4 The LDA+U Approach: A Simple Hubbard Correction for Correlated Ground States

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One of the most well known and well documented failures of Density Functional Theory (DFT) [1, 2] is certainly represented by Mott insulators . In these systems the insulating character of the ground state stems from the strong Coulomb repulsion between electrons that, prevailing on their kinetic energy (minimized by delocalization), forces them to localize on atomic-like orbitals (Mott localization) [3]. The precise description of this behavior requires the full account of the multi-determinant nature of the N-electron wave function and of the many-body terms of the electronic interactions. In molecular dissociation processes, for example, the localization of electrons on the resulting fragments can only be properly described if the so-called *ionic terms* (describing multiple valence electrons on the same site) of the ground state wave function are allowed to decrease their weight (e.g., in a variational calculation) while the distance between the fragments increases. This is only possible if the N-electron wave function is constructed as a linear combination of multiple Slater determinants. In other words, when electrons are strongly localized their motion becomes "correlated" and their wave function acquires a marked many-body character. Thus, the Hartree-Fock (HF) method, that describes the electronic ground state with a variationally optimized single determinant, cannot capture the physics of Mott insulators. The insulating character of these materials is also beyond reach for band theory.For these reasons they are generally classified as "strongly-correlated" materials (in fact, the formal definition of correlation energy is $E_c = E_{exact} - E_{HF}$ where E_{HF} represents the HF approximation to the exact quantity). Describing the behavior of these systems within (approximate) DFT is a formidable task (although the unknown exact exchange-correlation energy functional would be able to predict their ground state properties) due to the expression of the electron-electron interaction as a functional of the electronic charge density, and to the use of an effective single particle (Kohn-Sham) representation of this quantity [2]. In fact, most commonly used approximate exchange-correlation (xc) functionals such as, the Local Density Approximation (LDA) [4–6], or the Generalized Gradient Approximation (GGA), fail quite dramatically in predicting the insulating character of these materials and also provide a quite poor representation of other physical properties, including their equilibrium crystal structure, their magnetic moments, their vibrational spectrum, etc. In general, these problems can be traced back to the tendency of most approximate xc functionals to over-delocalize valence electrons and to over-stabilize metallic ground states. Other inaccuracies of approximate xc functionals such as, the imprecise account of the exchange interaction and the consequent incomplete cancellation of the electronic self-interaction contained in classical (density-density) Coulomb integrals may sometimes concur to the over-delocalization of electronic states.

One of the simplest models that have been formulated to rationalize (albeit in a semi-quantitative way) the physics of correlated materials, is the Hubbard model [7–12] whose real-space second-quantization formalism is ideally suited to describe systems with electrons localized on atomic orbitals. In its simplest, one-band incarnation, the Hubbard Hamiltonian can be written as follows:

$$H_{Hub} = t \sum_{\langle i,j \rangle, \sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow} \tag{1}$$

where $\langle i, j \rangle$ denotes nearest-neighbor atomic sites, $c^{\dagger}_{i,\sigma}$, $c_{j,\sigma}$, and $n_{i,\sigma}$ are electronic creation,

annihilation and number operators for electrons of spin σ on site i. When electrons are strongly localized, their motion is described by a "hopping" process from one atomic site to its neighbors (first term of Eq. (1)) whose amplitude t is proportional to the dispersion (the bandwidth) of the valence electronic states and represents the single-particle term of the total energy. In virtue of the strong localization, the Coulomb repulsion is only accounted for between electrons on the same atom through a term proportional to the product of the occupation numbers of atomic states on the same site, whose strength is U (the "Hubbard U"). The hopping amplitude and the on-site Coulomb repulsion represent the minimal set of parameters necessary to capture the physics of Mott insulators. In fact, in these systems, the insulating character of the ground state emerges when single-particle terms of the energy (generally minimized by electronic delocalization on more extended states) [3] are overcome by short-range Coulomb interactions (the energy cost of double occupancy of the same site): $t << U$. In other words, the system becomes insulator (even at half-filling conditions, when band theory would predict a metal) when electrons cannot hop around because they don't have sufficient energy to overcome the repulsion from other electrons on neighbor sites. Therefore, the balance between U and t controls the behavior of these systems and the character of their electronic ground state. While the regime dominated by single-particle terms of the energy ($t >> U$) is generally well described by approximate DFT, the opposite one ($t << U$) is far more problematic.
The LDA+U (by this name I indicate a "+U" correction applied to a generic approximate DFT functionals, not necessarily LDA) is one of the simplest corrective approaches that were formulated to improve the accuracy of DFT functionals in describing the ground state of correlated systems [13–17]. The idea it is based on is quite simple and consists in using the the Hubbard Hamiltonian to describe "strongly correlated" electronic states (typically, localized d or f orbitals), while the rest of valence electrons are treated at the "standard" level of approximation. Within LDA+U the total energy of a system can be written as follows:

$$E_{LDA+U}[\rho(\mathrm{r})] = E_{LDA}[\rho(\mathrm{r})] + E_{Hub}[\{n^{I\sigma}_{mm'}\}] - E_{dc}[\{n^{I\sigma}\}]. \tag{2}$$

In this equation E$_{Hub}$ is the term that contains electron-electron interactions as modeled in the Hubbard Hamiltonian. Because of the additive nature of this correction it is necessary to eliminate from the (approximate) DFT energy functional E_{LDA} the part of the interaction energy already contained in E_{Hub} to avoid double-counting problems. This task is accomplished by the subtraction of the so-called "double-counting" (dc) term E_{dc} that models the contribution to the DFT energy from correlated electrons as a mean-field approximation to E_{Hub}. Due to the lack of a precise diagrammatic expansion of the DFT total energy, the dc term is not uniquely defined, and different possible formulations and implementations will be discussed in section 2.1 It is important to stress that the Hubbard correction is only applied to the localized states of the system (typically the ones most affected by correlation effects). In fact, it is a functional of occupation numbers that are often defined as projections of occupied Kohn-Sham orbitals (ψ^{σ}_{kv}) on the states of a localized basis set (ϕ^{I}_{m}):

$$n^{I\sigma}_{m,m'} = \sum_{k,v} f^{\sigma}_{kv} \langle \psi^{\sigma}_{kv} | \phi^{I}_{m'} \rangle \langle \phi^{I}_{m} | \psi^{\sigma}_{kv} \rangle \tag{3}$$

where f^{σ}_{kv} are the Fermi-Dirac occupations of the Kohn-Sham (KS) states (k and v being, respectively, the k-point and band indexes). Using the occupations defined in Eq. (3) in the functional of Eq. (2) corresponds to substituting the number operators appearing in Eq. (1) with their (mean-field) average on the occupied manifold of the system. While this operation is necessary to use the Hubbard model in current implementations of DFT, the choice of the localized basis set is not unique. Some of the most popular choices, as atomic orbitals or maximally localized Wannier functions, are briefly discussed in section 2.3.

The reminder of this chapter is organized as follows. In section 1 I will review the historical formulation of LDA+U and the most widely used implementations, discussing the theoretical background of the method in the framework of DFT. In section 2 I will compare different flavors of LDA+U obtained from different choices of the corrective functional, of the set of interactions, of the localized basis set to define atomic occupations. In section 3 I will review different methods to compute the necessary interaction parameters, particularly focusing on one based on linear-response. Section 4 will illustrate the calculation of energy derivatives (forces, stress, dynamical matrix) in LDA+U. In section 5 I will present a recently introduced extension to the LDA+U that contains both on-site and inter-site effective interactions. Finally, in section 6 I will offer some conclusions and an outlook on the future of this method.

1 Basic formulations and approximations

1.1 General formulation

In Eq. (2) the general structure of the LDA+U energy functional was introduced. I will now discuss the most common implementations of this corrective approach starting from the simplest and most general one. The LDA+U approach was first introduced in Refs. [14–16] and consisted of an energy functional that, when specialized to on-site interactions, can be written as follows:

$$E = E_{LDA} + \sum_I \left[\frac{U^I}{2} \sum_{m,\sigma \neq m',\sigma'} n^{I\sigma}_m n^{I\sigma'}_{m'} - \frac{U^I}{2} n^I (n^I - 1) \right]. \tag{4}$$

In Eq. (4) $n^{I\sigma}_m = n^{I\sigma}_{mm}$, and $n^I = \sum_{m,\sigma} n^{I\sigma}_m$, and the index m labels the localized states of the same atomic site I. The second and the third terms of the right-hand side of this equation represent, respectively, the Hubbard and the double-counting terms of Eq. (2). Using the definition of atomic orbital occupations given in Eq. (3), one can easily define the action of the Hubbard corrective potential on the Kohn-Sham wave functions needed for the minimization process:

$$V|\psi^{\sigma}_{k,v}\rangle = V_{LDA}|\psi^{\sigma}_{k,v}\rangle + \sum_{I,m} U^I \left(\frac{1}{2} - n^{I\sigma}_m \right) |\phi^I_m\rangle\langle\phi^I_m|\psi^{\sigma}_{k,v}\rangle. \tag{5}$$

It is important to notice that, because the definition of the atomic occupations (Eq. (3)), the Hubbard potential is non-local. Therefore, the LDA+U energy functional (Eq. (4)) is out of the validity domain of the Hohenberg-Kohn theorem [1]. It respects, however, the conditions of the Gilbert theorem [18]; the Kohn-Sham equations obtained from Eq. (4) will thus yield the ground state one-body density matrix of the system. As evident from Eq. (5), the Hubbard potential is repulsive for less than half-filled orbitals ($n^{I\sigma}_m < 1/2$), attractive for the others. This is the mechanism through which the Hubbard correction discourages fractional occupations of localized orbitals (often indicating significant hybridization with neighbor atoms) and favors the Mott localization of electrons ($n^{I\sigma}_m \to 1$). The difference between the potential acting on occupied and unoccupied states (whose size is of the order of U) also gives a measure of the energy gap opening between their eigenvalues. Thus, consistently with the predictions of the Hubbard model, the explicit account of on-site electron-electron interactions favors electronic localization and may lead to a band gap in the KS spectrum of the system, provided the on-site Coulomb repulsion prevails on the kinetic term of the energy, minimized through delocalization. Although this appears as a significant improvement over the result of approximate DFT, it is important to remark that a gap only appears in the band structure if possible degeneracies between the (localized) states around the Fermi level are lifted. To achieve this result it is sometimes necessary to artificially impose the symmetry of the electronic system to be lower than the point group of the crystal as, for example, in the case of FeO [19] and CuO [20]. This operation corresponds to "preparing" the system in one of the possibly degenerate insulating states (having electrons localized on different subsets of orbitals), characterized by a finite gap in the band structure of the corresponding KS spectrum. As will be discussed in sections 1.4 and 3.3, this result highlights that the LDA+U is out of the realm of DFT, as the Kohn-Sham spectrum of the exact functional is not constrained to reflect any physical property (while the charge density should maintain the whole symmetry of the crystal).

1.2 Rotationally-invariant formulation

While able to capture the main essence of the LDA+U approach, the formulation presented in Eq. (4) is not invariant under rotation of the atomic orbital basis set used to define the occupation of d states $n^I_{m\sigma}$, which produces an undesirable dependence of the results on the specific choice of the localized basis set. To solve these problems, A. Liechtenstein and coworkers [21] introduced a basis set independent formulation of LDA+U in which E_{Hub} and E_{dc} are given a more general expression borrowed from the HF method:

$$\begin{aligned} E_{Hub}[\{n^I_{mm'}\}] = \frac{1}{2} \sum_{\{m\},\sigma,I} \{ & \langle m,m''|V_{ee}|m',m'''\rangle n^{I\sigma}_{mm'} n^{I-\sigma}_{m''m'''} + \\ & (\langle m,m''|V_{ee}|m',m'''\rangle - \langle m,m''|V_{ee}|m''',m'\rangle) n^{I\sigma}_{mm'} n^{I\sigma}_{m''m'''} \} \end{aligned} \tag{6}$$

$$E_{dc}[\{n^I_{mm'}\}] = \sum_I \{ \frac{U^I}{2} n^I (n^I - 1) - \frac{J^I}{2} [n^{I\uparrow}(n^{I\uparrow} - 1) + n^{I\downarrow}(n^{I\downarrow} - 1)] \}. \tag{7}$$

The invariance of the "Hubbard" term (Eq. (6)) stems from the fact that the interaction parameters transform as quadruplets of localized wavefunctions, thus compensating the variation of the (product of) occupations associated with them. In Eq. (7), instead, the invariance stems from the dependence of the functional on the trace of the occupation matrices. In Eq. (6) the V_{ee} integrals represents the electron-electron interactions computed on the wave functions of the localized basis set (e.g., d atomic states) that are labeled by the index m. Assuming that atomic (e.g., d or f) states are chosen as the localized basis, these quantities can be computed from the expansion of the $e^2/|r-r'|$ Coulomb kernel in terms of spherical harmonics (see [21] and references quoted therein):

$$\langle m, m''|V_{ee}|m', m'''\rangle = \sum_k a_k(m, m', m'', m''')F^k \tag{8}$$

where $0 \leq k \leq 2l$ (l is the angular moment of the localized manifold; $-l \leq m \leq l$) and the a_k factors can be obtained as products of Clebsh-Gordan coefficients:

$$a_k(m, m', m'', m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} \langle lm|Y_{kq}|lm'\rangle\langle lm''|Y^*_{kq}|lm'''\rangle. \tag{9}$$

In Eq. (8) the F^k coefficients are the radial Slater integrals computed on the Coulomb kernel [21]. For d electrons only F^0, F^2, and F^4 are needed to compute the V_{ee} matrix elements (for higher k values the corresponding a_k would vanish) while f electrons also require F^6. Consistently with the definition of the dc term (Eq. (7)) as the mean-field approximation of the Hubbard correction (Eq. (6)), the effective Coulomb and exchange interactions, U and J, can be computed as atomic averages of the corresponding Coulomb integrals over the states of the localized manifold (in this example, atomic orbitals of fixed l):

$$U = \frac{1}{(2l+1)^2} \sum_{m,m'} \langle m, m'|V_{ee}|m, m'\rangle = F^0, \tag{10}$$

$$J = \frac{1}{2l(2l+1)} \sum_{m \neq m', m'} \langle m, m'|V_{ee}|m', m\rangle = \frac{F^2+F^4}{14}. \tag{11}$$

These equations have often been used (assuming that F^2/F^4 has the same value as in isolated atoms) to evaluate *screened* Slater integrals F^k from the values of U and J, computed from the ground state of the system of interest (some methods to calculate these quantities will be illustrated in section 3). The *screened* V_{ee} integrals, to be used in the corrective functional of Eq. (6), can then be easily obtained from the computed F^k using Eqs. (8) and (9). Although Eqs. (8)-(11) are strictly valid for atomic states and *unscreened* Coulomb kernels, this procedure can be assumed quite accurate for solids if the localized orbitals retain their atomic character.

