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Density functional theory for local defects in crystalline materials

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We present a new variational model for computing the perturbation of the electronic first-order density matrix generated by a defect in a crystalline material. A natural way to obtain variational discretizations of this model is to expand the perturbation 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.

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Describing the electronic state of crystals with local defects is a major issue in solid-state physics, materials science and nano-electronics [1–3]. Usually, the energy of a local defect is computed by subtracting the energy of the perfect crystal from the energy of the crystal with the defect, using a supercell model [4, 5]. However, the supercell model has 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 [6].

In a recent article [7], we have used rigorous thermodynamic limit arguments to derive a variational model allowing to directly compute the perturbation of the electronic first order density matrix generated by a (neutral or charged) local defect, when the host crystal is an insulator (or a semi-conductor). This model has a structure similar to the Chaix-Iracane model in quantum electrodynamics [8–10]. This similarity originates from formal analogies between the Fermi sea of a perturbed crystal and the Dirac sea in presence of atomic nuclei. For technical reasons, the reference model considered in [7] 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 Letter 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 perturbation 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.

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 $E^{\text{xc}}(\rho)$. 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

$$\inf \{ E_{\rho^{\text{nuc}}}^{\text{KS}}(\gamma), 0 \leq \gamma \leq 1, \text{tr}(\gamma) = \mathcal{N} \}, \quad (1)$$

$$E_{\rho^{\text{nuc}}}^{\text{KS}}(\gamma) = \text{tr} \left(-\frac{1}{2} \Delta \gamma \right) - D(\rho^{\text{nuc}}, \rho_{\gamma}) + \frac{1}{2} D(\rho_{\gamma}, \rho_{\gamma}) + E^{\text{xc}}(\rho_{\gamma}), \quad (2)$$

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

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

is the Coulomb interaction. Still for simplicity, we detail the case of the $X\alpha$ exchange-correlation functional

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

the extension to more general LDA or GGA functionals being straightforward.

The above model describes a *finite* system of \mathcal{N} electrons in the electrostatic field created by the external density ρ^{nuc} . Our goal is to describe an *infinite* crystalline material obtained in the thermodynamic limit $\mathcal{N} \rightarrow \infty$. 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:

$$\rho^{\text{nuc}} \rightarrow \rho_{\text{per}}^{\text{nuc}}, \quad (4)$$

$\rho_{\text{per}}^{\text{nuc}}$ being a periodic function. The second system is a perturbation of the previous crystal by a defect:

$$\rho^{\text{nuc}} \rightarrow \rho_{\text{per}}^{\text{nuc}} + \nu. \quad (5)$$

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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.

The form of the density matrix γ_{per}^0 of the *perfect crystal* obtained in the thermodynamic limit (4) is well-known. Let us denote by \mathcal{R} the Bravais lattice of the host crystal and by Ω a reference unit cell. The matrix γ_{per}^0 is a solution of the self-consistent equation

$$\gamma_{\text{per}}^0 = \chi_{(-\infty; \mu]}(H_{\text{per}}^0) \quad (6)$$

$$H_{\text{per}}^0 = -\frac{1}{2}\Delta + \Phi_{\text{per}} - \frac{4}{3}C_{X\alpha}\rho_{\text{per}}^{0/3}, \quad (7)$$

$$-\Delta\Phi_{\text{per}} = 4\pi(\rho_{\text{per}}^0 - \rho_{\text{per}}^{\text{nucl}}), \quad \Phi_{\text{per}} \text{ } \mathcal{R}\text{-periodic.}$$

The notation $P = \chi_{(-\infty; \mu]}(A)$ means that P is the spectral orthogonal projector of the operator A corresponding to filling all the energies up to the Fermi level μ . The density of the periodic Fermi sea is $\rho_{\text{per}}^0(r) = \gamma_{\text{per}}^0(r, r)$. Note that the system is locally neutral:

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

the Fermi level μ being chosen to ensure this equality. For the rest of the Letter, we assume the host crystal is an insulator (or a semi-conductor), 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 $\Sigma^- \leq \mu < \Sigma^+$.

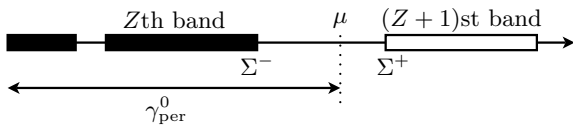


FIG. 1: Spectrum of H_{per}^0 .

