Non-perturbative embedding of local defects in crystalline materials

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Abstract
We present a new variational model for computing the electronic first-order density matrix of a
crystalline material in the presence of a local defect. A natural way to obtain variational
discretizations of this model is to expand the difference Q between the density matrix of the
defective crystal and the density matrix of the perfect crystal, in a basis of precomputed
maximally localized Wannier functions of the reference perfect crystal. This approach can be
used within any semi-empirical or density functional theory framework.

(Some figures in this article are in colour only in the electronic version)

Describing the electronic state of crystals with local defects is a major issue in solid-state physics, materials science and nano-electronics [1–3]. The first self-consistent electronic structure calculations for defective crystals were performed in the late 1970s, by means of nonlinear Green function methods [4–6]. In the 1990s, it became possible to solve the Kohn–Sham equations [7] for systems with several hundred electrons, and Green function methods were superseded by supercell methods [8, 9]. However, supercell methods have several drawbacks. First, the defect interacts with its periodic images. Second, the supercell must have a neutral total charge, so that in the simulation of charged defects an artificial charge distribution (a jellium for instance) needs to be introduced to counterbalance the charge of the defect. These two drawbacks may lead to large, uncontrolled errors in the estimation of the energy of the defect. In practice, ad hoc correction terms are introduced to account for these errors [10]. A refinement of the supercell approach, based on a more careful treatment of the Coulomb interaction, has also been proposed in [11].

In a recent article [12] we used rigorous thermodynamic limit arguments to derive a variational model allowing us to directly compute the modification of the electronic first-order density matrix generated by a (neutral or charged) local defect, when the host crystal is an insulator (or a semiconductor). This model has a structure similar to the Chaix–Iracane model in quantum electrodynamics [13, 14]. This similarity originates from formal analogies between the Fermi sea of a defective crystal and the Dirac sea in the presence of atomic nuclei. For technical reasons, the reference model considered in [12] was the reduced Hartree–Fock model, or in other words a Kohn–Sham model with fractional occupancies and exchange–correlation energy set to zero.

The purpose of the present paper is twofold. First, the extension of our model to a generic exchange–correlation functional is discussed. Second, a rigorous justification of the numerical method consisting in expanding the difference between the density matrix of the defective crystal and the density matrix of the perfect crystal, in a basis of well-chosen Wannier functions of the reference perfect crystal, is provided: this method can be seen as a variational approximation of our model.

1. Derivation of the model

We consider a generic Kohn–Sham model (or rather a generic *extended* Kohn–Sham model in which fractional occupancies are allowed) with exchange–correlation energy functional $E^{xc}(\rho)$. For the sake of simplicity, we omit the spin variable. The ground state of a molecular system with nuclear charge density ρ^{nuc} and $\mathcal{N}$ electrons is obtained by solving

$$\inf \left\{ E^{KS}_{\rho^{nuc}}(\gamma), 0 \leqslant \gamma \leqslant 1, \mathrm{Tr}(\gamma) = \mathcal{N} \right\}, \tag{1}$$
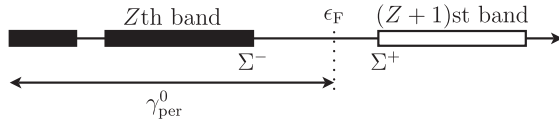
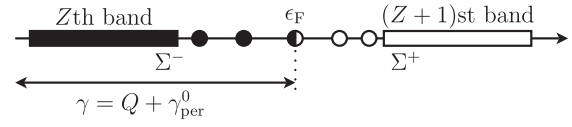**Figure 1.** Spectrum of H_{per}^0.

Figure 2. Spectrum of H_Q.

$$E_{\rho^{\text{nuc}}}^{\text{KS}}(\gamma) = \text{Tr}(-\tfrac{1}{2}\Delta\gamma) - D(\rho^{\text{nuc}}, \rho_\gamma)$$
$$+ \tfrac{1}{2}D(\rho_\gamma, \rho_\gamma) + E^{\text{xc}}(\rho_\gamma), \qquad (2)$$

where $\rho_\gamma(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$ and where

$$D(f, g) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{f(\mathbf{r})g(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'$$

is the Coulomb interaction. Still for simplicity, we detail the case of the Xα exchange–correlation functional

$$E^{\text{xc}}(\rho) = -C_{\text{X}\alpha}\int_{\mathbb{R}^3} \rho^{4/3},$$

the extension to more accurate LDA functionals being straightforward. Likewise, replacing the all-electron model considered here with a valence electron model with pseudopotentials does not cause any additional difficulty.

