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**A NEW APPROACH TO THE MODELING OF LOCAL DEFECTS
IN CRYSTALS:
THE REDUCED HARTREE-FOCK CASE**

ÉRIC CANCÈS, AMÉLIE DELEURENCE, AND MATHIEU LEWIN

ABSTRACT. This article is concerned with the derivation and the mathematical study of a new mean-field model for the description of interacting electrons in crystals with local defects. We work with a reduced Hartree-Fock model, obtained from the usual Hartree-Fock model by neglecting the exchange term.

First, we recall the definition of the self-consistent Fermi sea of the perfect crystal, which is obtained as a minimizer of some periodic problem, as was shown by Catto, Le Bris and Lions. We also prove some of its properties which were not mentioned before.

Then, we define and study in details a nonlinear model for the electrons of the crystal in the presence of a defect. We use formal analogies between the Fermi sea of a perturbed crystal and the Dirac sea in Quantum Electrodynamics in the presence of an external electrostatic field. The latter was recently studied by Hainzl, Lewin, Séré and Solovej, based on ideas from Chaix and Iracane. This enables us to define the ground state of the self-consistent Fermi sea in the presence of a defect.

We end the paper by proving that our model is in fact the thermodynamic limit of the so-called supercell model, widely used in numerical simulations.

Describing the electronic state of crystals with local defects is a major issue in solid-state physics, materials science and nano-electronics [25, 17, 33].

In this article, we develop a theory based on formal analogies between the Fermi sea of a perturbed crystal and the polarized Dirac sea in Quantum Electrodynamics in the presence of an external electrostatic field. Recently, the latter model was extensively studied by Hainzl, Lewin, Séré and Solovej in the Hartree-Fock approximation [10, 11, 13, 12], based on ideas from Chaix and Iracane [6] (see also [7, 1]). This was summarized in the review [14]. Using and adapting these methods, we are able to propose a new mathematical approach for the self-consistent description of a crystal in the presence of local defects.

We focus in this article on the *reduced Hartree-Fock* (rHF) model in which the so-called *exchange term* is neglected. To further simplify the mathematical formulas, we do not explicitly take the spin variable into account and we assume that the host crystal is cubic with a single atom of charge Z per unit cell. The arguments below can be easily extended to the general case.

In the whole paper, the main object of interest will be the so-called *density matrix* of the electrons. This is a self-adjoint operator $0 \leq \gamma \leq 1$ acting on the one-body space $L^2(\mathbb{R}^3)$. When γ has a finite rank, it models a finite number of electrons. In the periodic case, the ground state density matrix γ_{per}^0 has an infinite rank (it describes infinitely many electrons) and commutes with the translations of the lattice. We will see in the sequel that the ground state density matrix of a crystal with a local defect can be written as $\gamma = \gamma_{\text{per}}^0 + Q$, where Q is a compact perturbation of the periodic density matrix γ_{per}^0 of the reference perfect crystal.

In each of the above three cases (finite number of electrons, perfect crystal, defective crystal), the ground state density matrix can be obtained by minimizing some nonlinear energy functional depending on a set of admissible density matrices. In the case of a crystal with a local defect, the perturbation Q is a minimizer of some nonlinear minimization problem set in the whole space \mathbb{R}^3 , with a possible lack of compactness at infinity. The main unusual feature compared to standard variational problems is that Q is a self-adjoint operator of infinite rank. This was already the case in [10, 11, 12, 13].

The paper is organized as follows. In Section 1, we recall the definition of the reduced Hartree-Fock model for a *finite* number of electrons, which serves as a basis for the theories of infinitely many electrons in a (possibly perturbed) periodic nuclear distribution. Section 2 is devoted to the definition of the model for the infinite periodic crystal, following mainly [4, 5] (but we provide some additional material compared to what was done in [4, 5]). In Section 3, we define a model for the crystal with local defects which takes the perfect crystal as reference. In Section 4, we prove that this model is the thermodynamic limit of the supercell model.

For the convenience of the reader, we have gathered all the proofs in Section 5. Often, the proofs follow the same lines as those in [10, 11, 12, 13] and we shall not detail identical arguments. But there are many difficulties associated with the particular model under study which do not appear in previous works and which are addressed in details here.

1. THE REDUCED HARTREE-FOCK MODEL FOR N ELECTRONS

We start by recalling the definition of the reduced Hartree-Fock model [31] for a *finite* number of electrons. Note that the *reduced* Hartree-Fock model should not be confused with the *restricted* Hartree-Fock model commonly used in numerical simulations (see e.g. [8]). We consider a system containing N nonrelativistic quantum electrons and a set of nuclei having a density of charge ρ_{nuc} . If for instance there are K nuclei of charges $z_1, \dots, z_K \in \mathbb{N} \setminus \{0\}$ located at $R_1, \dots, R_K \in \mathbb{R}^3$, then

$$\rho_{\text{nuc}}(x) := \sum_{k=1}^K z_k m_k(x - R_k),$$

where m_1, \dots, m_K are positive measures on \mathbb{R}^3 of total mass one. Point-like nuclei would correspond to $m_k = \delta$ (the Dirac measure) but for convenience we shall deal with smeared nuclei in the sequel, i.e. we assume that for all $k = 1 \dots K$, m_k is a smooth nonnegative function such that $\int_{\mathbb{R}^3} m_k = 1$. The technical difficulties arising with point-like nuclei will be dealt with elsewhere.

