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# A nonlinear Bloch model for Coulomb interaction in quantum dots

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## Abstract

In this paper we first derive a Coulomb Hamiltonian for electron-electron interaction in quantum dots in the Heisenberg picture. Then we use this Hamiltonian to enhance a Bloch model, which happens to be nonlinear in the density matrix. The coupling with Maxwell equations when interaction with an electromagnetic field is also considered from the Cauchy problem point of view. The study is completed by numerical results and a discussion about the advisability of neglecting intra-band coherences, as is done in part of the literature.

Keywords: Maxwell-Bloch model, quantum dot, Coulomb interaction, Cauchy problem, Liouville model, positiveness properties.

## 1 Introduction

Bloch model is a very common model to describe the time evolution of a system of electrons in different contexts such as gases of electrons, glasses or crystals. The very classical case of gases and glasses involves isotropic media. The electrons are supposed to be localized and non interacting. Their behavior is averaged at the mesoscopic scale. This leads to relatively simple models where matter energy levels are quantized and labelled by integers. The case of crystals [BBFB+04] also involves levels integer indexed levels, but symmetries and directions in matter have to be taken into account.

Bloch model has also been extended for the description of quantum wells [HK96, KR92], and quantum dots [GH02, BF10]. In these models matter is described by the state of two species of particles (electrons and holes, or equivalently valence and conduction electrons). In quantum wells, energy levels are

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indexed by vectors. In contrast the confinement of electrons in quantum dots leads to integer indexed levels like in gases, which often leads to consider quantum dots as pseudo-atoms, but this is a very raw vision. In particular, among other differences, electrons at the same mesoscopic location do interact directly *via* Coulomb interaction.

[BF10] is a preliminary paper that derives raw Bloch equations for two species of electrons (conduction and valence) only taking into account the free electron Hamiltonian and the interaction with a laser electric field. The aim of the present paper is to include properly Coulomb interaction in this model. Beyond the sole derivation of the model, we want in particular to study its mathematical properties. In the continuation of [Bid01, BBR01], we want to show that a certain number of properties are preserved through the time evolution, such as Hermiticity and positiveness of the density matrix.

## 1.1 The raw Bloch model

Let us first recall the main results obtained in [BF10] and fix the notations.

### 1.1.1 Commutators and Heisenberg equation

Let  $A$  and  $B$  be two operators, we define their commutator by  $[A, B] = AB - BA$  and their skew-commutator by  $\{A, B\} = AB + BA$ . For an operator  $A$ , we will define the associated observable  $\langle A \rangle = \text{Tr}(S_0 A)$  by averaging with respect to the initial state density  $S_0$  of the system. If the system is described by an Hamiltonian  $H$ , the time-evolution for this observable is given by the Heisenberg equation

$$i\hbar\partial_t\langle A \rangle = \langle [A, H] \rangle. \quad (1)$$

When the observable is the density matrix, the Heisenberg equation of motion is called the Bloch equation.

### 1.1.2 Operators for quantum dots

A quantum dot is defined as a collection of conduction and valence electrons. There is of course no conduction in quantum dots since the electrons are confined in every direction, but this terminology is useful to distinguish between the valence electrons — which are in fact the absence of holes in the valence band, see Section 2.2 — and the free, but confined, electrons. For each species, energy levels are quantized and indexed by a set of integers,  $I^c$  and  $I^v$ , for conduction and valence electrons respectively. For  $i \in I^c$ , we define the creation and annihilation operators  $c_i^\dagger$  and  $c_i$ . Electrons are fermions and should respect the Pauli exclusion principle. The corresponding skew-commutation rules are

$$\{c_i, c_j\} = \{c_i^\dagger, c_j^\dagger\} = 0, \quad \{c_i, c_j^\dagger\} = \delta_{i,j}.$$

This implies in particular that  $c_i c_i = c_i^\dagger c_i^\dagger = 0$ , which means clearly that it is impossible to create twice or annihilate twice the same electron. This is the Pauli exclusion rule.

Likewise, for valence electrons, we define the creation and annihilation operators  $v_i^\dagger$  and  $v_i$ , for which

$$\{v_i, v_j\} = \{v_i^\dagger, v_j^\dagger\} = 0, \quad \{v_i, v_j^\dagger\} = \delta_{i,j}.$$

Of course any conduction operator commutes with any valence operator.

### 1.1.3 Observables for quantum dots

The observable we are interested in is the *density matrix*. It includes a *conduction density matrix*, which elements are the  $\rho_{ij}^c = \langle c_j^\dagger c_i \rangle$ . This matrix is clearly Hermitian. Its diagonal terms  $\rho_{ii}^c = \langle c_i^\dagger c_i \rangle$  are also called *populations* and give the probability to find an electron in state  $i$ . The off-diagonal terms,  $\rho_{ij}^c$ ,  $i \neq j$  are called (*intra-band*) *coherences*. Of course we also define a *valence density matrix*, which elements are the  $\rho_{ij}^v = \langle v_j^\dagger v_i \rangle$ . Besides we are interested in *inter-band coherences* defined by  $\rho_{ij}^{cv} = \langle v_j^\dagger c_i \rangle$ . The entries of these matrices are the variables of the Bloch equation. They are cast in a single density matrix

$$\rho = \begin{pmatrix} \rho^c & \rho^{cv} \\ \rho^{vc} & \rho^v \end{pmatrix}$$

where  $\rho^{vc} = \rho^{cv*}$ , which ensures that  $\rho$  is Hermitian.

### 1.1.4 Free electron Hamiltonians and interaction with a laser

The raw Bloch equation for quantum dot is derived in [BF10]. It takes into account two types of Hamiltonians in the Heisenberg equation for the density matrix, namely free electron Hamiltonians and interaction Hamiltonians with a laser field. The free electron Hamiltonians read

$$H_0^c = \sum_{k \in I^c} \epsilon_k^c c_k^\dagger c_k, \quad H_0^v = \sum_{k \in I^v} \epsilon_k^v v_k^\dagger v_k,$$

for conduction and valence electrons respectively. The coefficients  $\epsilon_k^c$  and  $\epsilon_k^v$  are the free electron energies associated to each electron level (eigen-state). The interaction with a laser characterized by its time-dependent electric field  $\mathbf{E}(t)$  is described by the Hamiltonians

$$\begin{aligned} H^{Lc} &= \frac{1}{2} \sum_{(k,l) \in (I^c)^2} (\mathbf{E}(t) \cdot \mathbf{M}_{kl}^c c_k^\dagger c_l + \mathbf{E}^*(t) \cdot \mathbf{M}_{kl}^{c*} c_l^\dagger c_k), \\ H^{Lv} &= \frac{1}{2} \sum_{(k,l) \in (I^v)^2} (\mathbf{E}(t) \cdot \mathbf{M}_{kl}^v v_k^\dagger v_l + \mathbf{E}^*(t) \cdot \mathbf{M}_{kl}^{v*} v_l^\dagger v_k), \\ H^{Lcv} &= \sum_{(k,l) \in I^c \times I^v} (\mathbf{E}(t) \cdot \mathbf{M}_{kl}^{cv} c_k^\dagger v_l + \mathbf{E}^*(t) \cdot \mathbf{M}_{kl}^{cv*} v_l^\dagger c_k), \end{aligned}$$

where the dipolar moment matrices may be expressed in terms of the wave functions associated to each level:

$$\begin{aligned}\mathbf{M}_{kl}^c &= \int dr \psi_l^{c*}(r) r \psi_k^c(r), \\ \mathbf{M}_{kl}^v &= \int dr \psi_l^{v*}(r) r \psi_k^v(r), \\ \mathbf{M}_{kl}^{cv} &= \int dr \psi_l^{v*}(r) r \psi_k^c(r).\end{aligned}$$

Injecting these Hamiltonians in the Heisenberg equation, the raw Bloch equations can be cast in Liouville form

$$i\hbar\partial_t\rho = [V_0(t), \rho]. \quad (2)$$

In equation (2),  $V_0(t) = V^F + V^E(t)$  is a sum of a constant term  $V^F$  stemming from the free energies collected in diagonal matrices  $E_0^c = \text{diag}(\{\epsilon_i^c\}_{i \in I^c})$  and  $E_0^v = \text{diag}(\{\epsilon_i^v\}_{i \in I^v})$ , and a time dependent term due to the interaction with the electric field:

$$V^F = \begin{pmatrix} E_0^c & 0 \\ 0 & E_0^v \end{pmatrix} \text{ and } V^E(t) = \begin{pmatrix} \Re\mathbf{E}(t) \cdot \mathbf{M}^c & \mathbf{E}(t) \cdot \mathbf{M}^{cv} \\ \mathbf{E}^*(t) \cdot \mathbf{M}^{cv*} & \Re\mathbf{E}(t) \cdot \mathbf{M}^v \end{pmatrix}.$$

### 1.1.5 Mathematical properties of the Liouville equation

Equation (2) clearly preserves the Hermitian structure of  $\rho$ . Its exact solution is

$$\rho(t) = \exp\left(-\frac{i}{\hbar} \int_0^t V_0(\tau) d\tau\right) \rho(0) \exp\left(\frac{i}{\hbar} \int_0^t V_0(\tau) d\tau\right). \quad (3)$$

This expression allows to prove a certain number of properties (see [BF10]), in particular:

- Equation (2) is globally well-posed,
- for all time  $\rho(t)$  is a positive matrix,
- its trace is conserved through the time evolution.

## 1.2 Issues related to the Coulomb Hamiltonian

The outline of this paper is as follows. In Section 2 we derive the Coulomb Hamiltonian in terms of the conduction and valence operators. The associated Heisenberg equation is derived in Section 3, but it ends up with an open system of equations. The system is closed in Section 4 using Hartree-Fock approximation, and the final Bloch equation has a Liouville form, but is nonlinear. This nonlinearity does not allow to use previous literature directly and we prove anew the Hermiticity, positiveness and boundedness results in Section 5. In Section 6 we show the impact of the Coulomb contribution in numerical results and also compare our model with a vanishing inter-band coherence model defined in [GH02].

