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Executive Summary of the Thesis

QED Solver for ab-initio cavity materials engineering

Laurea Magistrale in Physics Engineering - Ingegneria Fisica

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1. Introduction

Controlling the properties of materials is a central theme in our societies since the beginning of human history [1]. Nowadays, thanks to all of the advances in science and technologies, we are able to modify the fundamental properties of materials to their very core, for instance by creating nanostructures that can confine electrons [2, 3] or by inducing new behaviors, such as changing the ground state properties [4] or enabling a superconductive phase [5], when the material is strongly perturbed. One way to control such properties is using the interaction between light and matter [6–8]. The phenomena arising from the coupling between them have been studied for a long time, starting from the first laws on the static description of the electric and magnetic field, then through the Maxwell's equations, the semi-classical, and finally the modern full quantum light-matter interaction theories. For the light to modify the properties of materials, the coupling must be in the so-called strong regime. It only became possible to reach such a regime in the last century, firstly thanks to the laser, and in more recent times thanks to the optical cavities, which can confine light in a small region in space. This allows to achieve strong coupling by using a low-intensity field or just by exploiting the quantum fluctuations of light, therefore opening many possibilities for controlling materials even at equilibrium [4, 7, 9]. All these exciting possibilities are made possible by the strong light-matter coupling, which mixes the electronic and photonic states, to generate the so-called polaritons [10, 11]. However, while molecules and finite systems have been deeply studied in the strong light-matter coupling regime, much less has been done for crystals/solids. Such systems are characterized by a greater physical and computational complexity with respect to finite ones. In this work, a tool for computing the polaritonic states arising from materials in optical cavities is presented. We use a quantum description of both the matter (using Slater determinants built from the single-particle states calculated using Density Functional Theory) and of the cavity field (using Fock states). After defining and solving the QED Hamiltonian on that basis, we use the obtained polaritonic states to compute response functions in the framework of linear response theory.

This executive summary uses the same structure as the thesis manuscript, with the exception that here the implementation of software is only men-

tioned. As a consequence, section 2 contains a theoretical overview of QED, starting from the quantization of the electromagnetic field and the description of electrons in condensed matter. Section 3 deals with the methods and approximations used in this work, as well as a brief mention of the implementation. Finally, section 4 contains the main results of the thesis. The software is released under the TDDFT code Octopus [12], with the name of *QED Solver*.

2. Theoretical background

To study the strong light-matter coupling regime, one needs to treat both the electromagnetic field and the matter with a full quantum description using the Quantum Electrodynamics (QED) theory in the non-relativistic approximation.

One should start by describing the two main ingredients (the radiation field and the behavior of electrons in matter) in a quantum way. For the former, one can follow Dirac's Canonical Quantization Protocol [13], which states that one should first write the Hamiltonian of the field in terms of classical conjugated variables, then substitute them with the quantum operator and finally impose the commutation relations. By following this recipe, it is possible to write the expression of the Hamiltonian of the electromagnetic field as

$$\widehat{H} = \sum_{\boldsymbol{k}} \sum_{\lambda=1,2} \omega_{\boldsymbol{k}} \left(\widehat{a}^{\dagger}_{\boldsymbol{k},\lambda} \widehat{a}_{\boldsymbol{k},\lambda} + \frac{1}{2} \right) \tag{1}$$

where $\widehat{a}^{\dagger}_{\boldsymbol{k},\lambda}, \widehat{a}_{\boldsymbol{k},\lambda}$ are the creation and annihilation operators for the mode $\boldsymbol{k}$ and the polarization λ. If we assume that the light is linearly polarized, then the vector potential reads

$$\begin{aligned} \boldsymbol{A}(\boldsymbol{r},t) = \sum_{\boldsymbol{k}} \sum_{\lambda=1,2} \boldsymbol{e}_{\boldsymbol{k},\lambda} A_{\boldsymbol{k}} \\ \left[\widehat{a}_{\boldsymbol{k},\lambda} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_{\boldsymbol{k}}t)} + \widehat{a}^{\dagger}_{\boldsymbol{k},\lambda} e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_{\boldsymbol{k}}t)} \right] \end{aligned} \tag{2}$$

where $A_{\boldsymbol{k}} = \frac{1}{2\epsilon_0 V \omega_{\boldsymbol{k}}}$, from which it is possible to retrieve the expression for the electronic and magnetic field [14].