The above model describes a *finite* system of $\mathcal{N}$ electrons in the electrostatic field created by the density ρ^{nuc}. Our goal is to describe an *infinite* crystalline material obtained in the thermodynamic limit $\mathcal{N} \to \infty$. In fact we shall consider two such systems. The first one is the periodic crystal obtained when, in the thermodynamic limit, the nuclear density approaches the periodic nuclear distribution of the perfect crystal:

$$\rho^{\text{nuc}} \to \rho_{\text{per}}^{\text{nuc}}, \qquad (3)$$

$\rho_{\text{per}}^{\text{nuc}}$ being a periodic distribution. The second system is the previous crystal in the presence of a local defect:

$$\rho^{\text{nuc}} \to \rho_{\text{per}}^{\text{nuc}} + \nu. \qquad (4)$$

Typically, ν describes nuclear vacancies, interstitial nuclei, or impurities together with possible local rearrangement of the nuclei of the host crystal in the vicinity of the defect. In the simple case of a reference perfect crystal with a single atom per unit cell

$$\rho_{\text{per}}^{\text{nuc}} = \sum_{\mathbf{R}\in\mathcal{R}} z\delta_{\mathbf{R}}$$

where $\mathcal{R}$ is the Bravais lattice of the host crystal and $\delta_{\mathbf{R}}$ is the Dirac delta measure at $\mathbf{R}$. If the defect consists of an impurity (the nucleus of charge z at $\mathbf{R} = \mathbf{0}$ being replaced with a nucleus of charge z'), the charge distribution ν reads

$$\nu = z'\delta_{\mathbf{U}(\mathbf{0})} - z\delta_{\mathbf{0}} + \sum_{\mathbf{R}\in\mathcal{R}\setminus\{0\}} z\left(\delta_{\mathbf{R}+\mathbf{U}(\mathbf{R})} - \delta_{\mathbf{R}}\right),$$

where $\mathbf{U}$ is the displacement field of the nuclei generated by the relaxation of the crystal. It is therefore composed of nuclei of positive charges and of 'ghost nuclei' of negative charges. In this paper we assume that ν is given, and we focus on the calculation of the electronic density matrix.

The form of the density matrix γ_{per}^0 of the *perfect crystal* obtained in the thermodynamic limit (3) is well known. The matrix γ_{per}^0 is a solution to the self-consistent equation

$$\gamma_{\text{per}}^0 = \chi_{(-\infty;\epsilon_F]}(H_{\text{per}}^0) \qquad (5)$$

$$H_{\text{per}}^0 = -\tfrac{1}{2}\Delta + \Phi_{\text{per}} - \tfrac{4}{3}C_{\text{X}\alpha}\rho_{\text{per}}^{0\,1/3}, \qquad (6)$$

$$-\Delta\Phi_{\text{per}} = 4\pi\left(\rho_{\text{per}}^0 - \rho_{\text{per}}^{\text{nuc}}\right), \qquad \Phi_{\text{per}}\ \mathcal{R}\text{-periodic}.$$

The notation $P = \chi_{(-\infty;\epsilon_F]}(A)$ means that P is the spectral orthogonal projector of the self-adjoint operator A corresponding to filling all the energies up to the Fermi level ϵ_F (see for instance [15]). In our case, (5) means that γ_{per}^0 is the spectral projector which fills all the energies of H_{per}^0 up to the Fermi level ϵ_F (see figure 1).

The density of the periodic Fermi sea is $\rho_{\text{per}}^0(\mathbf{r}) = \gamma_{\text{per}}^0(\mathbf{r}, \mathbf{r})$. Note that the system is locally neutral:

$$\int_\Omega \rho_{\text{per}}^0 = \int_\Omega \rho_{\text{per}}^{\text{nuc}},$$

where Ω is a reference unit cell, the Fermi level ϵ_F being chosen to ensure this equality. For the rest of the paper we assume that the host crystal is an insulator (or a semiconductor), i.e. that there is a gap $g = \Sigma^+ - \Sigma^- > 0$ between the highest occupied and the lowest virtual bands. Then the Fermi level can be any number $\Sigma^- \leqslant \epsilon_F < \Sigma^+$.

