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A Closed Local-Orbital Unified Description of DFT and Many-Body Effects

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Abstract

Density Functional Theory (DFT) is usually formulated in terms of the electron density as a function of position $n(\mathbf{r})$. Here we discuss an alternative formulation of DFT in terms of the orbital occupation numbers $\{n_\alpha\}$ associated with a local-orbital orthonormal basis set $\{\phi_\alpha\}$. First, we discuss how the building blocks of DFT, namely the Hohenberg-Kohn theorems, the Levy-Lieb approach and the Kohn-Sham method, can be adapted for a description in terms of $\{n_\alpha\}$. In particular, the total energy is now a function of $\{n_\alpha\}$, $E[\{n_\alpha\}]$, and a Kohn-Sham-like Hamiltonian is derived introducing the effects of the electron-electron interactions via effective potentials, $\{V_\alpha^{\text{eff}} = \partial E_{ee}[\{n_\beta\}]/\partial n_\alpha\}$. In a second step we consider the Hartree and Exchange energies and discuss how to describe them, in the spirit of a DFT approach, in terms of the orbital occupation numbers. In this contribution special attention is paid to the description of the (intra-atomic) correlation energy and corresponding correlation potentials $\{V_{\text{corr},\alpha}\}$. For this purpose, a model system is analyzed in detail, whereby an atomic Hamiltonian interacts with the environment via a simplified model; the use of this model allows us to obtain the correlation energy and potentials (in terms of $\{n_\alpha\}$) for different cases corresponding to low, intermediate and high electron correlations.

I. INTRODUCTION

Density Functional Theory (DFT) is probably the most appealing method for analyzing the properties of solids and chemical systems [1, 2]. In this approach, by means of the Kohn-Sham (KS) prescription, the problem of calculating the properties of an interacting electron system is solved by using an auxiliary one-body problem, where a single particle moves in an effective potential, $V_{ee}(\mathbf{r})$, created by all the other electrons. In DFT, this potential is introduced as a function of the local charge density, $n(\mathbf{r})$, which plays the central role in this theory; alternatively, in GGA methods [3] this potential also depends on the local gradient, $\nabla n(\mathbf{r})$.

These approximations, however, do not describe properly the properties of highly correlated systems, typically solids or molecules with transition metal or rare earth atoms. Different many-body schemes have been developed, based on a GW-approach [4] and/or a Dynamical Mean Field approximation [5] as well as a Reduced Density Matrix Functional method [6–8], to analyze those highly correlated systems; we also mention the DFT+U method [9, 10], much easier to manage computationally speaking and frequently used in the computational scientific community. [11–14]

In all these developments, researchers have been using either plane-waves or local-orbitals as the basis set to describe the electron wave-functions; these local orbital basis approaches have been very important in the early descriptions of molecular systems (in this regards it is worth mentioning the pioneering work of Enrico Clementi for his seminal work on this area [15] and on the many-body problem of these systems [16]). However, in both cases, researchers have been calculating $V_{ee}(\mathbf{r})$ by means of the local charge, $n(\mathbf{r})$, provided by the electron wave-functions as calculated by using any basis set. This way of proceeding may appear unsatisfactory when using a local orbital set, because in this calculation one returns to the point-like description of the charge, $n(\mathbf{r})$, more appropriate for a plane-wave set formulation. In other words, one wonders why not try and look for an alternative approach, whereby instead of $V_{ee}(\mathbf{r})$, and the local charge $n(\mathbf{r})$, one takes the potential V_α and the local charge n_α associated with the local orbital, ϕ_α , as the key variables. Obviously, the problem in this case is to calculate V_α by means of the local charge, n_α .

In this paper, we present a closed description of a DFT-method that uses n_α instead of $n(\mathbf{r})$ as the independent variable; as it will be proved below n_α fixes the electron-electron

energy of the system, $E_{ee}[\{n_\alpha\}]$, and the corresponding potential, $V_{\alpha,ee} = \frac{\partial E_{ee}[\{n_\beta\}]}{\partial n_\alpha}$ in a KS-like equation for the electrons. The work presented here is mainly a kind of review paper where, trying to honour the memory of Enrico Clementi, we present a summary of our previous publications [17–22], and also some new results for the description of the many-body properties in this closed local orbital formulation of DFT. This approach also unifies two different ways of understanding the properties of realistic systems: (a) the calculation of its electronic structure using a local orbital DFT-method and (b) the analysis of sophisticated many-body techniques that allow us to describe accurately the correlation contributions to $E_{ee}[\{n_\alpha\}]$, even for highly correlated materials.

In section II we start reformulating the Hohenberg-Kohn (HK) theorem, Levy-Lieb approach and the Kohn-Sham (KS) method taking n_α (or more properly, $n_{i\mu\sigma}$, see below) as the independent variables. In section III, we present the basic local-orbital Hamiltonian and show how to obtain the quantity $V_{ee}(n_{i\mu\sigma})$ that provides the Hartree-Fock (HF) solution and some related DFT-equations. In section IV, we discuss in detail how to obtain the appropriate correlation energy for lowly and highly correlated materials: the corresponding correlation potential, combined with the results of section III, completely defines the solution for the local-orbital DFT-method we present here. We stress that in this approach, our solution only depends on the atomic charge, $n_{i\mu\sigma}$, that is obtained from the KS-equations that themselves depend self-consistently on $n_{i\mu\sigma}$; this means that in this approach the potential $V_{ee}(\mathbf{r})$ is neither calculated nor needed in order to obtain a consistent solution of the initial local orbital Hamiltonian.

II. GENERAL FORMALISM

The crucial point is to adapt Hohenberg-Kohn (HK) theorems, the Levy-Lieb formulation of DFT and the Kohn-Sham (KS) approach to a formalism where the orbital occupation numbers, $\{n_{i\mu\sigma}\}$, associated with the orbital basis set $\phi_{i\mu\sigma}$ (i defines the site, μ the orbital and σ the spin), appear as the independent variables, instead of the conventional one, $n_\sigma(\mathbf{r})$.

Hohenberg-Kohn theorems and Levy-Lieb formulation.

We consider the following Hamiltonian: $\hat{H} = \hat{H}_0 + \sum_{i\mu\sigma} v_{i\mu\sigma}^0 \hat{n}_{i\mu\sigma}$; \hat{H} defines the initial many-body system we are interested in, and $\hat{n}_{i\mu\sigma} = \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma}$ where $\hat{c}_{i\mu\sigma}^\dagger$ and $\hat{c}_{i\mu\sigma}$ are the creation and annihilation operators associated with the orthonormal basis set $\{\phi_{i\mu\sigma}\}$, while

$\{v_{i\mu\sigma}^0\}$ represent the external potentials of our problem.

We consider first the Levy-Lieb formulation of DFT which offers a straightforward approach to the essential DFT result. Adapting it to our present case, we define the total energy as a *function* of the orbital occupation numbers, $E[\{n_{i\mu\sigma}\}]$, as follows [23]:

$$E[\{n_{i\mu\sigma}\}] = \min_{|\Phi\rangle \rightarrow \{n_{i\mu\sigma}\}} \langle \Phi | \hat{H}_0 | \Phi \rangle + \sum_{i\mu\sigma} v_{i\mu\sigma}^0 n_{i\mu\sigma} , \quad (1)$$

where the first term on the r.h.s. is the smallest possible value of $\langle \Phi | \hat{H}_0 | \Phi \rangle$ out of all the normalized N -electron antisymmetric wavefunctions $|\Phi\rangle$ that yield the same set of occupation numbers $\{n_{i\mu\sigma}\}$. Then, it can be shown [23] that:

$$E[\{n_{i\mu\sigma}\}] \geq E[\{n_{i\mu\sigma}^0\}] = E_0 , \quad (2)$$

where E_0 is the ground state energy and $\{n_{i\mu\sigma}^0\}$ are the ground state occupation numbers. Equation (2) is the essential result for a DFT theory in terms of the $\{n_{i\mu\sigma}\}$.

It is instructive, however, to analyze also the HK total energy functional. In the standard $n(\mathbf{r})$ case, this functional is formally defined as $E[n(\mathbf{r})] = \langle \Phi | \hat{H} | \Phi \rangle$ where $|\Phi\rangle$ is the ground state for a Hamiltonian with external potential $v(\mathbf{r})$ such that $|\Phi\rangle$ yields $n(\mathbf{r})$ (*i.e.* V -representable densities). In our present $\{n_{i\mu\sigma}\}$ case, we then have: $E[\{n_{i\mu\sigma}\}] = \langle \Phi | \hat{H} | \Phi \rangle$, where $|\Phi\rangle$ is now the ground state for a Hamiltonian $\hat{H}_v = \hat{H}_0 + \sum_{i\mu\sigma} v_{i\mu\sigma} \hat{n}_{i\mu\sigma}$ with potentials $\{v_{i\mu\sigma}\}$ such that $|\Phi\rangle$ yields $\{n_{i\mu\sigma}\}$. The HK definition for E is based on the HK theorem that, in the standard $n(\mathbf{r})$ case, states if two Hamiltonians corresponding to two different external potentials, $v_A(\mathbf{r})$ and $v_B(\mathbf{r})$, have the same ground state density $n(\mathbf{r})$, then $v_A(\mathbf{r})$ and $v_B(\mathbf{r})$ can only differ by a constant. In order to analyze the HK theorem in our present $\{n_{i\mu\sigma}\}$ case, we follow ref. [24] and split the theorem in two parts. In part 1, it is shown that if two Hamiltonians, $\hat{H}_A = \hat{H}_0 + \sum_{i\mu\sigma} v_{i\mu\sigma}^A \hat{n}_{i\mu\sigma}$ and $\hat{H}_B = \hat{H}_0 + \sum_{i\mu\sigma} v_{i\mu\sigma}^B \hat{n}_{i\mu\sigma}$, that differ only in the external potentials, $\{v_{i\mu\sigma}^A\}$ and $\{v_{i\mu\sigma}^B\}$, have the same ground state $\{n_{i\mu\sigma}\}$, then a ground state wavefunction $|\Phi\rangle$ of \hat{H}_A is also a ground state of \hat{H}_B , and viceversa. See ref. [24] (theorem 7) for a proof of this result, which can also be viewed as a consequence of the relationship between $\{n_{i\mu\sigma}\}$ and $|\Phi\rangle$ in equation (1). This result already shows that the HK $E[\{n_{i\mu\sigma}\}]$ is well-defined even when there is no biunivocal correspondence $\{v_{i\mu\sigma}\} \leftrightarrow \{n_{i\mu\sigma}\}$, *i.e.* when different $\{v_{i\mu\sigma}\}$ yield the same $\{n_{i\mu\sigma}\}$, since those potentials yield the same ground state $|\Phi\rangle$.

For the sake of completeness, we also discuss here part 2 of the HK theorem. Now, we assume that we have two different Hamiltonians, \hat{H}_A and \hat{H}_B , that differ only in their external potentials, but have the same ground state occupation numbers $\{n_{i\mu\sigma}\}$ and thus the same ground state wavefunction $|\Phi\rangle$. Then, subtract $\hat{H}_A|\Phi\rangle = E_A|\Phi\rangle$ from $\hat{H}_B|\Phi\rangle = E_B|\Phi\rangle$; this yields:

$$\sum_{i\mu\sigma} (v_{i\mu\sigma}^A - v_{i\mu\sigma}^B) \hat{n}_{i\mu\sigma} |\Phi\rangle = (E_A - E_B) |\Phi\rangle ;$$

projecting this equation over the many-body basis set of Slater determinants $|\Psi_{\vec{\alpha}}\rangle$ (where $\vec{\alpha} \equiv (\alpha_1, \alpha_2, \dots, \alpha_N)$ is a multi-index that indicates the set of N orbitals $\{\phi_{\alpha_k}\}$ from the basis set $\{\phi_{i\mu\sigma}\}$ that define each $|\Psi_{\vec{\alpha}}\rangle$), yields the set of equations

$$\sum_k (v_{\alpha_k}^A - v_{\alpha_k}^B) \langle \Psi_{\vec{\alpha}} | \Phi \rangle = (E_A - E_B) \langle \Psi_{\vec{\alpha}} | \Phi \rangle .$$

If enough coefficients $\langle \Psi_{\vec{\alpha}} | \Phi \rangle$ are non-zero (out of all the many-body basis wavefunctions $|\Psi_{\vec{\alpha}}\rangle$), the resulting system of linear equations has a unique solution, $(v_{i\mu\sigma}^A - v_{i\mu\sigma}^B) = \frac{1}{N}(E_A - E_B)$ (a constant) for all $i\mu\sigma$, indicating that there is a biunivocal correspondence between $\{n_{i\mu\sigma}\}$ and $\{v_{i\mu\sigma}\}$ (except for a constant in the potentials).

