Mathematical modeling of point defects in materials science

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Abstract

We survey some recent mathematical works we have contributed to that are related to the modeling of defects in materials science at different scales. We emphasize the similarities (need of a reference, often periodic system; renormalization procedure; etc) shared by models arising in different contexts. Our illustrative examples are taken from electronic structure models, atomistic models, homogenization problems. The exposition is pedagogic and deliberately kept elementary. Both theoretical and numerical aspects are addressed.

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Contents

1 Introduction

This article is not a state-of-the-art survey of all existing mathematical approaches for addressing the question of the modeling of defects in materials science. The field is enormous. International conferences, thematic programs worldwide are organized around this topic. Our article is rather a recollection of some of our own works and the works by the group of researchers we belong to in this direction. Because we have no expertise in Physics, Chemistry or Mechanics, we will keep the exposition on a purely mathematical footing. We are interested in mathematical methodologies that allow, starting from an ideal medium, to model the same medium in the presence of imperfections. On purpose, we say here "medium" and "imperfections", in order not to let our mathematical constructions unintentionally carry a physical meaning. We do not want to discuss the physical relevance of the models we study or derive. Our colleagues from other disciplines will assess this. However, we acknowledge that the primary applications we have in mind concern "materials" as examples of "media". Likewise, if one wants to equip our mathematical discussion with a physical relevance, "point defects" (such as a vacancy in a crystalline structure) rather than general defects in these materials are to be born in mind. Thus our specific choice of title for this article and the slight abuse of terminology we allow ourselves. The modeling of more sophisticated defects (such as dislocations), or the application to other contexts, is perhaps possible using similar techniques, or improvements of those. We will not claim this is the case, nor proceed further in this direction.

Before we definitively turn to exclusively mathematical considerations, we would like to make the following points on the relevance of our mathematical endeavour for materials science, or other applied contexts. The *defects* we are considering are essential elements of the modeling because they allow to pass from an idealized model, which nowhere exists in the real world, to a practically relevant model. In that sense, they are not *defects* but just part of reality. In addition to this, and for what specifically regards materials science, the *point defects* we consider here have been much less studied than other types of defects, such as e.g. dislocations, for which the mathematical literature is much broader (at least for phenomenological models at the mesoscale). An important remark we would like to emphasize is that we do realize that there exists an extensive literature in mechanical engineering, nuclear engineering and materials science about all types of defects and all possible modeling strategies for those. Our endeavour is systematic and mathematical, and therefore is, to this extent, different and new.

In order to readily present our line of thought, we start with a simple example: a set of interacting particles clamped on the real line. Consider $2N+1$ point particles, at the positions X_k, $k=-N,-N+1,\cdots N-1,N$, with the convention $X_{-N}\leq X_{-N+1}\leq\cdots\leq X_N$. Assume that a given particle in X_k only interacts with the particles in X_{k-1} and X_{k+1} (with the obvious adaptation when $k=-N$ or N). The interaction is a nearest neighbor interaction modeled by a potential $V(|X_j-X_i|)$ for $|i-j|=1$, and zero otherwise. When N is finite (as in a finite size *molecular* system), the energy of the system is clearly

$$E_N=\sum_{k=-N}^{N-1}V(|X_{k+1}-X_k|). \tag{1.1}$$

Suppose now that the particles are clamped at integer positions, $X_k = k$, and let their number N grow to infinity. The energy E_N clearly diverges: it has value $E_N^0 = 2NV(1)$ since the interparticle distance is everywhere set to 1. Only the *energy per particle* $\frac{E_N^0}{2N+1}$ (also equal to the energy per unit "volume" in that simplified case) converges, to the value $V(1)$. The latter value can be given the name of *energy of the periodic system*, since it evidently models the energy of the infinite periodic system we have just constructed letting N grow to infinity.

Let us now depart from this ideal (that is, periodic) system. We have, at least, two ways to do so.

First, we may modify the positions of *all* particles. This may be achieved assuming now that the k-th particle has a random position $X_k(\omega) = k + Y_k(\omega)$ where, say, all the random variables Y_k, $-N \leq k \leq N$, are independent and identically distributed. The same argument as above, this time formalized by the law of large numbers, yields the expectation value $\mathbb{E}(V(1 + Y_1 - Y_0))$ (when this exists) as the *energy* of the infinite, now imperfect, system we have constructed. Note that randomness, although a possible track, is not the only track. For instance, the deterministic system $X_k = k + 1/2$ for $(2n)^2 < |k| \leq (2n+1)^2$, $X_k = k$ for $(2n+1)^2 < |k| \leq (2n+2)^2$, clearly admits an energy per particle (which, incidentally, is identical to that of the original periodic system), even though the system is by no means periodic and the "perturbation", measured with respect to the original system, does not vanish at infinity. In other terms, the perturbation is *global*, as in the random case, although entirely deterministic. We leave to the reader the exercise of constructing a similar perturbation that does modify the energy per particle obtained in the limit and likewise an example of an infinite system that does not have an energy per particle for a generic interaction potential V.

Another direction we may take is to modify our periodic system *locally*. Instead of, as above, perturbing each and every position $X_k = k$ of the particles, we leave all the particles unperturbed *except one*, say the particle $k = 0$. This is now a *local* perturbation. We assume that $X_0 = a \neq 0$. The energy of the finite system with $2N+1$ particles is now

$$E_N^{\text{defect}} = \sum_{k=-N}^{-2} V(|X_{k+1} - X_k|) + V(|1+a|) + V(|1-a|) + \sum_{k=1}^{N-1} V(|X_{k+1} - X_k|). \quad (1.2)$$

Of course, if we now mimic the argument of the previous paragraph and consider $\frac{E_N^{\text{defect}}}{2N+1}$, we immediately find that this quantity shares the same limit as $\dfrac{E_N^0}{2N+1}$ when N grows to infinity. Our "defect" being unique and localized, it does not show up in the limit of an infinite number of particles. In order to get a nontrivial effect, we have to proceed otherwise and model the energy of the perturbed system differently. Considering the difference

$$E_N^{\text{defect}} - E_N^0 = V(|1+a|) + V(|1-a|) - 2V(1) \quad (1.3)$$

allows for all unperturbed terms (those for $|k| > 1$) to cancel out, leaving a quantity that has a limit when N goes to infinity (in this simplified case, it is even independent of N). Clearly, $V(|1+a|) + V(|1-a|) - 2V(1)$ may be seen as the energy of the periodic system

with a defect at zero, being understood that the energy is counted *with reference to the ideal periodic system.*

One step further is to combine the above two directions of perturbation and either *randomly* perturb a periodic system, or deterministically perturb a perfect random system (or both!). Since we do not want to bore our reader with unnecessary technicalities, we will postpone such developments. Likewise, we may combine all the ideas briefly outlined above with the notion of change of scale: the same thinking allows to derive models at the macroscale from the models manipulated at the microscale. Again, we postpone ...

In a nutshell, our whole article is devoted to showing that the above line of thought is quite general. It allows one to obtain energy models in the presence of defects, for a large range of models (atomistic models as above, quantum models such as Thomas-Fermi type and Kohn-Sham type models) and at different scales. It also allows one to define homogenized limits of some elliptic problems with oscillatory, not necessarily periodic coefficients with the same degree of "explicitness" as that of the periodic case.

Our article is articulated as follows. The formal simplified argument above has demonstrated the need to have an appropriate renormalized notion of energy, whether it is an energy *per unit volume* (or *per particle*), or an energy counted *with respect to* some reference "perfect" system. Often, the latter system is a periodic system. Occasionally, it can be a random ergodic stationary system. To start with, we therefore have to, at least briefly, survey the mathematical modeling of such periodic, or random, systems, all ideal in some sense. We will first do so in the context of *homogenization theory* in Section 2. The same issue, this time in the context of electronic structure models for materials, is postponed until Section 5. As is well known, the questions of limit energy for an infinite system of particles and homogenization limit for a partial differential equation are intimately related to one another, and this is why we consider both contexts in this review article. In addition, the question of change of scale for a microscopic system (with the purpose to obtain theories for the energy at the macroscopic scale) is also very much related to homogenization. When perfect (meaning, periodic or random stationary) models are recalled, we are in position to progressively introduce imperfections in our ideal settings. We will do so using random modeling in Section 3 and entirely deterministic modeling in Section 4, both in the context of homogenization (with the exception of Section 4.2 which considers the adaptation of our arguments to electronic structure theory). Then, after Section 5 we already mentioned, we will consider in Section 6 defects for materials and their effect on the electronic structure.

We conclude this introduction emphasizing that we will simply outline, or even sketch the mathematical derivations and results. The reader is referred to the publications in reference for all the mathematical details. Our purpose here is to give the reader a flavour of what the difficulties are and how they have been solved or circumvented to give rise to a consistent scientific scheme that allows to model, in particular, defects in materials.

2 Periodic and random homogenization

As mentioned in the introduction, we cannot address the modeling of *defects* embedded in a perfect structure without being able to model this perfect structure beforehand. The present section therefore starts with, in Section 2.1, an extremely brief survey of the homogenization of elliptic equation with *periodic* coefficients. We then proceed with Section 2.2 to the case of *random (stationary ergodic)* coefficients. Of course, this setting itself can be seen as a perturbation of the periodic setting, although it is quite a major perturbation! It can alternatively be seen as a perfect structure itself, where defects can be possibly superimposed. We will not go in the latter direction. We will rather use the random setting as a general context and consider within this general context some specific situations that can indeed model *small* (in a sense made precise in the body of Section 3) perturbations (therefore defects) of the periodic setting.

2.1 Periodic homogenization

To begin with, we recall some basic ingredients of elliptic homogenization theory in the periodic setting. We refer *e.g.* to the monographs [9, 27, 43] for more details on homogenization theory.

We consider, in a regular domain $\mathcal{D}$ in $\mathbb{R}^d$, the problem

$$\left\{ \begin{array}{l} -\mathrm{div}\left[A_{per}\left(\frac{x}{\varepsilon}\right)\nabla u^\varepsilon\right] = f \quad \text{in} \quad \mathcal{D}, \\ \\ u^\varepsilon = 0 \quad \text{on} \quad \partial\mathcal{D}, \end{array} \right. \tag{2.1}$$

where $f \in H^{-1}(\mathcal{D})$ and the matrix A_{per} is symmetric and $\mathbb{Z}^d$-periodic. We manipulate for simplicity *symmetric* matrices, but the discussion carries over to non symmetric matrices up to slight modifications. We assume A_{per} satisfies the usual properties of coercivity and boundedness (made precise in (3.1)-(3.2) below).

The corrector problem associated to (2.1) reads, for p fixed in $\mathbb{R}^d$,

$$\left\{ \begin{array}{l} -\mathrm{div}\left(A_{per}(y)\left(p + \nabla w_p\right)\right) = 0, \\ \\ w_p \text{ is } \mathbb{Z}^d\text{-periodic.} \end{array} \right. \tag{2.2}$$

It has a unique solution up to the addition of a constant. Then, the homogenized coefficients read

$$[A_*]_{ij} = \int_Q \left(e_i + \nabla w_{e_i}(y)\right)^T A_{per}(y)\left(e_j + \nabla w_{e_j}(y)\right) dy = \int_Q e_i^T A_{per}(y)\left(e_j + \nabla w_{e_j}(y)\right) dy,$$

where e_i, $i = 1, \ldots, d$, denote the canonical vectors of $\mathbb{R}^d$ and Q is the unit cube. The main result of periodic homogenization theory is that, as ε goes to zero, the solution u^ε to (2.1) converges to u^* solution to

$$\left\{ \begin{array}{l} -\mathrm{div}\left[A_*\nabla u^*\right] = f \quad \text{in} \quad \mathcal{D}, \\ \\ u^* = 0 \quad \text{on} \quad \partial\mathcal{D}. \end{array} \right. \tag{2.3}$$

The convergence holds in $L^2(\mathcal{D})$, and weakly in $H_0^1(\mathcal{D})$. The correctors w_{e_i} may then also be used to "correct" u^* in order to identify the behavior of u^ε in the strong topology $H_0^1(\mathcal{D})$. Several other convergences on various products involving $A_{per}\left(\frac{x}{\varepsilon}\right)$ and u^ε also hold. All this is well documented.

The practical interest of the approach is evident. No small scale ε is present in the homogenized problem (2.3). At the price of only computing d periodic problems (2.2) (as many problems as dimensions in the ambient space, take indeed p the vectors of the canonical basis of $\mathbb{R}^d$), the solution to problem (2.1) can be efficiently approached for ε small. A direct attack of problem (2.1) would require taking a meshsize smaller than ε. The difficulty has been circumvented. Of course, many improvements and alternatives exist in the literature.

2.2 Random ergodic stationary homogenization

The present section introduces the classical *stationary ergodic setting*. We choose to present the theory in a *discrete* stationary setting, which is more appropriate for our specific purpose in the next sections. Random homogenization is more often presented in the *continuous* stationary setting. Although the two settings are different (neither of them being an extension of the other), the modifications needed to pass from one setting to the other are easy.

Let $(\Omega, \mathcal{F}, \mathbb{P})$ denote a probability space. For any random variable $X \in L^1(\Omega, d\mathbb{P})$, we denote by $\mathbb{E}(X) = \int_\Omega X(\omega) d\mathbb{P}(\omega)$ its expectation value. We fix $d \in \mathbb{N}^*$, and assume that the group $(\mathbb{Z}^d, +)$ acts on Ω. We denote by $(\tau_k)_{k\in\mathbb{Z}^d}$ this action, and assume that it preserves the measure $\mathbb{P}$, i.e

$$\forall k \in \mathbb{Z}^d, \quad \forall A \in \mathcal{F}, \quad \mathbb{P}(\tau_k A) = \mathbb{P}(A).$$

We assume that τ is *ergodic*, that is,

$$\forall A \in \mathcal{F}, \quad \big(\forall k \in \mathbb{Z}^d,\ \tau_k A = A\big) \Rightarrow (\mathbb{P}(A) = 0 \text{ or } 1).$$

In addition, we define the following notion of stationarity: any $F \in L^1_{\text{loc}}\left(\mathbb{R}^d, L^1(\Omega)\right)$ is said to be *stationary* if

$$\forall k \in \mathbb{Z}^d, \quad F(x+k, \omega) = F(x, \tau_k \omega) \text{ almost everywhere in } x, \text{ almost surely.} \tag{2.4}$$

In this setting, the ergodic theorem can be stated as follows (see [46, 70]). Let $F \in L^\infty\left(\mathbb{R}^d, L^1(\Omega)\right)$ be a stationary function in the sense of (2.4). For $k = (k_1, k_2, \cdots k_d) \in \mathbb{R}^d$, we set $|k|_\infty = \sup_{1\le i\le d} |k_i|$. Then

$$\frac{1}{(2N+1)^d} \sum_{|k|_\infty \le N} F(x, \tau_k \omega) \underset{N\to\infty}{\longrightarrow} \mathbb{E}\left(F(x, \cdot)\right) \quad \text{in } L^\infty(\mathbb{R}^d), \text{ almost surely.}$$

This implies that (denoting by Q the unit cube in $\mathbb{R}^d$)

$$F\left(\frac{x}{\varepsilon}, \omega\right) \underset{\varepsilon\to 0}{\overset{*}{\longrightarrow}} \mathbb{E}\left(\int_Q F(x, \cdot) dx\right) \quad \text{in } L^\infty(\mathbb{R}^d), \text{ almost surely.}$$

It is useful to intuitively define stationarity and ergodicity in terms of material modeling. Pick two points x and $y \neq x$ that differ from an integer shift at the microscale in the material. The particular local environment seen from x (that is, the microstructure present at x) is generically different from what is seen from y (that is, the microstructure present at y). However, the *average* local environment in x is identical to that in y (considering the various realizations of the random material). In mathematical terms, the *law* of microstructures is the same at all points. This is *stationarity*. On the other hand, *ergodicity* means that considering all the points in the material amounts to fixing a point x in this material and considering all the possible microstructures present within $x + Q$.

We now fix $\mathcal{D}$ an open, smooth and bounded subset of $\mathbb{R}^d$, and A a square matrix of size d, which is assumed stationary in the sense defined above, and which is assumed to enjoy the classical assumptions of uniform ellipticity and boundedness. Then we consider the boundary value problem

$$\left\{ \begin{array}{l} -\mathrm{div}\left(A\left(\frac{x}{\varepsilon},\omega\right)\nabla u^\varepsilon\right) = f \quad \text{in} \quad \mathcal{D}, \\ \\ u^\varepsilon = 0 \quad \text{on} \quad \partial\mathcal{D}. \end{array} \right. \tag{2.5}$$

Standard results of stochastic homogenization [9, 43] apply and allow to find the homogenized problem for problem (2.5). These results generalize the periodic results recalled in Section 2.1. The solution u^ε to (2.5) converges to the solution to (2.3) where the homogenized matrix is now defined as:

$$[A_*]_{ij} = \mathbb{E}\left(\int_Q e_i^T A\left(y,\cdot\right)\left(e_j + \nabla w_{e_j}(y,\cdot)\right)\, dy\right),$$

where for any $p \in \mathbb{R}^d$, w_p is the solution (unique up to the addition of a random constant) in $\left\{w \in L^2_{\mathrm{loc}}(\mathbb{R}^d, L^2(\Omega)) \mid \nabla w \in L^2_{\mathrm{unif}}(\mathbb{R}^d, L^2(\Omega))\right\}$ to

$$\left\{ \begin{array}{l} -\mathrm{div}\left[A\left(y,\omega\right)\left(p + \nabla w_p(y,\omega)\right)\right] = 0, \quad \text{a.s. on} \quad \mathbb{R}^d \\ \\ \nabla w_p \quad \text{is stationary in the sense of (2.4)}, \\ \\ \mathbb{E}\left(\displaystyle\int_Q \nabla w_p(y,\cdot)\, dy\right) = 0. \end{array} \right. \tag{2.6}$$

We have used above the notation L^2_{unif} for the *uniform* L^2 space, that is the space of functions for which, say, the L^2 norm on a ball of unit size is bounded above independently from the center of the ball.

A striking difference between the stochastic setting and the periodic setting can be observed comparing (2.2) and (2.6). In the periodic case, the corrector problem is posed on a bounded domain (namely, the periodic cell Q), since the corrector w_p is periodic. In sharp contrast, the corrector problem (2.6) of the random case is posed on the whole space $\mathbb{R}^d$, and cannot be reduced to a problem posed on a bounded domain. The fact that the random corrector problem is posed on the entire space has far reaching consequences for numerical practice. Truncations of problem (2.6) have to be considered, and the actual homogenized coefficients are only correctly captured in the asymptotic regime.

3 Different tracks for modeling imperfections using randomness

As announced above, we now use the random setting as a general context, that is *a tool*, to generate perturbations of the periodic setting. To each type of perturbation we consider corresponds a specific type of defects. These defects all have in common some repetitive character. Localized defects will be addressed later on in this article.

3.1 Random deformations of the periodic setting

A specific stochastic setting has been introduced and studied in [12]. It is motivated by the consideration of random geometries (we mean, materials) that have some relation to the periodic setting. Here, and not unexpectedly given what we mentioned so far in this article, the periodic setting is taken as a *reference* configuration. The actual configuration is seen *via* a *mapping* from the reference configuration to the actual configuration.

We fix some $\mathbb{Z}^d$-periodic, square matrix A_{per} of size d, assumed to satisfy

$$\exists \gamma > 0 \quad | \quad \forall \xi \in \mathbb{R}^d, \quad \xi^T A_{per}(y)\xi \geq \gamma |\xi|^2, \quad \text{almost everywhere in } y \in \mathbb{R}^d, \tag{3.1}$$

$$\forall i,j \in \{1,2,\cdots,d\}, \quad [A_{per}]_{ij} \in L^\infty\left(\mathbb{R}^d\right). \tag{3.2}$$

We consider the following problem:

$$\begin{cases} -\text{div}\left(A_{per}\left(\Phi^{-1}\left(\frac{x}{\varepsilon},\omega\right)\right)\nabla u^\varepsilon\right) = f \quad \text{in} \quad \mathcal{D}, \\ \\ u^\varepsilon = 0 \quad \text{on} \quad \partial\mathcal{D}, \end{cases} \tag{3.3}$$

where the function $\Phi(\cdot,\omega)$ is assumed to be a diffeomorphism from $\mathbb{R}^d$ to $\mathbb{R}^d$ for $\mathbb{P}$-almost every ω. The diffeomorphism is assumed to additionally satisfy

$$\underset{\omega\in\Omega,\, x\in\mathbb{R}^d}{\text{EssInf}}\left[\det(\nabla\Phi(x,\omega))\right] = \nu > 0, \tag{3.4}$$

$$\underset{\omega\in\Omega,\, x\in\mathbb{R}^d}{\text{EssSup}}\left(|\nabla\Phi(x,\omega)|\right) = M < \infty, \tag{3.5}$$

$$\nabla\Phi(x,\omega) \quad \text{is stationary in the sense of (2.4).} \tag{3.6}$$

Such a Φ is called a *random stationary diffeomorphism.*

The following result is proved in [12]:

Theorem 1 *Let $\mathcal{D}$ be a bounded smooth open subset of $\mathbb{R}^d$, and let $f \in H^{-1}(\mathcal{D})$. Let A_{per} be a square matrix which is $\mathbb{Z}^d$-periodic and satisfies (3.1)-(3.2). Let Φ be a random stationary diffeomorphism satisfying hypotheses (3.4)-(3.5)-(3.6). Then the solution $u^\varepsilon(x,\omega)$ to (3.3) satisfies the following properties:*

(i) $u^\varepsilon(x,\omega)$ converges to some $u^*(x)$ strongly in $L^2(\mathcal{D})$ and weakly in $H^1(\mathcal{D})$, almost surely;

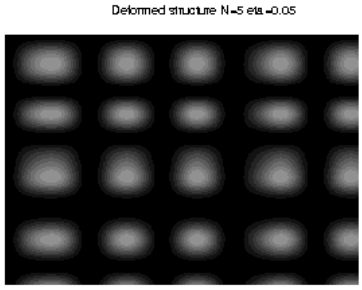

Figure 1: We show a particular realization of $A_{per} \circ \Phi^{-1}(x, \omega)$ for $\eta = 0.05$. Reprinted from [28]

(ii) the function u^* is the solution to the homogenized problem:

$$\begin{cases} -\mathrm{div}\,(A_* \nabla u^*) = f \quad in \quad \mathcal{D}, \\ \\ u^* = 0 \quad on \quad \partial\mathcal{D}. \end{cases} \tag{3.7}$$

In (3.7), the homogenized matrix A_* is defined by:

$$[A_*]_{ij} = \det\left(\mathbb{E}\left(\int_Q \nabla\Phi(z,\cdot)dz\right)\right)^{-1} \mathbb{E}\left(\int_{\Phi(Q,\cdot)} \left(e_i + \nabla w_{e_i}(y,\cdot)\right)^T A_{per}\left(\Phi^{-1}(y,\cdot)\right) e_j \, dy\right), \tag{3.8}$$

where for any $p \in \mathbb{R}^d$, w_p is the solution (unique up to the addition of a random constant) in $\left\{w \in L^2_{\mathrm{loc}}(\mathbb{R}^d, L^2(\Omega)) \mid \nabla w \in L^2_{\mathrm{unif}}(\mathbb{R}^d, L^2(\Omega))\right\}$ to

$$\begin{cases} -\mathrm{div}\left[A_{per}\left(\Phi^{-1}(y,\omega)\right)(p + \nabla w_p)\right] = 0, \\ \\ w_p(y,\omega) = \tilde{w}_p\left(\Phi^{-1}(y,\omega),\omega\right), \quad \nabla\tilde{w}_p \quad \textit{is stationary in the sense of (2.4)}, \\ \\ \mathbb{E}\left(\displaystyle\int_{\Phi(Q,\cdot)} \nabla w_p(y,\cdot)dy\right) = 0. \end{cases} \tag{3.9}$$

3.2 Small random perturbations of the periodic setting

The next step is to superimpose to the setting defined in the previous section an actual assumption that encodes that the material considered is a perturbation of a periodic material. This is achieved by writing (see Figure 1)

$$\Phi(x,\omega) = x + \eta\,\Psi(x,\omega) + O(\eta^2). \tag{3.10}$$

It has been shown in [12] that, when Φ in (3.3) is such a perturbation of the identity map, the solution to the corrector problem (3.9) may be developed in powers of the small parameter η. It reads $\widetilde{w}_p(x,\omega) = w_p^0(x) + \eta w_p^1(x,\omega) + O(\eta^2)$, where w_p^0 solves

$$-\mathrm{div}\,\left[A_{per}\left(p + \nabla w_p^0\right)\right] = 0, \quad w_p^0 \text{ is } Q\text{-periodic}, \tag{3.11}$$

and where w_p^1 solves

$$\begin{cases} -\text{div}\left[A_{per}\,\nabla w_p^1\right] = \text{div}\left[-A_{per}\,\nabla\Psi\,\nabla w_p^0 - (\nabla\Psi^T - (\text{div}\,\Psi)\text{Id})\,A_{per}\,(p+\nabla w_p^0)\right], \\ \nabla w_p^1 \text{ is stationary and } \mathbb{E}\left(\displaystyle\int_Q \nabla w_p^1\right) = 0. \end{cases} \tag{3.12}$$

The problem (3.12) in w_p^1 is random in nature, but it is in fact easy to see, taking the expectation, that $\overline{w}_p^1 = \mathbb{E}(w_p^1)$ is Q-periodic and solves the *deterministic* problem

$$-\text{div}\left[A_{per}\,\nabla\overline{w}_p^1\right] = \text{div}\left[-A_{per}\,\mathbb{E}(\nabla\Psi)\,\nabla w_p^0 - (\mathbb{E}(\nabla\Psi^T) - \mathbb{E}(\text{div}\,\Psi)\text{Id})\,A_{per}\,(p+\nabla w_p^0)\right].$$

This is useful because, on the other hand, the knowledge of w_p^0 and $\overline{w}_p^1$ suffices to obtain a first order expansion (in η) of the homogenized matrix. Define $A_{ij}^0 = \displaystyle\int_Q \left(e_i + \nabla w_{e_i}^0\right)^T A_{per}\,e_j$ and

$$A_{ij}^1 = -\int_Q \mathbb{E}(\text{div}\,\Psi)\,A_{ij}^0 + \int_Q (e_i+\nabla w_{e_i}^0)^T A_{per}\,e_j\,\mathbb{E}(\text{div}\,\Psi) + \int_Q \left(\nabla\overline{w}_{e_i}^1 - \mathbb{E}(\nabla\Psi)\nabla w_{e_i}^0\right)^T A_{per}\,e_j,$$

we then have

$$A_* = A^0 + \eta A^1 + O(\eta^2). \tag{3.13}$$

As subsequently shown in [28], a similar approach can be applied to the problem once *discretized* by a finite element approach. More details on this approach can be found in [28].

