Recent mathematical results on the quantum modeling of crystals

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Abstract : We describe in this paper a strategy, the so-called thermodynamic limit process, to build in a rigorous mathematical manner quantum-mechanical models for the ground-state energy of solid crystals. These models are the analogues for the solid state of well-known models issued from Quantum Chemistry, namely Thomas-Fermi, Hartree and Hartree-Fock type models. We shall present a broad overview on recent mathematical studies on this topic. We shall in particular report on some new results on the so-called crystal problem within the framework of Thomas-Fermi type models.

1 Introduction

Many mathematical studies have been devoted to the thermodynamic limit problem as stated in its full generality within the Statistical Mechanics, and we refer in particular the reader to the works by Ruelle [52], Lebowitz and Lieb [35, 39, 40], and Fefferman [28, 29]. We shall not deal here with the physical background of this theoretical problem, and we refer the reader to the textbooks [7, 59] and the articles [36, 40]. The works we shall present here are focused on models for charged particles at the zero temperature limit, where in some sense, they are frozen at their ground-state, and even more specifically on the crystalline phase.

Briefly speaking, the so-called thermodynamic limit problem consists in examining the behaviour of models for particles in a finite volume of matter when the volume under consideration goes to infinity. Since the energy is an extensive thermodynamic quantity, it is expected that the energy per unit volume goes to a finite limit when the volume goes to infinity. It is also expected that the function representing the state of the matter goes also to a limit in some sense. The thermodynamic limit problem we study (that is, for crystals, and at zero temperature) may be stated as follows.

We consider a neutral molecular system consisting of N electrons and N nuclei of unit charge (atomic units will be adopted in all that follows). According to the Born-Oppenheimer approximation, the electronic ground-state is first determined for a given nuclear configuration. The geometry of the nuclei and their electric charge will be taken as fixed and arranged according to a crystalline lattice. To fix ideas, from now on, our reference lattice will be the lattice of points of integer coordinates—that is, $\mathbf{Z}^3$ —and therefore the primitive cell of the crystal will be the unit cube, denoted by Q in the sequel. The N point nuclei of unit charge being located on a finite subset Λ_N of $\mathbf{Z}^3$ (each point being at the center of a cubic unit cell), we asymptotically let the set Λ_N fill in the entire lattice $\mathbf{Z}^3$. The union of all cubic cells whose center is a point of Λ_N is denoted by $\Gamma(\Lambda_N)$; it has volume N . It is important to note that, in all that follows, $\Gamma(\Lambda_N)$ may be viewed as a big box to which the molecule is confined. (This claim may actually be checked in a rigorous mathematical way.) This assumption is standard for statistical physicists, and is compulsory at positive temperature. It turns out that, at zero temperature, any boundary conditions for the wave functions or the electronic density on a big box one may think of (like Neumann, Dirichlet or periodic boundary conditions) gives rise to the same periodic model after passing to the thermodynamic limit. The boundary conditions may therefore be chosen conveniently according to everyone's own prefer-

ences, for numerical purposes, for instance. Let us simply mention that Solid State physicists seem to prefer to work with the so-called Born-Von Karman conditions, which are simply periodic boundary conditions on the boundary of a big parallelepiped box.

Suppose that for any subset of $\mathbf{Z}^3$ fixed, we have a well-posed model for the ground-state of the neutral molecule consisting of N electrons and N nuclei located at the points of Λ_N . Let us denote by I_{Λ_N} the ground-state energy, and by ρ_{Λ_N} the minimizing electronic density. Then, the question of the existence of the thermodynamic limit for the model under consideration may be stated as follows :

- (i) Does there exist a limit for the energy per unit volume $\frac{1}{N}I_{\Lambda_N}$ when N goes to infinity Γ
- (ii) Does the minimizing electronic density ρ_{Λ_N} approach a limit ρ_∞ (in a sense to be made precise later) when N goes to infinity Γ
- (iii) Does the limit density ρ_∞ have the same periodicity as the assumed periodicity of the nuclei Γ

We investigate the behaviour of the ground-state energy per unit volume, as N goes to infinity, within standard approximation theories in Quantum Chemistry for the ground-state energy; namely, models from Density Functional Theory, like Thomas-Fermi type models on the one hand, and the restricted Hartree, the Hartree, the reduced Hartree-Fock and the Hartree-Fock models, on the other hand. Let us emphasize the fact that in all that follows we shall not deal with more advanced models from Density Functional Theory like the Kohn-Sham or the $X\alpha$ model (see *e. g.* [25]), since from a mere mathematical viewpoint this kind of models features the same structure, and thereby the same difficulties, as the Hartree-Fock model. In particular, the results that we describe within the setting of the Hartree-Fock model carry through just as they are to a wide class of models from modern Density Functional Theory.

By applying this strategy to various models, we have different purposes in mind. Firstly, we want to check that the molecular model under consideration does have the good behaviour in the limit of large volumes, thereby validating it a bit further for large molecules, or, on the contrary, limiting its efficiency to modeling true phenomena. Secondly, bearing in mind that our purpose is to build new models for the solid phase, we wish to set a limit problem that is well-posed mathematically and that can be justified in the most rigorous way. With this model at our disposal, we intend to give

a sound ground to numerical simulations of the condensed phase. Thirdly, this method aims at linking non-linear quantum-mechanical descriptions of crystals to concepts and techniques issued from Solid State Physics. A further step beyond is next to make use of these models to calculate macroscopic quantities, such as elasticity constants, for example.

Let us first summarize the results which are available on these issues, as far as we know. It has been proved by Lieb and Simon [41] for the Thomas-Fermi model, and by the authors in [16] for the Thomas-Fermi-von Weizsäcker model (which is a variant of the Thomas-Fermi model—see below) that the ground-state energy per unit volume converges to a periodic minimization problem, which is set on the unit cell of the crystal, and that the electronic density also converges to a periodic electronic density, which is precisely the minimizer of the limit periodic minimization problem.

The situation is far more complicated for more realistic models which involve the electronic wave-functions for describing the electronic state, as the Hartree and the Hartree-Fock models. One obvious reason is that we have to analyze the behaviour of an increasing number N of wave-functions and not only of one function, the electronic density. For simplified forms of the Hartree and the Hartree-Fock models, the restricted Hartree and the reduced Hartree-Fock models respectively, we completely determine the asymptotic behaviour, proving that the limit is actually a minimization problem set on the unit cell of the lattice. However, we have only extremely weak results on the behaviour of the electronic density to a periodic density, which are not very satisfactory.

For the Hartree and the Hartree-Fock models, we are only able to define periodic problems that are likely to be the thermodynamic limits. Within these models, the mere definition of the limit problem turns out to be a substantial piece of the work (writing a periodic problem that has some rigorous mathematical sense is not straightforward at all). In order to prepare and stimulate future works on the subject, we prove that the periodic limit problems that we define are well-posed. In particular, they allow to derive Hartree and Hartree-Fock type equations for crystals, which may be found in Solid State physics textbooks, thereby validating our method. Let us finally mention that, in order to set the periodic models which are the analogues for the crystalline phase of the molecular version of the Hartree-Fock and the reduced Hartree-Fock models, we extensively rely upon the decomposition of operators commuting with the group of translations of $\mathbf{Z}^3$. Consequently, we observe that the theory of Bloch waves, which is commonly used by Solid State physicists, appears naturally in the nonlinear framework we are considering.