As for electrons in solids, one has to deal with a many-body problem. In principle, one can write the full quantum Hamiltonian of the system by considering all the kinetic energies of both electrons and nuclei, as well as the Coulomb interaction between every couple of particles. The complexity of this problem is very high, but thanks to the Density Functional Theory (DFT) [15] it is possible to link the energy of the ground state to the electronic density. Such theory comes from the Hohenberg-Kohn theorems (1964) [16] and it is exact. The way in which it is implemented is to build a system of independent particles whose ground state density is the same of the one of the interacting many-body system. Then, since the ground state energy is a universal functional of the density, having the density of the system of independent particles allows computing the ground state energy. Such a system is described by the set of the Kohn-Sham equations (one for each particle), which in atomic units read:

$$\begin{aligned} \left[-\frac{\nabla^2}{2} + V_n(\boldsymbol{r}) + V_H(\boldsymbol{r}) + V_{xc}(\boldsymbol{r}) \right] \phi_i(\boldsymbol{r}) \\ = \epsilon_i \phi_i(\boldsymbol{r}) \end{aligned} \tag{3}$$

where $V_n(\boldsymbol{r})$ is the potential generated by the nuclei, $V_H(\boldsymbol{r})$ is the Hartree potential and $V_{xc}(\boldsymbol{r})$ is the exchange-correlation potential. However, to this day an analytical expression for the latter is not known. As a consequence, the way in which these equations are implemented is usually by using a self-consistent cycle for the ground state density, so that it is possible to compute the energy and the single-particle states. Finally, one can retrieve the solution to the many-body problem by building Slater determinants from these single-particle states.

Once both the electromagnetic field and the matter are quantized, it is possible to study their interaction. To do that, one has to start from equation (3) and perform the canonical momentum substitution $\widehat{\mathbf{p}} \rightarrow \widehat{\mathbf{p}} - \widehat{\mathbf{A}}$ for every particle. After some algebra, and also introducing the single-mode approximation for the electromagnetic field, one obtains:

$$\begin{aligned} \widehat{H}_{QED} = \sum_{i=1}^{N_{el}} \left(\frac{\widehat{\mathbf{p}}_{\mathbf{i}}^{\,2}}{2} + \widehat{V}_{tot}(\mathbf{r}_{\mathbf{i}}) \right) \\ + \omega \left(\frac{1}{2} + \widehat{a}^{\dagger}\widehat{a} \right) + \frac{N_{el}\widehat{\mathbf{A}}^2}{2} - \sum_{i=1}^{N_{el}} \widehat{\mathbf{p}}_{\mathbf{i}} \cdot \widehat{\mathbf{A}} \end{aligned} \tag{4}$$

where N_{el} represents the total number of electrons in each unit cell. It is easy to see that the first term corresponds to a sum of single particles Hamiltonians. The second term corresponds

to the Hamiltonian of the radiation field and the last two terms are the ones that effectively couple the electrons with the field. The states that arise from the solution of such Hamiltonian are called polaritonic states, from the quasi-particle (the polariton) that is associated with the propagation of light in matter.

3. Methods

The software developed in this thesis work aims to apply equation (4) to study strongly coupled light-matter systems. As mentioned in the introduction, its solution is expected to be a mix of electronic and photonic states, called *dressed* or polaritonic states. As a consequence, the starting point is to define the basis of the Hamiltonian from the uncoupled electronic and photonic states (because each of those diagonalizes a part of the uncoupled Hamiltonian). In particular, we describe the matter part by using Slater determinants built on top of the single-particle Kohn-Sham states, and the radiation part using Fock states. For the former, we will have one Slater determinant representing the ground state and many others representing all possible transitions from the valence band to the conduction band: $\{el\} : \{|\Psi_{GS}\rangle, |\Psi_{ex,1}\rangle \dots |\Psi_{ex,n}\rangle\}$. We assume that the transitions can only be vertical and that the Slater determinants are singly-excited. As a consequence, $|\Psi_{ex,1}\rangle$ means that we are considering a transition from a certain state of the valence band to a certain state of the conduction band at a given k point. As for the photonic part, since we use the For states, the basis will be $\{|n\rangle\} = \{|0\rangle, |1\rangle, ..., |n\rangle\}$. For the electromagnetic field we only consider the mode at $\boldsymbol{k} = 0$, which justifies the vertical transitions. Finally, the basis for representing equation (4) will be the tensor product of the electron and photon part:

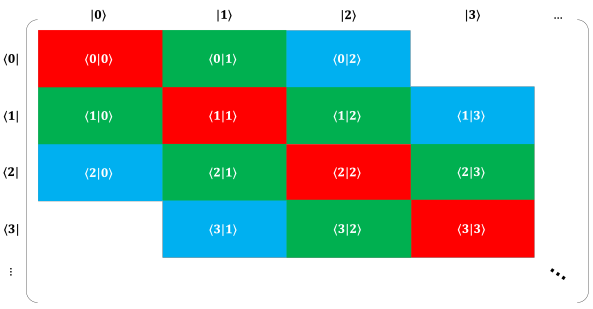

Figure 1: Block structure of the QED matrix.

$$\{|\Psi_{GS}\rangle, \{|\Psi_{ex}\rangle\}\} \otimes \{|n\rangle\} \tag{5}$$

and the generic matrix element of the Hamiltonian will be

$$\langle n| \langle \Psi_i| \widehat{H}_{QED} |\Psi_j\rangle |m\rangle \tag{6}$$

By applying all the aforementioned assumptions and by using the language of the second quantization, it is possible to rewrite equation (4) in:

$$\begin{aligned} \widehat{H}_{QED} &= \sum_{i,k} \epsilon^{KS}_{i,k} \widehat{c}^{\dagger}_{i,k} \widehat{c}_{i,k} + \omega \left(\frac{1}{2} + \widehat{a}^{\dagger} \widehat{a} \right) \\ &+ \frac{N_{el} A_0^2}{2} \left(\widehat{a}^{\dagger 2} + \widehat{a}^2 + 2\widehat{a}^{\dagger} \widehat{a} + 1 \right) \\ &- A_0 \sum_{i \neq j,k} \langle \phi_{i,k} | \, \widehat{\boldsymbol{p}} \cdot \boldsymbol{e} \, | \phi_{j,k} \rangle \, \widehat{c}^{\dagger}_{i,k} \widehat{c}_{j,k} \left(\widehat{a}^{\dagger} + \widehat{a} \right) \end{aligned} \tag{7}$$

where ϕ are the single-particle Kohn-Sham states coming from DFT. If one computes all the matrix elements of equation (6), then it is possible to give a matrix representation of equation (7). Such a matrix has a penta-diagonal block structure as in figure 1, which means that only the highlighted blocks have non-zero elements. Moreover, it is possible to show that the red and blue blocks are diagonal, which means that they only have non-zero elements on their main diagonal, while the green blocks (which correspond to the bilinear coupling) have non-zero elements mainly on the first row and column. The dimension of the matrix is given by the expression

$$\begin{aligned} DIM &= (1 + VB_{states} * CB_{states} * k_{points}) \\ &* (N_{ph} + 1) \end{aligned} \tag{8}$$

where VB_{states}, CB_{states} are the number of states in the valence band and conduction band, k_{points} the number of k points used in the calculation, and N_{ph} the number of Fock states included.

From equation (8) it can be understood that the dimension of the matrix is quite large, especially for systems for which a high number of k points are required. An example is Graphene, for which one needs to sample the Brillouin zone around the Dirac cones with a dense grid. This can push the dimension of the QED Matrix well above 100000×100000. To deal with such computational complexity, the software is highly parallelized, which means that the storage of the matrix as well as the computation is distributed

among a large number of CPUs. Each of them manages a small part of the matrix, and then they communicate to make sure that they are all aware of the others (otherwise the parallelization leads to erroneous results). The code developed in this thesis work is written in Fortran 90 and is designed to run on computer clusters, in the framework of HPC (High Performance Computing).