The energy of the whole system in the reduced Hartree-Fock model reads [31, 5]

$$(1.1) \quad \mathcal{E}_{\rho_{\text{nuc}}}^{\text{rHF}}(\gamma) = \text{Tr} \left(-\frac{1}{2} \Delta \gamma \right) + \frac{1}{2} D(\rho_\gamma - \rho_{\text{nuc}}, \rho_\gamma - \rho_{\text{nuc}}).$$

We have chosen a system of units such that $\hbar = m = e = \frac{1}{4\pi\epsilon_0} = 1$ where m and e are respectively the mass and the charge of an electron, \hbar is the reduced Planck constant and ϵ_0 is the dielectric permittivity of the vacuum. The first term in the right-hand side of (1.1) is the kinetic energy of the electrons and $D(\cdot, \cdot)$ is the classical Coulomb interaction, which reads for f and g in $L^{6/5}(\mathbb{R}^3)$ as

$$(1.2) \quad D(f, g) = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f(x)g(y)}{|x-y|} dx dy = 4\pi \int_{\mathbb{R}^3} \frac{\widehat{f}(k)\widehat{g}(k)}{|k|^2} dk.$$

where \widehat{f} denotes the Fourier transform of f . In this mean-field model, the state of the N electrons is described by the one-body density matrix γ , which is an element of the following class

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

Here and below, $\mathcal{S}(\mathfrak{H})$ denotes the space of bounded self-adjoint operators acting on the Hilbert space \mathfrak{H} . Also we define $\operatorname{Tr}((-\Delta)\gamma) := \operatorname{Tr}(\sqrt{-\Delta}\gamma\sqrt{-\Delta})$ which makes sense when $\gamma \in \mathcal{P}^N$. The set \mathcal{P}^N is the closed convex hull of the set of orthogonal projectors of rank N acting on $L^2(\mathbb{R}^3)$ and having a finite kinetic energy. Each such projector $\gamma = \sum_{i=1}^N |\varphi_i\rangle\langle\varphi_i|$ is the density matrix of a Hartree-Fock state

$$(1.3) \quad \Psi = \varphi_1 \wedge \cdots \wedge \varphi_N$$

in the usual N -body space of fermionic wavefunctions with finite kinetic energy $\bigwedge_{i=1}^N H^1(\mathbb{R}^3)$.

The function ρ_γ appearing in (1.1) is the density associated with the operator γ , defined by $\rho_\gamma(x) = \gamma(x, x)$ where $\gamma(x, y)$ is the kernel of the trace class operator γ . Notice that for all $\gamma \in \mathcal{P}^N$, one has $\rho_\gamma \geq 0$ and $\sqrt{\rho_\gamma} \in H^1(\mathbb{R}^3)$, hence the last term of (1.1) is well-defined, since $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \subset L^{6/5}(\mathbb{R}^3)$.

It can be proved (see the appendix of [31]) that if $N \leq \sum_{k=1}^M z_k$ (neutral or positively charged systems), the variational problem

$$(1.4) \quad I_{\text{HF}}(\rho_{\text{nuc}}, N) = \inf \{ \mathcal{E}_{\rho_{\text{nuc}}}^{\text{rHF}}(\gamma), \quad \gamma \in \mathcal{P}^N \}$$

has a minimizer γ and that the corresponding minimizing density ρ_γ is unique.

The Hartree-Fock model [21] is the variational approximation of the time-independent Schrödinger equation obtained by restricting the set of fermionic wavefunctions under consideration to the subset of functions of the form (1.3). The HF functional reads

$$(1.5) \quad \mathcal{E}_{\rho_{\text{nuc}}}^{\text{HF}}(\gamma) = \mathcal{E}_{\rho_{\text{nuc}}}^{\text{rHF}}(\gamma) - \frac{1}{2} \iint_{\mathbb{R}^6} \frac{|\gamma(x, y)|^2}{|x - y|} dx dy,$$

the last term being called the *exchange energy*. As the Hartree-Fock energy functional is nonconvex, there is little hope to obtain rigorous thermodynamic limits in this setting, at least with current state-of-the-art techniques. For this reason, the exchange term is often neglected in mathematical studies.

2. THE REDUCED HARTREE-FOCK MODEL FOR A PERFECT CRYSTAL

In this article, we clamp the nuclei on a periodic lattice, optimizing only over the state of the electrons. More precisely we are interested in the change of the electronic state of the crystal when a local defect is introduced. To this end, we shall rely heavily on the rHF model for the infinite perfect crystal (with no defect) which was studied by Catto, Le Bris and Lions in [4, 5]. The latter can be obtained as the thermodynamical limit of the rHF model for finite systems which was introduced in the previous section. This will be explained in Section 4 below.

