x).$$

In the next step, we transform the Hamiltonian into its length gauge form [13] by the unitary transformation

$$\hat{U} = \exp\left[\frac{\mathrm{i}}{\hbar}\left(\frac{\mathcal{C}e}{c}\vec{\epsilon}\cdot\vec{r}q\right)\right].$$

If we then perform a canonical variable transformation, which exchanges the photon coordinate and momentum, $\mathrm{i}\mathrm{d}/\mathrm{d}q \to p$ and $q \to -\mathrm{i}\mathrm{d}/\mathrm{d}p$, leaving the commutation relations unchanged, we find

$$\begin{aligned}\hat{H}(t) = &-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{\hbar}{2}\frac{\mathrm{d}^2}{\mathrm{d}p^2} + \frac{\hbar\omega^2}{2}\left(p - \frac{\mathcal{C}e}{\hbar c}\frac{\vec{\epsilon}\cdot\vec{r}}{\omega}\right)^2 \\ &+ ea^0_{\mathrm{ext}}(x) + \frac{\mathrm{i}\mathcal{C}}{c\omega}\vec{\epsilon}\cdot\vec{j}_{\mathrm{ext}}(t)\frac{\mathrm{d}}{\mathrm{d}p}.\end{aligned} \tag{3.68}$$

Then, we perform yet another time-dependent gauge transformation

$$\hat{U}(t) = \exp\left[\frac{\mathrm{i}\mathcal{C}}{\hbar c\omega}\left(j_{\mathrm{ext}}(t)p - \frac{\mathcal{C}}{2c\omega}\int_0^t j^2_{\mathrm{ext}}(t')dt'\right)\right],$$

where $j_{\mathrm{ext}}(t) = \vec{\epsilon}\cdot\vec{j}_{\mathrm{ext}}(t)$ is the projection of the external current on the direction of the photon polarization. The above transformation is aimed at eliminating the linear in p-derivative term in Eq. (3.68). Using the general transformation rule $H \mapsto -\mathrm{i}\hbar\hat{U}^\dagger\partial_t\hat{U} + \hat{U}^\dagger\hat{H}\hat{U}$, we obtain

$$\begin{aligned}\hat{H}(t) = &-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{\hbar}{2}\frac{\mathrm{d}^2}{\mathrm{d}p^2} + \frac{\hbar\omega^2}{2}\left(p - \frac{\mathcal{C}e}{\hbar c}\frac{\vec{\epsilon}\cdot\vec{r}}{\omega}\right)^2 \\ &+ ea^0_{\mathrm{ext}}(x) - \frac{\mathcal{C}}{\omega c}p\,\partial_t j_{\mathrm{ext}}(t).\end{aligned} \tag{3.69}$$

Here, we see that the photonic variable p is shifted by the dipole moment $e\vec{r}$, which indicates that p is actually proportional to the electric displacement field D (this point will be discussed in detail in Sec. 4.2).

In the last step, we discretize the matter part of the problem and employ a two-site approximation, such that

$$
\begin{aligned}
&-\frac{\hbar^2}{2m}\vec{\nabla}^2 \rightarrow -T\hat{\sigma}_x, \\
&e\vec{\epsilon}\cdot\vec{r} \rightarrow e\vec{\epsilon}\cdot\vec{l}\hat{\sigma}_z \equiv \frac{c}{\omega}\hat{J}^0, \\
&ea^0_{\text{ext}}(x) \rightarrow ea^0_{\text{ext}}(t)\hat{\sigma}_z,
\end{aligned}
$$

where T is the kinetic (hopping) energy, $\vec{l}$ is the vector connecting the two sites, $\hat{J}^0$ is the dipole moment operator, and $a^0_{\text{ext}}(t)$ corresponds to the potential difference between the sites. To highlight the general structure of the matter-photon Hamiltonian, we also redefine the external current, the external potential, and the photon field as follows

$$
\begin{aligned}
&\partial_t j_{\text{ext}}(t) \rightarrow \omega c\, \tilde{j}^0_{\text{ext}}(t), \\
&ea^0_{\text{ext}}(t)\hat{\sigma}_z \rightarrow -\frac{1}{c}a^0_{\text{ext}}(t)\hat{J}^0, \\
&\frac{\omega}{c}\mathcal{C}p \rightarrow \hat{D} = \sqrt{\frac{\hbar\omega}{2\epsilon_0 L^3}}(\hat{a}^\dagger + \hat{a}).
\end{aligned}
$$

Implementing the above redefinitions in Eq. (3.69), and neglecting irrelevant constant terms, we arrive at the Hamiltonian

$$
\begin{aligned}
\hat{H}(t) = &-T\hat{\sigma}_x + \hbar\omega\hat{a}^\dagger\hat{a} - \frac{\lambda}{k}\hat{J}^0\hat{D} - \frac{1}{c}a^0_{\text{ext}}(t)\hat{J}^0 \\
&- \frac{1}{k}j^0_{\text{ext}}(t)\hat{D}.
\end{aligned} \tag{3.70}
$$

Here, $k = \omega/c$, and we have introduced an appropriate dimensionless strength λ of the electron-photon coupling. We note that the same Hamiltonian could be derived by assuming a gauge condition for the external vector potential such that $a^0_{\text{ext}} = 0$ and $\vec{a}_{\text{ext}} \neq 0$. In that case, Eq. (3.67) would include terms of the form $\vec{a}_{\text{ext}}\cdot\vec{\nabla}$, $\vec{a}^2_{\text{ext}}$ and mixed terms of internal and external vector potential. However, by going into the length gauge also for the external potential,

and performing the same steps as above, one would end up with the same two-site one-mode Hamiltonian of Eq. (3.70). For clarity of presentation, though, we have chosen to start from the scalar potential case.

The basic functional variables for the Hamiltonian of Eq. (3.70) are the dipole moment J^0 and the displacement field D. The equations of motion for these variables read as

$$(\mathrm{i}\partial_0)^2\,\hat{J}^0 = \frac{4T^2}{\hbar^2 c^2}\hat{J}^0 - \frac{\lambda}{k}\hat{n}\hat{D} - \hat{n}a^0_{\mathrm{ext}}(t), \tag{3.71}$$

$$(\mathrm{i}\partial_0)^2\,\hat{D} = k^2\hat{D} - \frac{\omega}{\epsilon_0 L^3}\left(\lambda\hat{J}^0 + j^0_{\mathrm{ext}}(t)\right), \tag{3.72}$$

where

$$\hat{n} = \frac{4T(e\omega l)^2}{\hbar^2 c^4}\hat{\sigma}_x, \tag{3.73}$$

and $\epsilon_0 = 1/(\mu_0 c^2)$. Here, Eq. (3.71) is the discretized version of $\partial_t^2 n$ of standard TDDFT [15, 28] and Eq. (3.72) is the inhomogeneous Maxwell equation for the displacement field of a single mode. Solving the coupled problem starting from $|\Psi_0\rangle$ and subject to the external pair $(a^0_{\mathrm{ext}}, j^0_{\mathrm{ext}})$ is formally equivalent to solve the uncoupled non-linear problem with initial state $|\Phi_0\rangle$ and the KS fields $(a^0_{\mathrm{KS}}, j^0_{\mathrm{KS}})$

$$\mathrm{i}\hbar c\partial_0\,|\mathrm{M}(t)\rangle = \left[-T\hat{\sigma}_x - \frac{1}{c}\hat{J}^0 a^0_{\mathrm{KS}}(t)\right]|\mathrm{M}(t)\rangle\,, \tag{3.74}$$

$$\left(\partial_0^2 + k^2\right)D(t) = \frac{\omega}{\epsilon_0 L^3}j^0_{\mathrm{KS}}(t). \tag{3.75}$$

Here, $(a^0_{\mathrm{KS}}, j^0_{\mathrm{KS}})$ are defined by the equations

$$\begin{aligned} n([\Phi_0, J^0, D]; t)a^0_{\mathrm{KS}}(t) =& \frac{\lambda}{k}\langle\hat{n}\hat{D}\rangle([\Psi_0, J^0, D]; t) \\ &+ n([\Psi_0, J^0, D]; t)a^0_{\mathrm{ext}}(t) \end{aligned} \tag{3.76}$$

$$j^0_{\mathrm{KS}}(t) = \lambda J^0(t) + j^0_{\mathrm{ext}}(t). \tag{3.77}$$

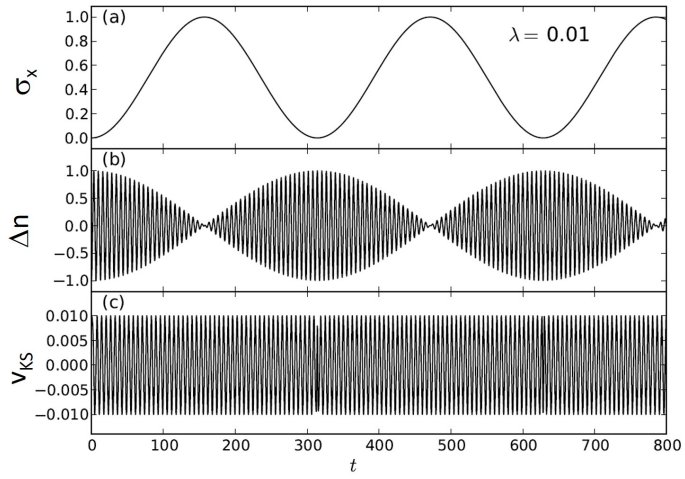

Figure 3.2: Exact results for the Rabi Hamiltonian of Eq. (3.78) in the weak coupling regime. (a) Inversion $\sigma_x(t)$, (b) density $\Delta n(t)$ and (c) exact KS potential $v_{\rm KS}(t)$ for the case of regular Rabi oscillations.

We point out that in Eq. (3.75) we do not need any approximate functional and merely need to solve a Maxwell equation. However, in practice it might be useful, especially when calculating non-trivial photonic expectation values, that one solves an actual uncoupled photon problem to have a first approximation to the photonic wave function. We also observe that in this discretized case the existence of the above KS construction can be proved by mapping the problem onto a special nonlinear Schrödinger equation [14, 15, 56, 73].

3.4.1 Numerical example

In this section we show numerical results for the simple electron-photon system introduced above. We use the density-functional framework presented in the previous sections, and explicitly construct the corresponding exact KS potentials. To illustrate our QED-TDDFT approach, we focus on two different examples. The first example treats a setup in resonance, where regular Rabi oscillations occur. We show results both in the weak and in the strong coupling regime. The second example includes the photon field initially in a

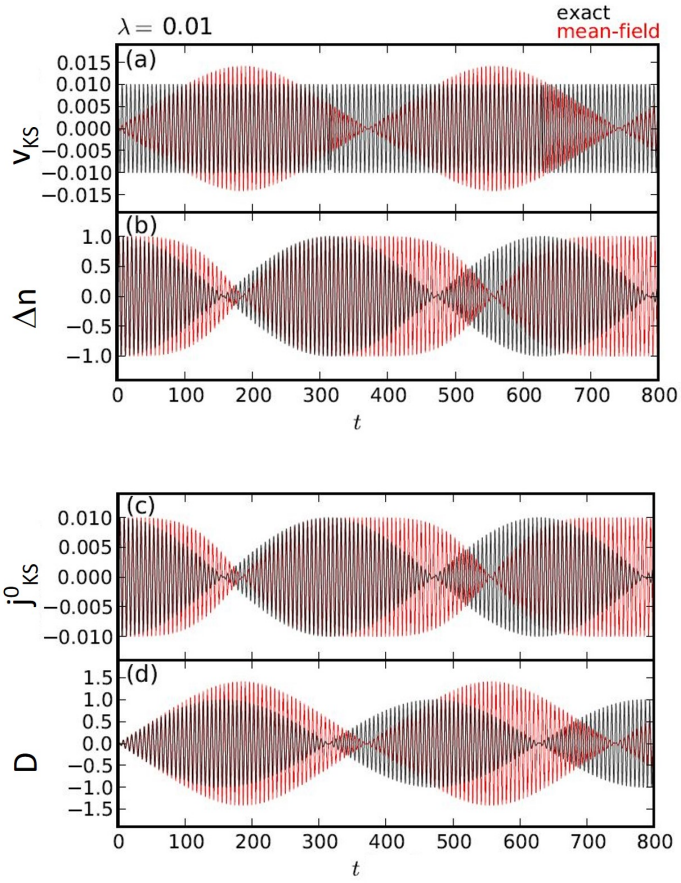

Figure 3.3: Exact potentials and densities (solid black line) compared to mean field potentials and densities (dashed red line) for the case of regular Rabi oscillations in the weak coupling regime. (a) KS potential $v_{\mathrm{KS}}(t)$ and (b) density $\Delta n(t)$. (c) KS potential $j^0_{\mathrm{KS}}(t)$ and (d) density $D(t)$.

coherent state. For this case, we study collapses and revivals of Rabi oscillations.

The Hamiltonian of Eq. (3.70) corresponds to the Rabi Hamiltonian [7, 19, 49, 50], which is heavily investigated in quantum optics. It has been studied in the context of Rabi oscillations, field fluctuations, oscillation collapses, revivals, coherences and entanglement (see Ref. [50] and references therein). To directly see this connection, we divide the Hamiltonian of Eq. (3.70) by $I = n\left(\frac{e\omega l}{c}\right)\left(\frac{\hbar c^2}{2\epsilon_0 L^3\omega}\right)^{\frac{1}{2}}$, where n is an arbitrary dimensionless scaling factor. Thus, we make the Hamiltonian and the corresponding Schrödinger equation dimensionless. The Hamiltonian of Eq. (3.70) can then be rewritten in a

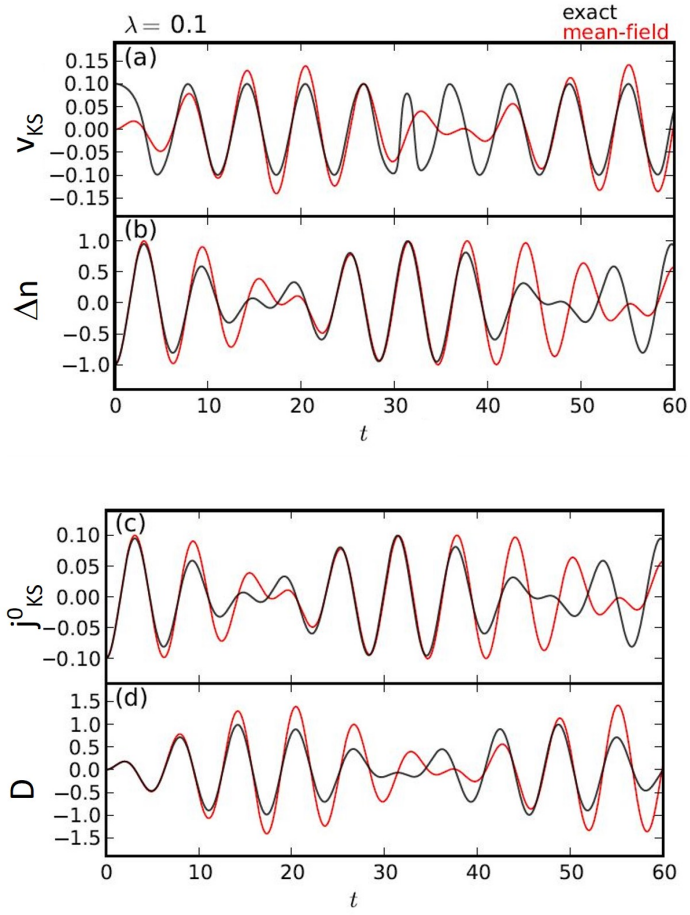

Figure 3.4: Exact potentials and densities (solid black line) compared to mean field potentials and densities (dashed red line) for the case of regular Rabi oscillations in the strong coupling regime. (a) KS potential $v_{\mathrm{KS}}(t)$ and (b) density $\Delta n(t)$. (c) KS potential $j^0_{\mathrm{KS}}(t)$ and (d) density $D(t)$.

similar form as usually found in the literature

$$\hat{H}(t) = -\frac{T}{I}\hat{\sigma}_x + \frac{\hbar\omega}{I}\hat{a}^\dagger\hat{a} - \lambda\left(\hat{a}+\hat{a}^\dagger\right)\hat{\sigma}_z \\ - j^0_{\mathrm{ext}}(t)\left(\hat{a}+\hat{a}^\dagger\right) - v_{\mathrm{ext}}(t)\hat{\sigma}_z. \tag{3.78}$$

Here, we have transformed to the dimensionless external potential $\frac{1}{n}\left(\frac{\hbar c^2}{2\epsilon_0 L^3\omega}\right)^{-\frac{1}{2}}$ $a^0_{\mathrm{ext}} \to v_{\mathrm{ext}}$ and the dimensionless external dipole moment $\frac{1}{n}\left(\frac{1}{e\omega l}\right) j^0_{\mathrm{ext}} \to j^0_{\mathrm{ext}}$. Further, we have also transformed to a dimensionless time variable $\frac{I}{\hbar}t \to t$. To perform numerical calculations, we take from the literature values for the free parameters, i.e., $T/I = 0.5$, $\hbar\omega/I = 1$, $\lambda = (0.01, 0.1)$, while setting to zero the external fields, i.e., $j^0_{\mathrm{ext}}(t) = v_{\mathrm{ext}}(t) = 0$. This set of parameters describes

a resonance situation, i.e., with no detuning between the transition energy of the atomic levels and the frequency of the field mode. As discussed above, the basic densities for the system are the dipole moment J^0 and the displacement field D. In this two-site example J^0 reduces to the on-site occupation difference $\Delta n = n_1 - n_2$ (in matrix notation σ_z).