The above condition ("if enough coefficients $\langle \Psi_{\vec{\alpha}} | \Phi \rangle$ are non-zero") deserves a comment. Although this condition is satisfied in almost all cases, specific exceptions may be found for particular model Hamiltonians (see a detailed discussion in ref. [24]). In any case, even for these cases the HK (and Levy-Lieb) $E[\{n_{i\mu\sigma}\}]$ is a well-defined *function* of the $\{n_{i\mu\sigma}\}$, as the above discussion of the part 1 of HK theorem (and equation (1)) shows.

The energy $E[\{n_{i\mu\sigma}\}]$ is a minimum w.r.t. the variations of $n_{i\mu\sigma}$, subjected to the condition $\sum_{i\mu\sigma} n_{i\mu\sigma} = N$; this leads to the following equation for each $n_{i\mu\sigma}$:

$$\frac{\partial E[\{n_{j\nu\sigma}\}]}{\partial n_{i\mu\sigma}} = E_F. \quad (3)$$

Kohn-Sham approach

It is convenient at this point to consider the independent electron Hamiltonian:

$$\hat{H} = \sum_{i\mu\sigma} \varepsilon_{i\mu\sigma} \hat{n}_{i\mu\sigma} + \sum_{i\mu \neq j\nu, \sigma} T_{i\mu, j\nu\sigma} \hat{n}_{i\mu, j\nu\sigma} \quad (4)$$

where $\hat{n}_{i\mu\sigma} = \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma}$ and $\hat{n}_{i\mu, j\nu\sigma} = \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma}$. In this Hamiltonian, $E[\{n_{i\mu\sigma}\}] = \sum_{i\mu\sigma} \varepsilon_{i\mu\sigma} n_{i\mu\sigma} + \sum_{i\mu \neq j\nu, \sigma} T_{i\mu, j\nu\sigma} n_{i\mu, j\nu\sigma}$; with $n_{i\mu\sigma} = \langle 0 | \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma} | 0 \rangle$ and $n_{i\mu, j\nu\sigma} = \langle 0 | \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma} | 0 \rangle$, $|0\rangle$ being the

ground state (a Slater determinant) of the independent-electron Hamiltonian. The HK-equation for $n_{i\mu\sigma}$ reads as follows:

$$\varepsilon_{i\mu\sigma} + \frac{\partial T[\{n_{i\nu\sigma}\}]}{\partial n_{i\mu\sigma}} = E_F, \quad (5)$$

where the functional $T[\{n_{i\mu\sigma}\}] = \sum_{kl,j\nu,\sigma'} T_{kl,j\nu,\sigma'} n_{kl,j\nu,\sigma'}$ plays a role similar to the one played by the kinetic energy functional in the conventional DFT-formulation. Solving equations (3) is equivalent to solving equation (2) and calculating from its ground state, $|0\rangle$, $\{n_{i\mu\sigma}\}$ and $\{n_{kl,j\nu,\sigma}\}$. In the KS method for a general many-body Hamiltonian, the functional $T[\{n_{i\mu\sigma}\}]$ is introduced by writing the total energy as:

$$E[\{n_{i\mu\sigma}\}] = \sum_{i\mu\sigma} \varepsilon_{i\mu\sigma} n_{i\mu\sigma} + T[\{n_{i\mu\sigma}\}] + E_{ee}[\{n_{i\mu\sigma}\}], \quad (6)$$

where $T[\{n_{i\mu\sigma}\}]$ is the kinetic energy of an independent-electron system defined by the same $\{T_{i\mu,j\nu\sigma}\}$ of the many-body Hamiltonian, and having at each site, $i\mu\sigma$, the same charge as the exact Hamiltonian. In equation (4), $E_{ee}[\{n_{i\mu\sigma}\}]$ includes the many-body Hartree, Exchange and correlation energies of the system. Notice that, as in the conventional DFT-approach, $T[\{n_{i\mu\sigma}\}]$ is not the actual kinetic energy of the interacting electrons; the difference to the actual one is included however in the correlation contribution. Equation (4) indicates that the functional equation for $n_{i\mu\sigma}$ is:

$$\varepsilon_{i\mu\sigma} + \frac{\partial T[\{n_{i\mu\sigma}\}]}{\partial n_{i\mu\sigma}} + \frac{\partial E_{ee}[\{n_{i\mu\sigma}\}]}{\partial n_{i\mu\sigma}} = E_F \quad (7)$$

and comparing with equation (3), we conclude that the KS-Hamiltonian in this local representation is given by:

$$\hat{H}_{\text{DFT}} = \sum_{i\mu\sigma} \varepsilon_{i\mu\sigma} \hat{n}_{i\mu\sigma} + \sum_{i\mu \neq j\nu,\sigma} T_{i\mu,j\nu\sigma} \hat{n}_{i\mu,j\nu\sigma} + \sum_{i\mu\sigma} V_{ee,i\mu\sigma} \hat{n}_{i\mu\sigma}, \quad (8)$$

where the many-body potential, $V_{ee,i\mu\sigma} = \frac{\partial E_{ee}[\{n_{j\nu\sigma}\}]}{\partial n_{i\mu\sigma}}$ has been introduced. A word of caution should be put here, because in some cases we find in the total energy terms going like $\sum_{i\mu \neq j\nu,\sigma} A_{i\mu,j\nu\sigma} n_{i\mu,j\nu\sigma}$; then, minimizing w.r.t. $n_{i\mu\sigma}$ yields non-diagonal contributions in the DFT-Hamiltonian going like $\sum_{i\mu \neq j\nu\sigma} A_{i\mu,j\nu\sigma} \hat{n}_{i\mu,j\nu\sigma}$, much in the same way as we have proceeded for the $T[\{n_{i\mu\sigma}\}]$ functional in the equivalence between equations (2) and (3).

III. THE LOCAL ORBITAL HAMILTONIAN. HARTREE AND EXCHANGE ENERGIES.

We start this section by writing the following local orbital Hamiltonian that defines the general problem we are interested in:

$$\hat{H} = \sum_{i\mu\sigma} \varepsilon_{i\mu\sigma} \hat{n}_{i\mu\sigma} + \sum_{i\mu \neq j\nu, \sigma} t_{i\mu, j\nu\sigma} \hat{n}_{i\mu, j\nu\sigma} + \frac{1}{2} \sum_{i\mu l\omega j\nu k\lambda\sigma\sigma'} O_{j\nu, k\lambda}^{i\mu, l\omega} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{l\omega\sigma'}^\dagger \hat{c}_{k\lambda\sigma'} \hat{c}_{j\nu\sigma} ; \quad (9)$$

In this equation the operators $\hat{c}_{i\mu\sigma}^\dagger$, $\hat{c}_{j\nu\sigma}$, $\hat{n}_{i\mu\sigma} = \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma}$ and $\hat{n}_{i\mu, j\nu\sigma} = \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma}$ are associated with a given orthonormal local orbital basis set $\{\phi_{i\mu}\}$ such as *e.g.* the Löwdin basis set defined as $\phi_{i\mu} = \sum_{j\nu} (S^{-1/2})_{i\mu, j\nu} \psi_{j\nu}$, where $S_{i\mu, j\nu} = \langle \psi_{i\mu} | \psi_{j\nu} \rangle$ is the orbital overlap matrix for the initial atomic-like basis set, $\{\psi_{i\nu}\}$. The discussion presented in this paper is independent, however, of the chosen initial orthonormal basis set used to define equation (9), since we assume the Hamiltonian (9) to be completely defined by the parameters included in it. In particular, we assume that in equation (9), $\varepsilon_{i\mu\sigma}$ and $t_{i\mu, j\nu\sigma}$ define the one electron terms of our initial Hamiltonian, with the ion-electron and pseudo-potential contributions included. On the other hand, $O_{j\nu, k\lambda}^{i\mu, l\omega}$ defines the spin independent electron-electron interaction:

$$O_{j\nu, k\lambda}^{i\mu, l\omega} = \int \phi_{i\mu}^*(\mathbf{r}) \phi_{l\omega}^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{k\lambda}(\mathbf{r}') \phi_{j\nu}(\mathbf{r}) d\mathbf{r} d\mathbf{r}' . \quad (10)$$

A Hartree-Fock (HF) solution to this Hamiltonian can be obtained by taking the mean value of the electron-electron interaction term in the following way:

$$E_{\text{HF}} = \frac{1}{2} \sum_{\substack{i\mu\sigma \neq l\omega\sigma' \\ j\nu\sigma \neq k\lambda\sigma'}} O_{j\nu, k\lambda}^{i\mu, l\omega} n_{i\mu, j\nu\sigma} n_{l\omega, k\lambda\sigma'} - \frac{1}{2} \sum_{\substack{i\mu \neq l\omega \\ j\nu \neq k\lambda, \sigma}} O_{j\nu, k\lambda}^{i\mu, l\omega} n_{i\mu, k\lambda\sigma} n_{l\omega, j\nu\sigma} , \quad (11)$$

where $n_{i\mu, j\nu\sigma} = \langle \Phi_0 | \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma} | \Phi_0 \rangle$, $|\Phi_0\rangle$ being the assumed non-degenerate ground state (a Slater determinant). The first term of equation (11) represents the Hartree energy while the second represents the Exchange. Notice that for $i\mu\sigma = l\omega\sigma'$ or $j\nu\sigma = k\lambda\sigma'$, the terms excluded in the Hartree and Exchange energies are the same; this allows us to rewrite equation (11) as follows:

$$E_{\text{HF}} = \frac{1}{2} \sum_{i\mu, l\omega, j\nu, k\lambda, \sigma, \sigma'} O_{j\nu, k\lambda}^{i\mu, l\omega} n_{i\mu, j\nu\sigma} n_{l\omega, k\lambda\sigma'} - \frac{1}{2} \sum_{i\mu, l\omega, j\nu, k\lambda, \sigma} O_{j\nu, k\lambda}^{i\mu, l\omega} n_{i\mu, k\lambda\sigma} n_{l\omega, j\nu\sigma} , \quad (12)$$

where the first term is a Hartree energy that includes also all the self-interaction contributions; while the second term is an Exchange energy with all the self-interaction corrections. Taking the derivative of this equation w.r.t. $n_{i\mu\sigma}$ yields $V_{\text{HF},i\mu\sigma}$ (or $V_{\text{HF},i\mu,j\nu\sigma}$), and the corresponding KS-equations, which represents an appropriate HF-solution.

At this point, instead of presenting the different approximations we have made in equation (12) for obtaining an appropriate and accurate HF solution for crystals, we discuss these approximations from the point of view of the initial Hamiltonian (9) which offers a more intuitive view of our way of proceeding. We should stress that these approximations have been inspired by some calculations performed for Si, Ge and Graphene [21]; moreover, we believe that these approximations have a more general application because the rationale behind them is that the neglected terms are found small if the overlap between orbitals, S , is used as an expansion parameter [17, 25].

In general, a good approximation to the solution of Hamiltonian (9) is obtained [21] by neglecting all the $O_{j\nu,k\lambda}^{i\mu,l\omega}$ terms with four different orbitals, $i\mu, j\nu, k\lambda$ and $l\omega$, except if they belong to either the same atom or two nearest-neighbour (NN) sites. The terms associated with only one atom will be represented by $\sum_i \hat{H}_i^A = \hat{H}_1$ and will be analysed in section IV. Terms associated with two orbitals and two different sites ($i\mu$ and $j\nu$) are:

$$\hat{H}_2 = \frac{1}{2} \sum_{i \neq j, \mu\sigma, \nu\sigma'} V_{i\mu,j\nu} \hat{n}_{i\mu\sigma} \hat{n}_{j\nu\sigma'} + \frac{1}{2} \sum_{i \neq j, \mu\sigma, \nu\sigma'} V_{i\mu,j\nu}^x \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma'}^\dagger \hat{c}_{i\mu\sigma'} \hat{c}_{j\nu\sigma} , \quad (13)$$

while the ones associated with three different orbitals (μ, ν and λ) read:

$$\hat{H}_3 = \sum_{\substack{i\mu j\nu k\lambda\sigma\sigma' \\ i \neq j}} h_{k\lambda,i\mu j\nu} \hat{c}_{k\lambda\sigma'}^\dagger \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma} \hat{c}_{k\lambda\sigma'} + \sum_{\substack{i\mu j\nu k\lambda\sigma\sigma' \\ i \neq j}} h_{k\lambda,i\mu j\nu}^x \hat{c}_{k\lambda\sigma'}^\dagger \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{k\lambda\sigma} \hat{c}_{j\nu\sigma'} . \quad (14)$$

The different values for V, V^x, h and h^x in these equations can be explicitly found using equation (10) and the indices indicated for each case. Notice that in equation (12), for $k = i$ or j , we also have a two center contribution not included in \hat{H}_2 ; however, the terms with $k\lambda\sigma = i\mu\sigma$ or $j\nu\sigma$ are zero because $\hat{c}_{i\mu\sigma}^\dagger \hat{c}_{i\mu\sigma}^\dagger = \hat{c}_{j\nu\sigma} \hat{c}_{j\nu\sigma} = 0$. Moreover, as discussed in [21] the contribution from the term h^x in equation (14) can be neglected, as well as the ones coming from the terms going like $\hat{c}_{k\lambda\sigma'}^\dagger \hat{c}_{k\lambda\sigma}^\dagger \hat{c}_{j\nu\sigma} \hat{c}_{i\mu\sigma'}$ or $\hat{c}_{j\nu\sigma'}^\dagger \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{k\lambda\sigma} \hat{c}_{k\lambda\sigma'}$ not included in equation (14).