3.3 Rare but possibly large random perturbations

We now consider a slightly different perturbative approach, described in full details in [3, 4, 5]. It could equally well be presented in the setting of random diffeormophisms introduced in Section 3.1 above, but for simplicity we present it in the more classical setting of Section 2.2.

As above, we consider our random material as a small perturbation of a periodic material. The matrix that models its response is thus written as

$$A_\eta(x,\omega) = A_{per}(x) + b_\eta(x,\omega)C_{per}(x), \tag{3.14}$$

where, with evident notation, A_{per} is a periodic matrix modeling the unperturbed material, and where C_{per} is a periodic matrix modeling the perturbation. The amplitude of the perturbation, which used to be modeled by a *deterministic* coefficient η in the previous section, is now a scalar stationary *random* field $b_\eta(x,\omega)$. We assume that this field satisfies

$$\|b_\eta\|_{L^\infty(Q;L^p(\Omega))} \underset{\eta\to 0}{\to} 0, \tag{3.15}$$

for some $1 \le p < \infty$. For well-posedness of the problem, we also assume there exists $0 < \alpha \le \beta$ such that for almost all $x \in \mathbb{R}^d$ and for almost all $\omega \in \Omega$,

$$\forall \xi \in \mathbb{R}^d,\ \forall \eta > 0, \quad \alpha|\xi|^2 \le A_\eta(x,\omega)\xi\cdot\xi \quad \text{and} \quad |A_\eta(x,\omega)\xi| \le \beta|\xi|.$$

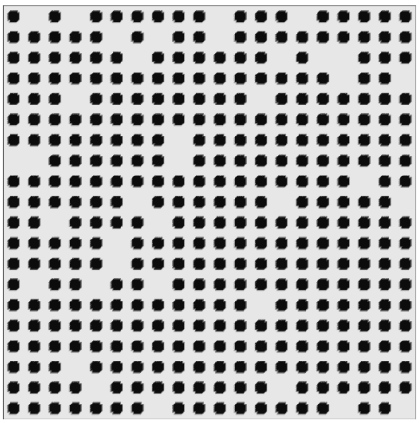

Figure 2: A typical random realization of the Bernoulli law for the perturbed periodic material.

Condition (3.15) states that the perturbation in (3.14) is small *on average*. However, it does not prevent the perturbation to be large, once in a while, because we only have $p < \infty$ (note that the setting of the previous section corresponds to a situation where $p = \infty$). Whereas the idea underlying the setting of the previous section was *"perturb the periodic material possibly often but only slightly"*, the intuitive image behind the present setting is *"perturb the periodic material only rarely, but then possibly largely"*.

When the exponent p in (3.15) is strictly larger than one, a theory similar to that of the previous section can be developed. Assuming that $m_\eta = \|b_\eta\|_{L^\infty(Q;L^p(\Omega))} \longrightarrow 0$ as η vanishes, it may be proved, up to the extraction of a subsequence, that the homogenized tensor $A_{\eta,*}$ admits a first order expansion in terms of the small "coefficient" m_η. The coefficients are easily expressed using periodic corrector problems built from the matrices A_{per} and C_{per}. The remainder in the expansion can indeed be shown to be $o(m_\eta)$ in a certain sense and under appropriate assumptions.

We now address a case that is very different in nature (see Figure 2). Consider the prototypical case

$$b_\eta(x,\omega) = \sum_{k\in\mathbb{Z}^d} \mathbf{1}_{\{Q+k\}}(x) B^k_\eta(\omega), \tag{3.16}$$

where the B^k_η are independent identically distributed random variables. Their common law is assumed to be a Bernoulli law of parameter η. This setting satisfies condition (3.15) for all $1 \leq p < +\infty$. The difficulty with a possible expansion in "powers" of b_η is intuitively that, a Bernoulli variable B, being valued in $\{0,1\}$, is such that $B^p = B$ for all p. So all terms in the expansion are potentially of the same order. A different strategy is needed. We now explain an alternative, *formal* approach, for which we do not know any rigorous foundation to date. The recent work [60] is a first step towards the mathematical foundation of our ideas. Although definite conclusions on the validity of the approach have yet to be obtained, the numerical tests we have performed (and reported upon in [4]) show its practical rectitude and efficiency.

The starting point of the formal argument consists in noticing that in the corrector problem

$$-\mathrm{div}\left[A\left(y,\omega\right)\left(p+\nabla w_p(y,\omega)\right)\right]=0, \tag{3.17}$$

the only source of randomness comes from the coefficient $A\left(y,\omega\right)$. Therefore, in theory, if one knows the law of this coefficient, one knows the law of the corrector function $w_p(y,\omega)$ and therefore may compute the homogenized coefficient A^*, the latter being a function of this law. When the law of A is an expansion in terms of a small coefficient, so is the law of w_p. Consequently A^* can be obtained as an expansion. The difficulty to make this argument rigorous is that the laws we are talking about are laws of infinite dimensional processes, since A and w_p are random *fields*. We are therefore only able to give a formal presentation. Heuristically, on the cube $Q_N=[0,N]^d$ and at order 1 in η, the probability to get the perfect periodic material (entirely modeled by the matrix A_{per}) is $(1-\eta)^{N^d}\approx 1-N^d\eta+O(\eta^2)$, while the probability to obtain the unperturbed material on all cells except one (where the material has matrix $A_{per}+C_{per}$) is $N^d\left(1-\eta\right)^{N^d-1}\eta\approx N^d\eta+O(\eta^2)$. All other configurations, with more than two cells perturbed, yield contributions of orders higher than or equal to η^2. This gives the intuition (and this intuition can be turned into a mathematical proof when one restricts the problem to considering truncations of the corrector problem on large domains, see [4]) that the first order correction indeed comes from the difference between the material perfectly periodic except on one cell and the perfect material itself. At least formally, $A_{\eta,*}=A_{per,*}+\eta A_{1,*}+o(\eta)$ where $A_{per,*}$ is the homogenized matrix for the unperturbed periodic material and

$$A_{1,*}\,e_i=\lim_{N\to+\infty}\int_{Q_N}\left[(A_{per}+\mathbf{1}_Q C_{per})(\nabla w_{e_i}^N+e_i)-A_{per}(\nabla w_{e_i}^0+e_i)\right], \tag{3.18}$$

where $w_{e_i}^0$ is the corrector for A_{per}, and $w_{e_i}^N$ solves

$$-\mathrm{div}\left((A_{per}(x)+\mathbf{1}_Q C_{per}(x))(\nabla w_{e_i}^N(x)+e_i)\right)=0\quad\text{in}\quad Q_N,\quad w_{e_i}^N\,Q_N-\text{periodic.} \tag{3.19}$$

Note that the integral appearing in the right-hand side of (3.18) is *not* normalized: it *a priori* scales as the volume N^d of Q_N and has finite limit only because of cancellation effects between the two terms in the integrand. This is very similar in nature to the modeling strategy taken in Section 6.1: a flawless (periodic) environment is subtracted to the actual environment and serves as a normalization. This is also reminiscent of our simple example (1.3).

There actually exists (see the references mentioned above) a formal generalization of (3.18) that allows for recovering the setting of the previous cases. The approach of the present section therefore appears to be the most general approach to the modeling of "small" random perturbations.

The approach has been extensively tested. It is observed that, using the perturbative approach, the large N limit for cubes of size N is already very well approached for small values of N. As in the previous section, the computational efficiency of the approach is clear: solving the two periodic problems with coefficients A_{per} and $A_{per}+\mathbf{1}_Q C_{per}$ for a limited size N is much less expensive than solving the original, random corrector problem for a much larger size N.

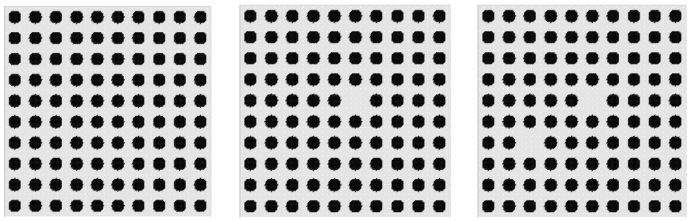

Figure 3: From left to right: zero defect, one defect and two defects.

An interesting follow-up is examined in [49]: when the second order term is needed, configurations with two defects have to be computed (see Figure 3). They all can be seen as a family of PDEs, parameterized by the geometrical location of the defects. Reduced basis techniques have been shown to be useful and allow for a definite speed-up in the computation.

4 Modeling imperfections deterministically

In sharp contrast to the previous sections, we will now follow a different route to model defects in a perfect structure. We will not resort to any random modeling and will proceed entirely deterministically. The theories we will construct are no stranger to random theories (some relation is thoroughly examined in [12], and we will not proceed in this direction here) but they remain very different in nature and allow for different developments.

Our starting point is a theory developed in [10], and summarized in Section 4.1, that allows for defining the energy per particle of infinite systems of interacting particles, provided the locations of these particles satisfy rather general geometric assumptions. To some extent, these assumptions are generalizations of more classical assumptions such as the prototypical periodicity assumption. To already get an idea of the type of generality these assumptions carry, the reader can for instance consider the simple case of a periodic lattice where a finite number of sites have been displaced. This is exactly the case we introduced in (1.2). It is clear that the local failure of periodicity is no obstacle to the definition of an energy per particle. We will show that much more general perturbations can be considered. Actually the set of particles may even *globally* depart from a periodic lattice and still be admissible for defining an energy per particle. We have again seen an example in the introduction. Whether or not some difference with the periodic case shows up in the energy per particle is another issue. We will survey the question of energy per particle of these "general" structures in Section 4.2.

We will next move on to the application of the above ideas to the context of homogenization. Our construction of general sets of points can be adapted to this context and be useful there, on a very abstract level. Schematically, to the notion of energy per particle in an infinite system corresponds the notion of homogenized limit for an oscillatory system. Both are *averaged* (*renormalized*, *homogenized*, ...) quantities. The assumptions set on the location of points for the definition of the energy per particle can be adapted and give appropriate assumptions on the obstacles, perforations, microscopic structure for the

homogenization problem to admit a homogenized limit. In contrast to the mathematical endeavours that also aim at addressing homogenization for very general structures, our own line of thought is to reach generality but not at the price of giving up *explicitness*. We want computable expressions for all the objects we manipulate: averages, homogenized coefficients, corrector functions. This will be exposed in Section 4.3. We however only have preliminary results in this direction. So our Section 4.4 will be devoted to a specific, concrete case where the situation is completely clear. The type of construction and the tools we have introduced allow us to consider the question of localized defects in periodic structures and how they affect the macroscopic, homogenized limit. Like in the case of a localized defect for a set of particles (bear in mind our elementary example (1.2)), no specific interesting phenomenon (that is, difference in energy, or, in the language of homogenization, difference in the homogenized limit) shows up if we consider averaged quantities. The idea, in homogenization, is to zoom in at the vicinity of the defect and compare with the periodic situation (exactly like we considered *differences* in energy in (1.3)).

4.1 Deterministic nonperiodic structures

In [10], we have considered an infinite set of points in $\mathbb{R}^d$, denoted by $\{X_i\}_{i\in\mathbb{N}}$, and have established some geometric properties that allow us to define its average energy. More precisely, we have proved that the following properties allowed us to define the average energy of the infinite set of particles $\{X_i\}_{i\in\mathbb{N}}$ for a large class of models:

Definition 1 *We shall say that a set of points $\{X_i\}_{i\in\mathbb{N}}$ is admissible if it satisfies the following:*

(H1) $\sup_{x\in\mathbb{R}^d} \#\big\{i\in\mathbb{N} \quad / \quad |x-X_i|<1\big\} < +\infty$*;*

(H2) $\exists R>0$ *such that* $\inf_{x\in\mathbb{R}^d} \#\big\{i\in\mathbb{N} \quad / \quad |x-X_i|<R\big\} > 0$*;*

(H3) for any $n\in\mathbb{N}$, the following limit exists

$$\lim_{R\to\infty} \frac{1}{|B_R|} \sum_{X_{i_0}\in B_R} \cdots \sum_{X_{i_n}\in B_R} \delta_{(X_{i_0}-X_{i_1},\cdots X_{i_0}-X_{i_n})} = l^n, \tag{4.1}$$

and is a non-negative uniformly locally bounded measure.

We use here the convention that if $n=0$, l^0 is the constant function equal to

$$l^0 = \lim_{R\to\infty} \frac{1}{|B_R|} \#\big\{i\in\mathbb{N} \quad / \quad X_i\in B_R\big\}.$$

Here and below, B_R denotes the open ball of $\mathbb{R}^d$ with center 0 and radius R, and δ_Y, with $Y\in\mathbb{R}^d$, denotes the Dirac mass at the point Y.

Remark 4.1 *It is also possible to give a fully geometric characterization by replacing (H3) with the following property:* $\forall n \in \mathbb{N}$, $\forall (\eta_0, \eta_1, \cdots \eta_n) \in \left(\mathbb{R}_+^*\right)^{n+1}$, $\forall (h_1 \cdots, h_n) \in (R^d)^n$, *the following limit exists:*

$$f_n(\eta_0, h_1, \eta_1, h_2, \eta_2, \cdots, h_n, \eta_n) = \lim_{R\to\infty} \frac{1}{|B_R|} \# \Big\{ (i_0, i_1, \cdots, i_n) \in \mathbb{N}^{n+1}, \\ |X_{i_0}| \leq \eta_0 R, \quad |X_{i_0} - X_{i_1} - h_1| \leq \eta_1, \cdots, |X_{i_0} - X_{i_n} - h_n| \leq \eta_n \Big\}, \quad (4.2)$$

with convergence in L^∞.

Intuitively, (H1) means there is no arbitrarily large cluster of particles, whereas (H2) means there is no arbitrarily large ball in $\mathbb{R}^d$ containing none of the X_i.

Assumption (H3) may be seen as a condition on correlations. It is therefore rather natural in a context where we aim to define averages. However, the set of assumptions (H1)-(H2)-(H3) is for genericity. In some particular cases of simple models of energy, such as a two-body potential, there is no need for a condition on correlations of order higher than 2. In such a case, only (H1)-(H2) and (H3) for $n = 0, 1$ are needed for the definition of the energy per particle. For the energy per unit volume, it is even sufficient to have (H1)-(H2) and (H3) for $n = 1$. On the other hand, in the case of quantum models (such as Thomas-Fermi type theories), nonlinearities imply the need of (H3) for all $n \in \mathbb{N}$. None of the properties (H1), (H2) and (H3) implies another one, as is proved in [10].

Given Definition 1, we introduce the corresponding functional spaces:

Definition 2 *Let* $\{X_i\}_{i\in\mathbb{N}}$ *be an admissible set, and denote by* $\mathcal{A}(\{X_i\})$ *the vector space generated by the functions of the form*

$$f(x) = \sum_{i_1\in\mathbb{N}} \sum_{i_2\in\mathbb{N}} \cdots \sum_{i_n\in\mathbb{N}} \varphi(x - X_{i_1}, x - X_{i_2}, \cdots, x - X_{i_n}), \quad (4.3)$$

with $\varphi \in \mathcal{D}(\mathbb{R}^{3n})$. *Then, for any* $k \in \mathbb{N}$ *and any* $p \in [1, +\infty)$, *we denote by* $\mathcal{A}^{k,p}(\{X_i\})$, *or simply* $\mathcal{A}^{k,p}$ *when there is no ambiguity, the closure of* $\mathcal{A}(\{X_i\})$ *for the norm* $\|\cdot\|_{W^{k,p}_{\rm unif}}$.

When $k = 0$, *we use the notation* $\mathcal{A}^p$ *for* $\mathcal{A}^{0,p}$. *The closure of* $\mathcal{A}$ *for the norm* $\|\cdot\|_{L^\infty(\mathbb{R}^d)}$ *being a set of continuous functions, we will denote it by* $\mathcal{A}_c$. *We will call* $\mathcal{A}^\infty$ *the closure for the* $L^\infty(\mathbb{R}^d)$ *norm of the space of functions of the form (4.3), with* $\varphi \in L^\infty(\mathbb{R}^d)$ *having compact support.*

Remark 4.2 *In the above definition, hypothesis (H2) is actually not needed. It was only needed in [10] to deal with a definition of nonlocal N-body energies. This is not the case here.*

Note that $\mathcal{A}^{k,p}$ is the closure for the $W^{k,p}_{\rm unif}$ norm of the algebra generated by functions of the form

$$f(x) = \sum_{i\in\mathbb{N}} \varphi(x - X_i), \quad \varphi \in \mathcal{D}(\mathbb{R}^d).$$

We also point out that in the particular case of a periodic lattice $\{X_i\}_{i\in\mathbb{N}}$, $\mathcal{A}^{k,p}(\{X_i\}_{i\in\mathbb{N}})$ is the algebra of periodic functions with the appropriate period and regularity.

The point is, any function in the spaces $\mathcal{A}^{k,p}$ has an average (see the proof in [10]):

Lemma 1 *Let $\{X_i\}_{i\in\mathbb{N}}$ be an admissible set of points. Then, for any $f \in \mathcal{A}^{k,p}$, the following limit exists:*

$$\langle f\rangle = \lim_{R\to\infty} \frac{1}{|B_R|}\int_{B_R} f.$$

In addition, in the special case of an f of the form (4.3), we have

$$\langle f\rangle = \int_{\mathbb{R}^d}\int_{\mathbb{R}^{d(n-1)}} \varphi(x, x-h_1, \cdots, x-h_{n-1}) dl^{n-1}(h_1,\cdots,h_{n-1})dx.$$

Examples of $\{X_i\}$ satisfying (H1)-(H2)-(H3) In dimension 3, besides the evident periodic case, when the set $\{X_i\}_{i\in\mathbb{N}}$ is a periodic lattice, for instance $\mathbb{Z}^3$, and the almost periodic case, when the set $\{X_i\}_{i\in\mathbb{N}}$ is almost periodic (see [69]), we wish to cite two prototypical examples:

- the case of a *compactly perturbed periodic system*: $\{X_i\}_{i\in\mathbb{N}}$ is a periodic set, except for a finite number of points. For instance, $\mathbb{Z}^3\setminus\{0\}$, or $\mathbb{Z}^3\cup\{(0,0,\frac{1}{2})\}$ satisfy this condition. Then it is possible to show that we have: $\mathcal{A}^p(\{X_i\}) = L^p_{\rm per}(\mathbb{Z}^3) + L^p_0(\mathbb{R}^3)$, where $L^p_0(\mathbb{R}^3) = \{f\in L^p_{\rm loc}(\mathbb{R}^3),\quad \lim_{|x|\to\infty}\|f\|_{L^p(B+x)} = 0\}$ (with B the unit ball). In other words, in this case, the algebra consists of periodic functions up to local perturbations, clearly reflecting the geometry of the set of points $\{X_i\}$.
- the case of *two semi-crystals glued together*: the set $\{X_i\}_{i\in\mathbb{N}}$ is equal to some lattice ℓ_1 on a half space, and to some (other) lattice ℓ_2 on the other half space: $\{X_i\}_{i\in\mathbb{N}} = (\ell_1\cap H^+)\cup(\ell_2\cap H^-)$, where $H^+ = \{x\in\mathbb{R}^3, x\cdot a\geq 0\}$ and $H^- = \{x\in\mathbb{R}^3, x\cdot a<0\}$, for some vector $a\neq 0$.

4.2 Energy of nonperiodic structures

We now consider a set of points $\{X_i\}_{i\in\mathbb{N}}$ satisfying our assumptions (H1)-(H2)-(H3) of the previous section, and place a nucleus, say of unit charge, at each X_i. We then equip this nuclear system with an equal (infinite) number of electrons. Our purpose is to define a quantum energy for this system. In doing so, we will assume that the reader is familiar with quantum models, and in particular with the Thomas-Fermi-von Weizsäcker (TFW) model we will manipulate. If that is not the case, the reader might consider skipping this section altogether and return to its reading after that of Section 5.

For simplicity, we will only consider the case of smeared out nuclei, that is, the measure defining the set of nuclei is

$$m = \sum_{i\in\mathbb{N}} m_0(\cdot - X_i)$$

for some smooth, nonnegative, normalized function m_0. In view of the classical expressions of the periodic setting for the TFW model (that is, expressions (5.29), (5.30), (5.31) of Section 5), the model expected to be found (and indeed obtained) for a general geometry of nuclei as defined in the previous section formally reads:

$$I^{TFW}_\infty = \inf\left\{\langle|\nabla\sqrt{\rho}|^2\rangle + \langle\rho^{5/3}\rangle + \frac{1}{2}\langle|\nabla\Phi|^2\rangle,\quad \rho\geq 0,\quad \langle\rho\rangle = 1,\quad -\Delta\Phi = 4\pi(m-\rho)\right\}. \tag{4.4}$$

The symbol $\langle\cdot\rangle$ of course denotes the average in the sense given by Lemma 1, and we need to check that the functional setting we have developed in the previous section allows us to correctly pose the variational problem, in such a way that a minimizer can be appropriately defined and determined.

