



# From Bloch model to the rate equations II: the case of almost degenerate energy levels

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## Abstract

Bloch equations give a quantum description of the coupling between an atom and a driving electric force. In this article, we address the asymptotics of these equations for high frequency electric fields, in a weakly coupled regime. We prove the convergence towards rate equations (*i.e.* linear Boltzmann equations, describing the transitions between energy levels of the atom). We give an explicit form for the transition rates.

This has already been performed in [BFCD03] in the case when the energy levels are fixed, and for different classes of electric fields: quasi or almost periodic, KBM, or with continuous spectrum. Here, we extend the study to the case when energy levels are possibly almost degenerate. However, we need to restrict to quasiperiodic forcings. The techniques used stem from manipulations on the density matrix and the averaging theory for ordinary differential equations. Possibly perturbed small divisor estimates play a key rôle in the analysis.

In the case of a finite number of energy levels, we also precisely analyze the initial time-layer in the rate equation, as well as the long-time convergence towards equilibrium. We give hints and counterexamples in the infinite dimensional case.

**Keywords:** density matrix, Bloch equations, rate equations, linear Boltzmann equation, averaging theory, small divisor estimates, degenerate energy levels.

## 1 Introduction

Bloch equations model the time evolution of a quantum mechanical system described in the density matrix formulation and driven by an electromagnetic field. This formalism is very precise but sometimes difficult to interpret and to use in practical simulations. It is therefore useful to find asymptotic models under appropriate scaling assumptions. In a former article [BFCD03] such a program is performed and leads to the rigorous derivation of rate equations, which are often used in the physics literature. Here, we want to extend these results to the case when the energy levels of the system are almost degenerate. There are many examples of such almost degeneracies. This is the case for example of Zeemann hyperfine structures in complex molecules, or quantum dots submitted to an external magnetic field. High levels of an atom are also almost degenerate since there is an infinite number of levels with accumulation value at the ionisation energy.

### 1.1 Bloch equations

According to the quantum theory, matter is described *via* a density matrix  $\rho$ , whose diagonal entry  $\rho(t, n, n)$  is –in the eigenstates basis– the population of the  $n$ -th energy level at time  $t$ , and the off-diagonal entry  $\rho(t, n, m)$  is linked to the transition probability from level  $n$  to level  $m$  (conditioned by the corresponding populations). One may think of a collection of identical, uncoupled atoms, with discrete energy levels. We refer the reader to [Boh79, Boy92, CTDRG88, Lou91, NM92, SSL77, Bid03] for textbooks about wave/matter interaction issues, where Bloch equations occur. To treat the mathematical problem, we use a dimensionless version of these equations and consider that the density matrix  $\rho(t, n, m)$  is governed by:

$$\begin{aligned} \varepsilon^2 \partial_t \rho(t, n, m) &= -i\omega_\varepsilon(n, m)\rho(t, n, m) + Q_\varepsilon(\rho)(n, m) \\ &+ i\varepsilon \sum_k \left[ \mathcal{V}\left(\frac{t}{\varepsilon^2}, n, k\right) \rho(t, k, m) - \mathcal{V}\left(\frac{t}{\varepsilon^2}, k, m\right) \rho(t, n, k) \right]. \end{aligned} \quad (1)$$

Integers  $n \in \mathbb{N}$ ,  $m \in \mathbb{N}$ , and  $k \in \mathbb{N}$  are labelling discrete energy levels, and time  $t$  belongs to  $\mathbb{R}^+$ . In the case of a finite number of energy levels, we add the restriction  $n \leq N$ ,  $m \leq N$ ,  $k \leq N$ .

The dependence of the density matrix on the small parameter  $\varepsilon$  will always be implicit. Here, the system is forced by a high frequency electromagnetic wave which is described by its oscillatory amplitude  $\phi(t/\varepsilon^2)$  and contributes to the quantity

$$\mathcal{V}\left(\frac{t}{\varepsilon^2}, n, m\right) = \phi\left(\frac{t}{\varepsilon^2}\right) V(n, m),$$

where the interaction coefficient  $V(n, m) \in \mathbb{C}$  is (up to a rescaling) an entry in the dipole moment matrix which is Hermitian:  $V(m, n) = V(n, m)^*$ .

The parameter  $\varepsilon$  occurring in the scaling plays two rôles. First, the coupling between atoms and the wave is small, of order  $\varepsilon$ , and its cumulated effects are considered over long time scales, of size  $1/\varepsilon^2$ . This is the setting of the so-called weak coupling regime (see [Spo80, Spo91, vH55, vH57]). Second, the scaling in Eq. (1) produces resonances between the eigenfrequencies  $\omega_k/\varepsilon$  of the free atom and the electromagnetic source  $\phi(t/\varepsilon^2)$ .

The quantity  $\omega_\varepsilon(n, m) = \omega(n, m) + \varepsilon^p \delta(n, m)$  is the transition energy between levels  $n$  and  $m$ . In the non-degenerate framework  $\omega(n, m) = \omega(n) - \omega(m) \in \mathbb{R}$  is the difference between the energies  $\omega(n)$  and  $\omega(m)$  of levels  $n$  and  $m$  respectively. Here we model almost degenerate levels replacing the energy  $\omega(n)$  by  $\omega(n) + \varepsilon^p \delta(n)$  where  $p > 0$  and  $\delta(n) \in \mathbb{R}$ . Therefore  $\delta(n, m) = \delta(n) - \delta(m)$ . We notice that a large value for  $p$  means that levels  $n$  and  $m$  are very close from one another if  $\omega(n, m) = 0$ .

Last, relaxation terms are modelled by the operator  $Q_\varepsilon$  which reads

$$\begin{aligned} Q_\varepsilon(\rho)(n, m) &= -\varepsilon^\mu \gamma(n, m) \rho(t, n, m), & \text{if } n \neq m, \\ &= \varepsilon^2 \left( \sum_k [W(k, n) \rho(t, k, k) - W(n, k) \rho(t, n, n)] \right), & \text{if } n = m. \end{aligned}$$

We assume that the Pauli coefficient  $W(n, m)$  is non-negative, as well as the longitudinal coefficient  $\gamma(n, m)$ , which is besides symmetric:  $\gamma(n, m) = \gamma(m, n)$ . To simplify further notations, we extend its definition to the case when  $n = m$  introducing  $\gamma(n, n) = 0$ .

We assume that  $0 \leq \mu < 1/2$ . This is already the case in the nondegenerate case [BFCD03]. This threshold value for  $\mu$  arises in the estimates and we do not know whether it is optimal or not. However it is no wonder that there is a threshold value. Indeed, in the case when  $\mu = 0$ , the initial Bloch equation (1) is time-irreversible and the asymptotic equation that we derive in this paper is also time-irreversible. On the other hand, in the opposite case when every coefficient  $\gamma(n, m)$  is identically zero (which can also be interpreted as  $\mu = \infty$ ), the initial Bloch equation is time-reversible and the nature of the problem has changed.

The relaxation operator  $Q_\varepsilon$  determines an equilibrium state, to which the system has a tendency to relax when no electromagnetic wave is applied. If the threshold  $\mu < 1/2$  is not necessarily optimal, it is very important that  $\mu < 2$ . This means that the off-diagonal terms of the density matrix are more rapidly decreasing than the diagonal terms. We therefore expect them to play no significant rôle on the time scale  $1/\varepsilon^2$ .

Finally, we associate to Eq. (1) an initial datum  $\rho(0, n, m)$  which satisfies

$$\rho(0, n, m) = 0, \quad \forall n \neq m, \quad \text{and} \quad \rho(0, n, n) \geq 0, \quad \forall n. \quad (2)$$

The vanishing of the off-diagonal entries means that we are dealing with “well prepared” initial data. This is a standard assumption in the field (see *e.g.* [KL57, LK58, Zwa66]).

**Remark.** Note that the small coupling in Eq. (1) a priori induces perturbations of size  $1/\varepsilon$  on time scales  $1/\varepsilon^2$ . As we shall see, the very Hamiltonian nature of the equation actually makes these perturbations of size 1.

## 1.2 Rate equations

To describe the asymptotic dynamics, we are only interested in the diagonal part of the density matrix (the populations) and set

$$\rho_d(t, n) := \rho(t, n, n),$$

which is the occupation number of the  $n$ -th level. The limiting model we look for as  $\varepsilon \rightarrow 0$  is a system of rate equations which are Boltzmann type equations, in the form

$$\partial_t \rho_d^{\text{app}} = (W_\varepsilon^{\text{mod}})_\# \rho_d^{\text{app}}, \quad (3)$$

where the approximate populations  $\rho_d^{\text{app}}$  are viewed as a vector, and the modified relaxation matrix operator  $(W_\varepsilon^{\text{mod}})_\#$  is defined from coefficients  $W_\varepsilon^{\text{mod}}(n, k)$  via the following notation.

**Notation 1.** To coefficients  $A(n, k)$ ,  $n \neq k$  (which may possibly be time dependent:  $A(t, n, k)$ ) we associate the matrix  $A_\#$  (respectively  $A_\#(t)$ ) through

$$\begin{aligned} A_\#(n, k) &:= A(k, n) && \text{if } n \neq k, \\ A_\#(n, n) &:= - \sum_{m \neq n} A(n, m) && \text{else.} \end{aligned}$$

If  $A(n, k) \in l_n^\infty l_k^1 \cap l_k^\infty l_n^1$ ,  $A_\#$  is a bounded operator on  $l^p$ ,  $1 \leq p \leq \infty$  (see Appendix 8.1).

Apart from [BFCD03], in the past few years an extensive attention has been paid on the rigorous derivation of Boltzmann type equations from dynamical models of (classical or quantum) particles or models for the interaction of waves with random media. Convergence results in the case of an electron in a periodic box may be found in [Cas99, Cas02, Cas01]. We also mention the non-convergence result established in [CP02, CP03] in a particular, periodic situation. For the case when an electron is weakly coupled to random obstacles, the reader may refer to [EY00, Spo77, Spo80, Spo91] and [KPR96] for the formal analysis performed. The computation of the relevant cross-sections is performed in [Nie96]. All these results address the case of a linear Boltzmann equation. A nonlinear case is studied in [BCEP03].

As proved in [BFCD03], in the non-perturbed case ( $\delta(n) \equiv 0$ ) the action of the wave transforms the relaxation operator  $W_\#$  associated with matrix  $W$  into a limit relaxation operator  $(W_\varepsilon^{\text{mod}})_\#$ .

The goal of this article is to specify the precise form of matrix  $W_\varepsilon^{\text{mod}}(n, k)$  for the perturbed case for a fixed  $\varepsilon$ . Once this rate equation is derived, we also give results about the limit  $\varepsilon \rightarrow 0$  and the size of the time-layer leading to equilibrium according to the value of  $\mu/p$ .

## 1.3 Main results

### 1.3.1 The modified relation operator $(W_\varepsilon^{\text{mod}})_\#$

The modified transition rates  $W_\varepsilon^{\text{mod}}(n, k)$  is defined by

$$W_\varepsilon^{\text{mod}}(n, k) := \langle \Psi_\varepsilon \rangle^{\text{dom}}(n, k) + W(n, k),$$

and the non-negative coefficient  $\langle \Psi_\varepsilon \rangle^{\text{dom}}(n, k)$  is given (see Proposition 4 and Theorem 6) by

$$\begin{aligned} \langle \Psi_\varepsilon \rangle^{\text{dom}}(n, k) &:= 2|V(n, k)|^2 \sum_{\beta \in \mathbb{Z}^r} \frac{\gamma(k, n)}{\gamma(k, n)^2 + |\omega(n, k) + \beta \cdot \omega + \varepsilon^p \delta(k, n)|^2} |\phi_\beta|^2 \quad \text{if } \mu = 0, \\ &:= 2|V(n, k)|^2 \frac{\varepsilon^\mu \gamma(k, n)}{\varepsilon^{2\mu} \gamma(k, n)^2 + \varepsilon^{2p} \delta(k, n)^2} \sum_{\beta \in \mathbb{Z}^r; \omega(k, n) + \beta \cdot \omega = 0} |\phi_\beta|^2 \quad \text{if } \mu > 0. \end{aligned}$$

Here, the electromagnetic wave  $\phi$  is determined by its frequency vector  $\omega \in \mathbb{R}^r$  and its Fourier coefficients  $\phi_\alpha$ :

$$\phi(t) = \sum_{\alpha \in \mathbb{Z}^r} \phi_\alpha \exp(i\alpha \cdot \omega t), \quad \text{where we denote } \alpha \cdot \omega := \alpha_1 \omega_1 + \dots + \alpha_r \omega_r.$$

Under assumptions that we specify in Section 2), we prove the following: if  $\rho$  is a solution to Eq. (1), and  $\rho_d^{\text{app}}$  the solution to Eq. (3) with the same initial datum, then for all  $T > 0$ , there exists  $C > 0$  such that

$$\|\rho_{\text{od}}\|_{L^\infty([0, T], l^1)} \leq C\varepsilon^{1-\mu} \quad \text{and} \quad \|\rho_d - \rho_d^{\text{app}}\|_{L^\infty([0, T], l^2)} \leq C(\varepsilon^\mu + \varepsilon^{1-2\mu}).$$

### 1.3.2 The asymptotic state

We study the convergence of the solution  $\rho$  to Bloch equation (1) on some *fixed* time interval  $[0, T]$ , as  $\varepsilon$  goes to zero. This dynamics is thus given by the corresponding solution  $\rho_d^{\text{app}}$  to Eq. (3). Since the operator  $(W_\varepsilon^{\text{mod}})_\sharp$  has a non-positive spectrum (see the Appendix 8.1), one may think that, as time grows,  $\rho_d^{\text{app}}$  approaches some equilibrium state, *i.e.* a stationary state  $\underline{\rho} \in l^2$  belonging to the kernel of  $(W_\varepsilon^{\text{mod}})_\sharp$ . We describe this convergence carefully in the case of a finite number of quantum levels. In the case of an infinite number of levels, we exhibit simple examples for which convergence does not occur.

### 1.3.3 The case of a finite number of levels

The evolution of  $\rho_d$  can be summarized as:

- (i) The levels  $n$  which do not resonate with the wave ( $\langle \Psi_\varepsilon \rangle^{\text{dom}}(n, k) = 0$  for all  $k$ ) and are not coupled to others *via* relaxations either ( $W(n, k) = 0$  for all  $k$ ) remain constant.
- (ii) Polarization: the remaining levels belonging to the space  $(l^2)$ -orthogonal to the kernel of the singular part  $\langle \Psi_\varepsilon \rangle_\sharp^{\text{sing}}$  of  $\langle \Psi_\varepsilon \rangle_\sharp^{\text{dom}}$  vanish in time  $O(\varepsilon^\sigma)$ . The precise definitions of  $\langle \Psi_\varepsilon \rangle_\sharp^{\text{sing}}$  and  $\sigma > 0$  are given in Section 6.
- (iii) After this time, the evolution of the remaining levels is given by an  $\varepsilon$ -independent system for  $\Pi \rho_d^{\text{app}}$ ,

$$\partial_t \Pi \rho_d^{\text{app}} = \Pi (W + \Psi_0^{\text{nonsing}})_\sharp \Pi \rho_d^{\text{app}}.$$

Here,  $\Pi$  is the orthogonal projector onto the space orthogonal to the ones treated in the first two steps. Also, we set  $\langle \Psi_\varepsilon \rangle^{\text{nonsing}} := \langle \Psi_\varepsilon \rangle^{\text{dom}} - \langle \Psi_\varepsilon \rangle^{\text{sing}}$ , and  $\Psi_0^{\text{nonsing}}$  is the value of  $\langle \Psi_\varepsilon \rangle^{\text{nonsing}}$  as  $\varepsilon$  vanishes. For each initial datum  $\rho(0)$ , the solution to this system converges, as  $t$  goes to infinity, to some (unique) equilibrium state  $\underline{\rho}$  (see Appendix 8.1).