Finally, the interaction between NN-atoms and four different orbitals is the following:

$$\hat{H}_4 = \frac{1}{2} \sum_{\substack{i,j \rightarrow NN \\ \mu \neq \nu \neq \omega \neq \lambda}} O_{i\nu,j\lambda}^{i\mu,j\omega} \hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\omega\sigma'}^\dagger \hat{c}_{j\lambda\sigma'} \hat{c}_{i\nu\sigma} = \frac{1}{2} \sum_{\substack{i,j \rightarrow NN \\ \mu \neq \nu \neq \omega \neq \lambda}} O_{i\nu,j\lambda}^{i\mu,j\omega} \hat{n}_{i\mu,i\nu\sigma} \hat{n}_{j\omega,j\lambda\sigma'} ; \quad (15)$$

this term represents basically the interaction between the dipoles associated with the operators $\hat{n}_{i\mu,j\nu\sigma}$ and $\hat{n}_{j\omega,j\lambda\sigma'}$ in the NN-atoms i and j of the crystal. In other systems, say molecules with a small symmetry, equation (15) should be extended to other pair of atoms.

Combining $\hat{H}_1, \hat{H}_2, \hat{H}_3$ and \hat{H}_4 gives a fair approximation to the initial Hamiltonian (9). The corresponding Hartree and Exchange energies can be obtained by calculating the mean value of the different terms as explained above; for example $\hat{c}_{i\mu\sigma}^\dagger \hat{c}_{j\nu\sigma'}^\dagger \hat{c}_{i\mu\sigma'} \hat{c}_{j\nu\sigma}$ yields the Hartree, $n_{i\mu,j\nu\sigma} n_{j\nu,i\mu\sigma'}$, and the Exchange, $-\delta_{\sigma,\sigma'} n_{i\mu,i\mu\sigma'} n_{j\nu,j\nu\sigma'}$, contributions. Writing all these contributions together leads to the following Hartree, E_H , and Exchange, E_X , energies:

$$E_H = \sum_i E_{i,H}^A + \frac{1}{2} \sum_{i \neq j, \mu\sigma, \nu\sigma'} V_{i\mu,j\nu} n_{i\mu\sigma} n_{j\nu\sigma'} + \frac{1}{2} \sum_{i \neq j, \mu\nu, \sigma\sigma'} V_{i\mu,j\nu}^x n_{i\mu,j\nu\sigma'} n_{j\nu,i\mu\sigma} \\ + \sum_{\substack{i\mu j\nu k\lambda\sigma\sigma' \\ i \neq j}} h_{k\lambda,i\mu j\nu} n_{k\lambda\sigma} n_{j\nu,i\mu\sigma'} + \frac{1}{2} \sum_{\substack{i,j \rightarrow NN \\ \mu \neq \nu \neq \omega \neq \lambda}} O_{i\omega,j\lambda}^{i\mu,j\nu} n_{i\mu,i\omega\sigma} n_{j\nu,j\lambda\sigma'} , \quad (16)$$

$$E_X = \sum_i E_{i,X}^A - \frac{1}{2} \sum_{i \neq j, \mu, \nu\sigma} V_{i\mu,j\nu} n_{i\mu,j\nu\sigma} n_{j\nu,i\mu\sigma} - \frac{1}{2} \sum_{i \neq j, \mu\nu, \sigma} V_{i\mu,j\nu}^x n_{i\mu\sigma} n_{j\nu\sigma} \\ - \sum_{\substack{i\mu j\nu k\lambda\sigma\sigma' \\ i \neq j}} h_{k\lambda,i\mu j\nu} n_{k\lambda,i\mu\sigma} n_{j\nu,k\lambda\sigma} \quad (17)$$

The contributions from \hat{H}_1 are represented by $\sum_i E_{i,H}^A$ and $\sum_i E_{i,X}^A$. In equation (17) the possible contribution $(-\frac{1}{2} \sum_{i,j \rightarrow NN} O_{i\nu,j\lambda}^{i\mu,j\omega} n_{i\mu\sigma,j\lambda\sigma} n_{j\omega\sigma,i\nu\sigma})$ is very small (see [21]) and has been neglected. Notice also that, in equations (16) and (17), the terms going like $\sum_{i\mu \neq j\nu, k\lambda, \sigma} h_{k\lambda,i\mu j\nu}$ do not have the restriction $k\lambda\sigma \neq i\mu\sigma$ or $j\nu\sigma$, because both contributions for $k\lambda\sigma = i\mu\sigma$ or $j\nu\sigma$ cancel each other. This leaves equation (16) as a typical Hartree contribution that includes all the relevant extra-atomic electron-electron interactions, with the self-interaction included, that are cancelled out by the self-interaction correction of the Exchange contribution of equation (17) (this is equivalent to the discussion going from (11) to (12)).

Equations (16,17) define our HF-approximation to Hamiltonian (9); the corresponding derivatives w.r.t. $n_{i\mu\sigma}$ yield the HF-potentials associated with this HF-approximation. Notice that the derivatives of $n_{i\mu,j\nu\sigma}$ should be treated as done above in the independent-electron

Hamiltonian example; thus, the term $(-\frac{1}{2} \sum_{i \neq j, \mu, \nu \sigma} V_{i\mu, j\nu} n_{i\mu, j\nu \sigma} n_{j\nu, i\mu \sigma})$ in (17) yields the following non-local potential: $(-\sum_{i \neq j, \mu, \nu \sigma} V_{i\mu, j\nu} n_{j\nu, i\mu \sigma} \hat{c}_{i\mu \sigma}^\dagger \hat{c}_{j\nu \sigma})$.

One step forward can be taken, however, reducing some Exchange contributions to simpler forms, more in the spirit of a DFT-formulation. In particular, consider the following terms in equation (17), $(-\frac{1}{2} \sum_{i \neq j, \mu, \nu \sigma} V_{i\mu, j\nu} n_{i\mu, j\nu \sigma} n_{j\nu, i\mu \sigma})$ and $(-\sum_{i \neq j, \mu \nu, k \lambda, \sigma} h_{k\lambda, i\mu j\nu} n_{k\lambda, i\mu \sigma} n_{j\nu, k\lambda \sigma})$. Regarding $(-\frac{1}{2} \sum_{i \neq j, \mu, \nu \sigma} V_{i\mu, j\nu} n_{i\mu, j\nu \sigma} n_{j\nu, i\mu \sigma})$, the identity $\sum_{j\nu \neq i\mu} n_{i\mu, j\nu \sigma} n_{j\nu, i\mu \sigma} = n_{i\mu \sigma} (1 - n_{i\mu \sigma})$ suggests to write: $-\frac{1}{2} \sum_{i \neq j, \mu, \nu \sigma} V_{i\mu, j\nu} n_{i\mu, j\nu \sigma} n_{j\nu, i\mu \sigma} = -\frac{1}{2} \sum_{i\mu \sigma} V_{i\mu}^{\text{eff}} n_{i\mu \sigma} (1 - n_{i\mu \sigma})$, where $V_{i\mu}^{\text{eff}}$ is the effective interaction between the charge $n_{i\mu \sigma}$ and its hole $(1 - n_{i\mu \sigma})$ [19], assuming in this argument that this hole is outside the i -site (see below); then, $V_{i\mu}^{\text{eff}}$ is close to the interaction between $i\mu$ and its NNs orbitals.

Likewise, the contribution $(-\sum_{i \neq j, \mu \nu, k \lambda, \sigma} h_{k\lambda, i\mu j\nu} n_{k\lambda, i\mu \sigma} n_{j\nu, k\lambda \sigma})$ can be reduced to a simpler form by noticing that $\sum_{k\lambda} n_{k\lambda, i\mu \sigma} n_{j\nu, k\lambda \sigma} = n_{j\nu, i\mu \sigma}$; this suggests that $\sum_{i \neq j, \mu \nu, k \lambda, \sigma} h_{k\lambda, i\mu j\nu} n_{k\lambda, i\mu \sigma} n_{j\nu, k\lambda \sigma} = \sum_{j \neq i, \nu \mu, \sigma} h_{j\nu, i\mu}^{\text{eff}} n_{j\nu, i\mu \sigma}$, where $h_{j\nu, i\mu}^{\text{eff}}$ is the effective interaction between the $(j\nu, i\mu)$ -bond charge and its hole. In reference [19], it was found that $h_{j\nu, i\mu}^{\text{eff}}$ is an average of $h_{i\mu, i\mu j\nu}$ and $h_{j\nu, i\mu j\nu}$.

These two transformations allow us to rewrite equation (17) as follows:

$$E_{\text{DFT}, X} = \sum_i E_{i, X}^A - \frac{1}{2} \sum_{i\mu, \sigma} V_{i\mu}^{\text{eff}} n_{i\mu \sigma} (1 - n_{i\mu \sigma}) - \frac{1}{2} \sum_{i \neq j, \mu \nu, \sigma} V_{i\mu, j\nu}^x n_{i\mu \sigma} n_{j\nu \sigma} - \sum_{j \neq i, \nu \mu, \sigma} h_{j\nu, i\mu}^{\text{eff}} n_{j\nu, i\mu \sigma}; \quad (18)$$

leaving apart the $\sum_i E_{i, X}^A$ term, it is interesting to realize that the corresponding contribution of this equation to the DFT-Hamiltonian is: $-\sum_{i\mu, \sigma} V_{i\mu}^{\text{eff}} \left(\frac{1}{2} - n_{i\mu \sigma}\right) \hat{c}_{i\mu \sigma}^\dagger \hat{c}_{i\mu \sigma} - \sum_{i \neq j, \mu \nu, \sigma} V_{i\mu, j\nu}^x n_{j\nu \sigma} \hat{c}_{i\mu \sigma}^\dagger \hat{c}_{i\mu \sigma} - \sum_{j \neq i, \nu \mu, \sigma} h_{j\nu, i\mu}^{\text{eff}} \hat{c}_{j\nu \sigma}^\dagger \hat{c}_{i\mu \sigma}$ whose structure explains by itself why we have called it a DFT-approximation to the Exchange of Hamiltonian (9).

We end up this section by mentioning that the two Exchange contributions, equations (17) and (18), can be combined into a kind of “hybrid” Exchange energy defined by:

$$E_X(\text{hybrid}) = \beta E_X(\text{eq. 17}) + (1 - \beta) E_{\text{DFT}, X}(\text{eq. 18}), \quad (19)$$

with $0 < \beta < 1$. Similar hybrid energies and potentials have been introduced in the literature (see [26–28] as well as the first attempts in this direction by Enrico Clementi [29]), and they have been shown to improve a lot the description of the materials band gaps [30–32].

IV. THE ATOMIC HAMILTONIAN. CORRELATION ENERGY.

We analyze the many-body properties associated with a site i , by means of the following Hamiltonian:

$$\hat{H}^A = \sum_{\mu\sigma} \varepsilon_{\mu\sigma} \hat{n}_{\mu\sigma} + \frac{1}{2} \sum_{\mu\nu\sigma\sigma'} U' \hat{c}_{\mu\sigma}^\dagger \hat{c}_{\nu\sigma'}^\dagger \hat{c}_{\nu\sigma'} \hat{c}_{\mu\sigma} + \frac{1}{2} \sum_{\mu\nu\sigma\sigma'} J \hat{c}_{\mu\sigma}^\dagger \hat{c}_{\nu\sigma'}^\dagger \hat{c}_{\mu\sigma'} \hat{c}_{\nu\sigma}, \quad (20)$$

where the site index, i , has been dropped for simplicity. This equation is usually written as follows [33]:

$$\begin{aligned} \hat{H}^A = & \sum_{\mu\sigma} \varepsilon_{\mu\sigma} \hat{n}_{\mu\sigma} + \sum_{\mu} U \hat{c}_{\mu\uparrow}^\dagger \hat{c}_{\mu\uparrow} \hat{c}_{\mu\downarrow}^\dagger \hat{c}_{\mu\downarrow} + \frac{1}{2} \sum_{\mu\sigma \neq \nu\sigma'} U' \hat{c}_{\mu\sigma}^\dagger \hat{c}_{\mu\sigma} \hat{c}_{\nu\sigma'}^\dagger \hat{c}_{\nu\sigma'} - \\ & \frac{1}{2} \sum_{\mu \neq \nu, \sigma} J \hat{c}_{\mu\sigma}^\dagger \hat{c}_{\mu\sigma} \hat{c}_{\nu\sigma}^\dagger \hat{c}_{\nu\sigma} - \frac{1}{2} \sum_{\mu \neq \nu, \sigma} J \hat{c}_{\mu\sigma}^\dagger \hat{c}_{\mu, \bar{\sigma}} \hat{c}_{\nu, \bar{\sigma}}^\dagger \hat{c}_{\nu\sigma}, \end{aligned} \quad (21)$$

where $U = U' + J$; U (U') is the Coulomb interaction between the $\mu \uparrow, \mu \downarrow$ ($\mu\sigma, \nu\sigma'$) orbitals, while J represents the Exchange interaction between orbitals, μ and ν , having the same spin. The last term of Hamiltonian (21) represents a spin-flip term for the $(\mu\bar{\sigma}, \nu\sigma)$ states; this spin-flip term is needed, as expected from equation (20), in order to have a rotationally invariant Hamiltonian with $U = U' + J$ [34].