1.3 A simpler formulation

The one presented in section 1.2 is the most complete formulation of the LDA+U, based on a multi-band Hubbard model. However, in many occasions, a much simpler expression of the Hubbard correction (E_{Hub}), introduced in Ref. [22], is actually adopted and implemented. This simplified functional can be obtained from the full formulation discussed in section 1.2 by retaining only the lower order Slater integrals F^0 and throwing away the others: $F^2 = F^4 = J = 0$. This simplification corresponds to neglecting the non-sphericity of the electronic interactions ($a_0(m, m', m'', m''') = \delta_{m,m'}\delta_{m'',m'''}$) and the differences among the couplings between parallel spin and anti-parallel spin electrons (i.e., the exchange interaction J). The energy functional can be recalculated from Eqs. (6) and (7) and one easily obtains:

$$\begin{aligned} E_U[\{n^{I\sigma}_{mm'}\}] &= E_{Hub}[\{n^{I}_{mm'}\}] - E_{dc}[\{n^I\}] \\ &= \sum_I \frac{U^I}{2}\left[\left(n^I\right)^2 - \sum_\sigma \mathrm{Tr}\,[(\mathbf{n}^{I\sigma})^2]\right] - \sum_I \frac{U^I}{2} n^I(n^I - 1) \\ &= \sum_{I,\sigma} \frac{U^I}{2} \mathrm{Tr}\,[\mathbf{n}^{I\sigma}(1 - \mathbf{n}^{I\sigma})]. \end{aligned} \tag{12}$$

It is important to stress that the simplified functional in Eq. (12) still preserves the rotational invariance of the one in Eqs. (6) and (7), that is guaranteed by the dependence of the "+U" functional on the trace of occupation matrices and of their products. On the other hand, the formal resemblance to the HF energy functional is lost and only one interaction parameter (U^I) is needed to specify the corrective functional. This simplified version of the Hubbard correction has been successfully used in several studies and for most materials it shows similar results as the fully rotationally invariant one (Eqs. (6) and (7)). Some recent literature has shown, however, that the Hund's rule coupling J is crucial to describe the ground state of systems characterized by non-collinear magnetism [23, 24], to capture correlation effects in multiband metals [25, 26], or to study heavy-fermion systems, typically characterized by f valence electrons and subject to strong spin-orbit couplings [23, 24, 27]. A recent study [28] also showed that in some Fe-based superconductors a sizeable J (actually exceeding the value of U and resulting in negative $U_{eff} = U - J$) is needed to reproduce (with LDA+U) the magnetic moment of Fe atoms measured experimentally. Several different flavors of corrective functionals with exchange interactions were also discussed in Ref. [29]. Due to the spin-diagonal form of the simplified LDA+U approach in Eq. (12), it is customary to attribute the Coulomb interaction U an effective value that accounts for the exchange correction: $U_{eff} = U - J$. As discussed in section 2.2, this assumption is actually not completely justifiable as the resulting functional is missing other terms of the same order in J as the one included.

1.4 Conceptual and practical remarks

After introducing the general formulation of the LDA+U approach I think it is appropriate to clarify in a more detailed way its theoretical foundation (possibly in comparison with other corrective methods) and to discuss the range of systems it can be applied to, its strengths and its limitations.

The formal resemblance of the full rotationally invariant Hubbard functional (Eqs. (6)) with the HF interaction energy could be misleading: how can a corrective approach provide a better description of electronic correlation if it is based on a functional that, by definition, can not capture correlation? Some differences are, of course, to be stressed: $i)$ the effective interactions in the LDA+U functional are *screened* rather than based on the *bare* Coulomb kernel (as in HF); $ii)$ the LDA+U functional only acts on a subset of states (e.g., localized atomic orbitals of d or

f kind) rather than on all the states in the system; iii) the effective interactions have an orbital-independent value and correspond to atomically averaged quantities. These differences between LDA+U and HF, while making the first approach more computationally efficient than the latter (and related ones as exact-exchange - EXX - and hybrid functionals), do not dissolve the doubts raised above, and actually make HF appear more accurate and general. In order to clarify this point one needs to keep in mind that LDA+U is designed to capture the *effects* of electronic correlation (more precisely, of the *static* correlation, descending from the multi-determinant nature of the electronic wave function) into an effective one-electron (KS) description of the ground state. From this point of view significant improvements in the description of a correlated system may result from the application of an HF-like correction to KS states. In other words, the main difference between LDA+U and HF is that the first approach applies a corrective functional (resembling a *screened* HF) to a sub-group of single-particle (KS) wave functions that do not have any physical meaning (except being constrained to produce the ground state density), in the assumption that this correction can help a better description of the properties of the correlated system they represent through the effects it has on the exchange-correlation functional. In real HF calculations, instead, no xc energy exist and the optimized single particle wave functions are associated with a physical meaning. In Mott insulators, for example, a more precise evaluation of the structural and the vibrational properties can be obtained using the LDA+U approach through improving the size of the fundamental gap (possibly after lowering the symmetry of their electronic system) that can be computed from total energy finite differences when varying the number of electrons in the system around a reference value (in a molecule this quantity corresponds to the difference between the first ionization potential and the electron affinity).

An equivalent way to look at this problem is to study the dependence of the total energy of a system on the number of electrons in its orbitals. As explained in Ref. [30], for example, the energy of a system exchanging electrons with a "bath" (a reservoir of charge), should be linear with the number of electrons (in either part) and the finite discontinuity in its derivative at integer values of this number, represents the fundamental gap. Approximate DFT functionals do not satisfy this condition and result in upward convex energy profiles (this flaw can be seen as caused by a residual self-interaction). The linearization of the total energy imposed by the Hubbard correction is more transparent from its simpler formulation (Eq. (12)) where it is evident that the corrective functional subtracts from the DFT energy the spurious quadratic term and substitutes it with a linear one. This topic will be discussed with more details in section 3 that describes a linear-response approach to the calculation of the Hubbard U. Self-interaction corrected (SIC) functionals [4] are specifically designed to eliminate the residual self-interaction that manifests itself with the lack of linearity of the energy profile. In HF, the exchange functional exactly cancels the self-Coulomb interaction contained in the Hartree term, but usually produces a downward convex energy profile. Therefore, in HF-related methods as hybrid functionals, the strength of the exchange interaction must be properly tuned by a scaling factor (see, for example, [31]). However, the value of the scaling factor (generally in the 0.2 - 0.3 range) is usually determined semi-empirically and has no immediate physical meaning. LDA+U performs a linearization of the energy only with respect to the electronic degrees of freedom for which self-interaction is expected to be stronger (localized atomic states) and with an effective coupling that, although orbital-independent (indeed corresponding to an atomically averaged quantity), can be evaluated ab-initio. Thus it results, at the same time, more computationally efficient and (arguably) more physically transparent than EXX and hybrid functionals as a corrective scheme to DFT. The formal similarity with SIC and EXX approaches suggests that LDA+U should be also effective in correcting the underestimated band gap of covalent insulators (e.g., Si, Ge, or GaAs), for which a more precise account of the exchange interaction proves to be useful. Indeed, while the "standard" "+U" functional is not effective on these systems, this result is actually achievable through a generalized formulation of the "+U" functional (with inter-site couplings) that will be discussed in section 5.

It is important to notice that the orbital independence of the effective electronic interaction, makes the simpler version of the "+U" correction, Eq. (12), effectively equivalent to a penalty functional that forces the on-site occupation matrix to be idempotent. This action corresponds to enforcing a ground state described by a set of KS states with integer occupations (either 0 or 1) and thus with a gap in its band structure. While this is another way to see how the "+U" correction helps improving the description of insulators, it should be kept in mind that the linearization of the energy as a function of (localized) orbital occupations is a more general and important effect to be obtained. In fact, in case of degenerate ground states, charge densities with fractional occupations (corresponding to a metallic Kohn-Sham system) can, in principle, represent linear combinations of insulating states (with different subgroups of occupied single particle states), as long as the total energy is equal to the corresponding linear combination of the energies of the single configurations. Thus, the insulating character of the KS system should not be expected/pursued unless the symmetry of the electronic state is broken. An example of a degenerate ground state is provided by FeO. In fact, the energy of this system is minimized when the minority-spin d electron of Fe is described by a combination of states on the (111) plane of the crystal (lower left panel of Fig. 1) rather than by the z^2 state along the [111] (upper left panel of Fig. 1). This combination can only be obtained through lowering the symmetry of the lattice and breaking the equivalence between d states on the same (111) plane as explained in Ref. [19]. The right panel in Fig. 1 shows that the orbital-ordered broken symmetry phase not only gives a good estimate of the band gap but also reproduces the rhombohedral distortion of the crystal under pressure. The real material has to be understood as resulting from the superposition of equivalent orbital-ordered phases that re-establish the symmetry of the crystal.

In spite of the appealing characteristics described above, LDA+U provides a quite approximate description of correlated ground states. Being a correction for atomically localized states, their possible dispersion is totally ignored and so is the k-point dependence of the effective interaction (the Hubbard U). This limit can be alleviated, in part, by taking into account inter-site electronic interactions as explained in Ref. [34]. LDA+U also completely neglects the frequency dependence of the electronic interaction and, in fact, it has been shown [17] to correspond to the static limit of GW [35–44]. This particular aspect implies that LDA+U completely misses the role of fluctuations around the ground state which also corresponds to neglecting its pos-

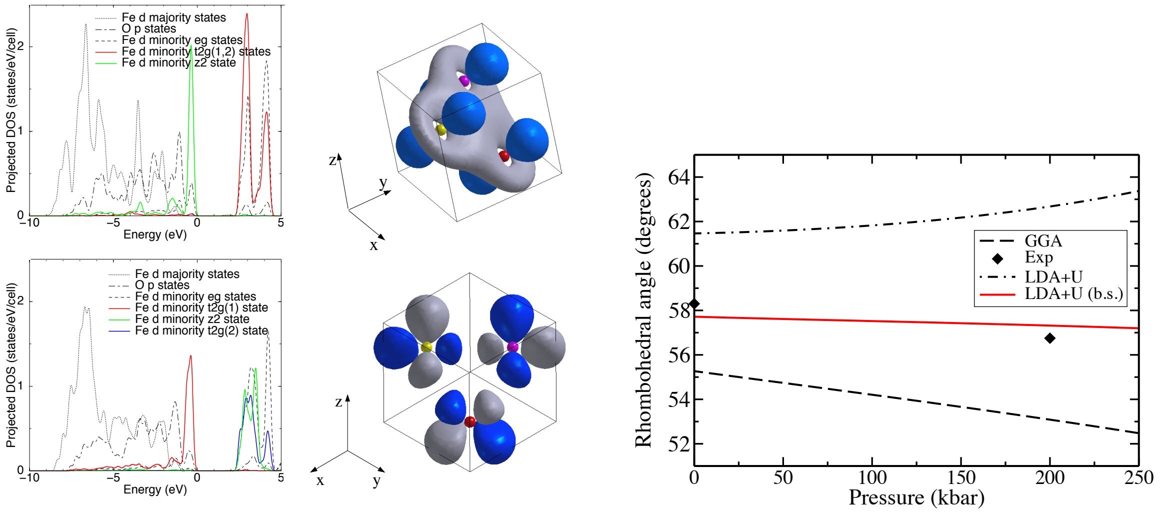

Fig. 1: *(From [19]). Projected density of states (left) and highest energy occupied orbital of FeO (center) in the unbroken symmetry (upper panels) and broken symmetry states (lower panels). In the graph on the right the rhombohedral angle is plotted as a function of pressure. The solid line describes DFT+U results in the broken-symmetry phase (from [19]). Diamonds represent the experimental data from [32, 33].*

sible multi-configurational character. In order to account for these dynamical effects higher order corrections are needed as, for example, the one provided by DMFT [45–50]. However, DFT+DMFT also solves a Hubbard model on each atom (treated as an impurity in contact with a “bath” represented by the rest of the crystal) and the final result depends quite strongly on the choice of the interaction parameter U. Recently, LDA+U has also been successfully used in conjunction with GW [51] and TDDFT [52] to compute the photo-emission spectra and quasi-particle energies of systems from their correlated ground states. Thus, in spite of its limits, LDA+U still plays an important role in the description of these materials (besides being one of the most inexpensive approaches to provide their ground state, at least) and improving its accuracy and its descriptive and predictive capabilities is very important.

