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First-Principles Calculation of Atomic Forces and Structural Distortions in Strongly Correlated Materials

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We introduce a novel computational approach for the investigation of complex correlated electron materials which makes it possible to evaluate interatomic forces and, thereby, determine atomic displacements and structural transformations induced by electronic correlations. It combines *ab initio* band structure and dynamical mean-field theory and is implemented with the linear-response formalism regarding atomic displacements. We apply this new technique to explore structural transitions of prototypical correlated systems such as elemental hydrogen, $SrVO_3$, and $KCuF_3$.

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A unified description of the electronic structure and the lattice properties of correlated materials is one of the most important goals of modern condensed matter physics. This is particularly desirable for correlated electron materials where the complex interplay between electronic and lattice degrees of freedom leads to rich phase diagrams which makes them interesting not only for fundamental research, but also for technological applications [1]. Clearly, there is a great need for theoretical approaches that are able to compute the properties of such materials from first principles.

State of the art techniques for the calculation of electronic band structures based on density functional theory often provide a good quantitative description of the electronic and lattice properties of a variety of transition metals and semiconductors. The lattice structure of such materials can be obtained, e.g., on the basis of total-energy calculations. These investigations are computationally very demanding even for simple materials, since they require the minimization of the total energy as a function of all atomic displacements. Thus, the computational effort increases exponentially, which limits the applicability of this line of approach. Such a problem does not occur when the lattice structure is calculated by means of the forces acting on the atoms. Indeed, only by computing the complete set of interatomic forces using the Hellmann-Feynman theorem [2] is it possible to calculate the lattice structure of complex materials. However, even this approach does not lead to satisfactory results in the case of correlated materials such as the metals Ce, Pu, or the Mott-Hubbard insulators NiO, MnO. Extensions of the local density approximation (LDA) or the generalized-gradient approximation, such as the LDA + U approach [3], can considerably improve results, e.g., for the band gaps and magnetic moments, but only for magnetically ordered states.

The LDA + DMFT approach, a combination of *ab initio* band-structure methods with the dynamical mean-field theory (DMFT) of correlated electrons [4] has made it possible to compute even the electronic structure of complex, correlated materials [5], thereby providing important insights into our understanding of their properties [6–14]. In particular, employing this technique, one is now able to study materials located at the proximity of a Mott-Hubbard metal-insulator transition as encountered in many transition-metal oxides. Moreover, LDA + DMFT calculations can determine both the electronic structure and lattice properties of correlated materials, irrespective of whether they are in a paramagnetic or a magnetically ordered state [9–14]. Although these studies take the lattice into account only on the basis of total-energy calculations, they already demonstrate the crucial importance of electronic correlations for the structural stability of correlated materials [9,13]. Furthermore, by implementing the LDA + DMFT scheme within the linear-response formalism [10], one can now investigate the influence of electronic correlations on dynamical properties of the lattice. Indeed, this approach provides a good quantitative description of the electronic properties and lattice dynamics of correlated metals and insulators [9,10]. Nevertheless, the approximations needed to solve the quantum impurity model (e.g., the Hubbard I approximation) prevent this method from being applicable to correlated materials near a Mott metal-insulator transition. Therefore, even today it remains a great theoretical challenge to treat the electronic and lattice properties of correlated materials in a nonperturbative and thermodynamically consistent way.

In this Letter, we present a new approach for the calculation of interatomic forces and structural distortions in strongly correlated materials based on the implementation of LDA + DMFT within the linear-response formalism. The calculation of forces opens the way to compute atomic displacements and determine equilibrium atomic positions and, hence, explain the origin of lattice transformations induced by electronic correlations. This makes it possible to calculate the equilibrium lattice structure of correlated systems even in the vicinity of a Mott metal-insulator transition—a computation which was not feasible up to now.