If the rotating-wave approximation is applied to the Rabi Hamiltonian of Eq. (3.78), one recovers the Jaynes-Cummings Hamiltonian. This Hamiltonian is analytically solvable. The rotating-wave approximation is only valid in conditions of resonance and weak coupling regime ($\lambda \approx 0.01$), while it breaks down in the strong coupling regime ($\lambda \geq 0.1$). Only recently, analytic results without the rotating-wave approximation have been published [7]. Here, we emphasize that the QED-TDDFT approach presented in this chapter is exact and does not rely on the rotating-wave approximation, hence it also allows one to treat strong coupling situations.

In our first example we choose as initial state for both the interacting many-body system and the uncoupled KS problem

$$|\Psi_0\rangle = |\Phi_0\rangle = |1\rangle \otimes |0\rangle \,,$$

meaning that the electron initially populates site one and the field is in the vacuum state. Therefore, no photon is present in the field initially. In Fig. 3.2, we show the inversion $\sigma_x(t)$, the density $\Delta n(t)$ and the corresponding exact KS potential $v_{\mathrm{KS}}(t)$ for the weak coupling case. The atomic inversion $\sigma_x(t)$ shows regular Rabi oscillations. Rabi oscillations are also visible in $\Delta n(t)$, where we observe the typical neck-like features [17] at $t \approx 150$ and at later points in time.

The exact KS potential for this case is determined by following a fixed-point construction similar to [37]. As an input for the fixed-point construction, we use the exact many-body densities. In addition, we also compare to

an analytic formula for the KS potential [15, 29]. We note that such an explicit formula is only known in a few cases, while the fixed-point construction is generally valid. However, both methods yield in the present case the same results.

We emphasize that a propagation of the uncoupled KS system with the exact KS potential $v_{\mathrm{KS}}(t)$ obtained in Fig. 3.2 reproduces by construction the exact many-body density ($\Delta n(t)$ in the present case). However, if a KS propagation is used, the numerical expenses can be drastically reduced as the KS construction effectively decouples the quantum system.

In practical calculations the exact KS potentials are normally not available and one has to rely on approximations. In the present case, the simplest approximation for $v_{\mathrm{KS}}[\Psi_0, \Phi_0, \Delta n, D, v_{\mathrm{ext}}]$ in Eq. (3.76) is straightforward if we assume $n[\Phi_0, \Delta n, D] \approx n[\Psi_0, \Delta n, D]$ and $\langle \hat{n}\hat{D} \rangle \approx nD$. Then, from Eq. (3.76) we find the mean field approximation to the KS potential

$$v_{\mathrm{MF}}([D, v_{\mathrm{ext}}]; t) = \lambda D(t) + v_{\mathrm{ext}}(t). \tag{3.79}$$

The mean field approximation is actually identical to the Maxwell-Schrödinger approach, i.e., we treat the electromagnetic field as being essentially classical. Further, for $\lambda \to 0$ and $\lambda \to \infty$, the mean field approximation becomes asymptotically exact. In Fig. 3.3 and Fig. 3.4, we compare the exact densities and exact KS potentials to densities and potentials obtained from a self-consistent mean field propagation. Already in the weak coupling limit, Fig. 3.3, quite sizable differences between the exact and mean field results become visible. The exact KS potential deviates from the mean field potential already at $t = 0$. In the case of the densities, this leads to a frequency shift, where the mean field density oscillates slower than the exact density. In the strong coupling regime shown in Fig. 3.4, effects beyond the rotating-wave approximation are visible. In the exact KS potential, we see a non regular feature at

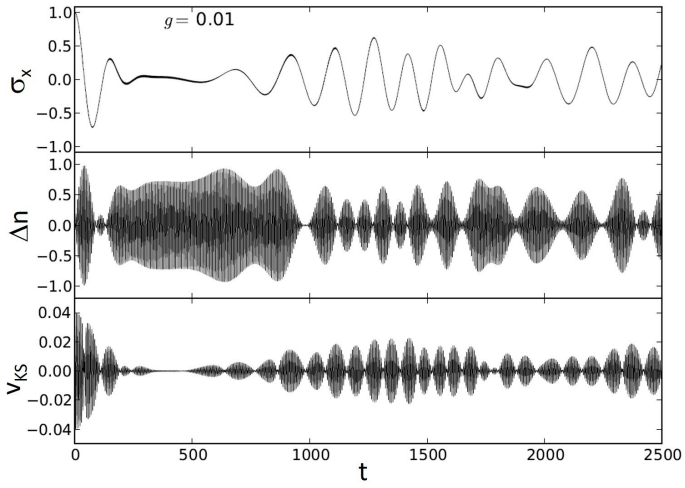

Figure 3.5: Exact results for the Rabi Hamiltonian in the weak coupling limit. (a) Inversion $\sigma_x(t)$, (b) density $\Delta n(t)$ and (c) exact KS potential $v_{\mathrm{KS}}(t)$ in the case of coherent states (see panel 3 in Fig. 4 Ref. [50]).

$t = 30$, which is also not covered by the mean field approximation. However, the mean field approximation reproduces at least some dynamical features of the propagation.

For the second example in this section, we start with the field initially in a coherent state. For a single field mode, coherent states [20, 21] can be written as follows

$$|a\rangle = \sum_{n=0}^{\infty} f_n(\alpha)\,|n\rangle\,, \quad \text{with} \quad f_n(\alpha) = \frac{\alpha^n}{\sqrt{n!}} \exp\left(-\frac{1}{2}|\alpha|^2\right).$$

In this example, we use as initial state for the many-body propagation and the KS propagation

$$|\Psi_0\rangle = |\Phi_0\rangle = |g\rangle \otimes |\alpha\rangle\,.$$

Here, the atomic state $|g\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ is the ground state of the electronic Hamiltonian. For the field state we choose $|\alpha|^2 = \langle \hat{a}^\dagger \hat{a}\rangle = 4$. This example is in the spirit of the calculation of panel 3 in Ref. [50]. Hence, as shown in

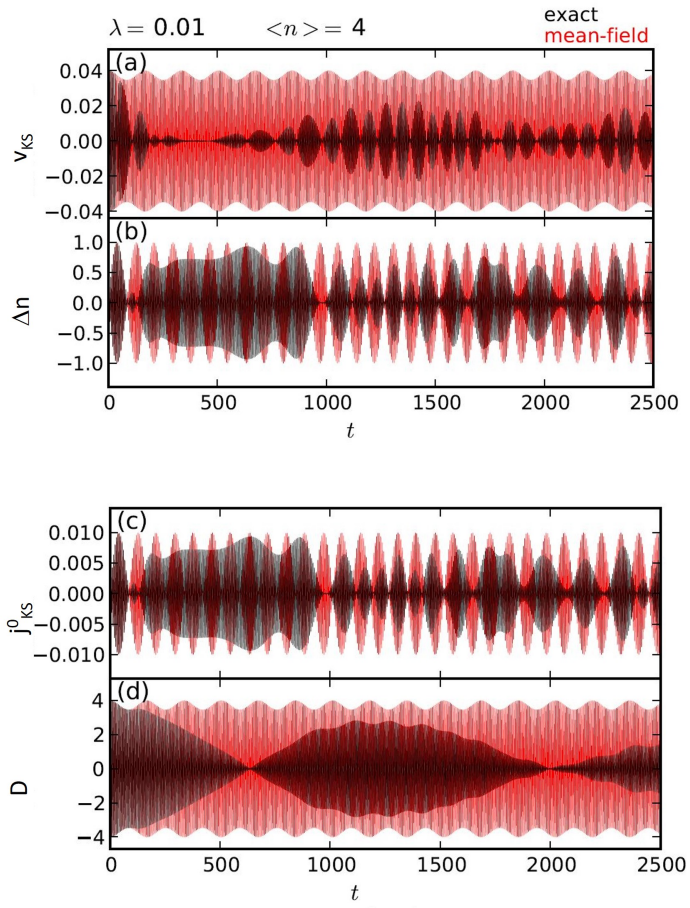

Figure 3.6: Exact densities and potentials (solid black line) compared to mean field densities and potentials (dashed red line) in the case of regular Rabi oscillations for coherent states. (a) KS potential $v_{\mathrm{KS}}(t)$ and (b) density $\Delta n(t)$. (c) KS potential $j^0_{\mathrm{KS}}(t)$ and (d) density $D(t)$.

Fig. 3.5, we obtain a similar time evolution for the inversion $\sigma_x(t)$. A Cummings collapse of Rabi oscillations occurs at $t = 250$ followed by a quiescence up to $t = 500$. After $t = 500$, we see a revival of Rabi oscillations. We also observe, as shown in [35], that the density $\Delta n(t)$ continues to change during the interval of quiescence after the inversion collapse. As before, we show in the lowest panel the corresponding exact KS potential obtained via fixed-point iterations.

In Fig. 3.6 we show a comparison of the exact KS potentials and densities to the mean field propagation. Here, we see that the mean field approximation performs rather poorly. For this case the simple ansatz in Eq. (3.79) is not sufficient, and more sophisticated approximations to the exact KS potential

are necessary to reach a better agreement [30, 32].

In summary, we have shown in this section the exact KS potentials, which reproduce the dynamics of the exact many-body densities in the Rabi model. In particular, the coherent state example shows that there is a clear need for better approximations to the exact KS potential [55], that go beyond the mean field level and include xc contributions. One promising possibility along these lines is provided by the OEP method [33, 58, 71]. In the next chapter we develop such an approach and show how for the present system the corresponding results improve quite considerably over the mean field approximation.

Chapter 4

QED Optimized Effective Potential

4.1 Introduction

In chapter 3 we discussed the advantages of non-relativistic QED for the description of condensed-matter systems. One obtains the standard non-relativistic quantum mechanical theory for the electrons, but with additional terms, which correct for relativity and electron-photon interactions. We proposed a reformulation of non-relativistic QED in terms of functional variables, that (in principle) accounts exactly for both corrections. However, any application of this theory requires approximations to the xc functional. In this chapter, we construct such an approximation for the description of electron-photon interaction effects in an optical cavity, (the theory of reference is then QED-TDDFT for electronic systems coupled to cavity modes [76]). In chapter 5, we will discuss the inclusion of relativistic spin-spin effects into the functional of standard SDFT.

In Sec. 4.2 we introduce the Hamiltonian of a localized many-electron system arbitrarily coupled to a set of discrete photon modes (this Hamiltonian corresponds to the many-body generalization of the Rabi Hamiltonian discussed in Sec. 3.4). In Sec. 4.3 we construct the functional for the coupled electron-photon system by extending the OEP approach (see Sec. 2.2.1) to the photon-mediated electron-electron coupling. In Sec. 4.4 the new functional is tested from the weak to the strong coupling regime in the Rabi model,

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 for describing complex strongly coupled matter-photon systems.

4.2 Stating the problem

Let us consider a system with an arbitrary 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 $\hat{H}_0 = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}}$ the Hamiltonian of the electronic system with kinetic energy $\hat{T}$, Coulomb interaction $\hat{V}_{\text{ee}}$, and generally time-dependent external potential $\hat{V}_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i t)$, due to the nuclear attraction and any classical field applied to the electrons. From the derivation of Sec. 3.4 for the case of many electrons, one obtains, in the dipole approximation,[1] the following length-gauge Hamiltonian [**Cohen**, **Craig**, 76] of the total electron-photon system

$$\hat{H} = \hat{H}_0 + \frac{1}{2}\sum_\alpha \left[\hat{q}_\alpha^2 + \omega_\alpha^2\left(\hat{p}_\alpha - \frac{\boldsymbol{\lambda}_\alpha}{\omega_\alpha}\hat{\mathbf{R}}\right)^2\right]. \tag{4.1}$$

Here, the second term corresponds to the usual expression $\frac{1}{8\pi}\int(\hat{\mathbf{B}}^2 + \hat{\mathbf{E}}^2)d\mathbf{r}$ for the energy of the transverse radiation field. The magnetic field $\hat{\mathrm{B}}_\alpha = \sqrt{4\pi}\hat{q}_\alpha$ in the α mode is proportional to the photon canonical coordinate $\hat{q}_\alpha$, while the electric field $\hat{\mathrm{E}}_\alpha = \sqrt{4\pi}(\omega_\alpha\hat{p}_\alpha - \boldsymbol{\lambda}_\alpha\hat{\mathbf{R}})$ is related to the photon momentum $\hat{p}_\alpha$. This is expressed in terms of the displacement field $\hat{\mathrm{D}}_\alpha = \sqrt{4\pi}\omega_\alpha\hat{p}_\alpha$. In fact, since $\boldsymbol{\nabla}\times\mathbf{B} = \partial\mathbf{D}/\partial t$, the displacement field D is the proper dynamical variable conjugated to the magnetic field B. D then properly describes the dynamics of transverse electromagnetic waves (photons), and when quantizing

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

the electromagnetic field, photon creation and annihilation operators refer to the quanta of D. Here, we define $\hat{p}_\alpha = -(\hat{a}_\alpha + \hat{a}_\alpha^\dagger)/\sqrt{2\omega_\alpha}$. Finally, $\boldsymbol{\lambda_\alpha}$ describes the polarization direction and normalized amplitude of the D_α mode at the position of the electronic system with dipole moment operator $\hat{\mathbf{R}} = \sum_{i=1}^{\mathbf{N}} \mathbf{r}_i$. We see that the photon-induced interaction Hamiltonian of Eq. (4.1) consists of two terms: (i) the "cross term" $\sim \hat{p}_\alpha \hat{R}$

$$\hat{V}_{\text{el-ph}} = \sum_\alpha \sqrt{\frac{\omega_\alpha}{2}} (\hat{a}_\alpha + \hat{a}_\alpha^\dagger) \int d^3\mathbf{r}\, (\boldsymbol{\lambda}_\alpha \mathbf{r})\, \hat{n}(\mathbf{r}), \tag{4.2}$$

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

$$W_{\text{ee}}(1,2) = \sum_\alpha (\boldsymbol{\lambda}_\alpha \mathbf{r}_1)(\boldsymbol{\lambda}_\alpha \mathbf{r}_2) \mathcal{W}_\alpha(t_1, t_2), \tag{4.3}$$

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

where we have used the compact notation $1 = (\mathbf{r}_1 t_1)$. Here, the first term actually corresponds to the photon displacement D_α propagator $\mathrm{i}\mathcal{D}_\alpha(t_1, t_2) \equiv \langle \mathcal{T}\{p_\alpha(t_1) p_\alpha(t_2)\rangle$, derived from Eq. (4.2). This describes the response of the displacement field D generated by the polarization, as it follows from the wave equation for D. However, this propagator does not correspond to the complete physical interaction between the electrons. The important point is that D in electrostatics can assume a non-zero value. In this regards an illustrative example is that of a ferroelectric material, whose polarization varies perpendicularly to its direction. In this case no forces are exerted on the charges, but D equals the (finite) transverse polarization. On the contrary, the electric force acting on the electrons ($F = \mathrm{E}$), and the electric part of the

energy (E^2), are determined by the electric field E. From the operational point of view this is the real physical quantity. The second instantaneous term in W_{ee}, due to the polarization contribution in the Hamiltonian, accounts for this point. It removes the instantaneous part of the D_α propagator, (i.e., the static D_α response generated by the transverse polarization), and brings it to the physical interaction given by the E_α propagator. This propagator follows from the wave equation for the electric field, in which the source term is the second time derivative of the polarization. Then $W_{ee} \sim -\sum_\alpha \omega^2/(\omega^2 - \omega_\alpha^2)$, which is proportional to the frequency, correctly describes the physical interaction of accelerated electrons via transverse electromagnetic waves.