Notice that equations (20) or (21) show that:

$$\begin{aligned} E_H^A = & \sum_{\mu} U n_{\mu\uparrow} n_{\mu\downarrow} + \frac{1}{2} \sum_{\mu\sigma \neq \nu\sigma'} U' n_{\mu\sigma} n_{\nu\sigma'} + \frac{1}{2} \sum_{\mu \neq \nu, \sigma} J n_{\mu\nu, \nu\mu, \sigma} = \\ & \frac{U'}{2} \mathcal{N}(\mathcal{N} - 1) + \frac{U'}{2} \sum_{\mu\sigma} n_{\mu\sigma} (1 - n_{\mu\sigma}) + J \sum_{\mu} n_{\mu\uparrow} n_{\mu\downarrow} + \frac{1}{2} \sum_{\mu \neq \nu, \sigma} J n_{\mu, \nu, \sigma} n_{\nu, \mu, \sigma} \end{aligned} \quad (22)$$

and:

$$\begin{aligned} E_X^A = & -\frac{1}{2} \sum_{\mu \neq \nu, \sigma} J n_{\mu, \sigma} n_{\nu, \sigma} - \frac{U'}{2} \sum_{\mu \neq \nu, \sigma} n_{\mu, \nu\sigma} n_{\nu, \mu\sigma} = \\ & -\frac{U'}{2} \sum_{\mu \neq \nu, \sigma} n_{\mu, \nu\sigma} n_{\nu, \mu\sigma} - \frac{J}{2} \mathcal{N}(\mathcal{N} - 1) - \frac{J}{2} \sum_{\mu\sigma} n_{\mu\sigma} (1 - n_{\mu\sigma}) + J \mathcal{N}_{\uparrow} \mathcal{N}_{\downarrow}, \end{aligned} \quad (23)$$

so that:

$$\begin{aligned} E_H^A + E_X^A = & \frac{U' - J}{2} \mathcal{N}(\mathcal{N} - 1) + \sum_{\mu\sigma} \frac{U' - J}{2} n_{\mu\sigma} (1 - n_{\mu\sigma}) + \\ & J \left(\mathcal{N}_{\uparrow} \mathcal{N}_{\downarrow} + \sum_{\mu} n_{\mu\uparrow} n_{\mu\downarrow} \right) - \frac{U' - J}{2} \sum_{\mu \neq \nu\sigma} n_{\mu\nu\sigma} n_{\nu\mu\sigma}; \end{aligned} \quad (24)$$

this equation completes the HF-equations (16,17) for E_H , E_X given above. In these equations $\mathcal{N}_\sigma = \sum_\mu \mathcal{N}_{\mu\sigma}$ and $\mathcal{N} = \mathcal{N}_\uparrow + \mathcal{N}_\downarrow$.

A DFT-approximation to this HF energy can be obtained by combining the term, $-\frac{1}{2} \sum_{i \neq j, \mu\nu\sigma} V_{i\mu,j\nu} n_{i\mu,j\nu\sigma} n_{j\nu,i\mu\sigma}$, with $-\frac{1}{2} \sum_{i, \mu \neq \nu, \sigma} (U' - J) n_{i\mu,i\nu\sigma} n_{i\nu,i\mu\sigma}$ in equation (24) (including here the index i). Thus, we can write:

$$\begin{aligned} & -\frac{1}{2} \sum_{i \neq j, \mu\nu\sigma} V_{i\mu,j\nu} n_{i\mu,j\nu\sigma} n_{j\nu,i\mu\sigma} - \frac{1}{2} \sum_{i, \mu \neq \nu, \sigma} (U' - J) n_{i\mu,i\nu\sigma} n_{i\nu,i\mu\sigma} = \\ & -\frac{1}{2} \sum_{i\mu\sigma} V_{i\mu\sigma}'^{\text{eff}} n_{i\mu\sigma} (1 - n_{i\mu\sigma}) \end{aligned} \quad (25)$$

where $V_{i\mu\sigma}'^{\text{eff}}$ is the effective interaction between $n_{i\mu\sigma}$ and its hole $(1 - n_{i\mu\sigma})$; $V_{i\mu\sigma}'^{\text{eff}}$ differs from $V_{i\mu\sigma}^{\text{eff}}$ in equation (18) because in $V_{i\mu\sigma}'^{\text{eff}}$ we also include the effect of the possible intra-atomic hole associated with $-\frac{1}{2} \sum_{\mu \neq \nu, \sigma} (U' - J) n_{i\mu,i\nu\sigma} n_{i\nu,i\mu\sigma}$, which disappears however in crystals of high symmetry if $n_{i\mu,i\nu\sigma} = 0$. Then, making use of the identity $-\sum_{i \neq j, \mu\nu, k\lambda, \sigma} h_{k\lambda, i\mu j\nu} n_{k\lambda, i\mu\sigma} n_{j\nu, k\lambda\sigma} = -\sum_{j \neq i, \nu\mu, \sigma} h_{j\nu, i\mu}^{\text{eff}} n_{j\nu, i\mu\sigma}$, leads to:

$$\begin{aligned} & \sum_i (E_{i,H}^A + E_{i,X}^A) - \frac{1}{2} \sum_{i \neq j, \mu, \nu\sigma} V_{i\mu,j\nu} n_{i\mu,j\nu\sigma} n_{j\nu,i\mu\sigma} - \sum_{i \neq j, \mu\nu, k\lambda, \sigma} h_{k\lambda, i\mu j\nu} n_{k\lambda, i\mu\sigma} n_{j\nu, k\lambda\sigma} = \\ & \frac{1}{2} \sum_i (U'_i - J_i) \mathcal{N}_i (\mathcal{N}_i - 1) + \sum_{i\mu\sigma} \frac{1}{2} (U'_i - V_{i\mu\sigma}'^{\text{eff}} - J_i) n_{i\mu\sigma} (1 - n_{i\mu\sigma}) + \sum_i J_i \mathcal{N}_{i\uparrow} \mathcal{N}_{i\downarrow} + \\ & \sum_{i\mu} J_i n_{i\mu\uparrow} n_{i\mu\downarrow} - \sum_{j \neq i, \nu\mu, \sigma} h_{j\nu, i\mu}^{\text{eff}} n_{j\nu, i\mu\sigma}, \end{aligned} \quad (26)$$

which defines with equations (16) and (18) the energy of the DFT-approximation to the HF-solution of Hamiltonian (9).

For analyzing the correlation energy associated with Hamiltonian (21), the atom should be embedded within a material that we model by assuming each atomic orbital to interact with a semi-infinite 1D-chain (figure 1); in our calculations, the number of orbitals μ in the atom will be $M = 2, 3$ or 5 . This interaction is described by the following one- electron Hamiltonian:

$$\hat{H}^{\text{oe}} = \sum_{\mu\alpha\sigma} \varepsilon_{\mu\alpha\sigma} \hat{n}_{\mu\alpha\sigma} + \sum_{NN, \mu, \alpha \neq \beta, \sigma} t \left(\hat{c}_{\mu\alpha\sigma}^\dagger \hat{c}_{\mu\beta\sigma} + \hat{c}_{\mu\beta\sigma}^\dagger \hat{c}_{\mu\alpha\sigma} \right) + \sum_{\mu, \sigma} T (\hat{c}_{\mu\sigma}^\dagger \hat{c}_{\mu\alpha_1, \sigma} + \hat{c}_{\mu\alpha_1, \sigma}^\dagger \hat{c}_{\mu\sigma}) , \quad (27)$$

where the (α, β) -indices refer to states of one chain, and μ to the superchain $\{\mu, \mu\alpha_1, \dots\}$ (see reference [22]). In this particular model, we have independent channels, say μ and ν ,

and $n_{\mu\nu\sigma} = \langle \Phi_0 | \hat{c}_{\mu\sigma}^\dagger \hat{c}_{\nu\sigma} | \Phi_0 \rangle = 0$ for $\mu \neq \nu$. Then, the HF-energy for the atomic model we are considering is given by:

$$E_{\text{HF}}^A = \sum_{\mu} U n_{\mu\uparrow} n_{\mu\downarrow} + \frac{1}{2} \sum_{\mu\sigma \neq \nu\sigma'} U' n_{\mu\sigma} n_{\nu\sigma'} - \frac{1}{2} \sum_{\mu \neq \nu, \sigma} J n_{\mu\sigma} n_{\nu\sigma} . \quad (28)$$

There still remains a point to be discussed: how to calculate the different parameters, U' and J , introduced in our model for analyzing the atomic correlation energy of the general Hamiltonian (9). Apparently, following our initial Hamiltonian (9), U' and J should be calculated from equation (10) introducing the local atomic wave-functions associated with the local orthonormal orbitals. While the value of J , a short-ranged Exchange interaction, is well approximated in this way, U' and U appear to be too large when compared with more conventional values used in the literature [10, 35–37]; as a first consideration, this can be related to the extra-atomic Exchange energy, $-\frac{1}{2} \sum_{i\mu, \sigma} V_{i\mu}^{\text{eff}} n_{i\mu\sigma} (1 - n_{i\mu\sigma})$, introduced in equation (18). As mentioned above, this equation collects the interaction between the charge $n_{i\mu\sigma}$ and the hole $(1 - n_{i\mu\sigma})$ located practically in the NNs atoms; it should also be realized that the rest of the total electron hole, $1 - (1 - n_{i\mu\sigma}) = n_{i\mu\sigma}$, is associated with the Exchange self-interaction correction, $-\frac{1}{2} U n_{i\mu\sigma}^2$, not included in equation (23) because the corresponding self-interaction Hartree energy does not appear in equation (22). On the other hand, correlation effects in the atom should be associated with a fraction, of the extra-atomic Exchange hole, $r_{i\mu\sigma}(1 - n_{i\mu\sigma})$, being transferred to the orbital $i\mu$. This means that the extra-atomic Exchange energy, $-\frac{1}{2} \sum_{i\mu\sigma} V_{i\mu}^{\text{eff}} n_{i\mu\sigma} (1 - n_{i\mu\sigma})$, should be reduced to $-\frac{1}{2} \sum_{i\mu\sigma} V_{i\mu}^{\text{eff}} (1 - r_{i\mu\sigma}) n_{i\mu\sigma} (1 - n_{i\mu\sigma})$, while an intra-atomic correlation energy given by, $-\frac{1}{2} \sum_{i\mu\sigma} U'_{i\mu} r_{i\mu\sigma} n_{i\mu\sigma} (1 - n_{i\mu\sigma})$, should appear. These two effects can be combined in the following correlation energy:

$$E_{\text{corr}} = -1/2 \sum_{i\mu\sigma} (U'_{i\mu} - V_{i\mu}^{\text{eff}}) r_{i\mu\sigma} n_{i\mu\sigma} (1 - n_{i\mu\sigma}) , \quad (29)$$

where $r_{i\mu\sigma}$ can be calculated in a further step, working out some specific model. Equation (29) suggests to introduce the following effective interactions, $U^{\text{eff}} = (U - V^{\text{eff}})$ and $U'_{\text{eff}} = (U' - V^{\text{eff}})$, in our model Hamiltonian for calculating the atomic correlation energy. Notice also that in equation (26) we have found the following intra-atomic contribution to $(E_{i,H}^A + E_{i,X}^A)$:

$$\frac{1}{2} \sum_i (U'_i - J_i) \mathcal{N}_i (\mathcal{N}_i - 1) + \sum_{i\mu\sigma} \frac{1}{2} (U'_i - V_{i\mu\sigma}^{\text{eff}} - J_i) n_{i\mu\sigma} (1 - n_{i\mu\sigma}) + \sum_i J_i \mathcal{N}_{i\uparrow} \mathcal{N}_{i\downarrow} + \sum_{i\mu} J_i n_{i\mu\uparrow} n_{i\mu\downarrow} ,$$

where $\frac{1}{2} \sum_{i\mu\sigma} (U'_i - V_{i\mu\sigma}'^{eff} - J_i) n_{i\mu\sigma} (1 - n_{i\mu\sigma})$ already includes the effective interaction $(U'_i - V_{i\mu\sigma}'^{eff})$ instead of U'_i . However, we still find the bare interaction U' in the Hartree contribution $\frac{1}{2} \sum_i (U'_i - J_i) \mathcal{N}_i (\mathcal{N}_i - 1)$, in apparent contradiction with our initial model. The point here is that in the atomic Hamiltonian used for analyzing correlations effects we neglect the Coulomb interaction between the atom i and any other center, say $i \neq j$: this means that the screening effects associated with those (i, j) -interactions should be introduced in the atomic Hamiltonian by screening appropriately the value of U'_i in the contribution $\frac{1}{2} \sum_i (U'_i - J_i) \mathcal{N}_i (\mathcal{N}_i - 1)$. The value found for the term $\frac{1}{2} \sum_{i\mu\sigma} (U'_i - V_{i\mu\sigma}'^{eff} - J_i) n_{i\mu\sigma} (1 - n_{i\mu\sigma})$ suggests that taking $\frac{1}{2} (U'_i - V_{i\mu\sigma}'^{eff} - J_i) \mathcal{N}_i (\mathcal{N}_i - 1)$ is the consistent and symmetric way of screening that U'_i in the Hartree contribution.