We start from the total energy functional of a correlated system [11,12]

$$E = E_{\mathrm{LDA}}[\rho] + \langle \hat{H}_{\mathrm{LDA}} \rangle - \sum_{m,k} \epsilon^{\mathrm{LDA}}_{m,k} + \frac{1}{2} \sum_{imm',\sigma\sigma'} U^{\sigma\sigma'}_{mm'} \langle \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \rangle - E_{\mathrm{DC}}. \tag{1}$$

Here $E_{\mathrm{LDA}}[\rho]$ denotes the total energy obtained by LDA, $\hat{H}_{\mathrm{LDA}}$ is the effective low-energy Hamiltonian [15] obtained from the LDA band structure by employing a projection technique to evaluate the atomic-centered symmetry-constrained Wannier orbitals [16–18], $\langle \hat{H}_{\mathrm{LDA}} \rangle$ is evaluated as the thermal average of $\hat{H}_{\mathrm{LDA}}$, and $\sum_{m,k} \epsilon^{\mathrm{LDA}}_{m,k}$ is the sum of the valence-state eigenvalues. The interaction energy, the fourth term on the right-hand side of Eq. (1), is computed from the double occupancy matrix $\langle \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \rangle$ which is evaluated in DMFT. The double-counting (DC) correction $E_{\mathrm{DC}} = \frac{1}{2} \sum_{imm',\sigma\sigma'} U^{\sigma\sigma'}_{mm'} \langle \hat{n}_{im\sigma} \rangle \langle \hat{n}_{im'\sigma'} \rangle$ corresponds to the average Coulomb repulsion between the interacting electrons and is calculated from the self-consistently determined local occupations.

To evaluate the correlation induced atomic displacements, we calculate the force acting on the atom s from the first-order derivative of the total energy

$$F_s = F^s_{\mathrm{LDA}} - \delta_s \langle \hat{H}_{\mathrm{LDA}} \rangle + \sum_{m,k} \delta_s \epsilon^{\mathrm{LDA}}_{m,k} - \frac{1}{2} \sum_{imm',\sigma\sigma'} U^{\sigma\sigma'}_{mm'} \delta_s \langle \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \rangle - F^s_{\mathrm{DC}}. \tag{2}$$

Here, $\delta_s \equiv d/d\mathbf{R}_s$ denotes the first-order derivative with respect to the atomic position $\mathbf{R}_s$, and F^s_{LDA} is the force acting on the atom s calculated within LDA. Furthermore, $\delta_s \langle \hat{H}_{\mathrm{LDA}} \rangle$ is evaluated as the thermal average of the force operator $\delta_s \hat{H}_{\mathrm{LDA}}$, which yields the Hellmann-Feynman contribution due to the first-order changes of the LDA Wannier Hamiltonian $\hat{H}_{\mathrm{LDA}}$, plus the term due to the explicit dependence of the local Green function on the atomic positions

$$\delta_s \langle \hat{H}_{\mathrm{LDA}} \rangle = \langle \delta_s \hat{H}_{\mathrm{LDA}} \rangle + \mathrm{Tr} \sum_{\mathbf{k},i\omega_n} \hat{H}^{\mathbf{k}}_{\mathrm{LDA}} \delta_s \hat{G}_{\mathbf{k}}(i\omega_n) e^{i\omega_n 0+}. \tag{3}$$

The first-order derivative of the local Green function is found as

$$\delta_s \hat{G}_{\mathbf{k}}(\omega) = \hat{G}_{\mathbf{k}}(\omega) [\delta_s \hat{H}^{\mathbf{k}}_{\mathrm{LDA}} + \delta_s \hat{\Sigma}(\omega) - \delta_s \mu] \hat{G}_{\mathbf{k}}(\omega). \tag{4}$$

Interatomic forces due to the Coulomb interaction, the fourth term on the right-hand side of Eq. (2), can be calculated [19] as the first-order derivative of the Galitskii-Migdal formula [20] for the interaction energy $F^s_{\mathrm{U}} = -\frac{1}{2} \mathrm{Tr} \sum_{i\omega_n} [\delta_s \hat{\Sigma}(i\omega_n) \hat{G}(i\omega_n) + \hat{\Sigma}(i\omega_n) \delta_s \hat{G}(i\omega_n)] e^{i\omega_n 0+}$. We assume, here, that the average Coulomb interaction $\bar{U}$ and Hund's rule coupling J remain constant when the atomic positions change. It turns out that the force operator $\delta_s \hat{H}_{\mathrm{LDA}}$ and the first-order change of the self-energy $\delta_s \hat{\Sigma}(\omega)$ are the two independent variables in the force functional [Eq. (2)] which have to be evaluated to compute interatomic forces [21].