The wave function of the total system $\Psi(\{\mathbf{r}_j\}, \{p_\alpha\}, t)$ 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 momenta $P_\alpha(t) = \langle\Psi|\hat{p}_\alpha\,|\Psi\rangle$ [76]. The former can be calculated for a fictitious KS system of N non-interacting particles, whose orbitals $\{\phi_j\}$ satisfy the self-consistent equations $\mathrm{i}\partial_t\phi_j(\mathbf{r}t) = [-\nabla^2/2 + v_s(\mathbf{r}t)]\,\phi_j(\mathbf{r}t)$ with the potential $v_\mathrm{s} = v_\mathrm{ext} + v_\mathrm{Hxc}^\mathrm{el} + v_\mathrm{eff}^\alpha$. Here, we assume [76] the separate description of the Coulomb interaction V_ee and the photon-mediated interaction W_ee, by the standard TDDFT Hartree-xc term $v_\mathrm{Hxc}^\mathrm{el}[n]$ and the effective potential $v_\mathrm{eff}^\alpha[n, P_\alpha]$. The latter is defined as $v_\mathrm{eff}^\alpha = v_\mathrm{MF}^\alpha + v_\mathrm{xc}^\alpha$, where

$$v_\mathrm{MF}^\alpha(\mathbf{r}t) = \int d1\, W_\mathrm{ee}^R(\mathbf{r}t, \mathbf{r}_1t_1)\, n(\mathbf{r}_1t_1) \tag{4.4}$$

is the mean-field contribution due to M classical electromagnetic modes, whose expectation values P_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 $v_\mathrm{xc}^\mathrm{el}$ by standard TDDFT functionals (e.g. x-only OEP or KLI [80], ALDA, GGA), we generalize the OEP approach to construct approximations to the photonic contribution v_xc^α.

4.3 QED-TDOEP equation

We derive the TDOEP equation for the electron-photon system starting from the linearized Sham-Schlüter equation on the Keldysh contour [81]

$$\int d2 G_{\mathrm{s}}(1,2) v_{\mathrm{xc}}(2) G_{\mathrm{s}}(2,1) = \int d2 \int d3 G_{\mathrm{s}}(1,2) \Sigma(2,3) G_{\mathrm{s}}(3,1), \tag{4.5}$$

where the electron self-energy Σ contains the interaction W_{ee} of Eq. (4.3) and G_{s} is the Green's function of the time-dependent KS system. Eq. (4.5) allows one to perturbatively construct the local potential v_{xc} that mimics the effects of the self-energy Σ, in principle up to any desired order in the coupling strength λ_α. Analogously to the GW approximation [82, 83] for electronic structure methods, we approximate the electron self-energy by the exchange-like diagram

$$\Sigma(1,2) = \mathrm{i}\, G_{\mathrm{s}}(1,2) W_{\mathrm{ee}}(2,1), \tag{4.6}$$

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 photon displacement propagator $\mathcal{D}_\alpha$ in Eq. (4.3). This part describes the processes of emission and absorption of a photon. Neglecting the above dynamical contribution to v_{eff} therefore corresponds to the classical treatment of the electromagnetic field. Making use of the Langreth rules [51], we rewrite Eq. (4.5) more explicitly as

$$\begin{aligned} &\mathrm{i} \int_{-\infty}^{t} dt_1 G^R(t,t_1) v_{\mathrm{xc}}(t_1) G^<(t_1,t) + c.c. = \\ &\mathrm{i} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2\, G^R(t,t_1) [\Sigma^>(t_1,t_2) G^<(t_2,t) - \Sigma^<(t_1,t_2) G^>(t_2,t)] + c.c., \end{aligned} \tag{4.7}$$

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. (4.7) 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. (4.6) for the self-energy, Eq. (4.7) becomes

$$\mathrm{i}\sum_{i,j}\int_{-\infty}^{t} dt_1[\langle\phi_i(t_1)|v_{\mathrm{x}}(t_1)\,|\phi_j(t_1)\rangle\, f_i - S_{ij}(t_1)]\,\phi_j^*(t)\phi_i(t)$$
$$+\, c.c. = 0, \tag{4.8}$$

where we define

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

with $\mathcal{W}_{\alpha}^{\gtrless}(t_1,t_2) = \omega_{\alpha}^2\left(\frac{-\mathrm{i}}{2\omega_{\alpha}}\right)e^{\pm\mathrm{i}\omega_{\alpha}(t_2-t_1)} \pm \delta(t_1-t_2)$. Here, f_i is the fermion occupation number and $d_{ik}^{\alpha}(t) = \boldsymbol{\lambda}_{\alpha}\langle\phi_i(t)|\mathbf{r}\,|\phi_k(t)\rangle$ 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 $t < 0$. Hence, the orbitals $\{\phi_j\}$ are solutions of the time-dependent KS equations with the initial condition $\phi_j(\mathbf{r}t) = \phi_j(\mathbf{r})e^{-\mathrm{i}\varepsilon_j t}$ for $-\infty < t \leq 0$. In Eq. (4.8) the matrix elements of v_{x} are constructed from the matrix elements S_{ij} of the self-energy Σ. These include the combination of occupied-unoccupied electronic states (i,k) and the D$_{\alpha}$ propagator $\mathcal{W}_{\alpha}^{\gtrless}$, describing the physical processes of excitation (annihilation) of electron-hole pairs by photon absorption (emission). Alternatively, Eq. (4.8) can be derived via variational principle from the Keldysh action functional, with the exchange part given by

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

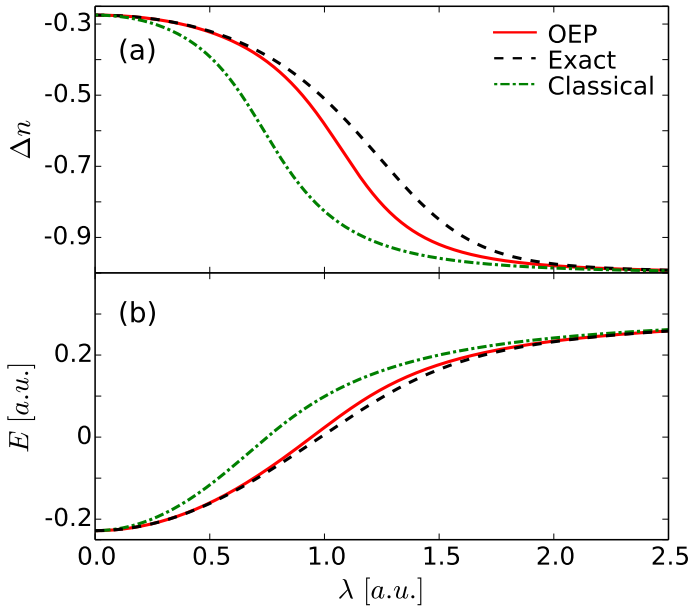

Figure 4.1: Comparison of the OEP (red), exact (black) and classical (green) (a) density Δn and (b) energy E versus the coupling parameter λ in a.u.. Other parameters: $\omega = 1$, $v_{\text{ext}} = 0.2$, $T = 0.7$.

where z denotes the contour variable. Furthermore, the time-dependent mean-field potential is evaluated from Eq. (4.4) as

$$v_{\text{MF}}(\mathbf{r}t) = -\sum_{\alpha} \omega_\alpha(\boldsymbol{\lambda}_\alpha \mathbf{r}) \int_0^t dt_1 \sin[\omega_\alpha(t-t_1)](\boldsymbol{\lambda}_\alpha \mathbf{R}(t_1))$$
$$-\sum_{\alpha} (\boldsymbol{\lambda}_\alpha \mathbf{r}) \left[(\boldsymbol{\lambda}_\alpha \mathbf{R}(0)) \cos(\omega_\alpha t) - (\boldsymbol{\lambda}_\alpha \mathbf{R}(t))\right], \tag{4.9}$$

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 special case of the electron-photon system in equilibrium at time $t = 0$ with $V_{\text{ext}} = V_{\text{ext}}(0)$, Eq. (4.8) reduces to the stationary OEP equation

$$\sum_{i,j} \left[\frac{\langle \phi_i | v_{\text{x}} | \phi_j \rangle}{\varepsilon_i - \varepsilon_j - \mathrm{i}\eta} f_i - S_{ij} \right] \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r}) + c.c. = 0, \tag{4.10}$$

where

$$S_{ij} = \sum_{k,\alpha} \frac{d^{\alpha}_{ik} d^{\alpha}_{kj} (\varepsilon_i - \varepsilon_k - i\eta)}{2(\varepsilon_i - \varepsilon_j - \mathrm{i}\eta)} \Big[\frac{f_i(1-f_k)}{\varepsilon_i - \varepsilon_k - \omega_\alpha - \mathrm{i}\eta} + \frac{(1-f_i)f_k}{\varepsilon_i - \varepsilon_k + \omega_\alpha - \mathrm{i}\eta} \Big]. \tag{4.11}$$

Here, we assume the limit $\eta \to 0$. Eq. (4.11) describes the virtual process of excitation of electron-hole pairs, supplemented with the virtual emission of a photon. Eq. (4.10) can be variationally derived employing the second-order correction to the ground-state energy

$$E_{\mathrm{x}} = -\frac{1}{2} \sum_{i,k,\alpha} |d^{\alpha}_{ik}|^2 \left\{ \omega_\alpha \frac{(1-f_i)f_k}{\varepsilon_i - \varepsilon_k + \omega_\alpha} - (1-f_i)f_k \right\}, \tag{4.12}$$

that is the Lamb shift due to the virtual emission of photons [84]. The second term in Eq. (4.12) comes from the counter-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 $\omega_\alpha \to \infty$.

4.4 Numerical example

As a proof of principles, we now apply these results to the (exactly solvable) tight binding model of 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 $v^{\mathrm{el}}_{\mathrm{xc}}$, thus allowing to assess the accuracy of our approximation to the electron-photon potential v_{xc}. As already discussed, the TDDFT density for the model corresponds to the on-site occupation difference $\Delta n = n_1 - n_2$.The projected Hamiltonian

$$\hat{H} = -T\hat{\sigma}_x + \left[\sqrt{\frac{\omega}{2}} \lambda (\hat{a} + \hat{a}^\dagger) + v_{\mathrm{ext}}(t) \right] \hat{\sigma}_z + \omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) + \frac{\lambda^2}{2} \tag{4.13}$$

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

We consider first the description of the system in equilibrium at time $t=0$ with $v_{\text{ext}} = v_{\text{ext}}(0)$. Eq. (4.10), projected onto the KS orbitals $\phi_g^\dagger = (\bar{v}\ \ \bar{u})$ and $\phi_e^\dagger = (\bar{u}\ \ -\bar{v})$, with related eigenvalues $\varepsilon_g = -W$ and $\varepsilon_e = W$, where $\bar{u}, \bar{v} = \sqrt{(1 \pm v_{\text{s}}/W)/2}$ and $W = \sqrt{v_{\text{s}}^2 + T^2}$, gives

$$v_{\text{x}} = -\lambda^2 \frac{v_{\text{s}}}{W}\left[\frac{\omega(\omega+3W)}{(\omega+2W)^2} - 1\right]. \tag{4.14}$$

Here, the second term corresponds to the classical contribution associated with the first interaction term in Eq. (4.3). The total energy functional takes the form

$$E[v_{\text{s}}] = -T\langle\sigma_x\rangle + v_{\text{ext}}\,\Delta n + E_{\text{x}}[v_{\text{s}}] + \frac{1}{2}\omega, \tag{4.15}$$

where $\Delta n = -v_{\text{s}}/W$ and Eq. (4.12) reduces to

$$E_{\text{x}} = \frac{\lambda^2 T^2}{W\,(\omega + 2\,W)}. \tag{4.16}$$

The x-energy in Eq. (4.16) vanishes in the classical limit of coupling $\lambda \to \infty$, as expected. In Fig. 4.1 we show the calculated OEP density 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. Here, $\lambda \sim 10^{-2}$, $0.1 \lesssim \lambda \lesssim 1$ and $\lambda \gtrsim 1$ are respectively circuit QED, ultrastrong [85] and deep strong coupling [86] values. The eigenvalue problem for the static Rabi Hamiltonian in Eq. (4.13) is solved by employing the exact diagonalization technique [87, 88], after proper truncation of the Fock space. We observe that both the OEP and the classical approximation reproduce qualitatively the electron's confinement 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 densities Δn shown in (a), we see excellent agreement between the OEP and the exact results up to $\lambda = 0.5$ and above $\lambda = 2$. In contrast, the classical approximation performs reliably only in the limits of very small or very high interaction strength. Regarding the energies E shown in (b), the improvement of the OEP with respect to the classical approach is evident. Here, the classical result is only asymptotically accurate and largely underestimating in between. On the contrary, the OEP energy is close to the exact values in the whole coupling range, with only small deviations around $\lambda = 1.25$.

The TDOEP Eq. (4.8) for the Rabi model simplifies to

$$\begin{aligned} &\mathrm{i}\int_{-\infty}^{t} dt_1 \tilde{v}_{\mathrm{x}}(t_1) d_{ge}(t_1) d_{eg}(t) + c.c. \\ &= \lambda^2 \omega \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2\, c(t,t_1)\, d_{eg}(t_2) e^{\mathrm{i}\omega(t_2-t_1)} + c.c., \end{aligned} \tag{4.17}$$

where $\tilde{v}_{\mathrm{x}} = v_{\mathrm{x}}(t) + \lambda^2 \Delta n(t)$ 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. (4.9) explicitly reads as

$$\begin{aligned} v_{\mathrm{MF}}(t) = &-\lambda^2 \omega \int_0^t dt_1 \sin[\omega(t-t_1)] \Delta n(t_1) - \lambda^2 \Delta n \cos(\omega t) \\ &+ \lambda^2 \Delta n(t). \end{aligned}$$

Employing the numerical algorithm presented in [89], we solve Eq. (4.17) 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 [90]. The latter is propagated with a predictor-corrector scheme using an exponential midpoint propagator [91]. In Fig. 4.2, we compare the time-evolution of the calculated TDOEP density Δn and effective potential

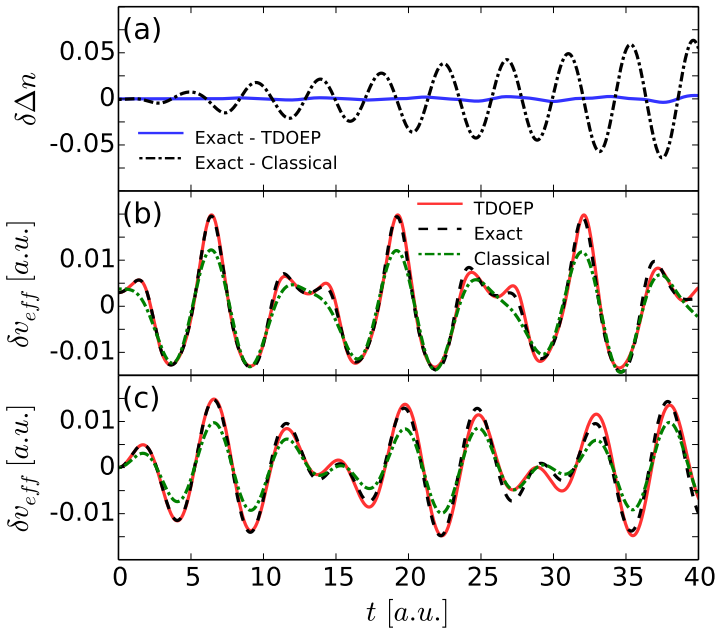

Figure 4.2: Comparison of the (a) errors $\delta\Delta n$ in the TDOEP (black) and classical (blue) density difference Δn and (b),(c) TDOEP (red), exact (black), and classical (green) effective potential v_{eff} versus time t in a.u. for the configurations: (a, b) $v_{\text{ext}} = -0.2\,\text{sign}(t)$, $\lambda = 0.1$ and (c) $v_{\text{ext}} = 0$, $\lambda = 0.1\theta(t)$. Other parameters: $\omega = 1$, $T = 0.7$.

v_{eff} with the exact and classical results, approaching 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 $v_{\text{ext}}(t) = -0.2\,\text{sign}(t)$. In the second configuration, we choose a non-interacting 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 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 densities of the two setups undergo off-resonant Rabi oscillations with nearly identical relative behavior. This is shown in (a) for the sudden-switch example. Within the plotted range, the TDOEP and exact results are practically on top of each other. In contrast, the classical density starts to deviate around $t = 20$ a.u., and the error becomes quite sizable at

$t = 40$ a.u.. More significant is the improvement of the TDOEP approach against the classical approximation in the effective potential. As we can see in (b) for the sudden-switch case, and in (c) for the non-interacting 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, we showed that the lowest order (TD)OEP for the off-resonant Rabi model gives accurate stationary properties (dynamics) 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 [80]. We point out that formally Eq. 4.1 is a version of the Caldeira-Leggett model [120]. Therefore, we also obtained an approximate xc functional for open quantum systems coupled to the Caldeira-Leggett bath of harmonic oscillators. Already at the zero level of approximation (Eq. 4.9) we recover the friction contribution to the dissipation [76]

Chapter 5

Exchange energy functional for the spin-spin interaction

5.1 Introduction

Design and manipulation of domain walls and skyrmions in ferromagnetic nanowires are at the core of novel low-cost, high-performing spintronic information technology, such as racetrack memories and domain wall operated logic devices [110–113]. Optimizing the magnetization setting in these systems requires an accurate evaluation of the dipolar energy, which is responsible for magnetic inhomogeneities. Currently, most modelling of magnetic structures in nanomaterials makes use of semiclassical micromagnetic simulations based on the continuous medium approximation [114, 115]. Here, the total energy is computed as a function of the classical magnetization vector $\mathbf{M}(\mathrm{x})$, which is defined as the mesoscopic average of the local magnetization density over a cell of a few nanometers size (the upper limit of the cell being the smallest exchange length of the material). In accordance with Maxwell equations for the magnetostatics, the dipolar contribution to the micromagnetic energy takes the form $E_d = -\frac{1}{2}\int d^3\mathrm{x}\,\mu_B \mathbf{H}_d \cdot \mathbf{M}$, where $\mathbf{H}_d$ is the demagnetizing field. However, both domain walls and spin vortices are nanoscale objects comparable in size with the discretization cell used in micromagnetic

calculations. In this case the fundamental assumption underlying micromagnetism, i.e., of slowly varying magnetization on a mesoscopic scale, breaks down. A new theoretical approach to these spin configurations is thus required, which accounts for sub-nanometric variations of the magnetization and related quantum effects [114, 115].