This paper is organized as follows. In the following section, we state the thermodynamic limit problem within the framework of Density Functional Theory, and more precisely, in the Thomas-Fermi setting (and related more advanced models). We are aware that these models are neither the most efficient ones nor the ones which are usually used for calculations. Nevertheless, very fundamental (and difficult) issues are already raised within these models, which one has also to face while dealing with more relevant models, like Hartree-Fock for example. By testing first our method on the Thomas-Fermi type models, we actually try to overcome the technical difficulties step by step as the complexity (together with the relevance) of the model increases. Section 3 is devoted to Hartree type models, while Hartree-Fock type models are treated in Section 4.

In Section 5, we shall report on recent progress made by Blanc and one of us [9, 11, 12] on the existence of a minimal energy configuration of the nuclei inside the class of all possible periodic lattices for the TFW model.

Finally, in Section 6, we suggest different extensions of all these works.

2 Models from Density Functional Theory

This section is devoted to the well-known Thomas-Fermi model and some of its variants. These models belong to a large class of models that are today identified as the models arising in Density Functional Theory. We refer the reader to [25, 46] for an introduction to the general features and the physical foundations of such models, and to [14, 21, 22] for a comprehensive list of recent mathematical results on all the models which are considered throughout this paper.

Within the Thomas-Fermi type models, the density functional may be written as follows :

$$\begin{aligned} E_{\Lambda_N}^{TFW}(\rho) = & c_0 \int_{\mathbf{R}^3} |\nabla \sqrt{\rho}|^2 + c_1 \int_{\mathbf{R}^3} \rho^{5/3} - \sum_{k \in \Lambda_N} \int_{\mathbf{R}^3} \frac{\rho(x)}{|x - k|} dx \\ & + \frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{\rho(x)\rho(y)}{|x - y|} dx dy + \frac{1}{2} \sum_{y \neq z \in \Lambda_N} \frac{1}{|y - z|}, \quad (1) \end{aligned}$$

and the ground-state energy is given by

$$I_{\Lambda_N}^{TFW} = \inf \left\{ E_{\Lambda_N}^{TFW}(\rho); \rho \geq 0, \sqrt{\rho} \in H^1(\mathbf{R}^3), \int_{\mathbf{R}^3} \rho = N \right\}. \quad (2)$$

In (1) above, c_0 and c_1 are non-negative constants (whose exact values are irrelevant from a mathematical view-point). The Thomas-Fermi model (TF,

for short) corresponds to the case when $c_0 = 0$, while the full model is referred to as the Thomas-Fermi-von Weizsäcker model (TFW, for short). In all that follows, we shall make the convention that $c_0 = c_1 = 1$ in the TFW setting. It is to be noticed, that in both cases, the energy functional is strictly convex with respect to the electronic density.

Many mathematical studies have been devoted to these models, and, in particular, it is a well-known fact that the problem (1)–(2) has a unique minimizing density, denoted by ρ_{Λ_N} . This fact has been proved by Lieb and Simon [41] (see also [37]) for the Thomas-Fermi model, and by Benguria, Brézis and Lieb [8] (see also [37]) for the TFW model.

Before turning to the thermodynamic limit problem *per se*, let us make some comments. The TFW model remedies major non-physical features of the Thomas-Fermi model. First of all, it predicts the expected behaviour of the density near the nuclei (*cusp conditions*) and at large distance (*exponential fall-off of the electronic density*). Moreover, as shown by two of us in [20], binding of neutral molecules holds in this model, at the difference with Teller’s no binding theorem for Thomas-Fermi model.

We have on purpose omitted to mention until now the ground-breaking work [41] by Lieb and Simon on the thermodynamic limit in the framework of the Thomas-Fermi theory. Indeed, this work is at the origin of our own study [16] on the Thomas-Fermi-von Weizsäcker model, and has therefore a far larger impact on our work than the, however fundamental, works that we have quoted in the introduction. Lieb and Simon proved in [41] that the three questions (i)-(ii)-(iii) of the thermodynamic limit problem that we have addressed in the introduction can be answered positively in the setting of the TF theory. In particular, they set a Thomas-Fermi type model for crystals. It is to be mentioned however that their strategy of proof relies very much upon Teller’s no binding theorem, and therefore, it cannot be carried through the TFW setting. In [16], we have proved that the three questions (i)-(ii)-(iii) of the thermodynamic limit problem can also be answered positively in the setting of the TFW theory. In addition, the new strategy of proof which we apply in [16] actually allows to extend the results of Lieb and Simon on the Thomas-Fermi model. Moreover, some of the techniques developed there also carry through the Hartree and the Hartree-Fock model.

Let us now introduce the periodic minimization problems obtained by passing to the thermodynamic limit. We then define the following periodic

minimization problem set on the unit cell Q of the lattice

$$I_{per}^{TFW} = \inf\{E_{per}^{TFW}(\rho); \rho \geq 0, \sqrt{\rho} \in H_{per}^1(Q), \int_Q \rho = 1\}, \quad (3)$$

$$\begin{aligned} E_{per}^{TFW}(\rho) &= \int_Q |\nabla \sqrt{\rho}|^2 + \int_Q \rho^{5/3} - \int_Q \rho(x) G(x) dx \\ &+ \frac{1}{2} \iint_{Q \times Q} \rho(x) \rho(y) G(x-y) dx dy, \end{aligned} \quad (4)$$

where $H_{per}^1(Q)$ is the subset of $H_{loc}^1(\mathbf{R}^3)$ consisting of functions which satisfy the periodic boundary conditions on the boundary of Q . The potential G which appears in the definition (4) of the TFW functional is defined, in a unique way, by

$$-\Delta G = 4\pi \left(-1 + \sum_{y \in \mathbf{Z}^3} \delta(\cdot - y) \right), \quad (5)$$

and

$$\int_Q G = 0. \quad (6)$$

The main results we obtain in [16] (which were announced in [15]) may be stated as follows. (We need technical assumptions that we do not make precise here.) We first prove the **convergence of the energy per unit volume**:

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

where $\frac{M}{2}$ is a universal constant, that only depends on G , through $M = \lim_{x \rightarrow 0} [G(x) - \frac{1}{|x|}]$, and which is just a matter of normalization. In particular, the ground state energy behaves linearly with respect to the total volume of the large molecule, and we have rigorously obtained a model for the ground-state energy of the crystal. Independently of this first result, we also establish in [16] the **convergence of the electronic density** in the following sense. The electronic density ρ_{Λ_N} converges to ρ_{per} , the unique periodic minimizing density of I_{per}^{TFW} , uniformly on sequences of domains approaching $\mathbf{R}^3$ in a sense defined precisely in [16]. Roughly speaking, these domains, which are included in the “big box” $\Gamma(\Lambda_N)$, fill in asymptotically the whole space; their complementary subset in $\Gamma(\Lambda_N)$ has a volume which is small compared to N , and they stay “very far away” from the boundary of the big box. We shall only briefly mention at this stage that, in order to avoid surface effects, technical assumptions are required in [16] on the sequence Λ_N of admissible finite subsets of the lattice. These technical

assumptions are well-identified and commonly used in Statistical Physics, and are satisfied by “reasonable big boxes”, like cubes, for example.