To obtain $\delta_s \hat{H}_{\mathrm{LDA}}$, we need to generalize the projection scheme used to evaluate the LDA Wannier Hamiltonian [17,18]. The former is based on the projection of the set of site-centered atomiclike trial orbitals $|\phi_n\rangle$ on the Bloch functions $|\psi_{ik}\rangle$ of the chosen bands with band indices N_a to N_b. Therefore, the force operator can be expressed as

$$(\delta_s \hat{H}^{\mathbf{k}}_{\mathrm{LDA}})_{nm} = \sum_{i=N_a}^{N_b} \langle \phi_n | \psi_{i\mathbf{k}} \rangle \langle \psi_{i\mathbf{k}} | \phi_m \rangle \times (\delta_s V^{\mathrm{KS}}_{i\mathbf{k}} + \delta_s V^{\mathrm{HXC}}_{i\mathbf{k}}), \tag{5}$$

where $\delta_s V^{\mathrm{KS}}_{i\mathbf{k}}$ and $\delta_s V^{\mathrm{HXC}}_{i\mathbf{k}}$ denote the first-order changes in the LDA Kohn-Sham (KS) and the Hartree and exchange-correlation (HXC) potentials, respectively [22]. The Kohn-Sham contribution $\delta_s V^{\mathrm{KS}}_{i\mathbf{k}}$ can be calculated within the plane-wave pseudopotential approach [23] as

$$\delta_s V^{\mathrm{KS}}_{i\mathbf{k}} \propto -i \sum_{\mathbf{G},\mathbf{G}'} c^{*}_{i,\mathbf{k}+\mathbf{G}} c_{i,\mathbf{k}+G'} e^{-i(\mathbf{G}-\mathbf{G}')\mathbf{R}_s} \times (\mathbf{G}-\mathbf{G}') V^{\mathrm{KS}}_s(\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}'), \tag{6}$$

where $V^{\mathrm{KS}}_s(\mathbf{G}, \mathbf{G}')$ is the Kohn-Sham potential for the atom s (for details, see Ref. [24]). The contribution $\delta_s V^{\mathrm{HXC}}_{i\mathbf{k}}$ is obtained from linear-response LDA calculations [24].

To evaluate the change of the self-energy $\delta_s \hat{\Sigma}(\omega)$, we perform a functional derivative of the impurity Green function (here, we drop the spin or orbital indices and assume summation over repeated indices)

$$\delta_s \hat{G}(\tau_1 - \tau_2) = -\hat{\chi}(\tau_1, \tau_2, \tau_3, \tau_4) \delta_s \hat{\mathscr{G}}^{-1}(\tau_3, \tau_4), \tag{7}$$

with

$$\hat{\chi}(\tau_1, \tau_2, \tau_3, \tau_4) = \langle \mathscr{T}_\tau \hat{c}(\tau_1) \hat{c}^\dagger(\tau_2) \hat{c}^\dagger(\tau_3) \hat{c}(\tau_4) \rangle - \langle \mathscr{T}_\tau \hat{c}(\tau_1) \hat{c}^\dagger(\tau_2) \rangle \langle \mathscr{T}_\tau \hat{c}^\dagger(\tau_3) \hat{c}(\tau_4) \rangle, \tag{8}$$

and use the first-order derivative of the local Green function [Eq. (4)]. We solve Eqs. (4) and (7) self-consistently by employing $\delta_s \hat{\mathscr{G}}^{-1} = \delta_s \hat{G}^{-1} + \delta_s \hat{\Sigma}$ and the two-particle

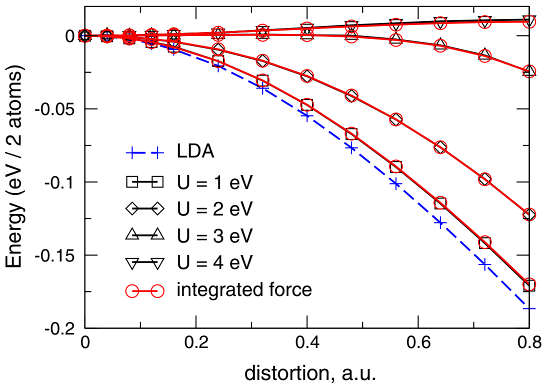

FIG. 1 (color online). Comparison of the total energies of paramagnetic hydrogen computed by LDA + DMFT with the results obtained by numerical integration of the corresponding force with respect to an atomic displacement. The calculations are performed using different values of Coulomb interaction U.

correlation function, i.e., the generalized susceptibility, $\chi(\tau_1, \tau_2, \tau_3, \tau_4)$ calculated within DMFT. The proposed method is implemented using the Hirsch-Fye quantum Monte Carlo method [25].