Let $\Gamma = [-1/2, 1/2]^3$ be the unit cell. We denote by $\Gamma^* = [-\pi, \pi]^3$ the first Brillouin zone of the lattice, and by τ_k the translation operator on $L_{\text{loc}}^2(\mathbb{R}^3)$ defined by $\tau_k u(x) = u(x - k)$. We then introduce

$$\mathcal{P}_{\text{per}} = \left\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 1, \forall k \in \mathbb{Z}^3, \tau_k \gamma = \gamma \tau_k, \right. \\ \left. \int_{\Gamma^*} \operatorname{Tr}_{L_\xi^2(\Gamma)}((1 - \Delta_\xi)^{1/2} \gamma_\xi (1 - \Delta_\xi)^{1/2}) d\xi < \infty \right\}$$

where $(\gamma_\xi)_{\xi \in \Gamma^*}$ is the Bloch waves decomposition of γ , see [27, 5]:

$$\gamma = \frac{1}{(2\pi)^3} \int_{\Gamma^*} \gamma_\xi d\xi, \quad \gamma_\xi \in \mathcal{S}(L_\xi^2(\Gamma)),$$

$$L_\xi^2(\Gamma) = \{u \in L_{\text{loc}}^2(\mathbb{R}^3) \mid \tau_k u = e^{-ik \cdot \xi} u, \forall k \in \mathbb{Z}^3\}$$

which corresponds to the decomposition in fibers $L^2(\mathbb{R}^3) = \int_{\Gamma^*}^\oplus L_\xi^2(\Gamma) d\xi$. For any $\gamma \in \mathcal{P}_{\text{per}}$, we denote by $\gamma_\xi(x, y)$ the integral kernel of γ_ξ . The density of γ is then the nonnegative \mathbb{Z}^3 -periodic function of $L_{\text{loc}}^1(\mathbb{R}^3) \cap L_{\text{loc}}^3(\mathbb{R}^3)$ defined as

$$\rho_\gamma(x) := \frac{1}{(2\pi)^3} \int_{\Gamma^*} \gamma_\xi(x, x) d\xi.$$

Notice that for any $\gamma \in \mathcal{P}_{\text{per}}$

$$\int_\Gamma \rho_\gamma(x) dx = \frac{1}{(2\pi)^3} \int_{\Gamma^*} \text{Tr}_{L_\xi^2(\Gamma)}(\gamma_\xi) d\xi,$$

i.e. this gives the number of electrons per unit cell. Later we shall add the constraint that the system is neutral and restrict to states $\gamma \in \mathcal{P}_{\text{per}}$ satisfying

$$\int_\Gamma \rho_\gamma(x) dx = Z$$

where Z is the total charge of the nuclei in each unit cell.

We also introduce the \mathbb{Z}^3 -periodic Green kernel of the Poisson interaction [22], denoted by G_1 and uniquely defined by

$$\begin{cases} -\Delta G_1 = 4\pi \left(\sum_{k \in \mathbb{Z}^3} \delta_k - 1 \right) \\ G_1 \text{ } \mathbb{Z}^3\text{-periodic, } \min_{\mathbb{R}^3} G_1 = 0. \end{cases}$$

The Fourier expansion of G_1 is

$$G_1(x) = c + \sum_{k \in 2\pi\mathbb{Z}^3 \setminus \{0\}} \frac{4\pi}{|k|^2} e^{ik \cdot x}$$

with $c = \int_\Gamma G_1 > 0$. The electrostatic potential associated with a \mathbb{Z}^3 -periodic density $\rho \in L_{\text{loc}}^1(\mathbb{R}^3) \cap L_{\text{loc}}^3(\mathbb{R}^3)$ is the \mathbb{Z}^3 -periodic function defined as

$$(\rho \star_\Gamma G_1)(x) := \int_\Gamma G_1(x - y) \rho(y) dy.$$

We also set for any \mathbb{Z}^3 -periodic functions f and g

$$D_{G_1}(f, g) := \int_\Gamma \int_\Gamma G_1(x - y) f(x) g(y) dx dy.$$

Throughout this article, we will denote by χ_I the characteristic function of the set $I \subset \mathbb{R}$ and by $\chi_I(A)$ the spectral projector on I of the self-adjoint operator A .

The periodic density of the nuclei is given by

$$(2.1) \quad \mu_{\text{per}}(x) = \sum_{R \in \mathbb{Z}^3} Z m(x - R).$$

We assume for simplicity that m is a nonnegative function of $C_c^\infty(\mathbb{R}^3)$ with support in Γ , and that $\int_{\mathbb{R}^3} m(x) dx = 1$. Hence $\int_\Gamma \mu_{\text{per}}(x) dx = Z$, the total charge of the nuclei in each unit cell. The periodic rHF energy is then defined for $\gamma \in \mathcal{P}_{\text{per}}$ as

$$(2.2) \quad \boxed{\mathcal{E}_{\text{per}}^0(\gamma) = \frac{1}{(2\pi)^3} \int_{\Gamma^*} \text{Tr}_{L_\xi^2(\Gamma)} \left(-\frac{1}{2} \Delta \gamma_\xi \right) + \frac{1}{2} D_{G_1}(\rho_\gamma - \mu_{\text{per}}, \rho_\gamma - \mu_{\text{per}})}.$$