Now we consider the system obtained in the thermodynamic limit (4) when there is a defect ν and derive a nonlinear variational model for it. We shall describe the variations of the Fermi sea with respect to the periodic state γ_{per}^0. The relevant variable therefore is

$$Q = \gamma - \gamma_{\text{per}}^0$$

where γ is the density matrix of the defective Fermi sea. Notice that the constraint that γ is a density matrix ($0 \leqslant \gamma \leqslant 1$) translates into $-\gamma_{\text{per}}^0 \leqslant Q \leqslant 1 - \gamma_{\text{per}}^0$ for the new variable Q.

The energy of Q is by definition the difference of two infinite quantities: the energy of the state γ and the energy of the periodic Fermi sea γ_{per}^0. Using (2), one obtains:

$$\mathcal{E}^\nu(Q) = \text{Tr}(H_{\text{per}}^0 Q) - D(\nu, \rho_Q) + \tfrac{1}{2}D(\rho_Q, \rho_Q)$$
$$+ \epsilon^{\text{xc}}(\rho_Q) \qquad (7)$$

where

$$\epsilon^{\text{xc}}(\rho_Q) = -C_{\text{X}\alpha}\int_{\mathbb{R}^3} (\rho_{\text{per}}^0 + \rho_Q)^{4/3} - \rho_{\text{per}}^{0\,4/3} - \tfrac{4}{3}\rho_{\text{per}}^{0\,1/3}\rho_Q.$$

If we want to describe a defective crystal of electronic charge q (q electrons in excess with respect to the perfect

crystal if $q > 0$, or $-q$ holes if $q < 0$ interacting with the self-consistent Fermi sea in the presence of the defect, we have to consider the minimization principle

$$E^\nu(q) = \inf\{\mathcal{E}^\nu(Q), -\gamma_{\mathrm{per}}^0 \leqslant Q \leqslant 1 - \gamma_{\mathrm{per}}^0, \mathrm{Tr}(Q) = q\}. \quad (8)$$

We obtain in this way a model which apparently renders possible the direct calculation of the defective Fermi sea in the presence of the nuclear charge defect ν, when q electrons (or $-q$ holes) are trapped by the defect. A globally neutral system would correspond to $q = \int_{\mathbb{R}^3} \nu$ but there is no obstacle in applying (8) to charged defects.

Alternatively, one can, instead of imposing *a priori* the total charge q of the system (microcanonical viewpoint), rather fix the Fermi level $\epsilon_F \in (\Sigma^-, \Sigma^+)$ (grand-canonical viewpoint). This amounts to considering the Legendre transform of (8):

$$E^\nu_{\epsilon_F} = \inf\{\mathcal{E}^\nu(Q) - \epsilon_F \mathrm{Tr}(Q), -\gamma_{\mathrm{per}}^0 \leqslant Q \leqslant 1 - \gamma_{\mathrm{per}}^0\}. \quad (9)$$

Any solution of (8) or (9) satisfies the SCF equation

$$Q = \chi_{(-\infty,\epsilon_F)}(H_Q) - \gamma_{\mathrm{per}}^0 + \delta, \quad (10)$$

where

$$H_Q = -\frac{\Delta}{2} + \Phi_{\mathrm{per}} + (\rho_Q - \nu) * \frac{1}{|x|}$$
$$- \frac{4}{3} C_{X\alpha}(\rho_{\mathrm{per}}^0 + \rho_Q)^{1/3}$$

and where $0 \leqslant \delta \leqslant 1$ is a finite-rank self-adjoint operator on $L^2(\mathbb{R}^3)$ such that $\mathrm{Ran}(\delta) \subset \mathrm{Ker}(H_Q - \epsilon_F)$. In the case of (8), the Fermi level ϵ_F is the Lagrange multiplier associated with the constraint $\mathrm{Tr}(Q) = q$. The essential spectrum of H_Q is the same as that of H_{per}^0 and is therefore composed of bands. On the other hand, the discrete spectrum of H_{per}^0 is empty, while the discrete spectrum of H_Q may contain isolated eigenvalues of finite multiplicities located below the essential spectrum and between the bands (see figure 2). Each filled (or unfilled) eigenvalue may correspond to electrons (or holes) which are trapped by the defect.

The SCF equation (10) is equivalent to the usual Dyson equation, which is at the basis of Green function methods.

2. Proper definition of the variational set

The variational models (8) and (9) may look similar to the usual Kohn–Sham models for molecules and perfect crystals. Their mathematical structure is, however, dramatically more complex. To design consistent numerical methods for solving (8) and (9), a deeper understanding of the mathematical setting is needed.