Although the values of U_i^{eff} and $U_i'^{eff}$ are much smaller than the initial ones, they are still too large; however, as argued below for 3d-magnetic atoms, correlation effects associated with the 3d-electrons described in our model Hamiltonian, taking in it the interactions U^{eff} and U'^{eff} , screens these effective interactions to values in good agreement with standard quantities [38, 39].

These effective interactions can also be understood by means of an alternative and complementary argument: due to the fluctuations of the electrons between the environment and the atom changes do appear in the energy of the system associated with U (or U'), the new electron-electron interaction after the fluctuation, minus the interaction of the fluctuating electron with the hole left behind; this yields the effective interactions just mentioned.

For the sake of simplicity, from now on, we will still analyze correlation effects with Hamiltonian (21), using U and U' , but keeping in mind that these quantities should be reduced to $U^{\text{eff}} = U - V^{\text{eff}}$ and $U'^{\text{eff}} = U' - V^{\text{eff}}$ for calculating the correlation energy.

Then, we have analyzed Hamiltonian (21) for two cases: (a) $U = U'$ and $J = 0$ (the Hubbard case), and (b) $J = 0.1U$, $U' = 0.9U$ (the Hubbard-Hund case, where the first Hund rule is important) [22]. Analyzing numerically this many-body Hamiltonian is a formidable task; thus, in a first step we have taken in each one-dimensional chain only three levels and consider the space of electronic configurations defined by having initially zero total S_z -spin and four electrons in each super-chain, as well as all the other configurations obtained by applying \hat{H}^A to that initial set.

A. The Hubbard case ($J = 0$)

In our occupation number formulation:

$$E^A = \sum_{\mu\sigma} \varepsilon_{\mu\sigma} n_{\mu\sigma} + E_{\text{HF}}^A[\{n_{\mu\sigma}\}] + E_{\text{corr}}^A[\{n_{\mu\sigma}\}], \quad (30)$$

so that $V_{\text{HF}}^A = \frac{\partial E_{\text{HF}}^A[\{n_{\nu\sigma}\}]}{\partial n_{\mu\sigma}}$, $V_{\text{corr}}^A = \frac{\partial E_{\text{corr}}^A[\{n_{\nu\sigma}\}]}{\partial n_{\mu\sigma}}$. From equations (22) and (23), we find $E_X^A = 0$, $E_{\text{HF}}^A = E_H^A$ with:

$$E_H^A = \sum_{\mu} U n_{\mu\uparrow} n_{\mu\downarrow} + \frac{1}{2} \sum_{\mu\sigma \neq \nu\sigma'} U n_{\mu\sigma} n_{\nu\sigma'} = \frac{U}{2} \mathcal{N}(\mathcal{N} - 1) + \frac{U}{2} \sum_{\mu\sigma} n_{\mu\sigma} (1 - n_{\mu\sigma}), \quad (31)$$

where $\mathcal{N} = \sum_{\mu\sigma} n_{\mu\sigma}$ is the total number of electrons in the atom. For calculating $E_{\text{corr}}^A[\{n_{\mu\sigma}\}]$, it is convenient to consider first the $U/T \rightarrow \infty$ limit. Assume that the atomic charge is \mathcal{N} , with $N \leq \mathcal{N} \leq N + 1$; the atomic charge fluctuates in this limit between N and $N + 1$ electrons, with probabilities weights a and b ($a + b = 1$), respectively. Then, $\mathcal{N} = aN + b(N + 1)$, so that $a = N - \mathcal{N} + 1$, $b = \mathcal{N} - N$, and the electron-electron interaction energy is given by:

$$E_{ee}^A(\mathcal{N}) = aE_{ee}^A(N) + bE_{ee}^A(N + 1) = \frac{1}{2}NU(2\mathcal{N} - N - 1), \quad (32)$$

where use of the equations $E_{ee}^A(N) = \frac{1}{2}UN(N - 1)$ and $E_{ee}^A(N + 1) = \frac{1}{2}U(N + 1)N$ has been made. Combining equations (31) and (32) leads to the following correlation energy:

$$E_{\text{corr}}^A = E_{ee}^A - E_H^A = \frac{1}{2}U\delta\mathcal{N}(1 - \delta\mathcal{N}) - \frac{1}{2}U \sum_{\mu\sigma} n_{\mu\sigma} (1 - n_{\mu\sigma}), \quad (U/T \rightarrow \infty), \quad (33)$$

where $\delta\mathcal{N} = \mathcal{N} - N$ takes values between 0 and 1: $0 < \delta\mathcal{N} < 1$. As the Hartree potential, for $J = 0$, is given by:

$$V_{H,\mu\sigma}^A = \frac{\partial E_H^A}{\partial n_{\mu\sigma}} = U(\mathcal{N} - 1/2) + U \left(\frac{1}{2} - n_{\mu\sigma} \right), \quad (34)$$

and the correlation potential for $U/T \rightarrow \infty$ by:

$$V_{\text{corr},\mu\sigma}^A = \frac{\partial E_{\text{corr}}^A}{\partial n_{\mu\sigma}} = U \left(\frac{1}{2} - \delta\mathcal{N} \right) - U \left(\frac{1}{2} - n_{\mu\sigma} \right), \quad (35)$$

the effective atomic potential, $V_{\mu\sigma}^{A,\text{eff}} = V_{H,\mu\sigma}^A + V_{\text{corr},\mu\sigma}^A$, is equal to $U(\mathcal{N} - \delta\mathcal{N}) = UN$, jumping by U when \mathcal{N} crosses an integer number, as corresponds to the atomic levels of an isolated

atom. Figure 2 shows for $U/T \rightarrow \infty$, $V_{\text{corr},\mu\sigma}^A$ for $M = 3$ as a function of $n_{\mu\sigma} = \mathcal{N}/2M$; notice the jump by U in this potential for \mathcal{N} equal to an integer number. For U/T finite, it was found in reference [22] by means of numerical calculations, that the atomic correlation potential can be expressed, with a good approximation, as:

$$V_{\text{corr},\mu\sigma}^A = -F_1 U \left(\frac{1}{2} - n_{\mu\sigma} \right) + F_2 U \left(\frac{1}{2} - \delta\mathcal{N} \right), \quad (36)$$

where:

$$\begin{aligned} F_1 &= f_1 \tanh[\alpha_1 n_{\mu\sigma} (1 - n_{\mu\sigma})] \\ F_2 &= f_2 \tanh[\alpha_2 \delta\mathcal{N} (1 - \delta\mathcal{N})], \end{aligned} \quad (37)$$

α_i being constants determined in each case for different values of U/T and M . It is convenient to show in figure 3, $V_{\text{corr},\mu\sigma}^A$ for $M = 2$ (two atomic levels), and for $U/T = 4, 6$ and 8 ; the corresponding values of f_1, f_2, α_1 and α_2 are given in Table I. The important point to notice from this figure is that the contribution of $F_2 U (1/2 - \delta\mathcal{N})$ is very small for $U/T = 4$, suggesting that in the limit, $U/T \sim 4$, equation (36) can be approximated by:

$$V_{\text{corr},\mu\sigma}^A = -F_1 U \left(\frac{1}{2} - n_{\mu\sigma} \right), \quad (U/T \sim 4). \quad (38)$$

It is interesting to realize that this value of $U/T = 4$ is in the frontier between lowly correlated materials (normal metals or conventional semiconductors) and highly correlated materials (magnetic metals or 3d-transition metal oxides). For normal metals or conventional semiconductors, the total bandwidth of the valence and conduction electrons is in the order of 20 eVs, while for 3d-magnetic metal atoms that total bandwidth is around 4.5 eVs.

Since in the 1-dimensional chains of the model shown in figure 1 the bandwidth is around $\sqrt{12}/T$ [40], we conclude that the values of T in that model should be around 6 eVs for lowly correlated materials, and around 1.3 eV in the highly correlated ones. On the other hand, the corresponding values of U (in this case, the value of $U - V^{\text{eff}}$ mentioned above) are around 3-5 (6-9) eVs in the lowly (highly) correlated materials. These values suggest that U/T is around 0.7 or 6 for the lowly or highly correlated systems. Therefore, we concentrate our discussion on the Hubbard case (appropriate for lowly correlated materials) for low values of U/T , say for $U/T < 4$. On the contrary, in the next section we will discuss the Hund-Hubbard case, including the Hund interaction in the atom, for $U/T > 4$, a limit more appropriate for 3d-magnetic systems.

Before discussing in detail the case $U/T < 4$ for the Hubbard case, it is convenient to make a comment: in the calculations performed in reference [22] for $M = 2$ and $m = 3$ (three levels in the chain), the hopping t has been changed from 0 to $2T$, exploring the effect of that hopping, t , on the correlation energy of the atom. Our calculations have shown only minor changes in the correlation energy and potential with the changes of t , indicating that the fluctuations of charge in the atomic levels are mainly controlled by T , the hopping between the atom and the first atomic level of each chain.

Accordingly, the results presented below have been calculated taking the simplest case $t = 0$, reducing each chain to only one atom (in our notation this means $m = 1$). Figures 4, 5 and 6 show the correlation potential, $V_{\text{corr},\mu\sigma}^A$, for $U/T = 4, 2$ and 1 , and for different number of atomic orbitals, $M = 2, 3$ and 5 . In the fitting of these potentials we have found that f_2 can be neglected completely (only for $U/T = 4$ and $M = 2$, we have found a slight contribution of f_2), so that $V_{\text{corr},\mu\sigma}^A$ reads as:

$$V_{\text{corr},\mu\sigma}^A = -f_1 \tanh[\alpha_1 n_{\mu\sigma}^{3/2} (1 - n_{\mu\sigma})^{3/2}] U \left(\frac{1}{2} - n_{\mu\sigma} \right); \quad (39)$$

where we have found a better fitting using $[\alpha_1 n_{\mu\sigma}^{3/2} (1 - n_{\mu\sigma})^{3/2}]$ instead of $[\alpha_1 n_{\mu\sigma} (1 - n_{\mu\sigma})]$ as done in equation (37). Equation (39) also yields the effective potential, $V_{\mu\sigma}^{A,\text{eff}}$, as:

$$V_{\mu\sigma}^{A,\text{eff}} = V_{H,\mu\sigma}^A + V_{\text{corr},\mu\sigma}^A = 1 - f_1 \tanh[\alpha_1 n_{\mu\sigma}^{3/2} (1 - n_{\mu\sigma})^{3/2}] U (1/2 - n_{\mu\sigma}), \quad (40)$$

Table II gives the different values of f_1 and α_1 used in the fitting of this potential; from the values shown in this Table, we can see that the correlation potential increases slightly with the number of atomic orbitals, M , although the cases $M = 3$ and $M = 5$ are very similar. In all cases, however, the correlation potential is still important for $U/T = 1$, because in this case f_1 is still around 0.5 indicating an important screening of the Hubbard interaction, U , as shown by equation (40). Notice that for $0.25 < n_{\mu\sigma} < 0.75$, $\tanh[\alpha_1 n_{\mu\sigma}^{3/2} (1 - n_{\mu\sigma})^{3/2}] \sim 1$, so that $V_{\mu\sigma}^{A,\text{eff}} = (1 - f_1) U \left(\frac{1}{2} - n_{\mu\sigma} \right)$; this equation shows that $(1 - f_1)$ is a good parameter measuring how important the screening of correlation effects is.