Atomistic modelling, with parameters from ab-initio spin density functional theory (SDFT), has been successfully applied to magnetic nanomaterials for describing complex phenomena such as surface anisotropy, ultrafast laser-induced spin dynamics, exchange bias and spin torque [114]. At present the only source of magnetic coupling in SDFT is the exchange interaction, which originates from the Pauli exclusion principle and favors spin alignment. In this chapter, we propose a full quantum microscopic approach to highly inhomogeneous magnetic structures by treating the dipole-dipole coupling as a pairwise interaction within SDFT.

The interaction between the spin magnetic dipole moments of two electrons is a second order term in the $1/c$ expansion of the QED Hamiltonian [116]. It arises from the non-relativistic limit of the Breit Hamiltonian of Eq. (3.40) as

$$\hat{H}_{dip} = \frac{\mu_B^2}{2} \int d^3\mathrm{x} \int d^3\mathrm{x}'\, \hat{m}^i(\mathbf{x}) \delta^{\perp}_{ij}(\mathbf{x}-\mathbf{x}') \hat{m}^j(\mathbf{x}'), \tag{5.1a}$$

$$\delta^{\perp}_{ij}(\mathbf{x}-\mathbf{x}') = d_{ij}(\mathbf{x}-\mathbf{x}') - \frac{8\pi}{3}\delta_{ij}\delta^3(\mathbf{x}-\mathbf{x}'). \tag{5.1b}$$

Here, $\delta^{\perp}$ denotes the transverse delta function and $\hat{\boldsymbol{m}}(\mathbf{x}) = \hat{\psi}^{\dagger}(\mathbf{x})\boldsymbol{\sigma}\hat{\psi}(\mathbf{x})$ is the magnetization density operator, expressed in terms of the Pauli bispinor $\hat{\psi}(\mathbf{x})$ and the vector of Pauli $\boldsymbol{\sigma}$ matrices. Repeated indices are to be summed over. Eq. (5.1a) is the sum of two contributions. The first contribution comes

from the dipole-dipole interaction tensor d_{ij} of Eq. (5.1b), which is defined as

$$\begin{aligned} d_{ij}(\mathbf{x}-\mathbf{x}') \equiv & -\frac{\partial^2}{\partial \mathrm{x}_i \partial \mathrm{x}'_j}\frac{1}{|\mathbf{x}-\mathbf{x}'|} - \frac{4\pi}{3}\delta_{ij}\delta^3(\mathbf{x}-\mathbf{x}') \\ = & \frac{1}{r^3}(\delta_{ij} - 3\hat{\boldsymbol{r}}_i\hat{\boldsymbol{r}}_j), \end{aligned} \tag{5.2}$$

where $\boldsymbol{r} = \mathbf{x} - \mathbf{x}'$ and $\hat{\boldsymbol{r}}$ denotes the unit vector along $\boldsymbol{r}$. Eq. (5.2) is assumed to be valid for $r \neq 0$. Physically, it describes the interaction between the magnetization density at $\mathbf{x}$ and the dipolar field created by the magnetization distribution at all the other points $\mathbf{x}' \neq \mathbf{x}$. The contact term δ_{ij} here, ensures that the diagonal elements of d_{ij} satisfy the Laplace equation $-\Delta(1/|\mathbf{x}-\mathbf{x}'|) = 4\pi\delta^3(\mathbf{x}-\mathbf{x}')$ for the scalar potential generated by the magnetic charge density in the ferromagnet. Equivalently, this term is required because the dipolar magnetic field must have zero divergence. Its inclusion in Eq. (5.2) makes the dipolar tensor d_{ij} traceless as well as symmetric. The second contribution to Eq. (5.1a) comes from the second term in Eq. (5.1b) and is a contact interaction, which depends on the magnetization density at the same point.

In Sec. 5.2.1 we recover the micromagnetic dipolar energy as the Hartree term of SDFT for the dipole-dipole interaction. In Sec. 5.2.2 we derive the first approximate exchange functional for calculations of magnetic inhomogeneities beyond the mean field micromagnetic approach. In Sec. 5.3 we conclude with a remark on the functional treatment of the spin contact contribution to the dipolar interaction.

5.2 Dipole-dipole functional

5.2.1 Hartree energy functional

The Hartree term is straightforward to write down. It is simply obtained by replacing the magnetization density operator $\hat{\boldsymbol{m}}(\mathbf{x})$ in the expression for the dipole-dipole interaction with its expectation value $\boldsymbol{m}(\mathbf{x})$

$$E_H^{dip} = \frac{\mu_B^2}{2} \int d^3\mathrm{x} \int d^3\mathrm{x}'\, m^i(\mathbf{x}) d_{ij}(\mathbf{x}-\mathbf{x}') m^j(\mathbf{x}'), \tag{5.3}$$

where d_{ij} is given by Eq. (5.2). Eq. (5.3) represents the exact magnetostatic energy, of which the dipolar micromagnetic energy is a mesoscopic approximation (here $\boldsymbol{m}(\mathbf{x})$ is a microscopic quantity not to be confused with the magnetization $\boldsymbol{M}(\mathbf{x})$ averaged over a mesoscopic volume of atomic cells). We point out that at present only this mean field contribution to the dipolar energy is implemented in actual calculations of inhomogeneous magnetic structures. However, the Hartree treatment of a pairwise interaction is a very crude approximation, (see, e.g., the case of the Coulomb interaction). In addition to completely neglecting quantum many-body effects, it is affected by a self-interaction error. An improved estimate of the real interaction energy is given by the Hartree-Fock approximation, which significantly lowers the Hartree energy by inclusion of the exchange (Fock) term. In the next section we go beyond the current mean field description by deriving an approximate exchange energy functional for the dipole-dipole interaction.

5.2.2 Exchange energy functional

The approximation to the exchange (x) energy functional most widely used in SDFT is the local spin density approximation (LSDA) [12]. In the LSDA, the x energy of a non-uniform magnetic system is given at each point by the x energy of the homogeneous electron gas (HEG), with the same spin density

as the local density. Choosing a local coordinate system, with the z-axis along the direction of the local spin, we evaluate the x energy density of the spin polarised non-relativistic HEG with dipole-dipole interaction as

$$e_x^{dip}(\mathbf{x}) = -\frac{\mu_B^2}{2}\int d^3\mathrm{y}\rho_{\alpha\beta}(\boldsymbol{r})\sigma^i_{\nu\alpha}d_{ij}(\boldsymbol{r})\sigma^j_{\beta\mu}\rho_{\mu\nu}(-\boldsymbol{r}), \tag{5.4}$$

where $\rho_{\alpha\beta}(\boldsymbol{r}) = \int d^3k\psi^\dagger_{\boldsymbol{k}\sigma}(\mathbf{x}\alpha)\psi_{\boldsymbol{k}\sigma}(\mathbf{y}\beta)$ is the one-body density matrix with spin orbitals $\psi_{\boldsymbol{k}\sigma}(\mathbf{x}\alpha) = (2\pi)^{-3/2}e^{i\boldsymbol{k}\cdot\mathbf{x}}\delta_{\sigma\alpha}$. After tracing over the spin in Eq. (5.4), one obtains

$$\begin{aligned} e_x^{dip}(\mathbf{x}) = -\frac{\mu_B^2}{2}\int d^3\mathrm{y}\Bigg\{&\left[\int\int^{k_F{}^\uparrow} + \int\int^{k_F{}^\downarrow}\right]\frac{d^3k}{(2\pi)^3}\frac{d^3k'}{(2\pi)^3}e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}}d_{zz} \\ &+\left[\int\int^{k_F{}^\uparrow k_F{}^\downarrow k_F{}^\downarrow k_F{}^\uparrow} + \int\int\right]\frac{d^3k}{(2\pi)^3}\frac{d^3k'}{(2\pi)^3}e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}}(d_{xx}+d_{yy})\Bigg\}, \end{aligned} \tag{5.5}$$

where the spin polarisation is taken into account by different Fermi vectors $k_F{}^{\uparrow,\downarrow}$ for the different spin components along z. We observe that since the uniform electron gas is spherically symmetric, the density matrix depends only on the modulus of the distance, i.e., $\rho(\boldsymbol{r}) = \rho(r)$. Moreover, we can replace in Eq. (5.5) for the diagonal components of the dipolar tensor d_{ij} (Eq. (5.2)) $\hat{r}_x^2$ (as well as $\hat{r}_y^2$ and $\hat{r}_z^2$) by the average value $1/3\,\hat{\boldsymbol{r}}^2$. It immediately follows that the x energy density e_x^{dip} is equal to zero. We thus conclude that for the HEG, regardless of the spin polarization, the leading relativistic correction to the energy due to the dipole-dipole interaction vanishes. This is a general property, and the obtained result is not affected by employing a fully relativistic description for the HEG.

We then proceed to derive nonlocal corrections to the LSDA for the dipole-dipole x energy functional. Corrections to the standard LSDA in SDFT are systematically constructed via the gradient expansion and the linear response

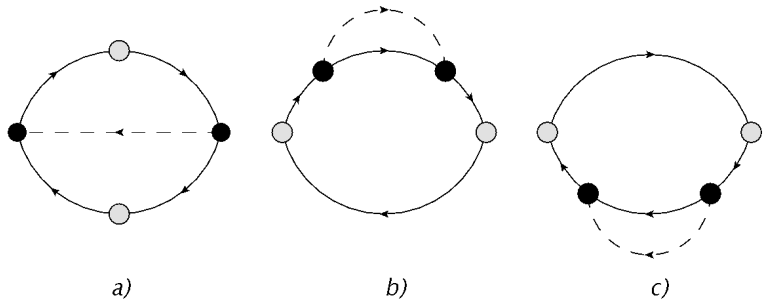

Figure 5.1: First order Feynman diagrams for the spin density response function with magnetic dipole-dipole interaction.

[12]. Here, we follow the second strategy, as it allows one to describe variations of the magnetization $\boldsymbol{m}(\mathbf{x})$ also at small $\mathbf{x}$. We thus consider the dipolar HEG subject to a weak external perturbation in the form of the magnetic field $\delta V^i_{\boldsymbol{q}}(\mathbf{x}) = e^{i\boldsymbol{q}\cdot\mathbf{x}}\sigma^i$, which couples to the spin density n_i. The wave vector $\boldsymbol{q}$ is arbitrary. The dipole-dipole contribution to the x energy can be evaluated as

$$E_x^{dip} = -\frac{1}{2}\int \frac{d^3q}{(2\pi)^3} K_x^{ij}(q)\delta n(\boldsymbol{q})_i \delta n(-\boldsymbol{q})_j, \tag{5.6}$$

where $\delta n(\boldsymbol{q})_i$ is the induced spin density variation (from an actual calculation), and the x kernel is given by

$$K_x^{ij}(q) \equiv \frac{\partial^2 E_x^{dip}}{\partial n_i(\boldsymbol{q})\,\partial n_j(-\boldsymbol{q})} = g_{kl}\left(\chi^{-1}\right)_{ik}\left(\chi^{-1}\right)_{jl}. \tag{5.7}$$

Here, we have used the chain rule to express K_x^{ij} in terms of the response function of the HEG $\chi_{ik} = \partial n_i/\partial V_k$ and the linear response contribution to the dipolar x energy functional $g_{kl} \equiv \partial^2 E_x^{dip}/\partial V^k_{\boldsymbol{q}}\partial V^l_{-\boldsymbol{q}}$. This is represented diagrammatically in Fig. (5.1). The vertex correction diagram a) has the analytic expression

$$g^{lk}(\boldsymbol{q},0) = \frac{1}{\beta^2}\sum_{n,m}\int\frac{d^3k}{(2\pi)^3}\int\frac{d^3k'}{(2\pi)^3} v^{ij}_{\boldsymbol{k}-\boldsymbol{k}'}\sigma^i_{\alpha\delta}G^0_{\delta\epsilon}(k,i\epsilon_n)\sigma^l_{\epsilon\eta}$$
$$\times G^0_{\eta\gamma}(|\boldsymbol{k}+\boldsymbol{q}|,i\epsilon_n)\sigma^j_{\gamma\beta}G^0_{\beta\zeta}(|\boldsymbol{k}'+\boldsymbol{q}|,i\epsilon'_m)\sigma^k_{\zeta\theta}G^0_{\theta\alpha}(k',i\epsilon'_m), \tag{5.8}$$

where $v^{ij}_{\boldsymbol{k}} = 4\pi\mu_B^2/3(3\hat{\boldsymbol{k}}_i\hat{\boldsymbol{k}}_j - \delta_{ij})$ is the Fourier transform of the dipolar interaction in Eq. (5.2), and $G^0_{\alpha\beta}(k, i\omega_n) = \delta_{\alpha\beta}/(i\omega_n - \varepsilon_{\boldsymbol{k}})$ is the unperturbed Matsubara Green's function for the paramagnetic electron gas. Summing over the spin indices in Eq. (5.8) gives

$$Tr\{\sigma^i\sigma^l\sigma^j\sigma^k\} = 4\delta_{il}\delta_{jk}. \tag{5.9}$$

From Eq. (5.9), since the system is isotropic, we observe that Eq. (5.8) takes the form

$$g^{ij}(\boldsymbol{q}, 0) = f(q)(3\hat{\boldsymbol{q}}_i\hat{\boldsymbol{q}}_j - \delta_{ij}), \tag{5.10}$$

where $f(q)$ denotes a function of the modulus of $\boldsymbol{q}$ and the angular dependence of g on the indices of $\boldsymbol{q}$ is while the traceless symmetric interaction tensor $v^{ij}_{\boldsymbol{k}-\boldsymbol{k}'}$. Performing the summation over the Matsubara frequencies and spin indices we obtain for g^{zz} ($g^{xx} = g^{yy} = -1/2\, g^{zz}$) the expression

$$\begin{aligned} g^{zz} =& 8\frac{4\pi\mu_B^2}{3}\int\frac{d^3k}{(2\pi)^3}\int\frac{d^3k'}{(2\pi)^3}\left(\frac{n_{\boldsymbol{k}} - n_{\boldsymbol{k}+\boldsymbol{q}}}{\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}}}\right) \\ &\times\left(\frac{n_{\boldsymbol{k}'} - n_{\boldsymbol{k}'+\boldsymbol{q}}}{\varepsilon_{\boldsymbol{k}'} - \varepsilon_{\boldsymbol{k}'+\boldsymbol{q}}}\right) P_2(\cos\theta_{\boldsymbol{k}-\boldsymbol{k}'}), \end{aligned} \tag{5.11}$$

where $n_{\boldsymbol{k}}$ is the Fermi distribution function and $P_2(\cos\theta_{\boldsymbol{k}}) = 1/2(3\cos^2\theta_{\boldsymbol{k}} - 1)$ is the Legendre polynomial of second order with $\cos\theta_{\boldsymbol{k}} = \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{q}}$. The main result of this chapter is the exact evaluation of Eq. (5.11) in terms of one quadrature. Using the transformations $\boldsymbol{k}^{(\prime)} \to \pm\boldsymbol{k}^{(\prime)} - \boldsymbol{q}/2$, we recast the $\sim\cos^2\theta_{\boldsymbol{k}-\boldsymbol{k}'}$ term in the form