## 2 Second quantification Coulomb Hamiltonian

### 2.1 Electron–hole model

Coulomb interaction is easier to introduce first in the electron–hole picture and using field operators. We denote by  $\hat{\psi}_e^\dagger(r)$  and  $\hat{\psi}_h^\dagger(r)$  the creation field-operators of respectively an electron and a hole at the space location  $r$ , and  $\hat{\psi}_e(r)$  and  $\hat{\psi}_h(r)$  the corresponding annihilation field-operators. Then considering that there are  $N$  relevant electrons in the quantum dot, we can simply write the Coulomb Hamiltonians as

$$H^{e-e} = \frac{1}{2} \sum_{i,j=1}^N \iint dr_i dr_j \hat{\psi}_e^\dagger(r_i) \hat{\psi}_e^\dagger(r_j) V^e(r_i, r_j) \hat{\psi}_e(r_j) \hat{\psi}_e(r_i), \quad (4a)$$

$$H^{h-h} = \frac{1}{2} \sum_{i,j=1}^N \iint dr_i dr_j \hat{\psi}_h^\dagger(r_i) \hat{\psi}_h^\dagger(r_j) V^h(r_i, r_j) \hat{\psi}_h(r_j) \hat{\psi}_h(r_i), \quad (4b)$$

$$H^{e-h} = \sum_{i,j=1}^N \iint dr_i dr_j \hat{\psi}_e^\dagger(r_i) \hat{\psi}_h^\dagger(r_j) V^{e-h}(r_i, r_j) \hat{\psi}_h(r_j) \hat{\psi}_e(r_i), \quad (4c)$$

where  $V^e$ ,  $V^h$  and  $V^{e-h}$  are the electron–electron, hole–hole and electron–hole Coulomb potentials. The total Coulomb Hamiltonian is  $H^C = H^{e-e} + H^{h-h} + H^{e-h}$ . We want to derive Bloch-type equations for the Coulomb interaction. Bloch equations have the advantage not to depend explicitly on the exact form of the field-operators. To this aim we write

$$\hat{\psi}_e(r) = \sum_{\alpha \in I^e} \psi_\alpha^e(r) c_\alpha, \quad \hat{\psi}_e^\dagger(r) = \sum_{\alpha \in I^e} \psi_\alpha^{e*}(r) c_\alpha^\dagger, \quad (5a)$$

$$\hat{\psi}_h(r) = \sum_{\alpha \in I^h} \psi_\alpha^h(r) d_\alpha, \quad \hat{\psi}_h^\dagger(r) = \sum_{\alpha \in I^h} \psi_\alpha^{h*}(r) d_\alpha^\dagger. \quad (5b)$$

In this decomposition  $c_\alpha$  (resp.  $d_\alpha$ ) is the annihilation operator for electrons (resp. holes) and  $c_\alpha^\dagger$  (resp.  $d_\alpha^\dagger$ ) is the corresponding creation operator, where  $\alpha$  take its values in the set of indices  $I^e$  (resp.  $I^h$ ) for electrons (resp. holes) states. They are weighted by the electron and hole wave functions  $\psi_\alpha^e(r)$  and  $\psi_\alpha^h(r)$ . In the sequel, to avoid unnecessary written complexity, we will often omit to specify which set the indices belong to. Pauli exclusion principle is ensured by skew-commutation properties. Of course electron operators commute with hole operators. The properties are expressed using skew-commutators  $\{A, B\} = AB + BA$  and the Kronecker symbol  $\delta$ .

#### Property 1.

$$\begin{aligned} \{c_\alpha, c_\beta^\dagger\} &= \delta_{\alpha\beta}, & \{c_\alpha, c_\beta\} &= \{c_\alpha^\dagger, c_\beta^\dagger\} = 0, \\ \{d_\alpha, d_\beta^\dagger\} &= \delta_{\alpha\beta}, & \{d_\alpha, d_\beta\} &= \{d_\alpha^\dagger, d_\beta^\dagger\} = 0. \end{aligned}$$

Inserting decompositions (5) in Hamiltonians (4) we obtain

$$H^{e-e} = \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^e c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1}, \quad (6a)$$

$$H^{h-h} = \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^h d_{\alpha_1}^\dagger d_{\alpha_2}^\dagger d_{\alpha'_2} d_{\alpha'_1}, \quad (6b)$$

$$H^{e-h} = \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{e-h} c_{\alpha_1}^\dagger d_{\alpha_2}^\dagger d_{\alpha'_2} c_{\alpha'_1}, \quad (6c)$$

where

$$R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^e = \frac{N^2}{2} \iint dr dr' \psi_{\alpha_1}^{e*}(r) \psi_{\alpha_2}^{e*}(r') V^e(r, r') \psi_{\alpha'_2}^e(r') \psi_{\alpha'_1}^e(r), \quad (7a)$$

$$R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^h = \frac{N^2}{2} \iint dr dr' \psi_{\alpha_1}^{h*}(r) \psi_{\alpha_2}^{h*}(r') V^h(r, r') \psi_{\alpha'_2}^h(r') \psi_{\alpha'_1}^h(r), \quad (7b)$$

$$R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{e-h} = N^2 \iint dr dr' \psi_{\alpha_1}^{e*}(r) \psi_{\alpha_2}^{h*}(r') V^{e-h}(r, r') \psi_{\alpha'_2}^h(r') \psi_{\alpha'_1}^e(r). \quad (7c)$$

The symmetries in the integrands induce the following properties.

**Property 2.** Since  $V(r, r')$  is an even function of  $r - r'$ , variables  $r$  and  $r'$  play the same role and

$$R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^e = R_{\alpha_2 \alpha_1 \alpha'_2 \alpha'_1}^e, \quad R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^h = R_{\alpha_2 \alpha_1 \alpha'_2 \alpha'_1}^h.$$

Since  $V(r, r')$  is a real valued function

$$R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^e = R_{\alpha'_1 \alpha'_2 \alpha_1 \alpha_2}^{e*}, \quad R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^h = R_{\alpha'_1 \alpha'_2 \alpha_1 \alpha_2}^{h*},$$

$$R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{e-h} = R_{\alpha'_1 \alpha'_2 \alpha_1 \alpha_2}^{e-h*}.$$

The Pauli exclusion principle (skew-commutation, Property 1) also induces that some terms in  $H^{e-e}$  and  $H^{h-h}$  are necessarily zero.

**Property 3.** If  $\alpha_1 = \alpha_2$  or  $\alpha'_1 = \alpha'_2$ ,

$$c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1} = 0, \quad d_{\alpha_1}^\dagger d_{\alpha_2}^\dagger d_{\alpha'_2} d_{\alpha'_1} = 0.$$

The Coulomb interaction is intended to be included in a global Bloch-type model. It has been shown in [BF10] that the electron-hole formulation is not proper to write a Bloch model and that a conduction-valence electron model should be used instead.

## 2.2 Conduction–valence electron model

The electrons described in the previous section are viewed as conduction electrons. The presence of a hole in the valence band is the absence of the corresponding valence electron. Creating a hole is annihilating a valence electron and vice-versa. We can therefore recover creation and annihilation operators for valence electrons already used in Section 1.1.2 as  $v_\alpha^\dagger = d_\alpha$  and  $v_\alpha = d_\alpha^\dagger$ .

The order of the operators (which has to be read from the right to the left) in the Coulomb Hamiltonians (4) has a meaning: in order that two particles interact via Coulomb interact they have to pre-exist at locations  $r_i$  and  $r_j$ . Then they are annihilated while interacting and recreated at the same locations. The transformed Coulomb Hamiltonians (6) obey the same rule.

**Definition 1.** A product of operators will be said to be in the *canonical form*, if the annihilation operators are on the right and the creation operators on the left.

If we replace hole operators by valence electron operators in the Hamiltonians (6), we do not obtain canonical forms.

$$H^{\text{h-h}} = \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{\text{h}} v_{\alpha_1} v_{\alpha_2} v_{\alpha'_2}^\dagger v_{\alpha'_1}^\dagger,$$

$$H^{\text{e-h}} = \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{\text{e-h}} c_{\alpha_1}^\dagger v_{\alpha_2} v_{\alpha'_2}^\dagger c_{\alpha'_1},$$

**Notation 1.** In computations we underline the part of the expression which is transformed at the next step, e.g.

$$\underline{v_\alpha v_\beta^\dagger} = \delta_{\alpha\beta} - v_\beta^\dagger v_\alpha.$$

For the reader's convenience, many details of the computations using the (skew-)commutation rules and Notation 1 are postponed to an appendix.

To express  $H^{\text{h-h}}$  we need to compute a canonical form of  $v_{\alpha_1} v_{\alpha_2} v_{\alpha'_2}^\dagger v_{\alpha'_1}^\dagger$  (see details in Appendix A)

$$\begin{aligned} v_{\alpha_1} v_{\alpha_2} v_{\alpha'_2}^\dagger v_{\alpha'_1}^\dagger &= \delta_{\alpha_1 \alpha'_1} \delta_{\alpha_2 \alpha'_2} - \delta_{\alpha_1 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_2} - \delta_{\alpha_2 \alpha'_1} \delta_{\alpha_1 \alpha'_2} + \delta_{\alpha_2 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_1} \\ &\quad + \delta_{\alpha_1 \alpha'_2} v_{\alpha'_1}^\dagger v_{\alpha_2} - \delta_{\alpha_2 \alpha'_2} v_{\alpha'_1}^\dagger v_{\alpha_1} + v_{\alpha'_1}^\dagger v_{\alpha'_2}^\dagger v_{\alpha_2} v_{\alpha_1}. \end{aligned}$$

Thanks to Property 2,  $R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{\text{h}} = R_{\alpha_2 \alpha_1 \alpha'_2 \alpha'_1}^{\text{h}}$ , therefore  $-\delta_{\alpha_1 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_2}$  and  $-\delta_{\alpha_2 \alpha'_2} v_{\alpha'_1}^\dagger v_{\alpha_1}$  lead to the same contribution. The same argument can be applied to  $\delta_{\alpha_2 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_1}$  and  $\delta_{\alpha_1 \alpha'_2} v_{\alpha'_1}^\dagger v_{\alpha_2}$ . Hence

$$H^{\text{v-v}} = 2 \sum_{\alpha, \alpha', \beta} (R_{\alpha\beta\beta\alpha'}^{\text{h}} - R_{\beta\alpha\beta\alpha'}^{\text{h}}) v_{\alpha'}^\dagger v_\alpha + \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{\text{h}} v_{\alpha'_1}^\dagger v_{\alpha'_2}^\dagger v_{\alpha_2} v_{\alpha_1}.$$



In the definition of  $H^{v-v}$  we have dropped the  $\delta_{\alpha_1\alpha'_1}\delta_{\alpha_2\alpha'_2}$  and  $-\delta_{\alpha_2\alpha'_1}\delta_{\alpha_1\alpha'_2}$  terms which would lead to zero contributions in the Heisenberg equation.

In the same way  $c_{\alpha_1}^\dagger v_{\alpha_2} v_{\alpha'_2}^\dagger c_{\alpha'_1} = \delta_{\alpha_2\alpha'_2} c_{\alpha_1}^\dagger c_{\alpha'_1} - c_{\alpha_1}^\dagger v_{\alpha'_2}^\dagger v_{\alpha_2} c_{\alpha'_1}$ , hence

$$H^{e-h} = \sum_{\alpha,\alpha',\beta} R_{\alpha\beta\alpha'\beta}^{e-h} c_\alpha^\dagger c_{\alpha'} - \sum_{\substack{\alpha_1,\alpha_2, \\ \alpha'_1,\alpha'_2}} R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^{e-h} c_{\alpha_1}^\dagger v_{\alpha'_2}^\dagger v_{\alpha_2} c_{\alpha'_1}.$$

Setting

$$R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^c = R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^e, \quad R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^v = R_{\alpha'_1\alpha'_2\alpha_1\alpha_2}^h, \quad R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^{c-v} = -R_{\alpha_1\alpha'_2\alpha'_1\alpha_2}^{e-h},$$

we can define the Coulomb Hamiltonian in the conduction–valence electron picture

$$H^{c-c} = \sum_{\substack{\alpha_1,\alpha_2, \\ \alpha'_1,\alpha'_2}} R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^c c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1}, \quad (8a)$$

$$H^{v-v} = \sum_{\substack{\alpha_1,\alpha_2, \\ \alpha'_1,\alpha'_2}} R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^v v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_2} v_{\alpha'_1} + 2 \sum_{\alpha,\alpha',\beta} (R_{\beta\alpha\alpha'\beta}^v - R_{\beta\alpha\beta\alpha'}^v) v_\alpha^\dagger v_{\alpha'}, \quad (8b)$$

$$H^{c-v} = \sum_{\substack{\alpha_1,\alpha_2, \\ \alpha'_1,\alpha'_2}} R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^{c-v} c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_2} c_{\alpha'_1} - \sum_{\alpha,\alpha',\beta} R_{\alpha\beta\alpha'\beta}^{c-v} c_\alpha^\dagger c_{\alpha'}. \quad (8c)$$

### 3 Exact formulation of the Heisenberg equation

We now write Heisenberg equation (1) where  $A$  are operators  $c_j^\dagger c_i$ ,  $v_j^\dagger v_i$  or  $v_j^\dagger c_i$  and  $H$  are the Hamiltonians defined by Equation (8).