2 Functionals and implementations

In this section I will discuss some particular aspects of the formulation and the implementation of LDA+U that can influence its effectiveness and accuracy.

2.1 Which double counting?

The lack of a diagrammatic expansion of the DFT total energy makes it quite difficult to model the electronic correlation already contained in semilocal xc functionals through simple dc terms (Eqs. (7) and (12)) that are general and flexible enough to work for many different classes of systems. As a result, the choice of E_{dc} is not univocal and different formulations have been proposed in literature for different kinds of materials.

The first one to be introduced was the one given in Eq. (7). that was obtained as a mean-field approximation to the Hubbard correction (Eq. 6) in the so-called "fully-localized" limit (FLL), in which each localized (e.g., atomic) orbital is either full or completely empty. This formulation of the dc term is consistent with the idea behind the Hubbard model as an expansion of the electronic energy around the strongly localized limit and thus tends to work quite well for strongly correlated materials with very localized orbitals. For other systems such as, for example, metals or "weakly correlated" materials in general, the excessive stabilization of occupied states due to the "+U" corrective potential (see Eq. 5) can lead to a description of the ground state inconsistent with experimental data and to quite unphysical results (such as, e.g., the enhancement of the Stoner factor [53]) that seriously question its applicability in these cases. In order to alleviate these difficulties a different Hubbard corrective functional, called "around mean-field" (AMF), was introduced in Ref. [54] and further developed in Ref. [53]. This functional can be expressed as follows:

$$E_{DFT+U} = E_{DFT} - \sum_I \frac{U^I}{2} \, \mathrm{Tr} \, \left(\mathbf{n}^I - \langle n^I \rangle\right)^2 \tag{13}$$

where $n^I = \mathrm{Tr}\ \mathbf{n}^I$ and $\langle n^I \rangle$ is the average diagonal element of the occupation matrix $\mathbf{n}^I$ (multiplied by the unit matrix). As evident from Eq. (13), this functional encourages deviations from a state with uniform occupations (i.e., with all the localized states equally occupied) representing the approximate DFT ground state. Its expression can be obtained from the combination of the E_{Hub} term of Eq. (12) and a modified dc that reads:

$$E_{dc}^{AMF} = \sum_I \frac{U^I}{2} n^I (n^I - \langle n^I \rangle) \qquad . \tag{14}$$

In Ref. [53] a linear combination of the AMF and the FLL flavors of LDA+U is proposed, also used in [27]. The mixing parameter has to be determined for each material and is a function of various quantities related to its electronic structure. In spite of this connection between the two schemes, the AMF one has had limited success and diffusion, except for relatively few works [27, 29]. Because of its derivation from the Hubbard model, the LDA+U approach is generally viewed as a corrective scheme for systems with localized orbitals and the FLL limit is usually adopted. In cases where these are embedded in a "background" of more delocalized or hybridized states the use of the FLL flavor is still justifiable with a corrective functional that selectively correct only the most localized orbitals. This approach has recently shown promising results (to be published elsewhere) for bulk Fe with a FLL LDA+U applied on e_g states only.

2.2 Which corrective functional?

Another source of uncertainty when using LDA+U derives from the level of approximation in the corrective Hamiltonian. While rotational invariance is widely recognized as a necessary feature of the functional, whether to use the full rotationally invariant correction, Eqs. (6) and (7), or the simpler version of it, Eq. (12), seems more a question of taste or of availability in current implementations. In fact, the two corrective schemes give very similar results for a large number of systems in which electronic localization is not critically dependent on Hund's rule magnetism. However, as mentioned in section 1.3, in some materials that have recently attracted considerable interest, this equivalence does not hold anymore and the explicit inclusion of the exchange interaction (J) in the corrective functional appears to be necessary. Examples of systems in this group include recently discovered Fe-pnictides superconductors [28], heavy-fermion [27, 24], non-collinear spin materials [23], or multiband metals for which the Hund's rule coupling, promotes, depending on the filling, metallic or insulating behavior [25, 26]. In our recent work on CuO [20] the necessity to explicitly include the Hund's coupling J in the corrective functional was determined by a competition (likely to exist in other Cu compounds as well, such as high T$_c$ superconductors), between the tendency to complete the external $3d$ shell and the one towards a magnetic ground state (dictated by Hund's rule) with 9 electrons on the d manifold. The precise account of exchange interactions between localized d electrons beyond the simple approach of Eq. (12) (with $U_{eff} = U - J$) turned out to be crucial to predict the electronic and structural properties of this material. In this work we used a simpler J-dependent corrective functional than the full rotationally invariant one to reach this aim. The expression of the functional was obtained from the full second-quantization formulation of the electronic interaction potential,

$$\hat{V}_{\text{int}} = \frac{1}{2} \sum_{I,J,K,L} \sum_{i,j,k,l} \sum_{\sigma,\sigma'} \langle \phi_i^I \phi_j^J | V_{ee} | \phi_k^K \phi_l^L \rangle \, \hat{c}^\dagger_{I\,i\,\sigma} \, \hat{c}^\dagger_{J\,j\,\sigma'} \, \hat{c}_{K\,k\,\sigma'} \, \hat{c}_{L\,l\,\sigma} \tag{15}$$

(where V_{ee} represent the kernel of the effective interaction, upper- and lower-case indexes label atomic sites and orbitals respectively) keeping only on-site terms describing the interaction between up to two orbitals. Approximating on-site effective interactions with the (orbital-independent) atomic averages of Coulomb and exchange terms,

$$U^I = \frac{1}{(2l+1)^2} \sum_{i,j} \langle \phi_i^I \phi_j^I | V_{ee} | \phi_j^I \phi_i^I \rangle,$$

and

$$J^I = \frac{1}{(2l+1)^2} \sum_{i,j} \langle \phi_i^I \phi_j^I | V_{ee} | \phi_i^I \phi_j^I \rangle,$$

and substituting the product of creation and destruction operators with their averages, associated to the occupation matrices defined in Eq. 3, $n_{ij}^{I\sigma} = \langle \hat{c}^\dagger_{I\,i\,\sigma} \hat{c}_{I\,j\,\sigma} \rangle$, one arrives at the following expression:

$$E_{\text{Hub}} - E_{\text{dc}} = \sum_{I,\sigma} \frac{U^I - J^I}{2} \text{Tr}[\mathbf{n}^{I\sigma} (\mathbf{1} - \mathbf{n}^{I\sigma})] + \sum_{I,\sigma} \frac{J^I}{2} \text{Tr}[\mathbf{n}^{I\sigma} \, \mathbf{n}^{I\,-\sigma}]. \tag{16}$$

Comparing Eqs. (12) and (16), one can see that the on-site Coulomb repulsion parameter (U^I) is effectively reduced by J^I for interactions between electrons of parallel spin and a positive J term further discourages anti-aligned spins on the same site stabilizing magnetic ground states. The second term on the right-hand side of equation (16) can be explicated as

$\sum_{I,\sigma} (J^I/2)\, n^{I\sigma}_{m\,m'}\, n^{I\,-\sigma}_{m'\,m}$ which shows how it corresponds to an "orbital exchange" between electrons of opposite spins (e.g. up spin electron from m' to m and down spin electron from m to m'). It is important to notice that this term is genuinely beyond Hartree-Fock. In fact, a single Slater determinant containing the four states $m\uparrow$, $m\downarrow$, $m'\uparrow$, $m'\downarrow$ would produce no interaction term like the one above. Thus, the expression of the J term given in equation (16), based on a product of $\mathbf{n}^{I\,\sigma}$ and $\mathbf{n}^{I\,-\sigma}$ is an approximation of a functional that would require the calculation of the 2-body density matrix to be properly included. However, in the spirit of the elimination of the spurious quadratic behavior of the total energy, one can assume that the J term in Eq. (16) is a fair representation of the exchange energy contained in the approximate DFT functionals. Therefore its formulation and use in corrective functionals are legitimate. Similar terms in the corrective functional have already been proposed in literature [25, 26, 55–57] although with slightly different formulation than in Eq. (16) when used in model Hamiltonians.

Eq. (16) represents a significant simplification with respect to Eqs. (6) and (7) and proved effective to predict the insulating character of the cubic phase of CuO and to describe its tetragonal distortion [20]. The simplicity of its formulation greatly facilitates its use and the implementation of other algorithms (such as, for example, the calculation of forces, stresses or phonons that will be discussed below). It is also important to report that the LDA+U scheme has recently been implemented with a non-collinear formalism (see, e.g., Ref. [23]). to study correlated systems characterized by canted magnetic moments, magnetic anisotropy or strong spin-orbit interactions (as common in rare earth compounds) [24]. This extension will not be further discussed in this chapter.

2.3 Which localized basis set?

The formulation of the corrective LDA+U functional discussed so far is valid independently from the particular choice of the localized set used to define the occupation matrices that enter the expression of the same functional. Many different choices are indeed possible. The first formulations of LDA+U [14–16] were based on a linear muffin-tin orbital (LMTO) implementation and thus had muffin-tin-orbitals (MTOs - constructed using Bessel, Neumann and Henkel spherical functions and spherical harmonics) as a natural choice to define on-site occupations. In plane-wave - pseudo-potential implementations of DFT, the atomic wave functions used to construct the pseudopotentials probably represent the easiest basis to use. In this case, it is useful to keep in mind that, since the valence electrons wave functions are defined at every point in the unit cell and are expanded on a plane-wave basis set, the definition of the occupation of atomic orbitals requires a projection of valence states on the atomic one. This is reflected in the expression in Eq. (3) and obviously determines the way the Hubbard potential acts on the Kohn-Sham states (Eq. (5)). Other choices are also possible as, for example, atomically centered gaussians or maximally localized Wannier functions [58].

In principles, the final result (the description of the properties of a system obtained from the LDA+U) should not depend on the choice of the localized basis set, provided the effective interaction parameters appearing in the functional (U and possibly J) are computed consistently, as described in section 3. However, the approximations operated in the Hubbard functional (and the consequent lack of flexibility) may introduce some basis set dependence. Another source of (undesirable) dependence on the basis set is represented by the lack of invariance of the corrective functional with respect to possible rotations of its wave function. In sections 1.2 and 1.3 I highlighted the rotational invariance of the LDA+U formulated in Eqs. (6) and (7). However, it is important to stress that this formulation is only invariant for rotations of localized wave functions belonging to the *same atomic site*. In other words, if one mixes orbitals centered on different atoms the corrective energy changes. In these conditions different basis sets may show different ability to capture the localization of electrons and yield results somewhat different from each other. A particularly good choice in this context seems to be represented by Wannier functions [59, 60]. This choice may lead, however, to some additional computational cost related to the necessity to optimize the localized basis set and to adapt it to the system for optimal performance [60]. An alternative solution to the problem is represented by the extension of the corrective functional to include inter-site interactions (and, ideally higher order terms) that will be discussed in section 5.

3 Computing *U* (and *J*?)

3.1 The necessity to compute *U*

As evident from the expression of the Hubbard functionals discussed in previous sections, the "strength" of the correction to approximate DFT total energy functionals is controlled by the effective on-site electronic interaction - the Hubbard U - whose value is not known a-priori. Consistently with a wide-spread use of this approach as a means to roughly assess the role of electronic correlation, it has become common practice to tune the Hubbard U in a semiempirical way, through seeking agreement with available experimental measurements of certain properties and using the so determined value to make predictions on other aspects of the system behavior. Besides being not satisfactory from a conceptual point of view, this practice does not allow to appreciate the variations of the on-site electronic interaction U, e.g., during chemical reactions, structural transitions or under changing physical conditions. Therefore, in order to obtain quantitatively predictive results, it is crucial to have a method to compute the Hubbard U (and possibly J) in a consistent and reliable way. The interaction parameters should be calculated, in particular, for every atom the Hubbard correction is to be used on, for the crystal structural and the magnetic phase of interest. The obtained value depends not only on the atom, its crystallographic position in the lattice, the structural and magnetic properties of the crystal, but also on the localized basis set used to define the on-site occupation (the same as in the LDA+U calculation). Therefore, contrary to another practice quite common in literature, these values have limited portability, from one crystal to another, or from one implementation of LDA+U to another.