B. B. The Hubbard-Hund case ($J = 0.1U$)

The case $J \neq 0$ can be analyzed following a similar path to the one taken in the Hubbard case. First, consider the $U/T \rightarrow \infty$ limit, and calculate the electron-electron interaction

energy; as shown in reference [22], this is given by:

$$E_{ee}^A = \frac{1}{2}(U' - J)N(2\mathcal{N} - N - 1) + J(M + 1)(\mathcal{N} - M)\Theta(\mathcal{N} - M). \quad (41)$$

Combining this equation with equation (28) for the atomic HF-energy, yields the following correlation energy

$$\begin{aligned} E_{\text{corr}}^A[\{n_{\mu\sigma}\}] = & \frac{1}{2}(U' - J)\delta\mathcal{N}(1 - \delta\mathcal{N}) - \frac{1}{2}(U' - J)\sum_{\mu\sigma} n_{\mu\sigma}(1 - n_{\mu\sigma}) \\ & + J(M + 1)(\mathcal{N} - M)\Theta(\mathcal{N} - M) - J\mathcal{N}_{\uparrow}\mathcal{N}_{\downarrow} - J\sum_{\mu} n_{\mu\uparrow}n_{\mu\downarrow}, \end{aligned} \quad (42)$$

and:

$$\begin{aligned} V_{\text{corr}}^A[\{n_{\mu\sigma}\}] = & \frac{\partial E_{\text{corr}}^A[\{n_{\nu\sigma}\}]}{\partial n_{\mu\sigma}} = (U' - J)(1/2 - \delta\mathcal{N}) - (U' - J)(1/2 - n_{\mu\sigma}) \\ & - J\{(\mathcal{N}_{\bar{\sigma}} + n_{\mu\bar{\sigma}}) - (M + 1)\Theta(\mathcal{N} - M)\} \quad (\text{for } U/T \rightarrow \infty). \end{aligned} \quad (43)$$

Comparing with the Hubbard case, equation (35), we find that: (a) U is changed to $(U' - J)$, and (b) that there appears a new term $-J\{(\mathcal{N}_{\bar{\sigma}} + n_{\mu\bar{\sigma}}) - (M + 1)\Theta(\mathcal{N} - M)\}$ associated with the Exchange interaction. Figure 7 shows the correlation potential, eq. 43, for $M = 3$, $n_{\mu\sigma} = \mathcal{N}/M$ and $U/T \rightarrow \infty$. Notice that the jump in $(M + 1)J$ for $n_{\mu\sigma} = 1/2$ (or $\mathcal{N} = M$), is related to the change between the atomic levels for 4 and 3 electrons, $(U' - J) + (M + 1)J$ (or $(U' - J) + 4J$ in the case of $M = 3$): in all the other cases, the difference between consecutive atomic levels is $(U' - J)$ (see figure 7b). This jump is also reflected in the different curves calculated for $V_{\text{corr}}^A[\{n_{\mu\sigma}\}]$. $V_{\text{corr}}^A[\{n_{\mu\sigma}\}]$ has been fitted by the equation:

$$\begin{aligned} V_{\text{corr}}^A[\{n_{\mu\sigma}\}] = & F_2(U' - J) \left(\frac{1}{2} - \delta\mathcal{N} \right) - F_1(U' - J) \left(\frac{1}{2} - n_{\mu\sigma} \right) - \\ & J\{F_3(\mathcal{N}_{\bar{\sigma}} + n_{\mu\bar{\sigma}}) - F_4(M + 1)\Theta(\mathcal{N} - M)\}, \end{aligned} \quad (44)$$

where F_1 and F_2 are also given by equations (37), and:

$$\begin{aligned} F_3 = & f' \tanh(\alpha_3 x (M + 1 - x)), \quad \text{with } x = \mathcal{N}_{\bar{\sigma}} + n_{\mu\bar{\sigma}}; \\ F_4 = & f' / [1 + \exp(-\alpha_4 (N - M))] \end{aligned} \quad (45)$$

Table III shows the values of $f_1, f_2, f', \alpha_1, \alpha_2, \alpha_3$, and α_4 as obtained in our fitting for $V_{\text{corr}}^A[\{n_{\mu\sigma}\}]$, taking $M = 3$ and 5, and $U/T = 4, 6$ or 8 [22]; from the curves shown in figure 8 we conclude that: (a) the term $F_2(U' - J) \left(\frac{1}{2} - \delta\mathcal{N} \right)$ is very small in all the cases except

for $M = 3$ and $U/T = 8$, where small oscillations associated with this term are still found. (b) The jump associated with the term $-J\{F_3(\mathcal{N}_{\bar{\sigma}} + n_{\mu\bar{\sigma}}) - F_4(M+1)\Theta(\mathcal{N} - M)\}$ is clearly seen for $U/T = 8$; however, its contribution disappears for $U/T = 4$, and is very small for $U/T = 6$. (c) For $U/T = 4$, only the term $-F_1(U' - J)\left(\frac{1}{2} - n_{\mu\sigma}\right)$ survives in all the cases. These results show that for $U/T \sim 6$, it is a good approximation to write:

$$V_{\text{corr},\mu\sigma}^A[\{n_{\mu\sigma}\}] = -F_1(U' - J)\left(\frac{1}{2} - n_{\mu\sigma}\right). \quad (46)$$

Since the HF-potential for this Hubbard-Hund case is given by:

$$V_{HF,\mu\sigma}^A[\{n_{\mu\sigma}\}] = \frac{\partial E_{HF}^A[\{n_{\mu\sigma}\}]}{\partial n_{\mu\sigma}} = (U' - J)\left(\mathcal{N} - \frac{1}{2}\right) + (U' - J)\left(\frac{1}{2} - n_{\mu\sigma}\right) + J(\mathcal{N}_{\bar{\sigma}} + n_{\mu\bar{\sigma}}),$$

the effective potential associated with the electron-electron interaction, $V^{A,\text{eff}}[\{n_{\mu\sigma}\}]$, is:

$$V_{\mu\sigma}^{A,\text{eff}}[\{n_{\mu\sigma}\}] = (U' - J)(\mathcal{N} - 1/2) + (1 - F_1)(U' - J)\left(\frac{1}{2} - n_{\mu\sigma}\right) + J(\mathcal{N}_{\bar{\sigma}} + n_{\mu\bar{\sigma}}). \quad (47)$$

This equation shows that for $U/T \sim 6$, only the term $(U' - J)(1/2 - n_{\mu\sigma})$ is screened to $(1 - F_1)(U' - J)\left(\frac{1}{2} - n_{\mu\sigma}\right)$. For $0.25 < n_{\mu\sigma} < 0.75$, $F_1 \sim f_1$, and $(1 - f_1) \sim 0.3$ (see Table III), indicating that these screening effects can be very important, reducing $(U' - J) \sim 5 - 7$ eV to $(U' - J)^{\text{eff}} \sim 1.8 \pm 0.3$ eV. This result explains why the values of $(U' - J)$ used in the semi-empirical DFT+U calculations for systems with 3d-atoms are much smaller than the ones afforded by a restricted DFT approach: *the crucial point to realize is that in the DFT+U calculations, U (or $U' - J$) should be screened by the correlation effects associated with the 3d-shell.* [9]

We complete this discussion about the Hubbard-Hund Hamiltonian, by analyzing the Stoner parameter afforded by equation (47). In this case we need to calculate the change of $V_{\mu\sigma}^{A,\text{eff}}$ associated with the atomic magnetization $\delta n_{\mu\sigma} = -\delta n_{\mu\bar{\sigma}}$, assuming that all the orbitals with the same spin change by the same value. Then, from equation (47) we get the following equation:

$$\begin{aligned} \delta V_{\mu\sigma}^{A,\text{eff}}[\{n_{\mu\sigma}\}] &= -(1 - F_1)(U' - J)\delta n_{\mu\sigma} + J(\delta \mathcal{N}_{\bar{\sigma}} + \delta n_{\mu\bar{\sigma}}) = \\ &= -((1 - F_1)(U' - J) + J(M + 1))\delta n_{\mu\sigma}, \end{aligned} \quad (48)$$

where we have assumed $\delta n_{\mu\bar{\sigma}} = -\delta n_{\mu\sigma}$, and $\delta \mathcal{N}_{\bar{\sigma}} = M\delta n_{\mu\bar{\sigma}}$. Equation (48) leads to the following Stoner parameter:

$$I = -\frac{\partial V_{\mu\sigma}^{A,\text{eff}}}{\partial n_{\mu\sigma}} = (1 - F_1)(U' - J) + J(M + 1). \quad (49)$$

In Fe, the bandwidth, Δ , is 4.5 eV [41], the atomic U , taking into account atomic relaxation effects, is 14.7 eV and $V^{eff} \sim 6.0$ eV [42], so that $U^{eff}/T \approx \sqrt{12}$, i.e. $U^{eff}/\Delta \approx 6.7$, and $F_1 \approx f_1 \approx 0.73$. As $J = 0.83$ eV [19], $(M+1)J \approx 5.0$ eV and $(1-f_1)(U'^{eff}-J) \approx 1.7$ eV, so that we conclude that: $I \approx 6.7$ eV and that magnetization in Fe is mainly controlled by the Exchange interaction (the first Hund rule). It should be mentioned that the parameter f_2 is not completely negligible in this case; for Fe we find that $f_2 \approx 0.2$ so that $(M+1)J$ is screened to $(M+1)(1-f_2)J \approx 4.0$ eV still much larger than $(1-f_1)(U'^{eff}-J) \approx 1.55$ eV.

V. CONCLUSIONS

We have presented a Closed Local Orbital formulation of DFT, whereby the effective local potential, $V_{i\mu\sigma}^{eff}$, created by all the electrons is described by means of the occupation numbers $n_{i\mu\sigma}$ associated with the orthonormal local orbitals $\phi_{i\mu\sigma}$. We have shown that the Hohenberg-Kohn and Kohn-Sham theorems hold taking as independent variable the charges $\{n_{i\mu\sigma}\}$ associated with the orthonormal local orbitals $\{\phi_{i\mu\sigma}\}$. This allows us to calculate $V_{i\mu\sigma}^{eff}$ without resorting to the conventional calculation of $V(\mathbf{r})$.

We have also analyzed the many-body local orbital Hamiltonian given by equation (9), and have calculated in this local representation, (a) the Hartree-Fock energy, (16),(17) and (24), and (b) the corresponding DFT energy given by equations (16),(18) and (26).

In section III we have analyzed the correlation energy of our many-body system by means of the Kanamori Hamiltonian that includes the Hubbard (U) and the Hund (J) interactions. We have shown that for both lowly and highly correlated 3d-materials, the atomic effective potential, $V_{i\mu\sigma}^{A,eff}[\{n_{\mu\sigma}\}]$, can be described by equation (47) where $-F_1(U'-J)\left(\frac{1}{2}-n_{i\mu\sigma}\right)$ collects the correlation contribution. The effect of this term is to screen $(U'-J)\left(\frac{1}{2}-\delta n_{i\mu\sigma}\right)$ to $(1-F_1)(U'-J)\left(\frac{1}{2}-\delta n_{i\mu\sigma}\right)$, with dramatic effects in the DFT+U calculations for 3d-materials and in the value of the Stoner parameter. Finally, we stress that in the calculation of the correlation effects we are using some many-body techniques that typically cannot be included in the conventional DFT-calculations. Our description in terms of $\{n_{i\mu\sigma}\}$ allows us, however, to incorporate those techniques in our DFT-formalism that, in this sense, is a kind of an unified description.

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U/T	4	6	8
f_1	0.60	0.67	0.78
f_2	0.09	0.20	0.30
α_1	8.6	9.1	9.8
α_2	0.01	0.4	5.6

TABLE I: Table I shows f_1 , f_2 , α_1 and α_2 , see eq. (36), for the Hubbard Hamiltonian, $M = 2$, $m = 3$; $U/T = 4, 6$ and 8 .

	$M = 2$			$M = 3$			$M = 5$		
U/T	4	2	1	4	2	1	4	2	1
f_1	0.72	0.58	0.45	0.72	0.60	0.52	0.75	0.65	0.55
α_1	15	10.5	7.4	21	15	10	30	21	15

TABLE II: Values of f_1 and α_1 , see eq. (39), for $M = 2, 3$ and 5 for $U/T = 4, 2$ and 1 .