#### 3.1 Commutators involving $c_j^\dagger c_i$

In order to derive the Heisenberg equation we have to compute  $[c_j^\dagger c_i, H^{c-c}]$  and  $[c_j^\dagger c_i, H^{c-v}]$  (since  $[c_j^\dagger c_i, H^{v-v}]$  is clearly zero).

##### 3.1.1 Commutator with $H^{c-c}$

According to Equation (8a)

$$[c_j^\dagger c_i, H^{c-c}] = \sum_{\substack{\alpha_1,\alpha_2, \\ \alpha'_1,\alpha'_2}} R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^c [c_j^\dagger c_i, c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1}].$$

*Remark 1.* We already know many situations where  $[c_j^\dagger c_i, c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1}]$  is necessarily zero:

- if none of the indices  $\alpha_1, \alpha_2, \alpha'_1, \alpha'_2$  is equal either to  $i$  or  $j$ ,

- if  $\alpha_1 = \alpha_2$  or  $\alpha'_1 = \alpha'_2$  (see Property 3),

We compute separately each commutator (see details in Appendix B)

$$\begin{aligned} [c_j^\dagger c_i, c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'}] &= \delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} + \delta_{i\alpha_2} c_j^\dagger c_{\alpha_1}^\dagger c_{\alpha_1'} c_{\alpha_2'} \\ &\quad - \delta_{j\alpha_2'} c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger c_{\alpha_1'} c_i - \delta_{j\alpha_1'} c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_i. \end{aligned}$$

Using Property 2, we see that

$$\begin{aligned} [c_j^\dagger c_i, H^{c-c}] &= \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha_1', \alpha_2'}} R_{\alpha_1 \alpha_2 \alpha_1' \alpha_2'}^c \left( 2\delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} - 2\delta_{j\alpha_1'} c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_i \right) \\ &= 2 \sum_{\substack{\alpha, \\ \alpha_1', \alpha_2'}} R_{i\alpha\alpha_1'\alpha_2'}^c c_j^\dagger c_\alpha^\dagger c_{\alpha_2'} c_{\alpha_1'} - 2 \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 j \alpha'}^c c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'} c_i. \end{aligned} \quad (9)$$

*Remark 2.* Here we have made an implicit choice. We could have written

$$\begin{aligned} [c_j^\dagger c_i, c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'}] &= -\delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_1'} c_{\alpha_2'} - \delta_{i\alpha_2} c_j^\dagger c_{\alpha_1}^\dagger c_{\alpha_2'} c_{\alpha_1'} \\ &\quad + \delta_{j\alpha_2'} c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_1'} c_i + \delta_{j\alpha_1'} c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger c_{\alpha_2'} c_i \end{aligned}$$

to obtain

$$[c_j^\dagger c_i, H^{c-c}] = -2 \sum_{\substack{\alpha, \\ \alpha_1', \alpha_2'}} R_{\alpha i \alpha_1' \alpha_2'}^c c_j^\dagger c_\alpha^\dagger c_{\alpha_2'} c_{\alpha_1'} + 2 \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 \alpha' j}^c c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'} c_i.$$

This choice is connected with the one mentioned in Remarks 3 and 4.

### 3.1.2 Commutator with $H^{c-v}$

According to Equation (8c)

$$[c_j^\dagger c_i, H^{c-v}] = \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha_1', \alpha_2'}} R_{\alpha_1 \alpha_2 \alpha_1' \alpha_2'}^{c-v} [c_j^\dagger c_i, c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'}] - \sum_{\alpha, \alpha', \beta} R_{\alpha \beta \alpha' \beta}^{c-v} [c_j^\dagger c_i, c_\alpha^\dagger c_{\alpha'}].$$

To evaluate the commutators we compute

$$\begin{aligned} c_j^\dagger c_i c_\alpha^\dagger c_{\alpha'} &= \delta_{i\alpha} c_j^\dagger c_{\alpha'} - \underline{c_j^\dagger c_\alpha^\dagger c_i c_{\alpha'}} = \delta_{i\alpha} c_j^\dagger c_{\alpha'} - c_\alpha^\dagger \underline{c_j^\dagger c_{\alpha'} c_i} \\ &= \delta_{i\alpha} c_j^\dagger c_{\alpha'} - \delta_{j\alpha'} c_\alpha^\dagger c_i + c_\alpha^\dagger c_{\alpha'} c_j^\dagger c_i. \end{aligned}$$

Applying this to  $(\alpha, \alpha') = (\alpha_1, \alpha_1')$  in the first sum we obtain

$$\begin{aligned} [c_j^\dagger c_i, H^{c-v}] &= \sum_{\substack{\alpha, \\ \alpha_1', \alpha_2'}} R_{i\alpha\alpha_1'\alpha_2'}^{c-v} c_j^\dagger v_\alpha^\dagger v_{\alpha_2'} c_{\alpha_1'} - \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 j \alpha'}^{c-v} c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'} c_i \\ &\quad - \sum_{\alpha', \beta} R_{i\beta\alpha'\beta}^{c-v} c_j^\dagger c_{\alpha'} + \sum_{\alpha, \beta} R_{\alpha\beta j \beta}^{c-v} c_\alpha^\dagger c_i. \end{aligned} \quad (10)$$

## 3.2 Commutators involving $v_j^\dagger v_i$

### 3.2.1 Commutator with $H^{v-v}$

According to Equation (8b), we have to evaluate two types of commutators to evaluate  $[v_j^\dagger v_i, H^{v-v}]$ . The first commutator is clearly computed in the same way as  $[c_j^\dagger c_i, H^{c-c}]$  replacing conduction electron operators by valence ones. For the second part, we have to compute  $[v_j^\dagger v_i, v_\alpha^\dagger v_{\alpha'}]$ . Since

$$\begin{aligned} v_j^\dagger v_i v_\alpha^\dagger v_{\alpha'} &= \delta_{i\alpha} v_j^\dagger v_{\alpha'} - v_j^\dagger v_\alpha^\dagger v_i v_{\alpha'} = \delta_{i\alpha} v_j^\dagger v_{\alpha'} - v_\alpha^\dagger v_j^\dagger v_{\alpha'} v_i \\ &= \delta_{i\alpha} v_j^\dagger v_{\alpha'} - \delta_{j\alpha'} v_\alpha^\dagger v_i + v_\alpha^\dagger v_{\alpha'} v_j^\dagger v_i, \end{aligned}$$

we have

$$\begin{aligned} \sum_{\alpha, \alpha', \beta} (R_{\beta\alpha\alpha'\beta}^v - R_{\beta\alpha\beta\alpha'}^v) [v_j^\dagger v_i, v_\alpha^\dagger v_{\alpha'}] \\ &= \sum_{\alpha, \alpha', \beta} (R_{\beta\alpha\alpha'\beta}^v - R_{\beta\alpha\beta\alpha'}^v) (\delta_{i\alpha} v_j^\dagger v_{\alpha'} - \delta_{j\alpha'} v_\alpha^\dagger v_i) \\ &= \sum_{\alpha', \beta} (R_{\beta i \alpha' \beta}^v - R_{\beta i \beta \alpha'}^v) v_j^\dagger v_{\alpha'} - \sum_{\alpha, \beta} (R_{\beta \alpha j \beta}^v - R_{\beta \alpha \beta j}^v) v_\alpha^\dagger v_i. \end{aligned}$$

Hence

$$\begin{aligned} [v_j^\dagger v_i, H^{v-v}] &= 2 \sum_{\substack{\alpha, \\ \alpha'_1, \alpha'_2}} R_{i\alpha\alpha'_1\alpha'_2}^v v_j^\dagger v_\alpha^\dagger v_{\alpha'_2} v_{\alpha'_1} - 2 \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1\alpha_2j\alpha'}^v v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'} v_i \\ &+ 2 \sum_{\alpha', \beta} (R_{\beta i \alpha' \beta}^v - R_{\beta i \beta \alpha'}^v) v_j^\dagger v_{\alpha'} - 2 \sum_{\alpha, \beta} (R_{\beta \alpha j \beta}^v - R_{\beta \alpha \beta j}^v) v_\alpha^\dagger v_i. \quad (11) \end{aligned}$$

### 3.2.2 Commutator with $H^{c-v}$

According to Equation (8c), the commutator  $[v_j^\dagger v_i, H^{c-v}]$  only involves the first term of  $H^{c-v}$ , which we can write as

$$[v_j^\dagger v_i, H^{c-v}] = \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^{c-v} c_{\alpha_1}^\dagger c_{\alpha'_1} [v_j^\dagger v_i, v_{\alpha_2}^\dagger v_{\alpha'_2}].$$

Setting  $(\alpha, \alpha') = (\alpha_2, \alpha'_2)$  in the previous commutator computation, we deduce that

$$\begin{aligned} [v_j^\dagger v_i, H^{c-v}] &= \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1\alpha_2\alpha'_1\alpha'_2}^{c-v} c_{\alpha_1}^\dagger c_{\alpha'_1} (\delta_{i\alpha_2} v_j^\dagger v_{\alpha'_2} - \delta_{j\alpha'_2} v_{\alpha_2}^\dagger v_i) \\ &= \sum_{\substack{\alpha, \\ \alpha'_1, \alpha'_2}} R_{\alpha i \alpha'_1 \alpha'_2}^{c-v} c_\alpha^\dagger v_j^\dagger v_{\alpha'_2} c_{\alpha'_1} - \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1\alpha_2\alpha'j}^{c-v} c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_i c_{\alpha'}. \quad (12) \end{aligned}$$

### 3.3 Commutators involving $v_j^\dagger c_i$

#### 3.3.1 Commutator with $H^{c-c}$

According to Equation (8a)

$$[v_j^\dagger c_i, H^{c-c}] = \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^c v_j^\dagger [c_i, c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1}].$$

We compute

$$\begin{aligned} \underline{c_i c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1}} &= \delta_{i\alpha_1} c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1} - c_{\alpha_1}^\dagger \underline{c_i c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1}} \\ &= \delta_{i\alpha_1} c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1} - \delta_{i\alpha_2} c_{\alpha_1}^\dagger c_{\alpha'_2} c_{\alpha'_1} + c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_i c_{\alpha'_2} c_{\alpha'_1} \\ &= \delta_{i\alpha_1} c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1} - \delta_{i\alpha_2} c_{\alpha_1}^\dagger c_{\alpha'_2} c_{\alpha'_1} + c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'_2} c_{\alpha'_1} c_i. \end{aligned}$$

Hence, using Property 2,

$$[v_j^\dagger c_i, H^{c-c}] = 2 \sum_{\substack{\alpha, \\ \alpha'_1, \alpha'_2}} R_{i\alpha\alpha'_1\alpha'_2}^c v_j^\dagger c_\alpha^\dagger c_{\alpha'_2} c_{\alpha'_1}. \quad (13)$$