In the unperturbed case  $\delta = 0$  [BFCD03], we have  $\sigma = \mu$ . The perturbation can affect the exponent  $\sigma$ , the transition rates given by  $\langle \Psi_\varepsilon \rangle_{\sharp}^{\text{sing}}$ , as well as the final equilibrium (determined by  $\langle \Psi_\varepsilon \rangle_{\sharp}^{\text{nonsing}}$ ). The precise value of  $\sigma$  and the possibility of modifying the limiting operator according to the value of  $\mu/p$  are given in Table 1.

$\mu/p$	$\sigma$	difference with the unperturbed case [BFCD03]
$0 \leq \mu/p < 1$	$\mu$	none
$\mu/p = 1$	$\mu$	transition rates
$1 < \mu/p < 2$	$2p - \mu$	transition rates and time-layer
$2 \leq \mu/p < \infty$	$\mu$	projector $\Pi$ and asymptotic state

Table 1: Consequences of the perturbation for a finite number of levels.

### 1.3.4 The case of an infinite number of levels

For an infinite number of levels, Proposition 4 and Theorem 6 hold. They give the approximation of the solution to Eq. (1) by the solution to Eq. (3). The transition rates  $W(n, k)$  are again transformed into  $W_\varepsilon^{\text{mod}}(n, k)$ . However, the analysis of the asymptotic behavior of the solution to Eq. (3) is more intricate than in the finite case. In Appendix 8.1.2, we give examples for which there *does not exist* any possible equilibrium state in  $l^2$  (see Corollary 16).

It is still true that non-interacting levels remain constant, as in item (i) of Section 1.3.3. Nevertheless, we are unable to prove the precise polarization property of the two other items, even if we expect that the results of Table 1 hold. An equivalent to Table 1 for an infinite number of levels is given in Section 6.5, for the values of  $\mu/p$  for which we can conclude.

## 1.4 Outline

The article is organized as follows. Section 2 is devoted to the introduction of the precise notations and assumptions needed in the sequel. In Section 3 a *closed* equation which governs populations only is derived from the Bloch equations up to an approximation of order  $O(\varepsilon^{2(1-\mu)})$ . This equation is already a Boltzmann type equation, but the transition rates depend on time and  $\varepsilon$ . The off-diagonal terms are proven to be negligible, of order  $O(\varepsilon^{1-\mu})$ . This transformation uses classical arguments for the Bloch equation in the weak coupling regime (see [Cas99, Cas02, Cas01] and also [KL57, LK58, Kre83, Zwa66] for this point).

In Section 4 a new Boltzmann type equation is derived removing the time-dependence of the transition rates up to an approximation of order  $O(\varepsilon^{1-2\mu})$ . These transition rates still include

some terms which do not correspond to a resonance between the wave and the matter. These contributions are removed in Section 5 with a new error of order  $O(\varepsilon^\mu)$ . The thus obtained equation is the rate equation we want to derive in this article. The main theorem in this Section (namely Theorem 6) yields the form of the transition rates in the rate equation. The techniques used are those of the averaging theory for ordinary differential equations (see [LM88, SV85]). Diophantine estimates play naturally a key rôle in the analysis. Lemma 7 ensures that although the Diophantine condition is not stable with respect to small perturbations, violations of the condition only occur for large values of the indices, that are compensated by extra smoothness assumptions (see [CCC<sup>+</sup>03] for a similar argument in another context).

The sequel of the article addresses the analysis of the limit process  $\varepsilon \rightarrow 0$  in this equation. Section 6 is devoted to the case study according to the value of  $\mu/p$  leading to Table 1 in the finite dimensional case (finite number of levels) and to partial results in the infinite dimensional case (see Table 2). The justification of the restriction to a finite number of levels is given in Section 7: we show that there exists a number  $N$  such that considering only the  $N$  first levels implies an additional error of order  $o(1)$ . The number  $N$  *a priori* depends on  $\varepsilon$ , except when resonances do not occur beyond some level.

Finally, we give in Section 8 the proofs of several lemmas, concerning continuity and non-positiveness of the relaxation operators first, then about existence and uniqueness of the associated equilibrium state, and finally, we show the genericity of the Diophantine condition 1 (see below).

## 2 Functional setting

The choice for functional spaces is first guided by some physical properties of the density matrix. Throughout this article the initial datum is taken such that

$$\rho(0, n, m) = 0, \text{ if } n \neq m, \quad \rho(0, n, n) \geq 0 \quad \text{and} \quad \sum_n \rho(0, n, n) < \infty. \quad (4)$$

The energy levels are assumed to be bounded:

$$(\omega(n))_{n \in \mathbb{N}} \in l^\infty \text{ and } (\delta(n))_{n \in \mathbb{N}} \in l^\infty$$

(which is physically relevant, since these energies are bounded by the ionisation energy), as well as the relaxation coefficients

$$(\gamma(n, m))_{n, m \in \mathbb{N}} \in l^\infty, \quad \inf_{n \neq m} \gamma(n, m) := \gamma > 0.$$

We also suppose that the Pauli coefficients satisfy

$$\|W\|_{l_k^\infty l_n^1 \cap l_n^\infty l_k^1} := \sup_k \sum_n |W(n, k)| + \sup_n \sum_k |W(n, k)| < \infty.$$

Matrix  $W$  describes the relaxation to a thermodynamic equilibrium. Entries  $W(n, m)$  and  $W(m, n)$  are therefore related by the standard microreversibility relation (see *e.g.* [BBR01,

Bid03])

$$W(n, m) = \exp\left(\frac{\omega(m, n)}{T}\right) W(m, n), \quad (5)$$

where  $T$  is a normalized temperature. This specific form is of great importance when describing the equilibrium states in Sections 6 and 8.1.

We recall that the interaction matrix  $V$  is Hermitian. Thus we simply assume that

$$\|V\|_{l^\infty l^1} := \sup_k \sum_n |V(n, k)| < \infty.$$

Classical ordinary differential equation arguments (see *e.g.* [Cas99]) allow to state the existence and uniqueness of solutions to System (1) for initial data in  $l^1$ . Indeed, since we assumed that  $\mathcal{V}(t, n, m)$  belongs to  $L^\infty(\mathbb{R}^+, l_m^\infty l_n^1 \cap l_n^\infty l_m^1)$ , and also that  $W(n, m) \in l_m^\infty l_n^1 \cap l_n^\infty l_m^1$ , we may use the estimate of Lemma 12. The operators involved in Eq. (1) are thus continuous on  $L^\infty(\mathbb{R}^+, l^1)$ . This implies in a straightforward way that these solutions exist and have the following regularity:  $\rho \in C^0(\mathbb{R}^+, l^1)$  and  $\partial_t \rho \in L^\infty(\mathbb{R}^+, l^1)$ , for each  $\varepsilon > 0$ .

A weaker result is the existence and uniqueness in  $l^2$  and we will have to restrict to this case from Section 4 on.

The summation and positiveness properties are preserved through the time evolution if the density matrix is solution to the Bloch equations (1). More precisely we have the following lemma (points (ii), (iii), (iv) are addressed in [Lin76, BBR01, Cas01]).

**Lemma 1.** *Let  $\rho(t = 0)$  satisfy conditions (4). Then, under the above assumptions, for all  $t \in \mathbb{R}$ ,*

(i) *there exists a unique solution  $\rho \in C^0(\mathbb{R}^+, l^1)$  to Eq. (1).*

(ii)  *$\rho(t)$  is Hermitian:  $\rho(t, n, m) = \rho(t, m, n)^*$ ,*

(iii) *the trace of  $\rho$  is conserved:*

$$\sum_n \rho(t, n, n) = \sum_n \rho(0, n, n) < \infty, \quad (6)$$

(iv) *positiveness of populations is conserved:  $\rho(t, n, n) \geq 0$ .*

We stress the importance of items (iii) and (iv), first established in [Lin76]. They give a nontrivial  $l^1$  estimate for the diagonal part  $\rho_d$ . This proves to be crucial in Proposition 2 (see also [Cas01] for a situation where the oscillations are much more difficult to handle).

The electromagnetic wave is real and bounded:  $\phi(t) \in \mathbb{R}$  and  $\phi \in L^\infty(\mathbb{R})$ . Although a larger class of high frequency waves is addressed in [BFCD03], we have to restrict here to the quasiperiodic case. The amplitude  $\phi$  is characterized *via* its frequency vector  $\omega \in \mathbb{R}^r$  and its Fourier coefficients  $\phi_\alpha$ :

$$\phi(t) = \sum_{\alpha \in \mathbb{Z}^r} \phi_\alpha \exp(i\alpha \cdot \omega t) \quad \text{where} \quad \phi_\alpha^* = \phi_{-\alpha} \quad \text{and} \quad \sum_{\alpha \in \mathbb{Z}^r} |\phi_\alpha|^2 < \infty. \quad (7)$$

Here we denote  $\alpha \cdot \omega := \alpha_1 \omega_1 + \dots + \alpha_r \omega_r$ .

We need a certain number of assumptions on the wave and the interaction coefficients. Those already stressed will be valid (and not recalled) in the whole article. However, in some places, we will have to reinforce the decay assumptions and therefore we also label some specific hypotheses.

As it is usual in the field of oscillations in ordinary differential equations and averaging techniques (see [Arn89, SV85, LM88]), we introduce a Diophantine condition on the frequency vector  $\omega$ .

**Hypothesis 1** (Diophantine condition). *There exists a (small) number  $\eta > 0$ , and a constant  $C_\eta > 0$ , such that*

$$\begin{aligned} \forall \alpha = (\alpha_1, \dots, \alpha_r) \in \mathbb{Z}^r \setminus \{0\}, \quad \forall (n, k) \in \mathbb{N}^2 \text{ such that } \alpha \cdot \omega + \omega(n, k) \neq 0, \\ |\alpha \cdot \omega + \omega(n, k)| \geq \frac{C_\eta}{(1 + |\alpha|)^{r-1+\eta}(1+n)^{1+\eta}(1+k)^{1+\eta}}, \end{aligned} \quad (8.a)$$

and similarly

$$\forall \alpha \in \mathbb{Z}^r \setminus \{0\}, \quad |\alpha \cdot \omega| \geq \frac{C_\eta}{(1 + |\alpha|)^{r-1+\eta}}. \quad (8.b)$$

**Remark.** *Given once and for all a fixed  $\eta > 0$ , we can classically claim (see [Arn89]) that there exists a constant  $C_\eta > 0$ , depending on  $\omega(n, m)$  and on  $\eta$ , such that for almost all value of the frequency vector  $\omega = (\omega_1, \dots, \omega_r)$  Hypothesis 1 is satisfied. This is proved in Appendix 8.2. This condition is therefore not much restrictive.*

The same kind of estimate is also needed in the case when  $\alpha = 0$ , which means that the energies do not converge too fast towards the ionisation energy.

**Hypothesis 2** (Convergence towards the ionisation energy). *There exists a constant  $C_\eta > 0$ , such that*

$$\forall (n, k) \in \mathbb{N}^2, \quad |\omega(n, k)| \geq \frac{C_\eta}{(1+n)^{1+\eta}(1+k)^{1+\eta}},$$

where  $\eta$  is the number occurring in the Diophantine assumption (Hypothesis 1).

From Section 4 on, we impose the following hypothesis in order to average transition rates in time.

**Hypothesis 3** (Smoothness assumption). *The Fourier coefficients  $\phi_\alpha$  satisfy*

$$\sum_{\alpha} (1 + |\alpha|)^{r-1+\eta} |\phi_\alpha|^2 < \infty,$$

where  $\eta$  is the number occurring in the Diophantine assumption (Hypothesis 1).

From Section 5 on, we need the following two hypotheses to justify the sorting out of resonant and non resonant contributions.

**Hypothesis 4** (Reinforced smoothness assumption). *There exists  $N_\eta > 2\mu/p$  such that the Fourier coefficients  $\phi_\alpha$  satisfy*

$$\sum_{\alpha} (1 + |\alpha|)^{(r-1+\eta)N_\eta} |\phi_\alpha|^2 < \infty,$$

where  $\eta$  is the number occurring in the Diophantine assumption (Hypothesis 1).

**Hypothesis 5** ("Far from continuum" assumption). *The interaction coefficients satisfy*

$$\sup_n \sum_m ((1+n)^{1+\eta}(1+m)^{1+\eta})^{N_\eta} |V(n, m)|^2 < \infty,$$

where  $\eta$  is the number occurring in the Diophantine assumption (Hypothesis 1) and  $N_\eta$  is given by Hypothesis 4.

This last hypothesis means that only low levels (*i.e.* levels which are far from the continuous spectrum or ionisation threshold) really interact with the wave with a significant contribution. To restrict to a finite number of levels we also use an assumption on the interaction of low and high levels *via* the relaxation operator.

**Hypothesis 6** (Weak interaction of low and high energy levels). *The longitudinal relaxation coefficients satisfy*

$$\sup_n \sum_m (1+n)^K (1+m)^K |W(n, m)| < \infty,$$

for some  $K > 0$ .

We introduce a last notation useful for describing approximations of  $\rho$ .

**Notation 2.** *For  $s \geq 0$ , and  $q \geq 1$ , the symbol  $O_{L^\infty_{\text{loc}}(\mathbb{R}, l^q)}(\varepsilon^s)$  means that for all  $T > 0$ , there exists a constant  $C > 0$ , that does not depend on  $\varepsilon$ , such that the corresponding term is bounded:*

$$\|O_{L^\infty([0, T], l^q)}(\varepsilon^s)\|_{L^\infty([0, T], l^q)} \leq C\varepsilon^s.$$

In the whole article  $C$  denotes constants which do not depend on the (small) parameter  $\varepsilon$ . It however possibly depends on all the coefficients of the problem and on the initial data, but we will never make this dependence explicit.