The first observation is that we cannot hope to define a unique minimizer if all what we ask to a minimizing function is to minimize (4.4). Indeed modifying ρ by adding a compactly supported function does not change the averages present in (4.4). In any event, we therefore need a more stringent definition of a minimizer. We do so using the notion of *local ground state*.

Definition 3 *Let $\{X_i\}_{i\in\mathbb{N}}$ be an admissible set of points. We will say that ρ is a local ground state of (4.4) if*

$$\begin{aligned}&\forall\varphi\in\mathcal{D}(\mathbb{R}^3)\ s.t.\ \rho+\varphi\geq 0\ and\ \int_{\mathbb{R}^3}\varphi=0,\\ &\int_{\mathbb{R}^3}\left(|\nabla\sqrt{\rho+\varphi}|^2-|\nabla\sqrt{\rho}|^2\right)+\int_{\mathbb{R}^3}\left((\rho+\varphi)^{5/3}-\rho^{5/3}\right)+\int_{\mathbb{R}^3}\Phi\varphi+\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\varphi(x)\varphi(y)}{|x-y|}\,dx\,dy\geq 0,\end{aligned}\tag{4.5}$$

where Φ is the effective potential, namely a solution to

$$-\Delta\Phi=4\pi(m-\rho).$$

The key step is next to prove, in line with Lemma 4:

Theorem 2 *Let $\{X_i\}_{i\in\mathbb{N}}$ be an admissible set, and let (u,Φ) be the unique solution in $L^\infty(\mathbb{R}^3)\times L^1_{\rm unif}(\mathbb{R}^3)$ to the system*

$$\left\{\begin{array}{l}-\Delta u+u^{7/3}-\Phi u=0,\\ -\Delta\Phi=4\pi(m-u^2),\\ u\geq 0.\end{array}\right.\tag{4.6}$$

Then, $u\in\mathcal{A}^{2,2}(\{X_i\}_{i\in\mathbb{N}})$, and $\Phi\in\mathcal{A}^p(\{X_i\}_{i\in\mathbb{N}})$ for any $p<3$.

This theorem, proved in [10] for point nuclei, also applies to the case of smeared out nuclei we consider here. It can then be shown that $\rho=u^2$ is a local ground state of the problem in the sense of Definition 3 if and only if u solves the above system of equations. Consequently, it is a minimizer to (4.4). The key ingredient for both facts to hold is of course the strict convexity of the TFW problem.

4.3 Application to homogenization theory

The question now under consideration is to know whether any infinite set of points satisfying properties (H1)-(H2)-(H3) gives rise to algebras $\mathcal{A}^{k,p}$ that allow to carry out the homogenization procedure. Actually, the answer is yes, at least if (H3) is modified in order to include a form of translation invariance. For instance, one may replace (H3) by

(H3') for any $n \in \mathbb{N}$, the following limit exists

$$\lim_{\varepsilon \to 0} \mu^n \left(\frac{x}{\varepsilon}, h_1, \cdots, h_n \right) = \nu^n(h_1, \cdots, h_n),$$

(and is independent of x), where

$$\mu^n(y, h_1, \cdots, h_n) = \sum_{i_0 \in \mathbb{Z}^d} \sum_{i_1 \in \mathbb{Z}^d} \cdots \sum_{i_n \in \mathbb{Z}^d} \delta_{(X_{i_0}, X_{i_0} - X_{i_1}, \cdots, X_{i_0} - X_{i_n})}(y, h_1, h_2, \cdots, h_n).$$

Under assumption (H3'), it is possible to prove that the corresponding algebras are particular cases of those considered by Nguetseng in [61, 62], for which a homogenization procedure may be carried out. The relation between all these assumptions, and their relation with other conditions such as those of the random stationary ergodic context, or variants of the latter context such as that seen earlier in this article, is examined in details in [12].

We wish to emphasize two differences between the endeavour we outline here and other existing works in the literature. The theory of H-convergence allows to homogenize very general problems and completely settle the issues. However, it does not always provide *explicit* expressions for the objects manipulated: "the" corrector function may be only a sequence of functions, not necessarily accessible to computations, and the homogenized coefficients may be obtained only as weak limits. Designing a numerical strategy to approximate these coefficients is unclear. Likewise, the theory developed by G. Nguetseng (summarized in [12]) also allows, in a different direction, to obtain homogenized limits for very general settings. As the theory summarized in the present review, it considers *algebras* $\mathcal{A}$ of functions that have *averages* (averages are quantities more amenable to computations in principle). However the generality of the setting comes at a price. The corrector problem is only set at a very abstract level, in a sense that is equivalent to an equation true *on average*:

$$\forall v \in \mathcal{A}, \quad \langle \nabla v^T A(\nabla w_p + p) \rangle = 0, \tag{4.7}$$

with the condition $\langle \nabla w_p \rangle = 0$. The homogenized coefficients then read

$$A^*_{ij} = \langle A_{ij} + A_{ik} \partial_k w_{e_j} \rangle,$$

with summation over repeated indices. The difficulty is that, although the setting is very well adapted for the theory, the numerical approximation of the problem is again unclear: equations "on average" such as (4.7) are not equations in the sense of distributions (solutions are stable under the addition of a compactly supported function. This is a difficulty similar to that mentioned for the minimization problem (4.4)). Hence, the question remains of finding a homogenization procedure making use of the "explicit" feature of the algebras $\mathcal{A}^{k,p}$ (in terms of $\{X_i\}_{i \in \mathbb{Z}^d}$). The corrector equation would then be obtained as a "classical" equation (as opposed to "equation on the average") in the original ambient space $\mathbb{R}^d$, that is,

$$\begin{cases} -\text{div } [A(y)(\nabla w_p(y) + p)] = 0, \\ \\ \nabla w_p \in \mathcal{A}, \quad \langle \nabla w_p \rangle = 0. \end{cases} \tag{4.8}$$

This is exactly the purpose of our mathematical endeavour. Several issues in this direction are currently under investigation [14]. Many actual situations considered are related to the modeling of defects, but our work is still in too preliminary a stage to be considered in the present review. So we prefer to consider a concrete case where the types of ideas developed above already bring an added value. The study considers a local defect in a periodic structure and shows how the paradigm of classical homogenization can be slightly twisted to develop interesting theoretical remarks and a corresponding numerical approach.

4.4 Defects and periodic homogenization

We now consider (equipped with the appropriate assumptions so that the problem is well-posed) the equation

$$-\text{div } (a(x/\varepsilon)\,\nabla u^\varepsilon) = f \tag{4.9}$$

with

$$a = a_{per} + b \tag{4.10}$$

where a_{per} is a periodic function and $b \in L^2(\mathbb{R}^d)$ models a localized *perturbation* b. We assume throughout this section that a_{per}, b and a are such that all the equations we will write enjoy all the appropriate, usual properties of unique solvability. In particular, a is bounded and bounded away from zero so that (4.9) is well posed. We see this mathematical example as an attempt to model a material with a periodic microstructure in the presence of a localized defect. The specific case considered here makes essential use of the Hilbert structure of $L^2(\mathbb{R}^d)$. More general cases of perturbations (such as b in functional spaces other than $L^2(\mathbb{R}^d)$, and for instance in $L^2_0(\mathbb{R}^d)$, the space mentioned in Section 4.1 when modeling a compactly supported defect in a periodic lattice) give rise to much more substantial mathematical difficulties and are discussed in [14].

Our purpose is then to theoretically derive an approximation of the solution u^ε to (4.9), which is less expensive to compute than u^ε itself but *everywhere accurate at the small scale* ε. It is indeed easy to realize that periodic homogenization can be readily applied to (4.9)-(4.10). Considering the homogenized equation

$$-\text{div } (A^*\,\nabla u^*) = f \tag{4.11}$$

provides an approximation for u^ε and, using the periodic corrector, its gradient ∇u^ε. All this will be briefly recalled below. The point is however that this approximation fails to accurately approximate the solution at the scale $\varepsilon\,x$ close to the "defect", that is where the perturbation b is large. This is of course not an unexpected shortcoming of homogenization theory, since such an approximation property at the small scale is not the purpose of homogenization theory, the aim of which is to approximate the solution at scale one. We however believe that the need may arise, in practice, to obtain effective inexpensive approximations of u^ε and its derivatives, at the small scale and in the vicinity of the defect. To this end, our approach consists, *at practically no substantial additional computational cost*, in computing a corrector w better adapted to the problem than the periodic corrector w_{per}. Even though both give the same homogenized matrix A^* and

allow for the same quality of approximation of u^ε at scale one, only the former performs uniformly well at scale ε.

On a more abstract level, the questions we investigate here are connected to the issues examined above: constructions of some general algebras and functional spaces that can be useful for homogenization theory. The specific functional space considered here is the space $L^2_{per} + L^2(\mathbb{R}^d)$ of sums of L^2 periodic functions and L^2 functions.

To start with (and this is actually sufficient to understand the bottom line of our argument) we consider the one-dimensional version of (4.9).

One-dimensional setting Consider $\mathcal{D} = [-1/2, 1/2]$, $f \in L^2(\mathcal{D})$, a_{per} a real-valued periodic function of period 1, $b \in L^2(\mathbb{R})$, $\varepsilon > 0$ presumably small and consider u^ε solution to

$$-\frac{d}{dx}\left((a_{per}(x/\varepsilon) + b(x/\varepsilon))\ \frac{d}{dx}\, u^\varepsilon \right) = f \tag{4.12}$$

with homogeneous boundary conditions $u^\varepsilon(-1/2) = u^\varepsilon(1/2) = 0$. It is straightforward to see that the homogenized limit of (4.12) is the equation

$$-a^*(u^*)'' = f, \tag{4.13}$$

where the homogenized coefficient a^* is actually equal to $a^*_{per} = \left(\langle a^{-1}_{per}\rangle\right)^{-1}$, the coefficient obtained in the absence of the perturbation b, since the function $b \in L^2(\mathbb{R})$ does not contribute to the large volume limit. We know that u^ε converges to u^* weakly in $H^1(\mathcal{D})$ and strongly in $L^2(\mathcal{D})$. The question then arises to approximate u^ε in H^1 norm.

In the absence of the perturbation b, homogenization theory provides such an approximation using the periodic corrector function w_{per} solution to

$$-\frac{d}{dx}\left(a_{per}(y)\ \left(1 + \frac{d}{dy}\, w_{per}(y)\right)\right) = 0. \tag{4.14}$$

Considering

$$u^{\varepsilon,1}_{per}(x) = u^*(x) + \varepsilon\,(u^*(x))'\,(1 + w_{per}(x/\varepsilon)), \tag{4.15}$$

it is then classical to observe that $u^\varepsilon - u^{\varepsilon,1}_{per}$ converges strongly to zero in H^1. Actually, one may even observe that the convergence still holds true at the small scale $\varepsilon\, x$. This will be recalled below.

Accounting for the perturbation, we now compute

$$\begin{aligned}\left[(u^\varepsilon)' - (1 + w'_{per}(./\varepsilon))\,(u^*)'\right](x) &= (a_{per} + b)^{-1}\,(x/\varepsilon)\ (F(x) + c_\varepsilon) \\ &\qquad -(a_{per})^{-1}(x/\varepsilon)\ (F(x) + c^*) \\ &= \left[(a_{per} + b)^{-1} - (a_{per})^{-1}\right](x/\varepsilon) \\ &\qquad \times (F(x) + c_\varepsilon) \\ &\qquad +(a_{per})^{-1}(x/\varepsilon)\ (c_\varepsilon - c^*)\,,\end{aligned} \tag{4.16}$$

where $F(x) = \displaystyle\int_0^x f$, $c_\varepsilon = -\left(\int_{-1/2}^{1/2} (a_{per} + b)\left(\frac{\cdot}{\varepsilon}\right)^{-1}\right)^{-1} \int_{-1/2}^{1/2} (a_{per} + b)\left(\frac{\cdot}{\varepsilon}\right)^{-1} F$, $c^* = -\displaystyle\int_{-1/2}^{1/2} F$. Not unexpectedly, both terms in the right-hand side of (4.16) vanish in L^2

norm as ε goes to zero. Consider now the same difference at the small scale:

$$\begin{aligned}\left[(u^\varepsilon)' - (1 + w'_{per}(./\varepsilon))\,(u^*)'\right](\varepsilon\,x) &= \left[(a_{per}+b)^{-1} - (a_{per})^{-1}\right](x) \\ &\quad \times (F(\varepsilon\,x) + c_\varepsilon) \\ &\quad +(a_{per})^{-1}(x)\;(c_\varepsilon - c^*)\,.\end{aligned}$$

We observe that, in sharp contrast to the situation at scale one, the first term of the right-hand side does not in general vanish as ε goes to zero. In the absence of the defect, that is when $b \equiv 0$, it does vanish (following our earlier claim that, at least in dimension one, but this is a general fact, periodic homogenization also allows for an accurate H^1 approximation at the small scale).

In order to recover this quality of approximation in the presence of b, we consider, instead of the periodic corrector equation (4.14), the equation

$$-\frac{d}{dy}\left((a_{per}+b)(y)\,\left(1+\frac{d}{dy}\,w(y)\right)\right) = 0, \tag{4.17}$$

the solution of which is

$$w'(y) = -1 + a^*_{per}\,(a_{per}+b)^{-1}(y), \tag{4.18}$$

defined up to an irrelevant additive constant. Note that the integration constant has been chosen so that w defined from (4.18) is sublinear at infinity. Using this particular function w, we observe that

$$\left[(u^\varepsilon)' - (1 + w'(./\varepsilon))\,(u^*)'\right](x) = (a_{per}+b)^{-1}(x/\varepsilon)\;(c_\varepsilon - c^*)\,, \tag{4.19}$$

which is to be compared with (4.16). Both at the scale x and at the scale $\varepsilon\,x$, we now have strong convergence. We have therefore reinstated the quality of approximation obtained in the purely periodic setting.

Nonperiodic approximation We now work in dimensions higher than or equal to 2. We return to (4.9), that is

$$-\mathrm{div}\;(a(x/\varepsilon)\,\nabla u^\varepsilon) = f,$$

and first make its mathematical setting precise. We take $\mathcal{D}$ a bounded domain in $\mathbb{R}^d$, $f \in L^2(\mathcal{D})$, $a = a_{per} + b$ where a_{per} is this time a real-valued $\mathbb{Z}^d$-periodic function, and where $b \in L^2(\mathbb{R}^d)$ is such that both a_{per} and $a_{per} + b$ are bounded away from zero and infinity. We supply (4.9) with homogeneous Dirichlet boundary conditions on $\partial\mathcal{D}$.

In the periodic case, the first order approximation for the solution u^ε to (4.9) is defined as

$$u^{\varepsilon,1}_{per}(x) = u^*(x) + \varepsilon \sum_{i=1}^{d} \partial_{x_i} u^*(x)\, w_{e_i,per}(x/\varepsilon), \tag{4.20}$$

where $w_{e_i,per}$ solves

$$-\,\mathrm{div}\,(a_{per}(y)\,(e_i + \nabla w_{e_i,per}(y))) = 0 \tag{4.21}$$

and where u^* is the solution to (4.11) with homogeneous Dirichlet boundary conditions on $\partial\mathcal{D}$ and where the entries of the matrix of homogenized coefficients read, for all $1 \leq i, j \leq d$,

$$[A^*]_{ij} = \int_Q a_{per}(y) \left(\delta_{ij} + \partial_j w_{e_i,per}(y)\right) dy,$$

where Q is the unit cube. The fact that $u^{\varepsilon,1}_{per}$ is an approximation in H^1 of u^ε (away from the boundary $\partial\mathcal{D}$, since specific, but well documented effects occur at the vicinity of $\partial\mathcal{D}$) is a standard fact.

We now consider the perturbed case (4.9). In the vein of our one-dimensional observations, and more precisely our corrector equation (4.17), we introduce, for $p \in \mathbb{R}^d$ fixed, the equation

$$-\operatorname{div}\left((a_{per} + b)(y)\left(p + \nabla w_p(y)\right)\right) = 0. \tag{4.22}$$

Equation (4.22) is the natural corrector equation suggested by homogenization theory (with here a constant homogenized coefficient). In a fully general setting, the left-hand side of (4.22) is employed to define a sequence of correctors $w_{p,\varepsilon}$. We use here that, in our particular framework, $w_{p,\varepsilon}$ can be chosen to be $w_p(\cdot/\varepsilon)$, with w_p a function solution to (4.22), independent of the scale ε, and of course, as usual in homogenization theory, also independent of the right-hand side f. Showing well-posedness of (4.22) in the appropriate functional space is the purpose of our next Lemma, the proof of which is an essential element of the theory and is provided in [13].

Lemma 2 *For all $p \in \mathbb{R}^d$, equation (4.22) admits a solution w_p such that $\nabla w_p \in L^2_{per} + L^2(\mathbb{R}^d)$ and $\lim_{R\to+\infty} \frac{1}{|B_R|} \int_{B_R} \nabla w_p = 0$ (where B_R evidently denotes the ball of radius R centered at the origin). Such a solution is unique up to an additive constant.*

Using the corrector the existence of which is claimed in Lemma 2, we then have

Lemma 3 *The solution u^ε to (4.9) is well approximated in H^1 norm, both at scale one and at scale ε, by the first order expansion $u^{\varepsilon,1}(x) = u^*(x) + \varepsilon \sum_{i=1}^d \partial_{x_i} u^*(x)\, w_{e_i}(x/\varepsilon)$ constructed using the solution w_p provided by Lemma 2, in the following sense:*

$$\begin{cases} \left\|\nabla\left(u^\varepsilon - u^{\varepsilon,1}\right)\right\|_{L^2(\mathcal{D})} \longrightarrow 0, \\ \left\|\nabla\left(u^\varepsilon - u^{\varepsilon,1}\right)(\varepsilon\,.)\right\|_{L^2(B_R)} \longrightarrow 0, \end{cases}$$

where B_R of course denotes any arbitrary fixed ball of radius R such that $\varepsilon B_R \subset \mathcal{D}$. The latter approximation property does not in general hold for the periodic first-order approximation $u^{\varepsilon,1}_{per}(x) = u^*(x) + \varepsilon \sum_{i=1}^d \partial_{x_i} u^*(x)\, w_{e_i,per}(x/\varepsilon)$ constructed using the periodic corrector $w_{p,per}$ solution to (4.21).

A numerical illustration For our numerical tests, extracted from [13], we consider problem (4.9) in dimension 2 with a defined by (4.10), that is, with

$$a_{per}(x_1, x_2) = 3 + \cos(2\pi x_1) + \cos(2\pi x_2),$$

and

$$b(x_1, x_2) = \exp\left(-(x_1^2 + x_2^2)\right).$$

The computational domain is the square $\mathcal{D} = (-1, 1)^2$, and we use periodic boundary conditions, in order to avoid boundary layer effects in the homogenization process (we also take $\varepsilon = 1/N$ for some integer N). The right-hand side f of (4.9) is chosen as

$$f(x_1, x_2) = \sin(\pi x_1)\cos(\pi x_2).$$

On this case, we compare the quality of approximation at the vicinity of the "defect", that is, at the vicinity of the origin, obtained at scale εx using the first order expansion and, on the one hand the periodic corrector or, on the other hand, the actual corrector constructed above. More precisely, we look at

$$\delta^\varepsilon_{per} = \frac{\left\|\nabla u^\varepsilon\left(\varepsilon\,\cdot\right) - \nabla u^{\varepsilon,1}_{per}\left(\varepsilon\,\cdot\right)\right\|_{L^2(\mathcal{D})}}{\left\|\nabla u^\varepsilon\left(\varepsilon\,\cdot\right)\right\|_{L^2(\mathcal{D})}},\ \delta^\varepsilon = \frac{\left\|\nabla u^\varepsilon\left(\varepsilon\,\cdot\right) - \nabla u^{\varepsilon,1}\left(\varepsilon\,\cdot\right)\right\|_{L^2(\mathcal{D})}}{\left\|\nabla u^\varepsilon\left(\varepsilon\,\cdot\right)\right\|_{L^2(\mathcal{D})}}. \tag{4.23}$$

Figure 4 and Table 1 present our results (all computations have been performed using a $\mathbb{P}_1$ finite element approximation on triangular meshes – the meshsize h is chosen sufficiently fine so that it does not perturb the results at the scale ε–, and implemented using the software FreeFem++ [33]). They unambiguously show the quality of the approximation provided by the non-periodic corrector, as opposed to the periodic one.

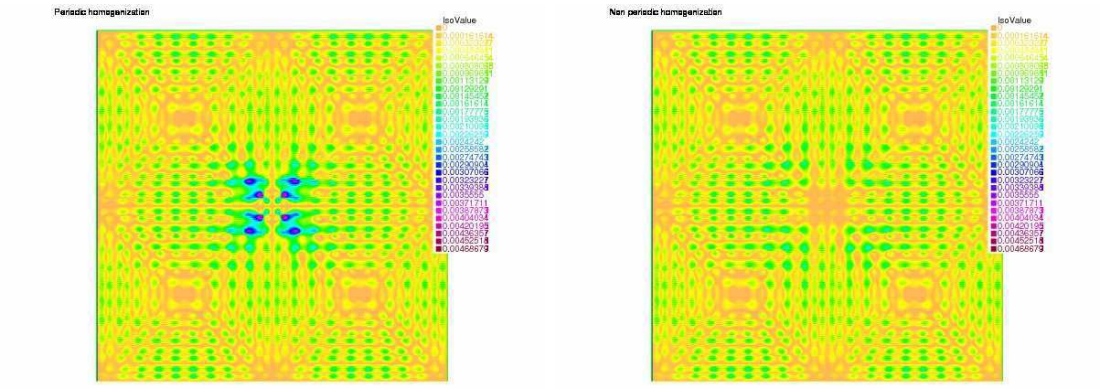

Figure 4: For $\varepsilon = 1/10$, we display the norm $\left|\nabla u^\varepsilon\left(\varepsilon\,\cdot\right) - \nabla u^{\varepsilon,1}_{per}\left(\varepsilon\,\cdot\right)\right|$ (left) and $\left|\nabla u^\varepsilon\left(\varepsilon\,\cdot\right) - \nabla u^{\varepsilon,1}\left(\varepsilon\,\cdot\right)\right|$ (right). Recall that the defect is located at the origin, and has essentially size ε. The quality of approximation at the vicinity of the defect is significantly improved. Reproduced from [13].

$1/\varepsilon$	$\delta^{\varepsilon}_{per}$	δ^{ε}
3	0.198112	0.0850091
5	0.191952	0.0425306
10	0.183784	0.0266084
20	0.175248	0.0139564

Table 1: Numerical results: Relative errors (defined by (4.23)) using the periodic corrector (left column) and the corrector adapted to the case with defect (right column). Reproduced from [13].

5 Electronic structure of perfect crystals

We present in this section models for the electronic structure of perfect crystals, with infinite periodic arrangements of nuclei. The models are mathematically, or at least formally, derived from analogous models for finite size molecular systems. Schematically, the derivation is a more sophisticated version of taking the limit of (1.1) as N grows to infinity. Atomistic models such as those we considered in our simplified example in the introduction are easy to deal with for periodic systems. We will therefore skip them and directly proceed to the consideration of systems of particles modeled quantum mechanically.

Consider a finite system, and a given energy model for this system. An infinite, periodic arrangement of nuclei is formally the limit of finite arrangements. It is thus desirable to establish that the electronic ground state of the finite system also becomes periodic in the limit. The basic question of interest is to define the energy of such an infinite system, as well as to check whether there exists a periodic ground-state. Both objects, the energy and the minimizer, should be *consistent* with those for the molecular system of finite size one has started from. Doing so, one aims at a threefold goal: first, rigorously define the energy per unit volume of the crystal; second, show the robustness of the molecular model as the size increases; third, assess the validity of the models for the crystalline phase that are used for numerical simulation.