$$\begin{aligned} I(q) =& \frac{e^2}{8\pi^5\hbar^2c^2q^2}\int d^3k\int d^3k'\frac{n_{\boldsymbol{k}-\boldsymbol{q}/2}n_{\boldsymbol{k}'-\boldsymbol{q}/2}}{(\boldsymbol{k}\cdot\boldsymbol{q})(\boldsymbol{k}'\cdot\boldsymbol{q})} \\ &\times\left\{\left[\frac{\boldsymbol{q}\cdot(\boldsymbol{k}+\boldsymbol{k}')}{|\boldsymbol{k}+\boldsymbol{k}'|}\right]^2 + \left[\frac{\boldsymbol{q}\cdot(\boldsymbol{k}-\boldsymbol{k}')}{|\boldsymbol{k}-\boldsymbol{k}'|}\right]^2\right\}, \end{aligned} \tag{5.12}$$

which looks structurally similar to the response function of the electron gas

with Coulomb interaction [117–119]. In evaluating Eq. (5.12) we generalize the analytic derivation presented in [119] (see appendix D). The additional term in Eq. (5.11) simply amounts to the square of the Lindhard function. We obtain for $g_{zz}(q)$ the following expression

$$\begin{aligned} g^{zz}(q) =& \frac{e^2 k_F^2}{16\pi^3 \hbar^2 c^2 q^2} \Big\{ \frac{2}{45q} \left(7q^5 - 15q^4 + 30q^3 - 20q^2 - 144\right) \ln|a| \\ &+ \frac{2}{45q} \left(7q^5 + 15q^4 + 30q^3 + 20q^2 + 144\right) \ln b \\ &+ \frac{4}{45} q^2 \left(7q^2 + 60\right) \ln \frac{2}{q} + \frac{16}{45} \left(11q^2 - 18\right) \\ &- \frac{2}{3} q \left[(2b)^3 \ln b \left(\ln b + \ln \frac{2}{q} \right) - (2a)^3 \ln|a| \left(\ln|a| + \ln \frac{2}{q} \right) \right] \\ &+ 8 \int_{-a}^{b} dz z \ln|z| \left[(a+z)(b-z) W_1(z) - (b+z)(z-a) W_2(z) \right] \\ &- \frac{4}{3} \left(q + ab \ln \left| \frac{b}{a} \right| \right)^2 \Big\}, \end{aligned} \tag{5.13}$$

where $W_1(z) = \ln \left| \frac{z+a}{z-b} \right|$ and $W_2(z) = \ln \left| \frac{z-a}{z+b} \right|$, with $a = 1 - q/2$ and $b = 1 + q/2$ in units of the Fermi vector. The self-energy diagrams b) and c) in Fig. (5.1) don't contribute to the corrections to the dipolar x energy, as it can be checked by evaluating the summation over the spin indices. In this regards it is worth noting that diagram a) corresponds to the x energy diagram for a ferromagnetic system with triplet Green's functions, while both diagrams b) and c) contain one singlet Green's function. For completeness we show the expansions of $g^{zz}(q)$ for small and large q:

$$g^{zz}(q) = \begin{cases} \frac{e^2 k_F^2}{1080\pi^3 \hbar^2 c^2} \left[\frac{(127 + 60\log 2 - 60\log q)\, q^2}{5} - \frac{97q^4}{70} - \frac{53q^6}{392} + \dots \right], q \to 0 \\ \frac{16 e^2 k_F^2}{675\pi^3 \hbar^2 c^2} \left(\frac{25}{q^4} + \frac{11}{q^6} + \dots \right), q \to \infty. \end{cases} \tag{5.14}$$

The second derivative of the result has a logarithmic divergence at $q = 0$. Due to the logarithmic factor, the dipolar linear response contribution to the x energy dominates over the Coulomb-exchange in the limit $q \to 0$. Since

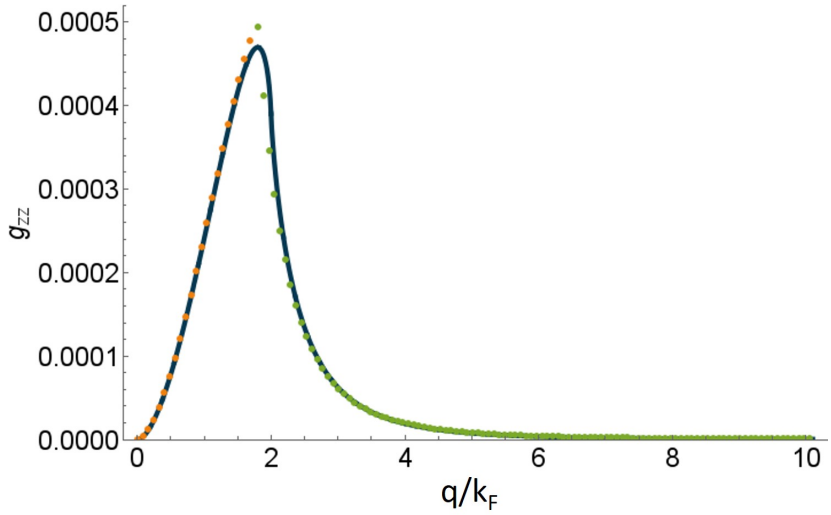

Figure 5.2: g_{zz} as a function of q in units of k_F. The blue curve is the exact result, the orange and green curves are the expansions at q equal to zero and infinity, respectively.

the ratio between dipolar and exchange interaction energies is of the order of 10^{-3} to 10^{-4}, the crossover to the exchange dominated regime takes place at values of q which are exponentially small. However, the ground state properties of the system, such as the spin polarization, are determined by the $q \to 0$ limit and thus by the dipolar interaction. Fig. 5.2 shows the analytic g_{zz} and both the limiting expansions. Using Eq. (5.7), one can calculate the dipolar x kernel via matrix multiplication with the response function χ of the HEG. The simplest choice is approximating χ by the Lindhard function χ_0 of the non-interacting paramagnetic electron gas, i.e., $K_x(k_F, q) = g\chi_0^{-1}\chi_0^{-1}$. The resulting x kernel is shown in Fig. 5.3, and reaches a constant value in the limit $q \to \infty$. A more sophisticated approach requires solving the Dyson's equation to include interacting effects into χ, so that Eq. (5.7) reads as

$$K_x\left(k_F, q\right) = g\left[\left(\frac{1}{1-\left(v_q + K_x\left(k_F, q\right)\right)\chi_0}\chi_0\right)^{-1}\right]^2. \tag{5.15}$$

This expression can be solved algebraically for K_x. However, as v_q is bounded and suppressed by a factor $1/c^2$, this is a very tiny correction. Additionally, v_q reintroduces an explicit directional dependence into the functional, which

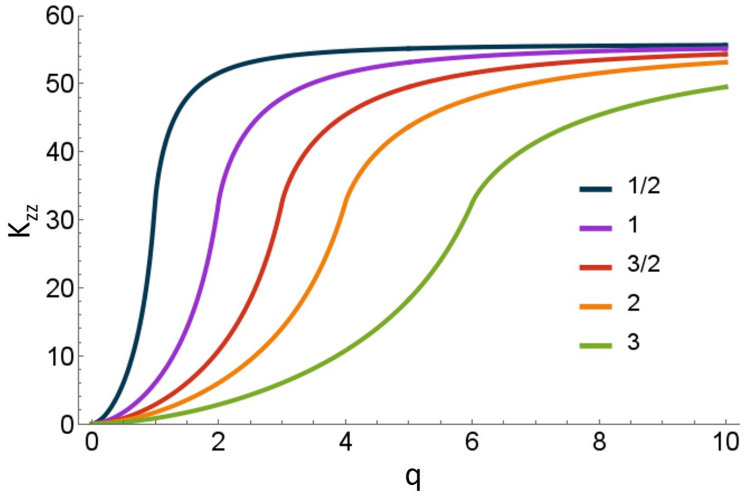

Figure 5.3: K^{zz} as a function of q for different values of k_F.

makes its evaluation much more complicated.

5.3 Spin contact functional

For completeness we include the expressions of the magnetostatic and x energy functionals for the spin contact interaction defined in Eqs. (5.1a,5.1b). The spin contact interaction has the same form of the exchange interaction, but is rescaled by the smaller factor μ_B^2 and is not localized. The magnetostatic term is easily obtained as

$$E_{\mathrm{H}}^{\mathrm{SC}} = -\frac{4\pi\mu_B^2}{3}\int d^3\mathrm{x}\,\mathbf{m}^2\left(\mathbf{x}\right), \tag{5.16}$$

while the LSDA for the x energy is given by

$$E_x^{\mathrm{SC}} = 2\pi\mu_B^2\int d^3\mathrm{x}\,n^2(\mathrm{x}) - \frac{1}{3}\mathbf{m}^2(\mathrm{x}), \tag{5.17}$$

where n is the total density.

Appendix A

Quantum Electrodynamics in Coulomb gauge

In this appendix we give a detailed derivation of QED in Coulomb gauge. We start from the classical QED Lagrangian density with external fields $a_\mu^{\text{ext}}(x)$ and $j_\mu^{\text{ext}}(x)$. This takes the following form [22]

$$\begin{aligned}\mathcal{L}_{\text{QED}}(x) = \mathcal{L}_{\text{M}}(x) - \frac{1}{c} J^\mu(x) a_\mu^{\text{ext}}(x) \\ + \ \mathcal{L}_{\text{E}}(x) - \frac{1}{c}\left(J_\mu(x) + j_\mu^{\text{ext}}(x)\right) A^\mu(x).\end{aligned} \tag{A.1}$$

Here, the classical Lagrangian of the Dirac field is defined as

$$\mathcal{L}_{\text{M}}(x) = \bar{\psi}(x)\left(\mathrm{i}\hbar c\gamma^\mu \partial_u - mc^2\right)\psi(x),$$

where

$$\psi(x) = \begin{pmatrix}\phi(x) \\ \chi(x)\end{pmatrix}$$

is the Dirac spinor with the two-component spin functions $\phi(x)$ and $\chi(x)$, the gamma matrices are given by

$$\gamma^i = \begin{pmatrix} 0 & \sigma^i \\ -\sigma^i & 0 \end{pmatrix}, \ \gamma^0 = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix},$$

where σ^i are the usual Pauli matrices, $\bar{\psi} = \psi^\dagger \gamma^0$, and

$$J_\mu(x) = ec\bar{\psi}(x)\gamma_\mu\psi(x)$$

is the conserved (Noether) current. Further, we use the Minkowski metric $g_{\mu\nu}) = (+,-,-,-)$ to raise and lower the indices. For the classical Maxwell field one has

$$\mathcal{L}_{\mathrm{E}}(x) = -\frac{\epsilon_0}{4} F^{\mu\nu}(x) F_{\mu\nu}(x), \tag{A.2}$$

where $F_{\mu\nu}(x) = \partial_\mu A_\nu(x) - \partial_\nu A_\mu(x)$ is the electric field tensor and $A_\mu(x)$ is the vector potential.

Now we employ the Coulomb gauge condition for the Maxwell field, i.e., $\vec{\nabla} \cdot \vec{A}(x) = 0$. Then, it holds that

$$-\Delta A^0(x) = \frac{1}{\epsilon_0 c} \left(J^0(x) + j^0_{\mathrm{ext}}(x) \right), \tag{A.3}$$

where Δ is the Laplacian. If we impose square-integrability on all of $\mathbb{R}^3$[1] the Green's function of the Laplacian becomes $\Delta^{-1} = -1/(4\pi|\vec{r} - \vec{r}'|)$, and therefore

$$A^0(x) = \frac{1}{c} \int \mathrm{d}^3 r' \, \frac{J^0(x') + j^0_{\mathrm{ext}}(x')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}. \tag{A.4}$$

[1] If we consider the situation of a finite volume, e.g., due to a perfect cavity, the boundary conditions change. These different boundary conditions, in principle, change the Green's function of the Laplacian, and thus the instantaneous interaction. We ignore these deviations from the Coulomb interaction in this work for simplicity.

Since the zero component of the four potential $A_\mu(x)$ is given in terms of the full current, it is not subject to quantization. The conjugate momenta of the photon field (that need to be quantized) are the same as in the current-free theory ,and thus the usual canonical quantization procedure applies [22], i.e.

$$\left[\hat{A}_k(\vec{r}), \epsilon_0 \hat{E}_l(\vec{r}')\right] = -\mathrm{i}\hbar c \delta^{\perp}_{kl}(\vec{r}-\vec{r}'), \tag{A.5}$$

where $\hat{E}_k$ is the electric field operator, $\delta^{\perp}_{kl}(\vec{r}-\vec{r}') = (\delta_{kl} - \partial_k \Delta^{-1} \partial_l)\delta^3(\vec{r}-\vec{r}')$ is the transverse delta function and k, l are spatial coordinates only. Equivalently, we can define these operators by their respective plane-wave expansions

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

where $\omega_k = ck$, $\vec{\epsilon}(\vec{k},\lambda)$ is the transverse polarization vector [22], and the annihilation and creation operators obey

$$\left[\hat{a}_{\vec{k}',\lambda'}, \hat{a}^{\dagger}_{\vec{k},\lambda}\right] = \delta^3(\vec{k}-\vec{k}')\delta_{\lambda\lambda'}.$$

If we further define the magnetic field operator by $c\hat{\vec{B}} = \vec{\nabla} \times \hat{\vec{A}}$, the Hamiltonian corresponding to $\mathcal{L}_{\mathrm{E}}$ is given in Eq. (3.3). We used normal ordering, (i.e., rearrange the annihilation parts of the operators to the right), to get rid of the infinite zero-point energy in this expression. Also, for the Dirac field, the coupling does not change the conjugate momenta. Therefore, we can perform the usual canonical quantization procedure for fermions, which leads to the (equal-time) anti-commutation relations [22]

$$\{\hat{\psi}_\alpha(\vec{r}), \hat{\bar{\psi}}_\beta(\vec{r}')\} = \gamma^0_{\alpha\beta}\delta^3(\vec{r}-\vec{r}').$$

The Hamiltonian corresponding to $\mathcal{L}_{\mathrm{M}}$ thus becomes the one of Eq. (3.2), where we used $\vec{r} \cdot \vec{y} = -x_k y^k$.

Using Eq. (A.4) it is straightforward to give the missing terms of the QED Hamiltonian due to the coupling to the external fields, as well as due to the coupling between the quantized fields.