#### 3.3.2 Commutator with $H^{v-v}$

In the same way, according to Equation (8b)

$$\begin{aligned} [v_j^\dagger c_i, H^{v-v}] &= \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^v [v_j^\dagger, v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_2} v_{\alpha'_1}] c_i \\ &\quad + 2 \sum_{\alpha, \alpha', \beta} (R_{\beta\alpha\alpha'\beta}^v - R_{\beta\alpha\beta\alpha'}^v) [v_j^\dagger, v_\alpha^\dagger v_{\alpha'}] c_i \end{aligned}$$

and

$$\begin{aligned} \underline{v_j^\dagger v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_2} v_{\alpha'_1}} &= v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger \underline{v_j^\dagger v_{\alpha'_2} v_{\alpha'_1}} \\ &= \delta_{j\alpha'_2} v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_1} - v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_2} \underline{v_j^\dagger v_{\alpha'_1}} \\ &= \delta_{j\alpha'_2} v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_1} - \delta_{j\alpha'_1} v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_2} + v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_2} v_{\alpha'_1} v_j^\dagger. \end{aligned}$$

Hence, using Property 2,

$$\sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^v [v_j^\dagger, v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_2} v_{\alpha'_1}] c_i = 2 \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 \alpha' j}^v v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'} c_i.$$

Since  $\underline{v_j^\dagger v_\alpha^\dagger v_{\alpha'}} = -v_\alpha^\dagger \underline{v_j^\dagger v_{\alpha'}} = -\delta_{j\alpha'} v_\alpha^\dagger + v_\alpha^\dagger v_{\alpha'} v_j^\dagger$ , we have

$$\sum_{\alpha, \alpha', \beta} (R_{\beta\alpha\alpha'\beta}^v - R_{\beta\alpha\beta\alpha'}^v) [v_j^\dagger, v_\alpha^\dagger v_{\alpha'}] c_i = - \sum_{\alpha, \beta} (R_{\beta\alpha j \beta}^v - R_{\beta\alpha\beta j}^v) v_\alpha^\dagger c_i.$$

Hence

$$[v_j^\dagger c_i, H^{v-v}] = 2 \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 \alpha' j}^v v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'} c_i - 2 \sum_{\alpha, \beta} (R_{\beta \alpha j \beta}^v - R_{\beta \alpha \beta j}^v) v_\alpha^\dagger c_i. \quad (14)$$

### 3.3.3 Commutator with $H^{c-v}$

According to Equation (8a)

$$\begin{aligned} [v_j^\dagger c_i, H^{c-v}] &= \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{c-v} [v_j^\dagger c_i, c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_1} c_{\alpha'_2}] \\ &\quad - \sum_{\alpha, \alpha', \beta} R_{\alpha \beta \alpha' \beta}^{c-v} v_j^\dagger [c_i, c_\alpha^\dagger c_{\alpha'}]. \end{aligned}$$

To evaluate the first sum (see details in Appendix C)

$$v_j^\dagger c_i c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_1} c_{\alpha'_2} = \delta_{i \alpha_1} v_j^\dagger v_{\alpha_2}^\dagger v_{\alpha'_1} c_{\alpha'_2} - \delta_{j \alpha'_2} c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger c_{\alpha'_1} c_i + c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_1} c_{\alpha'_2} v_j^\dagger c_i,$$

and

$$\begin{aligned} \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'_1, \alpha'_2}} R_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2}^{c-v} [v_j^\dagger c_i, c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'_1} c_{\alpha'_2}] &= \sum_{\substack{\alpha, \\ \alpha'_1, \alpha'_2}} R_{i \alpha \alpha'_1 \alpha'_2}^{c-v} v_j^\dagger v_\alpha^\dagger v_{\alpha'_1} c_{\alpha'_2} \\ &\quad - \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 \alpha' j}^{c-v} c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger c_{\alpha'} c_i. \end{aligned}$$

Last,  $\underline{c_i c_\alpha^\dagger c_{\alpha'}} = \delta_{i \alpha} c_{\alpha'} - c_\alpha^\dagger c_i c_{\alpha'} = \delta_{i \alpha} c_{\alpha'} + c_\alpha^\dagger c_{\alpha'} c_i$ , and

$$\sum_{\alpha, \alpha', \beta} R_{\alpha \beta \alpha' \beta}^{c-v} v_j^\dagger [c_i, c_\alpha^\dagger c_{\alpha'}] = \sum_{\alpha', \beta} R_{i \beta \alpha' \beta}^{c-v} v_j^\dagger c_{\alpha'}.$$

Hence

$$\begin{aligned} [v_j^\dagger c_i, H^{c-v}] &= \sum_{\substack{\alpha, \\ \alpha'_1, \alpha'_2}} R_{i \alpha \alpha'_1 \alpha'_2}^{c-v} v_j^\dagger v_\alpha^\dagger v_{\alpha'_1} c_{\alpha'_2} - \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 \alpha' j}^{c-v} c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger c_{\alpha'} c_i \\ &\quad - \sum_{\alpha', \beta} R_{i \beta \alpha' \beta}^{c-v} v_j^\dagger c_{\alpha'}. \end{aligned} \quad (15)$$

## 4 Hartree-Fock approximation

### 4.1 Principle

For the free Hamiltonians and the laser interactions the computation of the commutators led to expressions in terms of the two-operator densities, and therefore to a closed set of equations. This is not the case any more here,

since the commutators stemming from Coulomb Hamiltonians are expressed in terms of four-operator observables. To go further we should *a priori* have evolution equations for these observables *via* the Heisenberg equation, computing commutators with the already defined Coulomb Hamiltonians. This would lead inevitably to six-operator observables, and so on. To avoid this endless procedure, we have to close the system at some point. This is the goal of the Hartree–Fock approximation. In general, the Hartree–Fock approximation is one way to take into account the antisymmetry of  $N$ -electron wave functions. This approximation assumes that the  $N$ -electron wave function may be cast as a Slater determinant of 1-electron wave functions. In the Heisenberg operator formulation, this amounts to write the four-operator observables as products of two-operator densities.

To perform this, we first destroy the canonical form given by Definition 1, e.g.

$$c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} = \delta_{\alpha_2 \alpha_2'} c_{\alpha_1}^\dagger c_{\alpha_1'} - c_{\alpha_1}^\dagger c_{\alpha_2'} c_{\alpha_2}^\dagger c_{\alpha_1'},$$

and then approximate the mean of the four-operator by

$$\langle c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} \rangle \stackrel{\text{(HF)}}{=} \delta_{\alpha_2 \alpha_2'} \langle c_{\alpha_1}^\dagger c_{\alpha_1'} \rangle - \langle c_{\alpha_1}^\dagger c_{\alpha_2'} \rangle \langle c_{\alpha_2}^\dagger c_{\alpha_1'} \rangle,$$

where the symbol  $\stackrel{\text{(HF)}}{=}$  means "is approximated in the Hartree–Fock approximation by".

We use the approximation to compute the means of Equations (9) to (15).

*Remark 3.* In the above example, we chose to couple  $\alpha_1$  and  $\alpha_2'$  on the one hand and  $\alpha_2$  and  $\alpha_2'$  on the other hand. We could have also chosen to couple  $\alpha_1$  and  $\alpha_1'$  and  $\alpha_2$  and  $\alpha_2'$ .

## 4.2 Evolution of conduction electron densities

We apply the Hartree–Fock approximation to the two four-operators involved in Equation (9), which leads to

$$\begin{aligned} \langle c_j^\dagger c_\alpha^\dagger c_{\alpha_2'} c_{\alpha_1'} \rangle &\stackrel{\text{(HF)}}{=} \delta_{\alpha \alpha_2'} \langle c_j^\dagger c_{\alpha_1'} \rangle - \langle c_j^\dagger c_{\alpha_2'} \rangle \langle c_\alpha^\dagger c_{\alpha_1'} \rangle = \delta_{\alpha \alpha_2'} \rho_{\alpha_1' j}^c - \rho_{\alpha_2' j}^c \rho_{\alpha_1' \alpha}^c, \\ \langle c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha'} c_i \rangle &\stackrel{\text{(HF)}}{=} \delta_{\alpha_2 \alpha'} \langle c_{\alpha_1}^\dagger c_i \rangle - \langle c_{\alpha_1}^\dagger c_{\alpha'} \rangle \langle c_{\alpha_2}^\dagger c_i \rangle = \delta_{\alpha_2 \alpha'} \rho_{i \alpha_1}^c - \rho_{\alpha' \alpha_1}^c \rho_{i \alpha_2}^c. \end{aligned}$$

Hence

$$\begin{aligned} \langle [c_j^\dagger c_i, H^{c-c}] \rangle &\stackrel{\text{(HF)}}{=} 2 \sum_{\alpha, \alpha'} R_{i \alpha \alpha' \alpha}^c \rho_{\alpha' j}^c - 2 \sum_{\substack{\alpha, \\ \alpha_1', \alpha_2'}} R_{i \alpha \alpha_1' \alpha_2'}^c \rho_{\alpha_2' j}^c \rho_{\alpha_1' \alpha}^c \\ &\quad - 2 \sum_{\alpha, \alpha'} R_{\alpha \alpha' j \alpha'}^c \rho_{i \alpha}^c + 2 \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 j \alpha'}^c \rho_{\alpha' \alpha_1}^c \rho_{i \alpha_2}^c. \end{aligned}$$

Defining the matrices  $\Lambda^c$  and  $\gamma^c(\rho)$  as

$$\Lambda_{ik}^c = 2 \sum_{\alpha \in I^c} R_{i\alpha k \alpha}^c, \quad (16)$$

$$\gamma_{ik}^c(\rho) = -2 \sum_{(\alpha, \alpha') \in (I^c)^2} R_{i\alpha\alpha'k}^c \rho_{\alpha'\alpha}^c = -2 \sum_{(\alpha, \alpha') \in (I^c)^2} R_{\alpha i k \alpha'}^c \rho_{\alpha'\alpha}^c, \quad (17)$$

we can cast the result as

$$\left\langle [c_j^\dagger c_i, H^{c-c}] \right\rangle \stackrel{\text{(HF)}}{=} [\Lambda^c + \gamma^c(\rho), \rho^c]_{ij}.$$

*Remark 4.* The alternative choice mentioned in Remark 3 would result in the same equation but with

$$\Lambda_{ik}^c = -2 \sum_{\alpha} R_{i\alpha\alpha k}^c \text{ and } \gamma_{ik}^c(\rho) = +2 \sum_{\alpha, \alpha'} R_{i\alpha k \alpha'}^c \rho_{\alpha'\alpha}^c.$$

We apply the Hartree–Fock approximation to the two four-operators involved in Equation (10)

$$\begin{aligned} c_j^\dagger v_\alpha^\dagger v_{\alpha_2} c_{\alpha_1} &= \delta_{\alpha\alpha_2} c_j^\dagger c_{\alpha_1} - c_j^\dagger v_{\alpha_2} v_\alpha^\dagger c_{\alpha_1}, \\ c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'} c_i &= \delta_{\alpha_2\alpha'} c_{\alpha_1}^\dagger c_i - c_{\alpha_1}^\dagger v_{\alpha'} v_{\alpha_2}^\dagger c_i, \end{aligned}$$

which leads to the approximation

$$\begin{aligned} \left\langle c_j^\dagger v_\alpha^\dagger v_{\alpha_2} c_{\alpha_1} \right\rangle &\stackrel{\text{(HF)}}{=} \delta_{\alpha\alpha_2} \left\langle c_j^\dagger c_{\alpha_1} \right\rangle - \left\langle c_j^\dagger v_{\alpha_2} \right\rangle \left\langle v_\alpha^\dagger c_{\alpha_1} \right\rangle = \delta_{\alpha\alpha_2} \rho_{\alpha_1 j}^c - \rho_{\alpha_2 j}^{\text{vc}} \rho_{\alpha_1 \alpha}^{\text{cv}}, \\ \left\langle c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'} c_i \right\rangle &\stackrel{\text{(HF)}}{=} \delta_{\alpha_2\alpha'} \left\langle c_{\alpha_1}^\dagger c_i \right\rangle - \left\langle c_{\alpha_1}^\dagger v_{\alpha'} \right\rangle \left\langle v_{\alpha_2}^\dagger c_i \right\rangle = \delta_{\alpha_2\alpha'} \rho_{i\alpha_1}^c - \rho_{\alpha' \alpha_1}^{\text{vc}} \rho_{i\alpha_2}^{\text{cv}}. \end{aligned}$$