We now make somewhat more precise the above discussion. For simplicity, we assume in the sequel that the crystalline lattice is $\mathbb{Z}^3$, but all our arguments hold for a generic lattice. We consider a finite subset Λ_N (this is a historical notation) of N points of the lattice $\mathbb{Z}^3$, obtained by intersection of the lattice with a large cube. This is again for simplicity, as any sequence of domains, for which the number of sites on the boundary is asymptotically negligible with respect to the number of sites in the interior, would be convenient; such domains are called Van Hove sequences in statistical mechanics. We then assign a nucleus of unit charge (still for simplicity) to each of the points of Λ_N. We finally consider a well-posed model for the neutral molecular system of finite size composed of the N nuclei plus N electrons, and denote by I_{Λ_N} the ground state energy of this configuration.

The so-called *thermodynamic limit problem* (a more appropriate name for our discussion would be the *bulk limit problem*, since no finite temperature effect is considered here) consists in the following two questions on limits as N grows to infinity: (i) Does the

energy per unit volume $\frac{I_{\Lambda_N}}{N}$ converge to a limit ? Which limit ? (ii) Does the electronic ground state density ρ_N (or respectively the ground state density matrix γ_N) converge to a limit ? Which limit ?

To some extent, the question under consideration is both related to fundamental questions of Thermodynamics and to the question of defining effective properties of composite materials on the basis of the knowledge of the properties of their constitutive materials.

It is expected that there is some consistency between the limit of the energy and the limit of the density in the following sense: in good cases, the energy will converge to a scalar that can be recast as the infimum value of a minimization problem set on the unit cell of the lattice (here the unit cube), the minimizer of which is the limit of the sequences of densities ρ_N. We recover here a result in the spirit of standard results of the Γ-convergence theory.

The thermodynamic limit in the terms stated above has been the subject of many outstanding contributions in the context of various energy models and various physical systems [68, 56]. The monograph [24] gives a rather extensive account of the major contributions (by L. Van Hove, D. Ruelle, C. Fefferman, E. Lieb, B. Simon, and many other authors). It also presents the thermodynamic limit problem for a famous model in mathematical physics, namely the Thomas-Fermi-von Weizsäcker model, henceforth abbreviated as TFW model. For the Hartree-Fock and Kohn-Sham type models (abbreviated as HF and KS models, respectively), the fundamental issues (i)-(ii) remain open. All that is known (see [39]) is for HF that a limit exists, but that limit is not identified. The two key difficulties are first that the latter models are not convex (convexity plays a crucial role in the analysis of the TFW model) and second that the number of one-body molecular orbitals to be dealt with, or equivalently the rank of the one-body density matrix, are also growing to infinity (in the TFW model, only the density ρ is relevant). For the HF model, partial results have been established in [26] (see also [26] for results on another model called the Hartree model). The results are partial in the sense that it is needed to *postulate*, in addition to the periodicity of the set of nuclei, the periodicity of the ground state density matrix in the limit. A simplified version of the HF model, namely the *reduced Hartree-Fock* (rHF) model however allows for a complete proof. We will return to this specific model below.

5.1 Models for finite size systems

We now describe some models for finite size systems composed of K classical nuclei and N quantum electrons within the Born-Oppenheimer approximation. For more details on the physical background and on the mathematical properties of these models, we refer to [40, 31, 17] and [58, 52, 59, 73].

5.1.1 The N-body Schrödinger model

In the vast majority of problems of interest, nuclei can be considered as point-like classical particles, and electrons as quantum particles lying in their ground state. Denoting by X_k the positions in the space $\mathbb{R}^3$ of the K nuclei, the electronic Hamiltonian of the system

reads

$$H_{\{X_k\}} = -\sum_{i=1}^{N} \frac{1}{2}\Delta_{x_i} + \sum_{i=1}^{N} V_{\{X_k\}}(x_i) + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}. \tag{5.1}$$

We omit here the spin degrees of freedom for simplicity. The function $V_{\{X_k\}}$ models the potential created by the nuclei and experienced by the electrons in the system:

$$V_{\{X_k\}}(x) = -\sum_{k=1}^{K} \frac{z_k}{|x - X_k|},$$

where $z_k \in \mathbb{N}^*$ is the charge of the nucleus number k ($z_k = 1$ for Hydrogen, 2 for Helium, 3 for Lithium ...). Here and below, we use atomic units, obtained by setting to one the values of the reduced Planck constant $\hbar$, the elementary charge e, the electron mass m_e and the constant $4\pi\epsilon_0$, where ϵ_0 is the dielectric permittivity of the vacuum. The Hamiltonian $H_{\{X_k\}}$ is a self-adjoint operator on the fermionic space $\wedge^N L^2(\mathbb{R}^3)$ of the square integrable antisymmetric functions $\psi(x_1, \cdots, x_N)$:

$$\wedge^N L^2(\mathbb{R}^3) = \Big\{ \psi \in L^2(\mathbb{R}^{3N}) \quad \Big| \quad \int_{\mathbb{R}^{3N}} |\psi(x_1, \cdots, x_N)|^2 \, dx_1 \cdots dx_N < \infty,$$
$$\psi(x_{\sigma(1)}, \cdots, x_{\sigma(N)}) = \epsilon(\sigma)\psi(x_1, \cdots, x_N), \text{ for all permutation } \sigma \Big\},$$

where $\epsilon(\sigma)$ is the parity of σ. It is bounded from below and the ground state energy is defined as

$$I_{\{X_k\}} = \inf \left\{ \langle \psi, H_{\{X_k\}}\psi \rangle, \ \psi \in \wedge^N H^1(\mathbb{R}^3), \ \|\psi\|_{L^2} = 1 \right\}. \tag{5.2}$$

Here and in the sequel, $\langle \psi, A\psi \rangle$ denotes the quadratic form associated with the self-adjoint operator A. Note that $\wedge^N H^1(\mathbb{R}^3)$ is the form domain of $H_{\{X_k\}}$. The ground state potential energy surface defined as

$$W(X_1, \cdots, X_N) = I_{\{X_k\}} + \sum_{1\le k<l\le K} \frac{z_k z_l}{|X_k - X_l|}$$

can then be used to carry out geometry optimization or molecular dynamics simulations. In particular, the global and local minima of W respectively correspond to the stable and metastable states of the molecular system.

The number $I_{\{X_k\}}$ is always the bottom of the spectrum of the self-adjoint operator $H_{\{X_k\}}$. If the molecular system is neutral or positively charged, it is an eigenvalue of finite multiplicity [77, 78, 42], and the corresponding eigenfunctions are called electronic ground states.

The physical interpretation of an N-electron wavefunction $\psi \in \wedge^N H^1(\mathbb{R}^3)$ satisfying $\|\psi\|_{L^2} = 1$ is that the non-negative function $|\psi(x_1, \cdots, x_N)|^2$ is the probability density of observing the electron 1 in x_1, the electron 2 in x_2, ... In particular, the electronic density is the marginal

$$\rho_\psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \cdots, x_N)|^2 \, dx_2 \cdots dx_N, \tag{5.3}$$

and it holds

$$\langle \psi, \sum_{i=1}^{N} V_{\{X_k\}}(x_i)\psi \rangle = \int_{\mathbb{R}^3} \rho_\psi V_{\{X_k\}}.$$

An important remark due to Levy [50], and then mathematically formalized by Lieb [54], is that $I_{\{X_k\}}$ can be rewritten as

$$I_{\{X_k\}} = \inf \left\{ F(\rho) + \int_{\mathbb{R}^3} \rho V_{\{X_k\}},\ \rho \in \mathcal{R}_N \right\},$$

where $\mathcal{R}_N$ is the set of the N-representable densities, that is the set of electronic densities ρ for which there exists some N-body wavefunction ψ such that $\rho_\psi = \rho$. It turns out that this set is easily characterized:

$$\mathcal{R}_N = \left\{ \rho \geq 0 \mid \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \rho = N \right\}.$$

The functional $F(\rho)$ is a universal functional of the density defined by

$$F(\rho) = \inf \left\{ \langle \psi, \left(-\sum_{i=1}^{N} \frac{1}{2}\Delta_{x_i} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \right) \psi \rangle,\ \psi \in \wedge^N H^1(\mathbb{R}^3),\ \rho_\psi = \rho \right\},$$

the existence of which was first proved by Hohenberg and Kohn in their celebrated paper [41] founding Density Functional Theory (DFT). No explicit expression of F as a function of ρ is known. A major challenge in DFT is therefore to construct approximations of $F(\rho)$ amenable to numerical simulations for large molecular systems.

5.1.2 Thomas-Fermi type models

Although introduced decades before the works by Hohenberg and Kohn, Thomas-Fermi type models fall in the framework of DFT. They consist in approximating the functional $F(\rho)$ by explicit functionals of the density ρ. Examples of such models include:

- the original Thomas-Fermi model

$$F_{\mathrm{TF}}(\rho) = C_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy$$

  where $C_{\mathrm{TF}} = \frac{10}{3}(3\pi^2)^{2/3}$ is the Thomas-Fermi constant;

- the Thomas-Fermi-von Weizsäcker (TFW) model

$$F_{\mathrm{TFW}}(\rho) = C_{\mathrm{W}} \int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 + C_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy,$$

  where the constant C_{W} takes different values depending on how the TFW model is derived [31];

- the Thomas-Fermi-Dirac von Weizsäcker (TFDW) model

$$F_{\rm TFDW}(\rho) = C_{\rm W}\int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 + C_{\rm TF}\int_{\mathbb{R}^3}\rho^{5/3} + \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy - C_{\rm D}\int_{\mathbb{R}^3}\rho^{4/3},$$

  where $C_{\rm D} = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$ is the Dirac constant.

The first term in $F_{\rm TF}(\rho)$ models the kinetic energy of the electrons (note that $C_{\rm TF}\rho_0^{5/3}$ is the kinetic energy density of a homogeneous gas of non-interacting electrons of uniform density ρ_0). We recognize in the second component of $F_{\rm TF}(\rho)$ the electrostatic energy of a *classical* charge distribution of density ρ. The first term in $F_{\rm TFW}(\rho)$ is a correction to the Thomas-Fermi approximation of the kinetic energy of the electrons taking into account the fact that, in molecular systems, the electronic density is not uniform. The last term in $F_{\rm TFDW}(\rho)$ is called the Dirac exchange term. It is a quantum correction to the electrostatic energy. Its interpretation will be given in Section 5.1.3.

The above Thomas-Fermi type models provide crude approximations of $F(\rho)$, and are no longer used in quantum chemistry and materials science. On the other hand, some improvements of the TFW model, the so-called *orbital-free models* [76], are used for the simulation of specific materials (aluminum crystals with defects for example [66]). The reason why we focus on Thomas-Fermi like models, and in particular on the TFW model, is that these models are extremely useful in the mathematical analysis. They are indeed toy models upon which new mathematical techniques can be developed before being applied to the more sophisticated models actually used in quantum chemistry and materials science.

In order to simplify the notation, we take $C_{\rm W} = 1$, $C_{\rm TF} = 1$ and $C_{\rm D} = 1$ since these constants do not play any role in the mathematical analysis. Setting $\rho = v^2$, the TFW ground state energy is obtained by solving

$$I^{\rm TFW}_{\{X_k\}} = \inf\left\{\mathcal{E}^{\rm TFW}_{\{X_k\}}(v),\ v\in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} v^2 = N\right\}, \tag{5.4}$$

where

$$\mathcal{E}^{\rm TFW}_{\{X_k\}}(v) = \int_{\mathbb{R}^3}|\nabla v|^2 + \int_{\mathbb{R}^3}|v|^{10/3} + \int_{\mathbb{R}^3} V_{\{X_k\}}v^2 + \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{v(x)^2v(y)^2}{|x-y|}\,dx\,dy. \tag{5.5}$$

Under appropriate assumptions, and in particular when the system is globally neutral, that is when $N = \sum_{k=1}^K z_k$, problem (5.4)-(5.5) admits a minimizer $u > 0$, unique up to a global change of sign ($-u$ is the only other minimizer), which solves the Euler-Lagrange equation

$$-\Delta u + \frac{5}{3}u^{7/3} + V_{\{X_k\}}u + (u^2 \star |\cdot|^{-1})u + \theta u = 0 \tag{5.6}$$

(where $\star$ denotes the convolution product), at least in the distributional sense on $\mathbb{R}^3$, for some scalar θ, the Lagrange multiplier of the equality constraint $\int_{\mathbb{R}^3} v^2 = N$. It can be shown that θ is in fact positive. An excellent reference summarizing the mathematical knowledge on the TFW model at the time of its publication is [52].

5.1.3 The Hartree-Fock model

The HF model is somewhat mathematically close to the TFW model (5.4). The main difference is that we have to deal with an N-tuple of functions, the so-called molecular orbitals ϕ_i, where we used to consider *only one* function (the density ρ or its square root v) in the TFW model. An additional difficulty, which has far reaching consequences, is that the HF model is not convex. In particular, although existence may be proved by now relatively standard techniques, uniqueness seems out of reach in the general case (see however the interesting result in [35] for the particular case of a very positive atomic ion). The main two references addressing the HF problem in mathematical details are [58], and [59].

Recall for consistency the basic derivation of the HF model. Since problem (5.2) is computationally too complex to be treated directly, a possible approximation is to keep the same Hamiltonian (5.1), but minimize the energy $\langle\psi, H_{\{X_k\}}\psi\rangle$ upon less general functions ψ. This leads to the variational problem

$$I^{\mathcal{X}}_{\{X_k\}} = \inf\left\{\langle\psi, H_{\{X_k\}}\psi\rangle,\ \psi\in\mathcal{X},\ \|\psi\|_{L^2}=1\right\}, \tag{5.7}$$

where $\mathcal{X}$ is a subset of $\wedge^N H^1(\mathbb{R}^3)$. Obviously, $I^{\mathcal{X}}_{\{X_k\}}$ is an upper bound of the target value $I_{\{X_k\}}$. The Hartree-Fock approximation consists in considering the set $\mathcal{X}$ of the L^2-normalized N-electron wavefunctions that can be written as an antisymetrized product of single electron molecular orbitals ϕ_i:

$$\psi(x_1,\cdots,x_N) = \frac{1}{\sqrt{N!}}\det(\phi_i(x_j)). \tag{5.8}$$

Such functions are called *Slater determinants*. Since the determinant is an alternate multilinear map, it is possible to impose that the functions ϕ_i satisfy the orthonormality constraints

$$\int_{\mathbb{R}^3}\phi_i\phi_j = \delta_{ij}. \tag{5.9}$$

This implies, in particular, that $\|\psi\|_{L^2}=1$. Problem (5.7) for the functions (5.8) can then be rewritten, once the computation of $\langle\psi, H_{\{X_k\}}\psi\rangle$ is explicitly performed, as

$$I^{\rm HF}_{\{X_k\}} = \inf\left\{\mathcal{E}^{\rm HF}_{\{X_k\}}(\Phi),\ \Phi=(\phi_1,\cdots,\phi_N)\in(H^1(\mathbb{R}^3))^N,\ \int_{\mathbb{R}^3}\phi_i\phi_j=\delta_{ij}\right\}, \tag{5.10}$$

$$\begin{aligned}\mathcal{E}^{\rm HF}_{\{X_k\}}(\Phi) &= \frac{1}{2}\sum_{i=1}^N\int_{\mathbb{R}^3}|\nabla\phi_i|^2 + \int_{\mathbb{R}^3}\rho_\Phi V_{\{X_k\}} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\Phi(x)\rho_\Phi(y)}{|x-y|}\,dx\,dy\\ &\quad -\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|\gamma_\Phi(x,y)|^2}{|x-y|}\,dx\,dy,\end{aligned} \tag{5.11}$$

where the density matrix γ_Φ and the density ρ_Φ associated with the N-tuple $\Phi=(\phi_1,\cdots,\phi_N)$ are defined as

$$\gamma_\Phi(x,y) = \sum_{i=1}^N\phi_i(x)\phi_i(y), \qquad \rho_\Phi(x) = \gamma_\Phi(x,x) = \sum_{i=1}^N|\phi_i(x)|^2. \tag{5.12}$$

Note that the density ρ_Φ is in fact the density ρ_ψ defined by (5.3) of the N-body wavefunction ψ defined by (5.8).

The last term in the HF energy functional (5.11) is called the exchange term. It has a purely quantum nature (it arises from the antisymmetry of the electronic wavefunction) and has no classical counterpart. The exchange energy density of a homogeneous electron gas of uniform density ρ_0 can be computed analytically. It is equal to $-C_{\rm D}\rho_0^{4/3}$; this expression is used in the construction of the Dirac local exchange term in the TFDW energy functional.

It is important to emphasize that, for simplicity, we consider here a *spinless* HF model. Like the TFW problem, the HF problem admits a minimizer in the neutral case. Uniqueness is however an open issue. Any minimizer of the HF problem satisfies the associated Euler-Lagrange equations

$$-\frac{1}{2}\Delta\phi_i + V_{\{X_k\}}\phi_i + \left(\rho_\Phi \star |\cdot|^{-1}\right)\phi_i - \left(\int_{\mathbb{R}^3} \frac{\gamma_\Phi(\cdot,y)}{|\cdot - y|}\,\phi_i(y)\,dy\right) = \sum_{j=1}^{N} \lambda_{ij}\phi_j, \tag{5.13}$$

for a symmetric matrix of Lagrange multipliers $[\lambda_{ij}]$, the multiplier $\lambda_{ij} = \lambda_{ji}$ being associated to the constraint $\displaystyle\int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}$. Up to a change of $(\phi_1, \cdots, \phi_N)$ using an orthogonal transformation, which does not change the energy, one can diagonalize this symmetric matrix of Lagrange multipliers and obtain

$$\left\{\begin{array}{l} \displaystyle -\frac{1}{2}\Delta\phi_i + V_{\{X_k\}}\phi_i + \left(\rho_\Phi \star |\cdot|^{-1}\right)\phi_i + K_{\gamma_\Phi}\phi_i = \varepsilon_i\phi_i \\ \displaystyle \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}, \end{array}\right. \tag{5.14}$$

where K_{γ_Φ} is the nonlocal exchange operator defined for all $\phi \in L^2(\mathbb{R}^3)$ by

$$(K_{\gamma_\Phi}\phi)(x) = -\int_{\mathbb{R}^3} \frac{\gamma_\Phi(x,y)}{|x-y|}\,\phi(y)\,dy.$$

System (5.14) forms the *Hartree-Fock equations*. An important property is that if $\Phi = (\phi_1, \cdots, \phi_N)$ is a minimizer of the HF problem satisfying (5.14), then the eigenvalues $\varepsilon_1, \cdots, \varepsilon_N$ are the lowest N eigenvalues (counting multiplicities) of the HF operator [58, 59]

$$H_\Phi^{\rm HF} = -\frac{1}{2}\Delta + V_{\{X_k\}} + \rho_\Phi \star |\cdot|^{-1} + K_{\gamma_\Phi}$$

and that there is a positive gap between the N-th and $(N+1)$-st eigenvalues of $H_\Phi^{\rm HF}$ [6].

5.1.4 Kohn-Sham models

Kohn-Sham models are by far the most widely used electronic structure models in materials science. They all are of the form

$$I_{\{X_k\}}^{\rm KS} = \inf\left\{\mathcal{E}_{\{X_k\}}^{KS}(\Phi),\ \Phi = (\phi_1, \cdots, \phi_N) \in (H^1(\mathbb{R}^3))^N,\ \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}\right\}, \tag{5.15}$$

$$\mathcal{E}^{\rm KS}_{\{X_k\}}(\Phi) = \frac{1}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3}|\nabla\phi_i|^2 + \int_{\mathbb{R}^3}\rho_\Phi V_{\{X_k\}} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\Phi(x)\rho_\Phi(y)}{|x-y|}\,dx\,dy + E_{\rm xc}(\rho_\Phi) \quad (5.16)$$

where the density ρ_Φ is defined by (5.12). The functional $E_{\rm xc}(\rho)$, called the *exchange-correlation term*, is a correction term, accounting for the non-independence of the electrons. KS models originate from Density Functional Theory, and are *in principle* "exact": there exists a functional of the density $E_{\rm xc}$ for which $I^{KS}_{\{X_k\}} = I_{\{X_k\}}$ for all finite molecular systems. On the other hand, they are approximate models in practice since the exact exchange-correlation functional is not known and must be approximated to perform numerical calculations. The simplest KS model actually used in practice is obtained using the *Local Density Approximation* (LDA) introduced by Kohn and Sham [45] (see also [65]). The resulting model is mathematically very similar to the so-called Xα model [72] where the exchange-correlation functional is approximated by the Dirac local exchange term:

$$E^{\rm X\alpha}_{\rm xc}(\rho) = -C_D\int_{\mathbb{R}^3}\rho^{4/3}.$$

Other more refined exchange-correlation functionals have been developed in the past 30 years, leading to the *Generalized Gradient Approximation* (GGA) [64, 7, 63], hybrid functionals [8], ...

The Euler-Lagrange equations of problem (5.15) obtained after rotating the Kohn-Sham orbitals ϕ_i to diagonalize the matrix of the Lagrange multipliers (as for the HF model) are the *Kohn-Sham equations*

$$\left\{\begin{array}{l} -\dfrac{1}{2}\Delta\phi_i + V_{\{X_k\}}\phi_i + (\rho_\Phi \star |\cdot|^{-1})\phi_i + v_{\rm xc}(\rho_\Phi)\phi_i = \epsilon_i\phi_i, \\ \displaystyle\int_{\mathbb{R}^3}\phi_i\phi_j = \delta_{ij}, \end{array}\right. \quad (5.17)$$

where $v_{\rm xc}(\rho) = \dfrac{\partial E_{\rm xc}}{\partial\rho}(\rho)$ is the functional derivative of $E_{\rm xc}$. For the Xα model, we simply have $v^{\rm X\alpha}_{\rm xc}(\rho) = -\frac{4}{3}C_D\rho^{1/3}$.

The comparison of the energy functionals in the HF case and in the KS case (or that of their respective Euler-Lagrange equations) reveals at first sight the global similarity between the two approaches from a formal viewpoint. The HF problem (5.10)-(5.11) and the KS problems (5.15) obviously share some similarities. However, when it comes to mathematical details, the KS problem turns out to be more difficult than the HF problem to analyze [48, 1]. The difficulty owes to the presence of the *concave* exchange-correlation term. For $N = 1$ (that is for 2 electrons if spin is taken into account), the Xα KS model is close to the TFDW model introduced in Section 5.1.2. The only difference between the Xα KS model (5.15) for $N = 1$, and the TFDW model is the addition of the kinetic energy term $\displaystyle\int_{\mathbb{R}^3}|u|^{10/3}$. In fact, this term does not affect the mathematical analysis. So the TFDW model is an adequate prototypical model for understanding mathematically the KS model. More details can be found in [48].

5.1.5 One-electron density matrices

The one-electron density matrix, henceforth simply named the density matrix, associated with a normalized N-body wavefunction $\psi \in \wedge^N L^2(\mathbb{R}^3)$ is the bounded self-adjoint operator γ_ψ on $L^2(\mathbb{R}^3)$ defined by its kernel (also called density matrix and denoted by γ_ψ)

$$\gamma_\psi(x,x') = N \int_{\mathbb{R}^{3(N-1)}} \psi(x,x_2,\cdots,x_N)\psi(x',x_2,\cdots,x_N)\,dx_2\cdots dx_N. \tag{5.18}$$

If the N-body wavefunction is the Slater determinant (5.8), the two functions γ_ψ and γ_Φ respectively defined by (5.18) and (5.12) coincide.

