1. Introduction

A quantitative description of micro- and macroscopic properties of materials with strong electron–electron interactions has been a challenge for condensed matter physics over the past few decades. Density functional theory extensions, such as DFT + U and DFT + DMFT, that allow one to take into account electronic correlations, are under intensive development at the moment. The essence of DFT + correlations methods is a merging of the density functional and model approaches. The Hubbard model for correlated states is built on a result of \textit{ab initio} DFT calculation. Some localized atomic wave functions are chosen to describe correlated electrons. Then various Hubbard corrections for potential, charge density, total energy, atomic forces, etc are added to the DFT calculation results. A key point in this approach is the choice of the localized atomic wave functions.

Wannier functions basis has been widely used by many researchers for strongly correlated materials calculations in recent years, for example, see [1–4]. This basis is localized in direct space and could be expressed as a superposition of atomic orbitals of neighboring atoms.

A significant breakthrough was recently made by Leonov \textit{et al} [5] that allows one to compute not only the electronic structure of correlated materials within the DFT $\rightarrow$ Wannier $\rightarrow$ DMFT scheme, but even lets one obtain forces acting on atoms. However, calculations within the dynamical mean field theory are computationally expensive. Hence, we turn to a static limit of DMFT–DFT + U method that gives a reasonable description of the electronic structure for a large number of compounds and, what is more important, is less computer time demanding.

In our previous works [6, 7] we have formulated the DFT + U approach with Wannier functions (WF) for correlated states description. In the present paper we extend the approach with an atomic forces calculation technique. This will allow us to evaluate phonon spectra and perform molecular dynamics simulations for correlated materials with complex energy bands structure near the Fermi level.

With the fact that phonon calculations and molecular dynamics are common nowadays within the DFT + U approach [8–10], our goal was to shift from an atomic orbitals basis, commonly used for correlated states description, in the Wannier functions basis. Firstly, the WFs basis is more general, and secondly, it is the only basis that is able to describe correlated states in compounds with highly oxidated elements, such as BaBiO$_3$ [6]. In such compounds energy bands near the Fermi level correspond to a superposition of orbitals centered on correlated ion and the nearest ligands. The traditional DFT + U approach in atomic orbitals basis is unable to deal with such mixed character electronic states, whereas the WFs basis allows one to overcome this difficulty.
The present technique is formulated for pseudopotential plane-wave method and was implemented as a part of Quantum-ESPRESSO package [11]. We have successfully tested the approach on two typical correlated systems with different crystal structure, namely NiO and SrVO₃.

2. Method

The Hubbard contribution to the total energy could be expressed [12] as:

\[ E_H[n_{mf}^{\uparrow \downarrow}] = \frac{U}{2} \sum_{mf} \left( n_{mf}^{\uparrow \downarrow} - \frac{1}{2} n_{mf}^{\uparrow \uparrow} \right) \]

(1)

where \( U \) is on-site Coulomb interaction parameter and \( n_{mf}^{\uparrow \downarrow} \) is correlated states occupation matrix for site \( f \) and spin \( \sigma \). By using Hellmann–Feynman theorem one can write the Hubbard contribution to atomic forces as [13]:

\[ F_{ai}^{U} = - \sum_{mf} \frac{\partial E_H}{\partial n_{mf}^{\sigma \sigma}} \frac{\partial n_{mf}^{\sigma \sigma}}{\partial \tau_{ai}} \]

(2)

where \( \tau_{ai} \) is a displacement of atom \( a \) of the unit cell in \( i \)th direction. Therefore, the Hubbard contribution to the atomic forces is:

\[ F_{ai}^{U} = - \frac{U}{2} \sum_{mfn} \left( \delta_{mf} - 2n_{mf}^{\sigma \sigma} \right) \frac{\partial n_{mf}^{\sigma \sigma}}{\partial \tau_{ai}}. \]

(3)

The key point in the atomic forces calculation is an accurate computation of the occupation matrix derivative. The occupation number operator for \( \mathbf{k} \)-point in reciprocal space is:

\[ \hat{n}^{\sigma \sigma}_{\mathbf{k}} = \sum_{\nu} \theta(e_{\nu} - E_{\mathbf{k}}) \langle \psi_{\nu \mathbf{k}}^{\sigma} | \psi_{\nu \mathbf{k}}^{\sigma} \rangle, \]

(4)

where \( e_{\nu} \) is \( \nu \)th band energy, \( | \psi_{\nu \mathbf{k}}^{\sigma} \rangle \) is \( \nu \)th eigenvector of the Hamiltonian matrix and \( E_{\mathbf{k}} \) is the Fermi energy.