The biggest issue with problems (8) and (9) is to properly define the variational set, that is the set of all Qs on which one has to minimize the energy functional $\mathcal{E}^\nu(Q)$ or the free energy functional $\mathcal{E}^\nu(Q) - \epsilon_F \mathrm{Tr}(Q)$. For the usual Kohn–Sham models, the variational set is very simple: it is the largest set of density matrices for which each term of the energy functional is a well-defined number and the constraints are satisfied. This is the reason why it is not a problem to omit the precise definition

of the variational set when dealing with the usual Kohn–Sham models. For instance, the variational set for (1) is

$$\{\gamma | 0 \leqslant \gamma \leqslant 1, \mathrm{Tr}(\gamma) = \mathcal{N}, \mathrm{Tr}(|\nabla|\gamma|\nabla|) < \infty\}. \quad (11)$$

Let us recall (see [15] for instance) that if B is a non-negative self-adjoint operator on $L^2(\mathbb{R}^3)$ and if $(\psi_i)_{i\in\mathbb{N}}$ is an orthonormal basis of $L^2(\mathbb{R}^3)$, the series of non-negative numbers $\sum_{i=0}^{+\infty} \langle\psi_i|B|\psi_i\rangle$ converges in $\mathbb{R}_+ \cup \{+\infty\}$ towards a limit denoted by $\mathrm{Tr}(B)$, which does not depend on the chosen basis. The operator B is said to be trace-class if $\mathrm{Tr}(B) < \infty$. A bounded operator A on $L^2(\mathbb{R}^3)$ is trace-class if $\sqrt{A^*A}$ is trace-class. In this case, the scalar $\mathrm{Tr}(A) = \sum_{i=0}^{+\infty} \langle\psi_i|A|\psi_i\rangle$ is well-defined and does not depend on the chosen basis. On the other hand, if A is not trace-class, the series $\sum_{i=0}^{+\infty} \langle\psi_i|A|\psi_i\rangle$ may converge for one specific basis and diverge (or converge to a different limit) in another basis.

The condition $\mathrm{Tr}(|\nabla|\gamma|\nabla|) < \infty$ in (11) is a necessary and sufficient condition for each term of (2) being well-defined. In terms of Kohn–Sham orbitals, this condition means that each orbital ϕ_i is in the Sobolev space $H^1(\mathbb{R}^3) = \{\phi \in L^2(\mathbb{R}^3)|\nabla\phi \in (L^2(\mathbb{R}^3))^3\}$.

The difficulty with the variational models (8) and (9) is that the variational set does not have such a simple structure. It was shown in [12] that an appropriate variational set is the convex set

$$\mathcal{K} = \big\{Q| -\gamma_{\mathrm{per}}^0 \leqslant Q \leqslant 1 - \gamma_{\mathrm{per}}^0, \mathrm{Tr}(1 + |\nabla|)Q^2(1 + |\nabla|)$$
$$+ \mathrm{Tr}(1 + |\nabla|)(Q^{++} - Q^{--})(1 + |\nabla|) < \infty\big\}.$$

In the above expression, we have used the notation

$$Q = \left(\begin{array}{c|c} Q^{--} & Q^{-+} \\ \hline Q^{+-} & Q^{++} \end{array}\right)$$

with

$$Q^{--} = \gamma_{\mathrm{per}}^0 Q \gamma_{\mathrm{per}}^0, \qquad Q^{-+} = \gamma_{\mathrm{per}}^0 Q(1 - \gamma_{\mathrm{per}}^0),$$

$$Q^{+-} = (1 - \gamma_{\mathrm{per}}^0)Q\gamma_{\mathrm{per}}^0, \qquad Q^{++} = (1 - \gamma_{\mathrm{per}}^0)Q(1 - \gamma_{\mathrm{per}}^0),$$

corresponding to the decomposition

$$L^2(\mathbb{R}^3) = \mathcal{H}_- \oplus \mathcal{H}_+, \quad (12)$$

where $\mathcal{H}_- = \gamma_{\mathrm{per}}^0 L^2(\mathbb{R}^3)$ and $\mathcal{H}_+ = (1 - \gamma_{\mathrm{per}}^0)L^2(\mathbb{R}^3)$ are, respectively, the occupied and virtual spaces of the reference perfect crystal.