The above result on the asymptotic behaviour of the ground-state electronic density, when the molecule becomes larger and larger, roughly says that, while the nuclei spread over the whole lattice $\mathbf{Z}^3$, the electronic density becomes periodic, leaving asymptotically one electron per unit cell.

Let us now make some comments on the periodic TFW energy by itself. First of all, it mimics very well the usual TFW energy (1)–(2), except that the integrals involved in (4) are set on the unit cell and that the electronic density shares the same periodicity as the lattice of nuclei. It is also to be remarked that in (4), the periodic potential G which features the electrostatic interaction potential created by the lattice of nuclei models at the same time the self-interaction between the electrons. It is to be noticed that a key-point for the definition of the periodic problem is the definition of laws of interaction between particles, i.e. of the interaction potential(s). Indeed, owing to the long-range of the Coulomb potential, the electrostatic potential created by the infinite lattice of nuclei cannot be simply $\sum_{k \in \mathbf{Z}^3} \frac{1}{|x-k|}$, since this series obviously does not make sense. Besides, each of the three terms appearing in the electrostatic contributions to the ground-state energy (1), namely the *electrons-nuclei interaction* $-\sum_{k \in \Lambda_N} \int_{\mathbf{R}^3} \frac{1}{|x-k|} \rho(x) dx$, the *nuclei-nuclei interaction* $\sum_{y \neq z \in \Lambda_N} \frac{1}{|y-z|}$, and the *electrons-electrons interaction* $\frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{\rho(x) \rho(y)}{|x-y|} dx dy$, is of the order of $N^{5/3}$ as the volume of the box N (which is also the number of particles) goes to infinity. Still, their sum **globally** behaves linearly with respect to N . The compensating effects are explained by the so-called screening phenomenon, once again commonly playing this role in the thermodynamic limit issues—see, for instance, [35, 39, 40]. Let us noteworthy observe, still on this point, that the periodic potential G which was previously defined by (5) and (6) is also

$$G(x) = \sum_{k \in \mathbf{Z}^3} \left(\frac{1}{|x-k|} - \int_Q \frac{1}{|x-y-k|} dy \right)$$

(up to a constant); that is the sum over the lattice points of the Coulomb potential created by a point charge placed at the center of the unit cube, and which is screened, on each cell, by a uniform background of negative unit charge. Different techniques are proposed in Solid State physics to compute efficiently such electrostatic sums, like Ewald summation techniques (see, for example, [24, 27], and also [10]).

All these comments on the potential G and the screening effect already appear in Lieb and Simon’s work on the Thomas-Fermi model [41]. In

particular, in the TFW setting, the potential G is the same as the one appearing in the TF setting, and the periodic minimization problem is rather easy to guess in view of the one arising for the TF theory (they only differ from the gradient term). Likewise, it is easy to check that this periodic minimization problem is mathematically well-posed. In other words, taking benefit from the work by Lieb and Simon who had already defined the TF periodic problem, the idea to introduce the periodic problem (3)–(4) was straightforward. In [16], our “only” contribution was therefore to prove that the TFW model does converge in the thermodynamic limit to (3)–(4). However, concerning the Hartree and the Hartree-Fock models, the situation is much more difficult, owing in particular to the fact that the corresponding energy functional have no more a convex underlying structure, which was of crucial importance in the techniques employed in the TF and the TFW settings. In particular, for these models, guessing the limit periodic model is *per se* a fundamental and difficult step. A (small) part of the work has already been done within the framework of the Thomas-Fermi type models; in particular, one may expect that the limit of the electrostatic contribution to the ground-state energy should be the same; indeed, in every model which is dealt with in the sequel, the energy functional will contain, possibly among other electrostatic terms, the same expression for the electrostatic energy, that is

$$E_{\Lambda_N}^{elec}(\rho) = - \sum_{k \in \Lambda_N} \int_{\mathbf{R}^3} \frac{\rho(x)}{|x - k|} dx + \frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{\rho(x) \rho(y)}{|x - y|} dx dy + \frac{1}{2} \sum_{y \neq z \in \Lambda_N} \frac{1}{|y - z|}. \quad (7)$$

Therefore, we may expect that in all the models we shall consider, we shall always have, for a minimizing electronic density ρ_{Λ_N}

$$\begin{aligned} & \lim_{N \rightarrow +\infty} \frac{1}{N} E_{\Lambda_N}^{elec}(\rho_{\Lambda_N}) \\ &= - \int_Q G \rho + \frac{1}{2} \iint_{Q \times Q} \rho(x) \rho(y) G(x - y) dx dy + \frac{M}{2}, \end{aligned} \quad (8)$$

where ρ is the limit of ρ_{Λ_N} , and is Q -periodic. In spite of the fact that we have not been able until now to prove the thermodynamic limit for these models, we dispose of indications which help us to define periodic minimization problems, which are likely to be the crystalline analogues of the usual Hartree (H for short) and Hartree-Fock (HF for short) models in Molecular Chemistry. We prove that the periodic limit problems that we define are

well-posed: There exist minimizers and one may therefore derive meaningful Euler-Lagrange equations. These models will be presented in Sections 3 and 4 respectively; they have been studied by the authors in [18] and [19] respectively, and, for both models, the results have been announced in [17]. Nevertheless, as a preliminary stage to the modeling of the crystalline phase, we have also considered in [18] and [19] (see also [17]), simplified forms of the Hartree (respectively the Hartree-Fock) model, which are referred to as the Restricted Hartree (RH for short) (respectively Reduced Hartree-Fock (RHF for short)) model for which we are able to identify the limit of the energy per unit volume.

Let us begin with the Hartree model.

3 Hartree type models

Let us recall the Hartree model, historically introduced by Hartree in [32]. This model is obtained, when one does not take into account the Pauli exclusion principle for the electrons, and, then simply represents the electronic wave-function as a product of independent wave functions (atomic orbitals). The corresponding ground-state energy is then given by

$$I_{\Lambda_N}^H = \inf \left\{ E_{\Lambda_N}^H(\varphi_1; \dots; \varphi_N); \right. \\ \left. \varphi_i \in H^1(\mathbf{R}^3), \int_{\mathbf{R}^3} \varphi_i^2 = 1, 1 \leq i \leq N \right\},$$

where the φ_i 's are the atomic orbitals, and where

$$E_{\Lambda_N}^H(\varphi_1; \dots; \varphi_N) = \sum_{i=1}^N \left(\int_{\mathbf{R}^3} |\nabla \varphi_i|^2 - \frac{1}{2} D(\varphi_i^2, \varphi_i^2) \right) + E_{\Lambda_N}^{elec}(\rho)$$

with $\rho = \sum_{i=1}^N |\varphi_i|^2$, and $D(f, g) = \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{f(x)g(y)}{|x-y|} dx dy$. The existence of (at least) one minimizer for this problem has been established by Lieb and Simon [42], and the existence of infinitely many solutions to the corresponding Euler-Lagrange equations (in other words, infinitely many bound states) is due to Lions [43].