3.2 Other approaches: a quick overview

In the first implementations of LDA+U, based on the use of localized basis sets (e.g., in the LMTO approximation), the Hubbard U was calculated (consistently with its definition as the energy cost of the reaction $2d^n \to d^{n+1} + d^{n-1}$) from finite differences between Kohn-Sham energy eigenvalues computed (within the atomic sphere approximation) with one more or one less electron on the d states. [13]. This approach allows to obtain a value that is automatically screened by electrons of other kinds on the same atom (e.g., on $4s$ and $4p$ orbitals for a $3d$ transition metal). The use of the LMTO basis set also makes it possible to change the occupation of $3d$ states and to eliminate hopping terms between these atomic orbitals (for which U is calculated) and the rest of the crystal so that single-particle terms of the energy, accounted for explicitly in the Hubbard model, are not included in the calculation. These latter features are quite specific to implementations that use localized basis sets (e.g., LMTO); other implementations (based, e.g., on plane waves) require different procedures to compute the effective interaction parameters [61].
One of the latest methods to compute the effective (screened) Hubbard U is based on constrained RPA (cRPA) calculations and yields a screened, fully frequency dependent interaction parameter that can be used, e.g., in DFT+DMFT calculations [62]. This approach has been extensively described in one of the chapter of the 2011 volume of this same series [57] and will not be discussed here.

3.3 Computing *U* from linear-response

In the following I will describe a linear response approach to the calculation of the effective Hubbard U [19] that allows to use atomic occupations defined as projections of Kohn-Sham states on a generic localized basis set, as shown in Eq. (3). The one described below is the method implemented in the plane-wave pseudopotential total-energy code of the Quantum-ESPRESSO package [63]. The basic idea of this approach is the observation that the (approximate) DFT total energy is a quadratic function of on-site occupations (as also suggested in Ref. [64]). This is consistent with the definition of the dc term (Eq. (7)). In fact, if one considers a system able to exchange electrons with a reservoir (e.g., an atom exchanging electrons with a metallic surface or another atom) the approximate DFT energy is an analytic function of the number of electrons on the orbitals of the system. As demonstrated by quite abundant literature [65, 30, 66], it should consist, instead, of a series of straight segments joining the energies corresponding to integer occupations. Examining Fig. 2, that compares the DFT total energy with the piece-wise linear behavior of the exact energy (it should be noted that they represent cartoons as the energy of the system does not increase for larger N), it is easy to understand that, if the DFT energy profile is represented by a parabola (actually a very good approximation within single intervals between integer occupations [67]), the correction needed to recover the physical piece-wise linear behavior (blue curve) has the expression of the Hubbard functional of Eq. (12), provided that U represents the (spurious) curvature of the approximate total energy profile one aims to eliminate. It is important to notice that recovering the linear behav-

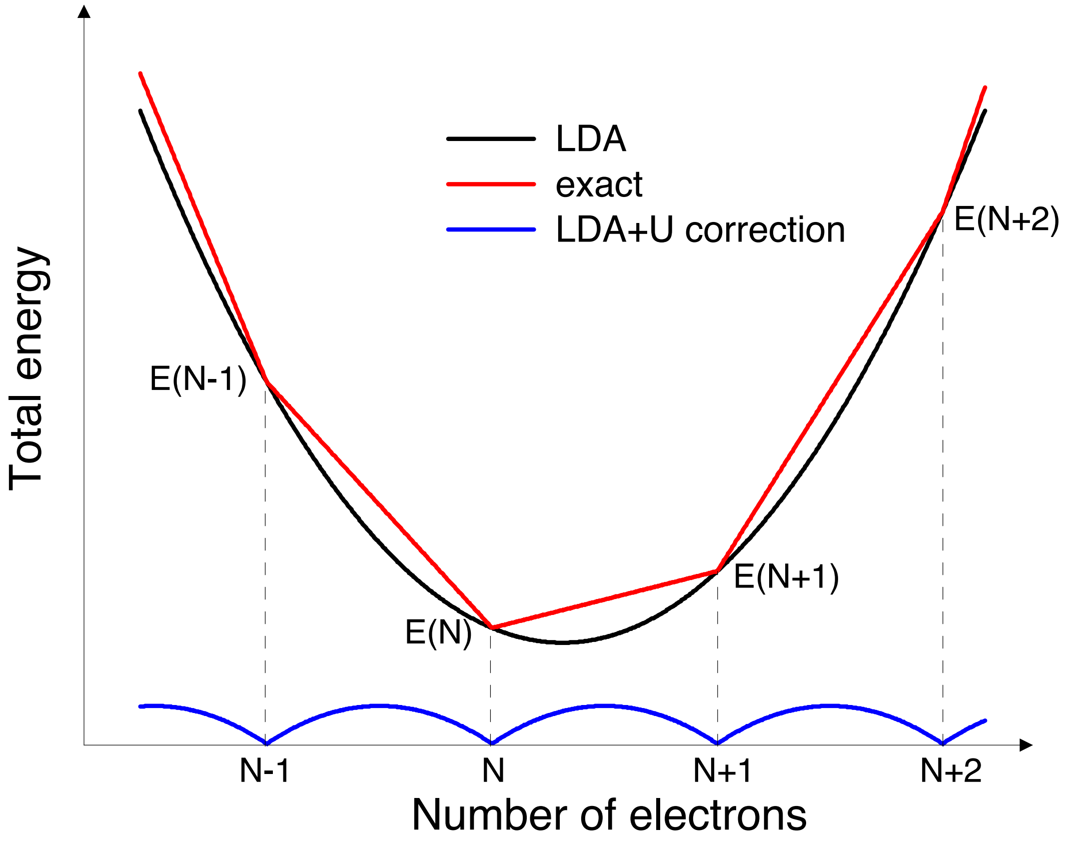

Fig. 2: *(From [19]) Sketch of the total energy profile as a function of the number of electrons in a generic atomic system in contact with a reservoir. The black line represents the DFT energy, the red the exact limit, the blue the difference between the two. The discontinuity in the slope of the red line for integer occupations, corresponds to the difference between ionization potential and electron affinity and thus measures the fundamental gap of the system.*

ior corresponds to reintroducing the discontinuity in the first derivative of the energy (i.e., the single-particle eigenvalue) when the number of electrons increases by one, from N to $N+1$. This discontinuity, also proportional to U, represents the fundamental gap of the system (i.e., the difference between ionization potential and electron affinity in molecules). Thus, the Hubbard U is associated to important physical quantities if calculated as the second derivative of the (approximate) DFT energy.

Unfortunately, when using plane waves (and, typically, pseudopotentials) the on-site occupations cannot be controlled or changed “by hand” because they are obtained as an outcome from the calculation after projecting Kohn-Sham states on the wave function of the localized basis set (Eq. (3)). Therefore, to obtain the second derivative of the total energy with respect to occupations we adopted a different approach that is based on a Legendre transform [19]. In practice, we add a perturbation to the Kohn-Sham potential that is proportional to the projector on the localized states ϕ^I_m of a certain atom I,

$$V_{tot}|\psi^{\sigma}_{kv}\rangle = V_{KS}|\psi^{\sigma}_{kv}\rangle + \alpha^I \sum_m |\phi^I_m\rangle\langle\phi^I_m|\psi^{\sigma}_{kv}\rangle \tag{17}$$

In this equation α^I represents the "strength" of the perturbation (usually chosen small enough to maintain a linear response regime). The potential in Eq. 17 is the one entering the Kohn-Sham equations of a modified energy functional that yields a α-dependent ground state:

$$E(\alpha^I) = \min_{\gamma} \left\{ E_{DFT}[\gamma] + \alpha^I n^I \right\} \tag{18}$$

where γ is the one-body density matrix. If one defines $E[\{n^I\}] = E(\alpha^I) - \alpha^I n^I$ (where n^I indicates the value of the on-site occupation computed when the minimum in Eq. (18) is achieved), the second derivative $d^2E/d(n^I)^2$ can be computed as $-d\alpha^I/d(n^I)$. In actual calculations, we change α^I on each "Hubbard" atom and, solving the minimization problem of Eq. (18) through modified Kohn-Sham equations, we collect the response of the system in terms of variation in all the n^J. Thus, the quantity that we can directly measure is the response function $\chi_{IJ} = d(n^I)/d\alpha^J$, where I and J are site indexes that label all the Hubbard atoms. The Hubbard U is obtained from the inverse of the response matrix: $U^I = -\chi^{-1}$. This definition is actually not complete. In fact, a term to the energy second derivative, coming from the reorganization (rehybridization) of the electronic wave functions in response to the perturbation of the potential, Eq. (17), would be present even for independent electron systems and is not related to electron-electron interactions. Thus, it must be subtracted out. The final expression of the Hubbard U then results:

$$U^I = (\chi_0^{-1} - \chi^{-1})_{II} \tag{19}$$

where χ_0 measures the response of the system that accounts for the rehybridization of the electronic states upon perturbation. Subtracting this term corresponds to eliminate the hopping between the localized "Hubbard" states and the rest of the system, or to kill the kinetic contribution to the second derivative of the energy as suggested in Ref. [61]. The necessity to compute χ_0 (besides χ) actually dictates the the way these calculations are performed. The first step is a well converged self-consistent calculation of the system of interest with the approximate xc functional of choice. Starting from the ground-state potential and wave functions we then switch the perturbation on and run separate DFT calculations (solving the problem in Eq. (18)) for each Hubbard atom and for each alpha in an interval of values typically centered around 0. The variation of on-site occupation at the *first iteration of the perturbed run* defines χ_0. In fact, at this stage electron-electron interactions have not yet come into play to screen the perturbation, and the response one obtains is that of a system that has the same electronic density of the ground state but the potential frozen to its self-consistent value. Thus it is entirely due to the re-hybridization of the orbitals. The response measured at self-consistency will give, instead, χ. More details about the theoretical aspects of this calculation can be found in Ref [19], and a useful hands-on tutorial with examples on these calculations is linked from the web-page of the Quantum-ESPRESSO package (http://wwww.quantumespresso.org).

The Hubbard U, calculated as in Eq. (19), is screened by other orbitals and atoms: in fact, when perturbing the system the "non-Hubbard" degrees of freedom silently participate to the redistribution of electrons and to the response of "Hubbard" orbitals. To account for this contribution more explicitly an extra row and column are added to the response matrices χ and χ_0 to contain the collective response (computed with a simultaneous perturbation) of these “background” states.

The calculation of J could, in principles, be performed along similar lines, adding a perturbation that effectively couples with the on-site magnetization $m^I = n^{I\uparrow} - n^{I\downarrow}$. However, the energy of a magnetic ground state is not generally quadratic in the magnetization as it is minimized on the domain-border. In other words, the magnetization is often the maximum it could be compatibly with the number of electronic localized states. In these circumstances n^I and m^I are not independent variables and one can only obtain linear combinations of U and J but not solve them separately. A possible way around this problem could be to perturb a state corresponding to a magnetization slightly decreased with respect to its ground state value (e.g., with a penalty functional) in order to allow for the independent variation of n^I and m^I. However, this calculation has not been actually attempted yet and it is impossible to comment on its reliability.

The approach described above renders the LDA+U ab-initio, eliminating any need of semi-empirical evaluations of the interaction parameters in the corrective functional. It also introduces the possibility to re-compute the values of these interactions in dependence of the crystal structure, the magnetic phase, the crystallographic position of atoms, etc. This ability proved critical to improve the predictive capability of LDA+U and the agreement of its results with available experimental data for a broad range of different materials and different conditions. The ability to consistently recompute the interaction parameters significantly improved the description of the structural, electronic and magnetic properties of a variety of transition-metal-containing crystals and was particularly useful in presence of structural [19, 68], magnetic [69] and chemical transformations [70, 71]. In Ref. [69] the use of the “self-consistent” Hubbard U (recomputed for different spin configurations) allowed to predict a ground state for the (Mg,Fe)(Si,Fe)O_3 perovskite with high-spin Fe atoms on both A and B sites, and a pressure-induced spin-state crossover of Fe atoms on the B sites that couples with a noticeable volume reduction, an increase in the quadrupole splitting (consistent with recent x-ray diffraction and Mössbauer spectroscopy measurements) and a marked anomaly in the bulk modulus of the material. These results have far-reaching consequences for understanding the physical behavior of the Earth’s lower mantle where this mineral is particularly abundant. The calculation of the Hubbard U also improved the energetics of chemical reactions [72, 73], and electron-transfer processes [74]. Thanks to this calculation, LDA+U has become significantly more versatile, flexible and accurate. A recent extension to the linear response approach has further improved its reliability through the self-consistent calculation of the U from an LDA+U ground state [34, 72]. This improved method, that is mostly useful for systems where the LDA and LDA+U ground states are qualitatively different, is based on a similar calculation to the one described above with a perturbed run performed on a LDA+U ground state for which the “+U” corrective *potential* is frozen to its self-consistent unperturbed value. This guarantees that the +U part does not contribute to the response and, consistently to its definition, the Hubbard U is measured as the curvature of the LDA energy in correspondence of the LDA+U ground state charge density.