	$M = 3$			$M = 5$		
U/T	4	6	8	4	6	8
f_1	0.55	0.68	0.71	0.57	0.70	0.73
f_2	0.00	0.03	0.09	0.01	0.09	0.17
f_3	0.15	0.20	0.24	0.15	0.21	0.33
α_1	10.1	11.2	12.3	12.1	22.1	27.2
α_2	0.08	0.40	4.7	0.08	0.3	5.1
α_3	25.2	41.2	48.7	25.2	41.2	48.7
α_4	17.5	24.2	36.6	11.3	14.0	31.5

TABLE III: f_i and α_i , see eq. (44), for the Hubbard-Hund Hamiltonian, $M = 3$ and $M = 5$ for $U/T = 4, 6$ and 8 .

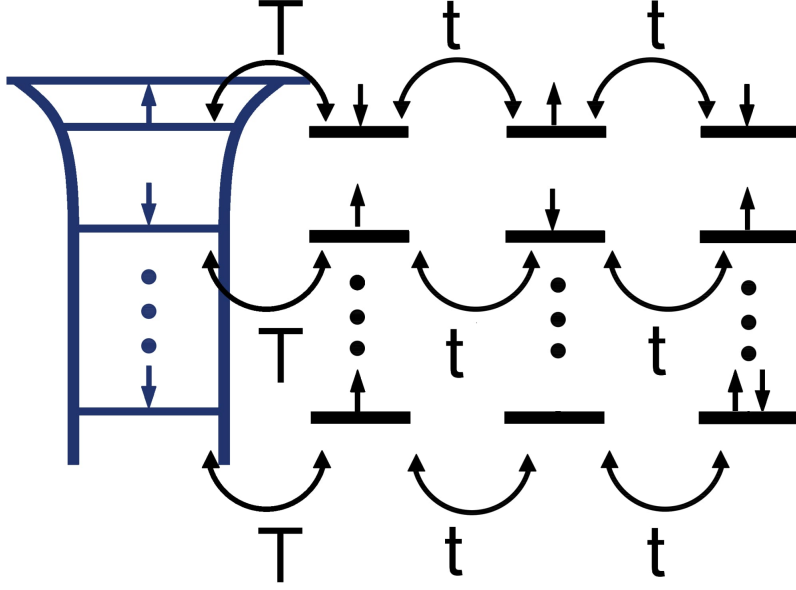


FIG. 1: (Color online) Schematic representation of our model system. An atomic shell of $2M$ $i\sigma$ -orbitals (left), described by the atomic Hamiltonian \hat{H}^A , eq. (20), is connected to different channels (right), that simulate the effect of the environment, by means of a one-electron Hamiltonian \hat{H}^{OE} , eq. (27). In our calculations, each channel is simulated by a chain of three sites; in each super-chain (the atomic level plus the chain) we assume to have always four electrons.

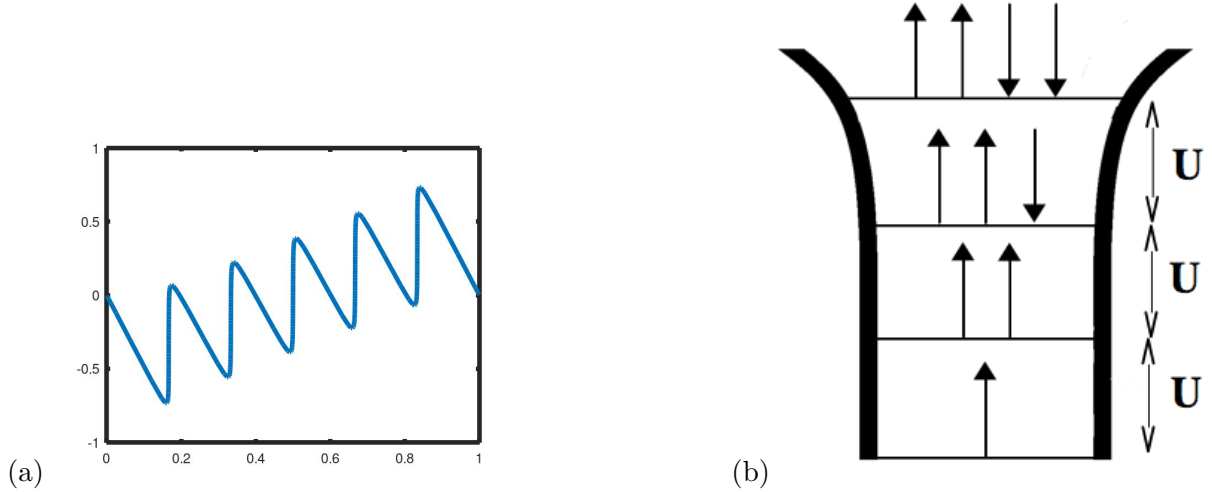


FIG. 2: (Color online) (a) V_{corr}^A (in units of U) as a function of $n_{\mu\sigma} = \mathcal{N}/2M$ for $M = 3$ and $U/T \rightarrow \infty$ (Hubbard case). Notice the jump by U for \mathcal{N} equal to an integer number.

(b) Atomic levels for $M = 2$.

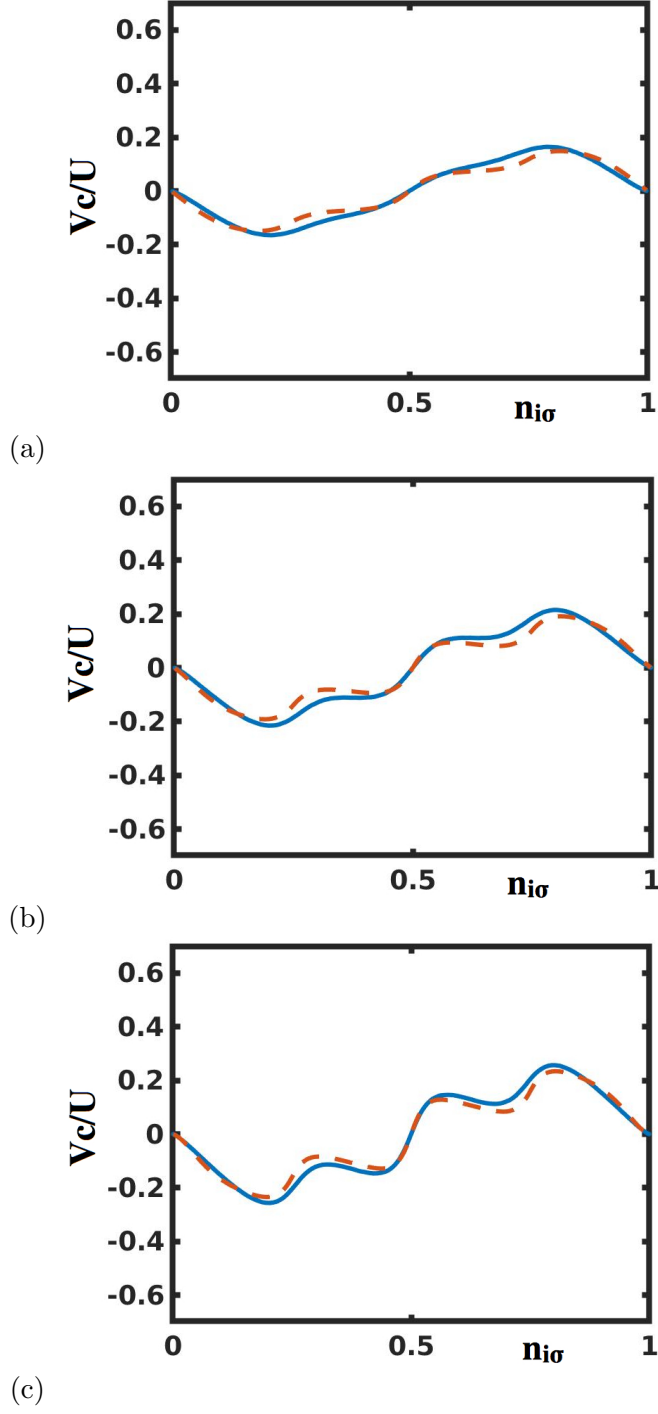


FIG. 3: (Color online) V_{corr}^A as a function of $n_{\mu\sigma} = \mathcal{N}/2M$ for $M = 2$ and $U/T = 4$ (a), 6 (b) and 8 (c). Dashed line: fitting using eq. (36).

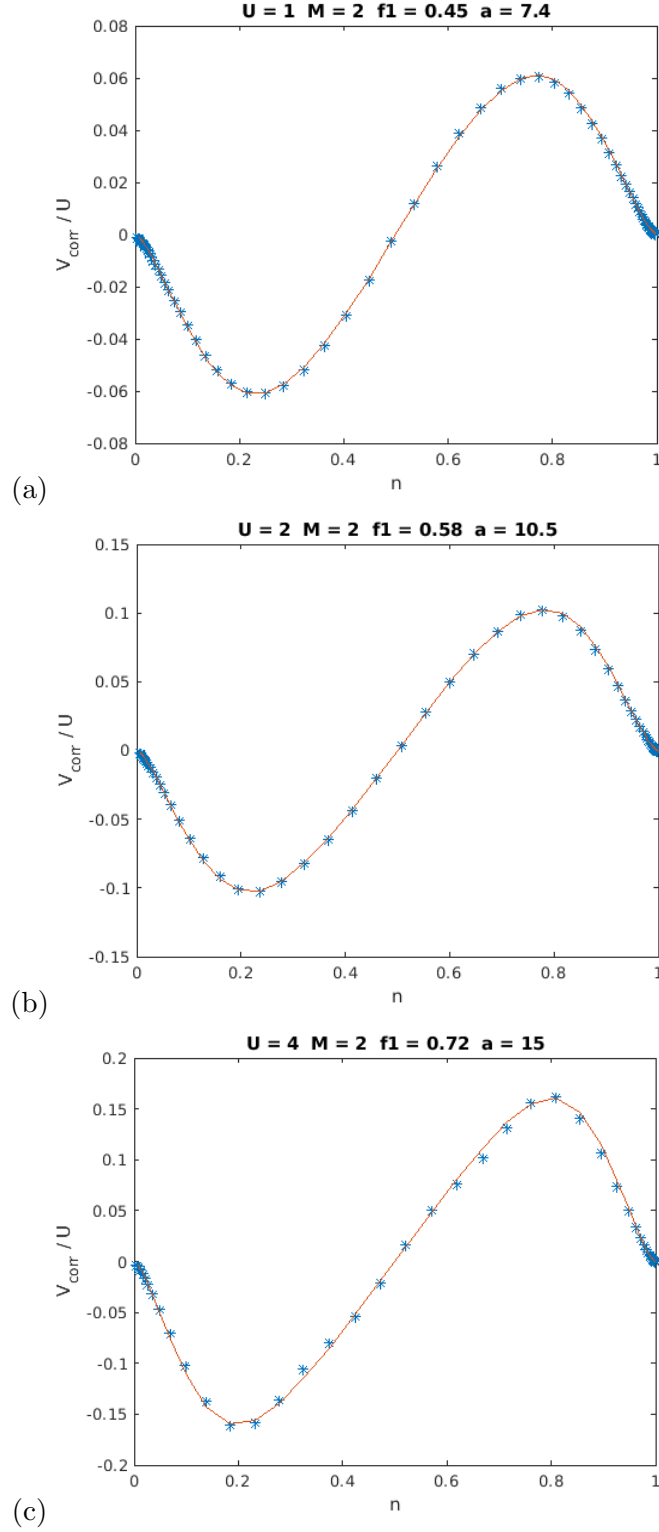


FIG. 4: (Color online) V_{corr}^A as a function of $n_{\mu\sigma} = \mathcal{N}/2M$ for $M = 2$ and $U/T = 1$ (a), 2 (b) and 4 (c). The blue asterisks (*) are the results of the calculations while the red solid line represents the fit using eq. (39).