The set of density matrices originating from a Slater determinant of finite kinetic energy is easily characterized. It is the set

$$\mathcal{P}_N = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid \gamma^2 = \gamma,\ \mathrm{Tr}(\gamma) = N,\ \mathrm{Tr}(-\Delta\gamma) < \infty\right\},$$

where $\mathcal{S}(L^2(\mathbb{R}^3))$ is the space of the bounded self-adjoint operators on $L^2(\mathbb{R}^3)$, and where $\mathrm{Tr}(-\Delta\gamma) = \mathrm{Tr}(|\nabla|\gamma|\nabla|)$. The condition $\gamma^2 = \gamma$ means that the self-adjoint operator γ is an orthogonal projector, and the condition $\mathrm{Tr}(\gamma) = N$ that the range of γ is of dimension N. Denoting by $(\phi_1,\cdots,\phi_N)$ an L^2-orthonormal basis of $\mathrm{Ran}(\gamma)$, we can see that

$$\mathrm{Tr}(-\Delta\gamma) = \sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla\phi_i|^2.$$

As a consequence, the HF energy functional is in fact a functional of the density matrix:

$$E^{\mathrm{HF}}_{\{X_k\}}(\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V_{\{X_k\}} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\gamma(x,y)|^2}{|x-y|}\,dx\,dy,$$

where

$$\rho_\gamma(x) = \gamma(x,x),$$

and the HF problem can be reformulated as

$$I^{\mathrm{HF}}_{\{X_k\}} = \inf\left\{E^{\mathrm{HF}}_{\{X_k\}}(\gamma),\ \gamma \in \mathcal{P}_N\right\}. \tag{5.19}$$

Likewise, the KS model can be reformulated in terms of density matrices:

$$I^{\mathrm{KS}}_{\{X_k\}} = \inf\left\{E^{\mathrm{KS}}_{\{X_k\}}(\gamma),\ \gamma \in \mathcal{P}_N\right\}, \tag{5.20}$$

where

$$E^{\mathrm{HF}}_{\{X_k\}}(\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V_{\{X_k\}} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy + E_{\mathrm{xc}}(\rho_\gamma).$$

There is however a difference between the HF and KS cases: a minimizer to (5.19) is, by construction of the KS model [45], an approximation of the ground state density matrix of the physical system of interacting electrons, while a minimizer to (5.20) is an

approximation of the ground state density matrix of an idealized system of non-interacting electrons with same ground state density as the actual physical system. This means that, in principle, it is not possible to use the ground state density matrices obtained with the KS model to compute properties depending on the density matrix, not only on the density $\rho_\gamma(x) = \gamma(x,x)$, but on the full density matrix $\gamma(x,y)$.

There is no simple characterization of the set of density matrices originating from an L^2-normalized N-body wavefunction of finite kinetic energy. On the other hand, the set Γ_N of the (one-body) density matrices originating from N-body density matrices with finite kinetic energy has a simple structure [29]:

$$\Gamma_N = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 1,\ \mathrm{Tr}(\gamma) = N,\ \mathrm{Tr}(-\Delta\gamma) < \infty\right\}.$$

Recall that in quantum mechanics, the states that can be defined by a single N-body wavefunction are called pure states, while those that need to be defined by N-body density matrices are called mixed states, or ensemble states [29]. Any operator $\gamma \in \Gamma_N$ is a bounded self-adjoint operator on $L^2(\mathbb{R}^3)$ satisfying the constraint $0 \leq \gamma \leq 1$ in the sense of operators. This condition, which is a mathematical translation of the Pauli principle, means that $0 \leq \langle\phi, \gamma\phi\rangle \leq \|\phi\|_{L^2}^2$ for all $\phi \in L^2(\mathbb{R}^3)$, or equivalently, that the spectrum of γ lies in the interval $[0,1]$. The trace of γ (which is always defined since γ is a positive operator) is equal to the number of electrons. Any $\gamma \in \Gamma_N$ being trace-class, hence compact, it can be diagonalized in an orthonormal basis set of $L^2(\mathbb{R}^3)$:

$$\gamma = \sum_{i=1}^{+\infty} n_i (\phi_i, \cdot)_{L^2} \phi_i \quad \text{where} \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}.$$

The constraints $0 \leq \gamma \leq 1$, $\mathrm{Tr}(\gamma) = N$ and $\mathrm{Tr}(-\Delta\gamma) < \infty$ are respectively equivalent to the constraints $0 \leq n_i \leq 1$ for all i, $\sum_{i=1}^{+\infty} n_i = N$, and $\sum_{i=1}^{+\infty} n_i \|\nabla\phi_i\|_{L^2}^2 < \infty$. The density ρ_γ associated with γ is defined as

$$\rho_\gamma(x) = \sum_{i=1}^{+\infty} n_i |\phi_i(x)|^2,$$

and is independent on the choice of the diagonalization basis ϕ_i. The function ρ_γ is of course in $L^1(\mathbb{R}^3)$ and

$$\int_{\mathbb{R}^3} \rho_\gamma = \mathrm{Tr}(\gamma). \tag{5.21}$$

Its square root is in fact in $H^1(\mathbb{R}^3)$, and satisfies the Hoffmann-Ostenhof inequality

$$\int_{\mathbb{R}^3} |\nabla\sqrt{\rho_\gamma}|^2 \leq \mathrm{Tr}(-\Delta\gamma).$$

Note that Γ_N is the convex hull of $\mathcal{P}_N$; in particular Γ_N is a convex set.

Lastly, the minimization problem

$$I_{\{X_k\}}^{\mathrm{EKS}} = \inf\left\{E_{\{X_k\}}^{\mathrm{KS}}(\gamma),\ \gamma \in \Gamma_N\right\}, \tag{5.22}$$

consisting in minimizing the KS energy functional on the set Γ_N has a physical interpretation in terms of Density Functional Theory for mixed states. It is known in the physical literature under the name of *extended Kohn-Sham* model [31]. With the exact exchange-correlation energy functional (which, we recall, has no known explicit expression), it holds $I^{\rm EKS}_{\{X_k\}} = I^{\rm KS}_{\{X_k\}} = I_{\{X_k\}}$. In practice, with approximate exchange-correlation functionals, these three numbers differ in general, but the first two are equal for many molecular systems. The extended Kohn-Sham model is also the zero-temperature limit of the finite temperature Kohn-Sham model [31] commonly used in materials science.

5.1.6 The reduced Hartree-Fock (rHF) model

An important result due to Lieb is that the minimizers of the HF energy functional $E^{\rm HF}_{\{X_k\}}$ on the set Γ_N coincides with the minimizers of $E^{\rm HF}_{\{X_k\}}$ on the set $\mathcal{P}_N$. In particular,

$$I^{\rm HF}_{\{X_k\}} = \inf\left\{E^{\rm HF}_{\{X_k\}}(\gamma),\ \gamma \in \Gamma_N\right\}. \tag{5.23}$$

A simplified version of the HF model (5.23), called the *reduced Hartree-Fock* (rHF) model, consists in eliminating the exchange term of the energy functional (5.11). The so-obtained model reads

$$I^{\rm rHF}_{\{X_k\}} = \inf\left\{E^{\rm rHF}_{\{X_k\}}(\gamma),\ \gamma \in \Gamma_N\right\}, \tag{5.24}$$

where

$$E^{\rm rHF}_{\{X_k\}}(\gamma) = {\rm Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V_{\{X_k\}} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy. \tag{5.25}$$

In contrast with the HF model, the rHF model is convex in the density matrix, and strictly convex in the density. It has been proved [73] that for neutral (or positively charged) molecular systems, (5.24) has at least one minimizer γ^0, that all the minimizers share the same density ρ^0, and that γ^0 satisfies the self-consistent equation

$$\gamma^0 = \mathbb{1}_{(-\infty,\epsilon^0_{\rm F})}(H_{\rho^0}) + \delta, \tag{5.26}$$

where

$$H_{\rho^0} = -\frac{1}{2}\Delta + V_{\{X_k\}} + \rho^0 \star |\cdot|^{-1} \tag{5.27}$$

is the mean-field Hamiltonian for the rHF model, $\epsilon^0_{\rm F}$ the Fermi level (the Lagrange multiplier of the constraint ${\rm Tr}(\gamma) = N$), $\mathbb{1}_{(-\infty,\epsilon_{\rm F})}(H_{\rho^0})$ the spectral projector of H_{ρ^0} on the range $(-\infty,\epsilon^0_{\rm F})$, and $0 \le \delta \le 1$ a finite rank operator such that ${\rm Ran}(\delta) \subset {\rm Ker}(H_{\rho^0} - \epsilon^0_{\rm F})$. Equation (5.26) is an adequate formulation of the Euler equation associated with the convex optimization problem (5.24), in the sense that it is concise and can be generalized to the periodic and stationary ergodic settings, in which there is an infinite number of electrons in the system (see Sections 5.3 and 6.2). For finite systems, H_{ρ^0} has at least N non-positive eigenvalues (counting multiplicities). Denoting by $\epsilon_1 \le \epsilon_2 \le \epsilon_3 \le ...$ the non-negative eigenvalues of H_{ρ^0}, two cases can be distinguished:

1. if H_{ρ^0} has exactly N negative eigenvalues, or if $\epsilon_N < \epsilon_{N+1}$, then $\delta = 0$, γ^0 is the orthogonal projector on the space spanned by the eigenvectors of H_{ρ^0} associated with the lowest N eigenvalues, and $\epsilon_{\rm F}^0$ can be any number in the range $(\epsilon_N, \epsilon_{N+1})$ (with the convention that $\epsilon_{N+1} = 0$ if H_{ρ^0} has exactly N negative eigenvalues);

2. if $\epsilon_N = \epsilon_{N+1}$, then $\epsilon_{\rm F}^0 = \epsilon_N$ and δ can be non-zero.

5.2 Thomas-Fermi type models for perfect crystals

In order to illustrate the difficulty of rigorously deriving a model for a crystal, we consider the TFW energy functional with $\{X_k\} = \Lambda_N \subset \mathbb{Z}^3$ and nuclei of unit charges. Without changing the notation, we consider the *total* energy functional of the system obtained by adding to the electronic energy functional an interaction term accounting for the repulsion between the nuclei:

$$\begin{aligned} E_{\Lambda_N}^{\rm TFW}(\rho) &= \int_{\mathbb{R}^3} |\nabla\sqrt{\rho}|^2 + \int_{\mathbb{R}^3} \rho^{5/3} \\ &\quad - \sum_{X_k\in\Lambda_N} \int_{\mathbb{R}^3} \frac{\rho(x)}{|x-X_k|} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy + \frac{1}{2}\sum_{X_j\neq X_k\in\Lambda_N} \frac{1}{|X_j-X_k|}, \end{aligned}$$

and recall that we expect the energy $E_{\Lambda_N}^{\rm TFW}(\rho)$ at the minimizer ρ_N to be asymptotically linear with respect to N. Now it is easy to see that each of the last three terms of the electrostatic energy

$$\begin{aligned} E_{\Lambda_N}^{\rm elec}(\rho) &= -\sum_{X_k\in\Lambda_N} \int_{\mathbb{R}^3} \frac{\rho(x)}{|x-X_k|}\,dx + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\,\rho(y)}{|x-y|}\,dx\,dy \\ &\quad + \frac{1}{2}\sum_{X_j\neq X_k\in\Lambda_N} \frac{1}{|X_j-X_k|}. \end{aligned} \tag{5.28}$$

scales as $N^{5/3}$. For instance, a rough evaluation as follows

$$\begin{aligned} \sum_{X_j\neq X_k\in\Lambda_N} \frac{1}{|X_j-X_k|} &\approx \iint_{(\text{Cube of volume } N)^2} \frac{dx\,dy}{|x-y|} \\ &= N^{5/3} \iint_{(\text{Unit cube})^2} \frac{dx\,dy}{|x-y|} \end{aligned}$$

using a change of variables in the integral, suffices to conclude for the last term.

Therefore, cancellation effects are needed to obtain a linear behaviour of the electrostatic energy $E_{\Lambda_N}^{\rm elec}(\rho)$. A key point in the strategy of proof is therefore to prove that the electronic density spreads in such a homogeneous way all over the cube of size N so that the effect of the electronic cloud is to screen the electrostatic interaction, thereby making possible the proper linear scaling law for the energy $E_{\Lambda_N}^{\rm elec}(\rho)$.

We now introduce the periodic minimization problems obtained in the thermodynamic limit. Define the following periodic minimization problem set on the unit cell Q of the

lattice (take $Q = [-1/2, 1/2]^3$ for simplicity):

$$I_{\rm per}^{\rm TFW} = \inf\{E_{\rm per}^{\rm TFW}(\rho),\ \rho \geq 0,\ \sqrt{\rho} \in H^1_{\rm per}(Q),\ \int_Q \rho = 1\}, \tag{5.29}$$

with

$$\begin{aligned} E_{\rm per}^{\rm TFW}(\rho) &= \int_Q |\nabla\sqrt{\rho}|^2 + \int_Q \rho^{5/3} - \int_Q \rho(x)G(x)dx \\ &+ \frac{1}{2}\iint_{Q\times Q} \rho(x)\rho(y)G(x-y)dxdy, \end{aligned} \tag{5.30}$$

where $H^1_{\rm per}(Q)$ is the subset of $H^1_{\rm loc}(\mathbb{R}^3)$ consisting of functions which satisfy the periodic boundary conditions on the boundary of Q. The potential G which appears in the definition (5.30) of the TFW functional is defined, in a unique way, by

$$\begin{cases} -\Delta G = 4\pi\ \left(-1 + \displaystyle\sum_{y\in\mathbb{Z}^3} \delta(\cdot - y)\right), \\ \displaystyle\int_Q G = 0. \end{cases} \tag{5.31}$$

From a physical viewpoint, G is the Coulomb potential generated by a periodic distributions of unit point charges located on the lattice $\mathbb{Z}^3$ and by a uniform negative charge distribution of density -1 (a jellium) so that the total charge per unit cell is neutral. The above PDE uniquely defines G up to an additive constant, and the constant is fixed by the condition $\int_Q G = 0$.

It is easily seen that problem (5.29) has a unique minimizer $\rho_{\rm per}$. The main results known to date are collected in the following theorem.

Theorem 3 *[24]* **Thermodynamic limit for the TFW model**
In the thermodynamic limit $N \to +\infty$, we have

- *(i) convergence of the energy per unit volume:*

$$\lim_{N\to+\infty} \frac{1}{N} I_{\Lambda_N}^{\rm TFW} = I_{\rm per}^{\rm TFW} + \frac{M}{2},$$

where $\dfrac{M}{2} = \dfrac{1}{2}\lim\limits_{x\to 0}\left(G(x) - \dfrac{1}{|x|}\right)$ *is just a normalization;*

- *(ii) convergence of the electronic density ρ_N to the minimizer $\rho_{\rm per}$ of $I_{\rm per}^{\rm TFW}$ in the following senses: $u_N = \sqrt{\rho}_N$ converges to $u_{\rm per} = \sqrt{\rho}_{\rm per}$ strongly in $H^1_{\rm loc}(\mathbb{R}^3) \cap L^p_{\rm loc}(\mathbb{R}^3)$ for all $1 \leq p < +\infty$, uniformly on the compact sets of $\mathbb{R}^3$, and*

$$\|\rho_N - \rho_{\rm per}\|_{L^\infty(\Omega_N)} \longrightarrow 0,$$

for any sequence of domains Ω_N included in the large cube of volume N, growing as this cube, and asymptotically far from its boundary (a sequence called an interior domain *in statistical mechanics).*

We now outline the proof of this Theorem. It is actually doable to write down a mathematical proof that follows the formal argument given above in terms of cancellations of the different terms in the energy (see [24, Chapters 2 & 3]), but a more elegant and powerful approach of the problem consists in treating the Euler-Lagrange equation, rather than the energy functional. In other words, proving (ii) of the Theorem before proving (i). In particular, this proof enables one to address more general geometries for the infinite set of nuclei, which is precisely the focus of this article. The set of nuclei need not be the periodic measure $\sum_{X_k\in\mathbb{Z}^3}\delta(\cdot-X_k)$ but only need to enjoy appropriate properties (see Section 4.1).

We recall that the TFW equation reads

$$-\Delta u_N+\frac{5}{3}\,u_N^{7/3}-\left(\sum_{X_k\in\Lambda_N}\frac{1}{|\cdot-X_k|}\right)u_N+\left(\rho_N\star|\cdot|^{-1}\right)u_N=-\theta_N u_N,$$

where $u_N=\sqrt{\rho_N}$. Introducing again the effective potential

$$\Phi_N(x)=\sum_{X_k\in\Lambda_N}\frac{1}{|x-X_k|}-\left(\rho_N\star|\cdot|^{-1}\right)(x)-\theta_N \tag{5.32}$$

it can be written in the form of the system

$$\left\{\begin{array}{l}-\Delta u_N+\dfrac{5}{3}\,u_N^{7/3}-\Phi_N\,u_N=0,\\ u_N\geq 0,\\ -\Delta\Phi_N=4\pi\left(\displaystyle\sum_{X_k\in\Lambda_N}\delta(\cdot-X_k)-u_N^2\right).\end{array}\right. \tag{5.33}$$

The strategy is as follows. First, we establish some *a priori bounds* on ρ_N and Φ_N, which allow us to pass to the limit in the Euler-Lagrange system (5.33) and obtain the system (5.35) below for the limits (u,Φ). The main result that will allow for the proof of Theorem 3 is the uniqueness result stated in Lemma 4 below. The proof of this latter lemma is the second step. Once this uniqueness is established, it suffices to suppose some additional structure hypothesis on the measure m, such as periodicity, to recover (by a straightforward argument) the same structure on the solution (u,Φ). Finally, the average energy (here the periodic energy) is then found by simply inserting the convergence of u_N and Φ_N in all terms of the energy functional (this will not be detailed here). The proof of Theorem 3 is then complete.

Lemma 4 *Let m be a locally bounded positive measure that satisfies*

$$\left\{\begin{array}{l}\displaystyle\sup_{x\in\mathbb{R}^3}m(x+B_1)<\infty,\\ \exists R<\infty\ \textit{s.t.}\ \displaystyle\inf_{x\in\mathbb{R}^3}m(x+B_R)>0.\end{array}\right. \tag{5.34}$$

Then there is one and only one solution (u,Φ) to the system

$$\left\{\begin{array}{l}-\Delta u+\dfrac{5}{3}\,u^{7/3}-\Phi\,u=0,\\ u\geq 0,\\ -\Delta\Phi=4\pi(m-u^2),\end{array}\right. \tag{5.35}$$

such that $u \in L^\infty(\mathbb{R}^3)$ *and* $\Phi \in L^1_{\rm unif}(\mathbb{R}^3)$. *In addition,*

$$\inf_{\mathbb{R}^3} u > 0,$$

and Φ *belongs to the uniform Marcinkiewitz space* $L^{3,\infty}_{\rm unif}(\mathbb{R}^3)$.

We recall that $L^1_{\rm unif}(\mathbb{R}^3) = \left\{ \Phi \in L^1_{\rm loc}(\mathbb{R}^3) \;\middle|\; \sup_{x\in\mathbb{R}^3} \|\Phi\|_{L^1(x+B_1)} < +\infty \right\}$ and that

$$L^{3,\infty}_{\rm unif}(\mathbb{R}^3) = \left\{ \Phi \in L^1_{\rm loc}(\mathbb{R}^3) \;\middle|\; \sup_{y\in\mathbb{R}^3} \quad \sup_{t>0} \quad t^3 \, |\{x \in y + B_1;\, |\Phi(x)| \geq t\}| < +\infty \right\},$$

where $|B|$ is the Lebesgue measure of the Borel set $B \subset \mathbb{R}^3$

Some remarks are needed on assumptions (5.34). Of course the case of the periodic lattice corresponds to $m = \sum_{X_k\in\mathbb{Z}^3} \delta(\cdot - X_k)$, which fulfills the above conditions. These conditions are known as those defining a *Delaunay lattice* in crystallography. Heuristically, Assumptions (5.34) exclude situations where the set of nuclei includes infinitely charged clusters of nuclei somewhere or infinitely large empty zones. These assumptions are equivalent to the assumptions (H1)-(H2) we have presented in Section 4.1.

It is worth emphasizing the fundamental reason why uniqueness holds for a system of type (5.35). Basically, the reason is the strict convexity of the TFW energy functional. As indicated by the condition $u \geq 0$, we deal here with the ground state, and this ground state is unique. However, the argument is not straightforward as the natural framework would be to work in the energy space, say H^1, or any space of functions that vanish at infinity, at least in some weak sense: now the solution we manipulate is definitely not in such a space, as we expect it to be periodic. The point is therefore to understand to which extent there is still sufficient convexity in the equations to enforce uniqueness even without "boundary condition"at infinity. In this respect, the argument is reminiscent of arguments by H. Brézis and collaborators in the 1980s on the equation

$$-\Delta\Phi + |\Phi|^{p-1}\Phi = m$$

with m a locally bounded measure. For $p = 3/2$, the latter equation can in fact be recovered as a degenerate case of our system (5.35) by forcefully eliminating the term $-\Delta u$ in the first equation and formally factoring out by u (which actually amounts to considering the Thomas-Fermi model itself).

5.3 Hartree-Fock and Kohn-Sham models for perfect crystals

No result to date gives the thermodynamic limit of the HF problem (5.19), the KS problem (5.20), or the extended KS problem (5.22) (for the standard exchange-correlation functionals). Nevertheless, there is such a result for the rHF model (5.24). The analysis is then far simpler because convexity is restored.

As in the previous section, we take $\{X_k\} = \Lambda_N$, and, without changing the notation, we consider the total rHF energy functional including the nuclear repulsion energy:

$$\begin{aligned} E^{\rm rHF}_{\Lambda_N}(\gamma) &= \mathrm{Tr}\left(\frac{1}{2}\Delta\gamma\right) - \sum_{X_k\in\Lambda_N}\int_{\mathbb{R}^3}\frac{\rho_\gamma(x)}{|x-X_k|} + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\gamma(x)\rho_\gamma(y)}{|x-y|}\,dx\,dy \\ &\quad + \frac{1}{2}\sum_{X_j\neq X_k\in\Lambda_N}\frac{1}{|X_j-X_k|}. \end{aligned}$$

The model

$$I^{\rm rHF}_{\Lambda_N} = \inf\left\{E^{\rm rHF}_{\Lambda_N}(\gamma),\ \gamma\in\Gamma_N\right\}$$

can be shown to converge [26], in the thermodynamic limit, to the rHF periodic model

$$I^{\rm rHF}_{\rm per} = \inf\{E^{\rm rHF}_{\rm per}(\gamma_{\rm per}),\ \gamma_{\rm per}\in\Gamma_{\rm per}\}. \tag{5.36}$$

The set $\Gamma_{\rm per}$ is the set of $\mathbb{Z}^3$-periodic density matrices with one electron per unit cell and finite kinetic energy, defined as

$$\begin{aligned} \Gamma_{\rm per} = \Big\{\gamma_{\rm per}\in\mathcal{S}(L^2(\mathbb{R}^3)) \quad | \quad & 0\le\gamma_{\rm per}\le 1,\ \tau_z\gamma_{\rm per} = \gamma_{\rm per}\tau_z,\ \forall z\in\mathbb{Z}^3, \\ & \underline{\mathrm{Tr}}^{\rm per}(\gamma_{\rm per}) = 1,\ \underline{\mathrm{Tr}}^{\rm per}(-\Delta\gamma_{\rm per})<\infty\Big\}, \end{aligned}$$

where τ_z denotes the translation operator of vector $z\in\mathbb{Z}^3$: $(\tau_z\phi)(x) = \phi(x-z)$ for all $\phi\in L^2(\mathbb{R}^3)$, and where the notation $\underline{\mathrm{Tr}}^{\rm per}$ is defined in (5.37). A positive self-adjoint operator $A\in\mathcal{S}(L^2(\mathbb{R}^3))$ is called locally trace class if $\mathbb{1}_B A\mathbb{1}_B$ is trace-class for any bounded Borel set B. The density ρ_A associated with a locally trace-class operator A is a locally integrable function and for all bounded Borel sets $B\subset\mathbb{R}^3$,

$$\mathrm{Tr}(\mathbb{1}_B A\mathbb{1}_B) = \int_B \rho_A.$$

It is easily seen that a $\mathbb{Z}^3$-periodic positive operator $A_{\rm per}\in\mathcal{S}(L^2(\mathbb{R}^3))$ (commuting with all the translations τ_z, $z\in\mathbb{Z}^3$) is locally trace-class if and only if $\underline{\mathrm{Tr}}^{\rm per}(A_{\rm per})<\infty$, where

$$\underline{\mathrm{Tr}}^{\rm per}(A_{\rm per}) = \mathrm{Tr}(\mathbb{1}_Q A_{\rm per}\mathbb{1}_Q). \tag{5.37}$$

If $\gamma_{\rm per}$ is a locally trace-class periodic density matrix, its density $\rho_{\gamma_{\rm per}}$ is a $\mathbb{Z}^3$-periodic function of $L^1_{\rm loc}(\mathbb{R}^3)$ and

$$\underline{\mathrm{Tr}}^{\rm per}(\gamma_{\rm per}) = \int_Q \rho_{\gamma_{\rm per}} = \text{ number of electrons per unit cell.}$$

Likewise,

$$\underline{\mathrm{Tr}}^{\rm per}(-\Delta\gamma_{\rm per}) = \sum_{j=1}^3 \underline{\mathrm{Tr}}^{\rm per}(P_j\gamma_{\rm per}P_j),$$

where $P_j = -i\partial_{x_j}$ is the j^{th} component of the momentum operator (note that $-\Delta = \sum_{j=1}^3 P_j^2$), is in fact the kinetic energy per unit cell of the periodic density matrix γ_{per}. The periodic rHF energy functional is defined as

$$E_{\text{per}}^{\text{rHF}}(\gamma_{\text{per}}) = \underline{\text{Tr}}^{\text{per}}\left(-\frac{1}{2}\Delta\gamma_{\text{per}}\right) - \int_Q G\,\rho_{\text{per}} + \frac{1}{2}\iint_{Q\times Q} \rho_{\text{per}}(x)\,G(x-y)\,\rho_{\text{per}}(y)\,dxdy.$$

It is possible to provide more explicit expressions for $\underline{\text{Tr}}^{\text{per}}(\gamma_{\text{per}})$ and $\underline{\text{Tr}}^{\text{per}}(-\Delta\gamma_{\text{per}})$ by means of Bloch theory, but we will not elaborate further on this point here and refer the reader to [26, 18] for more details. We however mention that numerical methods to solve (5.36) heavily rely on the Bloch decomposition of the trial density matrices γ_{per}.