The occupation matrix element in the WFs basis is ( \( \mathbf{k} \)-point weight is omitted here and below for simplicity):

\[ n_{mf}^{\sigma \sigma} = \sum_{\mathbf{k}} \langle \psi_{\nu \mathbf{k}}^{m \sigma} | \hat{S} | \psi_{\nu \mathbf{k}}^{f \sigma} \rangle \langle \psi_{\nu \mathbf{k}}^{f \sigma} | \hat{S}^{\dagger} | \psi_{\nu \mathbf{k}}^{m \sigma} \rangle. \]

(5)

The WFs used here are defined as projections of atomic orbitals \( | \psi_{\nu \mathbf{k}}^{m \sigma} \rangle \) onto a subspace of the Bloch functions (detailed description of WFs constructions procedure within pseudopotential method is given in [14]):

\[ |W_{mk}^{\uparrow \downarrow} \rangle = \frac{1}{N_{\lambda}} \sum_{\mu=1}^{N_{\lambda}} | \psi_{\nu \mathbf{k}}^{m \sigma} \rangle \langle \psi_{\nu \mathbf{k}}^{f \sigma} | \hat{S}^{\dagger} | \psi_{\nu \mathbf{k}}^{m \sigma} \rangle, \]

(6)

where \( \hat{S} \) is an overlap operator of the ultrasoft pseudopotential formalism [15] and it has the following form:

\[ \hat{S} = \hat{1} + \sum_{mfl} | \phi_{m}^{l \uparrow} \rangle q_{m}^{l \uparrow} \langle \phi_{m}^{l \downarrow} |, \]

(7)

where \( | \phi_{m}^{l \sigma} \rangle \) is a projector function that satisfies the condition \( \langle \phi_{m}^{l \uparrow} | \phi_{m}^{l \downarrow} \rangle = \delta_{m} \) and \( q_{m}^{l \sigma} = \langle \phi_{m}^{l \sigma} | \phi_{m}^{l \sigma} \rangle - \langle \phi_{m}^{l \uparrow} | \phi_{m}^{l \uparrow} \rangle \) within some cut-off atomic radius \( (r < r_{c}) \). The \( \tilde{\phi}_{\mathbf{k}}^{l \sigma} \) symbol corresponds to a pseudo atomic wave function inside a sphere with radius equals \( r_{c} \); \( | \tilde{\phi}_{\mathbf{k}}^{l \sigma} \rangle = \hat{S} \phi_{m}^{l \sigma} \), \( \forall r < r_{c} \). Orthonormality condition in the ultrasoft pseudopotential formalism has the following form: \( \langle \tilde{\phi}_{\mathbf{k}}^{l \sigma} | \tilde{\phi}_{\mathbf{k}}^{l \tau} \rangle = \delta_{\sigma \tau} \). Values of \( \tilde{\phi}_{\mathbf{k}}^{l \sigma} \) and \( q_{m}^{l \sigma} \) are defined during the pseudopotential generation procedure for selected atom and these quantities are not changed in self-consistent calculation.

We force the WFs to be orthonormal with standard procedure:

\[ |W_{mk}^{l \sigma} \rangle = \frac{1}{O_{mm}^{\uparrow \downarrow}} \sum_{\mu=1}^{N_{\lambda}} \langle \phi_{\mu \mathbf{k}}^{\uparrow \sigma} | \tilde{S} | \phi_{\mu \mathbf{k}}^{\downarrow \sigma} \rangle |W_{mk}^{\uparrow \downarrow} \rangle. \]

(8)

The WFs overlap matrix \( O_{mm}^{\uparrow \downarrow} \) could be written as:

\[ O_{mm}^{\uparrow \downarrow} = \sum_{\mu=1}^{N_{\lambda}} \langle \phi_{\mu \mathbf{k}}^{\uparrow \sigma} | \tilde{S} | \phi_{\mu \mathbf{k}}^{\downarrow \sigma} \rangle \langle \phi_{\mu \mathbf{k}}^{\downarrow \sigma} | \tilde{S} | \phi_{\mu \mathbf{k}}^{\uparrow \sigma} \rangle. \]

(9)