4 Energy derivatives

One of the most important advantages brought about by the simple formulation of the LDA+U corrective functional consists in the possibility to easily compute energy derivatives, as forces, stresses, dynamical matrices, etc. These are crucial quantities to identify and characterize the equilibrium structure of materials in different conditions, and to compute various other properties (as, e.g., vibrational spectra) or to account for finite temperature effects in insulators. In this section I will review the calculation of LDA+U forces, stresses, and second derivatives (see Refs. [75, 76] for details), that are contained in the total energy, Car-Parrinello MD, and phonon codes of the QUANTUM-ESPRESSO package [63]. In the last subsection I will also offer some comments on the importance of the derivative of the Hubbard interaction. In the remainder of this section I will present the implementation of energy derivatives in a code using a localized basis set of atomic orbitals taken from norm-conserving pseudo-potential. Mathematical complications deriving from the use of other kinds of pseudo-potentials (e.g., ultra-soft [77]) will not be addressed here.

4.1 The Hubbard forces

The Hubbard forces are defined as the derivative of the Hubbard energy with respect to the displacement of atoms. The force acting on the atom α in the direction i is defined as:

$$F^U_{\alpha,i} = -\frac{\partial E_U}{\partial \tau_{\alpha i}} = -\sum_{I,m,m',\sigma} \frac{\partial E_U}{\partial n^{I\sigma}_{m,m'}} \frac{\partial n^{I\sigma}_{m,m'}}{\partial \tau_{\alpha i}} = -\frac{U}{2} \sum_{I,m,m',\sigma} (\delta_{mm'} - 2n^{I\sigma}_{m'm}) \frac{\partial n^{I\sigma}_{m,m'}}{\partial \tau_{\alpha i}} \tag{20}$$

where $\tau_{\alpha i}$ is the component i of the position of atom α in the unit cell, E_U and $n^{I\sigma}_{m,m'}$ are the Hubbard energy and the elements of the occupation matrix as defined in Eq. (3). Based on that definition it is easy to derive the following formula:

$$\frac{\partial n^{I\sigma}_{m,m'}}{\partial \tau_{\alpha i}} = \sum_{k,v} f_{kv} [\frac{\partial}{\partial \tau_{\alpha i}} \left(\langle \varphi^I_{mk} | \psi^\sigma_{kv} \rangle\right) \langle \psi^\sigma_{kv} | \varphi^I_{m'k} \rangle + \langle \varphi^I_{mk} | \psi^\sigma_{kv} \rangle \frac{\partial}{\partial \tau_{\alpha i}} \langle \psi^\sigma_{kv} | \varphi^I_{m'k} \rangle] \tag{21}$$

(k and v being the k-point and band indexes, respectively) so that the problem is reduced to determine the quantities

$$\frac{\partial}{\partial \tau_{\alpha i}} \langle \varphi^I_{mk} | \psi^\sigma_{kv} \rangle \tag{22}$$

for each I, m, m', σ, k and v. Since the Hellmann-Feynman theorem applies, no response of the electronic wave function has to be taken into consideration for first derivatives of the energy. The quantities in Eq. (22) can thus be calculated considering only the derivative of the atomic wave functions:

$$\frac{\partial}{\partial \tau_{\alpha i}} \langle \varphi^I_{mk} | \psi^\sigma_{kv} \rangle = \left\langle \frac{\partial \varphi^I_{mk}}{\partial \tau_{\alpha i}} | \psi^\sigma_{kv} \right\rangle . \tag{23}$$

Although the atomic occupations are defined on localized atomic orbitals, the product with Kohn-Sham wavefunctions of a given **k**-vector (Eq. (3)) selects the Fourier component of the atomic wavefunction at the same k-point. This component can be constructed as a Bloch sum of localized atomic orbitals:

$$\varphi^{at}_{i,\mathbf{k},I}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}}\varphi^{at}_{i,I}(\mathbf{r}-\mathbf{R}-\tau_I) = e^{-i\mathbf{k}\cdot\mathbf{r}}\frac{1}{\sqrt{N}}\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\varphi^{at}_{i,I}(\mathbf{r}-\mathbf{R}-\tau_I). \quad (24)$$

In this equation i is the cumulative index for all the quantum numbers $\{n, l, m\}$ defining the atomic state, τ_I is the position of atom I inside the unit cell, N is the total number of k-points and the sum runs over all the N direct lattice vectors $\mathbf{R}$. The second factor in the right hand side of Eq. (24) is a function with the periodicity of the lattice. Its Fourier spectrum thus contains only reciprocal lattice vectors:

$$\varphi^{at}_{i,\mathbf{k},I}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}} e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}c_{i,I}(\mathbf{k}+\mathbf{G}). \quad (25)$$

In this equation $\mathbf{G}$ are reciprocal lattice vector ($\mathbf{G}\cdot\mathbf{R} = 2\pi n$), and V is the total volume of N unit cells: $V = N\Omega$). The response to the ionic displacement thus results:

$$\frac{\partial\varphi^{at}_{i,\mathbf{k},I}}{\partial\tau_{\alpha j}} = \delta_{I,\alpha}\frac{i}{\sqrt{\Omega}}\sum_{\mathbf{G}} e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}c_{i,\alpha}(\mathbf{k}+\mathbf{G})(\mathbf{k}+\mathbf{G})_j \quad (26)$$

where $(\mathbf{k}+\mathbf{G})_j$ is the component of the vector along direction j and i is the imaginary unit. Due to the presence of the Kronecker δ in front of its expression, the derivative of the atomic wave function is different from zero only in the case it is centered on the atom which is being displaced. Thus, the derivative in Eq. (23) only contributes to forces on atoms subject to the Hubbard correction. Finite off-site terms in the expression of the forces arise when using ultrasoft pseudopotentials. However this case is not explicitly treated in this chapter.

4.2 The Hubbard stresses

Starting from the the expression for the Hubbard energy functional, given in Eq. (12), we can compute the contribution to the stress tensor as:

$$\sigma^U_{\alpha\beta} = -\frac{1}{\Omega}\frac{\partial E_U}{\partial\varepsilon_{\alpha\beta}} \quad (27)$$

where Ω is the volume of the unit cell (the energy is also given per unit cell), $\varepsilon_{\alpha\beta}$ is the strain tensor that describes the deformation of the crystal:

$$\mathbf{r}_\alpha \to \mathbf{r}'_\alpha = \sum_\beta(\delta_{\alpha\beta}+\varepsilon_{\alpha\beta})\mathbf{r}_\beta \quad (28)$$

where $\mathbf{r}$ is the space coordinate internal to the unit cell. The procedure, already developed for the forces (see Eqs. (20), (21)), can be applied to the case of stresses as well. The problem thus reduces to evaluating the derivative

$$\frac{\partial}{\partial\varepsilon_{\alpha\beta}}\langle\varphi^I_{mk}|\psi^\sigma_{kv}\rangle. \quad (29)$$

In order to determine the functional dependence of atomic and KS wavefunctions on the strain we deform the lattice accordingly to Eq. (28) and study how these functions are modified by the distortion. Distortions will be assumed small enough to justify first order expansions of physical quantities around the values they have in the undeformed crystal. To linear order, the distortion of the reciprocal lattice is opposite to that of real space coordinates:

$$\mathbf{k}_\alpha \to \mathbf{k}'_\alpha = \sum_\beta (\delta_{\alpha\beta} - \varepsilon_{\alpha\beta})\mathbf{k}_\beta. \tag{30}$$

Thus, the products $(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}$ appearing in the plane wave (PW) expansion of the wave functions (see, for example, Eq. (25)) remain unchanged.

Let's first study the modification of the atomic wavefunctions taking in consideration the expression given in Eq. (25). The volume appearing in the normalization factor transforms as follows:

$$V \to V' = |1+\varepsilon|V \tag{31}$$

where $|1+\varepsilon|$ is the determinant of the matrix $\delta_{\alpha\beta}+\varepsilon_{\alpha\beta}$ that describes the deformation of the crystal. Applying the strain defined in Eq. (28), to the expression of the $\mathbf{k}+\mathbf{G}$ Fourier component of the atomic wave function one obtains:

$$\begin{aligned} c'_{i,I}(\mathbf{k}'+\mathbf{G}') &= \frac{1}{\sqrt{|1+\varepsilon|}\sqrt{N\Omega}} e^{i(\mathbf{k}'+\mathbf{G}')\cdot\tau'_I} \int_{V'} d\mathbf{r}' e^{i(\mathbf{k}'+\mathbf{G}')\cdot\mathbf{r}'} \varphi^{at}_{i,\mathbf{k},I}(\mathbf{r}') \\ &= \frac{1}{\sqrt{|1+\varepsilon|}} \frac{1}{\sqrt{N\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\tau_I} \int_{V'} d\mathbf{r} e^{i(\mathbf{k}'+\mathbf{G}')\cdot\mathbf{r}} \varphi^{at}_{i,\mathbf{k},I}(\mathbf{r}). \end{aligned} \tag{32}$$

Since the integral appearing in this expression does not change upon distorting the integration volume, defining

$$\tilde{c}_{i,I}(\mathbf{k}+\mathbf{G}) = c_{i,I}(\mathbf{k}+\mathbf{G}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\tau_I} \tag{33}$$

one obtains:

$$\tilde{c}'_{i,I}(\mathbf{k}'+\mathbf{G}') = \frac{1}{\sqrt{|1+\varepsilon|}} \tilde{c}_{i,I}(\mathbf{k}'+\mathbf{G}') = \frac{1}{\sqrt{|1+\varepsilon|}} \tilde{c}_{i,I}((1-\varepsilon)(\mathbf{k}+\mathbf{G})). \tag{34}$$

Thus, the "deformed" atomic wave function results:

$$\begin{aligned} \varphi^{at}_{i,\mathbf{k},I}(\mathbf{r}) &= \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} e^{i(\mathbf{k}+\mathbf{G})\cdot\tau_I} \tilde{c}_{i,I}(\mathbf{k}+\mathbf{G}) \to \\ & \frac{1}{\sqrt{\Omega'}} \sum_{\mathbf{G}'} e^{-i(\mathbf{k}'+\mathbf{G}')\cdot\mathbf{r}'} e^{i(\mathbf{k}'+\mathbf{G}')\cdot\tau'_I} \tilde{c}'_{i,I}(\mathbf{k}'+\mathbf{G}') \\ &= \frac{1}{|1+\varepsilon|} \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} e^{i(\mathbf{k}+\mathbf{G})\cdot\tau_I} \tilde{c}_{i,I}((1-\varepsilon)(\mathbf{k}+\mathbf{G})). \end{aligned} \tag{35}$$

According to the Bloch theorem Kohn-Sham (KS) wavefunctions can be expressed as follows:

$$\psi^\sigma_{kv}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_G e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} a^\sigma_{kv}(\mathbf{G}) \tag{36}$$

where

$$a^{\sigma}_{kv}(\mathbf{G}) = \frac{1}{\sqrt{V}} \int_V d\mathbf{r} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \psi^{\sigma}_{kv}(\mathbf{r}). \tag{37}$$

Upon distorting the lattice as described in Eq. (28) the electronic charge density is expected to rescale accordingly. One can thus imagine the electronic wave function in a point of the strained space to be proportional to its value in the corresponding point of the undistorted lattice:

$$\psi^{\sigma}_{kv}(\mathbf{r}) \rightarrow {\psi'}^{\sigma}_{k'v}(\mathbf{r}') = \alpha \psi^{\sigma}_{kv}((1-\varepsilon)\mathbf{r}') \tag{38}$$

where the proportionality constant α is to be determined by normalizing the wave function in the strained crystal. By a simple change of the integration variable we obtain:

$$1 = \int_{V'} d\mathbf{r}' |{\psi'}^{\sigma}_{kv}|^2 = |1+\varepsilon| \int_V d\mathbf{r} |\alpha \psi^{\sigma}_{kv}|^2 = |1+\varepsilon|\alpha^2 \tag{39}$$

from which, choosing α real, we have

$$\alpha = \frac{1}{\sqrt{|1+\varepsilon|}}. \tag{40}$$

Using this result we can determine the variation of the $\mathbf{k}+\mathbf{G}$ Fourier component of ψ^{σ}_{kv} (Eq. (37)). We easily obtain:

$$\begin{aligned} a^{\sigma}_{k'v}(\mathbf{G}') &= \frac{1}{\sqrt{V'}} \int_{V'} d\mathbf{r}' e^{i(\mathbf{k}'+\mathbf{G}')\cdot\mathbf{r}'} {\psi'}^{\sigma}_{k'v}(\mathbf{r}') \\ &= \frac{1}{\sqrt{|1+\varepsilon|}} \frac{1}{\sqrt{V}} \int_V |1+\varepsilon| d\mathbf{r} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \frac{1}{\sqrt{|1+\varepsilon|}} \psi^{\sigma}_{kv}(\mathbf{r}) = a^{\sigma}_{kv}(\mathbf{G}). \end{aligned} \tag{41}$$

We can now compute the first order variation of the scalar products between atomic and Kohn-Sham wavefunctions:

$$\langle \varphi^I_{mk} | \psi^{\sigma}_{kv} \rangle' = \frac{1}{\sqrt{|1+\varepsilon|}} \sum_G e^{i(\mathbf{k}+\mathbf{G})\cdot\tau_I} [c^I_{mk}((1-\varepsilon)(\mathbf{k}+\mathbf{G}))]^* a^{\sigma}_{kv}(G). \tag{42}$$

The expression of the derivative follows immediately (for small strains $|1+\varepsilon| \sim 1 + Tr(\varepsilon)$):

$$\begin{aligned} \frac{\partial}{\partial \varepsilon_{\alpha\beta}} \langle \varphi^I_{mk} | \psi^{\sigma}_{kv} \rangle |_{\varepsilon=0} &= -\frac{1}{2} \delta_{\alpha\beta} \langle \varphi^I_{mk} | \psi^{\sigma}_{kv} \rangle \\ &\quad - \sum_G e^{i(\mathbf{k}+\mathbf{G})\cdot\tau_I} a^{\sigma}_{kv}(G) \partial_\alpha [c^I_{mk}(\mathbf{k}+\mathbf{G})]^* (\mathbf{k}+\mathbf{G})_\beta. \end{aligned} \tag{43}$$

The explicit expression of the derivative of the Fourier components of the atomic wavefunctions won't be detailed here. In fact this quantity depends on the particular definition of the atomic orbitals that can vary in different implementations.