Appendix B

Non-relativistic equations of motion

To find the non-relativistic limit of Eq. (3.12), we cannot straightaway apply the decoupling to Eq. (3.51). Since we have to apply the decoupling consistently to the Hamiltonian, as well as the current, we need to rewrite the equation of motion. We start in the Heisenberg picture by

$$\begin{aligned}
&\mathrm{i}\partial_0 \left[ec\hat{\psi}^\dagger \gamma^0 \gamma^k \hat{\psi} \right] = \frac{2emc^2}{\hbar} \left[\hat{\chi}^\dagger \sigma^k \hat{\phi} - \hat{\phi}^\dagger \sigma^k \hat{\chi} \right] \\
&- \mathrm{i}ec \left[\hat{\phi}^\dagger \left(\sigma^k \sigma^l \partial_l + \overleftarrow{\partial}_l \sigma^l \sigma^k \right) \hat{\phi} + \hat{\chi}^\dagger \left(\sigma^k \sigma^l \partial_l + \overleftarrow{\partial}_l \sigma^l \sigma^k \right) \hat{\chi} \right] \\
&- \frac{2\mathrm{i}e^2}{\hbar} \epsilon^{klj} \hat{A}^{\mathrm{tot}}_l \left[\hat{\phi}^\dagger \sigma_j \hat{\phi} + \hat{\chi}^\dagger \sigma_j \hat{\chi} \right].
\end{aligned}$$

This leads with $\sigma^l \sigma^k = -g^{lk} - \mathrm{i}\epsilon^{lkj}\sigma_j$ and $\Im\{\hat{\phi}^\dagger \hat{A}^k_{\mathrm{tot}} \hat{\phi}\} \equiv 0$ to

$$\begin{aligned}
&\mathrm{i}\hbar\partial_0 \hat{J}^k = 2\Im \Big\{ -2emc^2 \hat{\chi}^\dagger \sigma^k \hat{\phi} + e^2 \hat{A}^{\mathrm{tot}}_l \left[\hat{\phi}^\dagger \sigma^k \sigma^l \hat{\phi} - \hat{\chi}^\dagger \sigma^l \sigma^k \hat{\chi} \right] \\
&- \mathrm{i}e\hbar c \hat{\chi}^\dagger \overleftarrow{\partial}_l \sigma^l \sigma^k \hat{\chi} - \mathrm{i}e\hbar c \hat{\phi}^\dagger \sigma^k \sigma^l \partial_l \hat{\phi} \Big\}.
\end{aligned}$$

Adding and subtracting on the r.h.s. the term $e\hat{\phi}^\dagger\sigma^k\left(\mathrm{i}\hbar c\partial_0 - \hat{D}\right)\hat{\chi}$, and employing Eq. (3.49) we find

$$\begin{aligned}\mathrm{i}\hbar\partial_0\hat{J}^k = 2e\Im\Big\{\Big[\hat{\chi}^\dagger\left(-\mathrm{i}\hbar c\overleftarrow{\nabla} + e\hat{\vec{A}}^{\mathrm{tot}}\right)\cdot\vec{\sigma} - \hat{\phi}^\dagger eA_0^{\mathrm{tot}} \\ -\hat{\phi}^\dagger e^2\int \mathrm{d}^3r' \frac{:\hat{\phi}^\dagger(\vec{r}')\hat{\phi}(x') + \hat{\chi}^\dagger(x')\hat{\chi}(x'):}{4\pi\epsilon_0|\vec{r}-\vec{r}'|} - mc^2\hat{\phi}^\dagger\Big]\sigma^k\hat{\chi} \\ +c\hat{\phi}^\dagger\sigma^k\mathrm{i}\hbar c\partial_0\hat{\chi}\Big\}.\end{aligned}$$

With the help of the definition $[...] = [\hat{D} + mc^2]^{-1}$, this can be rewritten as

$$\begin{aligned}&\mathrm{i}\hbar\partial_0\hat{J}^k = 2e\Im\Big\{\Big[-\hat{\phi}^\dagger\left(\mathrm{i}\hbar c\overleftarrow{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}\right)\cdot\vec{\sigma}[...]^\dagger\left(\mathrm{i}\hbar c\overleftarrow{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}\right)\cdot\vec{\sigma} - \hat{\phi}^\dagger eA_0^{\mathrm{tot}} \\ &-\hat{\phi}^\dagger e^2\int \mathrm{d}^3r' \frac{:\hat{\phi}^\dagger(x')\hat{\phi}(x') + \hat{\chi}^\dagger(x')\hat{\chi}(x'):}{4\pi\epsilon_0|\vec{r}-\vec{r}'|} - mc^2\hat{\phi}^\dagger\Big]\sigma^k[...]\vec{\sigma}\cdot\left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}\right)\hat{\phi} \\ &+\hat{\phi}^\dagger\sigma^k\left[\mathrm{i}\hbar c\partial_0[...]\vec{\sigma}\cdot\left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}\right)\right]\hat{\phi} + \hat{\phi}^\dagger\sigma^k[...]\vec{\sigma}\cdot\left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}\right) \\ &\Big[\vec{\sigma}\cdot\left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}\right)[...]\vec{\sigma}\cdot\left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}\right) + eA_0^{\mathrm{tot}} \\ &-e^2\int \mathrm{d}^3r' \frac{:\hat{\phi}^\dagger(x')\hat{\phi}(x') + \hat{\chi}^\dagger(x')\hat{\chi}(x'):}{4\pi\epsilon_0|\vec{r}-\vec{r}'|} - mc^2\Big]\hat{\phi}\Big\}.\end{aligned}$$

Now, if we employ the approximation $[...] \approx 1/2mc^2$, (also in the Coulomb terms), we end up with

$$\mathrm{i}\hbar\partial_0\hat{J}^k \approx \mathrm{i}\hbar\partial_0 2ec\Re\left\{\hat{\phi}^\dagger\sigma^k\frac{\vec{\sigma}}{2mc^2}\cdot\left(-\mathrm{i}\hbar c\vec{\nabla} - e\hat{\vec{A}}^{\mathrm{tot}}\right)\hat{\phi}\right\},$$

which is just the equation of motion for the non-relativistic current (3.53) with the Pauli-Fierz Hamiltonian.

For the Maxwell field, the non-relativistic limit of Eq. (3.15) is with the help of Eq. (3.53) straightforward. It is only important to see that this does agree with the equation of motion for $\hat{A}_k$ due to the Pauli-Fierz Hamiltonian (3.52). The main difference to the fully relativistic derivation is that now we

have a term of the form

$$\frac{e}{2mc^2}\int \mathrm{d}^3r\, \hat{J}_0(x)\left(\hat{A}^k(x)+a^k_{\mathrm{ext}}(x)\right)\left(\hat{A}_k(x)+a^{\mathrm{ext}}_k(x)\right).$$

This term does not change anything in the first order equation, i.e. $\partial_0\hat{A}_k = -\hat{E}_k$. In the second order, we find due to Eq. (A.5) that

$$\begin{aligned}\int \mathrm{d}^3r'\, \left[\hat{E}^k(x);\hat{A}^l(x')\hat{A}_l(x')\right]\hat{J}_0(x') \\ = 2\frac{\mathrm{i}\hbar c}{\epsilon_0}\hat{A}^l(x)\hat{J}_0(x) - 2\frac{\mathrm{i}\hbar c}{\epsilon_0}\partial^k\Delta^{-1}\partial^l\hat{A}_l(x)\hat{J}_0(x)\end{aligned}$$

and

$$\begin{aligned}2\int \mathrm{d}^3r'\, \left[\hat{E}^k(x);\hat{A}^l(x')\right]a^{\mathrm{ext}}_l(x')\hat{J}_0(x') \\ = 2\frac{\mathrm{i}\hbar c}{\epsilon_0}a^l_{\mathrm{ext}}(x)\hat{J}_0(x) - 2\frac{\mathrm{i}\hbar c}{\epsilon_0}\partial^k\Delta^{-1}\partial^l a^{\mathrm{ext}}_l(x)\hat{J}_0(x)\end{aligned}$$

Now, with the above definition for Δ^{-1} used in Eq. (A.4), we find that these commutators lead to the terms

$$\begin{aligned}-\partial^k\left(\frac{1}{c}\int \mathrm{d}^3r'\frac{\vec{\nabla}'\cdot\hat{\vec{A}}^{\mathrm{tot}}(x')\frac{e}{mc^2}\hat{J}_0(x')}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}\right) \\ +\mu_0 c\left(\hat{A}^k_{\mathrm{tot}}(x)\frac{e}{mc^2}\hat{J}_0(x)\right),\end{aligned}$$

of the equation of motion for the Maxwell field in the non-relativistic limit. The rest of the derivation is similar to the relativistic situation.

Appendix C

Mode expansion

If we restrict the allowed space for the photonic modes, we also need to impose appropriate boundary conditions. Let us first start with a cubic cavity of length L with periodic boundary condition. Given the allowed wave vectors $\vec{k}_n = \vec{n}(2\pi/L)$, and the corresponding dimensionless creation and annihilation operators $\hat{a}^\dagger_{\vec{n},\lambda}$, $\hat{a}_{\vec{n},\lambda}$, which are connected to their continuous counterparts by

$$\lim_{L\to 0} L^{3/2}\hat{a}_{\vec{n},\lambda} \to \hat{a}_{\vec{k},\lambda},$$

we find that

$$\hat{A}_k(\vec{r}) = \sqrt{\frac{\hbar c^2}{\epsilon_0 L^3}} \sum_{\vec{n},\lambda} \frac{\epsilon_k(\vec{n},\lambda)}{\sqrt{2\omega_n}} \left[\hat{a}_{\vec{n},\lambda} e^{\mathrm{i}\vec{k}_n\cdot\vec{r}} + \hat{a}^\dagger_{\vec{n},\lambda} e^{-\mathrm{i}\vec{k}_n\cdot\vec{r}}\right].$$

Here, $\omega_n = c|\vec{n}|(2\pi/L)$. If we change the conditions at the boundaries to zero-boundary conditions, then the allowed wave vectors change to $\vec{k}_n = \vec{n}(\pi/L)$, and the discrete operators obey

$$\lim_{L\to 0} (2L)^{3/2}\mathrm{i}\hat{a}^\dagger_{\vec{n},\lambda} \to \hat{a}^\dagger_{\vec{k},\lambda}.$$

With the normalized mode functions

$$\mathcal{S}(\vec{n}\cdot\vec{r}) = \left(\frac{2}{L}\right)^{3/2} \prod_{i=1}^{3} \sin\left(\frac{\pi n_i}{L} r_i\right), \tag{C.1}$$

the field operator reads as

$$\hat{A}_k(\vec{r}) = \sqrt{\frac{\hbar c^2}{\epsilon_0}} \sum_{\vec{n},\lambda} \frac{\epsilon_k(\vec{n},\lambda)}{\sqrt{2\omega_n}} \left[\hat{a}_{\vec{n},\lambda} + \hat{a}^{\dagger}_{\vec{n},\lambda}\right] \mathcal{S}(\vec{n}\cdot\vec{r}).$$

Here $\omega_n = c|\vec{n}|(\pi/L)$.

Appendix D

Evaluation of $I(q)$

For convenience we evaluate Eq. (5.12) in cylindrical coordinates with the polar axis along $\boldsymbol{q}$, where all the wave vectors are measured in units of k_F. The integrations over the azimuthal and radial coordinates of $\boldsymbol{k}$ and $\boldsymbol{k}'$ are readily carried through obtaining

$$I(q) = \frac{e^2 k_F^2}{16\pi^3 \hbar^2 c^2 q^2} \sum_{i=0}^{3} J_i, \tag{D.1}$$

where

$$\begin{aligned} J_0 = &-2 \iint_{-a}^{b} \frac{dz\, dz'}{z\, z'} \left[(z^2 + z'^2)(\lambda + \lambda')(2\ln 2 + 1) \right. \\ &\left. + z^4 + 6z^2 z'^2 + z'^4 \right], \end{aligned} \tag{D.2}$$

$$J_1 = 2 \iint_{-a}^{b} \frac{dz\, dz'}{z\, z'} \left[\alpha^2 \sqrt{R(z,z')} + \beta^2 |\beta| \right], \tag{D.3}$$

$$\begin{aligned} J_2 = &4 \iint_{-a}^{b} \frac{dz\, dz'}{z\, z'} \lambda \left[\alpha^2 \ln |2\sqrt{R(z,z')} + \lambda' - \lambda + \alpha^2| \right. \\ &\left. + \beta^2 \ln |2|\beta| + \lambda' - \lambda + \beta^2| \right], \end{aligned} \tag{D.4}$$

$$J_3 = -4 \iint_{-a}^{b} \frac{dz\, dz'}{z\, z'} \lambda \left[\beta^2 \ln |\beta^2| + \alpha^2 \ln |\alpha^2| \right]. \tag{D.5}$$

We adopt the same notation as in [119]. Here, $a = 1 - q/2$, $b = 1 + q/2$, $\alpha = z + z'$, $\beta = z - z'$ and $\lambda^{(\prime)} = (a + z^{(\prime)})(b - z^{(\prime)})$. The function R is defined as $R(z, z') = C_0(z)z'^2 + B_0(z)z' + A_0(z)$, where $A_0 = z^2$, $B_0 = (2 + 2qz - q^2)z$ and $C_0 = 1 + 2qz$. Evaluating J_0 is straightforward and the resulting expression is

$$J_0 = -(2 + \ln 2)8q^2 - 2q\left[q^2 \ln 2 - \frac{4}{3}(4 + 5\ln 2)\right] \ln\left|\frac{a}{b}\right|. \tag{D.6}$$

J_1 can be rewritten in the following form

$$J_1 = 4\iint_{-a}^{b} dzdz' \left(\frac{\alpha}{z'}\sqrt{R(z, z')} + \frac{\beta}{z'}|\beta|\right) = 4\int_{-a}^{b} dz \left(\bar{J}_1^A(z) + \bar{J}_1^B(z)\right), \tag{D.7}$$

where $\bar{J}_1^A(z)$ and $\bar{J}_1^B(z)$ are evaluated to be [119]

$$\begin{aligned}
\bar{J}_1^A(z) &= 1 + \frac{1}{4}q^2 + \frac{5}{2}qz + \left(2 - \ln\left|1 - \frac{4}{q^2}\right|\right) z^2 + \frac{B_0}{4C_0}(2z + q) \\
&\quad + \frac{1}{4C_0^{3/2}} z^2 \left[8 - q^4 + 4qz(6 - q^2) + 12q^2z^2\right] Y(z), \\
\bar{J}_1^B(z) &= 2qz - 1 - \frac{q^2}{4} - z^2(3 - 2\ln|z| + \ln|ab|),
\end{aligned}$$

with $Y(z) = \ln\left|\frac{\sqrt{C_0} + 1}{\sqrt{C_0} - 1}\right|$. The remaining integration in Eq. (D.7) can also be carried through obtaining

$$\begin{aligned}
J_1 = &-\frac{1}{q^2} - \frac{1}{9} + \frac{44}{3}q^2 + 4\left(\frac{4}{3} + q^2\right)\ln\frac{q}{2} + \frac{1}{3}\left[(q - 2)^3 \ln b - (q + 2)^3 \ln|a|\right] \\
&+ \frac{1}{2q^3}\left(q^2 - 1\right)^2 \ln\left|\frac{q + 1}{q - 1}\right| + \frac{3}{4q^3}\eta_5 - \frac{1}{2q}\eta_3 - \left(\frac{5}{2q^3} - \frac{3}{2q} + \frac{q}{4}\right)\eta_1 \\
&- \left(\frac{3}{2q} - \frac{2}{q^3} - \frac{q}{2}\right)\eta_{-1} + \left(\frac{1}{2q} - \frac{1}{4q^3} - \frac{q}{4}\right)\eta_{-3},
\end{aligned} \tag{D.8}$$

where $\eta_n = q\int_{-a}^{b} dz C_0^{n/2} Y(z)$. The explicit expressions for $\eta_{\pm 1,-3}$ are given in [119], for $\eta_{3,5}$ in appendix D.1. Next, we evaluate $J_{23} = J_2 + J_3$. This term is

conveniently rewritten as

$$\begin{aligned} J_{23} =& 4\iint_{-a}^{b} dz dz' \frac{\lambda}{z\,z'}\left(\alpha^2+\beta^2\right)\ln|4\lambda| \\ & - 4\int_{-a}^{b} dz \frac{\lambda}{z}\left[\bar{N}_1(z)+\bar{N}_2(z)\right], \end{aligned} \tag{D.9}$$

where $\bar{N}_1(z)$ and $\bar{N}_2(z)$ are defined as follows:

$$\bar{N}_1(z) = \int_{-a}^{b} dz' \frac{\alpha^2}{z'} \ln|\alpha^2+\lambda'-\lambda-2\sqrt{R(z,z')}|, \tag{D.10}$$

$$\bar{N}_2(z) = \int_{-a}^{z} dz' \frac{\beta^2}{z'} \ln|2\beta(z-b)| + \int_{z}^{b} dz' \frac{\beta^2}{z'} \ln|2\beta(z+a)|. \tag{D.11}$$

Eqs. (D.10) and (D.11) can be integrated by parts obtaining

$$\begin{aligned} \bar{N}_1(z) =& \int_{-a}^{b} \frac{dz'}{\alpha}\left(z^2\ln|z'|+\frac{1}{2}z'^2+2zz'\right)\left(\frac{qz}{\sqrt{R(z,z')}}-1\right) \\ & + \left(z^2\ln\left|\frac{b}{a}\right|+q+4z\right)\ln|2\lambda| \end{aligned} \tag{D.12}$$

$$\begin{aligned} \bar{N}_2(z) =& \left(z^2\ln\left|\frac{b}{a}\right|+q-4z\right)\ln|2\lambda| + \left(\frac{3}{2}z^2-\ln|z|z^2\right) \\ & \times W_1(z) + \int_{-a}^{b} dz'\left(z^2\ln|z'|+\frac{1}{2}z'^2-2zz'\right)\frac{1}{\beta}, \end{aligned} \tag{D.13}$$

where we have used the notation $W_1(z) = \ln|\frac{z+a}{z-b}|$. Subsequent substitution of Eqs. (D.12) and (D.13) in Eq. (D.9) gives

$$\begin{aligned} J_{23} =& 4q\left[q+\left(ab+\frac{2}{3}\right)\ln\left|\frac{b}{a}\right|\right](2\ln 2+1) - \frac{8}{3}q\ln\left|\frac{b}{a}\right| \\ & + 6\int_{-a}^{b} dz\lambda z W_2(z) - 4\left(q\Phi_1+2\Phi_2+q\Phi_3-\Phi_4\right). \end{aligned} \tag{D.14}$$