Notice that when Q satisfies the constraint $-\gamma_{\mathrm{per}}^0 \leqslant Q \leqslant 1 - \gamma_{\mathrm{per}}^0$, one has $Q^{++} \geqslant 0$ and $Q^{--} \leqslant 0$. A remarkable point, proved in [12], is that the density ρ_Q of any operator $Q \in \mathcal{K}$ is a well-defined function which satisfies

$$\int_{\mathbb{R}^3} \rho_Q^2 + D(\rho_Q, \rho_Q) < \infty.$$

This shows that the electrostatic components of the energy $\mathcal{E}^\nu(\gamma)$ are well defined and that so is the exchange–correlation contribution: as ρ_{per}^0 is periodic, continuous and positive on $\mathbb{R}^3$ and as $\rho_Q \in L^2(\mathbb{R}^3)$, the fifth term of (7), which was not

considered in [12], is also well defined. Finally, following [16], the generalized trace of an operator $Q \in \mathcal{K}$ is defined by

$$\mathrm{Tr}(Q) = \mathrm{Tr}(Q^{++}) + \mathrm{Tr}(Q^{--}), \qquad (13)$$

and for any $Q \in \mathcal{K}$, one sets

$$\mathrm{Tr}(H_{\mathrm{per}}^0 Q) = \mathrm{Tr}([H_{\mathrm{per}}^0]^{++} Q^{++}) + \mathrm{Tr}([H_{\mathrm{per}}^0]^{--} Q^{--}),$$

where $[H_{\mathrm{per}}^0]^{--}$ and $[H_{\mathrm{per}}^0]^{++}$ are, respectively, the restrictions to the occupied and virtual spaces of the periodic Kohn–Sham Hamiltonian of the perfect crystal. Note that H_{per}^0 is block diagonal in the decomposition (12):

$$H_{\mathrm{per}}^0 = \left(\begin{array}{c|c} [H_{\mathrm{per}}^0]^{--} & 0 \\ \hline 0 & [H_{\mathrm{per}}^0]^{++} \end{array} \right).$$

The definition (13) of the trace function is an extension of the standard trace function defined on the set of trace-class operators. Note that this extension depends on γ_{per}^0 through the decomposition (12) of the L^2 space. In the quantum electrodynamical model studied in [16–18, 14, 19], minimizers are never trace-class (this property being related to renormalization). Whether or not the minimizers of (8) and (9) are trace-class is still an open question.

To our knowledge, the variational interpretation of the ground state solutions of the self-consistent equation (10) as minimizers of the energy (7) on the set $\mathcal{K}$ with a constraint on the generalized trace (13) is new. This interpretation allows us to rigorously justify the numerical method described in section 4.

3. Interpretation in terms of Bogoliubov states

The density matrix formalism used in the previous section can be reinterpreted in terms of Bogoliubov states, following [13].

Let γ be an orthogonal projector acting on $L^2(\mathbb{R}^3)$ such that $Q = \gamma - \gamma_{\mathrm{per}}^0 \in \mathcal{K}$. It can be proved [18] that there exists an orthonormal basis $(\phi_i^-)_{i \geqslant -N_-}$ of $\mathcal{H}_-$ and an orthonormal basis $(\phi_i^+)_{i \geqslant -N_+}$ of $\mathcal{H}_+$ such that in this basis

$$Q = \left(\begin{array}{cc|cc} -I_{N_-} & 0 & 0 & 0 \\ 0 & \mathrm{diag}(-p_i) & 0 & \mathrm{diag}(p_i') \\ \hline 0 & 0 & I_{N_+} & 0 \\ 0 & \mathrm{diag}(p_i') & 0 & \mathrm{diag}(p_i) \end{array} \right) \qquad (14)$$

with $0 \leqslant p_i < 1$, $\sum_{i=0}^{+\infty} p_i < \infty$, $p_i' = \sqrt{p_i(1-p_i)}$. Notice that Q is a trace-class operator if and only if $\sum_{i=0}^{+\infty} \sqrt{p_i} < \infty$. Let us assume for simplicity that in equation (10) the Fermi level ϵ_F is either empty or fully occupied. In this case, $\chi_{(-\infty, \epsilon_F)}(H_Q) + \delta$ is an orthogonal projector, which implies that Q can be decomposed as in (14). It is important to mention that in this case, the generalized trace of Q is the integer $N_+ - N_-$.

Formula (14) can be interpreted in terms of Bogoliubov states. The orbitals $\phi_{-N_+}^+, \ldots, \phi_{-1}^+$ describe bound electrons in the virtual bands of the reference perfect crystal, while the orbitals $\phi_{-N_-}^-, \ldots, \phi_{-1}^-$ represent bound holes in the occupied

bands. Likewise, each pair (ϕ_i^+, ϕ_i^-) with $i \geqslant 0$ and $0 < p_i < 1$ is a virtual electron–hole pair, and ϕ_i^+ and ϕ_i^- are the states of the corresponding Bogoliubov quasiparticles. The angle $\theta_i = \mathrm{asin}(p_i)$ is then called the Bogoliubov angle of the virtual pair.