It is not difficult to check that the energy per unit volume is bounded (and, actually, its limit exists), and this implies (see [18]) that the sum of the self-interactions of the electrons, that is $\sum_{i=1}^N D(\varphi_i^2, \varphi_i^2)$, is of the order of N . Therefore, this electrostatic term features a different behaviour, compared to the other terms in $E_{\Lambda_N}^{elec}(\rho)$ (which are of the order of $N^{5/3}$). Hence, one

guess could be that this term does not affect the thermodynamic limit. The Restricted Hartree model is the model one obtains by getting rid of this contribution. This model may therefore be written as

$$I_{\Lambda_N}^{RH} = \inf \left\{ E_{\Lambda_N}^{RH}(\varphi_1; \dots; \varphi_N) ; \varphi_i \in H^1(\mathbf{R}^3), \int_{\mathbf{R}^3} \varphi_i^2 = 1, 1 \leq i \leq N \right\},$$

$$E_{\Lambda_N}^{RH}(\varphi_1; \dots; \varphi_N) = \sum_{i=1}^N \int_{\mathbf{R}^3} |\nabla \varphi_i|^2 + E_{\Lambda_N}^{elec}(\rho).$$

It turns out that the unique minimizer of $E_{\Lambda_N}^{RH}(\varphi_1; \dots; \varphi_N)$ is of the form $(\frac{\sqrt{\rho_{\Lambda_N}}}{N}; \dots; \frac{\sqrt{\rho_{\Lambda_N}}}{N})$. And, the limit of the energy per unit volume may be identified as

$$I_{per}^{RH} = \inf \left\{ E_{per}^{RH}(\rho) ; \rho \geq 0, \sqrt{\rho} \in H_{per}^1(Q) \int_Q \rho = 1 \right\} + \frac{M}{2},$$

where

$$E_{per}^{RH}(\rho) = \int_Q |\nabla \sqrt{\rho}|^2 - \int_Q G\rho + \iint_{Q \times Q} \rho(x) G(x-y) \rho(y) dx dy,$$

which is still a model from the Density Functional Theory. One can prove that our guess was wrong, and that, actually, the limit of the energy per unit volume in the Hartree model is strictly less than I_{per}^{RH} .

In the Hartree model, we are led to the following conjecture. We make first the natural assumption that the electronic density becomes periodic, by passing to the thermodynamic limit (we are not able to prove this claim), and we also postulate that, roughly speaking, each electron is represented by the same electronic wave-function φ up to a translation (which is known as a *Wannier function* in Solid State Physics literature). Within these assumptions, the periodic electronic density is given by $\rho = \sum_{k \in \mathbf{Z}^3} \varphi^2(\cdot + k)$. Our last **postulate** is then that the energy per unit volume converges to a periodic model I_{per}^H , which is given by

$$I_{per}^H = \inf \left\{ E_{per}^H(\varphi) ; \varphi \in H^1(\mathbf{R}^3), \int_{\mathbf{R}^3} \varphi^2 = 1 \right\} + \frac{M}{2}, \quad (9)$$

$$\begin{aligned} E_{per}^H(\varphi) &= \int_{\mathbf{R}^3} |\nabla \varphi|^2 - \frac{1}{2} D(\varphi^2, \varphi^2) - \int_{\mathbf{R}^3} G\varphi^2 \\ &\quad + \frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \varphi^2(x) G(x-y) \varphi^2(y) dx dy \end{aligned} \quad (10)$$

$$\begin{aligned}
&= \int_{\mathbf{R}^3} |\nabla \varphi|^2 - \frac{1}{2} D(\varphi^2, \varphi^2) \\
&\quad - \int_Q G \rho + \frac{1}{2} \iint_{Q \times Q} \rho(x) G(x-y) \rho(y) dx dy, \quad (11)
\end{aligned}$$

with $\rho(x) = \sum_{k \in \mathbf{Z}^3} \varphi^2(x+k)$. Let us observe at this stage that we recognize in (11) the same periodic electrostatic energy as in the TFW model.

Let us emphasize once more that we are not able to **prove** the convergence of the energy per unit volume to I_{per}^H , partly owing to the fact that the different strategies which are described in [16] only work for convex functionals. (Nevertheless, we provide in [18] an example of some Hartree model where the nuclei are smeared in a very specific manner, and for which we may establish the convergence of the energy per unit volume to the periodic model (9)–(10).) In [18], we give a proof of the well-posedness of the Hartree periodic model, in the sense that, **every** minimizing sequence of I_{per}^H admits a subsequence which is compact in $H^1(\mathbf{R}^3)$ (up to a translation along vectors which leave the crystalline lattice invariant). In particular, I_{per}^H admits a minimum φ_{per} , which is precisely the so-called Wannier function. The proof of this claim, which is given in [18], is very tricky and raises difficult mathematical questions. It is worth mentioning that the Euler-Lagrange equations satisfied by any minimizer φ_{per} of the periodic Hartree model already appear in Solid State Physics textbooks, which, in turn, gives us some confidence in the validity of our model. For the sake of consistency, let us write down here this “periodic Hartree equation” as

$$-\Delta \varphi_{per} - (|\varphi_{per}|^2 \star \frac{1}{|x|}) \varphi_{per} - G \varphi_{per} + (|\varphi_{per}|^2 \star G) \varphi + \theta \varphi_{per} = 0,$$

where $\theta > 0$ is the Lagrange multiplier.

We now turn to the next section which is devoted to Hartree-Fock type models.

4 Hartree-Fock type models

Before writing down the Hartree-Fock model, let us already say that, in all that follows, the spin effects are taken into account only through the Pauli exclusion principle; in particular, we shall only consider complex-valued wave-functions. In the absence of magnetic fields, re-incorporating the spin dependence does not affect neither our mathematical analysis nor our results.

Let us first recall the Hartree-Fock model. In this framework, the ground-state energy is defined by the following minimization problem :

$$I_{\Lambda_N}^{HF} = \inf \left\{ E_{\Lambda_N}^{HF}(\varphi_1, \dots, \varphi_N) ; \varphi_i \in H^1(\mathbf{R}^3), \int_{\mathbf{R}^3} \varphi_i \varphi_j^* = \delta_{i,j} \right\},$$

where

$$\begin{aligned} E_{\Lambda_N}^{HF}(\varphi_1, \dots, \varphi_N) &= \sum_{i=1}^N \int_{\mathbf{R}^3} |\nabla \varphi_i(x)|^2 dx + E_{\Lambda_N}^{elec}(\rho_N) \\ &\quad - \frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{|\rho_N(x, y)|^2}{|x - y|} dx dy, \end{aligned}$$

with $\rho_N(x, y) = \sum_{i=1}^N \varphi_i(x) \varphi_i^*(y)$ and $\rho_N(x) = \rho_N(x, x) = \sum_{i=1}^N |\varphi_i(x)|^2$.

The existence of a minimizer for the HF minimization problem is a standard fact due to Lieb and Simon [42], or Lions [43] (where a proof of the existence of infinitely many solutions to the Hartree-Fock equations is also provided).

In fact, it happens that, for the mathematical analysis of the thermodynamic limit problem of this model, it is more convenient to use an equivalent formulation of the ground-state energy in terms of density matrices. The proof that the two formulations are indeed equivalent is due to Lieb [38] (see also Bach [3] and Lions [44]).