Introducing

$$(2.3) \quad \mathcal{P}_{\text{per}}^Z := \left\{ \gamma \in \mathcal{P}_{\text{per}} \mid \int_{\Gamma} \rho_{\gamma} = Z \right\},$$

the periodic rHF ground state energy (per unit cell) is given by

$$(2.4) \quad \boxed{I_{\text{per}}^0 = \inf \{ \mathcal{E}_{\text{per}}^0(\gamma), \gamma \in \mathcal{P}_{\text{per}}^Z \}}.$$

It was proved by Catto, Le Bris and Lions in [5] that there exists a minimizer $\gamma_{\text{per}}^0 \in \mathcal{P}_{\text{per}}^Z$ to the minimization problem (2.4), and that all the minimizers of (2.4) share the same density $\rho_{\gamma_{\text{per}}^0}$. We give in Appendix A the proof of the following

Theorem 1 (Definition of the periodic rHF minimizer). *Let $Z \in \mathbb{N} \setminus \{0\}$. The minimization problem (2.4) admits a unique minimizer γ_{per}^0 . Denoting by*

$$(2.5) \quad H_{\text{per}}^0 := -\frac{\Delta}{2} + (\rho_{\gamma_{\text{per}}^0} - \mu_{\text{per}}) \star_{\Gamma} G_1,$$

the corresponding periodic mean-field Hamiltonian, γ_{per}^0 is solution to the self-consistent equation

$$(2.6) \quad \gamma_{\text{per}}^0 = \chi_{(-\infty, \epsilon_F]}(H_{\text{per}}^0),$$

where ϵ_F is a Lagrange multiplier called Fermi level, which can be interpreted as a chemical potential.

Additionally, for any $\epsilon_F \in \mathbb{R}$ such that (2.6) holds, γ_{per}^0 is the unique minimizer on \mathcal{P}_{per} of the energy functional

$$\gamma \mapsto \mathcal{E}_{\text{per}}^0(\gamma) - \epsilon_F \int_{\Gamma} \rho_{\gamma}.$$

Theorem 1 contains three main results that were not contained in [5]: first γ_{per}^0 is unique, second it is a projector, and third it satisfies Equation (2.6). These three properties are crucial for a proper construction of the model for the crystal with a defect.

It can easily be seen that $(\rho_{\gamma_{\text{per}}^0} - \mu_{\text{per}}) \star_{\Gamma} G_1$ belongs to $L_{\text{loc}}^2(\mathbb{R}^3)$. By a result of Thomas [34] this implies that the spectrum of H_{per}^0 is purely absolutely continuous. This is an essential property for the proof of the uniqueness of γ_{per}^0 . Let $(\lambda_n(\xi))_{n \geq 1}$ denote the nondecreasing sequence of the eigenvalues of $(H_{\text{per}}^0)_{\xi}$. Then

$$\sigma(H_{\text{per}}^0) = \bigcup_{n \geq 1} \lambda_n(\Gamma^*), \quad H_{\text{per}}^0 = \frac{1}{(2\pi)^3} \int_{\Gamma^*} (H_{\text{per}}^0)_{\xi} d\xi.$$

The projector γ_{per}^0 represents the state of the *Fermi sea*, i.e. of the infinite system of all the electrons in the periodic crystal. Of course, it is an infinite rank projector, meaning that

$$\gamma_{\text{per}}^0 = \sum_k |\varphi_k\rangle \langle \varphi_k|$$

should be interpreted as the one-body matrix of a formal infinite Slater determinant

$$\Psi = \varphi_1 \wedge \varphi_2 \wedge \cdots \wedge \varphi_k \wedge \cdots.$$

The fact that γ_{per}^0 is additionally a spectral projector associated with the continuous spectrum of an operator leads to the obvious analogy with the *Dirac sea* which is the projector on the negative spectral subspace of the Dirac operator [10, 11, 12, 13].

Most of our results will hold true for insulators (or semi-conductors) only. When necessary, we shall take $Z \in \mathbb{N} \setminus \{0\}$ and make the following assumption:

(A1) *There is a gap between the Z -th and the $(Z + 1)$ -st bands, i.e. $\Sigma_Z^+ < \Sigma_{Z+1}^-$, where Σ_Z^+ and Σ_{Z+1}^- are respectively the maximum and the minimum of the Z -th and the $(Z + 1)$ -st bands of H_{per}^0 .*

We emphasize that Assumption **(A1)** is a condition on the solution γ_{per}^0 of the *nonlinear* problem (2.4). Note that under **(A1)**, one has $\gamma_{\text{per}}^0 = \chi_{(-\infty, \epsilon_F]}(H_{\text{per}}^0)$ for any $\epsilon_F \in (\Sigma_Z^+, \Sigma_{Z+1}^-)$.

3. THE REDUCED HARTREE-FOCK MODEL FOR A CRYSTAL WITH A DEFECT

In this section, we define the reduced Hartree-Fock model describing the behavior of the Fermi sea and possibly of a finite number of bound electrons (or holes) close to a local defect. Our model is an obvious transposition of the Bogoliubov-Dirac-Fock model which was proposed by Chaix and Iracane [6] to describe the polarized Dirac sea (and a finite number of relativistic electrons) in the presence of an external potential. Our mathematical definition of the reduced energy functional follows mainly ideas from [10, 11]. We shall prove in Section 4 that this model can be obtained as the thermodynamic limit of the so-called supercell model. An analogous result was proved in [13] for the Bogoliubov-Dirac-Fock (BDF) model.