Hence

$$\begin{aligned} \left\langle [c_j^\dagger c_i, H^{c-v}] \right\rangle &\stackrel{\text{(HF)}}{=} \sum_{\alpha, \alpha'} R_{i\alpha\alpha'\alpha}^{c-v} \rho_{\alpha'j}^c - \sum_{\substack{\alpha, \\ \alpha_1', \alpha_2'}} R_{i\alpha\alpha_1'\alpha_2'}^{c-v} \rho_{\alpha_2'j}^{\text{vc}} \rho_{\alpha_1'\alpha}^{\text{cv}} \\ &\quad - \sum_{\alpha, \alpha'} R_{\alpha\alpha'j\alpha'}^{c-v} \rho_{i\alpha}^c + \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1\alpha_2j\alpha'}^{c-v} \rho_{\alpha'\alpha_1}^{\text{vc}} \rho_{i\alpha_2}^{\text{cv}} \\ &\quad - \sum_{\alpha', \beta} R_{i\beta\alpha'\beta}^{c-v} \rho_{\alpha'j}^c + \sum_{\alpha, \beta} R_{\alpha\beta j\beta}^{c-v} \rho_{i\alpha}^c. \end{aligned}$$

Using the matrix  $\gamma^{c-v}(\rho)$  where

$$\gamma_{ik}^{c-v}(\rho) = - \sum_{(\alpha, \alpha') \in I^v \times I^c} R_{i\alpha\alpha'k}^{c-v} \rho_{\alpha'\alpha}^{\text{cv}}, \quad (18)$$

and noticing that

$$\gamma_{ik}^{c-v}(\rho)^* = - \sum_{\alpha, \alpha'} R_{\alpha k i \alpha'}^{c-v} \rho_{\alpha'\alpha}^{\text{vc}},$$

we can rewrite this

$$\left\langle [c_j^\dagger c_i, H^{c-v}] \right\rangle \stackrel{\text{(HF)}}{=} \sum_k \gamma_{ik}^{c-v}(\rho) \rho_{kj}^{\text{vc}} - \sum_k \gamma_{jk}^{c-v}(\rho)^* \rho_{ik}^{\text{cv}},$$

which will prove useful for the matrix formulation in Section 4.5.

### 4.3 Evolution of valence electron densities

For valence operators, we use the choice described in Remark 4, and Equation (11) leads to

$$\begin{aligned} \left\langle [v_j^\dagger v_i, H^{v-v}] \right\rangle \stackrel{\text{(HF)}}{=} & -2 \sum_{\alpha, \alpha'} R_{i\alpha\alpha\alpha'}^v \rho_{\alpha'j}^v + 2 \sum_{\substack{\alpha, \\ \alpha'_1, \alpha'_2}} R_{i\alpha\alpha'_1\alpha'_2}^v \rho_{\alpha'_1j}^v \rho_{\alpha'_2\alpha}^v \\ & + 2 \sum_{\alpha, \alpha'} R_{\alpha\alpha'\alpha'j}^v \rho_{i\alpha}^v - 2 \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1\alpha_2j\alpha'}^v \rho_{\alpha'\alpha_2}^v \rho_{i\alpha_1}^v \\ & + 2 \sum_{\alpha', \beta} (R_{\beta i\alpha'\beta}^v - R_{\beta i\beta\alpha'}^v) \rho_{\alpha'j}^v - 2 \sum_{\alpha, \beta} (R_{\beta\alpha j\beta}^v - R_{\beta\alpha\beta j}^v) \rho_{i\alpha}^v. \end{aligned}$$

Defining the matrices  $\Lambda^v$  and  $\gamma^v(\rho)$  where

$$\Lambda_{ik}^v = -2 \sum_{\alpha \in I^v} R_{\alpha i\alpha k}^v, \quad (19)$$

$$\gamma_{ik}^v(\rho) = 2 \sum_{(\alpha, \alpha') \in (I^v)^2} R_{i\alpha k\alpha'}^v \rho_{\alpha'\alpha}^v = 2 \sum_{(\alpha, \alpha') \in (I^v)^2} R_{\alpha i\alpha'k}^v \rho_{\alpha'\alpha}^v, \quad (20)$$

we can cast the result as

$$\left\langle [v_j^\dagger v_i, H^{v-v}] \right\rangle \stackrel{\text{(HF)}}{=} [\Lambda^v + \gamma^v(\rho), \rho^v]_{ij}.$$

We apply the Hartree–Fock approximation to the two four-operators involved in Equation (12)

$$\begin{aligned} c_\alpha^\dagger v_j^\dagger v_{\alpha'_2} c_{\alpha'_1} &= v_j^\dagger c_\alpha^\dagger c_{\alpha'_1} v_{\alpha'_2} = \delta_{\alpha\alpha'_1} v_j^\dagger v_{\alpha'_2} - v_j^\dagger c_{\alpha'_1} c_\alpha^\dagger v_{\alpha'_2}, \\ c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_i c_{\alpha'} &= v_{\alpha_2}^\dagger c_{\alpha_1}^\dagger c_{\alpha'} v_i = \delta_{\alpha_1\alpha'} v_{\alpha_2}^\dagger v_i - v_{\alpha_2}^\dagger c_{\alpha'} c_{\alpha_1}^\dagger v_i, \end{aligned}$$

which leads to the approximation

$$\begin{aligned} \left\langle [v_j^\dagger v_i, H^{c-v}] \right\rangle \stackrel{\text{(HF)}}{=} & \sum_{\alpha, \alpha'} R_{\alpha i\alpha\alpha'}^{c-v} \rho_{\alpha'j}^v - \sum_{\substack{\alpha, \\ \alpha'_1, \alpha'_2}} R_{\alpha i\alpha'_1\alpha'_2}^{c-v} \rho_{\alpha'_1j}^{\text{cv}} \rho_{\alpha'_2\alpha}^{\text{vc}} \\ & - \sum_{\alpha, \alpha'} R_{\alpha'\alpha\alpha'j}^{c-v} \rho_{i\alpha}^v + \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1\alpha_2\alpha'j}^{c-v} \rho_{\alpha'\alpha_2}^{\text{cv}} \rho_{i\alpha_1}^{\text{vc}}. \end{aligned}$$



Anew, we can rewrite this

$$\begin{aligned} \left\langle [v_j^\dagger v_i, H^{c-v}] \right\rangle &\stackrel{\text{(HF)}}{=} \sum_k \Pi_{ik}^v \rho_{kj}^v + \sum_k \gamma_{ki}^{c-v}(\rho)^* \rho_{kj}^{cv} \\ &\quad - \sum_k \Pi_{kj}^v \rho_{ik}^v - \sum_k \gamma_{kj}^{c-v}(\rho) \rho_{ik}^{vc}, \end{aligned}$$

using  $\gamma^{c-v}(\rho)$  and the new matrix  $\Pi^v$  defined by

$$\Pi_{ik}^v = \sum_{\alpha \in I^c} R_{\alpha i \alpha k}^{c-v}. \quad (21)$$

#### 4.4 Evolution of inter-band coherences

We first apply the Hartree–Fock approximation to the four-operator involved in Equation (13):

$$v_j^\dagger c_\alpha^\dagger c_{\alpha_2'} c_{\alpha_1'} = \delta_{\alpha \alpha_2'} v_j^\dagger c_{\alpha_1'} - v_j^\dagger c_{\alpha_2'} c_\alpha^\dagger c_{\alpha_1'},$$

which, using  $\Lambda^c$  and  $\gamma^c(\rho)$ , leads to the approximation

$$\begin{aligned} \left\langle [v_j^\dagger c_i, H^{c-c}] \right\rangle &\stackrel{\text{(HF)}}{=} 2 \sum_{\alpha, \alpha'} R_{i \alpha \alpha' \alpha}^c \rho_{\alpha' j}^{cv} - 2 \sum_{\substack{\alpha, \\ \alpha_1', \alpha_2'}} R_{i \alpha \alpha_1' \alpha_2'}^c \rho_{\alpha_2' j}^{cv} \rho_{\alpha_1' \alpha}^c \\ &= \sum_k \Lambda_{ik}^c \rho_{kj}^{cv} + \sum_k \gamma_{ik}^c(\rho) \rho_{kj}^{cv}. \end{aligned}$$

Next we apply the Hartree–Fock approximation to the four-operator involved in Equation (14):

$$v_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha'} c_i = \delta_{\alpha_2 \alpha'} v_{\alpha_1}^\dagger c_i - v_{\alpha_1}^\dagger v_{\alpha'} v_{\alpha_2}^\dagger c_i,$$

which, using  $\Lambda^v$  and  $\gamma^v(\rho)$ , leads to the approximation

$$\begin{aligned} \left\langle [v_j^\dagger c_i, H^{v-v}] \right\rangle &\stackrel{\text{(HF)}}{=} 2 \sum_{\alpha, \alpha'} R_{\alpha \alpha' \alpha' j}^v \rho_{i \alpha}^{cv} - 2 \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1 \alpha_2 \alpha' j}^v \rho_{\alpha' \alpha_1}^v \rho_{i \alpha_2}^{cv} \\ &\quad - 2 \sum_\alpha \sum_\beta (R_{\beta \alpha j \beta}^v - R_{\beta \alpha \beta j}^v) \rho_{i \alpha}^{cv} \\ &= - \sum_k \Lambda_{kj}^v \rho_{ik}^{cv} - \sum_k \gamma_{kj}^v(\rho) \rho_{ik}^{cv}. \end{aligned}$$