Then the WFs overlap matrix is:

\[ O_{mn}^{\uparrow \downarrow} = \sum_{\mu=1}^{N_{\lambda}} \langle \phi_{\mu \mathbf{k}}^{\uparrow \sigma} | \tilde{S} | \phi_{\mu \mathbf{k}}^{\downarrow \sigma} \rangle \langle \phi_{\mu \mathbf{k}}^{\downarrow \sigma} | \tilde{S} | \phi_{\mu \mathbf{k}}^{\uparrow \sigma} \rangle, \]

(10)

and the occupation matrix (5) can be written as:

\[ n_{mf}^{\sigma \sigma} = \sum_{k} \sum_{m=1}^{N_{\lambda}} \theta(e_{\nu} - E_{\mathbf{k}}) \sum_{n=1}^{N_{\lambda}} \left( O_{mm}^{\uparrow \downarrow} \right)^{-\frac{1}{2}} p_{mn}^{\sigma \sigma} \sum_{n} (p_{nm}^{\sigma \sigma})^{\frac{1}{2}} O_{mm}^{\sigma \sigma} \]

(11)

The derivative of the occupation matrix with respect to the atomic displacements takes the form:

\[ \frac{\partial n_{mf}^{\sigma \sigma}}{\partial \tau_{ai}} = \sum_{\mathbf{k}} \sum_{\mu=1}^{N_{\lambda}} \theta(e_{\nu} - E_{\mathbf{k}}) \sum_{m=1}^{N_{\lambda}} \left( O_{mm}^{\uparrow \downarrow} \right)^{-\frac{1}{2}} \frac{\partial p_{mn}^{\sigma \sigma}}{\partial \tau_{ai}} \sum_{n} (p_{nm}^{\sigma \sigma})^{\frac{1}{2}} O_{mm}^{\sigma \sigma} \]

\[ + \sum_{\mathbf{k}} \left( O_{mm}^{\uparrow \downarrow} \right)^{-\frac{1}{2}} p_{mn}^{\sigma \sigma} \sum_{n} \langle O_{mn}^{\uparrow \downarrow} \rangle^{\frac{1}{2}} O_{mn}^{\sigma \sigma} \]

\[ + \sum_{\mathbf{k}} \left( O_{mm}^{\uparrow \downarrow} \right)^{-\frac{1}{2}} p_{mn}^{\sigma \sigma} \sum_{n} \langle O_{mn}^{\uparrow \downarrow} \rangle^{\frac{1}{2}} O_{mn}^{\sigma \sigma} \]

(13)

In a general case it is difficult to find an accurate analytical solution for the derivative \( \partial O_{mn}^{\uparrow \downarrow} / \partial \tau_{ai} \). Due to a flexibility of Wannier functions basis it is often possible to perform

\footnote{A detailed description of the ultrasoft pseudopotential generation procedure can be found in [16].}
the projection procedure in a special way. Usage of a linear combination of the atomic orbitals instead of one orbital, e.g. transformation into a local coordinate system, allows one to obtain the WFs overlap matrix in a form close to diagonal. Then one might deal only with the diagonal part of the overlap matrix derivative:

$$
\frac{\partial O_{m}}{\partial \tau_{ai}} = \frac{1}{2} \frac{\partial O_{m}}{\partial \tau_{ai}} O_{m}^{a},
$$

(14)

where

$$
\frac{\partial O_{m}}{\partial \tau_{ai}} = \sum_{\mu} O_{m}\left[ \frac{\partial P_{\mu}}{\partial \tau_{ai}} (P_{\mu})^{a} + P_{\mu} \left( \frac{\partial P_{\mu}}{\partial \tau_{ai}} \right)^{a}\right].
$$

(15)

The derivative of the $P_{\mu}$ can be written as:

$$
\frac{\partial P_{\mu}}{\partial \tau_{ai}} = \frac{\partial}{\partial \tau_{ai}} \langle \phi_{\mu}^{i} | \psi_{\mu}^{a} \rangle = \langle \frac{\partial \phi_{\mu}^{i}}{\partial \tau_{ai}} | \psi_{\mu}^{a} \rangle + \sum_{\mu} \langle \phi_{\mu}^{i} | \frac{\partial \phi_{\mu}^{i}}{\partial \tau_{ai}} | \psi_{\mu}^{a} \rangle + \langle \phi_{\mu}^{i} | \frac{\partial \phi_{\mu}^{i}}{\partial \tau_{ai}} | \psi_{\mu}^{a} \rangle.
$$

(16)

If one deals with some low-symmetry crystal cell and is unable to transform the WFs basis to obtain a diagonal overlap matrix, then more complicated operation is necessary. The problem of the derivative $\partial O_{m}/\partial \tau_{ai}$ calculation could be reformulated as a finding for numerical solution of the Sylvester equation. Then the classical numerical Bartels–Stewart algorithm could be used to obtain the derivative [17].