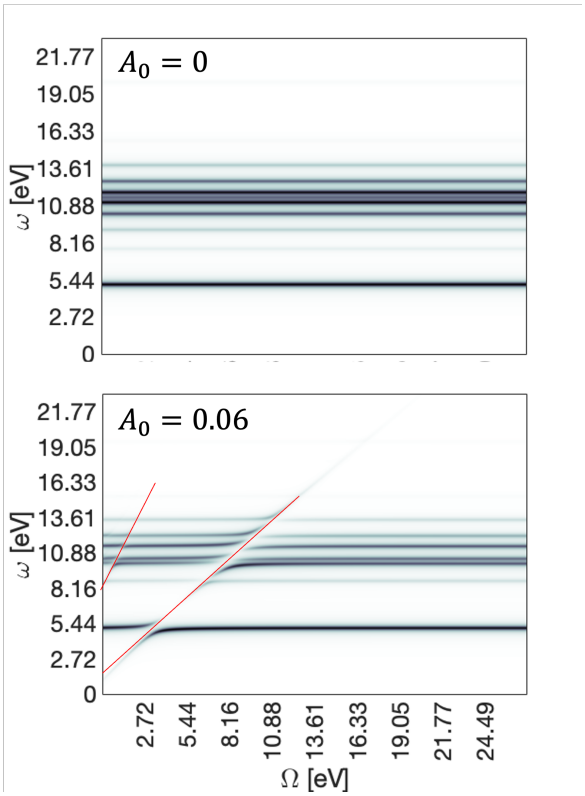

Figure 2: Linear optical response of Benzene for two values of the coupling parameter A_0

4. Results

The software developed in this work was used to study three different systems, in particular the Benzene molecule (as a finite system), the LiH chain (as a 1D system) and Graphene (2D system). In this executive summary we only briefly discuss the results of the linear optical response. To do that, firstly we compute the polaritonic states by diagonalizing the QED matrix, then we apply a probe field to study the behavior of the system. To investigate the effect of the probing field with we implemented the following response function [9, 17]:

$$\chi(\Omega,\omega) = \frac{1}{n}\sum_{I>1}\frac{\left|\langle\Psi_I|\,\widehat{\boldsymbol{P}}\cdot\boldsymbol{e}_{probe}\,|\Psi_0\rangle\right|^2}{\omega-(E_{pol,I}(\Omega)-E_{pol,0}(\Omega))+i\eta}$$

where Ψ_I are the polaritonic states, ω is the energy if the probe beam, $E_{pol,I}(\Omega)$ are the polariton eigenvalues for a given cavity resonance energy Ω and η is an artificial broadening.
Let us consider the Benzene molecule. By applying the formula above one gets the behavior in figure 2, where on the x axis there is the cavity energy Ω and on the y axis the probe energy ω. For the value of $A_0 = 0$ one gets the absorption spectrum of Benzene, because that case corresponds to not having the cavity. Indeed, the HOMO-LUMO transition of Benzene is at $5.11eV$. However, if one compares this result with the literature [18, 19], the transition should happen at $6.9eV$. This difference can be explained by the fact that in the present work the dynamic response was disregarded, while that was accounted for in both reference papers (which were using a time-dependent approach). In such a framework, they included the variation of the exchange-correlation potential that happens after the optical response, which gives the difference in the transition energy. When we switch on the cavity $A_0 = 0.06$, one can see that the linear response lines are split into two branches, which is proof of the appearance of the polariton. The split corresponds to the Rabi splitting. In the thesis we show that the split increases linearly with A_0, as one would expect.
Let us now consider the LiH chain, which constitutes a good introduction to periodic systems. Its Brillouin zone was sampled with 81 k points, and three conduction band states were observed. In the thesis work we show that the transitions from the valence band to the first two conduction bands (which are degenerate) are forbidden. When the cavity is switched on (top panel of figure 3) the band corresponding to transitions from the valence band to the third conduction band is split due to the appearance of the polariton. It is interesting to note that in this case we do have a band, as transitions are possible from any point of the valence band. As a consequence, apart from seeing a line we also see a shadowed region. In the panel below in figure 3, we consider the linear response for different values of A_0 at the cavity energy of $\Omega = 24.46eV$. It can be seen that by increasing the coupling strength A_0, the Rabi splitting between the upper polariton and the lower polariton (which are the two peaks) increases linearly.