## 3 A first closed equation for populations

### 3.1 Populations and coherences

In the same way as we defined the populations  $\rho_d(t, n)$ , we define the coherences as the off-diagonal part of the density matrix

$$\rho_{\text{od}}(t, n, m) = \rho(t, n, m)\mathbf{1}[n \neq m].$$

Set

$$\Omega^\varepsilon(n, m) := -i\omega(n, m) - i\varepsilon^p\delta(n, m) - \varepsilon^\mu\gamma(n, m),$$

where we stress that  $\Omega^\varepsilon(n, n) = 0$ . With these notations, Eq. (1) reads for the populations:

$$\begin{aligned} \partial_t \rho_d(t, n) &= \frac{i}{\varepsilon} \sum_k \left[ \mathcal{V} \left( \frac{t}{\varepsilon^2}, n, k \right) \rho_{od}(t, k, n) - \mathcal{V} \left( \frac{t}{\varepsilon^2}, k, n \right) \rho_{od}(t, n, k) \right] \\ &+ \sum_k [W(k, n) \rho_d(t, k) - W(n, k) \rho_d(t, n)], \end{aligned} \quad (9.a)$$

and for the coherences:

$$\begin{aligned} \partial_t \rho_{od}(t, n, m) &= \frac{1}{\varepsilon^2} \Omega^\varepsilon(n, m) \rho_{od}(t, n, m) \\ &+ \frac{i}{\varepsilon} \mathcal{V} \left( \frac{t}{\varepsilon^2}, n, m \right) [\rho_d(t, m) - \rho_d(t, n)] \\ &+ \frac{i}{\varepsilon} \sum_k \left[ \mathcal{V} \left( \frac{t}{\varepsilon^2}, n, k \right) \rho_{od}(t, k, m) - \mathcal{V} \left( \frac{t}{\varepsilon^2}, k, m \right) \rho_{od}(t, n, k) \right]. \end{aligned} \quad (9.b)$$

As a consequence of the Hermitian properties of Eq. (1) recalled in Lemma 1, Eq. (9.a) can also be cast as

$$\begin{aligned} \partial_t \rho_d(t, n) &= -\frac{2}{\varepsilon} \operatorname{Im} \sum_k \left[ \mathcal{V} \left( \frac{t}{\varepsilon^2}, n, k \right) \rho_{od}(t, k, n) \right] \\ &+ \sum_k [W(k, n) \rho_d(t, k) - W(n, k) \rho_d(t, n)]. \end{aligned} \quad (10)$$

### 3.2 An equation for populations only

In this section, we transform the coupled system (9.a)-(9.b) into one equation governing the populations  $\rho_d(t, n)$  only. More precisely, we show the following proposition.

**Proposition 2.** *Define the time dependent transition rate*

$$\Psi_\varepsilon \left( \frac{t}{\varepsilon^2}, k, n \right) := 2|V(n, k)|^2 \operatorname{Re} \int_0^{t/\varepsilon^2} ds \exp(\Omega^\varepsilon(k, n)s) \phi \left( \frac{t}{\varepsilon^2} \right) \phi \left( \frac{t}{\varepsilon^2} - s \right).$$

Then, for all  $T > 0$ , the vector  $\rho_d$  satisfies

$$\partial_t \rho_d(t) = \left( \Psi_\varepsilon \left( \frac{t}{\varepsilon^2} \right) + W \right)_\# \rho_d(t) + O_{L^\infty([0, T], l^1)}(\varepsilon^{1-2\mu}). \quad (11)$$

**Remark.** *Eq. (11) is a linear Boltzmann type equation with a time dependent transition rate. This is our first description of the behavior of the populations at leading order in  $\varepsilon$ .*

*We could likewise obtain approximations of  $\rho_d$  at each order (in  $\varepsilon$ ), thus providing a hierarchy of Boltzmann type equations for the successive orders.*

**Remark.** Using Lemma 11 and since  $\operatorname{Re} \Omega^\varepsilon(n, m) \leq -\varepsilon^\mu \gamma$ , uniformly in  $n$  and  $m$ ,  $n \neq m$ , operator  $\Psi_\varepsilon$  is a priori of order  $\varepsilon^{-\mu}$  on  $l^2$  or  $l^1$ . More precisely we have the following estimates.

$$\|\Psi_\varepsilon(t/\varepsilon^2)\#\rho_d\|_{l^1} \leq C\varepsilon^{-\mu} \|V(n, k)\|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1}^2 \|\phi\|_{L^\infty(\mathbb{R})}^2 \|\rho_d\|_{l^1}, \quad (12.a)$$

$$\|\Psi_\varepsilon(t/\varepsilon^2)\#\rho_d\|_{l^2} \leq C\varepsilon^{-\mu} \|V(n, k)\|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1}^2 \|\phi\|_{L^\infty(\mathbb{R})}^2 \|\rho_d\|_{l^2}. \quad (12.b)$$

*Proof.* Proposition 2 is proved in three steps that follow [BFCD03]. First, coherences  $\rho_{\text{od}}(t, n, k)$  are computed at leading order in  $\varepsilon$ . These leading order terms are expressed in terms of populations  $\rho_d(t, n)$  only as stated in Lemma 3 below. Next, we plug this result into Eq. (10) governing populations. The closed equation for populations (14) which is thus obtained is a linear Boltzmann equation with a time-delay term. To show this delay is indeed small and can be removed to obtain the delay-free equation (11) we then use calculations inspired by [Cas99, Cas02, Cas01].

*First step: computation of coherences*

Since the initial data for coherences is  $\rho_{\text{od}}(t = 0, n, m) \equiv 0$ , the integral form for Eq. (9.b) reads

$$\begin{aligned} \rho_{\text{od}}(t, n, m) &= i\varepsilon \int_0^{t/\varepsilon^2} ds \exp(\Omega^\varepsilon(n, m)s) \mathcal{V}\left(\frac{t}{\varepsilon^2} - s, n, m\right) [\rho_d(t - \varepsilon^2 s, m) - \rho_d(t - \varepsilon^2 s, n)] \\ &\quad + (A_\varepsilon \rho_{\text{od}})(t, n, m), \end{aligned} \quad (13)$$

where

$$\begin{aligned} (A_\varepsilon \rho_{\text{od}})(t, n, m) &:= i\varepsilon \int_0^{t/\varepsilon^2} ds \exp(\Omega^\varepsilon(n, m)s) \times \\ &\quad \times \sum_k \left[ \mathcal{V}\left(\frac{t}{\varepsilon^2} - s, n, k\right) \rho_{\text{od}}(t - \varepsilon^2 s, k, m) - \mathcal{V}\left(\frac{t}{\varepsilon^2} - s, k, m\right) \rho_{\text{od}}(t - \varepsilon^2 s, n, k) \right]. \end{aligned}$$

We are only interested in the first term in the expansion of  $\rho_{\text{od}}$ . Indeed, we only use leading order terms in  $\varepsilon$ . From the integral equation (13), we would however be able to express  $\rho_{\text{od}}$  as a *complete* expansion in powers of  $\varepsilon$ , in terms of  $\rho_d$ . The following lemma states that the remainder of the expansion is indeed small.

**Lemma 3.** *Set*

$$\rho_{\text{od}}^{(0)}(t, n, m) := i\varepsilon \int_0^{t/\varepsilon^2} ds \exp(\Omega^\varepsilon(n, m)s) \mathcal{V}\left(\frac{t}{\varepsilon^2} - s, n, m\right) [\rho_d(t - \varepsilon^2 s, m) - \rho_d(t - \varepsilon^2 s, n)].$$

*Then, for any given time  $T \geq 0$ , there exists a constant  $C$ , that does not depend on  $\varepsilon$ , such that we have the estimates*

$$\begin{aligned} \left\| \rho_{\text{od}} - \rho_{\text{od}}^{(0)} \right\|_{L^\infty([0, T], l^1)} &\leq C\varepsilon^{2(1-\mu)}, \\ \left\| \rho_{\text{od}} \right\|_{L^\infty([0, T], l^1)} &\leq C\varepsilon^{1-\mu}. \end{aligned}$$

*Proof.* (Lemma 3).

Let  $T \geq 0$  be given. Because  $\operatorname{Re} \Omega^\varepsilon(n, m) \leq -\varepsilon^\mu \gamma < 0$ , uniformly in  $n$  and  $m$ ,  $n \neq m$ , we have the estimate

$$\begin{aligned} \|A_\varepsilon \rho_{\text{od}}\|_{L^\infty([0, T], l^1)} &\leq 2\varepsilon \left\| \int_0^{+\infty} ds |\exp(\Omega^\varepsilon(n, m)s)| \right\|_{l_{n, m}^\infty} \|\mathcal{V}\|_{L^\infty(\mathbb{R}^+, l_n^\infty l_m^1 \cap l_m^\infty l_n^1)} \|\rho_{\text{od}}\|_{L^\infty([0, T], l^1)} \\ &\leq C\varepsilon^{1-\mu} \|\rho_{\text{od}}\|_{L^\infty([0, T], l^1)}. \end{aligned}$$

According to the definition of  $\rho_{\text{od}}^{(0)}(t, n, m)$ , Eq. (13)

$$\rho_{\text{od}}(t, n, m) = \rho_{\text{od}}^{(0)}(t, n, m) + (A_\varepsilon \rho_{\text{od}})(t, n, m),$$

and we can estimate the difference

$$\begin{aligned} \|\rho_{\text{od}} - \rho_{\text{od}}^{(0)}\|_{L^\infty([0, T], l^1)} &\leq C\varepsilon^{1-\mu} \|\rho_{\text{od}}\|_{L^\infty([0, T], l^1)} \\ &\leq C\varepsilon^{1-\mu} \|\rho_{\text{od}} - \rho_{\text{od}}^{(0)}\|_{L^\infty([0, T], l^1)} + C\varepsilon^{1-\mu} \|\rho_{\text{od}}^{(0)}\|_{L^\infty([0, T], l^1)}. \end{aligned}$$

Hence, if  $\varepsilon$  is small enough, we have

$$\|\rho_{\text{od}} - \rho_{\text{od}}^{(0)}\|_{L^\infty([0, T], l^1)} \leq C\varepsilon^{1-\mu} \|\rho_{\text{od}}^{(0)}\|_{L^\infty([0, T], l^1)}.$$

According to the definition of  $\rho_{\text{od}}^{(0)}(t, n, m)$ , and using the same type of estimates,

$$\|\rho_{\text{od}}^{(0)}\|_{L^\infty([0, T], l^1)} \leq C\varepsilon^{1-\mu} \|\mathcal{V}\|_{L^\infty(\mathbb{R}; l_n^\infty l_k^1 \cap l_k^\infty l_n^1)} \|\rho_{\text{d}}\|_{L^\infty([0, T], l^1)}.$$

Now the crucial estimate stems from the trace conservation property (6) which also reads  $\|\rho_{\text{d}}\|_{L^\infty([0, T], l^1)} = \|\rho_{\text{d}}(t=0)\|_{l^1}$ . This  $l^1$ -estimate on the diagonal terms of the density matrix is therefore sufficient to control all the off-diagonal terms in turn, and Lemma 3 follows.  $\square$

*Second step: the time-delayed differential equation for the populations*

Lemma 3 together with Eq. (10) governing  $\rho_{\text{d}}$  implies that

$$\begin{aligned} \partial_t \rho_{\text{d}}(t, n) &= \sum_k [W(k, n) \rho_{\text{d}}(t, k) - W(n, k) \rho_{\text{d}}(t, n)] \\ &+ \sum_k \int_0^{t/\varepsilon^2} ds [\rho_{\text{d}}(t - \varepsilon^2 s, k) - \rho_{\text{d}}(t - \varepsilon^2 s, n)] \times \\ &\quad \times 2 \operatorname{Re} \left\{ \exp(\Omega^\varepsilon(k, n)s) \mathcal{V} \left( \frac{t}{\varepsilon^2}, n, k \right) \mathcal{V} \left( \frac{t}{\varepsilon^2} - s, k, n \right) \right\} \\ &+ O_{L^\infty([0, T], l^1)}(\varepsilon^{1-2\mu}). \end{aligned} \tag{14}$$

*Third step: convergence to a delay-free equation*

From now on we will only deal with Boltzmann type equations and use extensively the shorter expressions defined in Notation 1. Hence Eq. (11) can be cast as

$$\partial_t \rho_d(t, n) = (\Psi_\varepsilon(t/\varepsilon^2)_\# \rho_d)(t, n) + (W_\# \rho_d)(t, n) + O_{L^\infty([0, T], l^1)}(\varepsilon^{1-2\mu}).$$

Moreover, if  $T \geq 0$  is given, the delayed terms  $\rho_d(t - \varepsilon^2 s)$  in Eq. (14) read

$$\rho_d(t - \varepsilon^2 s, n) = \rho_d(t, n) + O(\varepsilon^2 s \|\partial_t \rho_d(\cdot, n)\|_{L^\infty([0, T])}).$$

Thus, Eq. (14) yields

$$\partial_t \rho_d(t, n) = (\Psi_\varepsilon(t/\varepsilon^2)_\# \rho_d)(t, n) + (W_\# \rho_d)(t, n) + O_{L^\infty([0, T], l^1)}(\varepsilon^{1-2\mu}) + r_\varepsilon(t, n), \quad (15)$$

where the remainder  $r_\varepsilon$  can be estimated by

$$\begin{aligned} \|r_\varepsilon\|_{L^\infty([0, T], l^1)} &\leq C \|\partial_t \rho_d\|_{L^\infty([0, T], l^1)} \left\| \varepsilon^2 \int_0^{+\infty} ds \, s \exp(\Omega^\varepsilon(n, m)s) \right\|_{l_{n, m}^\infty} \\ &\leq C \varepsilon^{2-2\mu} \|\partial_t \rho_d\|_{L^\infty([0, T], l^1)} \\ &\leq C \varepsilon^{2-2\mu} \varepsilon^{-\mu} \|\rho_d\|_{L^\infty([0, T], l^1)} && \text{thanks to Eqs (15) and (12.a)} \\ &\leq C \varepsilon^{2-3\mu} && \text{thanks to Eq. (6),} \end{aligned}$$

for some constant  $C$ , that does not depend on  $\varepsilon$ , if  $\varepsilon$  is small enough. Including this new estimate in Eq. (15), we have

$$\partial_t \rho_d(t, n) = ((\Psi_\varepsilon)_\# \rho_d)(t, n) + (W_\# \rho_d)(t, n) + O_{L^\infty([0, T], l^1)}(\varepsilon^{1-2\mu} + \varepsilon^{2-3\mu}).$$

We recall that  $\mu < 1/2$  therefore  $1 - 2\mu < 2 - 3\mu$  and Proposition 2 follows.  $\square$

## 4 Time-averaging of transition rates

Proposition 2 reduces the problem to the asymptotic analysis of a leading order equation, namely Eq. (11). As  $\varepsilon$  goes to zero, the rapid oscillations of the time-dependent coefficient  $\Psi_\varepsilon(t/\varepsilon^2)$  are naturally smeared out, so that only the time average of  $\Psi_\varepsilon$  plays a significant rôle. The corresponding rigorous mathematical statement is proven here, as in [BFCD03], upon using averaging techniques (see *e.g.* [SV85]). This leads to substitute Eq. (11) by a new Boltzmann equation, with time-independent rates.

The result of these averaging procedures strongly depends on the specific form of the wave. In the present article, we need explicit forms for the averaged transition rates and therefore restrict to the case of a quasiperiodic wave, as described in Section 2. The small divisor problems that stem from this analysis are handled assuming strong decay properties on the Fourier coefficients, namely Hypothesis 3.

The averaged transitions rates we obtain in this section still depend on  $\varepsilon$ . Besides we do not discriminate dominant and negligible (with respect to  $\varepsilon$ ) contributions. We postpone this

sorting out to Section 5 where negligible contributions will be pointed out as non-resonant contributions.