Now we consider the system obtained in the thermodynamic limit (5) 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 . This means our variable is

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

where γ is the density matrix of the perturbed Fermi sea. Notice that the constraint that γ is a density matrix ($0 \leq \gamma \leq 1$) translates into $-\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0$ for the perturbation 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), the computation formally gives:

$$\begin{aligned} \mathcal{E}^\nu(Q) &= \text{tr}(H_{\text{per}}^0 Q) - D(\nu, \rho_Q) \\ &\quad + \frac{1}{2}D(\rho_Q, \rho_Q) + \epsilon^{\text{xc}}(\rho_Q) \end{aligned} \quad (8)$$

where this time

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

If we want to describe a system of total charge q (like q electrons 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

$$E^\nu(q) = \inf \{ \mathcal{E}^\nu(Q), -\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0, \text{tr}(Q) = q \}. \quad (9)$$

We obtain in this way a formal model which *a priori* renders possible the direct calculation of the perturbation of the Fermi sea generated by 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 (9) to charged defects.

Alternatively, one can, instead of imposing *a priori* the total charge q of the system (microcanonical viewpoint), rather fix the chemical potential $\mu \in (\Sigma^-, \Sigma^+)$ (grand-canonical viewpoint). This amounts to considering the Legendre transform of (9):

$$E_\mu^\nu = \inf \{ \mathcal{E}^\nu(Q) - \mu \text{tr}(Q), -\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0 \}. \quad (10)$$

Varying μ in the gap (Σ^-, Σ^+) should allow to describe all possible q 's in (9), i.e. all possible configurations in the presence of the defect.

It is however not clear how to construct numerical approximations of (9) (without coming back to the supercell model), nor even how to give a rigorous mathematical meaning to (8)-(9). The biggest issue is that there is *a priori* no reason why Q should be trace-class [11]. Indeed in the Quantum Electrodynamical model studied in [9, 10], minimizers are never trace-class, a property which is related to renormalization. For this reason, a mathematically correct definition of the variational set for Q (hence of ρ_Q , $\text{tr}(Q)$ and the right-hand side of (8)) is not obvious. It was shown in [7] that an appropriate set of admissible Q 's is the convex set

$$\begin{aligned} \mathcal{K} = \{ Q \mid & -\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0, \text{tr}(1 + |\nabla|)Q^2(1 + |\nabla|) \\ & + \text{tr}(1 + |\nabla|)(Q^{++} - Q^{--})(1 + |\nabla|) < \infty \}. \end{aligned}$$

Here we have introduced the notation

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

Notice that when Q satisfies the constraint $-\gamma_{\text{per}}^0 \leq Q \leq 1 - \gamma_{\text{per}}^0$, one has $Q^{++} \geq 0$ and $Q^{--} \leq 0$.

A remarkable point, proved in [7], 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 allows to give a rigorous formulation of the model described above: 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 (8)

which was not considered in [7] is also well-defined. Finally, following [9], the trace of any operator $Q \in \mathcal{K}$ is defined by $\text{tr}(Q) = \text{tr}(Q^{++}) + \text{tr}(Q^{--})$.

Any solution of (9) or (10) satisfies the SCF equation

$$Q = \chi_{(-\infty, \mu)}(H_Q) - \gamma_{\text{per}}^0 + \delta, \quad (11)$$

where

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

and where $0 \leq \delta \leq 1$ is a finite-rank self-adjoint operator on $L^2(\mathbb{R}^3)$ such that $\text{Ran}(\delta) \subset \text{Ker}(H_Q - \mu)$. In the case of (9), μ is a Fermi level (a Lagrange multiplier) which serves to ensure the constraint $\text{tr}(Q) = q$. The essential spectrum of H_Q is the same as the one 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. Each filled (or unfilled) eigenvalue may correspond to electrons (or holes) which are trapped by the defect.

The SCF equation (11) is equivalent to the usual Dyson equation on the Green functions. But its variational interpretation (namely (9) or (10) with the additional constraint $Q \in \mathcal{K}$) is new. This interpretation allows to rigorously justify the numerical method described below.

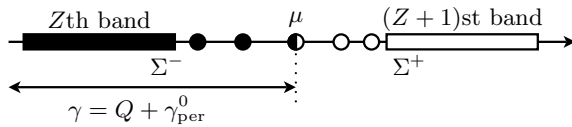


FIG. 2: Spectrum of H_Q .

Variational approximation

We consider the decomposition $L^2(\mathbb{R}^3) = \mathcal{H}_- \oplus \mathcal{H}_+$ where $\mathcal{H}_- = \gamma_{\text{per}}^0 L^2(\mathbb{R}^3)$ and $\mathcal{H}_+ = (1 - \gamma_{\text{per}}^0) L^2(\mathbb{R}^3)$.