The (reduced) one-particle density matrix, denoted by γ in the sequel, is a self-adjoint operator on $L^2(\mathbf{R}^3)$, with finite trace, such that

$$0 \leq \gamma \leq \mathbf{1}$$

(in the sense of self-adjoint operators) where $\mathbf{1}$ denotes the identity on $L^2(\mathbf{R}^3)$, and whose trace fits the number of electrons. To every such operator is associated a density ρ_γ , which is a non-negative function in $L^1(\mathbf{R}^3)$ such that

$$\text{Tr } \gamma = \int_{\mathbf{R}^3} \rho_\gamma.$$

Indeed, the density matrix being a Hilbert-Schmidt operator on $L^2(\mathbf{R}^3)$, its kernel (still denoted by γ) may be decomposed along a complete set of orthonormal eigenfunctions $(\varphi_n)_{n \geq 1} \in L^2(\mathbf{R}^3)$ of γ associated to the eigenvalues $0 \leq \lambda_n \leq 1$, in such a way that

$$\gamma(x, y) = \sum_{n \geq 1} \lambda_n \varphi_n(x) \varphi_n^*(y).$$

The density ρ_γ is then given by

$$\rho_\gamma(x) = \sum_{n \geq 1} \lambda_n |\varphi_n(x)|^2.$$

The Hartree-Fock functional may then be expressed in terms of density matrices as

$$E_{\Lambda_N}^{HF}(\gamma) = \text{Tr}[-\Delta \gamma] + E_{\Lambda_N}^{elec}(\rho_\gamma) - \frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{|\gamma(x, y)|^2}{|x - y|} dx dy,$$

where $E_{\Lambda_N}^{elec}(\rho_\gamma)$ is defined in (7). Let us note that, in the above expression of the energy, we have

$$\text{Tr} [-\Delta \gamma] = \sum_{n \geq 1} \lambda_n \int_{\mathbf{R}^3} |\nabla \varphi_n(x)|^2 dx,$$

and that the last term, namely, $-\frac{1}{2} \iint_{\mathbf{R}^3 \times \mathbf{R}^3} \frac{|\gamma(x, y)|^2}{|x - y|} dx dy$ is called the *exchange term*. The Hartree-Fock ground-state energy is then defined by

$$I_{\Lambda_N}^{HF} = \inf\{E_{\Lambda_N}^{HF}(\gamma) ; \gamma \in \Gamma_N\},$$

where the set of admissible density matrices Γ_N is composed of density matrices as above, satisfying in addition that $\text{Tr}(\gamma) = N$ and that $\text{Tr}[-\Delta \gamma] < +\infty$ (these conditions ensure that the energy functional takes finite values on the set of constraints).

Let us now turn to the thermodynamic limit of this model, which is studied in [19] (our results have been announced in [17]). The first result is that the energy per unit volume has the expected behaviour in the limit of large volumes. As a consequence of this fact, it is checked in [19] that the exchange term also behaves linearly with respect to N as N goes to infinity. This asymptotic behaviour however admitted in the Quantum Chemistry literature (see for example [47]) was not known so far, to the best of our knowledge, except in the simplified framework of the free electron gas by Friesecke [30]. Let us emphasize the fact that the exchange term features an asymptotic behaviour which is different from the other electrostatic terms. (Recall that each of them is of the order of $N^{5/3}$ as N goes to infinity.) The advantage of the formulation in terms of density matrices is that the set Γ_N of admissible density matrices is convex. Unfortunately, the Hartree-Fock functional itself is not convex with respect to the density matrix because of the exchange term. Therefore, the strategies of proofs proposed in [16] do not

apply here, and so far we have not been able to identify the thermodynamic limit of the Hartree-Fock energy per unit volume in a rigorous mathematical manner. We shall only propose in the following a periodic model which is likely to be the Hartree-Fock model for crystals. Nevertheless, before stating this model, we shall explain what kind of progress is at our reach for a simplified model, which is referred to as the Reduced Hartree-Fock model in the mathematical literature since it was introduced by Solovej in [56, 57], while it has nothing to do with the Reduced Hartree-Fock model in the sense of chemists ... This model is obtained from the Hartree-Fock model expressed in terms of density matrices, by getting rid of the exchange term. Since we have already observed that this term has a specific behaviour, by letting it apart at a first stage, we aim at understanding first the behaviour of the kinetic energy term $\text{Tr} [-\Delta \gamma]$ (since we still hope that the sum of the electrostatic terms should once more provide a known term according to (8)). Let us thus write down the RHF model in the following way

$$I_{\Lambda_N}^{RHF} = \inf\{E_{\Lambda_N}^{RHF}(\gamma); \gamma \in \Gamma_N\},$$

$$E_{\Lambda_N}^{RHF}(\gamma) = \text{Tr} [-\Delta \gamma] + E_{\Lambda_N}^{elec}(\rho_\gamma),$$

and make the following crucial observation: The RHF functional is convex with respect to the density matrix, and even strictly convex with respect to the associated density ρ_γ . Moreover, as shown by Solovej in [57], for every N and Λ_N , there exists a minimizer γ_{Λ_N} of $I_{\Lambda_N}^{RHF}$, and correspondingly, a unique electronic density ρ_{Λ_N} .

Thanks to this convexity property, and by adapting the arguments which are developed in [16], we prove in [19] the thermodynamic limit of the energy per unit volume for the RHF model. In order to state the RHF periodic model, we need to extend the definition of the reduced one-particle density matrices to this periodic framework. A *periodic density matrix* γ_{per} will be defined as a self-adjoint operator on $L^2(\mathbf{R}^3)$, still satisfying $0 \leq \gamma_{per} \leq \mathbf{1}$, and which commutes with the group of translations $\{\tau_k\}_{k \in \mathbf{Z}^3}$ which leave invariant the underlying crystalline lattice— $\mathbf{Z}^3$ here; this property may be simply written as

$$[\tau_k, \gamma_{per}] = 0, \text{ for every } k \in \mathbf{Z}^3. \quad (12)$$

This is precisely where the meeting point between our analysis and the standard theory of Bloch waves in Solid State physics stands (see, among other references, [1, 26] and also [33, 51] for a mathematical presentation). Indeed, thanks to the commutation relations (12) satisfied by the periodic density matrix, we may extend to our operator the famous Bloch theorem in Solid

State Physics, which determines the spectral decomposition of Schrödinger operators with periodic potentials in terms of Bloch waves. More precisely, Bloch's theorem states that a real number λ is in the spectrum of this kind of Schrödinger operators (*i. e.* $-\Delta + V_{per}$, with V_{per} being Q -periodic) if and only if it corresponds to a generalized eigenfunction, which is of the form of a plane wave $e^{i\xi \cdot x}$ times a periodic function, for some ξ in $\mathbf{R}^3$. (We recognize the well-known definition of *Bloch waves*.) A full description of the eigenfunctions is obtained by restricting the phase ξ to $[-\pi; +\pi]^3$, that we shall denote by Q^* in the following. (Actually, for general crystalline lattices, the phase is restricted to the dual (or reciprocal) lattice of the original lattice—see for example [10].) In other words, the spectral analysis of $-\Delta + V_{per}$ on $L^2(\mathbf{R}^3)$ reduces to the spectral analysis of the family of operators $-\Delta + V_{per}$ on $L^2_\xi(Q)$ ($\xi \in Q^*$), where $L^2_\xi(Q)$ is the space of locally square integrable Bloch waves associated to a given phase ξ in Q^* . By complete analogy with the model case of the Schrödinger operator with periodic potential, any periodic density matrix γ_{per} which enjoys the properties defined above may be diagonalized on $L^2_\xi(Q)$, one phase ξ at a time; to a fixed $\xi \in Q^*$ corresponds a self-adjoint operator γ_ξ on $L^2_\xi(Q)$ such that

$$0 \leq \gamma_\xi \leq \mathbf{1}, \quad (13)$$

(where this time $\mathbf{1}$ has to be understood as the identity on $L^2_\xi(Q)$). The aim of this diagonalization of our operator γ_{per} on stable subspaces is of course to obtain a family of operators γ_ξ which are easier to diagonalize than the original one. (Let us make the obvious remark that an operator which commutes with infinitely many translations cannot be compact.) Therefore, we shall make a further assumption on the admissible periodic density matrices, which is simply that, for every ξ in Q^* ,

the operator γ_ξ has a finite trace on $L^2_\xi(Q)$.