Using the explicit value of the wave  $\phi(t)$  given by Eq. (7), we compute from Eq. (11) the time-dependent transition rate  $\Psi_\varepsilon$ :

$$\Psi_\varepsilon\left(\frac{t}{\varepsilon^2}, k, n\right) = 2|V(n, k)|^2 \operatorname{Re} \sum_{\alpha, \beta \in \mathbb{Z}^r} \phi_\alpha \phi_\beta \exp\left(i(\alpha + \beta) \cdot \omega \frac{t}{\varepsilon^2}\right) \times \frac{1 - \exp\left([- \varepsilon^\mu \gamma(k, n) - i(\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n))]t/\varepsilon^2\right)}{\varepsilon^\mu \gamma(k, n) + i(\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n))}. \quad (16)$$

The goal of this section is to prove the following result.

**Proposition 4.** Define the averaged transition rate

$$\langle \Psi_\varepsilon \rangle(k, n) := \lim_{s \rightarrow +\infty} \frac{1}{s} \int_0^s ds \Psi_\varepsilon(s).$$

Its explicit value is

$$\langle \Psi_\varepsilon \rangle(k, n) = 2|V(n, k)|^2 \sum_{\beta \in \mathbb{Z}^r} \frac{\varepsilon^\mu \gamma(k, n)}{\varepsilon^{2\mu} \gamma(k, n)^2 + |\omega(n, k) + \beta \cdot \omega + \varepsilon^p \delta(k, n)|^2} |\phi_\beta|^2. \quad (17)$$

Define  $\rho_d^{(1)}$  as the vector solution to

$$\partial_t \rho_d^{(1)} = (\langle \Psi_\varepsilon \rangle + W)_\# \rho_d^{(1)} \quad (18)$$

with initial data  $\rho_d^{(1)}(0, n) = \rho_d(0, n)$ . Under Hypotheses 1 and 3, for all  $T > 0$ , there exists  $C > 0$  such that

$$\|\rho_d - \rho_d^{(1)}\|_{L^\infty([0, T], l^2)} \leq C \varepsilon^{1-2\mu}.$$

**Remark.** In the transition rate  $\langle \Psi_\varepsilon \rangle(k, n)$  there are still contributions of non-resonant waves, i.e. those such that  $\omega(n, k) + \beta \cdot \omega \neq 0$ . They are removed in the next section. However, we gained in defining a time-independent transition rate, in that we filtered oscillations.

The simple but crucial remark that leads from Proposition 2 to Proposition 4 is the fact that  $\langle \Psi_\varepsilon \rangle \in l_n^\infty l_k^1 \cap l_k^\infty l_n^1$  and its entries are non-negative. We can therefore apply Lemma 11 directly.

**Lemma 5.** For any  $\varepsilon > 0$ , operator  $\langle \Psi_\varepsilon \rangle_\#$  is a bounded non-positive operator on the Hilbert space  $l^2$ . In particular, the exponential  $\exp(t \langle \Psi_\varepsilon \rangle_\#)$  is well defined as an operator on  $l^2$  for  $t \geq 0$ , and its norm is less than 1, for all  $t \geq 0$ .

(Proof: see Appendix 8.1, Lemma 11)

**Remark.** This property proves to be crucial in the sequel, and therefore the asymptotic result in Proposition 4 and Theorem 6 may not hold when the transition rate has no sign. This is why we restrict the analysis to the case of a quasiperiodic wave when relaxations tend to zero with  $\varepsilon$ . The asymptotic result may also be false if applied to the time-dependent transition rate  $\Psi_\varepsilon(t/\varepsilon^2)$ , which clearly changes signs.

*Proof.* We follow [BFCD03] to prove Proposition 4.

*First step: splitting of  $\Psi_\varepsilon$*

Proposition 4 amounts to estimating the difference

$$\Delta(t) := \rho_d(t) - \rho_d^{(1)}(t).$$

To this aim, we first give shorter forms for the equations governing  $\rho_d$  and  $\rho_d^{(1)}$  respectively. Namely Eq. (11) can be cast as

$$\partial_t \rho_d(t) = \left( \Psi_\varepsilon \left( \frac{t}{\varepsilon^2} \right)_\# \rho_d \right) (t) + (W_\# \rho_d)(t) + O(\varepsilon^{1-2\mu}).$$

where the transition rate  $\Psi_\varepsilon(t/\varepsilon^2)$  is given by Eq. (16), and Eq. (18) also reads

$$\partial_t \rho_d^{(1)}(t) = \left( \langle \Psi_\varepsilon \rangle_\# \rho_d^{(1)} \right) (t) + \left( W_\# \rho_d^{(1)} \right) (t).$$

Hence the difference  $\Delta(t)$  satisfies the equation

$$\partial_t \Delta(t) = \left( \langle \Psi_\varepsilon \rangle_\# \Delta \right) (t) + \left( \Psi_\varepsilon^{\text{osc}} \left( \frac{t}{\varepsilon^2} \right)_\# \rho_d \right) (t) + (W_\# \Delta)(t) + O(\varepsilon^{1-2\mu}), \quad (19)$$

where

$$\Psi_\varepsilon^{\text{osc}} \left( \frac{t}{\varepsilon^2}, k, n \right) := \Psi_\varepsilon \left( \frac{t}{\varepsilon^2}, k, n \right) - \langle \Psi_\varepsilon \rangle(k, n)$$

contains the oscillatory contribution to the transition rate, which we want to prove to be negligible. Gathering the terms for which  $\alpha + \beta = 0$ , this contribution is equal to

$$\begin{aligned} \Psi_\varepsilon^{\text{osc}} \left( \frac{t}{\varepsilon^2}, k, n \right) &= 2|V(n, k)|^2 \text{Re} \left( - \sum_{\beta \in \mathbb{Z}^r} \frac{|\phi_\beta|^2}{\varepsilon^\mu \gamma(k, n) + i(\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n))} \times \right. \\ &\quad \times \exp\left( [-\varepsilon^\mu \gamma(k, n) - i(\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n))] \frac{t}{\varepsilon^2} \right) \\ &\quad + \sum_{\alpha \neq -\beta \in \mathbb{Z}^r} \frac{\phi_\alpha \phi_\beta \exp(i(\alpha + \beta) \cdot \omega t / \varepsilon^2)}{[\varepsilon^\mu \gamma(k, n) + i(\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n))]} \times \\ &\quad \left. \times [1 - \exp\left( [-\varepsilon^\mu \gamma(k, n) - i(\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n))] \frac{t}{\varepsilon^2} \right)] \right). \end{aligned} \quad (20)$$

This expression carries “time-oscillations” (at frequency  $\varepsilon^{-2+\mu}$  at least), which kill the possibly diverging factors  $\varepsilon^{-\mu}$  (due to the denominators), and make them of size  $\varepsilon^{2-2\mu}$ .

*Second step: preliminary bounds*

Since  $V \in l_n^\infty l_k^1 \cap l_k^\infty l_n^1$  and  $\sum_\beta |\phi_\beta|^2 < \infty$ , we first find that

$$\begin{aligned} \sup_n \sum_k |\langle \Psi_\varepsilon \rangle(k, n)| &\leq C\varepsilon^{-\mu}, & \sup_n \sum_k |\Psi_\varepsilon^{\text{osc}}(t/\varepsilon^2, k, n)| &\leq C\varepsilon^{-\mu}, \\ \sup_k \sum_n |\langle \Psi_\varepsilon \rangle(k, n)| &\leq C\varepsilon^{-\mu}, & \sup_k \sum_n |\Psi_\varepsilon^{\text{osc}}(t/\varepsilon^2, k, n)| &\leq C\varepsilon^{-\mu}, \end{aligned}$$

for some  $C > 0$  that does not depend on  $t$  and  $\varepsilon$ . Lemma 11 yields the operator estimates

$$\|\langle \Psi_\varepsilon \rangle_\# u\|_{l^2} \leq C\varepsilon^{-\mu} \|u\|_{l^2}, \quad \left\| \Psi_\varepsilon^{\text{osc}} \# u \right\|_{l^2} \leq C\varepsilon^{-\mu} \|u\|_{l^2}. \quad (21)$$

Besides, we have the upper bound

$$\sup_{0 \leq t \leq T} \left\| \int_0^{t/\varepsilon^2} ds \Psi_\varepsilon^{\text{osc}}(s, k, n) \right\|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} \leq C\varepsilon^{-2\mu}. \quad (22)$$

Now, according to Eq. (20),  $\Psi_\varepsilon^{\text{osc}}(t, k, n)$  is a sum of two different terms. We use the decay assumptions  $V \in l_n^\infty l_k^1 \cap l_k^\infty l_n^1$  and  $\phi_\alpha \in l^2$  to estimate the contribution of the first term to the integral by

$$C \left\| \sum_\beta |V(n, k)|^2 \frac{|\phi_\beta|^2}{|\varepsilon^\mu \gamma(k, n) + i(\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n))|^2} \right\|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} \leq C\varepsilon^{-2\mu}.$$

The second contribution is estimated by

$$\begin{aligned} & C \left\| \sum_{\alpha+\beta \neq 0} \frac{|V(n, k)|^2 |\phi_\alpha| |\phi_\beta|}{|\varepsilon^\mu \gamma(k, n) + i(\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n))|} \cdot \frac{1}{|(\alpha + \beta) \cdot \omega|} \right\|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} \\ & + C \left\| \sum_{\alpha+\beta \neq 0} \frac{|V(n, k)|^2 |\phi_\alpha| |\phi_\beta|}{|\varepsilon^\mu \gamma(k, n) + i((\alpha + \beta) \cdot \omega + \varepsilon^p \delta(k, n))|^2} \right\|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} \\ & \leq C\varepsilon^{-\mu} \sum_{\alpha, \beta} |\phi_\alpha| |\phi_\beta| |\alpha + \beta|^{r-1+\eta} + C\varepsilon^{-2\mu} \sum_{\alpha, \beta} |\phi_\alpha| |\phi_\beta| \\ & \leq C\varepsilon^{-2\mu}, \end{aligned}$$

thanks to the Diophantine estimate (Hypothesis 1), together with Hypothesis 3. This yields inequality (22).

*Third step: integral form of the equations*

Since  $\Delta(0) = 0$ , the integral form for Eq. (19) governing  $\Delta(t)$  reads

$$\Delta(t) := \Delta^{(1)}(t) + \Delta^{(2)}(t),$$

where

$$\begin{aligned} \Delta^{(1)}(t) &= \int_0^t ds \exp([t-s] \langle \Psi_\varepsilon \rangle) \Psi_\varepsilon^{\text{osc}} \left( \frac{s}{\varepsilon^2} \right)_\# \rho_d(s), \\ \Delta^{(2)}(t) &= \int_0^t ds \exp([t-s] \langle \Psi_\varepsilon \rangle) ((W_\# \Delta)(s) + O(\varepsilon^{1-2\mu})). \end{aligned}$$

Fourth step: estimating  $\Delta^{(1)}(t)$  and  $\Delta^{(2)}(t)$

Here Lemma 5 proves crucial, in that we use the exponential of the bounded operator  $\langle \Psi_\varepsilon \rangle$ . This together with Lemma 11 applied to operator  $W$  yields an estimate for  $\Delta^{(2)}$ :

$$\|\Delta^{(2)}(t)\|_{l^2} \leq C \left( \varepsilon^{1-2\mu} + \int_0^t ds \|\Delta(s)\|_{l^2} \right). \quad (23)$$

On the other hand, to take advantage of the time oscillations of the operator  $\Psi_\varepsilon^{\text{osc}}(t/\varepsilon^2)$ , we carry out a natural integration by parts in the expression for  $\Delta^{(1)}$ :

$$\begin{aligned} \Delta^{(1)}(t) &= \varepsilon^2 \left( \int_0^{t/\varepsilon^2} du \Psi_\varepsilon^{\text{osc}}(u) \right)_{\#} \rho_d(t) \\ &+ \varepsilon^2 \int_0^t ds \exp([t-s]\langle \Psi_\varepsilon \rangle) \langle \Psi_\varepsilon \rangle \left( \int_0^{s/\varepsilon^2} du \Psi_\varepsilon^{\text{osc}}(u) \right)_{\#} \rho_d(s) \\ &- \varepsilon^2 \int_0^t ds \exp([t-s]\langle \Psi_\varepsilon \rangle) \left( \int_0^{s/\varepsilon^2} du \Psi_\varepsilon^{\text{osc}}(u) \right) \times \\ &\quad \times \left( \langle \Psi_\varepsilon \rangle + \Psi_\varepsilon^{\text{osc}}\left(\frac{s}{\varepsilon^2}\right) + W + O(\varepsilon^{1-2\mu}) \right)_{\#} \rho_d(s), \end{aligned}$$

where we have used Eq. (11) to express  $\partial_t \rho_d(s)$ . Estimates (21) on the operators  $\langle \Psi_\varepsilon \rangle$  and  $\Psi_\varepsilon^{\text{osc}}(t)$  together with Lemma 11 and Lemma 5 (non-positiveness of  $\langle \Psi_\varepsilon \rangle$ ) lead to

$$\|\Delta^{(1)}\|_{L^\infty([0,T],l^2)} \leq C \varepsilon^{2-\mu} \sup_{0 \leq t \leq T} \left\| \int_0^{t/\varepsilon^2} ds \Psi_\varepsilon^{\text{osc}}(s) \right\|_{\mathcal{L}(l^2)} \|\rho_d\|_{L^\infty([0,T],l^2)}.$$

Besides we have  $\|\rho_d\|_{L^\infty([0,T],l^2)} \leq \|\rho_d\|_{L^\infty([0,T],l^1)} \leq C$ , and it follows that, for  $\varepsilon$  small enough, we have

$$\begin{aligned} \|\Delta^{(1)}\|_{L^\infty([0,T],l^2)} &\leq C \varepsilon^{2-\mu} \sup_{0 \leq t \leq T} \left\| \int_0^{t/\varepsilon^2} ds \Psi_\varepsilon^{\text{osc}}(s) \right\|_{\mathcal{L}(l^2)} \\ &\leq C \varepsilon^{2-\mu} \sup_{0 \leq t \leq T} \left\| \int_0^{t/\varepsilon^2} ds \Psi_\varepsilon^{\text{osc}}(s, k, n) \right\|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} \\ &\leq C \varepsilon^{2-3\mu}. \end{aligned}$$

This, together with estimate (23), and Gronwall lemma, yields

$$\|\Delta(t)\|_{L^\infty([0,T],l^2)} \leq C \varepsilon^{1-2\mu}.$$

and Proposition 4 is proved. □

## 5 Keeping only resonant contributions in transition rates: the main theorem

In this section we prove that the non-resonant contributions, which correspond to the triples  $(n, k, \beta)$  such that  $\omega(n, k) + \beta \cdot \omega \neq 0$  in the transition rate (17), are negligible in the limit  $\varepsilon \rightarrow 0$ . We therefore replace the transition rate  $\langle \Psi_\varepsilon \rangle$  by a purely resonant transition rate  $\langle \Psi_\varepsilon \rangle^{\text{dom}}$ , which however still depends on  $\varepsilon$ . To get rid of this last dependence, we will have to specify the value of  $p/\mu$ , which is the goal of the next section.