Calculation of the atomic wave function derivative on atom displacement is a well-run procedure in the plane-wave approaches [18]. For example, in Quantum-ESPRESSO package the derivative is calculated as:

$$
\frac{\partial \phi_{\mu}^{i}}{\partial \tau_{ai}} = \delta_{i,a} \frac{i}{\sqrt{V}} \sum_{G} e^{-i(k+G) \cdot \tau_{ai}} c_{i,a}(k + G)(k + G),
$$

(17)

where $V$ is the cell volume, $G$ is a reciprocal lattice vector and $c_{i,a}$ is a Fourier coefficient of an atomic wave functions Fourier expansion.

Thus, if we know the method of calculating $P_{\mu}$ and all components in (16) then we can calculate the occupation matrix derivative and hence the Hubbard contribution to the atomic forces.

3. Results and discussion

3.1. NiO

As the first step, the proposed approach was tested on one of typical objects for calculation schemes verification for correlated materials, nickel oxide. NiO is a charge-transfer insulator wherein the partially filled bands are formed by Ni-d and O-p orbitals of neighboring atoms. It is known that spin-polarized DFT + $U$ calculation is able to successfully reproduce bands structure of the compound [19]. Therefore, we calculated an atomic force acting on atoms at the end of

self-consistent cycle within spin-polarized DFT + $U$ approach in WFs basis [6, 7].

For the density-functional calculations, we used the Perdew–Burke–Ernzerhof GGA exchange–correlation functional together with Vanderbilt ultrasoft pseudopotentials. We used a kinetic energy cutoff of 45 Ry (360 Ry) for the plane-wave expansion of the electronic states (core-augmentation charge). The self-consistent calculations were performed with [6, 6, 6] Monkhorst–Pack k-points grid. Calculations were performed for a cell containing two formula units. The total energy during the calculations was converged up to to $10^{-7}$ Ry. One-site effective Coulomb interaction parameter $U = 8.0$ eV for Ni 3d states was chosen [19]. Constructed Wannier functions had a symmetry of Ni-d and O-p states. Total and partial densities of states for Ni ions are shown in figure 1. Obtained energy gap value equals 4 eV and it is in agreement with previous works [19] and photoelectron and XAS measurements [20, 21]. The upper Hubbard band above the Fermi level consists of Ni-d states and the lower Hubbard band is a mixture of Ni-d and O-p states due to a strong hybridization. To test the forces calculation procedure we displaced one nickel atom from its equilibrium position in the x-direction (the displacement direction within a cell is shown as a blue-color vector in figure 2).

To be sure that the assumption of small off-diagonal elements of the overlap matrix is reasonable, we checked these values numerically. The off-diagonal terms are 3 orders smaller than diagonal ones. Then the Hubbard contribution to the total force was computed using equations (3)–(17).

The resulting total force, obtained within DFT + $U$ in the WFs basis calculation, acting on the Ni atom is shown in figure 3 with blue-color dashed line. The force dependence was obtained for 12 various displacements and then interpolated with a straight line. The ‘analytical’ force compared with a numerical one (red solid line in figure 3) obtained as a numerical derivative of the total energy dependence (inset of the figure 3) is shown in the figure.

One can see that the atomic force obtained analytically is in a good agreement with the numerical derivative. Since the two
straight lines in figure 3 are almost coincide, we compared the slope of the forces versus displacement curves. The difference between the slopes for analytical and numerical force is 3.2%.

It is really useful to discuss various contributions to the total DFT + U force. We cannot compare directly the total force obtained within DFT and DFT + U approaches, since the DFT calculation is unable to reproduce experimentally observed insulating ground state of the NiO and the DFT gives absolutely different electronic density distribution.

To estimate the influence of the Hubbard correction on the total force one can compare the total force obtained within DFT + U and the Hubbard term contribution.