Therefore, for every ξ in Q^* , the Hilbert-Schmidt kernel of γ_ξ (which is still denoted by γ_ξ) may be decomposed along a complete sequence of eigenfunctions of γ_ξ , corresponding to eigenvalues $\lambda_n(\xi)$ between 0 and 1 (thanks to (13)), in the following way

$$\gamma_\xi(x, y) = \sum_{n \geq 1} \lambda_n(\xi) e^{-i\xi \cdot (x-y)} u_n(\xi; x) u_n^*(\xi; y)$$

where $u_n(\xi; x)$ is a hilbertian basis of $L^2(Q)$ consisting of Q -periodic functions. At each fixed phase, we may define a density $\rho_\xi(x)$ by

$$\rho_\xi(x) = \sum_{n \geq 1} \lambda_n(\xi) |u_n(\xi; x)|^2.$$

This function is clearly Q -periodic and satisfies $\int_Q \rho_\xi(x) dx = \sum_{n \geq 1} \lambda_n(\xi) = \text{Tr}_{L_\xi^2(Q)} \gamma_\xi$. The full periodic density matrix γ_{per} is then recovered from the family of γ_ξ 's through the relation

$$\gamma_{per}(x, y) = \frac{1}{(2\pi)^3} \int_{Q^*} \gamma_\xi(x, y) d\xi,$$

and the periodic electronic density is given by

$$\rho_{per}(x) = \frac{1}{(2\pi)^3} \int_{Q^*} \rho(\xi, x) d\xi.$$

(Let us also mention [47] where one can find definitions of periodic density matrices which are similar to ours.) The condition that each cell contains exactly one electron is now written in different equivalent manners as

$$1 = \int_Q \rho_{per} = \frac{1}{(2\pi)^3} \int_{Q^*} \sum_{n \geq 1} \lambda_n(\xi) d\xi = \frac{1}{(2\pi)^3} \iint_{Q \times Q^*} \rho_\xi(x) d\xi dx.$$

An extra condition on the γ_ξ 's is necessary in order to give a sense to the analogue of the kinetic energy term in the periodic setting. This condition is simply $\int_{Q^*} \text{Tr}_{L_\xi^2(Q)} [-\Delta_\xi \gamma_\xi] d\xi < +\infty$, where the notation $-\Delta_\xi$ stands for the Laplacian with quasi-periodic boundary conditions on the boundary of the cell. Finally, we denote by Γ , the set of periodic one-particle density matrices which fulfill the series of properties required before.

With these “new” objects at hand, we are able to define the RHF periodic model as

$$I_{per}^{RHF} = \inf \{ E_{per}^{RHF}(\gamma_{per}); \gamma_{per} \in \Gamma \},$$

$$\begin{aligned} E_{per}^{RHF}(\gamma_{per}) &= \frac{1}{(2\pi)^3} \int_{Q^*} \text{Tr}_{L_\xi^2(Q)} [-\Delta_\xi \gamma_\xi] d\xi \\ &\quad - \int_Q G \rho_{per} + \frac{1}{2} \iint_{Q \times Q} \rho_{per}(x) G(x-y) \rho_{per}(y) dx dy. \end{aligned}$$

We prove in [19] that this periodic minimization problem admits a minimum $\gamma \in \Gamma$, which corresponds to a unique minimizing density $\rho(x)$ (thanks to the strict convexity of the periodic energy functional with respect to the density). Moreover, we also establish there that this model is obtained by passing to the thermodynamic limit in the RHF energy per unit volume.

Let us return now to the Hartree-Fock model. In this setting, we are not able to prove rigorously that the electronic density becomes periodic, even

if it should be true in the absence of magnetic fields. (When magnetic fields are present, and within models with spins, one may observe periodicity on a larger cell; see [47] and [5].) However, we **postulate** that, should it indeed be the case, the Hartree-Fock energy per unit volume would converge to the following periodic model. :

$$I_{per}^{HF} = \inf\{E_{per}^{HF}(\gamma_{per}); \gamma_{per} \in \Gamma\},$$

$$\begin{aligned} E_{per}^{HF}(\gamma_{per}) &= \frac{1}{(2\pi)^3} \int_{Q^\star} \text{Tr}_{L^2_\xi(Q)}[-\Delta_\xi \gamma_\xi] d\xi - \int_Q G \rho_{per} \\ &+ \frac{1}{2} \iint_{Q \times Q} \rho_{per}(x) G(x-y) \rho_{per}(y) dx dy - \frac{1}{2} \iint_{Q \times \mathbf{R}^3} \frac{|\gamma_{per}(x, y)|^2}{|x-y|} dx dy. \end{aligned}$$

Comparing with the analogue periodic model in the RHF setting, the only new term is the exchange term $-\frac{1}{2} \iint_{Q \times \mathbf{R}^3} \frac{|\gamma_{per}(x, y)|^2}{|x-y|} dx dy$.

We prove in [19] that this Hartree-Fock periodic model is well-posed; in particular, I_{per}^{HF} admits a minimizer γ in Γ . Before writing down the HF periodic equations, we claim that the exchange term may be rewritten in the equivalent form

$$\begin{aligned} &\iint_{Q \times \mathbf{R}^3} \frac{|\gamma_{per}(x, y)|^2}{|x-y|} dx dy \\ &= \frac{1}{(2\pi)^6} \iiint_{(Q^\star)^2 \times Q^2} \gamma_\xi(x, y) W_\infty(\xi - \xi', x-y) \gamma_{\xi'}(x, y)^* d\xi d\xi' dx dy, \end{aligned}$$

where, for every η in $Q^\star$ and z in $\mathbf{R}^3$,

$$W_\infty(\eta, z) = \sum_{k \in \mathbf{Z}^3} \frac{e^{ik \cdot \eta}}{|z+k|}.$$

(Note that $e^{i\eta \cdot z} W_\infty(\eta, z)$ is Q -periodic with respect to z .) On this latter form the non-local feature of the exchange term is more easily seen. The Euler-Lagrange equation satisfied by any minimizer may be written as follows, at every fixed phase ξ in $Q^\star$, and for every $n \geq 1$,

$$\begin{aligned} &-(i\nabla + \xi)^2 u_n(\xi, \cdot) - G u_n(\xi, \cdot) + \left(\int_Q G(\cdot - y) \rho_\xi(y) dy \right) u_n(\xi, \cdot) \\ &- \frac{1}{(2\pi)^3} \iint_{Q^\star \times Q} \gamma(\xi'; \cdot; y) W_\infty(\xi - \xi'; \cdot - y) e^{i\xi \cdot y} u_n(\xi, y) dy d\xi' \\ &= \varepsilon_n(\xi) u_n(\xi, \cdot), \quad \text{on } Q, \end{aligned}$$

together with

$$\begin{cases} \lambda_n(\xi) = 0 \implies \varepsilon_n(\xi) \geq \pi, \\ 0 < \lambda_n(\xi) < 1 \implies \varepsilon_n(\xi) = \pi, \\ \lambda_n(\xi) = 1 \implies \varepsilon_n(\xi) \leq \pi, \end{cases}$$

where the real number π enters the equations as a Lagrange multiplier. It is worth noticing that these equations seem to be already known in Solid State Physics literature, thereby strengthening our feeling that our model should be the correct one.