Assume that the periodic nuclear density μ_{per} defined in (2.1) is replaced by a locally perturbed nuclear density $\mu_{\text{per}} + \nu$. The defect ν can model a vacancy, an interstitial atom, or an impurity, with possible local rearrangement of the neighboring atoms. The main idea underlying the model is to define a *finite* energy by subtracting the *infinite* energy of the periodic Fermi sea γ_{per}^0 defined in the previous section, from the *infinite* energy of the perturbed system under consideration. For the BDF model, this was proposed first in [13]. Formally, one obtains for a test state γ

$$(3.1) \quad \mathcal{E}_{\mu_{\text{per}} + \nu}^{\text{rHF}}(\gamma) - \mathcal{E}_{\mu_{\text{per}} + \nu}^{\text{rHF}}(\gamma_{\text{per}}^0) \text{ “ = ” } \text{Tr}(H_{\text{per}}^0(\gamma - \gamma_{\text{per}}^0)) \\ - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\nu(x)\rho_{[\gamma - \gamma_{\text{per}}^0]}(y)}{|x - y|} dx dy + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{[\gamma - \gamma_{\text{per}}^0]}(x)\rho_{[\gamma - \gamma_{\text{per}}^0]}(y)}{|x - y|} dx dy.$$

Of course the two terms in the left-hand side of (3.1) are not well-defined because μ_{per} is periodic and because γ and γ_{per}^0 have infinite ranks, but we shall be able to give a mathematical meaning to the right-hand side, exploiting the fact that $Q := \gamma - \gamma_{\text{per}}^0$ induces a small perturbation of the reference state γ_{per}^0 . The formal computation (3.1) will be justified by means of thermodynamic limit arguments in Section 4.

3.1. Definition of the reduced Hartree-Fock energy of a defect. We now define properly the reduced Hartree-Fock energy of the Fermi sea in the presence of the defect ν . We denote by \mathfrak{S}_p the Schatten class of operators Q acting on $L^2(\mathbb{R}^3)$ having a finite p trace, i.e. such that $\text{Tr}(|Q|^p) < \infty$. Note that \mathfrak{S}_1 is the space of trace-class operators, and that \mathfrak{S}_2 is the space of Hilbert-Schmidt operators. Let Π be an orthogonal projector on $L^2(\mathbb{R}^3)$ such that both Π and $1 - \Pi$ have infinite ranks. A self-adjoint compact operator Q is said to be Π -trace class ($Q \in \mathfrak{S}_1^\Pi$) when $Q \in \mathfrak{S}_2$ and $\Pi Q \Pi, (1 - \Pi)Q(1 - \Pi) \in \mathfrak{S}_1$. Its Π -trace is then defined as $\text{Tr}_\Pi(Q) = \text{Tr}(\Pi Q \Pi + (1 - \Pi)Q(1 - \Pi))$. Notice that if $Q \in \mathfrak{S}_1$, then $Q \in \mathfrak{S}_1^\Pi$ for any Π and $\text{Tr}_\Pi(Q) = \text{Tr}(Q)$. See [10, Section 2.1] for general properties related to this definition. In the following, we use the shorthand notation

$$Q^{--} := \gamma_{\text{per}}^0 Q \gamma_{\text{per}}^0, \quad Q^{++} := (1 - \gamma_{\text{per}}^0) Q (1 - \gamma_{\text{per}}^0),$$

$$\mathfrak{S}_1^0 := \mathfrak{S}_1^{\gamma_{\text{per}}^0} = \{Q \in \mathfrak{S}_2 \mid Q^{++} \in \mathfrak{S}_1, Q^{--} \in \mathfrak{S}_1\} \quad \text{and} \quad \text{Tr}_0(Q) := \text{Tr}_{\gamma_{\text{per}}^0}(Q).$$

We also introduce the Banach space

$$\mathcal{Q} = \{Q \in \mathfrak{S}_1^0 \mid Q^* = Q, |\nabla|Q \in \mathfrak{S}_2, |\nabla|Q^{++}|\nabla| \in \mathfrak{S}_1, |\nabla|Q^{--}|\nabla| \in \mathfrak{S}_1\},$$

endowed with its natural norm

$$(3.2) \quad \|Q\|_{\mathcal{Q}} := \|Q\|_{\mathfrak{S}_2} + \|Q^{++}\|_{\mathfrak{S}_1} + \|Q^{--}\|_{\mathfrak{S}_1} \\ + \| |\nabla|Q \|_{\mathfrak{S}_2} + \| |\nabla|Q^{++}|\nabla| \|_{\mathfrak{S}_1} + \| |\nabla|Q^{--}|\nabla| \|_{\mathfrak{S}_1}.$$

The convex set on which the energy will be defined is

$$(3.3) \quad \mathcal{K} := \{Q \in \mathcal{Q} \mid -\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0\}.$$