The total force obtained by DFT + U and acting on the displaced Ni atom equals $-0.01946$ Ry/Bohr (for the displacement of $0.095$ Bohr). The Hubbard contribution to the total force calculated using equations (2)–(16) equals $0.00194$ Ry/Bohr, i.e. the Hubbard term is about 10% of the total force and this contribution is small but it is important. Since the $+U$ force is proportional to the occupations matrix derivative, we demonstrate below, as an example, absolute values of this matrix (for the Ni displacement of $0.095$ Bohr). The occupation matrix derivative defined in equation (13) is (in $10^{-3}$ States/Bohr units):

$$\frac{\partial n}{\partial \alpha} = \begin{pmatrix} 1.64 & -0.70 & 0.48 & -9.24 & 1.97 \\ -0.70 & -2.31 & -0.75 & 2.68 & 1.44 \\ 0.48 & -0.75 & 3.92 & -0.84 & 0.75 \\ -9.24 & 2.68 & -0.84 & 12.2 & -1.94 \\ 1.97 & 1.44 & 0.75 & -1.94 & -2.31 \end{pmatrix}$$

The matrix elements are the same order as the resulting Hubbard force. Non-diagonal elements of the matrix with magnitude comparable to diagonal ones are the result of cubic symmetry breaking after one Ni atom displacement.

The equation (13) includes two terms proportional to the overlap matrix derivative $\partial O_{\alpha\beta}^{1/2}/\partial \alpha$. To estimate significance of this derivative for the Hubbard force value we performed several calculations with the derivative enforced to be zero. The change in the resulting total DFT + U force is $10^{-5}$ Ry/Bohr. Hence the overlap matrix derivative terms of equation (13) contribute about 1% to the Hubbard force. Despite the negligibility of this term it was taken into account in our calculations for NiO and for SrVO$_3$ cases.
3.2. SrVO₃

The next test compound for the proposed method is SrVO₃. It is paramagnetic correlated metal with the cubic perovskite crystal structure. This compound is often used as a test system for new methods with improved electronic correlations description [5, 22, 23] due to its clear crystal field splitting and simple electronic structure of vanadium d-states.

For the density-functional calculations, we also used the Perdew–Burke–Ernzerhof GGA exchange–correlation functional together with Vanderbilt ultrasoft pseudopotentials. Kinetic energy cutoff was set to 50 Ry (500 Ry) for the plane-wave expansion of the electronic states (core-augmentation charge). The self-consistent calculations were performed with (10, 10, 10) Monkhorst–Pack k-points grid. The total energy during the calculations was converged up to 10⁻⁶ Ry. One-site effective Coulomb interaction parameter \( U = 3.5\,\text{eV} \) for Ni 3d states was chosen [22]. Constructed Wannier functions had the symmetry of V-d states. For SrVO₃ we displaced one vanadium atom from its equilibrium position in the z-direction. The resulting total analytical and numerical forces, obtained within DFT + U in the WFs basis calculation, acting on the V atom are shown in figure 4. The agreement between the two lines is almost as good as for NiO. The difference between the slopes for analytical and numerical force for SrVO₃ is 5.7%.

To estimate the numerical accuracy of our calculations we have plotted the differences between the total forces obtained for every atomic displacement (see figure 5). The same values calculated within pure DFT approach are presented in the same figure for comparison. One can see that all four curves have the same character: the dependence is linear for small atomic displacements and there are the slopes, then the displacements are more than 0.1 Bohr. The difference for DFT calculation is the same order of magnitude as the difference obtained for DFT + U. One can conclude that our implementation of the proposed method has reasonable accuracy.

The most clear and straightforward method for phonon frequencies calculation is the ‘frozen phonon’ approach. The phonon frequency equals the second derivative of the total energy over atom displacement. On the other hand it could be computed as the first derivative of the total force acting on atom. Since in both cases the derivative is computed numerically, the second approach is more accurate and it is used nowadays more intensively than the first one. From the data presented in the figure 3 we computed the second derivative of the total energy and the first derivative of the total force over atom displacement for NiO. The obtained values 0.21 Ry/(Bohr)² and 0.2 Ry/(Bohr)² are in good agreement. Therefore, the presented technique could be used not only for forces calculation but additionally for vibrational properties computation within the ‘frozen phonons’ approach.

4. Conclusion

In the present work the approach to calculate the Hubbard term contribution to atomic forces within the Wannier functions basis in the DFT + U framework with the ultrasoft pseudopotential formalism is proposed. We have performed a calculation of the atomic force acting on a slightly displaced nickel atom in NiO and vanadium atom in SrVO₃. The good agreement between atomic force evaluated analytically and numerically is obtained, confirming the applicability and reliability of the proposed method.

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