4.3 Phonons and second energy derivatives

Many important properties of materials (such as, for example, their vibrational spectrum) are related to the second derivatives of their total energy. It was therefore important to develop the capability to compute these quantities from first principles for correlated systems. The main linear response technique to obtain second derivatives of the DFT energies is Density Functional Perturbation Theory (DFPT). In this section I present the recent extension of DFPT to the LDA+U energy functional to compute the vibrational spectrum (and other linear-response properties) of materials from their correlated (LDA+U) ground state [76].

DFPT is based on the application of first-order perturbation theory to the self-consistent DFT ground state. I refer to Ref. [78] for an extensive description and for the definition of the notation used here. The displacement of atom L in direction α from its equilibrium position induces a (linear) response $\Delta^\lambda V_{SCF}$ in the KS potential V_{SCF}, leading to a variation $\Delta^\lambda n(\mathbf{r})$ of the charge density ($\lambda \equiv \{L\alpha\}$). The Hubbard potential,

$$V_{Hub} = \sum_{I\sigma m_1 m_2} U^I \left[\frac{\delta_{m_1 m_2}}{2} - n^{I\sigma}_{m_1 m_2}\right] |\phi^I_{m_2}\rangle\langle\phi^I_{m_1}|,$$

also responds to the shift of atomic positions and its variation, to be added to $\Delta^\lambda V_{SCF}$, reads:

$$\begin{aligned}\Delta V_{Hub} &= \sum_{I\sigma m_1 m_2} U^I \left[\frac{\delta_{m_1 m_2}}{2} - n^{I\sigma}_{m_1 m_2}\right] \left[|\Delta\phi^I_{m_2}\rangle\langle\phi^I_{m_1}| + |\phi^I_{m_2}\rangle\langle\Delta\phi^I_{m_1}|\right] \\ &- \sum_{I\sigma m_1 m_2} U^I \Delta n^{I\sigma}_{m_1 m_2} |\phi^I_{m_2}\rangle\langle\phi^I_{m_1}| \end{aligned} \tag{44}$$

where $\Delta\phi^I_m$ is the variation of atomic wavefunctions due to the shift in the position of their centers and

$$\begin{aligned}\Delta n^{I\sigma}_{m_1 m_2} &= \sum_i^{occ} \{\langle\psi^\sigma_i|\Delta\phi^I_{m_1}\rangle\langle\phi^I_{m_2}|\psi^\sigma_i\rangle + \langle\psi^\sigma_i|\phi^I_{m_1}\rangle\langle\Delta\phi^I_{m_2}|\psi^\sigma_i\rangle\} \\ &+ \sum_i^{occ} \{\langle\Delta\psi^\sigma_i|\phi^I_{m_1}\rangle\langle\phi^I_{m_2}|\psi^\sigma_i\rangle + \langle\psi^\sigma_i|\phi^I_{m_1}\rangle\langle\phi^I_{m_2}|\Delta\psi^\sigma_i\rangle\}. \end{aligned} \tag{45}$$

In Eq. (45) $|\Delta\psi^\sigma_i\rangle$ is the linear response of the KS state $|\psi^\sigma_i\rangle$ to the atomic displacement and is to be computed solving the DFPT equations [78].

It is important to note that, in the approach discussed in this section, the derivative of the Hubbard U is assumed to be small and neglected.

Once the self-consistent density response $\Delta n(\mathbf{r})$ is obtained, the dynamical matrix of the system can be computed to calculate the phonon spectrum and the vibrational modes of the crystal. The Hubbard energy contributes to the dynamical matrix with the following term

$$\Delta^\mu(\partial^\lambda E_{\text{Hub}}) = \sum_{I\sigma mm'} U^I \left[\frac{\delta_{mm'}}{2} - n^{I\sigma}_{mm'}\right] \Delta^\mu\left(\partial^\lambda n^{I\sigma}_{mm'}\right) - \sum_{I\sigma mm'} U^I \Delta^\mu n^{I\sigma}_{mm'} \partial^\lambda n^{I\sigma}_{mm'} \tag{46}$$

which represents the total derivative of the Hellmann-Feynman Hubbard forces (Eq. (20)). In Eq. 46, the symbol ∂^λ indicates an explicit derivative (usually called “bare”) with respect to atomic positions that does not involve linear-response terms (i.e., the variation of the Kohn-Sham wave functions).

When computing phonons in ionic insulators and semiconductor materials a non-analytical term $C^{na}_{I\alpha,J\beta}$ must be added to the dynamical matrix to account for the coupling of longitudinal vibrations with a macroscopic electric field generated by ion displacement [79, 80]. This term, responsible for the LO-TO splitting at $\mathbf{q} = \Gamma$, depends on the Born effective charge tensor $\mathbf{Z}^*$ and the high-frequency dielectric tensors ε^∞: $C^{na}_{I\alpha,J\beta} = \frac{4\pi e^2}{\Omega}\frac{(\mathbf{q}\cdot\mathbf{Z}^*_I)_\alpha(\mathbf{q}\cdot\mathbf{Z}^*_J)_\beta}{\mathbf{q}\cdot\overleftrightarrow{\varepsilon}^\infty\cdot\mathbf{q}}$. The calculation of $\mathbf{Z}^*_{I,\alpha\beta}$ and $\varepsilon^\infty_{\alpha\beta}$ is based on the response of the electronic system to a macroscopic electric field and requires the evaluation of the transition amplitudes between valence and conduction KS states, promoted by the commutator of the KS Hamiltonian with the position operator $\mathbf{r}$, $\langle\psi_{c,\mathbf{k}}|[H_{SCF},\mathbf{r}]|\psi_{v,\mathbf{k}}\rangle$ [81]. A contribution to this quantity from the Hubbard potential must be also included:

$$\langle\psi_{c,\mathbf{k}}|[V^\sigma_{\text{Hub}}, r_\alpha]|\psi_{v,\mathbf{k}}\rangle = \sum_{Imm'} U^I\left[\frac{\delta_{mm'}}{2} - n^{I\sigma}_{mm'}\right]\left[-i\langle\psi_{c,\mathbf{k}}|\frac{d}{dk_\alpha}\left(|\phi^I_{m,\mathbf{k}}\rangle\langle\phi^I_{m',\mathbf{k}}|\right)|\psi_{v,\mathbf{k}}\rangle\right] \tag{47}$$

where $\phi^I_{m,\mathbf{k}}$ are Bloch sums of atomic wave functions and k_α represents one of the components of the Bloch vector $\mathbf{k}$.

To summarize, the extension of DFPT to the DFT+U functional requires three terms: the variation of the Hubbard potential $\Delta^\lambda V_{\text{Hub}}$ to be added to $\Delta^\lambda V_{\text{SCF}}$; the second derivative $\Delta^\mu(\partial^\lambda E_{\text{Hub}})$ to be added to the analytical part of the dynamical matrix; and the commutator of the Hubbard potential with the position operator to contribute to the non analytical part of the dynamical matrix. This extension of DFPT, called DFPT+U, was introduced in Ref. [76] and implemented in the PHONON code of the QUANTUM ESPRESSO package [63]. As an example of application I present below the results obtained from the DFPT+U calculation of the vibrational spectrum of MnO and NiO, also discussed in Ref. [76]. The Hubbard U for both systems was computed using the linear-response method discussed in one of the previous sections and resulted 5.25 eV for Mn and 5.77 eV for Ni.

As other transition metal mono-oxides, MnO and NiO crystallize in the cubic rock-salt structure but acquire a rhombohedral symmetry due to their antiferromagnetic order (called AFII) consisting of ferromagnetic planes of cations alternating with opposite spin. Because of the lower symmetry, the directions corresponding to the cubic diagonals lose their equivalence which leads to the splitting of the transverse optical modes (with oxygen and metal sublattices vibrating against each other) around the zone center [82]. Figure 3 compares the phonon dispersions of MnO and NiO obtained from the GGA+U ground state with those resulting from GGA. As it can be observed, the Hubbard correction determines an overall increase in the phonon frequencies for both materials, significantly improving the agreement with available experimental results [83–86]. Moreover, the phonon frequencies computed from the GGA+U ground state lead to a decreased splitting between transverse optical modes compared to GGA, which also is in better agreement with experimental data (although for NiO the sign of the splitting is still controversial [83, 87, 88]).

These results demonstrate that, on the contrary to what is sometimes expected or assumed, electronic correlations have significant effects on the structural and vibrational properties of materials and a corrected functional should be used when calculating properties related to the

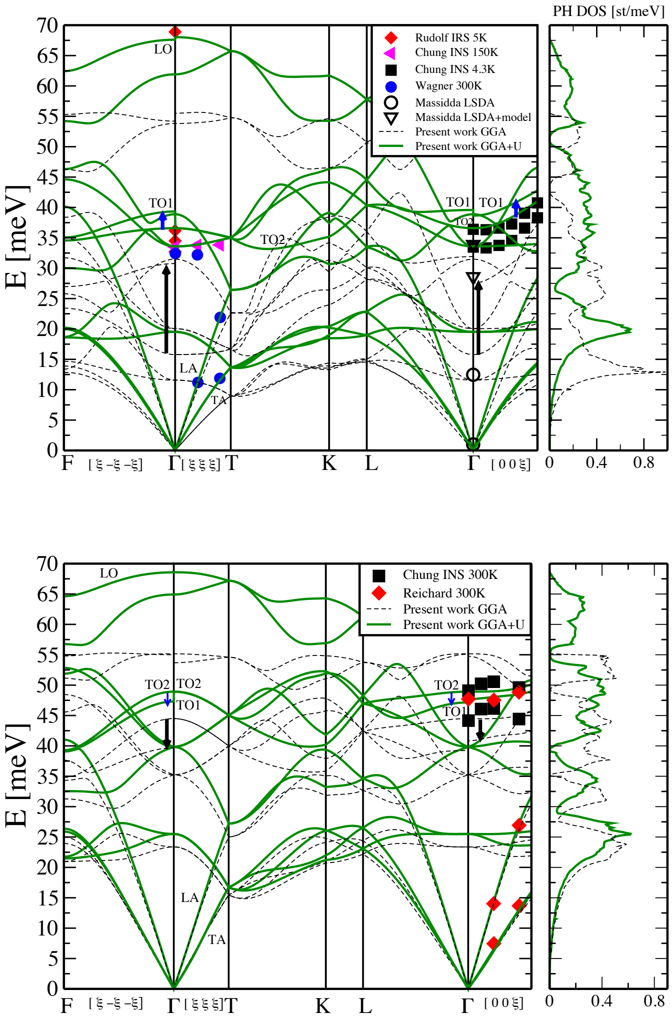

Fig. 3: *(From [76]) The phonon dispersion and the vibrational DOS of MnO (upper panel) and NiO (lower panel), calculated with GGA (dashed lines) and GGA+U (solid thick lines). Blue (black) arrows mark the GGA+U (GGA) magnetic splittings and their sign. Filled symbols: Experimental data [83–86]. Open symbols: Results of other calculations (at zone center) [82].*

vibrational spectrum, such as, e.g., Raman spectroscopy, or when integrating over the Brillouin zone to calculate thermodynamic quantities.