Notice that \mathcal{K} is the closed convex hull of states $Q \in \mathcal{Q}$ of the special form $Q = \gamma - \gamma_{\text{per}}^0$, γ being an orthogonal projector on $L^2(\mathbb{R}^3)$. Besides, the number $\text{Tr}_0(Q)$ can be interpreted as the charge of the system measured with respect to that of the unperturbed Fermi sea. It can be proved [10, Lemma 2] that $\text{Tr}_0(Q)$ is always an integer if Q is a Hilbert-Schmidt operator of the special form $Q = \gamma - \gamma_{\text{per}}^0$, with γ an orthogonal projector. Additionally, in this case, $\text{Tr}_0(Q) = 0$ when $\|Q\| < 1$.

Note that the constraint $-\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0$ in (3.3) is equivalent [1, 10] to the inequality

$$(3.4) \quad Q^2 \leq Q^{++} - Q^{--}$$

and implies in particular that $Q^{++} \geq 0$ and $Q^{--} \leq 0$ for any $Q \in \mathcal{K}$.

In order to define properly the energy of Q , we need to associate a density ρ_Q with any state $Q \in \mathcal{K}$. We shall see that ρ_Q can in fact be defined for any $Q \in \mathcal{Q}$. This is not obvious *a priori* since \mathcal{Q} does not only contain trace-class operators. Additionally we need to check that the last two terms of (3.1) are well-defined. For this purpose, we introduce the so-called Coulomb space

$$\mathcal{C} := \{\rho \in \mathcal{S}'(\mathbb{R}^3) \mid D(\rho, \rho) < \infty\}$$

where $D(f, g) = 4\pi \int_{\mathbb{R}^3} |k|^{-2} \overline{\widehat{f}(k)} \widehat{g}(k) dk$ was already defined before in (1.2). The dual space of \mathcal{C} is the Beppo-Levi space $\mathcal{C}' := \{V \in L^6(\mathbb{R}^3) \mid \nabla V \in L^2(\mathbb{R}^3)\}$. We now use a duality argument to define ρ_Q :

Proposition 1 (Definition of the density ρ_Q for $Q \in \mathcal{Q}$). *Assume that $Q \in \mathcal{Q}$. Then $QV \in \mathfrak{S}_1^0$ for any $V = V_1 + V_2 \in \mathcal{C}' + (L^2(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3))$ and moreover there exists a constant C (independent of Q and V) such that*

$$|\text{Tr}_0(QV)| \leq C \|Q\|_{\mathcal{Q}} (\|V_1\|_{\mathcal{C}'} + \|V_2\|_{L^2(\mathbb{R}^3)}).$$

Thus the linear form $V \in \mathcal{C}' + (L^2(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)) \mapsto \text{Tr}_0(QV)$ can be continuously extended to $\mathcal{C}' + L^2(\mathbb{R}^3)$ and there exists a uniquely defined function $\rho_Q \in \mathcal{C} \cap L^2(\mathbb{R}^3)$ such that

$$\forall V = V_1 + V_2 \in \mathcal{C}' + (L^2(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)), \quad \langle \rho_Q, V_1 \rangle_{\mathcal{C}, \mathcal{C}'} + \int_{\mathbb{R}^3} \rho_Q V_2 = \text{Tr}_0(QV).$$

The linear map $Q \in \mathcal{Q} \mapsto \rho_Q \in \mathcal{C} \cap L^2(\mathbb{R}^3)$ is continuous:

$$\|\rho_Q\|_{\mathcal{C}} + \|\rho_Q\|_{L^2(\mathbb{R}^3)} \leq C \|Q\|_{\mathcal{Q}}.$$

Eventually when $Q \in \mathfrak{S}_1 \subset \mathfrak{S}_1^0$, then $\rho_Q(x) = Q(x, x)$ where $Q(x, y)$ is the integral kernel of Q .

The proof of Proposition 1 is given in Section 5.2.

Assuming that **(A1)** holds true, we are now in a position to give a rigorous sense to the right-hand side of (3.1) for $\gamma - \gamma_{\text{per}}^0 = Q \in \mathcal{K}$. In the sequel, we use the following *notation* for any $Q \in \mathcal{Q}$:

$$(3.5) \quad \text{Tr}_0(H_{\text{per}}^0 Q) := \text{Tr}(|H_{\text{per}}^0 - \kappa|^{1/2} (Q^{++} - Q^{--}) |H_{\text{per}}^0 - \kappa|^{1/2}) + \kappa \text{Tr}_0(Q)$$

where κ is an arbitrary real number in the gap $(\Sigma_Z^+, \Sigma_{Z+1}^-)$ (this expression will be proved to be independent of κ , see Corollary 1 below). Then we define the energy of any state $Q \in \mathcal{K}$ as

$$(3.6) \quad \mathcal{E}^\nu(Q) := \text{Tr}_0(H_{\text{per}}^0 Q) - D(\rho_Q, \nu) + \frac{1}{2}D(\rho_Q, \rho_Q).$$