Finally, we used the software to study the behavior of Graphene. This material is much more complicated than the previous systems because a fine sampling of the Brillouin zone is needed to correctly describe the Dirac cones.

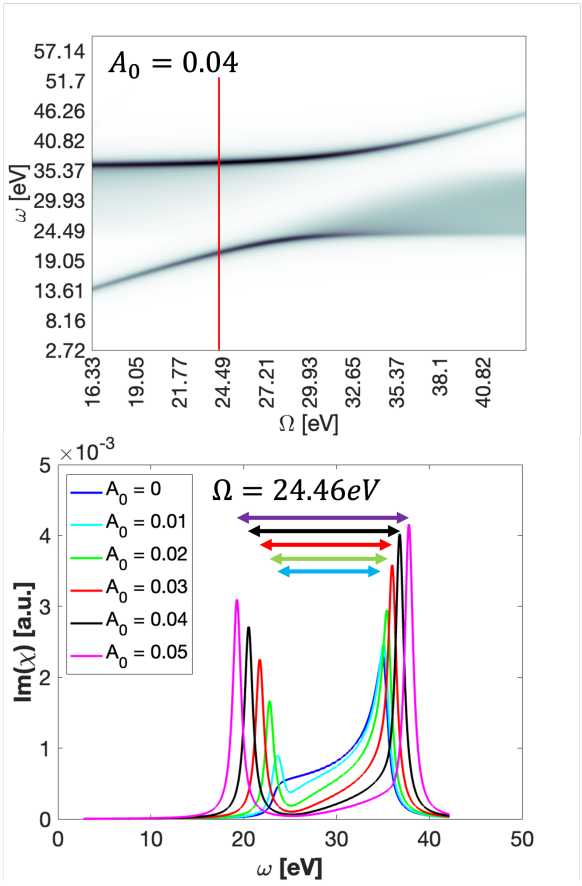

Figure 3: Linear optical response of LiH chain. On the panel above the contour plot for $A_0 = 0.04$, on the one below the response for various values of A_0 for $\Omega = 24.46eV$ (red line in the panel above).

This makes the calculations very heavy, to the point that it was not possible to generate a contour plot for χ. In the thesis we show that our software can reproduce the response of Graphene without the cavity and that there is an indication that a gap in the band structure is opened when chiral light is used. However, one also observes other features which are complicated to explain. As a consequence, understanding what happens in Graphene is to be considered a future development of this thesis work.

5. Conclusions

In this executive summary we introduced a new software for studying materials in the framework of cavity QED. We started by briefly describing the theoretical background, firstly by quantizing the electromagnetic field and by describing how it is possible to solve the electronic problem in condensed matter systems. Then we introduced QED by stating the Hamiltonian describing the full light-matter system, and finally we introduced the concept of polariton. Subsequently, we described how we solved the QED Hamiltonian, firstly by stating which approximations were used, then by defining the basis onto which to project Hamiltonian and finally by briefly describing the structure of the matrix representation. Moreover, we briefly introduced some computational challenges of the development of the software. We stress that the structure of this summary is the same as the thesis manuscript. Finally, we discussed the main results of the thesis, by showing the results for the Rabi splitting from both the LiH chain and the Benzene molecule.

In conclusion, in this thesis work we developed a software that allows studying any material in a QED cavity, starting only from the Kohn-Sham states (which can be easily computed using DFT). This is relevant because the flexibility of the code allows approaching systems spanning from molecular to bulk in an efficient and controllable way for any light-matter coupling regime. Moreover, since the code was parallelized and it was written with a programming language highly optimized for numeric computation, the complexity of the systems that we will be able to study in the future will increase significantly as scientists will be able to make use of this code in the computer clusters of their institutes.

Finally, the future developments of this project are twofold. On one hand, it will be interesting to use the software to study more complex systems such as Weyl semi-metals. For those, the number of k points required to correctly sample the Weyl points is very high due to the extra dimension (the material is 3D), which will require a big computational effort. The hope is to control the position of such points and affect the topological chiral currents associated with them. On the other hand, the development of the soft-

ware will continue to include new features, such as the correlation between electrons and the possibility of computing the ground-state electronic density from the polaritonic states and exploiting it to develop DFT functional with built-in light-matter correlation.

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