Formula (14) can itself be rewritten in a second-quantized form, using the Fock space built upon the decomposition (12). Let us introduce the N-electron sector $\mathcal{F}_+^N := \bigwedge_1^N \mathcal{H}_+$ and the M-hole sector $\mathcal{F}_-^M := \bigwedge_1^M \mathcal{H}_-$. The electron–hole Fock space is defined as

$$\mathcal{F} := \bigoplus_{N,M \geqslant 0} \mathcal{F}_+^N \otimes \mathcal{F}_-^M.$$

We denote by $a_i^\dagger$ the creation operator of an electron in the state ϕ_i^+ and by $b_i^\dagger$ the creation operator of a hole in the state ϕ_i^-. In this formalism, the vacuum state $\Omega_0 = 1 \otimes 1 \in \mathcal{F}_+^0 \otimes \mathcal{F}_-^0$ corresponds to the periodic Fermi sea of the perfect crystal, represented by the density matrix γ_{per}^0 in the usual Kohn–Sham description. We may also define the charge operator acting on the Fock space $\mathcal{F}$ by

$$\mathcal{Q} = \sum_{i \geqslant -N_+} a_i^\dagger a_i - \sum_{i \geqslant -N_-} b_i^\dagger b_i.$$

There is a special subclass of states in $\mathcal{F}$ called Bogoliubov states [13, 16, 20, 21]. Each Bogoliubov state $\Omega_\gamma \in \mathcal{F}$ is completely characterized by its one-body density matrix γ, an orthogonal projector acting on $L^2(\mathbb{R}^3)$. Conversely, any projector γ gives rise to a Bogoliubov state under the Shale–Stinespring [22, 23] condition that $Q = \gamma - \gamma_{\mathrm{per}}^0$ is a Hilbert–Schmidt operator (which means $\mathrm{Tr}(Q^2) < \infty$). The role of the Shale–Stinespring condition is to ensure that Ω_γ is a well-defined state in the same Fock space as the vacuum state Ω_0. In other words, this ensures that the Fock space representation associated with the splitting $L^2(\mathbb{R}^3) = \gamma L^2(\mathbb{R}^3) \oplus (1 - \gamma) L^2(\mathbb{R}^3)$ is equivalent to the one induced by (12) (i.e. $L^2(\mathbb{R}^3) = \gamma_{\mathrm{per}}^0 L^2(\mathbb{R}^3) \oplus (1 - \gamma_{\mathrm{per}}^0) L^2(\mathbb{R}^3)$). Notice that the Hilbert–Schmidt condition $\mathrm{Tr}(Q^2) < \infty$ is satisfied for any $Q = \gamma - \gamma_{\mathrm{per}}^0$ in $\mathcal{K}$. Hence the variational set $\mathcal{K}$ can be identified with a variational set of Bogoliubov states $\{\Omega_\gamma\}_{\gamma \in \mathcal{K}}$ in the Fock space $\mathcal{F}$.

The expression of the Bogoliubov state Ω_γ in the Fock space $\mathcal{F}$ is given by [21, 22, 24]

$$\Omega_\gamma = c a_{-N_+}^\dagger \cdots a_{-1}^\dagger b_{-N_-}^\dagger \cdots b_{-1}^\dagger \exp\left(\sum_{i \geqslant 0} \lambda_i a_i^\dagger b_i^\dagger \right) \Omega_0$$

where $\lambda_i = \tan(\theta_i)$, and where c is a normalization constant. The above expression can be considered as the second-quantized formulation of (14). It can then easily be checked [16] that the charge of each Bogoliubov state Ω_γ (counted relatively to that of the vacuum Ω_0) is actually given by (13):

$$\langle \Omega_\gamma | \mathcal{Q} | \Omega_\gamma \rangle = \mathrm{Tr}(Q^{++}) + \mathrm{Tr}(Q^{--}) = N_+ - N_-$$

where $Q = \gamma - \gamma_{\mathrm{per}}^0$.

4. Variational approximation

Let us now come to the discretization of problem (8).