The function ν is an external density of charge representing the nuclear charge of the defect. For the sake of simplicity, we shall assume that $\nu \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3) \subset \mathcal{C}$ throughout the paper, although some of our results are true with a weaker assumption. We shall need the following

Lemma 1. *Assume that (A1) holds true. For any fixed κ in the gap $(\Sigma_Z^+, \Sigma_{Z+1}^-)$, there exist two constants $c_1, c_2 > 0$ such that*

$$(3.7) \quad c_1(1 - \Delta) \leq |H_{\text{per}}^0 - \kappa| \leq c_2(1 - \Delta)$$

as operators on $L^2(\mathbb{R}^3)$. In particular

$$\left\| |H_{\text{per}}^0 - \kappa|^{1/2}(1 - \Delta)^{-1/2} \right\| \leq \sqrt{c_2}, \quad \left\| |H_{\text{per}}^0 - \kappa|^{-1/2}(1 - \Delta)^{1/2} \right\| \leq 1/\sqrt{c_1}.$$

Similarly, $(H_{\text{per}}^0 - \kappa)(1 - \Delta)^{-1}$ and its inverse are bounded operators.

The proof of the above lemma is elementary; it will be given in Section 5.1.1. By the definition of \mathcal{Q} and Lemma 1, it is clear that the right-hand side of (3.5) is a well-defined quantity for any $Q \in \mathcal{Q}$ and any $\kappa \in (\Sigma_Z^+, \Sigma_{Z+1}^-)$. By Proposition 1 which states that $\rho_Q \in \mathcal{C}$ for any $Q \in \mathcal{Q}$, we deduce that (3.6) is a well-defined functional.

We shall need the following space of more regular operators

$$(3.8) \quad \mathcal{Q}_r := \{Q \in \mathcal{Q} \mid (-\Delta)Q^2(-\Delta) \in \mathfrak{S}_1, (-\Delta)(Q^{++} - Q^{--})(-\Delta) \in \mathfrak{S}_1\}$$

and the associated convex set

$$\mathcal{K}_r := \mathcal{K} \cap \mathcal{Q}_r.$$

The following result will be useful (its proof will be given below in Section 5.3):

Lemma 2. *The space \mathcal{Q}_r (resp. the convex set \mathcal{K}_r) is dense in \mathcal{Q} (resp. in \mathcal{K}) for the topology of \mathcal{Q} .*

Corollary 1. *Assume that (A1) holds true. When $Q \in \mathcal{Q}_r$, then $H_{\text{per}}^0 Q \in \mathfrak{S}_1^0$. For any $Q \in \mathcal{Q}$, the expression (3.5) for $\text{Tr}_0(H_{\text{per}}^0 Q)$ does not depend on $\kappa \in (\Sigma_Z^+, \Sigma_{Z+1}^-)$. If $Q \in \mathcal{K}$, then*

$$(3.9) \quad \begin{aligned} 0 &\leq c_1 \text{Tr}((1 - \Delta)^{1/2} Q^2 (1 - \Delta)^{1/2}) \\ &\leq c_1 \text{Tr}((1 - \Delta)^{1/2} (Q^{++} - Q^{--}) (1 - \Delta)^{1/2}) \\ &\leq \text{Tr}_0(H_{\text{per}}^0 Q) - \kappa \text{Tr}_0(Q) \\ &\leq c_2 \text{Tr}((1 - \Delta)^{1/2} (Q^{++} - Q^{--}) (1 - \Delta)^{1/2}) \end{aligned}$$

where c_1 and c_2 are given by Lemma 1.

Proof. Let $Q \in \mathcal{Q}_r$ and $\kappa \in (\Sigma_Z^+, \Sigma_{Z+1}^-)$. Then $((H_{\text{per}}^0 - \kappa)Q)^{++} = |H_{\text{per}}^0 - \kappa|Q^{++} = |H_{\text{per}}^0 - \kappa|(1 - \Delta)^{-1}(1 - \Delta)Q^{++} \in \mathfrak{S}_1$ by Lemma 1 and the definition of \mathcal{Q}_r . A similar argument for $((H_{\text{per}}^0 - \kappa)Q)^{--}$ proves that $H_{\text{per}}^0 Q \in \mathfrak{S}_1^0$. Then for any $Q \in \mathcal{Q}_r$, (3.9) is a straightforward consequence of (3.7) and (3.4). We conclude using the density of \mathcal{Q}_r in \mathcal{Q} and the density of \mathcal{K}_r in \mathcal{K} . \square

The following is an adaptation of [10, Thm 1]:

Corollary 2. *Let $\nu \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$, $Z \in \mathbb{N} \setminus \{0\}$ and assume that **(A1)** holds. For any $\kappa \in (\Sigma_Z^+, \Sigma_{Z+1}^-)$, one has for some $d_1, d_2 > 0$*

$$(3.10) \quad \forall Q \in \mathcal{K}, \quad \mathcal{E}^\nu(Q) - \kappa \text{Tr}_0(Q) \geq d_1 \left(\|Q^{++}\|_{\mathfrak{S}_1} + \|Q^{--}\|_{\mathfrak{S}_1} \right. \\ \left. + \|\nabla|Q^{++}| \nabla\|_{\mathfrak{S}_1} + \|\nabla|Q^{--}| \nabla\|_{\mathfrak{S}_1} \right) + d_2 \left(\|Q\|_{\mathfrak{S}_2}^2 + \|\nabla|Q\|_{\mathfrak{S}_2}^2 \right) - \frac{1}{2}D(\nu, \nu)$$

Hence $\mathcal{E}^\nu - \kappa \text{Tr}_0$ is bounded from below and coercive on \mathcal{K} . Additionally, when $\nu \equiv 0$, $Q \mapsto \mathcal{E}^0(Q) - \kappa \text{Tr}_0(Q)$ is nonnegative, 0 being its unique minimizer.