Last we apply the Hartree–Fock approximation to the two four-operators involved in Equation (15):

$$\begin{aligned} v_j^\dagger v_\alpha^\dagger v_{\alpha_2'} c_{\alpha_1'} &= \delta_{\alpha \alpha_2'} v_j^\dagger c_{\alpha_1'} - v_j^\dagger v_{\alpha_2'} v_\alpha^\dagger c_{\alpha_1'}, \\ c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger c_{\alpha'} c_i &= v_{\alpha_2}^\dagger c_{\alpha_1}^\dagger c_{\alpha'} c_i = \delta_{\alpha_1 \alpha'} v_{\alpha_2}^\dagger c_i - v_{\alpha_2}^\dagger c_{\alpha'} c_{\alpha_1}^\dagger c_i, \end{aligned}$$

which leads to the approximation

$$\begin{aligned} \left\langle [v_j^\dagger c_i, H^{c-v}] \right\rangle &\stackrel{\text{(HF)}}{=} \sum_{\alpha, \alpha'} R_{i\alpha\alpha'\alpha}^{c-v} \rho_{\alpha'j}^{cv} - \sum_{\substack{\alpha, \\ \alpha'_1, \alpha'_2}} R_{i\alpha\alpha'_1\alpha'_2}^{c-v} \rho_{\alpha'_2j}^v \rho_{\alpha'_1\alpha}^{cv} \\ &- \sum_{\alpha, \alpha'} R_{\alpha'\alpha\alpha'j}^{c-v} \rho_{i\alpha}^{cv} + \sum_{\substack{\alpha_1, \alpha_2, \\ \alpha'}} R_{\alpha_1\alpha_2\alpha'j}^{c-v} \rho_{\alpha'\alpha_2}^{cv} \rho_{i\alpha_1}^c \\ &- \sum_{\alpha', \beta} R_{i\beta\alpha'\beta}^{c-v} \rho_{\alpha'j}^{cv}, \end{aligned}$$

where we recognize

$$\left\langle [v_j^\dagger c_i, H^{c-v}] \right\rangle \stackrel{\text{(HF)}}{=} \sum_k \gamma_{ik}^{c-v}(\rho) \rho_{kj}^v - \sum_k \Pi_{kj}^v \rho_{ik}^{cv} - \sum_k \gamma_{kj}^{c-v}(\rho) \rho_{ik}^c.$$

#### 4.5 Matrix formulation

We would like to cast the former results as

$$\left\langle \left[ \begin{pmatrix} c_j^\dagger c_i & v_j^\dagger c_i \\ c_j^\dagger v_i & v_j^\dagger v_i \end{pmatrix}, H^C \right] \right\rangle \stackrel{\text{(HF)}}{=} [V^C(\rho), \rho],$$

where

$$V^C(\rho) = \begin{pmatrix} V^c(\rho) & V^{c-v}(\rho) \\ V^{v-c}(\rho) & V^v(\rho) \end{pmatrix},$$

which implies

$$\begin{aligned} \left\langle [c_j^\dagger c_i, H^C] \right\rangle &\stackrel{\text{(HF)}}{=} V^c(\rho) \rho^c + V^{c-v}(\rho) \rho^{vc} - \rho^c V^c(\rho) - \rho^{cv} V^{v-c}(\rho), \\ \left\langle [v_j^\dagger v_i, H^C] \right\rangle &\stackrel{\text{(HF)}}{=} V^{v-c}(\rho) \rho^{cv} + V^v(\rho) \rho^v - \rho^{vc} V^{c-v}(\rho) - \rho^v V^v(\rho), \\ \left\langle [v_j^\dagger c_i, H^C] \right\rangle &\stackrel{\text{(HF)}}{=} V^c(\rho) \rho^{cv} + V^{c-v}(\rho) \rho^v - \rho^c V^{c-v}(\rho) - \rho^{cv} V^v(\rho). \end{aligned}$$

Identifying the coefficients computed in Sections 4.2, 4.3, and 4.4, we obtain that the result can indeed be cast as  $[V^C(\rho), \rho]$  where

$$\begin{aligned} V^c(\rho) &= \Lambda^c + \gamma^c(\rho), \\ V^{c-v}(\rho) &= \gamma^{c-v}(\rho), \\ V^{v-c}(\rho) &= \gamma^{c-v*}(\rho) = V^{c-v*}(\rho), \\ V^v(\rho) &= \Lambda^v + \gamma^v(\rho) + \Pi^v, \end{aligned}$$

and the various matrices have been defined by Equations (16) to (21).

The evolution equation for the density matrix including also the free electron Hamiltonians, the interaction with a laser field, and Coulomb interaction can therefore be cast in a Liouville form

$$i\hbar \partial_t \rho = [V(t, \rho(t)), \rho], \quad (22)$$

where  $V(t, \rho(t)) = V_0(t) + V^C(\rho(t))$ .

## 4.6 Energy shifts

Recall (see Equation (2)) the raw Bloch equation

$$i\hbar\partial_t\rho = [V_0(t), \rho],$$

where

$$V_0(t) = \begin{pmatrix} E_0^c + \Re\mathbf{E}(t) \cdot \mathbf{M}^c & \mathbf{E}(t) \cdot \mathbf{M}^{cv} \\ \mathbf{E}^*(t) \cdot \mathbf{M}^{cv*} & E_0^v + \Re\mathbf{E}(t) \cdot \mathbf{M}^v \end{pmatrix}.$$

The symmetries in the definition of  $\mathbf{M}^c$  and  $\mathbf{M}^v$  imply that their diagonal entries are zero. On the contrary for  $E_0^c$  and  $E_0^v$  there are only diagonal entries. In the evolution equation of  $\rho_{ij}^c$ , the  $\rho_{ij}^c$  term only involves  $E_0^c$ , and the other entries of  $\rho$  play a role through  $\mathbf{M}^c$  and  $\mathbf{M}^{cv}$ .

We can therefore easily analyze the Coulomb contributions in terms of shifts on the free electron energies and off-diagonal terms. Hence we compute

$$\begin{aligned} \delta\epsilon_i^c(\rho) &= 2 \sum_{\alpha \in I^c} R_{i\alpha i\alpha}^c - 2 \sum_{(\alpha, \alpha') \in (I^c)^2} R_{i\alpha\alpha' i}^c \rho_{\alpha'\alpha}^c, \\ \delta\epsilon_i^v(\rho) &= -2 \sum_{\alpha \in I^v} R_{i\alpha i\alpha}^v + 2 \sum_{(\alpha, \alpha') \in (I^v)^2} R_{i\alpha\alpha' i}^v \rho_{\alpha'\alpha}^v + \sum_{\alpha \in I^v} R_{i\alpha i\alpha}^{c-v}. \end{aligned}$$

We can define the energy shift matrices as  $\delta E^c(\rho) = \text{diag}(\{\delta\epsilon_i^c(\rho)\}_{i \in I^c})$  and  $\delta E^v(\rho) = \text{diag}(\{\delta\epsilon_i^v(\rho)\}_{i \in I^v})$ . Hence  $V(t, \rho(t)) = E(\rho(t)) + R(t, \rho(t))$ , where  $E(t, \rho(t)) = \text{diag}(E^c(t, \rho(t)), E^v(t, \rho(t)))$  and

$$E^c(\rho(t)) = E_0^c + \delta E^c(\rho(t)) \text{ and } E^v(\rho(t)) = E_0^v + \delta E^v(\rho(t)).$$

## 4.7 Vanishing intra-band coherence assumption

The model for quantum dots given in [GH02] has clearly been derived mimicking quantum well models as in [KR92]. In quantum wells electrons and holes can only interact if they "see each other" long enough, i.e. if they have (and are indexed by) the same wave vector. This leads morally to weakly coupled two-level systems. Therefore, in [GH02], the variables are the level populations and the inter-band coherences. In comparison with our model there are no intra-band coherence  $\rho_{ij}^c$  or  $\rho_{ij}^v$  for  $i \neq j$ .

We can therefore wonder what becomes of our model if we set intra-band coherences to zero. First we notice that in the evolution equation of e.g.  $\rho_{ij}^c$ , there is e.g. a contribution of  $V_{ij}^c(\rho_{jj}^c - \rho_{ii}^c)$ . Hence, even if intra-band coherences are initially zero, there are not always zero through the evolution with Equation (22). Setting artificially intra-band coherences to zero therefore destroys the Liouville structure of the system.

In our model, this hypothesis also changes the definition of  $\gamma^c(\rho)$  and  $\gamma^v(\rho)$ , which become

$$\gamma_{ik}^c(\rho) = -2 \sum_{\alpha \in I^c} R_{i\alpha\alpha k}^c \rho_{\alpha\alpha}^c \text{ and } \gamma_{ik}^v(\rho) = 2 \sum_{\alpha \in I^v} R_{i\alpha k\alpha}^v \rho_{\alpha\alpha}^v.$$

## 5 Mathematical analysis

### 5.1 Estimates on the density matrix

In the same way as in the usual Bloch case [BBR01], the Liouville structure allows to state that the density matrix remains Hermitian through time evolution. Its trace is conserved and it is a positive operator. Hence for a given electric field  $\mathbf{E}(t)$ , the elements of the density matrix are bounded, more precisely populations are bounded

$$|\rho_{ii}^c(t)|, |\rho_{jj}^v(t)| \leq \text{Tr}(\rho(t)) = \text{Tr}(\rho(0)), \quad \text{for all } i \in I^c \text{ and } j \in I^v,$$

as well as coherences

$$|\rho_{ij}^c(t)| \leq \sqrt{\rho_{ii}^c(t)\rho_{jj}^c(t)} \leq \frac{\text{Tr}(\rho(0))}{2}, \quad \text{for all } i, j \in I^c,$$

and likewise

$$|\rho_{jk}^v(t)|, |\rho_{ij}^{c-v}(t)| \leq \frac{\text{Tr}(\rho(0))}{2}, \quad \text{for all } i \in I^c \text{ and } j, k \in I^v.$$

### 5.2 Coupling with the Maxwell equations

The density matrix governed by Bloch equations in the previous section was only depending on time. We can now consider a collection of quantum dots which are scattered in space and interacting, not directly but through the interaction with an electromagnetic wave that propagates through the medium. This can be modeled by a density matrix, that now depends on time and space, which is coupled with Maxwell equations for the laser field through the expression of polarization. We therefore address the system

$$\begin{cases} \mu \partial_t \mathbf{H} = -\text{curl } \mathbf{E}, \\ \varepsilon \partial_t \mathbf{E} = \text{curl } \mathbf{H} - \partial_t \mathbf{P}, \\ \mathbf{P} = \mathcal{N}_b \text{Tr}(\mathbf{M}\rho), \\ \partial_t \rho = -\frac{i}{\hbar} [V(\rho), \rho], \end{cases} \quad (23)$$

where all the variables depend on time and space in 3 dimensions: the electric and magnetic fields  $\mathbf{E}$  and  $\mathbf{H}$ , the polarization  $\mathbf{P}$ , and the density matrix  $\rho$ . Such models have already been written and studied mathematically and numerically in a few physical contexts. Here the specificity is the fact that the Bloch equation is nonlinear in  $\rho$ . Note that even in the case when  $V$  does not depend on  $\rho$ , the full coupled model is already nonlinear since  $V$  is affine in  $\mathbf{E}$ .