The convex minimization problem (5.36) has a unique minimizer γ_{per}^0 [18] with density $\rho_{\text{per}}^0(x) = \gamma_{\text{per}}^0(x,x)$, which is the orthogonal projector

$$\gamma_{\text{per}}^0 = \mathbb{1}_{(-\infty,\epsilon_{\text{F}}^0)}(H_{\text{per}}^0),$$

with

$$H_{\text{per}}^0 = -\frac{1}{2}\Delta + V_{\text{per}}^0,$$

where the $\mathbb{Z}^3$-periodic potential $V_{\text{per}}^0 \in L^2_{\text{per}}(Q)$ is the unique $\mathbb{Z}^3$-periodic solution to the Poisson problem

$$\begin{cases} -\Delta V_{\text{per}}^0 = 4\pi\left(\rho_{\text{per}}^0 - \displaystyle\sum_{k\in\mathbb{Z}^3}\delta_k\right), \\ \displaystyle\int_Q V_{\text{per}}^0 = 0, \end{cases}$$

and where ϵ_{F}^0 is the Fermi level, that is the Lagrange multiplier of the constraint $\underline{\text{Tr}}^{\text{per}}(\gamma_{\text{per}}^0) = 1$. The spectral properties of periodic Schrödinger operators are well-known. Using again Bloch theory, it can be proved that the spectrum $\sigma(H_{\text{per}}^0)$ of H_{per}^0 is purely absolutely continuous, and consists of possibly overlapping bands:

$$\sigma(H_{\text{per}}^0) = \bigcup_{n=1}^{+\infty}[\Sigma_n^-, \Sigma_n^+],$$

where $(\Sigma_n^-)_{n\geq 1}$ is a non-decreasing sequence of real numbers converging to infinity, and $\Sigma_n^+ > \Sigma_n^-$. If there is a gap between the j^{th} and $(j+1)^{\text{st}}$ bands (i.e. if $\Sigma_{j+1}^- > \Sigma_j^+$), then for any $a \in [\Sigma_j^+, \Sigma_{j+1}^-]$, the orthogonal projector $\mathbb{1}_{(-\infty,a]}(H_{\text{per}}^0)$ is independent of a and its trace per unit volume is exactly equal to j. In the simple case we are considering here (one electron per unit cell), two cases are *a priori* possible (see Figure 5):

1. either $\Sigma_2^- > \Sigma_1^+$ (existence of a gap between the first and second bands), in which case we can choose for instance $\epsilon_{\text{F}}^0 = \frac{1}{2}(\Sigma_1^+ + \Sigma_2^-)$, though any value in the band gap is suitable. From a physical viewpoint, this corresponds to an insulating or semiconducting crystal, depending on the magnitude of the gap $g = \Sigma_2^- - \Sigma_1^+ > 0$;

2. or $\Sigma_2^- \leq \Sigma_1^+$ (overlap between the first and second bands), in which case the Fermi level has a well-defined fixed value. From a physical viewpoint, this models a conducting crystal.

This could be decided by means of numerical simulations, but this is not our point here. The two situations are encountered in practice for more general lattices and motifs.

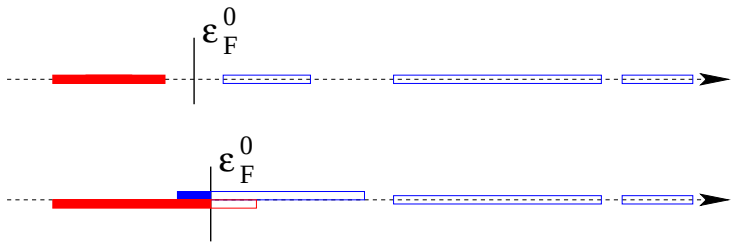

Figure 5: Electronic structure of an insulating or semiconducting crystal (top), and of a conducting crystal (bottom) with one electron per unit cell.

On the basis of the results obtained for the thermodynamic limit of the rHF model, it is natural to postulate that the HF and extended KS Xα ground state energies per unit volume and densities of the perfect crystal will be obtained by solving the following periodic models:

$$I_{\rm per}^{\rm HF} = \inf\{E_{\rm per}^{\rm HF}(\gamma_{\rm per}),\ \gamma_{\rm per} \in \Gamma_{\rm per}\}, \tag{5.38}$$

$$I_{\rm per}^{\rm KS} = \inf\{E_{\rm per}^{\rm KS}(\gamma_{\rm per}),\ \gamma_{\rm per} \in \Gamma_{\rm per}\}, \tag{5.39}$$

where

$$\begin{aligned} E_{\rm per}^{\rm HF}(\gamma_{\rm per}) &= \underline{\rm Tr}^{\rm per}\left(-\frac{1}{2}\Delta\gamma_{\rm per}\right) - \int_Q G\,\rho_{\gamma_{\rm per}} + \frac{1}{2}\iint_{Q\times Q} \rho_{\rm per}(x)\,G(x-y)\,\rho_{\rm per}(y)\,dxdy \\ &\quad -\frac{1}{2}\iint_{Q\times\mathbb{R}^3} \frac{|\gamma_{\rm per}(x,y)|^2}{|x-y|}\,dxdy, \end{aligned}$$

$$\begin{aligned} E_{\rm per}^{\rm KS}(\gamma_{\rm per}) &= \underline{\rm Tr}^{\rm per}\left(-\frac{1}{2}\Delta\gamma_{\rm per}\right) - \int_Q G\,\rho_{\gamma_{\rm per}} + \frac{1}{2}\iint_{Q\times Q} \rho_{\rm per}(x)\,G(x-y)\,\rho_{\rm per}(y)\,dxdy \\ &\quad -C_{\rm D}\int_Q \rho_{\gamma_{\rm per}}^{4/3}. \end{aligned}$$

The periodic HF model (5.38) can be shown to have a minimizer [26]. A recent contribution [34] provides a better mathematical knowledge on the above periodic HF problem. It establishes in particular that a minimizer is necessarily an orthogonal projector, a question left unsolved in [26]. It is easily seen that (5.39) has a minimizer, but its uniqueness is an open question.

6 Electronic structure of materials with defects

We now describe the results of [11, 18, 19, 20, 21] on the modeling of local defects in crystals in the framework of the TFW and rHF models. We first consider the case of a single local defect (or of a finite number of such defects) in Section 6.1. Then, we focus

on the case of a disordered crystal with an infinite number of randomly distributed local defects (possibly with very low concentration) in Section 6.2. Note that the electronic structure of crystals with local defects was first investigated in [57] in the framework of the Thomas-Fermi approximation for the particular case of a homogeneous host crystal with uniform nuclear and electronic densities.

6.1 The case of a local defect

Consider an insulating or semiconducting perfect crystal with a $\mathbb{Z}^3$-periodic nuclear charge density $\rho_{\rm per}^{\rm nuc}$. Our aim in this section is to investigate the case of a crystal with a local defect characterized by the nuclear charge distribution

$$\rho^{\rm nuc} = \rho_{\rm per}^{\rm nuc} + \nu, \tag{6.1}$$

where ν is localized (typically a compactly supported, or fast decaying perturbation of the periodic distribution $\rho_{\rm per}^{\rm nuc}$, see Figure 6.

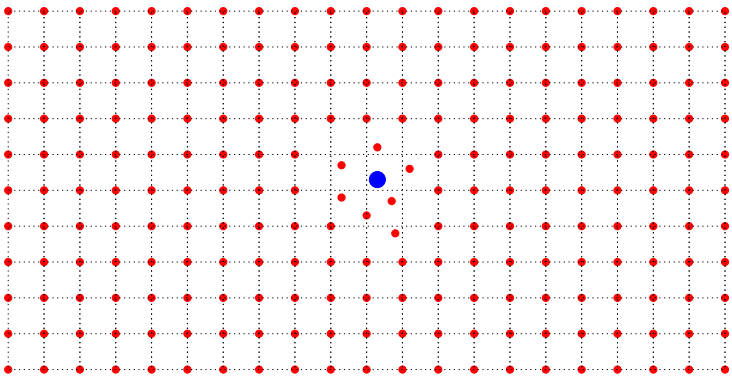

Figure 6: An example of a local defect: an impurity with relaxation of the neighboring atoms.

For both the TFW and rHF models, the electronic ground state of the perfect crystal is unique. It is indeed completely characterized

- in the TFW case, by the periodic ground state density $\rho_{\rm per}$, or equivalently by its square root $u_{\rm per} = \sqrt{\rho_{\rm per}}$ (see Section 5.2);
- in the rHF case, by the periodic ground state density matrix $\gamma_{\rm per}^0$ (see Section 5.3).

It is therefore natural to seek the ground state of the crystal with local defect of nuclear charge distribution $\rho^{\rm nuc} = \rho_{\rm per}^{\rm nuc} + \nu$, under the form

$$u_{\nu,q} = u_{\rm per} + v_{\nu,q} \qquad \text{(TFW)}, \tag{6.2}$$

$$\gamma_{\nu,\epsilon_{\rm F}^0} = \gamma_{\rm per}^0 + Q_{\nu,\epsilon_{\rm F}^0} \qquad \text{(rHF)}. \tag{6.3}$$

In (6.2), q denotes the charge of the defect. In (6.3), the charge of the defect is controlled by the Fermi level $\epsilon_{\rm F}^0$, which is, from the physical viewpoint, the chemical potential of the electrons in the crystal. The dual approach, in which the charge of the defect is imposed,

is also dealt with in [18]. A physical interpretation of these decompositions of $u_{\nu,q}$ (the square root of the ground state density) and $\gamma_{\nu,\epsilon_{\rm F}^0}$ (the ground state density matrix) is that the defect can be seen as a quasi-molecule with nuclear charge distribution ν and

- electronic ground state density

$$u_{\nu,q}^2 - u_{\rm per}^2 = 2u_{\rm per}v_{\nu,q} + v_{\nu,q}^2 \qquad \text{(TFW)};$$

- electronic density matrix

$$\gamma_{\nu,\epsilon_{\rm F}^0} - \gamma_{\rm per}^0 = Q_{\nu,\epsilon_{\rm F}^0} \qquad \text{(rHF)}.$$

It should be noticed that the charge densities ν, $2u_{\rm per}v_{\nu,q}+v_{\nu,q}^2$ and $\rho_{Q_{\nu,\epsilon_{\rm F}^0}}$ are not necessarily non-negative, since they are differences of two non-negative densities (note that we employ the physics terminology, where the term density does not assume non-negativity). For instance, if the host crystal has a nucleus of charge z at point X, the nuclear charge distribution of a vacancy at X is $\nu = -z\delta_X$.

Our goal is to exhibit variational problems allowing us to compute $v_{\nu,q}$ and $Q_{\nu,\epsilon_{\rm F}^0}$ from ν, q, $\epsilon_{\rm F}^0$ and the ground state of the perfect crystal. We proceed in four steps:

Step 1: guess a tentative variational problem by a formal calculation consisting in subtracting two infinite energies: the energy of the crystal with the defect, and the energy of the perfect crystal;

Step 2: find a functional setting to give a meaning to each term of the tentative problem;

Step 3: study the mathematical properties of the minimizers of the tentative problem;

Step 4: check that the tentative problem has a physical meaning by a thermodynamic limit argument.

This procedure falls into the scope of renormalization methods since we aim at giving a meaning to the difference of two infinite energies. Note that the renormalized model for defects in crystals we will obtain in the rHF case is formally very similar to the model introduced in [36, 37, 38] in the context of the no-photon approximation of quantum electrodynamics (QED) to describe atoms embedded in the QED vacuum.

Although the outline is identical for the TFW and rHF models, the technical details are quite different. The only common feature is that we will need in both cases to extend the definition of the Coulomb interaction energy to the Coulomb space $\mathcal{C}$ defined as

$$\mathcal{C} = \left\{ f \in \mathcal{S}'(\mathbb{R}^3) \mid \widehat{f} \in L^1_{\rm loc}(\mathbb{R}^3),\ D(f,f) = 4\pi \int_{\mathbb{R}^3} \frac{|\hat{f}(k)|^2}{|k|^2}\,dk < \infty \right\},$$

where $\mathcal{S}'(\mathbb{R}^3)$ is the space of tempered distributions on $\mathbb{R}^3$, and $\widehat{f}$ the Fourier transform of f (we use the normalization convention for which $\|\widehat{f}\|_{L^2} = \|f\|_{L^2}$ for all $f \in L^2(\mathbb{R}^3)$). Endowed with its natural inner product

$$D(f,g) = 4\pi \int_{\mathbb{R}^3} \frac{\overline{\hat{f}(k)}\,\hat{g}(k)}{|k|^2}\,dk, \tag{6.4}$$

$\mathcal{C}$ is a Hilbert space. It can be proved that $L^{6/5}(\mathbb{R}^3) \hookrightarrow \mathcal{C}$ and that for any $(f,g) \in L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$, it holds

$$4\pi \int_{\mathbb{R}^3} \frac{\overline{\hat{f}(k)}\,\hat{g}(k)}{|k|^2}\,dk = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{f(x)\,g(y)}{|x-y|}\,dx\,dy.$$

Hence, the definition (6.4) of $D(\cdot,\cdot)$ on $\mathcal{C}$ is consistent with the usual definition of the Coulomb interaction when the latter makes sense. The Coulomb space $\mathcal{C}$ therefore is the set of charge distributions of finite Coulomb energies. We denote by

$$\mathcal{C}' = \left\{ V \in L^6(\mathbb{R}^3) \,|\, \nabla V \in (L^2(\mathbb{R}^3))^3 \right\}.$$

the set of potentials generated by charge distributions of finite Coulomb energies, which can be identified with the dual of $\mathcal{C}$.

6.1.1 Crystals with local defects in the TFW setting

In the TFW setting, the methodology introduced in Section 6.1 can be put into practice as follows.

Step 1: formal derivation of a tentative variational problem.

We have previously seen that the periodic TFW problem (5.29) has a unique minimizer $\rho_{\rm per}$. The same holds if we replace the nuclear charge distribution $\sum_{X_k\in\mathbb{Z}^3}\delta_{X_k}$ with a more general $\mathbb{Z}^3$-periodic charge distribution $\rho^{\rm per}_{\rm nuc}$, and the constraint $\int_Q u^2 = 1$ with $\int_Q u^2 = N$, where N is the number of electrons per unit cell necessary to balance the nuclear charge distribution $\rho^{\rm per}_{\rm nuc}$. Reasoning as in Section 5.1.2, we obtain that the function $u_{\rm per} = \sqrt{\rho_{\rm per}}$ is solution in $H^1_{\rm per}(Q)$ to the Euler-Lagrange equation

$$H^{\rm TFW}_{\rm per} u_{\rm per} = \mu u_{\rm per}, \tag{6.5}$$

where μ is the Lagrange multiplier of the constraint $\int_Q u^2_{\rm per} = N$ and where $H^{\rm TFW}_{\rm per} = -\Delta + V_{\rm per}$ with

$$V_{\rm per} = \frac{5}{3}\rho^{2/3}_{\rm per} + (\rho_{\rm per} - \rho^{\rm nuc}_{\rm per}) \star G,$$

where G is the periodic Coulomb kernel defined by (5.31).

We now compute the difference between the TFW energy of a trial electronic density ρ interacting with the nuclear charge density $\rho^{\rm nuc}_{\rm per} + \nu$, and the TFW energy of the perfect crystal, without caring about mathematical rigor. Introducing the function v defined by $\sqrt{\rho} = u_{\rm per} + v$, and using the fact that the function $u_{\rm per}$ is solution to (6.5), we obtain

$$\begin{aligned} &E^{\rm TFW}_{\rho^{\rm nuc}_{\rm per}+\nu}(u_{\rm per}+v) - E^{\rm TFW}_{\rho^{\rm nuc}_{\rm per}}(u_{\rm per}) \\ &\overset{\rm formal}{=} \langle (H^{\rm TFW}_{\rm per} - \mu)v, v\rangle + \int_{\mathbb{R}^3} \left(|u_{\rm per}+v|^{10/3} - |u_{\rm per}|^{10/3} - \frac{5}{3}|u_{\rm per}|^{4/3}(2u_{\rm per}v + v^2) \right) \\ &\qquad + \frac{1}{2} D\left(2u_{\rm per}v + v^2 - \nu, 2u_{\rm per}v + v^2 - \nu\right) - \int_{\mathbb{R}^3} \nu V^0_{\rm per} + \mu q, \end{aligned} \tag{6.6}$$

where

$$q = \int_{\mathbb{R}^3} \left(|u_{\rm per} + v|^2 - |u_{\rm per}|^2 \right) = \int_{\mathbb{R}^3} (2u_{\rm per} v + v^2) \tag{6.7}$$

can be interpreted as the electronic charge of the defect. Of course, the left-hand side of (6.6) has *a priori* no mathematical sense since it is the difference of two infinite energies. On the other hand, the right-hand side is a well-defined mathematical expression.

Step 2: construction of a suitable functional setting.

The TFW Hamiltonian $H^{\rm TFW}_{\rm per}$ is a periodic Schrödinger operator. Using the fact that $u_{\rm per} = \sqrt{\rho_{\rm per}} \geq 0$, it can be shown that μ is in fact the bottom of the spectrum of $H^{\rm TFW}_{\rm per}$. It follows that the first term in the right-hand side of (6.6) is non-negative. So is the second one by convexity of the function $t \mapsto |t|^{10/3}$, as well as the third one by definition of the Coulomb energy. It is easy to see that the sum of these three terms is finite if and only if $v \in H^1(\mathbb{R}^3)$ and $u_{\rm per} v \in \mathcal{C}$. Besides, as v is defined by $\sqrt{\rho} = u_{\rm per} + v$, it obviously satisfies the constraint $v \geq -u_{\rm per}$. This leads us to introduce the set

$$\mathcal{Q}_+ = \left\{ v \in H^1(\mathbb{R}^3) \mid v \geq -u_{\rm per},\ u_{\rm per} v \in \mathcal{C} \right\},$$

and the minimization problem

$$I^\nu = \inf \left\{ \mathcal{E}^\nu(v),\ v \in \mathcal{Q}_+ \right\} \tag{6.8}$$

with

$$\begin{aligned} \mathcal{E}^\nu(v) &= \langle (H^{\rm TFW}_{\rm per} - \mu) v, v \rangle + \int_{\mathbb{R}^3} \left(|u_{\rm per} + v|^{10/3} - |u_{\rm per}|^{10/3} - \frac{5}{3} |u_{\rm per}|^{4/3} (2u_{\rm per} v + v^2) \right) \\ &\quad + \frac{1}{2} D\left(2u_{\rm per} v + v^2 - \nu, 2u_{\rm per} v + v^2 - \nu \right). \end{aligned} \tag{6.9}$$

The term $\int_{\mathbb{R}^3} \nu V^0_{\rm per}$ in the right-hand side of (6.6) is independent of v and can therefore be discarded. On purpose, we also ignore the term μq in (6.6), which yet depends on v through (6.7). The will be justified below.

Step 3: mathematical analysis of the minimization problem (6.8).

The following result is proved in [20].

Theorem 4 *[20] Let $\nu \in \mathcal{C}$. Then,*

1. Existence and uniqueness of the ground state density. *The minimization problem (6.8) has a unique minimizer v_ν. The function v_ν is such that $u_{\rm per} + v_\nu > 0$ in $\mathbb{R}^3$ and satisfies the Euler-Lagrange equation*

$$\begin{aligned} &(H^{\rm TFW}_{\rm per} - \epsilon^0_{\rm F}) v_\nu + \frac{5}{3} C_{\rm TF} \left(|u_{\rm per} + v_\nu|^{7/3} - |u_{\rm per}|^{7/3} - |u_{\rm per}|^{4/3} v_\nu \right) \\ &\qquad + \left((2u_{\rm per} v_\nu + v_\nu^2 - \nu) \star |\cdot|^{-1} \right) (u_{\rm per} + v_\nu) = 0. \end{aligned} \tag{6.10}$$

2. Neutrality of local defects. *We denote by* $\rho_\nu^0 = \nu - (2u_{\rm per}v_\nu + v_\nu^2)$ *the total charge density of the defect. It holds*

$$\lim_{r\to 0} \frac{1}{|B_r|} \int_{B_r} |\widehat{\rho_\nu^0}(k)|\, dk = 0. \tag{6.11}$$

In addition, the Coulomb potential $\Phi_\nu^0 = \rho_\nu^0 \star |\cdot|^{-1}$ *generated by* ρ_ν^0 *is in* $L^2(\mathbb{R}^3) \cap \mathcal{C}'$.

3. Compactness of the minimizing sequences. *Any minimizing sequence* $(v_n)_{n\in\mathbb{N}}$ *of (6.8) converges to* v_ν *weakly in* $H^1(\mathbb{R}^3)$ *and strongly in* $L^p_{\rm loc}(\mathbb{R}^3)$ *for* $1 \le p < 6$. *Besides,* $(u_{\rm per}v_n)_{n\in\mathbb{N}}$ *converges to* $u_{\rm per}v_\nu$ *weakly in* $\mathcal{C}$.