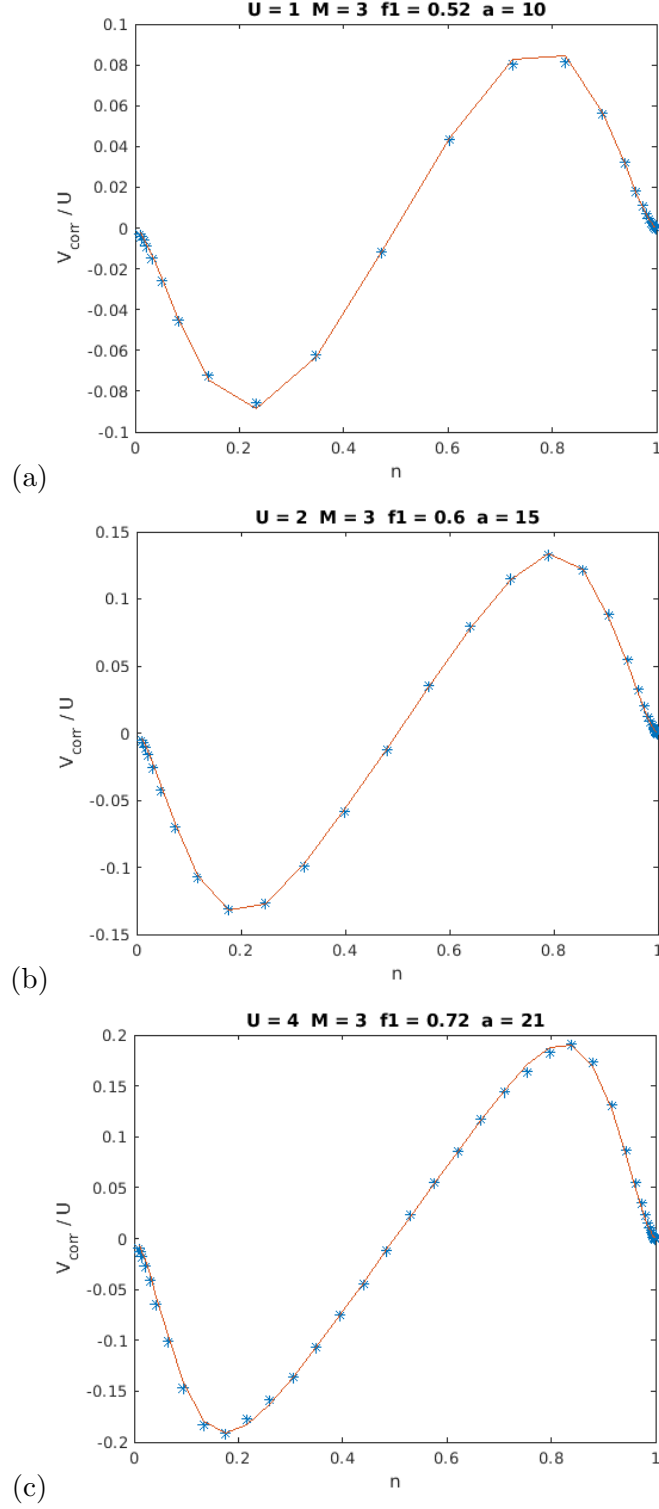


FIG. 5: (Color online) V_{corr}^A as a function of $n_{\mu\sigma} = \mathcal{N}/2M$ for $M = 3$ and $U/T = 1$ (a), 2 (b) and 4 (c). The blue asterisks (*) are the results of the calculations while the red solid line represents the fit using eq. (39).

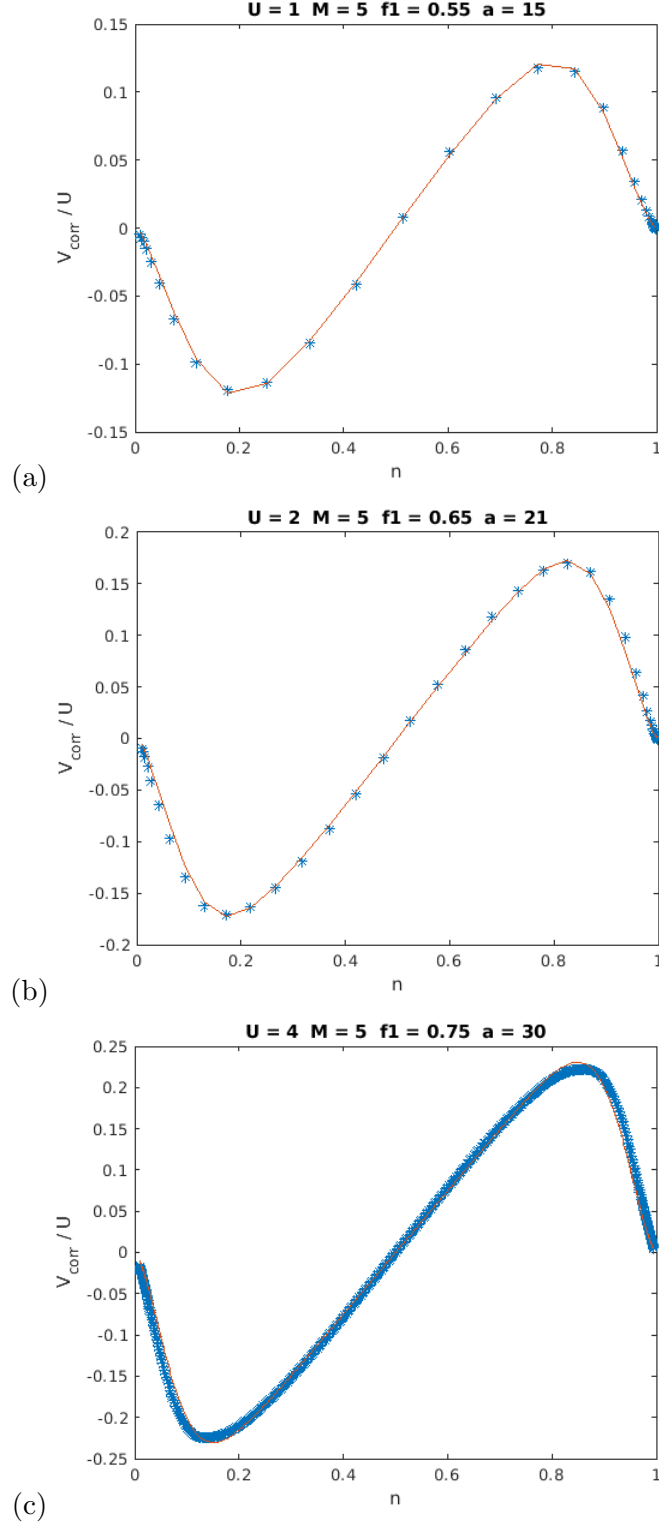


FIG. 6: (Color online) V_{corr}^A as a function of $n_{\mu\sigma} = \mathcal{N}/2M$ for $M = 5$ and $U/T = 1$ (a), 2 (b) and 4 (c). The blue asterisks (*) are the results of the calculations while the red solid line represents the fit using eq. (39).

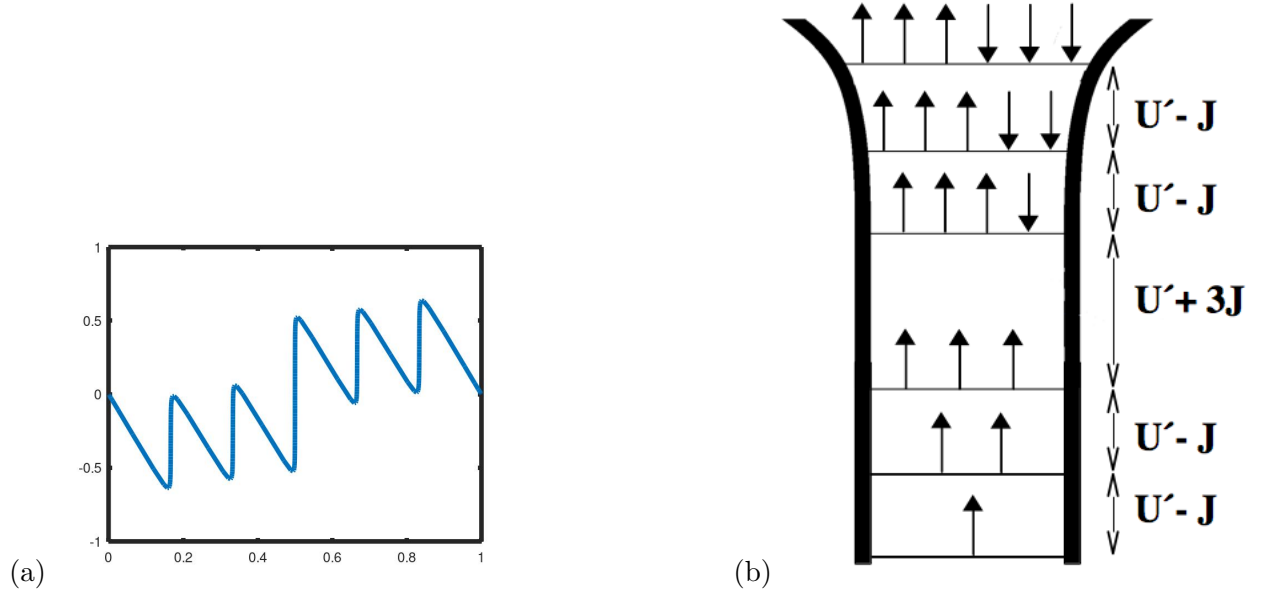


FIG. 7: (Color online) (a) V_{corr}^A (in units of U) as a function of $n_{\mu\sigma} = \mathcal{N}/2M$ for $M = 3$ and $U/T \rightarrow \infty$ (Hubbard-Hund case). (b) Atomic levels for $M = 3$.

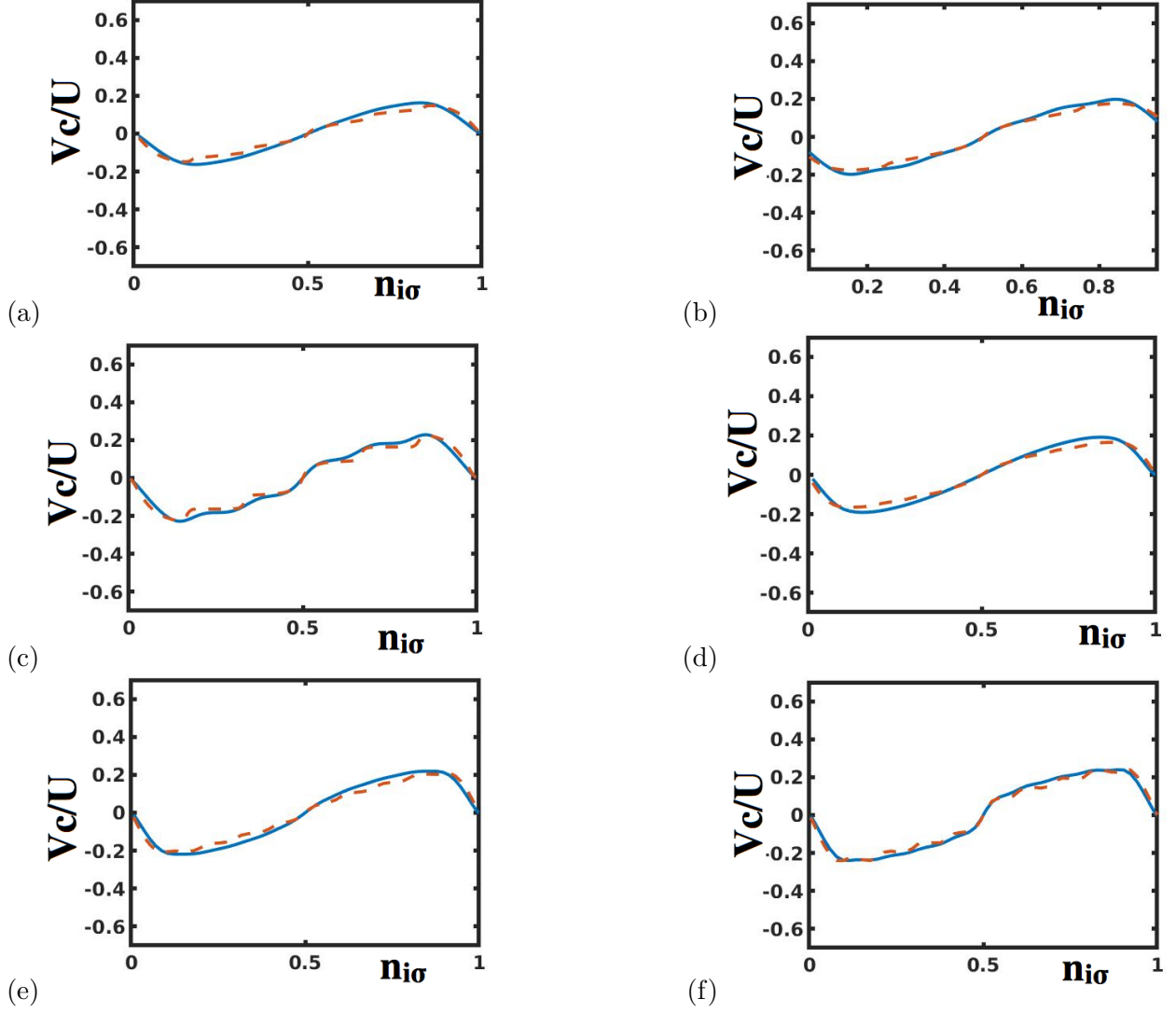


FIG. 8: (Color online) V_{corr}^A as a function of $n_{\mu\sigma} = \mathcal{N}/2M$ for (a) $M = 3, U/T = 4$; (b) $M = 3, U/T = 6$; (c) $M = 3, U/T = 8$; (d) $M = 5, U/T = 4$; (e) $M = 5, U/T = 6$; (f) $M = 5, U/T = 8$. Dashed line: fitting using eq. (44).