We still do not know whether any minimizer of our periodic model is a projector on the lowest eigenvalues of the Hartree-Fock periodic operator for each phase, as it is assumed to be the case for insulators (see the paper by Resta in [47]), and as it is known to be the case in the molecular HF model (see [4] and [43]).

5 The optimal periodic configuration for the nuclei

Hitherto we have concentrated our efforts on the first stage in the Born-Oppenheimer approximation, which consists in fixing *a priori* the locations of the nuclei, and then in determining the electronic ground-state energy, which is therefore parameterized by the nuclear configuration. We were also considering a finite number N of nuclei which were fixed at the points of a given periodic lattice, and we were interested in the asymptotic behaviour of quantities which describe the electronic state, like the electronic densities, and the ground-state energy per unit volume, when N goes to infinity and the nuclei fill in the entire periodic lattice. A question of great importance (but of outstanding mathematical difficulty) is the following. The second fundamental stage within the Born-Oppenheimer approximation consists next in minimizing the ground-state energy of the electrons with respect to all possible geometries of nuclei; the nuclei are therefore no more constrained to lie at points of a lattice, and we then obtain an “absolute ground-state”, taking into account the less-energy configuration for both the electrons and the nuclei. It is of course tempting to pass to the thermodynamic limit on the absolute ground-state energy per unit volume, and to raise the following issues. Being given a model within which such an optimal geometry exists for the nuclei (like TFW or Hartree—see [20]), what is the behaviour of this optimal geometry when the number of nuclei goes to infinity? Does it become periodic or do the nuclei arrange according to some ordered structures (think of quasi-crystals for example)? This would explain why crystals are

observed to have a tendency to form at absolute zero temperature. Some important preliminary results on the so-called crystal problem are available within some models for classical atoms in one or two dimensions (see, for example [31, 49, 50, 60]). In both cases, it is shown that the optimal configuration for the nuclei becomes periodic in the thermodynamic limit and, for two dimensional studies, the shape of the optimal cell is well-identified. Owing to the well-known Teller's no-binding theorem in the Thomas-Fermi setting (see [58, 6], and [41], for a rigorous mathematical proof), the simplest quantum models within which binding occurs are the Hartree and the TFW model (see [20]). Unfortunately, as far as we know, analogous results for quantum models are beyond one's reach, for the moment. However, we shall report in this section on recent works by Blanc and one of us [9, 11, 12] in the framework of the TFW model which may be seen as preliminary steps in this direction. (In the following, most of the notation is inherited from [12].) Indeed, one may define the periodic TFW model for general crystals, and not simply for a unit cubic cell with one point nucleus of unit charge, in the following way (see [16] and [12]). For every proper periodic lattice ℓ of $\mathbf{R}^3$, namely

$$\ell = \{k a_1 + l a_2 + m a_3; (k, l, m) \in \mathbf{Z}^3\},$$

where the three vectors a_i , $i = 1, 2, 3$, span $\mathbf{R}^3$, a primitive cell of the crystal is defined by

$$\Gamma(\ell) = \left\{ x a_1 + y a_2 + z a_3; (x, y, z) \in \left[-\frac{1}{2}; \frac{1}{2}[\right] \right\}.$$

We assume that one nucleus of unit charge lie at the center of each cell. The set of all proper lattices of $\mathbf{R}^3$ is denoted by $\mathcal{L}$. According to the results in [16], and by analogy with (3), (4), (5) and (6), the ground-state energy of the associated neutral crystal is given by

$$I(\ell) = \inf \left\{ E_\ell(\rho); \rho \geq 0, \sqrt{\rho} \in H_{per}^1(\Gamma(\ell)), \int_{\Gamma(\ell)} \rho = 1 \right\}, \quad (14)$$

where

$$\begin{aligned} E_\ell(\rho) = & \int_{\Gamma(\ell)} |\nabla \sqrt{\rho}|^2 + \int_{\Gamma(\ell)} \rho^{5/3} - \int_{\Gamma(\ell)} G_\ell(x) \rho(x) dx \\ & + \frac{1}{2} \iint_{\Gamma(\ell) \times \Gamma(\ell)} \rho(x) \rho(y) G_\ell(x - y) dx dy, \end{aligned} \quad (15)$$

with $H_{per}^1(\Gamma(\ell))$ being the subset of $H_{loc}^1(\mathbf{R}^3)$ consisting of functions which satisfy the periodic boundary conditions on the boundary of $\Gamma(\ell)$. The

potential G_ℓ which appears in the definition (15) of the TFW functional is defined, in a unique way, by

$$-\Delta G_\ell = 4\pi \left[\sum_{k \in \ell} \delta(\cdot - k) - \frac{1}{|\Gamma(\ell)|} \right], \quad (16)$$

and

$$\lim_{|x| \rightarrow 0} \left[G_\ell(x) - \frac{1}{|x|} \right] = 0, \quad (17)$$

where $|\Gamma(\ell)|$ is simply the volume of $\Gamma(\ell)$. (Note that G_ℓ is actually the Green function of the periodic Laplacian on $\Gamma(\ell)$, and that the normalization (17) on G_ℓ which is made in [9, 12], instead of $\int_{\Gamma(\ell)} G_\ell = 0$, simply helps for the calculations.) The problem under consideration in [9] consists in looking at the periodic ground-state energy (14)-(15) as a function of the primitive cell ℓ , and next in searching for a primitive cell which yields the smallest possible periodic ground-state energy in the framework of the TFW model. In other words, it is shown that every minimizing sequence $(\ell_n)_{n \geq 1}$ of the following minimization problem

$$I = \inf\{I(\ell); \ell \in \mathcal{L}\}$$

admits a subsequence which converges to some optimal cell. Interesting questions still remain to be solved on the uniqueness and the geometric properties (symmetries for instance) of this cell. The strategy of proof deserves some comments. Assuming that $(\ell_n)_{n \geq 1}$ is a minimizing sequence for I (*i.e.* $(\ell_n)_{n \geq 1}$ is a sequence of proper lattices of $\mathbf{R}^3$, and $\lim_{n \rightarrow +\infty} I(\ell_n) = I$), the point consists in verifying that $\ell_n = (a_1^n; a_2^n; a_3^n)$ converges to some proper lattice of $\mathbf{R}^3$. Any proper lattice ℓ_n is completely determined by the following data. We shall denote by R_i^n the respective length of a_i^n , for $i = 1, 2$ or 3 , and by $\vartheta_{i,j}^n$ the angle between a_i^n and a_j^n , for $i \neq j$, and we shall assume, without loss of generality that

$$R_1^n \leq R_2^n \leq R_3^n. \quad (18)$$

The first remark is borrowed by Blanc from crystallography textbooks, where one observes that the angles of proper lattices may be chosen in the compact segment $[\frac{\pi}{3}; \frac{\pi}{2}]$. Therefore, extracting a subsequence, if necessary, we already dispose of the convergence of the angles as n goes to infinity. It remains to check that the so-called radii R_i^n also converge (at least up to a further subsequence) to some positive quantities R_i , for $i = 1, 2$ or 3 . The first condition which has to be satisfied by the minimizing sequence is that