4.4 Derivatives of U

In all the preceding sections discussing the contribution of the Hubbard corrective functional to the first and second derivatives of the energy (forces, stresses, force-constant/dynamical matrices) the effective Hubbard U was held fixed. In fact, its dependence on the atomic positions and/or the cell parameters is usually assumed to be small and neglected. This is, of course, an approximation as the Hubbard U should be thought of as a functional of the charge density as well and thus depends on any factor able to change the electronic structure of the ground state. The validity of this approximation should be tested carefully, case by case. In fact, some recent works have shown that accounting for the variation of the interaction parameter with the ionic positions and the lattice parameter can be quite important to obtain quantitatively predictive results. In Ref. [68], focused on the properties of the low-spin ground state of $\mathrm{LaCoO_3}$ under pressure, the Hubbard U (necessary to reproduce the insulating character of this material and for a better description of its electronic and bonding structure) was recalculated for every volume explored. The structurally-consistent U proved crucial to predict the variation of the structural parameters of the material (lattice spacing, rhombohedral angle, Co-O distance and bond angles) with pressure in good agreement with experimental data. In Ref. [89] the linear-response calculation of the U as a function of the unit cell volume (or the applied pressure) allowed for a precise evaluation of the pressure-induced high-spin to low-spin transition in $(\mathrm{Mg}_{1-x}\mathrm{Fe}_x)\mathrm{O}$ Magnesiowüstite for different Fe concentrations.

The lack of an analytic expression for the Hubbard U makes it very difficult to account for its variation with the atomic position and lattice parameters. However, a recent article [90] has introduced a method to efficiently compute the derivative dU^I/dR^J that allows to capture (at least at first order) the variation of U with the ionic position. This extension is based on the linear-response approach to compute U [19] that was discussed in section 3 and, in particular, on the calculation of the linear-response of the ionic forces to the external perturbation α (see Eq. 17). The same method could be easily generalized to stress and used to evaluate $dU^I/d\epsilon_{\alpha\beta}$. In Ref. [90] this approach is used to account for the variation of U with atomic positions during chemical interactions involving bi-atomic molecules. It is demonstrated that a configuration-dependent effective interaction parameter significantly improves the quantitative description of the potential energy surfaces that the system explores during these processes and eliminates the inaccuracies related to the use of the same (average) value of U for all the configurations, that has become quite common practice in literature. The promising results obtained in this work give hope that analogous implementations could actually be completed for the calculation of stresses and second derivatives and to improve the accuracy of molecular dynamics simulations based on LDA+U [74, 91].

5 The LDA+U+V approach: when covalency is important

5.1 Extended Hubbard model and formulation of LDA+U+V functional

In this section I would like to introduce and briefly discuss one of the latest extensions to the LDA+U functional: the LDA+U+V [34]. This modification is shaped on the "extended" Hubbard model and includes both on-site and inter-site electronic interactions. The extended formulation of the Hubbard Hamiltonian (Eq. (1)) has been considered since the early days of this model [10, 11] and can be expressed as follows:

$$H_{Hub} = t \sum_{\langle i,j\rangle,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_i n_{i,\uparrow} n_{i,\downarrow} + V \sum_{\langle i,j\rangle} n_i n_j \tag{48}$$

where V represents the strength of the interaction between electrons on neighbor atomic sites.

The interest on the extended Hubbard model has been revamped in the last decades by the discovery of high T$_c$ superconductors and the intense research activity focusing around them. Whether the inter-site coupling V has a determinant role in inducing superconductivity is, however, still matter of debate. Although the "resonating valence bond" model [92] predicts a superconducting state (at least within mean-field theory) for a doped Mott insulator with only on-site couplings [93], several numerical studies suggest that the inter-site interaction plays indeed an important role [94, 95] and superconductivity is predicted in a regime with repulsive on-site ($U > 0$) and attractive inter-site ($V < 0$) couplings [96–99]. Several studies have also demonstrated that the relative strength of U and V controls many properties of the ground state of correlated materials, as, for example, the occurrence of possible phase separations [100], the magnetic order [101, 102], the onset of charge-density and spin-density-wave regimes [103]. In Refs. [17, 104] the inter-site coupling (between d states) was recognized to be important to determine a charge-ordered ground state in mixed-valence systems, while in Ref. [105] the extended Hubbard model was used to calculate the Green's function of two particles on a lattice and to refine the Auger core-valence-valence line shapes of solids. More recently, the extended Hubbard model has been used to study the conduction and the structural properties of polymers and carbon nano-structures and the interplay between U and V was shown to control, for example, the dimerization of graphene nanoribbons [106].

Our motivation to include inter-site interactions in the formulation of the corrective Hubbard Hamiltonian was the attempt to define a more flexible and general computational scheme able to account for (rather than just suppress) the possible hybridization of atomic states on different atoms. In order to understand the implementation of the LDA+U+V [34] it is useful to start from the second-quantization expression of the site- and orbital- dependent electronic interaction energy:

$$E_{int} = \frac{1}{2} \sum_{I,J,K,L} \sum_{i,j,k,l} \sum_{\sigma} \langle \phi_i^I \phi_j^J | V_{ee} | \phi_k^K \phi_l^L \rangle \left(n_{ki}^{KI\sigma} n_{lj}^{LJ\sigma'} - \delta_{\sigma\sigma'} n_{kj}^{KJ\sigma} n_{li}^{LI\sigma'} \right) \tag{49}$$

where $n_{ki}^{KI\sigma}$ represent the average values of number operators ($\langle c_i^{I\sigma\dagger} c_k^{K\sigma} \rangle$), to be associated to occupations defined as in Eq. (3). Generalizing the approach described for the on-site case, the E_{Hub} of the DFT+U+V can be obtained from Eq. (49) supposing that a significant contribution to the corrective potential also comes from the interactions between orbitals on couples of distinct sites: $\langle \phi_i^I \phi_j^J | V_{ee} | \phi_k^K \phi_l^L \rangle \rightarrow \delta_{IK} \delta_{JL} \delta_{ik} \delta_{jl} V^{IJ} + \delta_{IL} \delta_{JK} \delta_{il} \delta_{jk} K^{IJ}$. Similarly to the on-site case, the effective inter-site interactions are assumed to be all equal to their atomic averages over the states of the two atoms: $\langle \phi_i^I \phi_j^J | V_{ee} | \phi_k^K \phi_l^L \rangle \rightarrow \delta_{IK} \delta_{JL} \delta_{ik} \delta_{jl} V^{IJ} = \frac{\delta_{IK} \delta_{JL} \delta_{ik} \delta_{jl}}{(2l_I+1)(2l_J+1)} \sum_{i',j'} \langle \phi_{i'}^I \phi_{j'}^J | V_{ee} | \phi_{i'}^I \phi_{j'}^J \rangle$. Within this hypothesis it is easy to derive the following expression ($V^{II} = U^I$):

$$E_{Hub} = \sum_I \frac{U^I}{2} \left[(n^I)^2 - \sum_\sigma Tr \left[(\mathbf{n}^{II\sigma})^2 \right] \right] + \sum_{IJ}^{\star} \frac{V^{IJ}}{2} \left[n^I n^J - \sum_\sigma Tr (\mathbf{n}^{IJ\sigma} \mathbf{n}^{JI\sigma}) \right] \tag{50}$$

where the star in the sum operator reminds that for each atom I, index J covers all its neighbors up to a given distance (or belonging to a given shell). Eq. (50) uses a generalized formulation of the occupation matrix (Eq. (3)) to allow for the possibility that the two atomic wave functions involved in its definition belong to different atoms:

$$n^{IJ\sigma}_{m,m'} = \sum_{k,v} f^{\sigma}_{kv} \langle \psi^{\sigma}_{kv} | \phi^{J}_{m'} \rangle \langle \phi^{I}_{m} | \psi^{\sigma}_{kv} \rangle \tag{51}$$

where f^{σ}_{kv} are the occupations of the KS states. In Eq. (51) the indexes m and m' run over the angular momentum manifolds that are subjected to the Hubbard correction on atoms I and J respectively. It is important to notice that the occupation matrix defined in Eq. (51) contains information about all the atoms in the same unit cell and the on-site occupations defined in Eq. (3) correspond to its diagonal blocks ($\mathbf{n}^{I\sigma} = \mathbf{n}^{II\sigma}$). Generalizing the FLL expression of the on-site double-counting term we arrive at the following expression:

$$E_{dc} = \sum_{I} \frac{U^I}{2} n^I (n^I - 1) + \sum_{I,J}^{\star} \frac{V^{IJ}}{2} n^I n^J. \tag{52}$$

Subtracting Eq. (52) from Eq. (50) one finally gets:

$$E_{UV} = E_{Hub} - E_{dc} = \sum_{I,\sigma} \frac{U^I}{2} Tr\left[\mathbf{n}^{II\sigma}\left(\mathbf{1} - \mathbf{n}^{II\sigma}\right)\right] - \sum_{I,J,\sigma}^{*} \frac{V^{IJ}}{2} Tr\left[\mathbf{n}^{IJ\sigma}\mathbf{n}^{JI\sigma}\right]. \tag{53}$$

To better understand the effect of the inter-site part of the energy functional it is convenient to derive the contribution of the extended Hubbard correction to the KS potential (actually corresponding to $\frac{\delta E_{Hub}}{\delta (\psi^{\sigma}_{kv})^*}$):

$$V_{UV}|\psi^{\sigma}_{kv}\rangle = \sum_{I,m,m'} \frac{U^I}{2}\left(\delta_{mm'} - 2n^{II\sigma}_{m'm}\right)|\phi^{I}_{m}\rangle\langle\phi^{I}_{m'}|\psi^{\sigma}_{kv}\rangle - \sum_{I,J,m,m'}^{*} V^{IJ} n^{JI\sigma}_{m'm}|\phi^{I}_{m}\rangle\langle\phi^{J}_{m'}|\psi^{\sigma}_{kv}\rangle. \tag{54}$$

From Eq. (54) it is evident that while the *on-site* term of the potential is attractive for occupied states that are, at most, linear combinations of atomic orbitals of the *same atom* (resulting in on-site blocks of the occupation matrix, $\mathbf{n}^{II\sigma}$, dominant on others), the *inter-site* interaction stabilizes states that are linear combinations of atomic orbitals belonging to *different atoms* (e.g., molecular orbitals, that lead to large off-site blocks, $\mathbf{n}^{JI\sigma}$, of the occupation matrix). Thus, the two interactions are in competition with each other. The detailed balance between these quantities, controlling the character of the resulting ground state (e.g., the degree of localization), is guaranteed by the possibility to compute both parameters simultaneously through the linear-response approach described in [19]. In fact, the inter-site interaction parameters correspond to the off-diagonal terms of the interaction matrix defined in Eq. (19).

It is important to notice that the trace operator in the on-site functional guarantees the invariance of the energy only with respect to rotations of atomic orbitals *on the same atomic site*. In fact, the on-site corrective functional (Eq. (12)) is not invariant for general rotations of the atomic orbital basis set that mixes states from different atoms. In the inter-site term (Eq. (53)), the trace applied to the product of generalized occupation matrices is not sufficient to re-establish this invariance due to the lack of higher order terms (e.g., involving more than two sites) and to

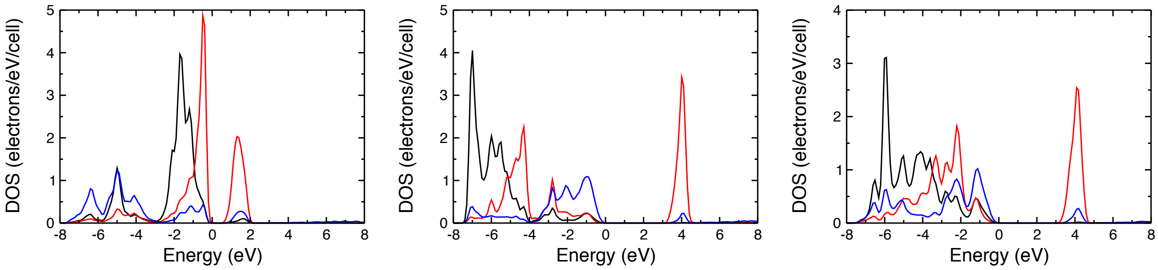

Fig. 4: *(From Ref. [34]) The density of states of NiO obtained with different approximations: GGA (left); GGA+U (center); GGA+U+V (right). The energies were shifted for the top of the valence band to correspond to the zero of the energy in all cases. The black line represents majority spin d states, the red line minority d states, the blue line oxygen p states.*

the use of site- and orbital- averaged interaction parameters. However, the inter-site extension of the corrective functional represents, with respect to the on-site case, a significant step towards general invariance as it contains, at least, some of the multiple-site terms that would be generated by the rotation of on-site ones. Site- and orbital-dependence of the corrective functional are implicitly included in Wannier-function-based implementations of the DFT+U [59, 107, 108] as it becomes evident by re-expressing Wannier functions on the basis of atomic orbitals. The two approaches would thus lead to equivalent results if all the relevant multiple-center interactions parameters are included in the corrective functionals and are computed consistently with the choice of the orbital basis. While on the basis of Wannier-functions the number of relevant electronic interactions to be computed is probably minimal (especially if maximally-localized orbitals are used [58]), the atomic orbital representation, besides providing a more intuitive and transparent scheme to select relevant interactions terms (e.g., based on inter-atomic distances), is more convenient to compute derivatives of the energy as, for example, forces and stresses that are crucial to evaluate the structural properties of systems.