Still due to small denominator problems, we need to reinforce the decay assumptions on the coefficients and assume Hypothesis 4 and 5 hold.

**Theorem 6.** *Define the transition rate*

$$\langle \Psi_\varepsilon \rangle^{\text{dom}}(k, n) := 2|V(n, k)|^2 \frac{\varepsilon^\mu \gamma(k, n)}{\varepsilon^{2\mu} \gamma(k, n)^2 + \varepsilon^{2p} \delta(k, n)^2} \sum_{\beta \in \mathbb{Z}^r; \omega(k, n) + \beta \cdot \omega = 0} |\phi_\beta|^2. \quad (24)$$

Let also  $\rho_d^{(2)}$  be solution to

$$\partial_t \rho_d^{(2)} = (\langle \Psi_\varepsilon \rangle^{\text{dom}} + W)_\# \rho_d^{(2)} \quad (25)$$

with initial data  $\rho_d^{(2)}(0, n) = \rho_d(0, n)$ . We assume that  $\mu < 1/2$ . Then, under Hypotheses 1, 2, 4 and 5, for all  $T > 0$ , there exists  $C > 0$  such that

$$\|\rho_d - \rho_d^{(2)}\|_{L^\infty([0, T], l^2)} \leq C(\varepsilon^\mu + \varepsilon^{1-2\mu}).$$

**Remark.** When  $\mu = 0$ , Theorem 6 does not give a good approximation of  $\rho_d$ , and we do not have a better description than the one from Proposition 4, where all (resonant and non-resonant) frequencies have a contribution to the transition rates.

The proof of Theorem 6 follows closely that of Proposition 4. However, we notice that the resonant values that play a rôle here satisfy  $\omega(n, k) + \beta \cdot \omega = 0$  and not  $\omega(n, k) + \beta \cdot \omega + \varepsilon^p \delta(n, k) = 0$ . Therefore we need to understand the effect of a perturbation on Diophantine estimates. Lemma 7 below answers this problem.

### 5.1 Perturbed Diophantine estimates

**Lemma 7.** *If  $\omega$  and  $\omega(n, k)$  satisfy the Diophantine condition (8.a) and Hypothesis 2 with constants  $\eta$  and  $C_\eta$ , then the following assertion holds.*

*If  $(n, k, \beta) \in \mathbb{N} \times \mathbb{N} \times \mathbb{Z}^d$  satisfies*

$$|\beta \cdot \omega + \omega(n, k) + \varepsilon^p \delta(n, k)| \leq \frac{1}{2} \frac{C_\eta}{(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}},$$

*then*

$$(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta} \geq \frac{C_\eta \varepsilon^{-p}}{2|\delta|_{l^\infty}}.$$

**Remark.** The Diophantine condition (8.a) is not stable with respect to small perturbations: coefficients  $\omega(n, k) + \varepsilon^p \delta(n, k)$ , that can be arbitrarily close to  $\omega(n, k)$ , are capable of violating the Diophantine condition (8.a). Indeed, for  $\varepsilon$  small, the condition

$$|\beta \cdot \omega + \omega(n, k) + \varepsilon^p \delta(n, k)| \geq \frac{1}{2} \frac{C_\eta}{(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}}$$

does therefore not necessarily hold, only assuming that the left hand-side is non-zero. Nevertheless, Lemma 7 claims that this condition may only be violated for values of the triple  $(n, k, \beta)$  which are very large when  $\varepsilon \rightarrow 0$ . See [CCC<sup>+</sup>03] for a similar argument.

*Proof.* Set  $K = C_\eta/2$  and take  $(n, k, \beta)$  such that

$$|\beta \cdot \omega + \omega(n, k) + \varepsilon^p \delta(n, k)| \leq \frac{K}{(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}}.$$

Then

$$|\beta \cdot \omega + \omega(n, k)| - \varepsilon^p |\delta(n, k)| \leq \frac{K}{(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}},$$

and according to condition (8.a) (or Hypothesis 2, when  $\beta = 0$ )

$$\frac{2K}{(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}} - \varepsilon^p |\delta(n, k)| \leq \frac{K}{(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}}.$$

Hence

$$\frac{K}{(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}} \leq \varepsilon^p |\delta(n, k)|,$$

which ends the proof of Lemma 7. □

## 5.2 Proof of the main theorem

*First step: Integral formulation*

To deduce Theorem 6 from Proposition 4 only amounts to estimate the difference

$$\Delta(t) = \rho_d^{(2)}(t) - \rho_d^{(1)}(t),$$

where we use once again the notation  $\Delta$ . Now  $\rho_d^{(2)}(t)$  and  $\rho_d^{(1)}(t)$  are respectively solution to

$$\partial_t \rho_d^{(2)}(t) = \left( \langle \Psi_\varepsilon \rangle_{\#}^{\text{dom}} \rho_d^{(2)} \right) (t) + \left( W_{\#} \rho_d^{(2)} \right) (t),$$

and

$$\partial_t \rho_d^{(1)}(t) = \left( \langle \Psi_\varepsilon \rangle_{\#} \rho_d^{(1)} \right) (t) + \left( W_{\#} \rho_d^{(1)} \right) (t).$$

Hence

$$\partial_t \Delta(t) = \left( \langle \Psi_\varepsilon \rangle_{\#} \Delta \right) (t) + \left( \langle \Psi_\varepsilon \rangle_{\#}^{\text{neg}} \rho_d^{(2)} \right) (t) + \left( W_{\#} \Delta \right) (t). \quad (26)$$

where

$$\langle \Psi_\varepsilon \rangle^{\text{neg}}(k, n) = \langle \Psi_\varepsilon \rangle^{\text{dom}}(k, n) - \langle \Psi_\varepsilon \rangle(k, n)$$

contains the contributions to the transition rate, that we want to prove to be negligible. Since  $\Delta(0) = 0$  the integral form for (26) reads

$$\Delta(t) = \int_0^t ds \exp([t-s]\langle \Psi_\varepsilon \rangle) \left( \langle \Psi_\varepsilon \rangle_{\#}^{\text{neg}} \rho_d^{(2)} \right) (s) + \int_0^t ds \exp([t-s]\langle \Psi_\varepsilon \rangle) (W_{\#} \Delta)(s).$$

*Second step: Estimating  $\langle \Psi_\varepsilon \rangle^{\text{neg}}$*

In view of Eqs (17) and (24), we have

$$\| \langle \Psi_\varepsilon \rangle^{\text{neg}} \|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} = \sup_n \sum_{k, \beta; \omega(n, k) + \beta \cdot \omega \neq 0} \frac{2|V(n, k)|^2 \varepsilon^\mu \gamma(k, n) |\phi_\beta|^2}{\varepsilon^{2\mu} \gamma(k, n)^2 + |\omega(k, n) + \beta \cdot \omega + \varepsilon^p \delta(k, n)|^2}.$$

We split this expression into two contributions according to the fact that

$$|\beta \cdot \omega + \omega(n, k) + \varepsilon^p \delta(n, k)| \geq \frac{1}{2} \frac{C_\eta}{(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}},$$

or not. Using Lemma 7 for the second contribution, we obtain

$$\begin{aligned} & \| \langle \Psi_\varepsilon \rangle^{\text{neg}} \|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} \\ & \leq \sup_n \left\{ \sum_{k, \beta; \omega(n, k) + \beta \cdot \omega \neq 0} \frac{4|V(n, k)|^2 \varepsilon^\mu \gamma(k, n) |\phi_\beta|^2}{C_\eta} (1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta} \right. \\ & \quad \left. + \sum_{k, \beta; \omega(n, k) + \beta \cdot \omega \neq 0} \mathbf{1} \left[ (1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta} \geq C\varepsilon^{-p} \right] \frac{2|V(n, k)|^2 \varepsilon^{-\mu} |\phi_\beta|^2}{\gamma} \right\}. \end{aligned}$$

The first sum is estimated using Hypotheses 4, 2 and 5. The second term is first multiplied and divided by the quantity  $[(1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta}]^{N_\eta}$ . Therefore we get

$$\begin{aligned} \| \langle \Psi_\varepsilon \rangle^{\text{neg}} \|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} & \leq C\varepsilon^\mu \\ & + C\varepsilon^{N_\eta p - \mu} \sum_{n, k, \beta} \left( (1 + |\beta|)^{r-1+\eta} (1+n)^{1+\eta} (1+k)^{1+\eta} \right)^{N_\eta} |V(n, k)|^2 |\phi_\beta|^2. \end{aligned}$$

Since we assumed that  $N_\eta > 2\mu/p$ , we finally have

$$\| \langle \Psi_\varepsilon \rangle^{\text{neg}} \|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} \leq C\varepsilon^\mu.$$

*Third step: Conclusion*

Using Lemma 5 (non-positiveness of  $\langle \Psi_\varepsilon \rangle$ ) leads to

$$\begin{aligned} \| \Delta(t) \|_{l^2} & \leq C \| \langle \Psi_\varepsilon \rangle^{\text{neg}} \|_{\mathcal{L}(l^2)} \| \rho_d^{(2)} \|_{L^\infty([0, T], l^2)} + C \int_0^t ds \| \Delta(s) \|_{l^2} \\ & \leq C \| \langle \Psi_\varepsilon \rangle^{\text{neg}}(n, k) \|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1} \left[ \| \Delta \|_{L^\infty([0, T], l^2)} + \| \rho_d^{(1)} \|_{L^\infty([0, T], l^2)} \right] + C \int_0^t ds \| \Delta(s) \|_{l^2}. \end{aligned}$$

A by-product of Proposition 4 is that the quantity  $\|\rho_d^{(1)}\|_{L^\infty([0,T],l^2)}$  can be estimated by a constant. Therefore

$$\begin{aligned} \|\Delta(t)\|_{l^2} &\leq C\|\langle\Psi_\varepsilon\rangle^{\text{neg}}(n,k)\|_{l_n^\infty l_k^1 \cap l_k^\infty l_n^1}(1+\|\Delta\|_{L^\infty([0,T],l^2)})+C\int_0^t ds\|\Delta(s)\|_{l^2} \\ &\leq C\varepsilon^\mu(1+\|\Delta\|_{L^\infty([0,T],l^2)})+C\int_0^t ds\|\Delta(s)\|_{l^2}. \end{aligned}$$

Thanks to the Gronwall lemma

$$\|\Delta\|_{L^\infty([0,T],l^2)}\leq C\varepsilon^\mu,$$

which proves Theorem 6. □

## 6 Time-layers and equilibrium states in the $\varepsilon \rightarrow 0$ limit

In the previous sections we have derived the rate equation (25), with the transition rates

$$W_\varepsilon^{\text{mod}}(n,m)=\langle\Psi_\varepsilon\rangle^{\text{dom}}(n,m)+W(n,m),$$

which may be considered as modified rates, *via* the interaction with the wave. We now turn to the study of the dynamics of the solution to Eq. (25).

For a fixed  $\varepsilon$ , this dynamics is described in Appendix 8.1. However, in most cases, the coefficients prove to be singular in  $\varepsilon$ . Therefore the time evolution of the solution obeys two different regimes as  $\varepsilon$  goes to zero: first a time-layer, and then relaxation to an "equilibrium" (if it exists, see Appendix 8.1). The duration of the time-layer is always less than  $O(1)$ , thus the Bloch equation (1) and the rate equation (25) behave in the same way on this time-range (as Theorem 6 asserts). On the contrary, the relaxation towards an equilibrium state, as time goes to infinity, is *a priori* specific for the rate equation, since Theorem 6 only applies on the fixed time-interval  $[0, T]$ .

In this section, we split the rate operator  $(W_\varepsilon^{\text{mod}})_\sharp$  into three contributions.

1. Some levels are decoupled from all other levels. The corresponding columns (and subsequently lines) in the matrix  $(W_\varepsilon^{\text{mod}})_\sharp$  are identically zero. These levels have a constant population for all time (exactly for the rate equation, and at leading order for the Bloch equation). They are excluded from the sequel of the argument. We call  $\Sigma_0$  the subspace spanned by these levels in  $l^2$  (this subspace does not depend on  $\varepsilon$ ). The projection onto the levels which have a non trivial time evolution is denoted by  $\Pi_0$ . Therefore  $\Sigma_0 = \text{Ker } \Pi_0$ .
2. We split  $\langle\Psi_\varepsilon\rangle^{\text{dom}}$  into two contributions:  $\langle\Psi_\varepsilon\rangle^{\text{sing}}$  collects the *singular* coefficients, which go to infinity as  $\varepsilon \rightarrow 0$ . Then,  $\langle\Psi_\varepsilon\rangle^{\text{nonsing}}$  gathers the non-singular coefficients, which are  $O(1)$ . The corresponding case study according to the value of  $\mu/p$  is performed in Section 6.1.
3. Finally we define the  $l^2$ -orthogonal projection  $\Pi$  onto the space  $l^2$ -orthogonal to  $\Sigma_0$  in  $\text{Ker}\langle\Psi_\varepsilon\rangle^{\text{sing}}$ . It does not depend on  $\varepsilon$  either. The quantity  $(1-\Pi)\rho_d$  will be proved

to vanish in time  $O(\varepsilon^\sigma)$ , where  $\sigma$  depends on the ratio  $\mu/p$  (see Table 1). After this time, *i.e.* past the initial time-layer, a polarized solution  $\rho_d^{\text{pol}}$  persists. It is given by the  $\varepsilon$ -independent system

$$\Pi \rho_d^{\text{pol}} = \rho_d^{\text{pol}}, \quad \partial_t \rho_d^{\text{pol}} = \Pi W_{\sharp}^{\text{pol}} \Pi \rho_d^{\text{pol}},$$

where  $W^{\text{pol}} = W + \Psi_0^{\text{nonsing}}$ .

This section is organized as follows: in Section 6.1 we set some notations and explain why the transition rates are in general splitted into three types of terms. Their respective sizes are given by powers of  $\varepsilon$ . Under the assumption that the number  $N$  of quantum levels is finite, a precise description of the time layer is given according to the value of  $\mu/p$  in Section 6.3. The key lemma for this analysis is given in Section 6.2. Section 6.4 is devoted to the particular case  $\mu = 0$ . In Section 6.5, we discuss the few cases (in terms of values of  $\mu/p$ ) when we may conclude for an infinite number of levels. A rigorous framework for the justification of the restriction to a finite number of levels is given in Section 7.