If one discretizes (8) in a local basis without taking care of the constraint $Q \in \mathcal{K}$ there is a risk of obtaining meaningless numerical results. On the other hand, selecting a basis set which respects the decomposition (12) will lead to a well-behaved variational approximation of (8) (the constraint $Q \in \mathcal{K}$ will be implicitly taken into account). Let $V_{\pm}^h$ be finite-dimensional subspaces of the occupied and virtual spaces $\mathcal{H}_{\pm}$ of the reference perfect crystal. Consider the finite-dimensional subspace $V^h = V_-^h \oplus V_+^h$ of $L^2(\mathbb{R}^3)$, the latter decomposition being the finite-dimensional counterpart of (12). Let $(\phi_1, \ldots, \phi_{m_-})$ (resp. $(\phi_{m_-+1}, \ldots, \phi_{N_b})$) be an orthonormal basis of V_-^h (resp. of V_+^h). We denote for simplicity $m_+ := N_b - m_-$. The approximation set for Q consists of the finite-rank operators

$$Q = \sum_{i,j=1}^{N_b} Q_{ij}^h |\phi_i\rangle\langle\phi_j| \qquad (15)$$

with $Q^h \in \mathcal{K}^h = \{Q^h = [Q^h]^T, \ 0 \leqslant \mathcal{I} + Q^h \leqslant 1\}$, where $\mathcal{I}$ is the $N_b \times N_b$ block diagonal matrix

$$\mathcal{I} = \begin{bmatrix} 1_{m_-} & 0 \\ 0 & 0_{m_+} \end{bmatrix}.$$

The matrix of H_{per}^0 in the basis (ϕ_i) is of the form

$$H^h = \begin{bmatrix} H^{--} & 0 \\ 0 & H^{++} \end{bmatrix}.$$

For Q of the form (15), it holds

$$\mathcal{E}^\nu(Q) = \mathcal{E}_h^\nu(Q^h)$$

with

$$\rho_{Q^h}(r) = \sum_{i,j=1}^{N_b} Q_{ij}^h \phi_i(r)\phi_j(r)$$

and

$$\mathcal{E}_h^\nu(Q^h) = \mathrm{Tr}(H^h Q^h) - D(\nu, \rho_{Q^h}) + \tfrac{1}{2}D(\rho_{Q^h}, \rho_{Q^h}) + \epsilon^{\mathrm{xc}}(\rho_{Q^h}).$$

We then end up with the finite-dimensional optimization problem

$$E_h^\nu(q) = \inf\left\{\mathcal{E}_h^\nu(Q^h), Q^h \in \mathcal{K}^h, \mathrm{Tr}(Q^h) = q\right\} \qquad (16)$$

which is a variational approximation of (8):

$$E_h^\nu(q) \geqslant E^\nu(q).$$

As $Q^h \in \mathcal{K}^h$ with $\mathrm{Tr}(Q^h) = q$ if and only if

$$\mathcal{I} + Q^h \in \{D = D^T \in \mathbb{R}^{2N_b}, \ D^2 \leqslant D,$$
$$\mathrm{Tr}(D) = q + N_-\},$$

problem (16) can be solved using relaxed constrained algorithms [25, 26].

The question is now to build spaces V_-^h and V_+^h that provide good approximations to (8) and (9). A natural choice is to use maximally localized (generalized) Wannier functions [27] (MLWFs) of the reference perfect crystal. A very interesting feature of these basis functions is that they can be precalculated once and for all for a given host crystal, independently of the local defect under consideration. To construct V_-^h, one can select the maximally localized (generalized) Wannier functions of the occupied bands that overlap with, for example, some ball B_{R_c} of radius R_c centered on the nuclear charge defect. Note that due to the variational nature of the approximation scheme, enlarging the radius R_c systematically improves the quality of the approximation. To obtain a basis set for V_+^h, one can select a number of active (unoccupied) bands using an energy cut-off and retain the maximally localized (generalized) Wannier functions of the active bands that overlap with the same ball B_{R_c}. The so-obtained basis set of the virtual space can be enriched by adding projected atomic orbitals of the atoms and ghost atoms involved in ν (using the localized Wannier functions of the occupied bands to project out the $\mathcal{H}_-$ component of atomic orbitals preserves the locality of these orbitals).