For any $q \in \mathbb{R}$, *there exists a minimizing sequence* $(v_n)_{n\in\mathbb{N}}$ *of (6.8) consisting of functions of* $\mathcal{Q}_+ \cap L^1(\mathbb{R}^3)$ *such that*

$$\forall n \in \mathbb{N}, \quad \int_{\mathbb{R}^3} \left(|u_{\rm per} + v_n|^2 - |u_{\rm per}|^2\right) = q. \tag{6.12}$$

Remark 6.1 *Let* $\nu \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$. *Assuming that* $v_\nu \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$ *(a property satisfied at least in the special case of homogeneous host crystals [20]), we obtain that* $\widehat{\rho_\nu^0} \in C^0(\mathbb{R}^3)$ *and (6.11) simply means that the continuous function* $\widehat{\rho_\nu^0}$ *vanishes at* $k = 0$, *or equivalently that*

$$\int_{\mathbb{R}^3} \rho_\nu^0 = 0. \tag{6.13}$$

The second part of the third statement of Theorem 4 means that there is no way to charge a defect within the TFW theory: loosely speaking, if we try to put too many (or not enough) electrons in the system, the electronic density will relax to $(u_{\rm per} + v_\nu)^2$ and the remaining (or missing) $q - \int_{\mathbb{R}^3} \nu$ electrons will escape to (or come from) infinity with an energy μ (the last term in (6.6)). At convergence of the minimizing sequence, the system will end up neutral. This justifies our choice to ignore the term μq in (6.6) in our definition of the defect problem (6.8).

Step 4: justification of the model by thermodynamic limit arguments.

There are several technical ways of performing thermodynamic limits. The method described in Sections 5.2-5.3 considers the set of nuclei Λ_N and the TFW, rHF or HF models for N electrons living *in the whole space*.

Another way for performing thermodynamic limits is to confine the nuclei *and* the electrons in a domain Ω_L with $|\Omega_L| \to \infty$, by means of Dirichlet boundary conditions for the electrons. The latter approach was chosen for the Schrödinger model with quantum nuclei in the canonical and grand canonical ensembles [68] in the seminal paper [55] (see also [51]), where the existence of a limit for the energy per unit volume is proved. The crystal case in the Schrödinger model was addressed in [32] (see also [39]).

Another possibility, perhaps less satisfactory from a physical viewpoint but more directly related to practical calculations (see e.g. [30]), is to consider the domain $\Omega_L = [-L/2, L/2]^3$ and to impose periodic boundary conditions on the box Ω_L. Usually the

Coulomb interaction is also replaced by a $(L\mathbb{Z}^3)$-periodic Coulomb potential, leading to the so-called *supercell model*. This approach has the advantage of respecting the symmetry of the system in the crystal case. For brevity, we do not detail the supercell model here and refer the reader to [20]. We just mention the fact that there are two ways to perform a supercell calculation for a crystal with a local defect in the TFW framework:

- either we fix the electronic charge q of the defect, by imposing a constraint of the form
$$\int_{\Omega_L} \rho_L = L^3 N + q$$
to the $L\mathbb{Z}^3$-periodic trial density ρ_L;
- or we do not fix q, and minimize over all $L\mathbb{Z}^3$-periodic trial densities.

In both cases, the ground state density obtained in the thermodynamic limit is given by $\rho = (u_{\rm per} + v_\nu)^2$, where v_ν is the unique solution of (6.8).

6.1.2 Crystals with local defects in the rHF setting

We now focus on the rHF case, and seek a ground state density matrix of the form (6.3) for the crystal with nuclear charge distribution given by (6.1). The constraints on the full density matrix (self-adjointness $(\gamma_{\nu,\epsilon_{\rm F}^0})^* = \gamma_{\nu,\epsilon_{\rm F}^0}$ and Pauli principle $0 \leq \gamma_{\nu,\epsilon_{\rm F}^0} \leq 1$) imply the following constraints on $Q_{\nu,\epsilon_{\rm F}^0}$:

$$(Q_{\nu,\epsilon_{\rm F}^0})^* = Q_{\nu,\epsilon_{\rm F}^0}, \qquad -\gamma^0_{\rm per} \leq Q_{\nu,\epsilon_{\rm F}^0} \leq 1 - \gamma^0_{\rm per}.$$

We also have $\rho_{Q_{\nu,\epsilon_{\rm F}^0}} \geq -\rho^0_{\rm per}$.

Step 1: formal derivation of a tentative variational problem.

Formally, the difference between the rHF free energy of some trial density matrix $\gamma = \gamma^0_{\rm per} + Q$ subjected to the nuclear potential generated by $\rho^{\rm nuc}_{\rm per} + \nu$, and the rHF free energy of the perfect crystal, is given by:

$$\begin{aligned}\left(E^{\rm rHF}_{\rho^{\rm nuc}_{\rm per}+\nu}(\gamma^0_{\rm per}+Q) - \epsilon_{\rm F}^0 {\rm Tr}(\gamma^0_{\rm per}+Q)\right) - \left(E^{\rm rHF}_{\rho^{\rm nuc}_{\rm per}}(\gamma^0_{\rm per}) - \epsilon_{\rm F}^0 {\rm Tr}(\gamma^0_{\rm per})\right)& \\ \overset{\rm formal}{=} {\rm Tr}\left(-\frac{1}{2}\Delta Q\right) + \int_{\mathbb{R}^3} \rho_Q V^0_{\rm per} - D(\nu,\rho_Q) + \frac{1}{2}D(\rho_Q,\rho_Q)& \\ -\epsilon_{\rm F}^0 {\rm Tr}(Q) - \int_{\mathbb{R}^3} \nu V^0_{\rm per} + \frac{1}{2}D(\nu,\nu).& \end{aligned} \tag{6.14}$$

The term "free energy" refers to the fact that we work here in the grand canonical ensemble in which the chemical potential of the electrons, that is the Fermi level $\epsilon_{\rm F}^0$, is fixed. The latter can be chosen equal to any number in the gap between the occupied and unoccupied energy bands of the spectrum of the perfect crystal. While the chosen value of $\epsilon_{\rm F}^0$ has no influence on the electronic state of the perfect crystal, it does impact on the electronic state of the crystal with defect since only the energy levels below $\epsilon_{\rm F}^0$ will be occupied (see Figure 7 below).

As for (6.6), the left-hand side of (6.14) has *a priori* no mathematical meaning (it is the difference of two infinite energies). On the other hand, we will see that it is possible to give a mathematical meaning to the right-hand side when Q belongs to some functional space $\mathcal{Q}$ defined below, and to characterize the ground state density operator $Q_{\nu,\epsilon_{\rm F}^0}$ of the defect (considered as a quasi-molecule embedded in the perfect crystal), by minimizing the so-defined energy functional on some convex set $\mathcal{K}$.

Step 2: construction of a suitable functional setting.

The terms $\int_{\mathbb{R}^3} \nu V_{\rm per}^0$ and $\frac{1}{2}D(\nu,\nu)$ are independent of Q and can therefore be ignored. It now turns out that the sum

$$\mathrm{Tr}\left(-\frac{1}{2}\Delta Q\right) + \int_{\mathbb{R}^3} \rho_Q V_{\rm per}^0 - \epsilon_{\rm F}^0 \mathrm{Tr}(Q)$$

can (still formally) be written as a non-negative quantity for any Q satisfying $Q = Q^*$ and $0 \le \gamma_{\rm per}^0 + Q \le 1$. In order to establish this result, we introduce, for any operator A on $L^2(\mathbb{R}^3)$, the notation

$$\begin{aligned} A^{--} &= \gamma_{\rm per}^0 A \gamma_{\rm per}^0, & A^{-+} &= \gamma_{\rm per}^0 A (1-\gamma_{\rm per}^0),\\ A^{+-} &= (1-\gamma_{\rm per}^0) A \gamma_{\rm per}^0, & A^{++} &= (1-\gamma_{\rm per}^0) A (1-\gamma_{\rm per}^0), \end{aligned}$$

and note that the constraints $Q = Q^*$ and $0 \le \gamma_{\rm per}^0 + Q \le 1$ are equivalent to

$$Q^* = Q, \qquad Q^{--} \le 0, \qquad Q^{++} \ge 0, \qquad Q^2 \le Q^{++} - Q^{--}. \tag{6.15}$$

The introduction of the operators $A^{\pm\pm}$ corresponds to a decomposition of the space $L^2(\mathbb{R}^3)$ into the direct sum of the two orthogonal spaces $\mathcal{H}^- = \mathrm{Ran}(\gamma_{\rm per}^0)$ (occupied states of the perfect crystals) and $\mathcal{H}^+ = \mathrm{Ker}(\gamma_{\rm per}^0) = \mathrm{Ran}(1-\gamma_{\rm per}^0)$ (unoccupied states of the perfect crystal). Using this decomposition, the operators $\gamma_{\rm per}^0$, $H_{\rm per}^0$ and Q have the following structures:

$$\gamma_{\rm per}^0 = \begin{pmatrix} 1_{\mathcal{H}^-} & 0 \\ 0 & 0 \end{pmatrix}, \qquad H_{\rm per}^0 = \begin{pmatrix} (H_{\rm per}^0)^{--} & 0 \\ 0 & (H_{\rm per}^0)^{++} \end{pmatrix}, \qquad Q = \begin{pmatrix} Q^{--} & Q^{-+} \\ Q^{+-} & Q^{++} \end{pmatrix}.$$

As $\mathrm{Tr}(V_{\rm per}^0 Q) = \int_{\mathbb{R}^3} \rho_Q V_{\rm per}^0$, we formally obtain

$$\begin{aligned} \mathrm{Tr}\left(-\frac{1}{2}\Delta Q\right) + \int_{\mathbb{R}^3} \rho_Q V_{\rm per}^0 - \epsilon_{\rm F}^0 \mathrm{Tr}(Q) &= \mathrm{Tr}((H_{\rm per}^0 - \epsilon_{\rm F}^0)Q)\\ &= \mathrm{Tr}((H_{\rm per}^0 - \epsilon_{\rm F}^0)^{++} Q^{++}) + \mathrm{Tr}((H_{\rm per}^0 - \epsilon_{\rm F}^0)^{--} Q^{--}). \end{aligned}$$

We now remark that, by definition of $\gamma_{\rm per}^0$, $(H_{\rm per}^0 - \epsilon_{\rm F}^0)^{++} \ge 0$ and $(H_{\rm per}^0 - \epsilon_{\rm F}^0)^{--} \le 0$, so that the right-hand side of the above expression is the sum of two non-negative terms, and can be rewritten as

$$\mathrm{Tr}(|H_{\rm per}^0 - \epsilon_{\rm F}^0|^{1/2}(Q^{++} - Q^{--})|H_{\rm per}^0 - \epsilon_{\rm F}^0|^{1/2}). \tag{6.16}$$

The above expression is well defined in $\mathbb{R}_+ \cup \{+\infty\}$ for all Q satisfying the constraints (6.15). It takes a finite value if Q is chosen in the vector space

$$\begin{aligned} \mathcal{Q} \;=\; \big\{ & Q \in \mathfrak{S}_2 \mid Q^* = Q,\ Q^{--} \in \mathfrak{S}_1,\ Q^{++} \in \mathfrak{S}_1, \\ & |\nabla| Q \in \mathfrak{S}_2,\ |\nabla| Q^{--} |\nabla| \in \mathfrak{S}_1,\ |\nabla| Q^{++} |\nabla| \in \mathfrak{S}_1 \big\}, \end{aligned} \tag{6.17}$$

where $\mathfrak{S}_1$ and $\mathfrak{S}_2$ respectively denote the spaces of trace-class and Hilbert-Schmidt operators [71] on $L^2(\mathbb{R}^3)$, and where $|\nabla| = \sqrt{-\Delta}$. Endowed with its natural norm, or with any equivalent norm such as

$$\|Q\|_{\mathcal{Q}} = \|(1+|\nabla|)Q\|_{\mathfrak{S}_2} + \|(1+|\nabla|)Q^{++}(1+|\nabla|)\|_{\mathfrak{S}_1} + \|(1+|\nabla|)Q^{--}(1+|\nabla|)\|_{\mathfrak{S}_1},$$

$\mathcal{Q}$ is a Banach space.

Before proceeding further, we comment on the definition of $\mathcal{Q}$. As the trial density operators Q must satisfy the constraints (6.15), it is natural to impose $Q^* = Q$. Since $|H^0_{\rm per} - \epsilon^0_{\rm F}|^{1/2}(1+|\nabla|)^{-1}$ is a bounded operator with bounded inverse (see [18]), the four conditions $Q^{--} \in \mathfrak{S}_1$, $Q^{++} \in \mathfrak{S}_1$, $|\nabla|Q^{--}|\nabla| \in \mathfrak{S}_1$ and $|\nabla|Q^{++}|\nabla| \in \mathfrak{S}_1$ are necessary and sufficient conditions for the expression (6.16) with Q satisfying (6.15) being finite. The other constraints imposed to the elements of $\mathcal{Q}$ ($Q \in \mathfrak{S}_2$ and $|\nabla|Q \in \mathfrak{S}_2$) follow from the fact that for any Q satisfying (6.15)

$$\begin{array}{rcl} \left(Q^{--} \in \mathfrak{S}_1,\ Q^{++} \in \mathfrak{S}_1\right) & \Rightarrow & \left(Q^2 \in \mathfrak{S}_1\right) \\ \left(|\nabla|Q^{--}|\nabla| \in \mathfrak{S}_1,\ |\nabla|Q^{++}|\nabla| \in \mathfrak{S}_1\right) & \Rightarrow & \left(|\nabla|Q^2|\nabla| \in \mathfrak{S}_1\right). \end{array}$$

In order to simplify the notation, we set for $Q \in \mathcal{Q}$,

$$\begin{aligned} &\mathrm{Tr}_0(Q) = \mathrm{Tr}(Q^{++} + Q^{--}), \\ &\mathrm{Tr}_0((H^0_{\rm per} - \epsilon^0_{\rm F})Q) = \mathrm{Tr}(|H^0_{\rm per} - \epsilon^0_{\rm F}|^{1/2}(Q^{++} - Q^{--})|H^0_{\rm per} - \epsilon^0_{\rm F}|^{1/2}). \end{aligned}$$

We finally need to check that the remaining two terms $\int_{\mathbb{R}^3} \rho_Q V_\nu$ and $\frac{1}{2}D(\rho_Q, \rho_Q)$ can be given a sense for $Q \in \mathcal{Q}$. This follows from the following important result: the linear mapping $Q \mapsto \rho_Q$ originally defined on the dense subset $\mathcal{Q} \cap \mathfrak{S}_1$ of $\mathcal{Q}$ can be extended in a unique way to a continuous linear mapping

$$\begin{array}{rcl} \mathcal{Q} & \to & L^2(\mathbb{R}^3) \cap \mathcal{C} \\ Q & \mapsto & \rho_Q. \end{array} \tag{6.18}$$

Note that the density associated with a generic element of $\mathcal{Q}$ is not necessarily an integrable function. On the other hand, its Coulomb energy is always finite.

In particular, if the nuclear charge distribution ν of the defect is such that $V_\nu = (\nu \star |\cdot|^{-1}) \in L^2(\mathbb{R}^3) + \mathcal{C}'$, the quantities $\int_{\mathbb{R}^3} \rho_Q V_\nu$, or more precisely the duality bracket $\langle V_\nu, \rho_Q \rangle_{L^2+\mathcal{C}', L^2\cap\mathcal{C}}$ and $D(\rho_Q, \rho_Q)$ can be given a mathematical sense.

It follows from the above arguments that the energy functional

$$E^{\nu,\epsilon^0_{\rm F}}(Q) = \mathrm{Tr}_0((H^0_{\rm per} - \epsilon^0_{\rm F})Q) - \langle V_\nu, \rho_Q \rangle_{L^2+\mathcal{C}', L^2\cap\mathcal{C}} + \frac{1}{2}D(\rho_Q, \rho_Q)$$

is well defined on $\mathcal{Q}$ and that a good candidate for a variational model allowing us to compute the ground state density matrix $Q_{\nu,\epsilon^0_{\rm F}}$ of the defect is

$$\inf\left\{E^{\nu,\epsilon^0_{\rm F}}(Q),\ Q \in \mathcal{K}\right\}, \tag{6.19}$$

where

$$\mathcal{K} = \left\{ Q \in \mathcal{Q} \mid -\gamma^0_{\rm per} \leq Q \leq 1 - \gamma^0_{\rm per} \right\}. \tag{6.20}$$

Note that $\mathcal{K}$ is a closed convex subset of $\mathcal{Q}$.

Step 3: mathematical analysis of the minimization problem (6.19).

The following existence theorem holds.

Theorem 5 *[18, 22] Let ν such that $(\nu \star |\cdot|^{-1}) \in L^2(\mathbb{R}^3) + \mathcal{C}'$. Then,*

1. *(6.19) has at least one minimizer $Q_{\nu,\epsilon_{\rm F}^0}$, and all the minimizers of (6.19) share the same density $\rho_{\nu,\epsilon_{\rm F}^0}$;*
2. *$Q_{\nu,\epsilon_{\rm F}^0}$ is solution to the self-consistent equation*

$$Q_{\nu,\epsilon_{\rm F}^0} = 1_{(-\infty,\epsilon_{\rm F}^0)}\left(H^0_{\rm per} + (\rho_{\nu,\epsilon_{\rm F}^0} - \nu) \star |\cdot|^{-1}\right) - 1_{(-\infty,\epsilon_{\rm F}^0]}\left(H^0_{\rm per}\right) + \delta, \tag{6.21}$$

where δ is a finite-rank self-adjoint operator on $L^2(\mathbb{R}^3)$ such that $0 \leq \delta \leq 1$ and $Ran(\delta) \subset Ker\left(H^0_{\rm per} + (\rho_{\nu,\epsilon_{\rm F}^0} - \nu) \star |\cdot|^{-1} - \epsilon_{\rm F}^0\right)$.

The interpretation of the Euler equation (6.21), which also reads

$$\gamma^0_{\rm per} + Q_{\nu,\epsilon_{\rm F}^0} = 1_{(-\infty,\epsilon_{\rm F}^0]}(H^0_{\nu,\epsilon_{\rm F}^0}) + \delta$$

with

$$H^0_{\nu,\epsilon_{\rm F}^0} = H^0_{\rm per} + (\rho_{\nu,\epsilon_{\rm F}^0} - \nu) \star |\cdot|^{-1}, \quad 0 \leq \delta \leq 1, \quad {\rm Ran}(\delta) \subset {\rm Ker}(H^0_{\nu,\epsilon_{\rm F}^0} - \epsilon_{\rm F}^0),$$

is the following. The mean-field Hamiltonian $H^0_{\nu,\epsilon_{\rm F}^0}$ is uniquely defined, since all the minimizers of (6.19) share the same density $\rho_{\nu,\epsilon_{\rm F}^0}$. Besides, the operator $(\rho_{\nu,\epsilon_{\rm F}^0} - \nu) \star |\cdot|^{-1}$ being a relatively compact perturbation of $H^0_{\rm per}$, it results from the Weyl theorem (see [67, Section XIII.4]) that the Hamiltonians $H^0_{\rm per}$ and $H^0_{\nu,\epsilon_{\rm F}^0}$ have the same essential spectra. On the other hand, while $H^0_{\rm per}$ has no eigenvalues, $H^0_{\nu,\epsilon_{\rm F}^0}$ may have a countable number of isolated eigenvalues of finite multiplicities in the gaps as well as below the bottom of the essential spectrum (see Figure 7). The only possible accumulation points of these eigenvalues are the edges of the bands.

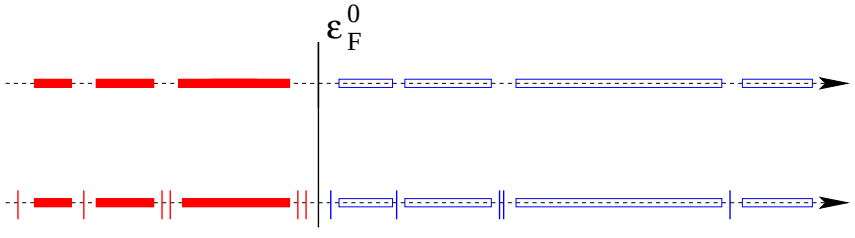

Figure 7: Typical spectra of $H^0_{\rm per}$ (up) and $H^0_{\nu,\epsilon_{\rm F}^0}$ (down).

If $\epsilon_{\rm F}^0 \notin \sigma(H^0_{\nu,\epsilon_{\rm F}^0})$, then $\delta = 0$ and the ground state density operator of the crystal in the presence of the defect is the orthogonal projector $\gamma^0_{\rm per} + Q_{\nu,\epsilon_{\rm F}^0}$: all the energy levels lower than the Fermi level are fully occupied while the other ones are empty. In this case, $Q_{\nu,\epsilon_{\rm F}^0}$ is both a Hilbert-Schmidt operator and the difference of two projectors. It therefore follows from [36, Lemma 2] that

$$\mathrm{Tr}_0(Q_{\nu,\epsilon_{\rm F}^0}) \in \mathbb{N}. \tag{6.22}$$

Assuming that $\nu \in L^1(\mathbb{R}^3)$ and $\int_{\mathbb{R}^3} \nu \in \mathbb{N}$, the integer

$$q = \int_{\mathbb{R}^3} \nu - \mathrm{Tr}_0(Q_{\nu,\epsilon_{\rm F}^0})$$

can be interpreted as the *bare* charge of the defect. We already know from (6.18) that the density $\rho_{\nu,\epsilon_{\rm F}^0}$ is in $L^2(\mathbb{R}^3) \cap \mathcal{C}$. Under some additional assumptions [22], it can be proved that its Fourier transform has a limit at $k = 0$, which we denote by $\int_{\mathbb{R}^3} \rho_{\nu,\epsilon_{\rm F}^0}$ by a slight abuse of notation. An interesting phenomenon is that, in general,

$$\mathrm{Tr}_0(Q_{\nu,\epsilon_{\rm F}^0}) \neq \int_{\mathbb{R}^3} \rho_{\nu,\epsilon_{\rm F}^0}.$$

The fact that the equality (5.21) is no longer true for the renormalized model is due to the polarization of the Fermi sea responsible for the dielectric permittivity of insulating and semiconducting crystals. More precisely, we obtain that (under the same assumptions)

$$q_r = \int_{\mathbb{R}^3} \nu - \int_{\mathbb{R}^3} \rho_{Q_{\nu,\epsilon_{\rm F}^0}} = \frac{q}{\epsilon_\mu},$$

where $\epsilon_\mu > 1$ is the microscopic dielectric permittivity of the crystal. We refer to [22] for details.

Step 4: justification of the model by thermodynamic limit arguments.

It is proved in [18] that the tentative variational problem (6.19) is indeed the thermodynamic limit of the supercell model when L goes to infinity.

All this allows us to conclude that the rHF ground state density operator of the crystal with nuclear charge density $\rho^{\rm nuc}_{\rm per} + \nu$ (the charge of the defect being controlled by the Fermi level $\epsilon_{\rm F}^0$) is therefore given by

$$\gamma_{\nu,\epsilon_{\rm F}^0} = \gamma^0_{\rm per} + Q_{\nu,\epsilon_{\rm F}^0}$$

where $Q_{\nu,\epsilon_{\rm F}^0}$ is obtained by solving (6.19).

6.2 Disordered crystals

A huge amount of literature has been devoted to modeling electrons in random materials. In most cases, electrons are considered as non-interacting particles subjected to a stationary empirical potential $V(\omega, x)$, in the sense defined in Section 2.2 (see in particular the definition (2.4)). The analysis of the electronic properties of the material then reduces to the analysis of the spectral properties of the associated random Schrödinger operator

$H(\omega) = -\frac{1}{2}\Delta + V(\omega, \cdot)$ acting on $L^2(\mathbb{R}^3)$. A remarkable property of random Schrödinger operators is that, under some integrability assumptions on V, the spectrum of $H(\omega)$ is deterministic: there exists a closed set $\Sigma \in \mathbb{R}$ such that $\sigma(H(\omega)) = \Sigma$ almost surely. Similar results hold for the density of states (that is, losely speaking, the number of quantum states per unit volume) of the Hamiltonian $H(\omega)$. Interesting questions are concerned with the nature of the spectrum (point spectrum, absolutely continuous spectrum, ...), which is related to the electronic transport properties of the material. We refer to [23, 74] and references therein for more details on the linear case.