This system can be cast in the abstract setting of [DS10]. In this paper, they introduce a general abstract setting able to treat both Maxwell–Landau–Lifschitz and classical Maxwell–Bloch equations. In this setting the electromagnetic field is supposed to exist in all space  $\mathbb{R}^3$ . Matter described by the density matrix is only occupying a subdomain  $\Omega$  of  $\mathbb{R}^3$ . The variables are gathered in

one variable  $U = (u, v)$ , where  $u = (u_1, u_2) = (\mathbf{H}, \mathbf{E})$  and  $v = \rho$ . The variable  $u$  can be view as 6 real variables and variable  $v$  as  $d = (\text{card}(I^c) + \text{card}(I^v))^2$  real variables. This variable  $U$  is supposed to be in  $\mathbf{L}^2 = L^2(\mathbb{R}^3; \mathbb{R}^6) \times L^2(\Omega; \mathbb{R}^d)$ . The abstract system reads

$$\begin{cases} (\partial_t + B)u = (\kappa^{-1} \cdot l)F(\bar{v}, u), & \text{for } x \in \mathbb{R}^3, \\ \partial_t v = F(v, u), & \text{for } x \in \Omega. \end{cases} \quad (24)$$

In this formulation  $\kappa(x) = (\kappa_1(x), \kappa_2(x)) = (\mu, \varepsilon)$ . It is uniformly positive as needed in [DS10]. The linear differential operator  $B$  is defined on  $H_{\text{curl}} \times H_{\text{curl}}$  by  $B(u_1, u_2) = (\kappa_1^{-1} \text{curl } u_2, -\kappa_2^{-1} \text{curl } u_1)$ . The variable  $v$  is extended by  $\bar{v}$  on the whole  $\mathbb{R}^3$  and is zero outside  $\Omega$ . We can identify  $l_1 = 0$ ,  $l_2 = -\mathcal{N}_b \text{Tr}(\mathbf{M} \cdot)$ , and  $F(v, u) = -\frac{i}{\hbar}[V(\rho), \rho]$ . The system (23) verifies the hypotheses given in [DS10], namely

- $F$  is affine in  $u$ :  $F(v, u) = F_0(v) + F_1(v)u$ ,
- for  $j = 0, 1$ ,  $F_j(0) = 0$ .
- for all  $R > 0$  there exists  $C_F(R)$  such that for all  $v \in B_R$  (ball of radius  $R$  in  $\mathbb{R}^d$ ),  $|F_j(v)| + |\partial_v F_j(v)| \leq C_F(R)$ .
- There exists  $K \geq 0$  such that for all  $(u, v) \in \mathbb{R}^6 \times \mathbb{R}^d$ ,  $F(v, u) \cdot v \leq K|u|^2$ .

We have in particular used the  $L^\infty$  bounds of the previous section, more precisely we look for

$$v \in L^\infty((0, \infty); L^\infty(\Omega; \mathbb{R}^d)). \quad (25)$$

Besides we suppose to have at time  $t = 0$  the conditions

$$\text{div}(\kappa_j u_j - l_j \bar{v}) = 0, \quad \text{for } j = 1, 2, \quad (26)$$

which are indeed the physical conditions  $\text{div} \mathbf{B} = 0$  and  $\text{div}(\varepsilon \mathbf{E} + \mathbf{P}) = 0$  [Dum05]. The structure of Equation (24) ensures that this condition holds for all time if it is valid at the initial time.

### 5.3 Cauchy problem

In this section, we state without proof the results obtained in [DS10] and that can apply to our context. The first result addresses the existence of global finite energy solutions.

**Theorem 1** (Theorem 3, [DS10]). *For any initial data  $U_0 = (u_0, v_0)$  satisfying (26), there exists  $U \in \mathcal{C}([0, \infty); \mathbf{L}^2)$  which is a global finite solution to (24)–(26). Moreover, for all  $T > 0$ , there exists a constant  $C$  that only depends on  $T, F, l$  and  $\|v_0\|_{L^\infty}$ , such that for all  $t \in [0, T]$ ,  $\|U(t)\|_{\mathbf{L}^2} \leq C\|U_0\|_{\mathbf{L}^2}$ .*

To have a uniqueness result we need some regularity on  $\varepsilon$  and  $\mu$ . Usually in physical contexts  $\varepsilon$  and  $\mu$  experiment jumps on the boundary of  $\Omega$ , but we do not know how to tackle with this problem. We hence assume that

$$\Omega \text{ is bounded and } \kappa_i - 1 \in C_{\Omega}^{\infty}(\mathbb{R}^3), \text{ for } i = 1, 2, \quad (27)$$

which means that  $\kappa_i$  is 1 outside  $\Omega$  and the transition across the boundary is smooth. We also assume that the initial data for the electromagnetic wave is smooth enough with Sobolev regularity.

**Theorem 2** (Theorem 5, [DS10]). *Under the assumptions of Theorem 1, and (27), let  $s \in (0, 1]$  and  $\text{curl } u_{0i} \in H^{s-1}(\mathbb{R}^3)$  for  $i = 1, 2$ . Then*

(i) *any solution given by Theorem 1 satisfies  $\text{curl } u_i \in C([0, \infty); H^{s-1}(\mathbb{R}^3))$  for  $i = 1, 2$ ;*

(ii) *if  $s = 1$ , there exists only one solution to (24)–(26) with initial data  $U_0$ .*

Item (ii) stems from the fact that  $l_1 = 0$  and  $F$  does not depend on  $u_1$  but only  $u_2$ .

## 6 Numerical experiments

### 6.1 Self-Induced Transparency

Self-Induced Transparency (SIT) is a typical two-level phenomenon: using a light pulse which is resonant with the transition, absorption and stimulated emission are combined to obtain exact population inversion and an unchanged electric field. This phenomenon has been predicted theoretically and confirmed experimentally [AE87, MH67, GS70].

The propagating field is a pulse given by

$$E(t, z) = \mathcal{E}(t, z) \sin(\omega_0(t - z/v)),$$

where  $v$  is the velocity of the pulse,  $\omega_0$  is both the center frequency of the pulse and the transition frequency of the medium, and  $\mathcal{E}(t, z)$  is the pulse envelope. It is shown that the envelope is not reshaped by the medium, only if it is a symmetric hyperbolic secant

$$\mathcal{E}(t, z) = \mathcal{E}_0 \operatorname{sech}\left(\frac{t - z/v}{\tau}\right), \text{ where } \mathcal{E}_0 = \frac{2}{m\tau}.$$

In this expression  $\tau$  is the pulse duration and  $m = M/\hbar$ , where  $M$  is the dipolar moment associated to the transition. According to the Area Theorem, the medium undergoes  $k$  exact inversions if

$$A = m \int_{-\infty}^{\infty} \mathcal{E}(t, z) dt = k\pi.$$

The corresponding pulse is called a  $k\pi$ -pulse. For our test-cases, we will use a  $2\pi$ -pulse, for which the medium is inverted and goes eventually to its original state. The return to the initial state is a easy-to-check criterion to validate numerical approaches, as has been already done in [BF06, ZAG95]. It is easy to compute that

$$A = m\tau\mathcal{E}_0 [\arctan(\sinh t)]_{-\infty}^{\infty} = m\tau\mathcal{E}_0\pi,$$

and hence a  $k\pi$ -pulse is obtained for the amplitude  $\mathcal{E}_0 = k\hbar/M\tau$ .

## 6.2 Adaption to the quantum dot context

In this paper we want in particular to investigate the validity of the vanishing intra-band assumption. To this aim we need a minimum of three levels and we therefore adapt the SIT experiment to our framework. We absolutely do not claim that SIT has any practical application in the quantum dot context, but only choose this test-case because of the easiness to interpret the results.

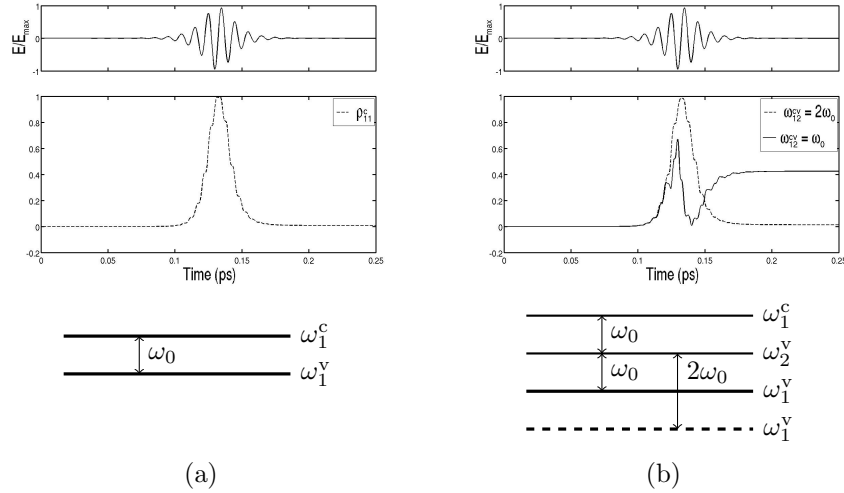


Figure 1: Adaption of the SIT test-case to the quantum dot context. (a) Original two-level case; (b) 2 three-level test cases.

In Figure 1(a) the original two-level test case is represented, for which there is a single conduction level and a single valence level, separated by the energy corresponding to the field frequency. The upper plot represents the (normalized) time-evolution of the electric field. The time-evolution of the population of the initially empty conduction level is given by the lower curve. We observe that the medium undergoes two complete population inversions.

In Figure 1(b) we have three-level test cases with a single conduction level and two valence levels. Coulomb interaction is not taken into account. In the

first case (represented by solid lines both on the plot and on the scheme) the transition between the two valence levels is also resonant with the field and this destroys the SIT phenomenon. It suffices to get both valence levels far apart enough (e.g.  $2\omega_0$  as in the second case, represented by dashed lines) to recover SIT. We use this last configuration as basis test-case for the following numerical experiments.

### 6.3 Numerical features

The simulations are performed using a code based on a finite difference Yee scheme and a relevant choice for the time discretization of the Bloch equation (see [Bid03]). It allows to keep the good properties of the original Yee scheme: second order and explicitness. A splitting scheme, first described in [BBR01], allows to preserve positiveness at the discrete level. It is strongly based on the exact solution given by Equation (3). It has been adapted to include also Coulomb interaction, still preserving positiveness, but at the cost of a loss of approximation order, which becomes one.

Integrating the zero intra-band coherences assumption is *a priori* a problem since it destroys the Liouville structure and an exact solution is no more available. It is however possible to solve a Liouville-like equation and set artificially intra-band coherences to zero. This adds a step at each time iteration but allows to preserve the general structure of the numerical code.

To determine the right envelope amplitude for numerics, we use the argument of [ZAG95]: in practice the input pulse is cut off on an interval  $t \in [-10\tau, 10\tau]$ , therefore the numerical area is

$$A_n = m\tau\mathcal{E}_0 [\arctan(\sinh t)]_{-10}^{10} = m\tau\mathcal{E}_0(0.999942\pi),$$

which slightly changes the value of  $\mathcal{E}_0$ .

## 6.4 Results

### 6.4.1 Impact of Coulomb terms

To include Coulomb interaction in the SIT test case, we have to give values to the coefficients given by Equation (7). Their exact computation is not in the scope of the present paper. We choose to take them all equal to a single value  $R_0$ .



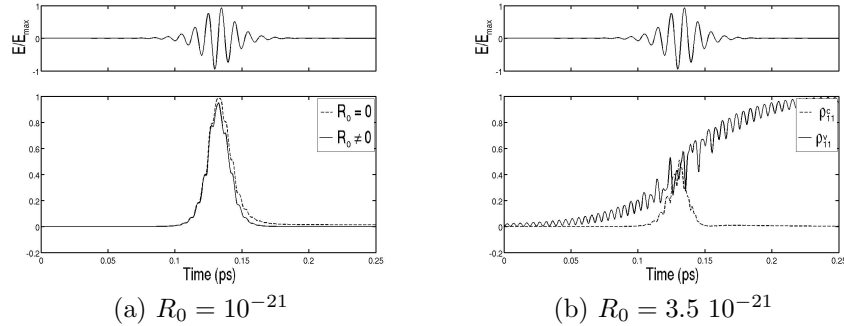


Figure 2: Impact of Coulomb terms for two interaction strengths.