Proof. Inequality (3.10) is a straightforward consequence of (3.9) and the fact that $D(\cdot, \cdot)$ defines a scalar product on \mathcal{C} . The rest of the proof is obvious. \square

Remark 1. The energy $\mathcal{E}^\nu(Q)$ measures the energy of a state $\gamma = \gamma_{\text{per}}^0 + Q$ with respect to that of γ_{per}^0 . Thus the last statement of Corollary 2 is another way of expressing the fact that γ_{per}^0 is the state of lowest energy of the periodic system when there is no defect.

3.2. Existence of minimizers with a chemical potential. In view of Corollary 2, it is natural to introduce the following minimization problem

$$(3.11) \quad \boxed{E_{\epsilon_F}^\nu := \inf\{\mathcal{E}^\nu(Q) - \epsilon_F \text{Tr}_0(Q), Q \in \mathcal{K}\} > -\infty}$$

for any Fermi level $\epsilon_F \in (\Sigma_Z^+, \Sigma_{Z+1}^-)$. The following result is proved in Section 5.5, following ideas from [11]:

Theorem 2 (Existence of minimizers with a chemical potential). *Let $\nu \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3)$, $Z \in \mathbb{N} \setminus \{0\}$ and assume that **(A1)** holds. Then for any $\epsilon_F \in (\Sigma_Z^+, \Sigma_{Z+1}^-)$, there exists a minimizer $\bar{Q} \in \mathcal{K}$ for (3.11). Problem (3.11) may have several minimizers, but they all share the same density $\bar{\rho} = \rho_{\bar{Q}}$. Any minimizer \bar{Q} of (3.11) satisfies the self-consistent equation*

$$(3.12) \quad \begin{cases} \bar{Q} = \chi_{(-\infty, \epsilon_F)}(H_{\bar{Q}}) - \gamma_{\text{per}}^0 + \delta, \\ H_{\bar{Q}} = H_{\text{per}}^0 + (\rho_{\bar{Q}} - \nu) * |\cdot|^{-1} \end{cases}$$

where δ is a finite rank self-adjoint operator satisfying $0 \leq \delta \leq 1$ and $\text{Ran}(\delta) \subseteq \ker(H_{\bar{Q}} - \epsilon_F)$.

Remark 2. It is easily seen that $(\rho_{\bar{Q}} - \nu) * |\cdot|^{-1}$ is a compact perturbation of H_{per}^0 , implying that $H_{\bar{Q}}$ is self-adjoint on $\mathcal{D}(H_{\text{per}}^0) = \mathcal{D}(-\Delta) = H^2(\mathbb{R}^3)$ and that $\sigma_{\text{ess}}(H_{\bar{Q}}) = \sigma(H_{\text{per}}^0)$. Thus the discrete spectrum of $H_{\bar{Q}}$ is composed of isolated eigenvalues of finite multiplicity, possibly accumulating at the ends of the bands.

Recall that the charge of the minimizing state \bar{Q} obtained in Theorem 2 is defined as $\text{Tr}_0(\bar{Q})$. Similarly to [10, 11], it can be proved by perturbation theory that for any fixed ϵ_F , there exists a constant $C(\epsilon_F)$ such that when $D(\nu, \nu) \leq C(\epsilon_F)$, one has $\ker(H_{\bar{Q}} - \epsilon_F) = \{0\}$ and $\text{Tr}_0(\bar{Q}) = 0$, i.e. the minimizer of the energy with chemical potential ϵ_F is a neutral perturbation of the periodic Fermi sea.

For a fixed external density ν and an adequately chosen chemical potential ϵ_F , one can have $\text{Tr}_0(\bar{Q}) \neq 0$ meaning either that electron-hole pairs have been created from the Fermi sea, and/or that the system of lowest energy contains a finite number of bound electrons or holes close to the defect. In the applications, one will usually have for a positively charged nuclear defect ($\nu \geq 0$) that the spectrum of $H_{\bar{Q}}$ contains a sequence of eigenvalues converging to the bottom Σ_{Z+1}^- of the lowest unfilled band (conduction band), and that ϵ_F is chosen such that exactly q eigenvalues are filled, corresponding to q bound electrons:

$$(3.13) \quad \bar{Q} = (\chi_{(-\infty, \Sigma)}(H_{\bar{Q}}) - \gamma_{\text{per}}^0) + (\chi_{[\Sigma, \epsilon_F)}(H_{\bar{Q}}) + \delta) := Q_{\text{pol}} + \gamma_{e^-},$$