In this article, we focus on models accounting for electron interactions. Consider for instance a disordered crystal whose nuclear charge distribution is modeled, for simplicity, by a non-negative stationary function $\rho^{\rm nuc}_{\rm sta} \in L^\infty(\Omega \times \mathbb{R}^3)$ satisfying

$$\forall k \in \mathbb{Z}^3, \quad \rho^{\rm nuc}_{\rm sta}(\omega, x+k) = \rho^{\rm nuc}_{\rm sta}(\tau_k(\omega), x) \quad \text{almost everywhere in } x, \text{ almost surely,}$$

for some ergodic group action $(\tau_k)_{k\in\mathbb{Z}^3}$ on the underlying probability space $(\Omega, \mathcal{F}, \mathbb{P})$. A particular instance of such a stationary nuclear charge distribution is

$$\rho^{\rm nuc}_{\rm sta}(\omega, x) = \sum_{k\in\mathbb{Z}^3} q_k(\omega)\chi(x-k), \qquad \int_{\mathbb{R}^3} \chi = 1, \quad q_k : \Omega \to \{1, \cdots, M\} \text{ i.i.d.,}$$

for which the positions of the nuclei are deterministic, while their charges are random (see Figure 8). The arguments below can be extended to treat point nuclei represented by Dirac masses, see [11].

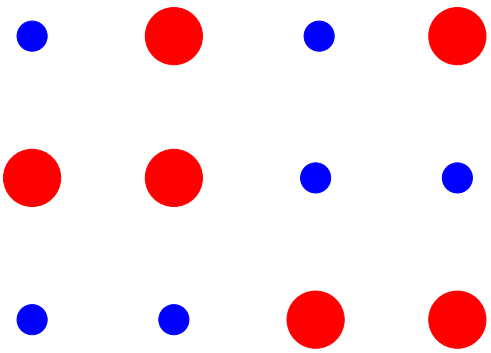

Figure 8: A realization of a random crystal with deterministic nuclear positions and random nuclear charges.

In this random setting (a disordered crystal with nuclear charge distribution $\rho^{\rm nuc}_{\rm sta}$), the expected thermodynamic limit of the rHF model reads, in view of equations (5.26)-(5.27),

$$\begin{cases} \gamma^0_{\rm sta}(\omega) = \mathbb{1}_{(-\infty,\epsilon^0_{\rm F})}(H(\omega)) + \delta(\omega), \\ H(\omega) = -\dfrac{1}{2}\Delta_x + V(\omega, x), \\ -\Delta_x V(\omega, x) = 4\pi\left(\rho_{\gamma^0_{\rm sta}}(\omega, x) - \rho^{\rm nuc}_{\rm sta}(\omega, x)\right), \end{cases} \tag{6.23}$$

with $\mathrm{Ran}(\delta(\omega)) \subset \mathrm{Ker}(H(\omega) - \epsilon^0_{\rm F})$. Here, the Fermi level $\epsilon^0_{\rm F}$ is the Lagrange multiplier of the constraint

$$\mathbb{E}\Big(\int_Q \rho_{\gamma^0_{\rm sta}}\Big) = \mathbb{E}\Big(\int_Q \rho^{\rm nuc}_{\rm sta}\Big),$$

ensuring the average neutrality per unit volume of the disordered crystal. The real number $\epsilon_{\rm F}^0$ is therefore a deterministic quantity.

The existence of solutions to the mean-field equation (6.23) still is an open question. The main difficulty is that the Poisson equation $-\Delta_x V(\omega,x) = 4\pi f(\omega,x)$ with a stationary charge distribution f does not have, in general, a stationary solution, even if the charge distribution is globally neutral, that is, $\mathbb{E}\left(\int_Q f\right) = 0$. The problem is that we do need a stationary potential to properly define the mean-field Hamiltonian as a random Schrödinger operator. The situation is therefore much more complex than in the case of a periodic function f, for which the Poisson equation has always a periodic solution, unique up to an additive constant, provided f is neutral on each unit cell.

We will see in Section 6.2.3 that it is however possible to define the rHF electronic ground states of a disordered crystal as the minimizers of some variational problem. Unfortunately, we do not have enough information on these minimizers to derive explicit optimality conditions of the form (6.23). The situation is more favorable for the TFW model (see Section 6.2.3), for which the electronic ground state of a disordered crystal can be defined both as the minimizer of some energy functional, and, using Lemma 4, as the unique solution of the self-consistent equations. Before presenting these results in more detail, we first have to define the Coulomb energy per unit volume of a stationary charge distribution. To prepare the ground for the last section of this article, we also consider the case of short-range Yukawa interactions.

6.2.1 Yukawa and Coulomb energies of stationary charge distributions

For convenience, we introduce the spaces $L^p_s(L^q)$ and L^p_s of stationary functions defined as follows:

$$L^p_s\left(L^q\right) = \left\{ f \in L^p\left(\Omega, L^q_{\rm loc}\left(\mathbb{R}^3\right)\right) \;|\; f \text{ is stationary} \right\}, \quad L^p_s = L^p_s(L^p).$$

The Coulomb energy per unit volume of a stationary charge distribution f can be defined, for instance, by means of a Yukawa regularization of the Coulomb potential. Recall that the Yukawa energy of a charge distribution $f \in L^2(\mathbb{R}^3)$ can be written in several equivalent ways:

$$\begin{aligned} D_m(f,f) &= \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} Y_m(x-y) f(x)\, f(y)\, dx\, dy \\ &= \left\| (4\pi)^{1/2} \left(-\Delta + m^2\right)^{-\frac{1}{2}} f \right\|^2_{L^2(\mathbb{R}^3)} = \|W_m \star f\|^2_{L^2(\mathbb{R}^3)}. \end{aligned}$$

In the above expressions, $Y_m(x) = \frac{e^{-m|x|}}{|x|}$ is the Yukawa kernel, and W_m the kernel of the integral operator $(4\pi)^{1/2}(-\Delta+m^2)^{-1/2}$. It can be shown that W_m is in $L^1(\mathbb{R}^3)$, behaves as $|x|^{-2}$ at zero, and decays exponentially at infinity.

Similar expressions can be obtained for the Yukawa energy per unit volume of a sta-

tionary charge distribution $f \in L^2_s$:

$$D^{\mathrm{sta}}_m(f,f) = \mathbb{E}\Big(\int_Q \int_{\mathbb{R}^3} Y_m(x-y) f(\cdot,x)\, f(\cdot,y)\, dx\, dy\Big)$$
$$= \left\| (4\pi)^{1/2} \left(-\Delta_s + m^2\right)^{-\frac{1}{2}} f \right\|^2_{L^2_s} = \|W_m \star f\|^2_{L^2_s}.$$

In the second formulation, the usual Laplacian is replaced with the self-adjoint operator Δ_s on L^2_s, called the stationary Laplacian [21], which formally acts as the Laplace operator on the space variable.

The fact that $W_m \star f \in L^2_s$ for all $f \in L^2_s$, follows from the Young inequality for stationary functions: for $1 \le p, q, r, t \le \infty$ such that $1 + r^{-1} = p^{-1} + q^{-1}$, there exists $C < \infty$ such that for all $f \in L^t_s(L^q)$ and all *deterministic* kernels $W(x)$,

$$\|W \star f\|_{L^t_s(L^r)} \le C \left(\sum_{k \in \mathbb{Z}^3} \|W\|_{L^p(Q+k)} \right) \|f\|_{L^t_s(L^q)}. \tag{6.24}$$

In particular, $W \star f \in L^p_s$ if $W \in L^1(\mathbb{R}^3)$ and $f \in L^p_s$.

As $W_m \in L^1(\mathbb{R}^3)$, we can define the Yukawa energy per unit volume $D^{\mathrm{sta}}_m(f,f) = \|W_m \star f\|^2_{L^2_s}$ for any $f \in L^1_s$ such that $W_m \star f \in L^2_s$. It is easily seen that the space

$$\mathcal{D}_Y = \left\{ f \in L^1_s \mid W_m \star f \in L^2_s \right\}$$

does not depend on the value of the positive parameter m. Endowed with the norm $\|f\|_{L^1_s} + D^{\mathrm{sta}}_1(f,f)^{1/2}$, $\mathcal{D}_Y$ is a Banach space and $L^2_s(L^{6/5}) \subset \mathcal{D}_Y \subset L^1_s$.

We now turn to the Coulomb case. First, we remark that, for any fixed $f \in \mathcal{D}_Y$, the function $m \mapsto D^{\mathrm{sta}}_m(f,f)$ is non-increasing. It is therefore natural to define the Coulomb energy per unit volume of f as

$$D^{\mathrm{sta}}_0(f,f) = \lim_{m \downarrow 0} D^{\mathrm{sta}}_m(f,f) \quad \in \mathbb{R}_+ \cup \{+\infty\}.$$

Note that $D^{\mathrm{sta}}_0(f,f) = +\infty$ whenever $\mathbb{E}\big(\int_Q f\big) \neq 0$ (i.e. whenever the charge distribution is not globally neutral). We finally introduce the space $\mathcal{D}_C = \{f \in \mathcal{D}_Y \mid D^{\mathrm{sta}}_0(f,f) < \infty\}$ of the locally integrable stationary charge distributions with finite Coulomb energy per unit volume.

It is also possible (see [11]) to define the Coulomb energy of a stationary charge distribution f such that $\mathbb{E}\big(\int_Q f\big) = 0$ as

$$D_0(f,f) = \frac{1}{4\pi} \mathbb{E}\left(\int_Q |\nabla \Phi_f|^2 \right),$$

where Φ_f is the unique solution (up to an additive constant) to the Poisson problem

$$\begin{cases} -\Delta_x \Phi_f(\omega, x) = 4\pi f(\omega, x), \\ \nabla_x \Phi_f \text{ stationary}, \ \mathbb{E}\big(\int_Q \nabla_x \Phi_f\big) = 0. \end{cases}$$

Note that the Coulomb potential Φ_f generated by a stationary charge distribution is not stationary in general. Only the electric field $E_{\Phi_f} = -\nabla_x \Phi_f$ enjoys the stationarity property.

6.2.2 Disordered crystals in the TFW setting

A natural definition of the TFW energy per unit volume of a stationary electronic charge distribution $\rho_{\rm sta}$ interacting with the stationary nuclear charge distribution $\rho_{\rm sta}^{\rm nuc} \in L_s^\infty$ is

$$E_{\rm sta}^{\rm TFW}(\rho_{\rm sta}) = \mathbb{E}\left(\int_Q |\nabla\sqrt{\rho_{\rm sta}}|^2\right) + \mathbb{E}\left(\int_Q \rho_{\rm sta}^{5/3}\right) + \frac{1}{2}D_0^{\rm sta}(\rho_{\rm sta}-\rho_{\rm sta}^{\rm nuc},\rho_{\rm sta}-\rho_{\rm sta}^{\rm nuc}).$$

The TFW problem for disordered crystals

$$I_{\rm sta}^{\rm TFW} = \inf\left\{E_{\rm sta}^{\rm TFW}(\rho_{\rm sta}),\ \rho_{\rm sta}\geq 0,\ \sqrt{\rho_{\rm sta}}\in L_s^2(H^1),\ \mathbb{E}\left(\int_Q \rho_{\rm sta}\right) = \mathbb{E}\left(\int_Q \rho_{\rm sta}^{\rm nuc}\right)\right\}, \tag{6.25}$$

where

$$L_s^2(H^1) = \left\{f\in L^2\left(\Omega, H^1_{\rm loc}\left(\mathbb{R}^3\right)\right)\ \middle|\ f \text{ is stationary}\right\},$$

has a unique minimizer $\rho_{\rm sta}^0$. The physical relevance of problem (6.25) comes from the fact that it is the thermodynamic limit of the problem

$$I_R^{\rm TFW}(\omega) = \left\{E_R^{\rm TFW}(\omega,\rho),\ \rho\geq 0,\ \sqrt{\rho}\in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3}\rho = |B_R|\mathbb{E}\left(\int_Q \rho_{\rm sta}^{\rm nuc}\right)\right\}, \tag{6.26}$$

where

$$E_R^{\rm TFW}(\omega,\rho) = \int_{\mathbb{R}^3}|\nabla_x\sqrt{\rho(\omega,\cdot)}|^2 + \int_{\mathbb{R}^3}\rho^{5/3}(\omega,\cdot) + \frac{1}{2}D(\rho-\rho_{\rm sta}^{\rm nuc}(\omega,\cdot)\mathbb{1}_{B_R},\rho-\rho_{\rm sta}^{\rm nuc}(\omega,\cdot)\mathbb{1}_{B_R}).$$

Indeed, proceeding as in [11], we obtain that

$$\lim_{R\to\infty}\frac{I_R^{\rm TFW}(\omega)}{|B_R|} = I_{\rm sta}^{\rm TFW} \quad \text{almost surely and in } L^1(\Omega),$$

and that, under the assumption

$$\exists A>0 \text{ such that } \inf_{x\in\mathbb{R}^3}\rho_{\rm sta}^{\rm nuc}(x+B_A,\omega) > 0 \text{ almost surely}, \tag{6.27}$$

the unique minimizer $\rho_R^0(\omega,\cdot)$ of (6.26) converges to $\rho_{\rm sta}^0(\omega,\cdot)$ in the following sense: for all sequences $S_R < R$ such that $\lim_{R\to\infty}(R-S_R) = +\infty$,

$$\lim_{R\to\infty}\|\rho_R^0(\omega,\cdot)-\rho_{\rm sta}^0(\omega,\cdot)\|_{L^\infty(B_{S_R})} = 0 \quad \text{almost surely.}$$

In addition, still under assumption (6.27), the unique solution $(u^0,\Phi^0)\in L^\infty(\Omega\times\mathbb{R}^3)\times L^\infty(\Omega, L^1_{\rm unif}(\mathbb{R}^3))$ to the TFW equations

$$\begin{cases} -\Delta_x u + \dfrac{5}{3}u^{7/3} - \Phi u = 0, \\ u\geq 0, \\ -\Delta_x\Phi = 4\pi(\rho_{\rm sta}^{\rm nuc}-u^2), \end{cases}$$

is in $L^2_s(H^1) \times L^\infty_s$, where $L^2_s(H^1) = \{u \in L^2(\Omega, H^1_{\rm loc}(\mathbb{R}^3)) \mid u \text{ stationary}\}$, and it holds $\rho^0_{\rm sta} = (u^0)^2$. This means in particular that the solution $\Phi^0(\omega, x)$ to the Poisson equation $-\Delta_x \Phi^0(\omega, x) = 4\pi(\rho^{\rm nuc}_{\rm sta}(\omega, x) - \rho^0_{\rm sta}(\omega, x))$ is stationary. The TFW self-consistent Hamiltonian $-\Delta_x + \dfrac{5}{3}(\rho^0_{\rm sta})^{4/3} - \Phi^0$ therefore is a well-defined random Schrödinger operator. All this is a consequence of the uniqueness result provided by Lemma 4. No analogue of Lemma 4 for the rHF model, which would state that, under the same assumptions on the nuclear charge density m as in Lemma 4, the rHF equations

$$\begin{cases} \gamma = \mathbb{1}_{(-\infty,0)}(H) + \delta, \quad \text{with } \mathrm{Ran}(\delta) \subset \mathrm{Ker}(H), \\ H = -\dfrac{1}{2}\Delta + V, \\ -\Delta V = 4\pi(m - \rho_\gamma), \end{cases}$$

have a solution such that $\rho_\gamma \in L^\infty(\mathbb{R}^3)$ and $V \in L^{3,\infty}_{\rm unif}(\mathbb{R}^3)$, and that all solutions share the same density, is available to date. This is the reason why we are not able to give a mathematical meaning to the stationary rHF equations (6.23).

6.2.3 Disordered crystals in the rHF setting

A variational formulation of the rHF model for disordered crystals has been proposed in [21]:

$$I^{\rm rHF}_{\rm sta} = \left\{ E^{\rm rHF}_{\rm sta}(\gamma_{\rm sta}),\ \gamma_{\rm sta} \in \Gamma_{\rm sta} \right\}, \tag{6.28}$$

where

$$E^{\rm rHF}_{\rm sta}(\gamma_{\rm sta}) = \underline{\rm Tr}^{\rm sta}\left(-\frac{1}{2}\Delta\gamma_{\rm sta}\right) + \frac{1}{2}D^{\rm sta}_0(\rho^{\rm nuc}_{\rm sta} - \rho_{\gamma_{\rm sta}}, \rho^{\rm nuc}_{\rm sta} - \rho_{\gamma_{\rm sta}}), \tag{6.29}$$

$$\Gamma_{\rm sta} = \left\{ \gamma_{\rm sta} \in \underline{\mathcal{S}}_{\rm sta} \mid 0 \le \gamma_{\rm sta}(\omega) \le 1 \text{ a.s.},\ \underline{\rm Tr}^{\rm sta}(\gamma_{\rm sta}) < \infty,\ \underline{\rm Tr}^{\rm sta}(-\Delta\gamma_{\rm sta}) < \infty \right\}. \tag{6.30}$$

The rHF energy per unit volume $E^{\rm rHF}_{\rm sta}(\gamma_{\rm sta})$ of an ergodic density matrix $\gamma_{\rm sta}$ is the sum of the kinetic energy per unit volume of $\gamma_{\rm sta}$, and of the Coulomb energy per unit volume of the total charge density $\rho^{\rm nuc}_{\rm sta} - \rho_{\gamma_{\rm sta}}$, both terms being non-negative. We now precisely define all the mathematical objects in (6.29)-(6.30).

The notation $\underline{\mathcal{S}}_{\rm sta}$ in (6.30) stands for the space of ergodic bounded self-adjoint operators. Recall that a bounded random operator A on $L^2(\mathbb{R}^3)$ is a family $(A(\omega))_{\omega\in\Omega}$ of bounded linear operators on $L^2(\mathbb{R}^3)$ such that the function $\omega \mapsto \langle A(\omega)x, y\rangle$ is measurable for all $x, y \in L^2(\mathbb{R}^3)$. The bounded random operator A is called *ergodic* if

$$A(\tau_k(\omega)) = U_k A(\omega) U_k^*,$$

where U_k is the space translation of vector $-k$, that is, $(U_k g)(\omega, x) = g(\omega, x + k)$. If A is an integral operator (which is the case for density matrices), this amount to saying that the kernel of A is a stationary function in the sense that $A(\tau_k(\omega), x, y) = A(\omega, x+k, y+k)$. Lastly, A is called *self-adjoint* if $A(\omega)$ is a.s. self-adjoint.

The constraint $0 \le \gamma_{\rm sta} \le 1$ corresponds to the Pauli principle. We now make precise the meaning of the notation $\underline{\rm Tr}^{\rm sta}$. A random operator A is called *locally trace-class* if $\chi A \chi \in L^1(\Omega, \mathfrak{S}_1)$, for all $\chi \in L^\infty_c(\mathbb{R}^3)$, where $L^\infty_c(\mathbb{R}^3)$ denotes the space of (deterministic)

compactly supported real-valued bounded functions on $\mathbb{R}^3$, and $\mathfrak{S}_1$ the space the trace-class operators on $L^2(\mathbb{R}^3)$. The *density* ρ_A associated with a locally trace-class ergodic operator A is the function of L^1_s characterized by

$$\forall \chi \in L^\infty_c(\mathbb{R}^3), \quad \mathrm{Tr}(\chi A(\omega)\chi) = \int_{\mathbb{R}^3} \chi^2(x)\, \rho_A(\omega, x)\, dx \quad \text{a.s.}$$

The *trace per unit volume* of a locally trace-class *ergodic* operator is defined as

$$\underline{\mathrm{Tr}}^{\mathrm{sta}}(A) = \mathbb{E}\big(\mathrm{Tr}(\mathbb{1}_Q A(\cdot)\mathbb{1}_Q)\big) = \mathbb{E}\Big(\int_Q \rho_A\Big).$$

The trace per unit volume of an ergodic density matrix therefore corresponds to the average number of particles per unit volume. Likewise, the *kinetic energy per unit volume* of an ergodic density matrix γ_{sta} can be defined as

$$\underline{\mathrm{Tr}}^{\mathrm{sta}}\left(-\frac{1}{2}\Delta\gamma_{\mathrm{sta}}\right) = \frac{1}{2}\sum_{j=1}^{3} \underline{\mathrm{Tr}}^{\mathrm{sta}}\left(P_j \gamma_{\mathrm{sta}} P_j\right),$$

where, again, $P_j = -i\partial_{x_j}$ is the momentum operator in the j^{th} direction.

It is proved in [21] that (6.28) has a ground state. On the other hand, for the reasons mentioned at the end of the previous section, it is not known whether the ground states of (6.28) satisfy the self-consistent equation (6.23).

More comprehensive results can be established for the Yukawa rHF model

$$I^{\mathrm{rHF},m}_{\mathrm{sta}} = \left\{ E^{\mathrm{rHF},m}_{\mathrm{sta}}(\gamma_{\mathrm{sta}}),\ \gamma_{\mathrm{sta}} \in \Gamma_{\mathrm{sta}},\ \underline{\mathrm{Tr}}^{\mathrm{sta}}(\gamma_{\mathrm{sta}}) = \mathbb{E}\left(\rho^{\mathrm{nuc}}_{\mathrm{sta}}\right) \right\}, \tag{6.31}$$

where

$$E^{\mathrm{rHF},m}_{\mathrm{sta}} = \underline{\mathrm{Tr}}^{\mathrm{sta}}\left(-\frac{1}{2}\Delta\gamma_{\mathrm{sta}}\right) + \frac{1}{2} D^{\mathrm{sta}}_m(\rho^{\mathrm{nuc}}_{\mathrm{sta}} - \rho_{\gamma_{\mathrm{sta}}}, \rho^{\mathrm{nuc}}_{\mathrm{sta}} - \rho_{\gamma_{\mathrm{sta}}}), \tag{6.32}$$

and where the neutrality constraint is explicitly enforced (this was not necessary for the Coulomb model since $D^{\mathrm{sta}}_0(f,f) = +\infty$ if f is not globally neutral).

For each $m > 0$, (6.31) has a minimizer, all the minimizers share the same density, and the minimizers are solutions to a self-consistent equation similar to (6.23), in which the Poisson equation $-\Delta_x V(\omega, x) = 4\pi\left(\rho^{\mathrm{nuc}}_{\mathrm{sta}}(\omega, x) - \rho_{\gamma^0_{\mathrm{sta}}}(\omega, x)\right)$ is replaced by the Yukawa equation

$$-\Delta_x V(\omega, x) + m^2 V(\omega, x) = 4\pi\left(\rho^{\mathrm{nuc}}_{\mathrm{sta}}(\omega, x) - \rho_{\gamma^0_{\mathrm{sta}}}(\omega, x)\right).$$

Let us emphasize that, in contrast to the Poisson equation, the Yukawa equation has a stationary solution for any stationary charge distribution in L^2_s. Under the assumption that we make here that $\rho^{\mathrm{nuc}}_{\mathrm{sta}} \in L^\infty_s$, it can be infered from the self-consistent equation, using results from [16], that the ground state density matrix is in fact unique. Lastly, it can be checked that, in the Yukawa setting, the ergodic rHF model introduced above is relevant from a physical viewpoint, by proving that it is the thermodynamic limit of the supercell model (we refer to [11, 12, 15, 75] for other recent works on the thermodynamic

limit of disordered quantum systems composed of interacting particles). Note that the Yukawa ground state converges, in some sense and up to extraction, to a Coulomb ground state when m goes to zero, but that this convergence seems not strong enough to pass to the limit in the self-consistent equation.

An interesting open problem consists in studying the case of rare but possibly large random perturbations, considered in Section 3.3 in the framework of homogenization theory, which corresponds here to the physical situation of doped semiconductors with low concentration of impurities. This question has been successfully addressed in [44] in the case of a linear model of non-interacting electrons. The case of interacting electrons with short-range interactions is dealt with in [47]. The problem is still open for electrons in Coulomb interactions.

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