Here, we have defined $W_2(z) = \ln|\frac{z-a}{z+b}|$,

$$\Phi_1 = \int_{-a}^{b} dz\lambda \int_{-a}^{b} dz'\left(\frac{1}{2}z'^2+2zz'\right)\frac{1}{\alpha\sqrt{R(z,z')}}, \tag{D.15}$$

$$\Phi_2 = \int_{-a}^{b} dz\lambda z \int_{-a}^{b} dz' \frac{z'}{\alpha\beta} \ln|z'|, \tag{D.16}$$

$$\Phi_3 = \int_{-a}^{b} dz\lambda \int_{-a}^{b} dz' z^2 \ln|z'| \frac{1}{\alpha\sqrt{R(z,z')}}, \tag{D.17}$$

$$\Phi_4 = \int_{-a}^{b} dz\lambda z W_1(z) \ln|z|. \tag{D.18}$$

By writing Φ_1 as

$$\Phi_1 = \frac{1}{2} \int_{-a}^{b} dz\lambda \int_{-a}^{b} dz' \frac{1}{\sqrt{R(z,z')}} \left[z' + 3z \left(1 - \frac{z}{\alpha} \right) \right], \tag{D.19}$$

and performing the integrations over z'

$$\int_{-a}^{b} dz' \frac{z'}{\sqrt{R(z,z')}} = \frac{1}{C_0}(2z+q) - \frac{B_0}{C_0^{3/2}} Y(z), \tag{D.20}$$

$$\int_{-a}^{b} dz' \frac{1}{\sqrt{R(z,z')}} = \frac{2}{\sqrt{C_0}} Y(z), \tag{D.21}$$

$$\int_{-a}^{b} dz' \frac{1}{\alpha\sqrt{R(z,z')}} = -\frac{1}{qz} W_2(z), \tag{D.22}$$

we get

$$\begin{aligned} \Phi_1 =& \frac{1}{2} \int_{-a}^{b} dz \frac{\lambda}{\sqrt{C_0}} \left[\frac{2z+q}{\sqrt{C_0}} + \left(6z - \frac{B_0}{C_0} \right) Y(z) \right] \\ &+ \frac{3}{2q} \int_{-a}^{b} dz\lambda z W_2(z). \end{aligned} \tag{D.23}$$

The last term in Eq. (D.23) cancels with the same contribution of opposite sign in Eq. (D.14). The remaining integrals can be carried out as follows

$$\frac{1}{2} \int_{-a}^{b} dz\lambda \frac{2z+q}{C_0} = \frac{1}{24q^4} \left[-6q + 16q^3 + 6q^5 - 3(q^2-1)^3 \ln\left| \frac{q+1}{q-1} \right| \right], \tag{D.24}$$

$$-\frac{1}{2}\int_{-a}^{b}dz\lambda\frac{Y(z)}{C_0^{3/2}}\left[B_0-6zC_0\right]=-\frac{5}{16q^4}\eta_5+\left(\frac{9}{16q^2}+\frac{1}{q^4}\right)\eta_3-\left(\frac{3}{16}-\frac{1}{16q^2}+\frac{9}{8q^4}\right)\eta_1$$
$$-\left(\frac{q^2}{16}-\frac{3}{8}+\frac{13}{16q^2}-\frac{1}{2q^4}\right)\eta_{-1}+\left(\frac{3}{16q^2}-\frac{1}{16q^4}-\frac{3}{16}+\frac{q^2}{16}\right)\eta_{-3}. \tag{D.25}$$

We then write Eq. (D.16) as

$$\Phi_2 \overset{z\leftrightarrow z'}{=} -\int_{-a}^{b}dzz\ln|z|\int_{-a}^{b}dz'\frac{\lambda' z'}{\alpha\beta} \tag{D.26}$$
$$=-\int_{-a}^{b}dzz\ln|z|\left[(b+z)(a-z)\int_{-a}^{b}dz'\frac{z'}{\alpha\beta}+(q+z)\int_{-a}^{b}dz'\frac{z'}{\beta}-\int_{-a}^{b}dz'\frac{z'^2}{\beta}\right], \tag{D.27}$$

where each of the integrations in z' can be performed

$$\int_{-a}^{b}dz'\frac{z'}{\alpha\beta}=\frac{1}{2}\left(W_1(z)+W_2(z)\right), \tag{D.28}$$

$$\int_{-a}^{b}dz'\frac{z'}{\beta}=-2+zW_1(z), \tag{D.29}$$

$$\int_{-a}^{b}dz'\frac{z'^2}{\beta}=\frac{1}{2}\left[a(a-2z)-b(b+2z)\right]+z^2W_1(z). \tag{D.30}$$

Substituting Eqs. (D.28-D.30) in Eq. (D.27), and carrying through the elementary integrations over z, we obtain the following result for Φ_2 in terms of one quadrature

$$\Phi_2=-\frac{1}{2}\int_{-a}^{b}dzz\left[\lambda W_1(z)-(b+z)(z-a)W_2(z)\right]\ln|z|-\frac{1}{2}q(q+a^2\ln|a|-b^2\ln|b|). \tag{D.31}$$

We follow the same procedure for Φ_3 given in Eq. (D.17)

$$\begin{aligned}\Phi_3 &\overset{z\leftrightarrow z'}{=} \int_{-a}^{b} dz \ln|z| \int_{-a}^{b} dz' \frac{\lambda' z'^2}{\alpha\sqrt{R(z,z')}} \\ &= \int_{-a}^{b} dz \ln|z| \left[(b+z)(a-z) \int_{-a}^{b} dz' \frac{z'^2}{\alpha\sqrt{R(z,z')}} + (q+z) \int_{-a}^{b} dz' \frac{z'^2}{\sqrt{R(z,z')}} \right. \\ &\left. - \int_{-a}^{b} dz' \frac{z'^3}{\sqrt{R(z,z')}} \right]. \end{aligned} \tag{D.32}$$

Here we have

$$\int_{-a}^{b} dz' \frac{z'^2}{\alpha\sqrt{R(z,z')}} = \frac{1}{C_0}(2z+q) - \frac{1}{C_0^{3/2}} (B_0 + 2zC_0)\, Y(z) - \frac{z}{q} W_2(z), \tag{D.33}$$

$$\begin{aligned}\int_{-a}^{b} dz' \frac{z'^2}{\sqrt{R(z,z')}} &= \left(\frac{b}{2C_0} - \frac{3B_0}{4C_0^2}\right)\sqrt{R(z,b)} + \left(\frac{a}{2C_0} + \frac{3B_0}{4C_0^2}\right)\sqrt{R(z,-a)} \\ &+ \frac{2}{\sqrt{C_0}} \left(\frac{3B_0^2}{8C_0^2} - \frac{A_0}{2C_0}\right) Y(z), \end{aligned} \tag{D.34}$$

$$\begin{aligned}\int_{-a}^{b} dz' \frac{z'^3}{\sqrt{R(z,z')}} &= \left(\frac{b^2}{3C_0} - \frac{5B_0 b}{12C_0^2} + \frac{5B_0^2}{8C_0^3} - \frac{2A_0}{3C_0^2}\right)\sqrt{R(z,b)} - \left(\frac{a^2}{3C_0} + \frac{5B_0 a}{12C_0^2}\right. \\ &\left. + \frac{5B_0^2}{8C_0^3} - \frac{2A_0}{3C_0^2}\right)\sqrt{R(z,-a)} - \left(\frac{5B_0^3}{16C_0^3} - \frac{3A_0 B_0}{4C_0^2}\right) \frac{2}{\sqrt{C_0}} Y(z). \end{aligned} \tag{D.35}$$

Substituting Eqs. (D.33-D.35) in Eq. (D.32), we obtain with some algebra

$$\Phi_3 = \bar{\Phi}_1 + \bar{\Phi}_2 + \bar{\Phi}_3, \tag{D.36}$$

where

$$\bar{\Phi}_1 = -\frac{1}{q} \int_{-a}^{b} dz\, z \ln|z| (b+z)(a-z) W_2(z), \tag{D.37}$$

$$\begin{aligned}\bar{\Phi}_2 = \int_{-a}^{b} dz \Big[&-\frac{19}{32q^3} C_0^2 + \left(\frac{139}{96q^3} - \frac{9}{32q}\right) C_0 - \frac{15}{16q^3} + \frac{25}{16q} - \frac{5}{32} q + \left(\frac{1}{16q^3} - \frac{3}{4q} + \frac{17}{32} q + \frac{q^3}{32}\right) C_0^{-1} \\ &+ \left(-\frac{1}{16q} - \frac{13}{96q^3} + \frac{5q}{32} + \frac{q^3}{24}\right) C_0^{-2} + \left(\frac{5}{32q^3} - \frac{15}{32q} + \frac{15}{32} q - \frac{5}{32} q^3\right) C_0^{-3} \Big] \ln|z|, \end{aligned} \tag{D.38}$$

$$\bar{\Phi}_3 = \int_{-a}^{b} dz\, C_0^{-7/2}\Big[\left(-4+2q^2-\frac{q^4}{4}\right)z+\left(-16q+\frac{11}{2}q^3-\frac{q^5}{4}\right)z^2 + \left(8-20q^2+\frac{11}{2}q^4-\frac{q^6}{8}\right)z^3+\left(36q+2q^3+\frac{5}{4}q^5\right)z^4 + \left(60q^2+\frac{25}{2}q^4\right)z^5+35q^3z^6\Big]\ln|z|Y(z). \tag{D.39}$$

Evaluating $\bar{\Phi}_2$ is elementary. Moreover, it can be shown [119] that $\bar{\Phi}_3$ is equivalent to

$$\bar{\Phi}_3 = \frac{1}{8q}\sum_{n=-3}^{3}\gamma_n\frac{1}{2n+1}\left[(1+q)^{2n+1}\ln b\ln\left|\frac{2b}{q}\right| - \tilde{q}^{2n+1}\ln|a|\ln\left|\frac{\tilde{q}+1}{\tilde{q}-1}\right|+\Omega_n\right], \tag{D.40}$$

where

$$\gamma_3=\frac{35}{8q^3},\gamma_2=-\frac{45}{4q^3}+\frac{25}{8q},\gamma_1=\frac{69}{8q^3}-\frac{117}{8q}+\frac{5}{8}q,\gamma_0=-\frac{3}{2q^3}+\frac{29}{4q}+3q-\frac{q^3}{8},$$
$$\gamma_{-1}=-\frac{3}{8q^3}+\frac{11}{4q}-\frac{7}{4}q-\frac{q^3}{8},\gamma_{-2}=\frac{3}{4q^3}-\frac{3}{8q}-\frac{3q^3}{8},\gamma_{-3}=-\frac{5}{8q^3}+\frac{15}{8q}-\frac{15}{8}q+\frac{5q^3}{8}.$$

Here $\tilde{q}=|1-q|$ and the explicit expressions for $\Omega_{0,\pm1}$ are given in [119], for $\Omega_{\pm2,\pm3}$ in Appendix D.1.

D.1

$$\eta_3=\frac{1}{5}\big[4q(2+q^2)-2q(5+10q^2+q^4)\ln q-2(1-2q+4q^2-3q^3+q^4)a\ln|2a| + 2(1+2q+4q^2+3q^3+q^4)b\ln 2b\big],$$
$$\eta_5=\frac{1}{7}\Big[4q\left(3+\frac{13}{3}q^2+q^4\right)-2q(7+35q^2+21q^4+q^6)\ln q-2(1-3q+9q^2-13q^3 + 11q^4-5q^5+q^6)a\ln|2a|+2(1+3q+9q^2+13q^3+11q^4+5q^5+q^6)b\ln 2b\Big],$$
$$\eta_{-5}=\frac{1}{3}\Big[\frac{4q}{(q^2-1)^2}+2\ln\left|\frac{q+1}{q-1}\right|-\left(1+\frac{1}{(1+q)^3}\right)\ln 2b+\left(1+\frac{1}{(1-q)^3}\right)\ln|2a| + \frac{2q(q^2+3)}{(q^2-1)^3}\ln q\Big].$$

$$\Omega_{-3} = h_0(q) - 2q\left[\int_{-a}^{b} dz\left(C_0^{-3} + C_0^{-2} + C_0^{-1}\right)\ln|z|\right] + 2(\eta_{-3} + \eta_{-5}),$$

$$\Omega_{-2} = h_0(q) - 2q\left[\int_{-a}^{b} dz\left(C_0^{-2} + C_0^{-1}\right)\ln|z|\right] + 2\eta_{-3},$$

$$\begin{aligned}\Omega_2 = h_0(q) - \frac{1}{30}\Big[&q(416 + 108q^2) + q(240 + 120q^2)\ln 2 - q(60 + 300q + 80q^2 + 75q^3 \\ &+ (2b)(92 - 16q + 38q^2 + 21q^3 + 12q^4)\ln 2b - (\tilde{q}+1)(137 - 77\tilde{q} + 47\tilde{q}^2 - 27\tilde{q}^3 \\ &+ 12\tilde{q}^4)\ln|\tilde{q}+1| + 12q^4)\ln q + (\tilde{q}-1)(137 + 77\tilde{q} + 47\tilde{q}^2 + 27\tilde{q}^3 + 12\tilde{q}^4)\ln|\tilde{q}-1|\Big],\end{aligned}$$

$$\begin{aligned}\Omega_3 = h_0(q) + \frac{1}{210}\Big[&- q\left(4472 + \frac{9028}{3}q^2 + 520q^4\right) - q(2520 + 3640q^2 + 840q^4)\ln 2 \\ &+ q(420 + 4410q + 1260q^2 + 3675q^3 + 924q^4 + 490q^5 + 60q^6)\ln q - 2b(704 - 142q \\ &+ 386q^2 + 437q^3 + 464q^4 + 230q^5 + 60q^6)\ln 2b + (\tilde{q}+1)(1089 - 669\tilde{q} + 459\tilde{q}^2 \\ &- 319\tilde{q}^3 + 214\tilde{q}^4 - 130\tilde{q}^5 + 60\tilde{q}^6)\ln|\tilde{q}+1| - (\tilde{q}-1)(1089 + 669\tilde{q} + 459\tilde{q}^2 \\ &+ 319\tilde{q}^3 + 214\tilde{q}^4 + 130\tilde{q}^5 + 60\tilde{q}^6)\ln|\tilde{q}-1|.\end{aligned}$$

Bibliography

[1]M. Di Ventra and R. D'Agosta, Phys. Rev. Lett. **98**, 226403 (2007).

[2]X. Andrade, J. Alberdi-Rodriguez, D. A. Strubbe, M. J. T. Oliveira, F. Nogueira, A. Castro, J. Muguerza, A. Arruabarrena, S. G. Louie, A. Aspuru-Guzik, A. Rubio, and M. A. L. Marques, Time-dependent density-functional theory in massively parallel computer architectures: the octopus project, Journal of Physics: Condensed Matter **24**, 233202 (2012).

[3]H. Appel and M. Di Ventra, Phys. Rev. B **80**, 212303 (2009).

[4]H. Appel and M. D. Ventra, Chem. Phys. **391**, 27–36 (2011).

[5]A. Blais, R.-S. Huang, A. Wallraff, S. M. Girvin, and R. J. Schoelkopf, Phys. Rev. A **69**, 062320 (2004).

[6]M. Bonitz, Quantum Kinetic Theory (Teubner-Verlag, Stuttgart/Leipzig, 1998).

[7]D. Braak, Integrability of the Rabi model, Phys. Rev. Lett. **107**, 100401 (2011).

[8]K. Burke, The Journal of Chemical Physics **136**, 150901, (2012).

[9]H. Chen, J. M. McMahon, M. A. Ratner, and G. C. Schatz, The Journal of Physical Chemistry C **114**, 14384–14392 (2010).

[10]R. Dicke, Physical Review **93**, 99 (1954).

[11]R. M. Dreizler and E. K. U. Gross, Density Functional Theory - An Approach to the Quantum Many-Body Problem (Springer-Verlag, Berlin, 1990).

[12]E. Engel and R. M. Dreizler, Density Functional Theory - An Advanced Course (Springer-Verlag, Berlin, 2011).

[13]F. H. Faisal, Theory of multiphoton processes (Springer-Verlag, Berlin, 1987).

[14]M. Farzanehpour and I. Tokatly, Quantum electrodynamical time-dependent density-functional theory for many-electron systems on a lattice, Phys. Rev. B **90**, 195149 (2014).

[15]M. Farzanehpour and I. V. Tokatly, Time-dependent density functional theory on a lattice, Phys. Rev. B **86**, 125130 (2012).

[16]A. Fratalocchi and G. Ruocco, Phys. Rev. Lett. **106**, 105504 (2011).

[17]J. I. Fuks, M. Farzanehpour, I. V. Tokatly, H. Appel, S. Kurth, and A. Rubio, Time-dependent exchange-correlation functional for a Hubbard dimer: Quantifying nonadiabatic effects, Phys. Rev. A **88**, 062512 (2013).

[18]C. V. Gardiner and Z. P., Quantum Noise (Springer-Verlag, Berlin, 2004).

[19]C. Gerry and P. Knight, Introductory Quantum Optics (Cambridge University Press, 2005).

[20]R. J. Glauber, The Quantum Theory of Optical Coherence, Phys. Rev. **130**, 2529–2539 (1963).