## 6.1 Setting for the time-layer

We first split  $\langle \Psi_\varepsilon \rangle^{\text{dom}}(n, m)$  into two contributions according to whether  $\delta(n, m) = 0$  or not. We restrict the discussion to the case when  $\mu > 0$  since the form of the transition rates in Section 5 does not apply when  $\mu = 0$ . This case is treated separately in Section 6.4. To simplify notations, we set

$$C(n, m) = 2|V(n, m)|^2 \sum_{\beta \in \mathbb{Z}^r; \omega(n, m) + \beta \cdot \omega = 0} |\phi_\beta|^2,$$

and  $\langle \Psi_\varepsilon \rangle^{\text{dom}}(n, m) = A_\varepsilon(n, m) + B_\varepsilon(n, m)$ , where

$$A_\varepsilon(n, m) := C(n, m) \frac{\varepsilon^\mu \gamma(n, m)}{\varepsilon^{2\mu} \gamma(n, m)^2 + \varepsilon^{2p} \delta(n, m)^2} \mathbf{1}(\delta(n, m) = 0), \quad (27.a)$$

$$B_\varepsilon(n, m) := C(n, m) \frac{\varepsilon^\mu \gamma(n, m)}{\varepsilon^{2\mu} \gamma(n, m)^2 + \varepsilon^{2p} \delta(n, m)^2} \mathbf{1}(\delta(n, m) \neq 0). \quad (27.b)$$

Of course Eq. (27.a) also reads

$$A_\varepsilon(n, m) = \varepsilon^{-\mu} C(n, m) \frac{1}{\gamma(n, m)} \mathbf{1}(\delta(n, m) = 0) =: \varepsilon^{-\mu} A(n, m).$$

In a similar way we rewrite Eq. (27.b) as

$$B_\varepsilon(n, m) =: \varepsilon^{-\nu} B^\varepsilon(n, m),$$

where  $\nu$  is chosen such that  $B^\varepsilon \rightarrow B^0$  in  $l^\infty l^1$ , as  $\varepsilon \rightarrow 0$ , and therefore also as an operator on  $l^2$ . To this aim we consider two cases, namely  $\mu \leq p$  and  $\mu \geq p$ . We set

$$\nu = \mu \text{ and } B^\varepsilon(n, m) := C(n, m) \frac{\gamma(n, m)}{\gamma(n, m)^2 + \varepsilon^{2(p-\mu)} \delta(n, m)^2} \mathbf{1}(\delta(n, m) \neq 0) \quad \text{if } \mu \leq p,$$

$$\nu = 2p - \mu \text{ and } B^\varepsilon(n, m) := C(n, m) \frac{\gamma(n, m)}{\varepsilon^{2(\mu-p)} \gamma(n, m)^2 + \delta(n, m)^2} \mathbf{1}(\delta(n, m) \neq 0) \quad \text{if } \mu \geq p.$$

With the above notations, we have cast Eq. (25) governing  $y = \rho_d^{(2)}$  as

$$\partial_t y = (\varepsilon^{-\mu} A + \varepsilon^{-\nu} B^\varepsilon + W)_\# y. \quad (28)$$

Using the block decomposition described in Appendix 8.1, we notice that  $\text{Ker}(B^\varepsilon) = \text{Ker}(B^0)$  is constant with respect to  $\varepsilon \geq 0$ . This is *a priori* only true if all the minimal stable eigenspaces are finite-dimensional.

Now, sorting between singular and non-singular contribution yields the different cases in Table 1. In the framework of [BFCD03]  $B_\varepsilon$  is identically zero. If  $\mu \leq p$  then  $B_\varepsilon$  contributes to singular terms at the same order  $\varepsilon^{-\mu}$  as  $A$ . If  $p < \mu < 2p$ , there are two orders of magnitude  $\varepsilon^{-\mu}$  and  $\varepsilon^{-\nu}$  in the singular term. Finally if  $2p \leq \mu$ , the effect of  $B_\varepsilon$  is of order  $O(1)$  and must be associated to that of  $W$ . In other words, if  $\mu < 2p$ , the non-zero entries in  $A$  and  $B_\varepsilon$  contribute to  $\langle \Psi_\varepsilon \rangle^{\text{sing}}$ , and  $\langle \Psi_\varepsilon \rangle^{\text{nonsing}} = 0$ . If  $\mu \geq 2p$ , only the non-zero entries in  $A$  contribute to  $\langle \Psi_\varepsilon \rangle^{\text{sing}}$ :  $\langle \Psi_\varepsilon \rangle^{\text{nonsing}} = B_\varepsilon$ , which has a non-vanishing value  $\Psi_0^{\text{nonsing}}$  only if  $\mu = 2p$ .

## 6.2 A finite dimensional lemma

**Lemma 8.** *Let  $0 \leq \nu \leq \mu$ . Let  $A$  and  $B^\varepsilon \in \mathcal{M}_N(\mathbb{R})$  be symmetric non-positive matrices such that  $B^\varepsilon \rightarrow B^0$ , and assume that  $\text{Ker}(B^\varepsilon)$  is constant for  $\varepsilon \geq 0$ . Let  $\Pi$  be the orthogonal projection onto  $\text{Ker} A \cap \text{Ker} B^0$ . Then there exists a constant  $c > 0$ , namely*

$$c = \min_{\|x\| \leq 1, \Pi x = 0} -((A + B^0)x, x),$$

such that any non-zero eigenvalue  $\lambda^\varepsilon$  of  $(1 - \Pi)(\varepsilon^{-\mu} A + \varepsilon^{-\nu} B^\varepsilon)(1 - \Pi)$  satisfies

$$\lambda^\varepsilon \leq -c\varepsilon^{-\nu}.$$

*Proof.* Since  $\mu \geq \nu$ , we write

$$(1 - \Pi)(\varepsilon^{-\mu} A + \varepsilon^{-\nu} B)(1 - \Pi) = \varepsilon^{-\nu}(1 - \Pi)(B + \varepsilon^{\nu-\mu} A)(1 - \Pi).$$

Let  $\kappa^\varepsilon$  be a non-zero eigenvalue of  $(1 - \Pi)(B^\varepsilon + \varepsilon^{\nu-\mu} A)(1 - \Pi)$ . Since  $A$  and  $B^\varepsilon$  are non-positive matrices, we have  $\kappa^\varepsilon < 0$ . We therefore want to prove that for the constant  $c$  defined in the lemma,  $\kappa^\varepsilon \leq -c$ . Let  $x^\varepsilon \in \text{Range}(1 - \Pi)$  be an eigenvector associated with the eigenvalue  $\kappa^\varepsilon$  and such that  $\|x^\varepsilon\| = 1$ . We have  $(1 - \Pi)(B^\varepsilon + \varepsilon^{\nu-\mu} A)(1 - \Pi)x^\varepsilon = \kappa^\varepsilon x^\varepsilon$ . Taking the scalar product with  $x^\varepsilon$ , we obtain

$$\kappa^\varepsilon \|x^\varepsilon\|^2 = ((B^\varepsilon + \varepsilon^{\nu-\mu} A)x^\varepsilon, x^\varepsilon) = (B^\varepsilon x^\varepsilon, x^\varepsilon) + \varepsilon^{\nu-\mu} (Ax^\varepsilon, x^\varepsilon).$$

Since  $\varepsilon \in [0, 1]$ ,  $\nu - \mu \leq 0$  and  $(Ax^\varepsilon, x^\varepsilon) \leq 0$ , we have  $\varepsilon^{\nu-\mu} (Ax^\varepsilon, x^\varepsilon) \leq (Ax^\varepsilon, x^\varepsilon)$ . A subsequence of  $x^\varepsilon$  converges to  $x^0$  and therefore

$$\sup_{\varepsilon \geq 0} \kappa^\varepsilon \|x^\varepsilon\|^2 \leq ((A + B^0)x^0, x^0) \leq -c\|x^0\|^2.$$

Finally, if  $c$  were zero, then  $((A + B^0)x, x) = 0$  that is  $(Ax, x) = 0$  and  $(B^0x, x) = 0$  and therefore  $x \in \text{Ker} A \cap \text{Ker} B^0$ . Thus  $(1 - \Pi)x = 0$  and  $x = 0$  which is impossible.  $\square$

**Remark.**

- (i) The above proof is restricted to the finite dimensional case for two reasons. First, in the infinite dimensional case the convergence of  $x^\varepsilon$  to  $x^0$  would only be weak. Second, the maximum of  $((A + B^0)x, x)$  on vectors  $x$  such that  $\|x\| = 1$  could be zero.
- (ii) To avoid such limitations we could think about replacing  $B^\varepsilon$  by the leading order terms (those which are not vanishing as  $\varepsilon \rightarrow 0$ ) in the series expansion of  $B_\varepsilon$  (Lemma 8 can clearly be extended to a finite number of matrices) extending the computations of Section 6.5 to sums of several powers of  $\varepsilon$ . This is not possible since such a procedure would not ensure the non-positiveness of the resulting operators, which is crucial in the proof.

Lemma 8 allows to split the solution  $y$  to Eq. (28) into two parts:  $(1 - \Pi)y$  vanishes exponentially and a solution  $z$  associated with the initial data  $\Pi y(0)$  survives.

**Corollary 9.** Let  $0 < \nu \leq \mu$ . Let  $A, B^\varepsilon \in \mathcal{M}_N(\mathbb{R})$  be two symmetric non-positive matrices such that  $B^\varepsilon \rightarrow B^0$ , and assume that  $\text{Ker}(B^\varepsilon)$  is constant for  $\varepsilon \geq 0$ . Let  $W \in \mathcal{M}_N(\mathbb{R})$ , and let  $\Pi$  be the orthogonal projection onto  $\text{Ker } A_\# \cap \text{Ker } B_\#^\varepsilon$ . If  $y$  is solution to

$$\partial_t y = (\varepsilon^{-\mu} A + \varepsilon^{-\nu} B^\varepsilon + W)_\# y$$

and if  $z$  is solution to

$$\partial_t z = \Pi W_\# \Pi z, \quad z(0) = \Pi y(0), \quad (29)$$

then

$$\|(1 - \Pi)y\| \leq C(\varepsilon^\nu + \exp(-ct\varepsilon^{-\nu})), \quad (30.a)$$

$$\|\Pi(y - z)\| \leq C(\varepsilon^\nu + \exp(-ct\varepsilon^{-\nu})), \quad (30.b)$$

where  $C$  depends on  $W$ ,  $y(0)$ ,  $T$  and  $c$  (the constant of the previous lemma). In particular,  $\lim_{\varepsilon \rightarrow 0} (1 - \Pi)y = 0$ .

*Proof.* The proof is standard. We reproduce it for the sake of completeness. We first prove estimate (30.a). Since  $\Pi$  is the orthogonal projection onto  $\text{Ker } A \cap \text{Ker } B^\varepsilon$ , we have  $\Pi A_\# = \Pi B_\#^\varepsilon = A_\# \Pi = B_\#^\varepsilon \Pi = 0$ , and therefore

$$\begin{aligned} \partial_t (1 - \Pi)y &= (1 - \Pi)\partial_t y = (1 - \Pi)(\varepsilon^{-\mu} A + \varepsilon^{-\nu} B^\varepsilon)_\# y + (1 - \Pi)W_\# y \\ &= (\varepsilon^{-\mu} A + \varepsilon^{-\nu} B^\varepsilon)_\# y + (1 - \Pi)W_\# y, \\ &= (\varepsilon^{-\mu} A + \varepsilon^{-\nu} B^\varepsilon)_\# (1 - \Pi)y + (1 - \Pi)W_\# y. \end{aligned}$$

The solution to this equation reads

$$\begin{aligned} (1 - \Pi)y(t) &= \exp(t(\varepsilon^{-\mu} A + \varepsilon^{-\nu} B^\varepsilon)_\#) (1 - \Pi)y(0) \\ &\quad + \int_0^t ds \exp((t - s)(\varepsilon^{-\mu} A + \varepsilon^{-\nu} B^\varepsilon)_\#) (1 - \Pi)W_\# y(s). \end{aligned}$$

Lemma 8 yields a bound for the spectrum of  $(\varepsilon^{-\mu}A + \varepsilon^{-\nu}B^\varepsilon)_\#$ , namely  $\text{Sp}(\varepsilon^{-\mu}A + \varepsilon^{-\nu}B^\varepsilon)_\# \leq -c\varepsilon^{-\nu}$  and we also have  $\|1 - \Pi\| \leq 1$ , therefore

$$\|(1 - \Pi)y\| \leq \exp(-ct\varepsilon^{-\nu})\|y(0)\| + C \int_0^t ds \exp(-(t-s)c\varepsilon^{-\nu}).$$

Finally  $\|(1 - \Pi)y\| \leq C(\varepsilon^\nu + \exp(-ct\varepsilon^{-\nu}))$  which is estimate (30.a).

We now prove estimate (30.b). We write  $y - z = \Pi(y - z) + (1 - \Pi)y - (1 - \Pi)z$ . By definition  $\Pi z = z$  and we already have estimated  $(1 - \Pi)y$ . Thus there remains to estimate the quantity  $\Pi(y - z)$ , which is solution to

$$\begin{aligned} \partial_t \Pi(y - z) &= \partial_t \Pi y - \partial_t \Pi z = \Pi \partial_t y - \partial_t z \\ &= \Pi(\varepsilon^{-\mu}A + \varepsilon^{-\nu}B)_\# y + \Pi W_\# y - \Pi W_\# \Pi z \\ &= \Pi W_\# y - \Pi W_\# \Pi z \\ &= \Pi W_\# \Pi y + \Pi W_\# (1 - \Pi)y - \Pi W_\# \Pi z \\ &= \Pi W_\# \Pi \Pi(y - z) + \Pi W_\# (1 - \Pi)y. \end{aligned}$$

The solution to this equation may be estimated by

$$\|\Pi(y - z)\| \leq \int_0^t ds \|\exp((t-s)\Pi W_\# \Pi)\| \times \|\Pi W_\# (1 - \Pi)y(s)\|$$

because  $\Pi y(0) = z(0) = \Pi z(0)$ . Since  $\Pi W_\# \Pi \leq 0$  we finally have

$$\|\Pi(y - z)\| \leq C(\varepsilon^\nu + \exp(-ct\varepsilon^{-\nu}))$$

and estimate (30.b) follows. □

**Remark.** If  $\Pi W_\# \Pi = 0$  then  $z' = 0$  and  $y$  is constant at leading order.

### 6.3 Finite dimensional case study

We now discuss the implications of Lemma 8 for the different values of  $\mu/p$ . We have already seen that a transition occurs in the definition of  $B^\varepsilon$  when  $p = \mu$ . Another transition happens when  $\nu = 0$ , *i.e.*  $\mu = 2p$ . The main results of this part are summarized in Table 1.

**Case when  $0 < \mu < p$ .** If  $0 < \mu < p$ , we may apply Corollary 9 with  $\nu = \mu$  and the limit operator  $B^0$  is

$$B^0(n, m) = C(n, m) \frac{1}{\gamma(n, m)} \mathbf{1}(\delta(n, m) \neq 0).$$

In this circumstance there is no need to separate the cases when  $\delta(n, m) \neq 0$ , since

$$(\varepsilon^{-\mu}A + \varepsilon^{-\nu}B^\varepsilon)(n, m) = \varepsilon^{-\mu} \left( \frac{C(n, m)}{\gamma(n, m)} + o(1) \right).$$

Hence for large values of  $p$  compared to  $\mu$ , the dynamics is the same for almost degenerate levels and for exactly degenerate levels. After a time-layer of size  $O(\varepsilon^\mu)$  the system is driven by Eq. (29), namely

$$\partial_t z = \Pi W_\# \Pi z, \quad z(0) = \Pi y(0),$$

where  $\Pi$  the orthogonal projection onto  $\text{Ker } A_\# \cap \text{Ker } B_\#^0 = \text{Ker} \langle \Psi_\varepsilon \rangle_\#^{\text{dom}}$ .