For small values of  $R_0$  (see the evolution of  $\rho_{11}^c$  described for  $R_0 = 10^{-21}$  in Figure 2(a), solid plot) SIT is only slightly affected. In this figure, the dashed plot corresponds to the reference case ( $R_0 = 0$ ) and is the same as the dashed plot of Figure 1(b). The effect is clearer for stronger values of  $R_0$  (e.g.  $R_0 = 3.5 \cdot 10^{-21}$  in Figure 2(b)). The total inversion is prevented by Coulomb interaction. By the time the electromagnetic wave arrives at the space point of interest, Coulomb interaction has relaxed part of the population of the higher valence level  $\rho_{22}^v$  to the lowest valence level  $\rho_{11}^v$  (solid plot)). Only the remaining electrons (about half of them in our example) take part in the phenomenon, which explain the dashed plot (and also the slight effect in Figure 2(a)). Although inversion is not complete, the return to zero of  $\rho_{11}^c$  is observed in this test case.

#### 6.4.2 Impact of vanishing intra-band coherences

We first test the impact of the vanishing intra-band coherence assumption on the Coulomb-free model. We always use the same experimental setting (see Figure 3(a)) and this assumption amounts to taking  $\rho_{12}^v = 0$ .

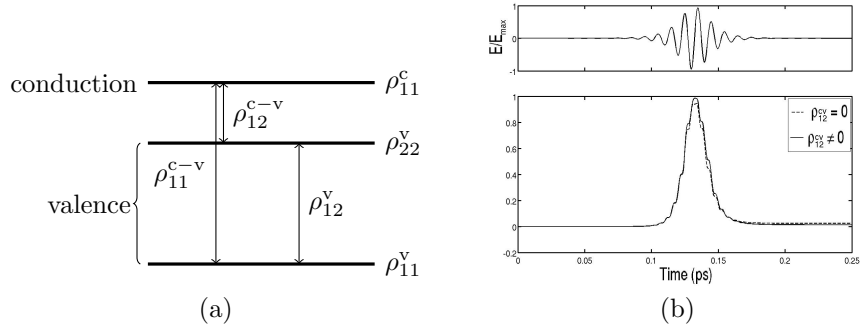


Figure 3: Impact of vanishing intra-band coherences on the Coulomb-free model.

The result is displayed in Figure 3(b). The final equilibrium state for matter is slightly changed and  $\rho_{11}^c$ , which is given by the solid curve, does not eventually return to zero. The last inversion is not a total one.

The test cases with Coulomb terms is much more interesting. If  $R_0$  is low (see Figure 4(a)), the result is not much affected by this assumption.

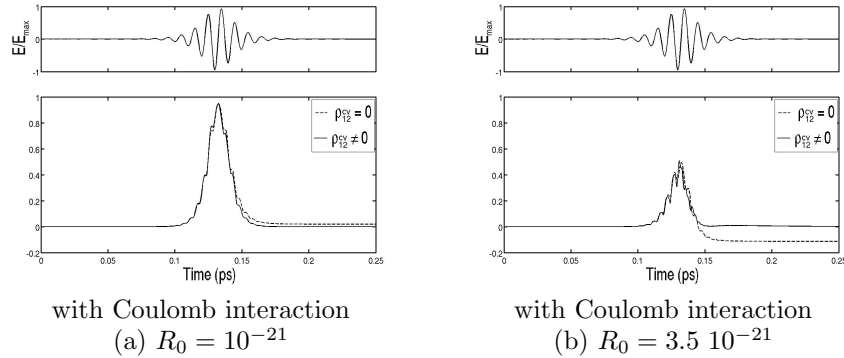


Figure 4: Impact of vanishing intra-band coherences on the full model.

In the case of  $R_0 = 3.5 \cdot 10^{-21}$ , we see in Figure 4(b) that the final equilibrium state is not physical ( $\rho_{11}^c < 0$ ). This is due to the destruction of the Liouville structure. We can easily explain why this is not observed when  $R_0$  is low. When we are close to the SIT experiment we have a typical two-level phenomenon:  $\rho_{11}^v \simeq 0$  during the whole experiment. For a two-level system, the positiveness of the density matrix is equivalent to

- the positiveness of each diagonal term (populations),
- the estimation of coherence by populations, here:  $|\rho_{12}^{c-v}|^2 \leq \rho_{11}^c \rho_{22}^v$ , if the second valence level would be the only relevant one (see [BBR01]).

Setting intra-band coherences to zero within the numerical process does not affect these properties, and the iteration use in the proof of the positiveness of the density matrix applies.

But for a three-level system (and the case  $R_0 = 3.5 \cdot 10^{-21}$  is a true three-level case) the positiveness of the matrix involves some more properties, which are affected by setting  $\rho_{12}^y$  to zero. Although trace is still conserved, the positiveness of the population is affected. We would of course have the same result with a dedicated code where intra-band coherences would simply not be computed. Besides the effect is clear enough in Figure 4(b) not to be attributed to simple round-off errors. The conclusion is that even if intra-band coherences seem not to be very relevant for some physical applications, it is very important to include them in the mathematical description and in the numerical computation to keep the natural mathematical structure of the density matrix.

*Remark 5.* In absence of electromagnetic field the evolution equation is reduced to

$$i\hbar\partial_t\rho_{11}^c = 0.$$

This is only due to the fact that there is only one conduction level in our test case, and does not depend on the intra-band coherence vanishing assumption, nor on the fact that we took a single  $R_0$  Coulomb coefficient. Hence, when the population of the coherence level has been set into a non-physical state (and this is due to the intra-band coherence vanishing assumption), it remains in this state for ever.

## 7 Conclusion

In this paper, Bloch-type equations have been derived considering Coulomb effects in quantum dots. We have shown analytically and numerically that Coulomb effects are not negligible in some quantum dot structures, and we have given the link between mathematical properties and physical relevancy of the Bloch model and more specifically in the treatment of intra-band coherences. Then this model has been coupled with the description of laser propagation in the quantum dot structures, leading to a Maxwell-Bloch system for which we have studied the local and global Cauchy problems. This system has been implemented numerically and simulations have been performed on a self-induced transparency test-case. In particular, we have tested the impact of Coulomb parameters and intra-band coherences. Further work will include additional effects in the same Bloch-type framework.

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## A Canonical form for $H^{\text{h-h}}$

$$\begin{aligned}
\underline{v_{\alpha_1} v_{\alpha_2}} \underline{v_{\alpha'_2}^\dagger v_{\alpha'_1}^\dagger} &= v_{\alpha_2} \underline{v_{\alpha_1} v_{\alpha'_1}^\dagger v_{\alpha'_2}^\dagger} = \delta_{\alpha_1 \alpha'_1} \underline{v_{\alpha_2} v_{\alpha'_2}^\dagger} - \underline{v_{\alpha_2} v_{\alpha'_1}^\dagger} v_{\alpha_1} v_{\alpha'_2}^\dagger \\
&= \delta_{\alpha_1 \alpha'_1} \delta_{\alpha_2 \alpha'_2} - \delta_{\alpha_1 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_2} \\
&\quad - \delta_{\alpha_2 \alpha'_1} \underline{v_{\alpha_1} v_{\alpha'_2}^\dagger} + v_{\alpha'_1}^\dagger v_{\alpha_2} \underline{v_{\alpha_1} v_{\alpha'_2}^\dagger} \\
&= \delta_{\alpha_1 \alpha'_1} \delta_{\alpha_2 \alpha'_2} - \delta_{\alpha_1 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_2} - \delta_{\alpha_2 \alpha'_1} \delta_{\alpha_1 \alpha'_2} + \delta_{\alpha_2 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_1} \\
&\quad + \delta_{\alpha_1 \alpha'_2} v_{\alpha'_1}^\dagger v_{\alpha_2} - \underline{v_{\alpha'_1}^\dagger v_{\alpha_2} v_{\alpha'_2}^\dagger} v_{\alpha_1} \\
&= \delta_{\alpha_1 \alpha'_1} \delta_{\alpha_2 \alpha'_2} - \delta_{\alpha_1 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_2} - \delta_{\alpha_2 \alpha'_1} \delta_{\alpha_1 \alpha'_2} + \delta_{\alpha_2 \alpha'_1} v_{\alpha'_2}^\dagger v_{\alpha_1} \\
&\quad + \delta_{\alpha_1 \alpha'_2} v_{\alpha'_1}^\dagger v_{\alpha_2} - \delta_{\alpha_2 \alpha'_2} v_{\alpha'_1}^\dagger v_{\alpha_1} + v_{\alpha'_1}^\dagger v_{\alpha'_2}^\dagger v_{\alpha_2} v_{\alpha_1}.
\end{aligned}$$

## B Commutator of $c_j^\dagger c_i$ with $H^{c-c}$

$$\begin{aligned}
c_j^\dagger c_i c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} &= \delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} - c_j^\dagger c_{\alpha_1}^\dagger c_i c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} \\
&= \delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} - \delta_{i\alpha_2} c_j^\dagger c_{\alpha_1}^\dagger c_{\alpha_2'} c_{\alpha_1'} + \underline{c_j^\dagger c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_i c_{\alpha_2'} c_{\alpha_1'}} \\
&= \delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} - \delta_{i\alpha_2} c_j^\dagger c_{\alpha_1}^\dagger c_{\alpha_2'} c_{\alpha_1'} + c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger \underline{c_j^\dagger c_{\alpha_2'} c_{\alpha_1'} c_i} \\
&= \delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} - \delta_{i\alpha_2} c_j^\dagger c_{\alpha_1}^\dagger c_{\alpha_2'} c_{\alpha_1'} \\
&\quad + \delta_{j\alpha_2'} c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_1'} c_i - c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} \underline{c_j^\dagger c_{\alpha_1'} c_i} \\
&= \delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} - \delta_{i\alpha_2} c_j^\dagger c_{\alpha_1}^\dagger c_{\alpha_2'} c_{\alpha_1'} \\
&\quad + \delta_{j\alpha_2'} c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_1'} c_i - \delta_{j\alpha_1'} c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_i + c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} c_j^\dagger c_i \\
&= \delta_{i\alpha_1} c_j^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} + \delta_{i\alpha_2} c_j^\dagger c_{\alpha_1}^\dagger c_{\alpha_1'} c_{\alpha_2'} \\
&\quad - \delta_{j\alpha_2'} c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger c_{\alpha_1'} c_i - \delta_{j\alpha_1'} c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_i + c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger c_{\alpha_2'} c_{\alpha_1'} c_j^\dagger c_i.
\end{aligned}$$

## C Commutator of $v_j^\dagger c_i$ with $H^{c-v}$

$$\begin{aligned}
v_j^\dagger c_i c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'} &= \delta_{i\alpha_1} v_j^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'} - v_j^\dagger c_{\alpha_1}^\dagger c_i v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'} \\
&= \delta_{i\alpha_1} v_j^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'} - c_{\alpha_1}^\dagger \underline{v_j^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_i c_{\alpha_1'}} \\
&= \delta_{i\alpha_1} v_j^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'} - c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger \underline{v_j^\dagger v_{\alpha_2'} c_{\alpha_1'} c_i} \\
&= \delta_{i\alpha_1} v_j^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'} - \delta_{j\alpha_2'} c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger c_{\alpha_1'} c_i + c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} \underline{v_j^\dagger c_{\alpha_1'} c_i} \\
&= \delta_{i\alpha_1} v_j^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'} - \delta_{j\alpha_2'} c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger c_{\alpha_1'} c_i + c_{\alpha_1}^\dagger v_{\alpha_2}^\dagger v_{\alpha_2'} c_{\alpha_1'} v_j^\dagger c_i,
\end{aligned}$$