In the implementation of Eq. (53) we have added the possibility for the corrective functional to act on two l manifolds per atom as, for example, the $3s$ and $3p$ orbitals of Si, or the $4s$ and $3d$ orbitals of Ni. The motivation for this extension consists in the fact that different manifolds of atomic states may require to be treated on the same theoretical ground in cases where hybridization is relevant (as, e.g., for bulk Si whose bonding structure is based on the sp^3 mixing of s and p orbitals).

5.2 LDA+U+V case studies: NiO, Si, and GaAs

The new LDA+U+V was first employed to study the electronic and structural properties of NiO, Si and GaAs [34], prototypical representatives of Mott or charge-transfer (NiO) and band insulators (Si and GaAs). The choice of these systems was made to test the ability of the new functional to bridge the description of Mott or charge-transfer insulators (NiO) with that of band insulators (Si and GaAs). In fact, the fundamental gap of a system is the sum of the KS gap and the discontinuity in the KS potential (usually missing in most approximate local or semi-local xc functionals) [109]. Since the main effect of the Hubbard correction consists in

	a	B	E_g
GGA	7.93	188	0.6
GGA+U	8.069	181	3.2
GGA+U+V	7.99	197	3.2
Exp	7.89	166-208	3.1-4.3

Table 1: *The equilibrium lattice parameter (a, in Bohr atomic radii), the bulk modulus (B, in GPa), and the band gap (E_g, in eV) of NiO obtained with different computational approaches: GGA, "traditional" GGA+U (with U only on the d states of Ni) and GGA+U+V with the interaction parameters computed "self-consistently" from the GGA+U+V ground state (see text). Comparison is made with experimental results on all the computed quantities.*

re-introducing the discontinuity of the KS potential at integer occupations it should be able to correct the description of the electronic properties for both classes of materials .

As mentioned in section 4.3, NiO has a cubic rock-salt structure with a rhombohedral symmetry brought about by its AFII ground state. Because of the balance between crystal field and exchange splittings of the d states of Ni, (nominally) occupied by 8 electrons, the material has a finite KS gap with oxygen p states occupying the top of the valence band. This gap, however, severely underestimates the one obtained from photoemission experiments (of about 4.3 eV [110]). LDA+U has been used quite successfully on this material (the spread of results is mostly due to the different values of U used) providing a band gap between 3.0 and 3.5 eV, and quite accurate estimates for both the magnetic moments and the equilibrium lattice parameter [111–113]. DFT+U has also been employed recently to compute the k-edge XAS spectrum of NiO using a novel, parameter-free computational approach [114] that has produced results consistent with experimental data. The use of GW on top of a LDA+U calculation has provided a better estimate of the energy gap compared to LDA+U, even though other details of the density of states were almost unchanged [115].

Besides the on-site U_{Ni}, the LDA+U+V calculations we performed also included the interactions between nearest neighbor Ni and O (V_{Ni-O}) and between second nearest neighbor Ni atoms (V_{Ni-Ni}). The corrective functional included interactions between d states, between d and p and between d and s (on-site). Other interactions were found to have a negligible effect on the results and were neglected. The numerical values of the interaction parameters, all determined through the linear-response approach discussed above, can be found in Ref [34]. Fig. 4 compares the density of states (DOS) of NiO as obtained from GGA, GGA+U and GGA+U+V calculations. It is easy to observe that the GGA+U+V obtains a band gap of the same width as GGA+U, also maintaining the charge-transfer character of the material with O p states at the top of the valence band, as observed in photoemission experiments. As anticipated, the GGA band gap is far too small if compared with experiments and also has Ni d states at the top of the valence band. As expected, the inter-site interactions between Ni and O electrons also results in a more significant overlap in energy between d and p states. In table 1 a comparison is made between experiments and calculations on the equilibrium lattice parameter, bulk modulus and

	U_{ss}	U_{sb}	U_{bs}	U_{bb}	V_{ss}	V_{sb}	V_{bs}	V_{bb}
Si-Si	2.82	3.18	3.18	3.65	1.34	1.36	1.36	1.40
Ga-Ga	3.14	3.56	3.56	4.17				
As-As	4.24	4.38	4.38	4.63				
Ga-As					1.72	1.68	1.76	1.75

Table 2: *Interaction parameters U and V (eV) for Si and GaAs (Ga $3d$ electrons as valence electrons). Inter-site terms are for first-neighbors and the listed values are for the equilibrium lattice parameters found with GGA+U+V. Indexes s and b stand for "standard" (higher l) and "background" (lower l) orbitals respectively.*

energy gap. One can see that while GGA provides the better estimate of the experimental lattice parameter, GGA+U+V improves on the result of GGA+U for the structural parameter and the bulk modulus is also corrected towards the experimental value. Thus, accounting for inter-site interactions does not destroy the quality of the LDA+U description of the ground state of correlated materials and has the potential to improve problematic aspects (e.g., structural properties) counter-balancing the effects of excessive electronic localization.

The application to Si and GaAs is, in some sense, the "proof of fire" for the LDA+U+V approach, as the insulating character of these materials is due to the hybridization of s and p orbitals) from neighbor atoms which leads to the formation of fully occupied bonding states and empty anti-bonding orbitals. The excessive stabilization of atomic orbitals induced by the on-site U suppresses the overlap with neighbor atoms and tends to reduces the gap between valence and conduction states [34]. While providing a quite good description of the ground state properties of these materials, the LDA and GGA functionals drastically underestimate the experimental band gap. A better estimate of the band gap has been obtained using SIC and hybrid functionals [116–118] or with the GW approach based on an LDA [119, 120] or a EXX [121] ground state.

As mentioned above, for the LDA+U+V method to work on these systems both on-site and inter-site interactions had to be computed for s and p states to account for the sp^3 hybridization. Table 2 collects all the interaction parameters computed for Si and GaAs. It is important to notice how, in virtue of the hybridization between s and p states the value of these parameters is almost constant both for on-site and inter-site interactions. In table 3, the equilibrium lattice parameter, the bulk modulus and the band energy gap obtained from GGA, GGA+U and GGA+U+V calculations on Si and GaAs can be directly compared with experimental measurements of the same quantities (we refer to the data collected in the web-database, Ref. [122]). As it can be observed from this table, the (on-site only) GGA+U predicts the equilibrium lattice parameter in better agreement with the experimental value than GGA for GaAs while it overcorrects GGA for Si; however, the bulk modulus is improved with respect to the GGA value only in the case of Si. Due to the suppression of the interatomic hybridization, in both cases, the energy band gap is lowered compared to GGA, further worsening the agreement with experiments. The use of the inter-site correction results in a systematic improvement for the evaluation

	Si			GaAs		
	a	B	E_g	a	B	E_g
GGA	5.479	83.0	0.64	5.774	58.4	0.19
GGA+U	5.363	93.9	0.39	5.736	52.6	0.00
GGA+U+V	5.370	102.5	1.36	5.654	67.7	0.90
Exp.	5.431	98.0	1.12	5.653	75.3	1.42

Table 3: *Comparative results for lattice parameter (a, in Å), bulk modulus (B, in GPa) and energy gap (E_g, in eV).*

of all these quantities. In fact, encouraging the occupations of hybrid states, the inter-site interactions not only enlarge the splittings between populated and empty orbitals (which increases the size of the band gap), but also make bonds shorter (so that hybridization is enhanced) and stronger, thus tuning both the equilibrium lattice parameter and the bulk modulus of these materials to values closer to the experimental results. Calculations on GaAs explicitly included Ga $3d$ states in the valence manifold as this was reported to produce a Ga pseudopotential of better quality [123].

Fig. 5 shows a comparison between the band structures of Si and GaAs obtained with GGA and GGA+U+V. As it can be observed, the increase in the band gap obtained with the "+U+V" correction is the result of an almost uniform shift of electronic energies (downwards for valence, upwards for conduction states) that maintains, however, the overall dispersion pattern.

These results confirm that the extended Hubbard correction is able to significantly improve the description of band insulators and semiconductors with respect to GGA, providing a more accurate estimate of structural and electronic properties. In view of the fact that these systems are normally treated with hybrid functionals or SIC approaches, the good results obtained with LDA+U+V are the demonstration that this approach has similar capabilities and the inaccuracy of the LDA+U (with on-site interactions only) is not inherent to the reference model but rather to the approximations used to obtain its final expression. These results also clarify that, within the single particle KS representation of the N-electron problem, band and Mott insulators can be treated within the same theoretical framework.

The fact that LDA+U+V can be equally accurate in the description of band and Mott insulators opens to the possibility to use it in a broad range of intermediate situations where (Mott) electronic localization coexists with or competes against the hybridization of atomic states from neighbor atoms, (as, e.g., in magnetic impurities in semiconductors or metals, high T_c superconductors, etc), or in the description of processes (such as, e.g., electronic charge transfers excitation [124]) involving a significant shift in the degree of electronic localization. In a recent work [90] LDA+U+V was used to study transition-metal dioxide molecules (e.g., MnO_2); the inclusion of the inter-site interaction was found to be crucial to predict the electronic configuration, the equilibrium structure and its deformations in agreement with experiments. The extended corrective functional has also been used as the starting point of DFT+DMFT calculations [125] and it has been demonstrated that the inclusion of the inter-site interaction in the

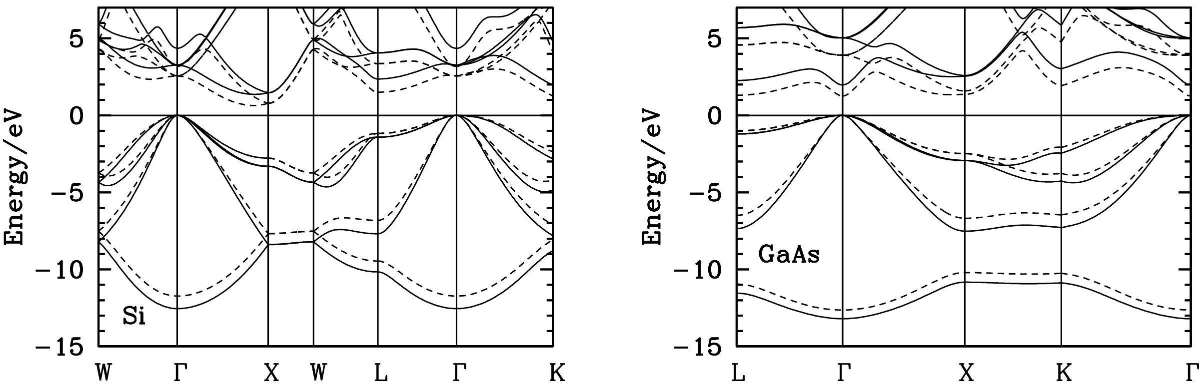

Fig. 5: *(From Ref. [34]) The band structure of Si (left) and GaAs (right). Continuous lines represent GGA+U+V results and dashed lines represent standard GGA results. All energies were shifted so that the top of valence bands are at zero energy.*

local part of the functional (not updated in the inner DMFT calculation) produced results of the same quality of cluster-DMFT but at the same computational cost of standard DMFT calculations.

6 Summary and outlook

Introduced as a simple correction to the DFT exchange-correlation functionals to improve the description of systems with strongly localized electrons, the LDA+U has become one of the most widely used numerical approaches to capture the effects of static electronic correlation. Much of the success this method continues to have in the scientific community is certainly related to the fact that it is quite easy to implement in existing DFT codes, it is very simple to use, allows to easily compute energy derivatives and also carries very limited additional computation costs. These characteristics, as also the availability of a single, easy-to-change interaction parameter to tune the strength of the correction, have encouraged the use of this scheme in a semiempirical way, as a first order, rough assessment of the (mostly qualitative) effects of electronic correlation on the physical properties of a given system. As a consequence, it has been regarded as a semiquantitative approach (as is the Hubbard model it is based on) or, at most, as a first order correction upon which to build higher level, more sophisticated approaches (as, for example, DMFT).

Notwithstanding the inherent limits of this approach (as, e.g., its static character and the consequent inability to capture dynamical, frequency dependent effects), I think it is important to stress the fact that it offers a unique possibility to compute properties related to energy derivatives from the correlated ground state of a system and thus allows to study (albeit in an approximate way) the effects of electronic correlation on equilibrium structural properties, on the dynamic evolution of systems, on phase stability and transitions, on the behavior at finite temperature. It also represents a better starting point than (uncorrected) approximate DFT functionals for higher order corrections or to compute the excitation spectrum of materials (e.g., with TDDFT or GW) thanks to the corrections it introduces to the KS spectrum.

In the present chapter I have illustrated the theoretical foundation of the LDA+U corrective approach, its prerogatives and limits, its historical construction and recent refinements. Above all, I hope I have provided a strong evidence of how this approach can represent a useful framework to capture some effects of electronic correlation and of how relatively minor extensions to its formulation can significantly improve its quantitative predictivity and the quality and numerical efficiency of computational approaches that are based on this simple correction. Therefore, further theoretical work on the "+U" functional (e.g., to include higher order many-body terms or to automatize the calculation of effective interactions) is highly desirable and can have far-reaching consequences for the definition of more accurate and efficient computational approaches able to capture the physics of correlated systems.

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