**Case when  $\mu = p$ .** If  $\mu = p$ , we again apply Corollary 9 with  $\nu = \mu$ , but the form of  $B^0$  is slightly different, and now  $\delta(n, m)$  plays a rôle, namely

$$B^\varepsilon(n, m) = B^0(n, m) = C(n, m) \frac{\gamma(n, m)}{\gamma(n, m)^2 + \delta(n, m)^2} \mathbf{1}(\delta(n, m) \neq 0).$$

The limit equation is as in the previous case.

**Case when  $p < \mu < 2p$ .** If  $p < \mu < 2p$ , we really have three different orders of magnitude in Eq. (28). The form for  $B^0$  is now

$$B^0(n, m) = C(n, m) \frac{\gamma(n, m)}{\delta(n, m)^2} \mathbf{1}(\delta(n, m) \neq 0),$$

and the size of the time-layer is  $O(\varepsilon^{2p-\mu})$ . The limit equation is still unchanged.

**Case when  $\mu = 2p$ .** If  $\mu = 2p$ , then  $\nu = 0$  and the contribution of  $B^0$  competes with that of  $W$ . Therefore the projector mentioned in Corollary 9 is here  $\Pi_A$ , the orthogonal projection on  $\text{Ker } A_\#$ , and the limit equation is

$$\partial_t z = \Pi_A (B^0 + W)_\# \Pi_A z, \quad z(0) = \Pi_A y(0),$$

where

$$B^0(n, m) = C(n, m) \frac{\gamma(n, m)}{\delta(n, m)^2} \mathbf{1}(\delta(n, m) \neq 0),$$

after a time-layer of size  $O(\varepsilon^\mu)$ . In this case, and in the following one, the projection only depends on  $A$  (and not on  $B^0$ ). The constant  $c$  is simply  $c = \min_{\|x\| \leq 1, \Pi_A x = 0} -(A_\# x, x)$ .

**Case when  $\mu > 2p$  or  $B_\varepsilon \equiv 0$ .** If  $\mu > 2p$ , then  $\nu < 0$  and  $B^\varepsilon \rightarrow 0$ . This case is therefore treated in the same way as when  $B_\varepsilon \equiv 0$ . In both cases, the limit equation is

$$\partial_t z = \Pi_A W_\# \Pi_A z, \quad z(0) = \Pi_A y(0),$$

after a time-layer of size  $O(\varepsilon^\mu)$ . Hence for small values of  $p$  compared to  $\mu$ , two almost degenerate levels  $n$  and  $m$  for which  $\delta(n, m) \neq 0$  are already too far apart to resonate with the wave.

## 6.4 Case when $\mu = 0$ .

In the case when  $\mu = 0$ , Section 5 does not yield an interesting result since  $\rho_d - \rho_d^{(2)}$  is of order  $O(1)$ . Therefore we have to use the transition rates obtained in Section 4, namely

$$\langle \Psi_\varepsilon \rangle(n, m) = 2|V(n, m)|^2 \sum_{\beta \in \mathbb{Z}^r} \frac{\gamma(n, m)}{\gamma(n, m)^2 + |\omega(m, n) + \beta \cdot \omega + \varepsilon^p \delta(n, m)|^2} |\phi_\beta|^2.$$

For a finite or an infinite number of energy levels, we have at leading order  $\rho_d = \rho_d^{\text{app}}$ , where

$$\partial_t \rho_d^{\text{app}} = (\langle \Psi_0 \rangle + W)_\# \rho_d^{\text{app}}$$

and

$$\langle \Psi_0 \rangle(n, m) = 2|V(n, m)|^2 \sum_{\beta \in \mathbb{Z}^r} \frac{\gamma(n, m)}{\gamma(n, m)^2 + |\omega(m, n) + \beta \cdot \omega|^2} |\phi_\beta|^2.$$

The discussion of the long time behavior and equilibrium state for such an equation is the same as for Eq. (25) (see Appendix 8.1).

## 6.5 Infinite dimensional case study

In the infinite dimensional case the convergence of  $B^\varepsilon$  towards  $B^0$  is not sufficient to conclude. However, we can use series expansions when they only include one non-positive order in  $\varepsilon$ , *i.e.*

$$\langle \Psi_\varepsilon \rangle^{\text{dom}} + W = \varepsilon^{-\sigma} \tilde{A} + o(1).$$

In this case, we consider at leading order the solution  $\rho_d^{\text{app}}$  of

$$\partial_t \rho_d^{\text{app}} = \varepsilon^{-\sigma} \Psi_\#^{\text{app}} \rho_d^{\text{app}} \quad (31)$$

where  $\Psi^{\text{app}}$  is homogeneous of order  $O(1)$ . In this case, time has to be changed into  $t' = \varepsilon^{-\nu} t$ . With this time scale, the equation is not singular any more. There remains to list the cases when such an homogeneous rate operator occurs, restricting the discussion to  $\mu > 0$ . As for a finite number of levels, the value of the ratio  $\mu/p$  is crucial. We once more have to consider the two cases  $\mu \leq p$  and  $\mu \geq p$ . The main results of this section are summarized in Table 2.

**Case when  $\mu < p$ .** If  $\mu < p$ , series expansions yield that

$$\langle \Psi_\varepsilon \rangle^{\text{dom}}(n, m) = C(n, m) \frac{\varepsilon^{-\mu}}{\gamma(n, m)} + O(\varepsilon^{2p-3\mu}).$$

If  $2p - 3\mu > 0$ , *i.e.*  $\mu < 2p/3$

$$\langle \Psi_\varepsilon \rangle^{\text{dom}}(n, m) =: \varepsilon^{-\mu} \Psi^{\text{app}}(n, m) + o(1).$$

Since  $\nu > 0$ ,  $\sigma = \mu$  and rates are homogeneous only if  $W = 0$ .

**Case when  $\mu = p$ .** In the case when  $\mu = p$  no series expansion is needed and we have exactly

$$\langle \Psi_\varepsilon \rangle^{\text{dom}}(n, m) = C(n, m) \frac{\varepsilon^{-\mu} \gamma(n, m)}{\gamma(n, m)^2 + \delta(n, m)^2} =: \varepsilon^{-\mu} \Psi^{\text{app}}(n, m).$$

Once more, we can only conclude if  $W = 0$ .

**Case when  $\mu > p$ .** If  $\mu < p$ , series expansions lead to

$$\begin{aligned} \langle \Psi_\varepsilon \rangle^{\text{dom}}(n, m) &= C(n, m) \frac{\varepsilon^{-\mu}}{\gamma(n, m)} \mathbf{1}(\delta(n, m) = 0) \\ &+ C(n, m) \frac{\varepsilon^{-(2p-\mu)} \gamma(n, m)}{\delta(n, m)^2} \mathbf{1}(\delta(n, m) \neq 0) + O(\varepsilon^{3\mu-4p}). \end{aligned}$$

Two cases lead to only one term  $\varepsilon^{-\sigma} \tilde{A} + o(1)$ , either  $\delta(n, m)$  is always nonzero,  $\mu > \frac{4}{3}p$  and  $W = 0$ . In this case  $\sigma = 2p - \mu$ . Or  $\mu > 2p$  and  $\sigma = \mu$ . We once more need to assume that  $W = 0$ .

In all the above cases, using the same type of estimates and integral formulations as in the proofs in Section 4 and 5, we define an approximate solution  $\rho_d^{\text{app}}$  to Eq. (31) such that

$$\|\rho_d - \rho_d^{\text{app}}\|_{L^\infty([0, T], l^2)} = o(1),$$

and  $\Psi^{\text{app}}$  has the properties described in Section 8.1.

$\mu/p$	$\sigma$	$\frac{\Psi^{\text{app}}(n, m)}{2 V(n, m) ^2 \sum_\beta  \phi_\beta ^2}$
$0 (\mu = 0, p > 0)$	$\mu$	$\frac{1}{\gamma(n, m)}$ (see caption)
$0 < \mu/p < 2/3$	$\mu$	$\frac{1}{\gamma(n, m)}$
$\mu/p = 1$	$\mu$	$\frac{\gamma(n, m)}{\gamma(n, m)^2 + \delta(n, m)^2}$
$4/3 < \mu/p < 2$	$2p - \mu$	$\frac{\gamma(n, m)}{\delta(n, m)^2}$
$\mu/p = 2$	$0$	$\frac{\gamma(n, m)}{\delta(n, m)^2}$
$2 < \mu/p < \infty$	$0$	$0$

Table 2: Cases when the transition rates are single powers of  $\varepsilon$ , for an infinite number of levels. The sum over  $\beta$ 's includes only resonant contributions in general, except when  $\mu = 0$  where  $\beta \in \mathbb{Z}^r$ .

## 7 Restriction to a finite number of levels

It is important to show that we can restrict the study to a finite number of levels since we have seen in Section 6 that we are able to give precise results on the time evolution of rate equations only in this case. Another perspective is numerical simulations, which in any case can only treat finite data.

Consider a solution  $\rho$  to Bloch equations (1) with initial datum  $\rho(0)$ , and infinitely many quantum levels. In this section, we show how  $\rho$  may be approximated by  $\rho^N$ , solution to Eq. (1) with only a finite number  $N$  of levels.

For this purpose, for all  $N \in \mathbb{N}$ , we define  $\pi^N$ , the projection of the space  $\mathbb{C}^{\mathbb{N}^2}$  of infinite matrices onto the space of  $N \times N$  matrices, by

$$(\pi^N u)(n, m) := u(n, m) \mathbf{1}[n, m < N].$$

Then, the  $N$ -level *truncated system* ( $1^N$ ) is defined from Eq. (1) by

$$\begin{aligned} \varepsilon^2 \partial_t \rho^N(t, n, m) = & -i\omega_\varepsilon(n, m) \rho^N(t, n, m) + (\pi^N Q_\varepsilon)(\rho^N)(n, m) \\ & + i\varepsilon \sum_{k < N} \left[ \mathcal{V} \left( \frac{t}{\varepsilon^2}, n, k \right) \rho^N(t, k, m) - \mathcal{V} \left( \frac{t}{\varepsilon^2}, k, m \right) \rho^N(t, n, k) \right]. \end{aligned} \quad (1^N)$$

The initial datum  $\rho^N(0)$  is also naturally defined as

$$\rho^N(0) := \pi^N \rho(0).$$

The analysis of the previous sections shows that, in the limit  $\varepsilon \rightarrow 0$ ,  $\rho$  is approximated by the diagonal solution  $\rho_d^{(2)}$  to rate equations (25). Theorem 6 also gives an approximation of  $\rho^N$  by  $\rho_d^{N,(2)}$ , which turns out to be solution to the truncated system obtained from Eq. (25):

$$\partial_t \rho_d^{N,(2)} = (\pi^N \langle \Psi_\varepsilon \rangle^{\text{dom}} + \pi^N W)_\# \rho_d^{N,(2)}, \quad \rho_d^{N,(2)}(0) = \pi^N \rho(0). \quad (25^N)$$

To apply Theorem 6, we need Hypotheses 1 to 5. Under the additional condition that longitudinal relaxation coefficients are decaying enough at infinity (Hypothesis 6), we show that this truncation procedure is compatible with the evolution according to Bloch equations and rate equations:

**Lemma 10.** *Under Hypotheses 1 to 6, for all  $\nu, T, \varepsilon > 0$ , there exists an integer  $N$  such that,*

$$\text{if } \|(1 - \pi^N) \rho(0)\|_{l^2} \leq \nu, \text{ then } \|\rho - \rho^N\|_{L^\infty([0, T], l^2)} \leq 2\nu + C(\varepsilon^\mu + \varepsilon^{1-2\mu}),$$

where  $C = C(T)$  is the constant from Theorem 6, and  $N$  has the form

$$N = N_0(\nu, T) \varepsilon^{-\frac{\mu}{(1+\eta)N_\eta}},$$

with  $\eta$  and  $N_\eta$  given by Hypotheses 1 and 4.

If, in addition, no resonance occurs between the wave and high energy levels (i.e. there exists  $M \in \mathbb{N}$  such that, when  $\min(n, k) > M$ , the set  $\{\beta \in \mathbb{Z}^r; \omega(n, k) + \beta \cdot \omega = 0\}$  is empty), then  $N$  has the form  $N = N_0(\nu, T)$ , uniformly with respect to  $\varepsilon$ .

*Proof.* Theorem 6 applies for both the infinite and the finite number of levels problems, therefore

$$\|\rho - \rho_d^{(2)}\|_{L^\infty([0,T],l^2)} \leq C(\varepsilon^\mu + \varepsilon^{1-2\mu})$$

and

$$\|\rho^N - \rho_d^{N,(2)}\|_{L^\infty([0,T],l^2)} \leq C(\varepsilon^\mu + \varepsilon^{1-2\mu}),$$

and we only need to estimate the difference  $\Delta := \rho_d^{(2)} - \rho_d^{N,(2)}$ , which is solution to

$$\partial_t \Delta = (\langle \Psi_\varepsilon \rangle^{\text{dom}} + W)_\# \Delta + (\langle \Psi_\varepsilon \rangle^{\text{dom}} - \langle \Psi_\varepsilon \rangle^{\text{dom},N})_\# \rho_d^{N,(2)} + (W - \pi^N W)_\# \rho_d^{N,(2)}.$$

Thanks to the non-positiveness property of the operators associated with  $\langle \Psi_\varepsilon \rangle^{\text{dom}}$  and  $W$ , an integral formulation leads to

$$\begin{aligned} \|\Delta\|_{L^\infty([0,T],l^2)} &\leq C \left( \|(1 - \pi^N)\rho(0)\|_{l^2} + \|(\langle \Psi_\varepsilon \rangle^{\text{dom}} - \pi^N \langle \Psi_\varepsilon \rangle^{\text{dom}})_\# \rho_d^{N,(2)}\|_{L^\infty([0,T],l^2)} \right. \\ &\quad \left. + \|(W - \pi^N W)_\# \rho_d^{N,(2)}\|_{L^\infty([0,T],l^2)} \right) \\ &\leq C \left( \|(1 - \pi^N)\rho(0)\|_{l^2} + \|\langle \Psi_\varepsilon \rangle^{\text{dom}} - \pi^N \langle \Psi_\varepsilon \rangle^{\text{dom}}\|_{l_k^\infty l_n^1 \cap l_n^\infty l_k^1} \right. \\ &\quad \left. + \|W - \pi^N W\|_{l_k^\infty l_n^1 \cap l_n^\infty l_k^1} \right). \end{aligned}$$

The first term goes to zero as  $N$  goes to infinity simply because the initial datum  $\rho(0)$  is in  $l^2$ . The third one reads

$$\begin{aligned} &\sup_{n>N} \sum_k |W(n,k)| + \sup_n \sum_{k>N} |W(n,k)| + \sup_{k>N} \sum_n |W(n,k)| + \sup_k \sum_{n>N} |W(n,k)| \\ &\leq C \left( \sup_{n>N} \sum_k |W(n,k)| + \sup_n \sum_{k>N} |W(n,k)| \right) \\ &\leq CN^{-K} \left( \sup_{n>N} \sum_k (1+n)^K |W(n,k)| + \sup_n \sum_{k>N} (1+k)^K |W(n,k)| \right) \\ &\leq CN^{-K}, \end{aligned}$$

thanks to Hypothesis 6. Thus, this term is also  $o(1)$  uniformly with respect to  $\varepsilon$  as  $N$  goes to infinity.