If one discretizes (9) in a local basis without taking care of the constraint $Q \in \mathcal{K}$, there is a risk to obtain meaningless numerical results. On the other hand, selecting a basis set which respects the above decomposition, will lead to a well-behaved variational approximation of (9). Let V_{\pm}^h be finite-dimensional subspaces of \mathcal{H}_{\pm} , and consider the finite-dimensional subspace $V^h = V_-^h \oplus V_+^h$ of $L^2(\mathbb{R}^3)$. Let $(\phi_1, \dots, \phi_{N_-})$ (resp. $(\phi_{N_-+1}, \dots, \phi_{N_b})$) be an orthonormal basis of V_-^h (resp. of V_+^h). The approximation set for Q consists of the finite-rank operators

$$Q = \sum_{i,j=1}^{N_b} Q_{ij}^h |\phi_i\rangle \langle \phi_j| \quad (12)$$

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

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

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 (12), one has $\mathcal{E}^\nu(Q) - \mu \text{tr}(Q) = \epsilon_{\nu, \mu}^h(Q^h)$ with $\rho_{Q^h}(r) = \sum_{i,j=1}^{N_b} Q_{ij}^h \phi_i(r) \phi_j(r)$ and

$$\begin{aligned} \epsilon_{\nu, \mu}^h(Q^h) &= \text{tr}((H^h - \mu)Q^h) - \int_{\mathbb{R}^3} V_\nu \rho_{Q^h} \\ &\quad + \frac{1}{2} D(\rho_{Q^h}, \rho_{Q^h}) + \epsilon^{\text{xc}}(\rho_{Q^h}). \end{aligned}$$

We then end up with the finite-dimensional problem

$$e_{\nu, \mu}^h = \inf \{ \epsilon_{\nu, \mu}^h(Q^h), Q^h \in \mathcal{Q}^h \} \quad (13)$$

which is a variational approximation of (10): $e_{\nu, \mu}^h \geq E_\mu^\nu$.

As $Q^h \in \mathcal{K}^h$ if and only if

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

problem (13) can be solved using relaxed constrained algorithms [13, 14].

The question is now to build spaces V_-^h and V_+^h that provide a good approximation to (10). A natural choice is to use the maximally localized (generalized) Wannier functions [12] (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 some ball B_{R_c} of radius R_c centered on the nuclear charge defect. 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} .

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 Yukawa interaction potential, for which the energy functional reads

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

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

In the numerical examples reported below, the host crystal is \mathbb{Z} -periodic and the nuclear density is a Dirac comb, i.e. $\rho_{\text{nuc}} = Z \sum_{j \in \mathbb{Z}} \delta_j$, with $Z \in \mathbb{N} \setminus \{0\}$. 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.

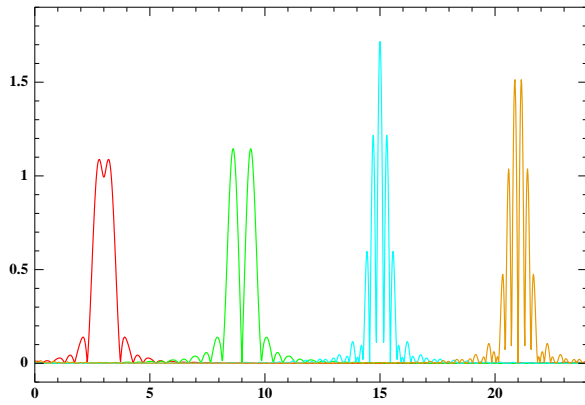


FIG. 3: Modulus of MLWFs associated with the two occupied bands (left) and with the lowest two virtual bands (right).

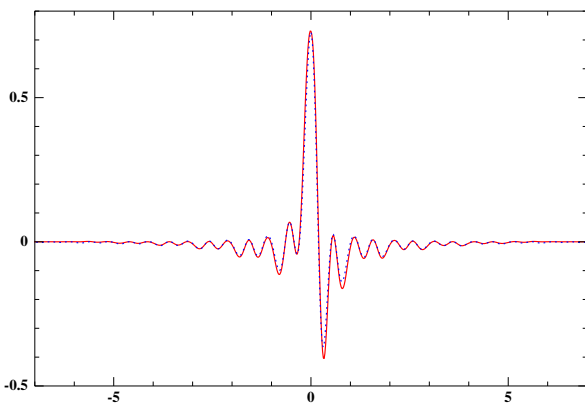


FIG. 4: Perturbation ρ_{Q^h} of the periodic ground state density with 28 MLWFs (line in red). The reference is a supercell calculation in a basis set of size 1224 (dashed line in blue).

The nuclear local defect is taken 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 [15]: 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 $\gamma = \gamma_{\text{per}}^0$), then N_a mother MLWFs corresponding to the lowest N_a virtual bands (taking for γ the spectral projector associated with the lowest N_a virtual bands). The so-obtained mother MLWFs are represented on Fig. 3.

The third stage consists in constructing a basis set $(\phi_j)_{1 \leq j \leq N_b}$ 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 (12) 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 Fig. 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.

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