[21]R. J. Glauber, Coherent and Incoherent States of the Radiation Field, Phys. Rev. **131**, 2766–2788 (1963).

[22]W. Greiner and J. Reinhard, Field Quantization (Springer-Verlag, Berlin, 1996).

[23]C. Hainzl and R. Seiringer, Mass renormalization and energy level shift in non-relativistic QED, Adv. Theor. Math. Phys **6**, 847–871 (2002).

[24]C. Hainzl and H. Siedentop, Non-Perturbative Mass and Charge Renormalization in Relativistic No-Photon Quantum Electrodynamics, English, Communications in Mathematical Physics **243**, 241–260 (2003).

[25]F. Hiroshima, Self-Adjointness of the Pauli-Fierz Hamiltonian for Arbitrary Values of Coupling Constants, English, Annales Henri Poincar **3**, 171–201 (2002).

[26]J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, and T. W. Ebbesen, Modifying Chemical Landscapes by Coupling to Vacuum Fields, Angewandte Chemie International Edition **51**, 1592–1596 (2012).

[27]T. Iwasa and K. Nobusada, Nonuniform light-matter interaction theory for near-field-induced electron dynamics, Physical Review A **80**, 043409 (2009).

[28]R. van Leeuwen, Mapping from Densities to Potentials in Time-Dependent Density-Functional Theory, Phys. Rev. Lett. **82**, 3863 (1999).

[29]Y. Li and C. A. Ullrich, Time-dependent V-representability on lattice systems, The Journal of Chemical Physics **129**, 044105 (2008).

[30]N. T. Maitra and K. Burke, Demonstration of initial-state dependence in time-dependent density-functional theory, Phys. Rev. A **63**, 042501 (2001).

[31]N. T. Maitra, K. Burke, H. Appel, E. K. U. Gross, and R. van Leeuwen, Ten topical questions in time-dependent density functional theory, in , edited by K. Sen (World Scientific, 2002), pp. 1186–1225.

[32]N. T. Maitra, K. Burke, and C. Woodward, Memory in Time-Dependent Density Functional Theory, Phys. Rev. Lett. **89**, 023002 (2002).

[33]M. A. Marques, N. T. Maitra, F. M. Nogueira, E. K. Gross, and A. Rubio, Fundamentals of time-dependent density functional theory, Vol. 837 (Springer, 2012).

[34]A. F. i Morral and F. Stellacci, Light-matter interactions: Ultrastrong routes to new chemistry, Nature Materials **11**, 272–273 (2012).

[35]N. B. Narozhny, J. J. Sanchez-Mondragon, and J. H. Eberly, Coherence versus incoherence: Collapse and revival in a simple quantum model, Phys. Rev. A **23**, 236–247 (1981).

[36]E. Nelson, Interaction of Nonrelativistic Particles with a Quantized Scalar Field, Journal of Mathematical Physics **5**, 1190–1197 (1964).

[37]S. E. B. Nielsen, M. Ruggenthaler, and R. van Leeuwen, Many-body quantum dynamics from the density, EPL (Europhysics Letters) **101**, 33001 (2013).

[38]J. M. Raimond, M. Brune, and S. Haroche, Manipulating quantum entanglement with atoms and photons in a cavity, Rev. Mod. Phys. **73**, 565–582 (2001).

[39]A. K. Rajagopal, Time-dependent functional theory of coupled electron and electromagnetic fields in condensed-matter systems, Phys. Rev. A **50**, 3759–3765 (1994).

[40]H. Ritsch, P. Domokos, F. Brennecke, and T. Esslinger, Cold atoms in cavity-generated dynamical optical potentials, Rev. Mod. Phys. **85**, 553–601 (2013).

[41]M. Ruggenthaler and R. van Leeuwen, Global fixed-point proof of time-dependent density-functional theory, EPL (Europhysics Letters) **95**, 13001 (2011).

[42]M. Ruggenthaler, F. Mackenroth, and D. Bauer, Time-dependent Kohn-Sham approach to quantum electrodynamics, Phys. Rev. A **84**, 042107 (2011).

[43]E. Runge and E. K. U. Gross, Density-functional theory for time-dependent systems, Phys. Rev. Lett. **52**, 997 (1984).

[44]L. H. Ryder, Quantum field theory (Cambridge University Press, Cambridge, 2006).

[45]K. Rzazewski and K. Wodkiewicz, Stability of matter interacting with photons, Phys. Rev. A **43**, 593–594 (1991).

[46]K. Rzazewski, K. Wodkiewicz, and W. Zakowicz, Phase Transitions, Two-Level Atoms, and the A^2 Term, Phys. Rev. Lett. **35**, 432–434 (1975).

[47]T. Schwartz, J. A. Hutchison, C. Genet, and T. W. Ebbesen, Reversible Switching of Ultrastrong Light-Molecule Coupling, Phys. Rev. Lett. **106**, 196405 (2011).

[48]M. O. Scully and M. S. Zubairyh, Quantum Optics (Cambridge University Press, Cambridge, 1997).

[49]B. Shore, The Theory of Coherent Atomic Excitation: Multilevel atoms and incoherence, The Theory of Coherent Atomic Excitation (Wiley, 1990).

[50]B. W. Shore and P. L. Knight, The Jaynes-Cummings Model, Journal of Modern Optics **40**, 1195–1238 (1993).

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

[52]P. Strange, Relativistic Quantum Mechanics: with applications in condensed matter and atomic physics (Cambridge University Press, Cambridge, 1998).

[53]T. Takaesu, On the spectral analysis of quantum electrodynamics with spatial cutoffs. I. Journal of Mathematical Physics **50**, 062302 (2009).

[54]Y. Todorov, A. M. Andrews, R. Colombelli, S. De Liberato, C. Ciuti, P. Klang, G. Strasser, and C. Sirtori, Ultrastrong Light-Matter Coupling Regime with Polariton Dots, Phys. Rev. Lett. **105**, 196402 (2010).

[55]I. V. Tokatly, Time-Dependent Density Functional Theory for Many-Electron Systems Interacting with Cavity Photons, Phys. Rev. Lett. **110**, 233001 (2013).

[56]I. V. Tokatly, Time-dependent current density functional theory on a lattice, Phys. Rev. B **83**, 035127 (2011).

[57]I. V. Tokatly, Quantum many-body dynamics in a Lagrangian frame: I. Equations of motion and conservation laws, Phys. Rev. B **71**, 165104 (2005).

[58]C. A. Ullrich, Time-Dependent Density-Functional Theory (Oxford University Press, Oxford, 2012).

[59]R. Van Leeuwen, Key concepts in time-dependent density-functional theory, International Journal of Modern Physics B **15**, 1969–2023 (2001).

[60]G. Vignale, Real-time resolution of the causality paradox of time-dependent density-functional theory, Phys. Rev. A **77**, 062511 (2008).

[61]G. Vignale, Mapping from current densities to vector potentials in time-dependent current density functional theory, Phys. Rev. B **70**, 201102 (2004).

[62]A. Vukics and P. Domokos, Adequacy of the Dicke model in cavity QED: A counter-no-go statement, Phys. Rev. A **86**, 053807 (2012).

[63]B. M. W. Greiner and J. Rafelski, Quantum Electrodynamics of Strong Fields (Springer-Verlag, Berlin, 1985).

[64]A. Wallraff, D. I. Schuster, A. Blais, L. Frunzio, R.-S. Huang, J. Majer, S. Kumar, S. M. Girvin, and R. J. Schoelkopf, Strong coupling of a single photon to a superconducting qubit using circuit quantum electrodynamics, Nature **431**, 162–167 (2004).

[65]H. Walther, B. T. Varcoe, B.-G. Englert, and T. Becker, Cavity quantum electrodynamics, Reports on Progress in Physics **69**, 1325 (2006).

[66]K. Yabana, T. Sugiyama, Y. Shinohara, T. Otobe, and G. F. Bertsch, Time-dependent density functional theory for strong electromagnetic fields in crystalline solids, Phys. Rev. B **85**, 045134 (2012).

[67]J. You and F. Nori, Atomic physics and quantum optics using superconducting circuits, Nature **474**, 589–597 (2011).

[68]J. Yuen-Zhou, C. Rodrıguez-Rosario, and A. Aspuru-Guzik, Time-dependent current-density functional theory for generalized open quantum systems, Phys. Chem. Chem. Phys. **11**, n/a, 4509–4522 (2009).

[69]J. Yuen-Zhou, D. G. Tempel, C. A. Rodrıguez-Rosario, and A. Aspuru-Guzik, Time-Dependent Density Functional Theory for Open Quantum Systems with Unitary Propagation, Phys. Rev. Lett. **104**, 043001 (2010).

[70]R. Baer, On the mapping of time-dependent densities onto potentials in quantum mechanics, The Journal of Chemical Physics **128**, 044103, (2008).

[71]S. Kümmel and L. Kronik, Orbital-dependent density functionals: Theory and applications, Rev. Mod. Phys. **80** (2008).

[72]D. Fausti, R. I. Tobey, N. Dean, S. Kaiser, A. Dienst, M. C. Hoffmann, S. Pyon, T. Takayama, H. Takagi, and A. Cavalleri, Light-Induced Superconductivity in a Stripe-Ordered Cuprate, Science **331**, 189–191 (2011).

[73]I. V. Tokatly, A unified approach to the density-potential mapping in a family of time-dependent density functional theories, Chem. Phys. **391** (2011).

[74]G. Breit, Dirac's Equation and the Spin-Spin Interactions of Two Electrons, Phys. Rev. **39**, 616 (1932).

[75]D. G. Tempel, M. A. Watson, R. Olivares-Amaya, and A. Aspuru-Guzik, Time-dependent density functional theory of open quantum systems in the linear-response regime, J. Chem. Phys. **134**, 074116 (2011).

[76]I. V. Tokatly, Time-Dependent Density Functional Theory for Many-Electron Systems Interacting with Cavity Photons, Phys. Rev Lett. **110**, 233001 (2013).

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

[78]D. P. Craig and T. Thirunamachandra, Molecular Quantum Electrodynamics (Academic Press, London, 1984).

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

[80]C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, Time-Dependent Optimized Effective Potential, Phys. Rev. Lett. **74**, 872 (1995).

[81]R. Leeuwen, The Sham-Schlüter Equation in Time-Dependent Density-Functional Theory, Phys. Rev. Lett. **76**, 3610 (1996).

[82]L. Hedin, New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem, Phys. Rev. **139**, A796 (1965).

[83]L. Onida, L. Reining, and A. Rubio, Electronic excitations: density-functional versus many-body Green?s-function approaches, Rev. Mod. Phys. **74**, 601 (2002).

[84]A. N. Mitra, Hans bethe, quantum mechanics, and the lamb shift, Resonance **10**, 33 (2005).

[85]T. Niemczyk, F. Deppe, H. Huebl, E. P. Menzel, F. Hocke, M. J. Schwarz, J. J. Garcia-Ripoli, D. Zueco, T. Hümmer, and E. e. a. Solano, Circuit quantum electrodynamics in the ultrastrong-coupling regime, Nat. Phys. **6**, 772 (2010).

[86]A. Crespi, S. Longhi, and R. Osellame, Photonic Realization of the Quantum Rabi Model, Phys. Rev. Lett. **108**, 163601 (2012).

[87]A. I. Streltsov, O. E. Alon, and L. S. Cederbaum, General mapping for bosonic and fermionic operators in Fock space, Phys. Rev. A **81**, 022124 (2010).

[88]J. Flick, H. Appel, and A. Rubio, Nonadiabatic and Time-Resolved Photoelectron Spectroscopy for Molecular Systems, J. Chem. Theory Comput. **10**, 4 (2014).

[89]H. O. Wijewardane and C. A. Ullrich, Real-Time Electron Dynamics with Exact-Exchange Time-Dependent Density-Functional Theory, Phys. Rev. Lett. **100**, 056404 (2008).

[90]P. Linz, Numerical methods for Volterra integral equations of the first kind, Comput J **12**, 4 (1969).

[91]A. Castro, M. A. Marques, and A. Rubio, Propagators for the time-dependent Kohn?Sham equations, J. Chem. Phys. **121**, 3425 (2004).

[92]W. M. Greiner and J. Reinhardt, Quantum Electrodynamics (Springer-Verlag, Berlin, 2009).

[93]J. J. Sakurai, Advanced Quantum Mechanics (Addison-Wesley, Reading, 1994).

[94]M. Fox, Quantum Optics-An Introduction (Oxford University Press, New York, 2006).

[95]M. M. Wilde, Quantum Information Theory (Cambridge University Press, Cambridge, 2013).

[96]W. Kohn, Nobel Lectures, Chemistry (World Scientific, Singapore, 2003).

[97]S. K. Ghosh and A. K. Dhara, Density-functional theory of many-electron systems subjected to time-dependent electric and magnetic fields, Phys. Rev. A **38**, 1149 (1988).

[98]G. Vignale and W. Kohn, Current-Dependent Exchange-Correlation Potential for Dynamical Linear Response Theory, Phys. Rev. Lett. **77**, 2037 (1996).

[99]G. Vignale and M. Rasolt, Current- and spin-density-functional theory for inhomogeneous electronic systems in strong magnetic fields, Phys. Rev. B. **37**, 10685 (1988).

[100]W. Kohn and L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Phys. Rev. **140**, A1133 (1965).

[101]K. Le Hur, H. Loïc, A. Petrescu, K. Plekhanov, G. Roux, and M. Schiró, Many-body quantum electrodynamics networks: Non-equilibrium condensed matter physics with light, Comptes Rendus Physique **17**, 808–835 (2016).

[102]K. Capelle and V. L. Líbero, Spin-density functional theory: Some open problems and application to inhomogeneous Heisenberg models, Int. J. Quantum Chem. **105**, 679–686 (2005).

[103]P. Hohenberg and W. Kohn, Inhomogeneous Electron Gas, Phys. Rev. 136 **136** (1964).

[104]R. van Leeuwen, The Sham-Schlüter Equation in Time-Dependent Density-Functional Theory, Phys. Rev. Lett. **76** (1996).

[105]C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, Time-Dependent Optimized Effective Potential, Phys. Rev. Lett. **74** (1995).

[106]C. A. Ullrich, U. J. Gossmann, and E. K. U. Gross, Density-functional approach to atoms in strong laser pulses, Ber. Bunsenges. Phys. Chem. **99**, 488–497 (1995).

[107]B. M. Garraway, The Dicke model in quantum optics: Dicke model revisited, Phil. Trans. R. Soc. A **369**, 1137–1155 (2011).

[108]D. Braak, Q.-H. Chen, M. T. Batchelor, and E. Solano, Semi-classical and quantum Rabi models: in celebration of 80 years, J. Phys. A: Mathematical and Theoretical **49** (2016).

[109]H. Walther, B. T. H. Varcoe, B.-G. Englert, and T. Becker, Cavity quantum electrodynamics, Reports on Progress in Physics **69** (2006).

[110]S. S. P. Parkin, M. Hayashi, and L. Thomas, Magnetic Domain-Wall Racetrack Memory, Science **320**, 190–194 (2008).

[111]S.-H. Parkin, S. and Yang, Memory on the racetrack, Nature Nanotechnology **10**, 195–198 (2015).

[112]D. A. e. a. Allwood, Magnetic Domain-Wall Logic, Science **309**, 1688 (2005).

[113]S. Krause and R. Wiesendanger, Skyrmionics gets hot, Nature Materials **15**, 493–494 (2016).

[114]R. F. L. Evans, J. W. Fan, P. Chureemart, T. A. Ostler, M. O. A. Ellis, and R. W. Chantrell, Atomistic spin model simulations of magnetic nanomaterials, J. of Phys.: Cond. Matt. **26**, 10 (2014).

[115]C. Andreas, S. Gliga, and R. Hertel, Numerical micromagnetism of strong inhomogeneities, Journal of Magnetism and Magnetic Materials **362**, 7–13 (2014).

[116]D. Belitz and T. R. Kirkpatrick, Quantum electrodynamics and the origins of the exchange, dipole-dipole, and Dzyaloshinsky-Moriya interactions in itinerant fermion systems, Phys. Rev. B **81**, 184419 (2010).

[117]E. Engel and H. Vosko, Wave-vector dependence of the exchange contribution to the electron-gas response functions: An analytic derivation, Phys. Rev. B **42**, 4940 (1990).

[118] M. L. Glasser, Exchange corrections to the static Lindhard screening function, Phys. Rev. B **51**, 7283 (1995).

[119] Z. Qian, Static dielectric function with exact exchange contribution in the electron liquid, J. Math. Phys. **56**, 111901 (2015).

[120] A. O. Caldeira, Quantum tunnelling in a dissipative system, Ann. of Phys. **149**, 2 (1983).