Finally, taking into account the fact that  $\langle \Psi_\varepsilon \rangle^{\text{dom}}$  is symmetric, the second term is

$$\begin{aligned} &2 \left( \sup_{n>N} \sum_k |\langle \Psi_\varepsilon \rangle^{\text{dom}}(n,k)| + \sup_n \sum_{k>N} |\langle \Psi_\varepsilon \rangle^{\text{dom}}(n,k)| \right) \\ &\leq C\varepsilon^{-\mu} \sup_{n>N} \sum_k \sum_{\beta; \omega(n,k)+\beta \cdot \omega=0} |\phi_\beta|^2 |V(n,k)|^2 \\ &\leq C\varepsilon^{-\mu} N^{-(1+\eta)N_\eta} \sup_{n>N} \sum_k (1+n)^{(1+\eta)N_\eta} \sum_{\beta; \omega(n,k)+\beta \cdot \omega=0} |\phi_\beta|^2 |V(n,k)|^2 \\ &\leq C\varepsilon^{-\mu} N^{-(1+\eta)N_\eta}, \end{aligned}$$

which vanishes in fact when no resonance occurs between the wave and high energy levels. Else, we obtain a  $o(1)$  as  $\varepsilon$  goes to zero under the condition

$$N \gg \varepsilon^{-\mu/N_\eta(1+\eta)}.$$

□

## 8 Appendix

In this section, we give the lemmas concerning the modified relaxation operator from Eq. (3), in order to describe the dynamics of the solution. We also give a proof of the genericity of the small divisor estimates of Hypothesis 1.

### 8.1 Relaxation operators

We first prove some non-positiveness properties of  $(W_\varepsilon^{\text{mod}})_\sharp$ .

#### 8.1.1 Continuity and non-positiveness

**Lemma 11.** *Let  $A(n, m) \in l_n^\infty l_m^1 \cap l_m^\infty l_n^1$ .*

*(i) Its associated operator  $A_\sharp$  is bounded on the spaces  $l^q$ ,  $1 \leq q \leq \infty$ , and*

$$\|A_\sharp u\|_{l^q} \leq \|A(n, m)\|_{l_n^\infty l_m^1 \cap l_m^\infty l_n^1} \|u\|_{l^q}.$$

*(ii) If in addition  $A(n, m) \geq 0$ , then for all positive integer  $N$ , the spectrum of the restriction of  $A_\sharp$  to  $\mathbb{R}^N$  is contained in  $\{\text{Re } \lambda < 0\} \cup \{0\}$ .*

*(iii) If  $A(n, m) \geq 0$  is symmetric,  $A_\sharp$  is non-positive on  $l^2$ , and the exponential  $\exp(tA_\sharp)$  is well defined as an operator on  $l^2$  when  $t \geq 0$ . Its norm is 1.*

*Proof.* (i) For  $q = \infty$  or  $q = 1$ , the result is immediate. The remaining cases are obtained by interpolation.

(ii) The localization of the eigenvalues of  $A_\sharp$  is obtained *via* the Hadamard-Gerschgorin method applied to  $M := \overline{A_\sharp} = {}^t A_\sharp$ , whose eigenvalues are the conjugates of those of  $A_\sharp$ : if  $\lambda$  is an eigenvalue of  $M$ , there exists an index  $n$  such that

$$|\lambda - M(n, n)| \leq \sum_{m \neq n} |M(n, m)|.$$

Remarking that for  $m \neq n$ ,  $M(n, m) = A_\sharp(m, n) \geq 0$ , and  $M(n, n) = -\sum_{m \neq n} M(n, m)$ , the conclusion is straightforward.

(iii) In the symmetric case, compute for all  $u \in l^2$ ,

$$\begin{aligned} (A_\sharp u, u) &= \sum_n \sum_{m \neq n} A_\sharp(n, m) u(m) u(n) + \sum_n A_\sharp(n, n) u(n)^2 \\ &\leq \frac{1}{2} \sum_n \sum_{m \neq n} A_\sharp(n, m) (|u(m)|^2 + |u(n)|^2) - \sum_n \sum_{m \neq n} A_\sharp(m, n) u(n)^2 = 0. \end{aligned}$$

The norm of  $\exp(tA_\sharp)$  is 1 on  $l^2$  for  $t > 0$  because  $A_\sharp$  has a non-trivial kernel (see below). □

In the same way as for item (i) of Lemma 11, we have the estimate usually called Schur's lemma.

**Lemma 12.** *Let  $A \in l_n^\infty l_k^1 \cap l_k^\infty l_n^1$  and  $1 \leq q \leq \infty$ . Then, if  $u \in l_{n,m}^q(\mathbb{N} \times \mathbb{N})$ ,*

$$\left\| \sum_k A(n, k)u(k, m) - A(k, m)u(n, k) \right\|_{l_{n,m}^q} \leq \|A(n, m)\|_{l_n^\infty l_m^1 \cap l_m^\infty l_n^1} \|u(n, m)\|_{l_{n,m}^q}.$$

### 8.1.2 Asymptotic states of the rate equation

We define the asymptotic state  $\underline{\rho}$  associated with Eq. (3) and with the initial datum  $\rho(0)$ , the limit (in  $l^1$ ), if it exists, of the solution  $\rho_d(t)$  to Eq. (3) with the initial value  $\rho(0)$  as  $t$  goes to infinity. Such an asymptotic state is necessarily an equilibrium state (*i.e.* it belongs to the kernel of  $(W_\varepsilon^{\text{mod}})_\#$ ). As an example, the usual thermodynamic equilibrium  $\underline{\rho}^{\text{therm}}$  (corresponding to  $W_\varepsilon^{\text{mod}} = W$  satisfying Eq. (5)) for the  $N$ -level Bloch model is given by

$$\underline{\rho}^{\text{therm}}(n) = \frac{\exp\left(-\frac{\omega_n}{T}\right)}{\sum_{k=1}^N \exp\left(-\frac{\omega_k}{T}\right)}.$$

We study the kernel of operators  $A_\#$  modelled on  $(W_\varepsilon^{\text{mod}})_\#$ : the  $-$ finite or infinite $-$  matrix  $A$ , written in the eigenstates basis  $e = (e_1, e_2, \dots)$ , has the property  $(\mathcal{P})$ .

$$A(m, n) = 0 \Leftrightarrow A(n, m) = 0. \quad (\mathcal{P})$$

In particular, thanks to this property, a vanishing column in  $A_\#$  corresponds to a vanishing line, and conversely.

The kernel of  $A_\#$  is linked to the spaces generated by elements of the basis  $e$ ,

$$E_L := \text{Span}\{e_m; m \in L\},$$

when  $L$  is a finite subset of indices.

**Proposition 13.** *Let  $A(m, n) \in l_m^\infty l_n^1 \cap l_n^\infty l_m^1$  satisfy property  $(\mathcal{P})$ , and  $A(m, n) \geq 0$  when  $m \neq n$ . In addition, suppose that there exists a decomposition of  $l^1$  into  $A_\#$ -stable subspaces of the form  $E_L$  (each with finite dimension).*

*Then, the restriction of  $A_\#$  to any such non-zero subspace with minimal size has a one-dimensional kernel.*

Such a minimal subset can be one dimensional, *i.e.* generated by a single  $e_n$ . This corresponds exactly to the case when the  $n$ -th line (or column) of  $A_\#$  vanishes. When the cardinality of  $L$  is greater or equal to two,  $E_L$  is characterized by:

$$\begin{aligned} m \leq n \in L \quad \Leftrightarrow \quad \exists m =: m_1 \leq \dots \leq m_s := n, \text{ such that} \\ m_j \in L \text{ for all } j = 1, \dots, s \\ \text{and } A_\#(m_j, m_{j+1}) \neq 0 \text{ for all } j = 1, \dots, s-1. \end{aligned}$$

*Proof.* When the dimension of  $E_L$  is one, the result is trivial. Now, suppose that the cardinality of  $L$  is at least 2.

Denote by  $A_{\#}^L$  the restriction of  $A_{\#}$  to  $E_L$ . Since the dimension of  $E_L$  is finite, the dimension of the kernel of  $A_{\#}^L$  is the same as the dimension of the kernel of the transposed matrix,  ${}^tA_{\#}^L$ . Let  $u$  belong to this kernel. Written relatively to the basis  $\{e_n; n \in L\}$ , the relation  ${}^tA_{\#}^L u = 0$  reads

$$\left( \sum_{k \in L \setminus \{n\}} A(n, k) \right) u(n) = \sum_{k \in L \setminus \{n\}} A(n, k) u(k)$$

for all  $n \in L$ . Each coefficient  $A(n, k)$  is non-negative, and thanks to the property  $(\mathcal{P})$ , the sum  $\sum_{k \in L \setminus \{n\}} A(n, k)$  is positive. Therefore,  $u(n)$  belongs to the convex hull of the other coordinates. Since this is valid for all  $n \in L$ , all the coordinates must be equal, and the kernel of  ${}^tA_{\#}^L$  is generated by  $\sum_{n \in L} e_n$ .  $\square$

**Corollary 14.** *Under the assumptions of Proposition 13, for each initial datum  $\rho(0) \in l^1$  satisfying Eq. (2), there is a unique  $\underline{\rho} \in l^1 \cap \text{Ker } A_{\#}$  such that for all minimal  $A_{\#}$ -stable subspace  $E_L$ ,*

$$\sum_{n \in L} \underline{\rho}(n) = \sum_{n \in L} \rho(0, n).$$

Since the decomposition of  $l^1$  into  $A_{\#}$ -stable finite dimensional subspaces corresponds to the splitting of Eq. (3) into a countable set of decoupled finite dimensional systems which have bounded solutions (thanks to the results of Lemma 11 on the spectrum of  $A_{\#}$ ), a diagonal argument allows to extract a converging subsequence of  $\rho_d(t)$ . Finally, the normalization of the trace on each minimal subspace ensures the uniqueness of the limit. This shows that the whole sequence  $(\rho_d(t))_{t \geq 0}$  converges to  $\underline{\rho}$ , which is actually an asymptotic state.

In the purely infinite dimensional case, *i.e.* when no decomposition into finite dimensional  $A_{\#}$ -stable subspaces exists, the results above may break down.

**Proposition 15.** *Consider  $A(m, n) \in l_m^{\infty} l_n^1 \cap l_n^{\infty} l_m^1$  satisfying property  $(\mathcal{P})$ ,  $A(m, n) \geq 0$  when  $m \neq n$ , and either symmetric, or in Pauli form (relation (5)). Suppose that there exists a minimal  $A_{\#}$ -stable subspace  $E$  of  $l^1$  generated by an infinite number of eigenstates  $e_n$ .*

*Then, the kernel of  $A_{\#|_E}$  (the restriction to  $E$  of the operator on  $l^1$ ) is  $\{0\}$ .*

*Proof.* Denoting  $A_{\#}^E$  the restriction of  $A_{\#}$  to  $E$ , we have a one-to-one relation between elements of the kernel of  $A_{\#}^E$  and elements of the kernel of  ${}^tA_{\#}^E$ :

$$\begin{aligned} u \in \text{Ker } A_{\#}^E &\Leftrightarrow {}^t u \in \text{Ker } {}^t A_{\#}^E && \text{in the symmetric case,} \\ &\Leftrightarrow \left( u(n) \exp\left(\frac{\omega(n)}{T}\right); n \in L \right) \in \text{Ker } {}^t A_{\#}^E && \text{in the "Pauli" case.} \end{aligned}$$

Since we have the bounds

$$0 < \exp\left(\frac{\omega(1)}{T}\right) \leq \exp\left(\frac{\omega(n)}{T}\right) \leq \exp\left(\frac{\omega_{\text{ionisation}}}{T}\right)$$

for all  $n$ , this correspondence preserves the summability property.

Finally, the proof of Proposition 13 shows that the kernel of  ${}^tA_{\#}^E$  (in  $l^1$ ) is  $\{0\}$ , and this gives the result.  $\square$

**Corollary 16.** *Under the assumptions of Proposition 15, for any initial datum  $\rho(0)$  with non-vanishing component in  $E$ , there is no equilibrium state  $\underline{\rho} \in l^1 \cap \text{Ker } A_{\#}$  with the same trace as  $\rho(0)$  in  $E$ .*

**Remark.** *In the symmetric case (when  $\langle \Psi_{\varepsilon} \rangle^{\text{dom}} = 0$ ,  $W_{\varepsilon}^{\text{mod}} = W$ ), according to Lemma 11, the  $l^2$ -norm of the solution  $\rho_d$  to Eq. (3) is decreasing in time; thus, it tends to a certain value  $r \geq 0$ . This means that  $\rho_d$  approaches a limit cycle in  $l^2$  belonging to the intersection of the sphere  $\|\rho_d\|_{l^2} = r$  and the hyperplane where the  $l^1$ -norm is one (assuming for simplicity that there is no strict  $A_{\#}$ -stable subspace of  $l^1$ ). In this case, only weak convergence (to zero) can occur.*

## 8.2 Diophantine estimates

We show the genericity of Hypothesis 1.

**Lemma 17.** *For all  $\eta > 0$  and all real sequence  $\omega(n, m)$ , there exists a constant  $C_{\eta} > 0$ , such that for almost all value of the frequency vector  $\omega = (\omega_1, \dots, \omega_r)$ ,*

$$\forall \alpha = (\alpha_1, \dots, \alpha_r) \in \mathbb{Z}^r \setminus \{0\}, \quad \forall (n, k) \in \mathbb{N}^2 \text{ such that } \alpha \cdot \omega + \omega(n, k) \neq 0,$$

$$|\alpha \cdot \omega + \omega(n, k)| \geq \frac{C_{\eta}}{(1 + |\alpha|)^{r-1+\eta}(1+n)^{1+\eta}(1+k)^{1+\eta}}.$$

*Proof.* We follow the standard approach (see e.g. [AG91]). Restricting  $\omega$  to a ball  $B$  in  $\mathbb{R}^r$ , we show that the measure of the set of “bad frequencies” violating the inequality for all constant  $C$  is zero.

For  $\eta, c > 0$ ,  $\alpha \in \mathbb{Z}^r \setminus \{0\}$  and  $(n, k) \in \mathbb{N}^2$  fixed, set

$$B_{\alpha, n, k}^{\eta, c} := \left\{ \omega \in B; |\alpha \cdot \omega + \omega(n, k)| \leq \frac{c}{(1 + |\alpha|)^{r-1+\eta}(1+n)^{1+\eta}(1+k)^{1+\eta}} \right\}.$$

This limitates  $\omega$  in the direction of  $\alpha$ . Introducing a constant  $K$  which depends on the size of  $B$  only, we obtain

$$\text{meas}(B_{\alpha, n, k}^{\eta, c}) \leq \frac{Kc}{(1 + |\alpha|)^{r-1+\eta}(1+n)^{1+\eta}(1+k)^{1+\eta}}.$$

Now, with  $\eta, c > 0$  fixed, the measure of the set of frequencies for which the inequality is false at least for some  $(\alpha, n, k)$  is less than the sum (over  $\alpha, n$  and  $k$ ) of the ones above, and thus is  $O(c)$ .  $\square$

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