R_1^n stays away from zero as n goes to infinity (and thus so do R_2^n and R_3^n , thanks to (18)). Otherwise, the minimizing cells shrink to a single point as n goes to infinity, and there is no cell remaining at all after passing to the limit. This condition is ensured by Teller's theorem for the TF energy which is an obvious bound from below for the TFW energy (see [9]). Secondly, a series of "stability type inequalities" have to be checked, which have a simple physical interpretation: They translate into mathematical language the fact that one has to bring energy to the system under consideration in order to increase the size of the cell to infinity (that is, some of the radii R_i^n to infinity). Owing to (18), such a situation may arise in three different manners. First of all, in order to avoid the case when R_1^n goes to infinity as n goes to infinity (and thus so do R_2^n and R_3^n), Blanc shows that the absolute periodic ground-state I corresponds to an energy which is strictly below the ground-state energy of a single isolated (neutral) atom. Secondly, in order to exclude the two other cases, namely the case when R_2^n (and thus R_3^n) goes to infinity, on the one hand, and the case when R_3^n goes to infinity on the other hand, Blanc checks that the absolute periodic ground-state I corresponds to an energy which is strictly below the ground-state energy of lineic polymers, on the one hand, and of thin films on the other hand. The TFW models for the ground-state energy of the lineic polymers, denoted by I_{pol}^{TFW} , and of the thin films, denoted by I_{film}^{TFW} , have been introduced by Blanc and one of us in [11]. They have been obtained from a thermodynamic limit strategy by extending the methods of [16] to the case of "infinite molecules", where the nuclei are arranged periodically along a line in a case of a lineic polymer or on a plane in the case of thin films. Let us now write down these models. Let ℓ be a one-dimensional periodic lattice of $\mathbf{R}^3$ which is defined by the vector e in $\mathbf{R}^3$. Then the ground-state energy of the lineic polymer whose nuclei stand at the points of $\mathbf{Z}e$ is given by

$$I_{pol}^{TFW}(\ell) = \inf \left\{ E_\ell(\rho); \rho \geq 0, \int_{\Gamma(\ell)} \rho = 1, \right. \\ \left. \sqrt{\rho} \in H_{per}^1(\Gamma(\ell)), \int_{\Gamma(\ell)} \log(2 + |x|) \rho < +\infty \right\},$$

with

$$\Gamma(\ell) = \mathbf{R}^2 \times \left\{ t e; t \in \left[-\frac{1}{2}; -\frac{1}{2}[\right] \right\},$$

and where the expression of $E_\ell(\rho)$ is the same as in (15), except for the fact that the potential G_ℓ is this time defined as a solution to

$$-\Delta G_\ell = 4\pi \sum_{k \in \mathbf{Z}} \delta(\cdot - k e)$$

which is periodic in the direction of e (and with additional normalization conditions which are made precise in [11]). The model for thin films is similarly written as :

$$I_{film}^{TFW}(\ell) = \inf \left\{ E_\ell(\rho); \rho \geq 0, \sqrt{\rho} \in H_{per}^1(\Gamma(\ell)), \int_{\Gamma(\ell)} |x| \rho < +\infty, \int_{\Gamma(\ell)} \rho = 1 \right\},$$

where ℓ is a periodic lattice in $\mathbf{R}^2$, defined by two linearly independent vectors e_1 and e_2 and

$$\Gamma(\ell) = \mathbf{R} \times \left\{ t e_1 + s e_2; t, s \in \left[-\frac{1}{2}; -\frac{1}{2}[\right] \right\}.$$

The corresponding potential G_ℓ which appears in the general definition (15) of the energy functional is a solution to

$$-\Delta G_\ell = 4\pi \sum_{(k;l) \in \mathbf{Z}^2} \delta(\cdot - k e_1 - l e_2)$$

which shares the periodicity of the two-dimensional lattice (further normalization conditions are also made precise in [11]).

In order to stimulate future work in this topic, we shall conclude this review by indicating in the forthcoming section some natural extensions of our work.

6 Extensions and perspectives

Let us recall from the introduction that, by applying the thermodynamic limit strategy to various models from Quantum Chemistry, we aimed at building new quantum-mechanical models for crystals. We have illustrated the efficiency of this method on a wide variety of models, from the toy model which is a Thomas-Fermi type model to the more sophisticated Hartree-Fock model. In any cases, this strategy provides a rigorous derivation of expressions for the ground-state energies. Moreover, since, for standard models

like Hartree and Hartree-Fock models, the corresponding Euler-Lagrange equations coincide with well-known equations in Solid State Physics, we are founded to think of applying the same strategy in order to construct new models. For example, by taking our Hartree-Fock periodic model as a starting point, it should be possible (while still much more difficult) to propose a Dirac-Fock type model for the crystalline phase, in order to take into account the relativistic effects (see the paper by Dolbeault, Esteban and Séré [23] for a presentation on the Dirac-Fock model).

Besides, we may now try to extend our models by allowing for more general geometries for the nuclei. In the framework of the Thomas-Fermi-von Weizsäcker model, we have already treated in [16] the case of general crystals, which may possibly contain local defects, like impurities, or, even some cases of non-periodic structures. We give in [16] some mathematical background which should allow to define a ground-state energy for quasi-crystals in a Thomas-Fermi type setting at a first stage, and next in the Hartree or even in the Hartree-Fock setting, within different mathematical definitions of quasi-crystals (see [2, 53]). In the same spirit of taking into account more general configurations for the nuclei, and still for the TFW model, we recall from the previous section that Blanc and one of us made use of the thermodynamic limit strategy to build models for polymers and two-dimensional films. Therefore, the general method exposed in [16] seems to allow the construction of ground-state energies for arrangements of infinitely many nuclei, which may be much more complicated than the model case of the crystalline lattice.

As also mentioned in the previous section, it is very challenging to tackle the thermodynamic limit problem of quantum models when the nuclei no more stand at the point of a periodic lattice but are rather disposed accordingly to a configuration where they minimize the ground-state energy. By understanding the behaviour of this optimal geometry when the number of nuclei goes to infinity, one tries to contribute to a theoretical explanation to the empirical observation that crystals forms at absolute zero temperature.

Eventually, having different models for the solid phase at our disposal, it would also be interesting to make use of them to build models for the macroscopic scale, with the help of homogenization techniques, and to calculate macroscopic quantities, say, for instance, elasticity constants. Besides their intrinsic interest, by addressing these natural questions, we also have in mind to validate a bit further our models.

Of course, beyond the mathematical analysis of the various equations

we may obtain, we also intend to give a sound ground to numerical computations based on them. We shall not develop further on the important question of the numerical aspects of the modeling of the solid phase, and we would rather refer the reader to Blanc [10].

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