5. Numerical results

In order to illustrate the efficiency of the variational approximation presented above, we take the example of a one-dimensional (1D) model with a Yukawa interaction potential, for which the energy functional reads

$$E_{1D}(\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\frac{\mathrm{d}^2\gamma}{\mathrm{d}x^2}\right) - D_\kappa(\rho_{\mathrm{nuc}}, \rho_\gamma) + \frac{1}{2}D_\kappa(\rho_\gamma, \rho_\gamma)$$

with

$$D_\kappa(f, g) = (A/2\kappa)\int_{\mathbb{R}}\int_{\mathbb{R}} f(x)\mathrm{e}^{-\kappa|x-x'|}g(x')\,\mathrm{d}x\,\mathrm{d}x'.$$

In the numerical examples reported below, the host crystal is $\mathbb{Z}$-periodic and the nuclear density is a Dirac comb, i.e.

$$\rho_{\mathrm{nuc}} = Z\sum_{j\in\mathbb{Z}}\delta_j,$$

with Z a positive integer. The values of the parameters ($A = 10$ and $\kappa = 5$) have been chosen in such a way that the ground state kinetic and potential energies are of the same order of magnitude.

The nuclear local defect is taken to be of the form

$$\nu = (Z-1)\delta_{0.25} - Z\delta_0.$$

This corresponds to moving one nucleus and lowering its charge by one unit.

The first stage of the calculation consists in solving the cell problem. For simplicity, we use a uniform discretization of the Brillouin zone $(-\pi, \pi]$, and a plane wave expansion of the crystalline orbitals.

The second stage is the construction of MLWFs. For this purpose, we make use of an argument specific to the one-dimensional case [28]: the MLWFs associated with the spectral projector γ are the eigenfunctions of the operator $\gamma x \gamma$. One first constructs N_e mother MLWFs (taking $\gamma = \gamma_{\mathrm{per}}^0$), then N_a mother MLWFs corresponding to the lowest N_a virtual
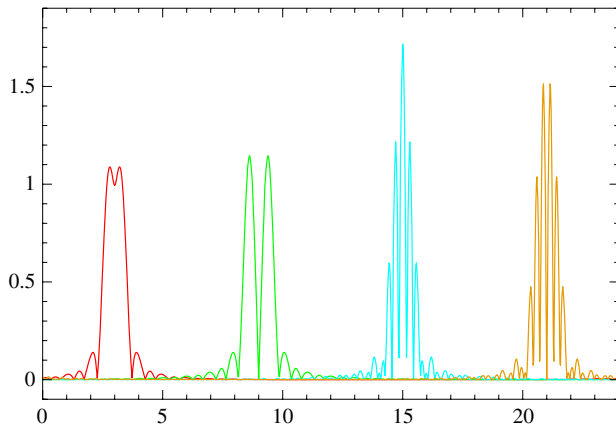
Figure 3. Modulus of MLWFs associated with the two occupied bands (left) and with the lowest two virtual bands (right).
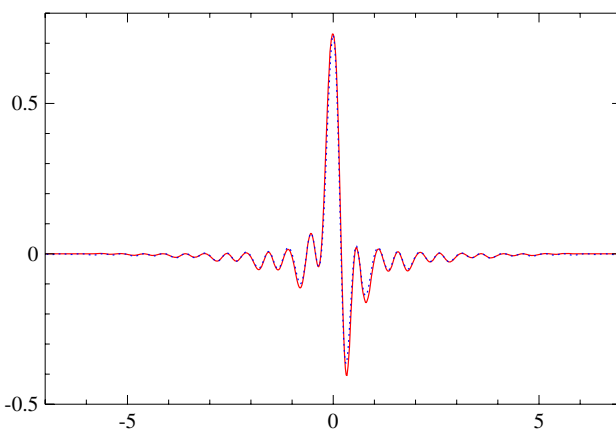

Figure 4. Density ρ_{Q^h} obtained with 28 MLWFs (solid line in red). The reference is a supercell calculation in a basis set of size 1224 (dashed line in blue).

bands (taking for γ the spectral projector associated with the lowest N_a virtual bands). The mother MLWFs thus obtained are represented in figure 3.

The third stage consists in constructing a basis set $(\phi_j)_{1 \leqslant j \leqslant N_b}$ of $N_b = N_v(N_e + N_a)$ MLWFs by selecting the N_v translations of the $(N_e + N_a)$ mother MLWFs that are closest to the local defect, and in computing the first-order density matrix of the form (15) which satisfies the constraints and minimizes the energy. The profile of the density ρ_{Q^h} obtained with $Z = 2$, $N_e = 2$, $N_a = 2$ and $N_b = 28$ is displayed on figure 4. It is compared with a reference supercell calculation with 1224 plane wave basis functions. A fairly good agreement is obtained with very few MLWFs.

The implementation of our method in the Quantum Espresso suite of programs [29], in the true 3D Kohn–Sham setting, is work in progress [30].

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