We now perform several test calculations to illustrate how the proposed method works in practice. To demonstrate its accuracy, we compare our results for the total energy calculated as a function of atomic displacement with those obtained by numerical integration of the corresponding forces. As the first test, we consider the simplest correlated electron problem, elemental hydrogen (H), with a cubic structure and lattice constant $a = 8$ atomic units (a.u.). The nonmagnetic LDA calculations for cubic hydrogen yield a metallic solution with a half-filled H s band of 3 eV width located at the Fermi level. To evaluate the force, we consider a supercell with two hydrogen atoms, in which one of the atoms is displaced by a distance δ with respect to its crystallographic position. In Fig. 1, we present our results for the total energy obtained by LDA as a function of δ. The nonmagnetic LDA calculations find the cubic lattice of hydrogen to be unstable since the total energy decreases with δ.

Now we take into account the electronic correlations by calculating the properties of paramagnetic hydrogen using the LDA + DMFT method. For the partially filled H s orbitals, a basis of atomic-centered symmetry constrained Wannier functions is constructed. By calculating at different values of the local Coulomb interaction U, we can explore the structural properties of correlated materials near a Mott metal-insulator phase transition—a challenging problem in solid state research. The calculations are performed for the U values in the range of 1–4 eV at a temperature $T = 0.1$ eV. Our results for the spectral function of paramagnetic hydrogen with $\delta = 0$ are shown in the inset of Fig. 2.

In Fig. 2, we present our results for the total energies calculated by LDA + DMFT for paramagnetic hydrogen as a function of the displacement δ. By changing the U values, we are able to check the accuracy of our method in calculating the kinetic and interaction contributions, respectively, to the total force. By integrating the corresponding force with respect to δ, we find an overall good quantitative agreement (within 1–2 meV) between the force and the total energy calculations. Even for large displacements δ (up to ∼10% of the lattice constant a) our force calculations show an excellent accuracy of ≤ 1 mRy/a.u. in the whole range of the U values. In Fig. 1, we provide a comparison of the total energy with the results of the numerical integration of the corresponding total force. Most interestingly, by increasing U, the cubic lattice (more precisely, the investigated displacive mode) becomes (meta-) stable for $U \geq 4$ eV. These results clearly demonstrate the crucial importance of electronic correlations for the lattice stability of correlated materials.

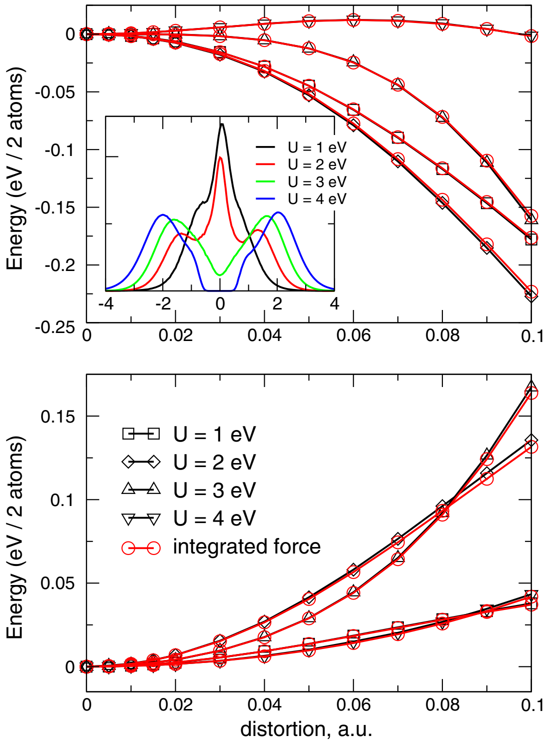

FIG. 2 (color online). Kinetic (top) and interaction (bottom) contributions to the total energy of paramagnetic hydrogen as calculated by LDA + DMFT in comparison to the results obtained by numerical integration of the corresponding force. Inset: Evolution of the resulting spectral function as a function of U.

Next, we apply our linear-response method to investigate a realistic correlated electron system, $SrVO_3$. This material has a cubic perovskite structure and a V $3d^1$ electronic configuration [26]. According to previous electronic-structure studies, $SrVO_3$ is a strongly correlated metal, with a well established three-peak structure in the spectral function [7]. It exhibits pronounced lower and upper Hubbard bands, which cannot be explained by conventional LDA. $SrVO_3$ is

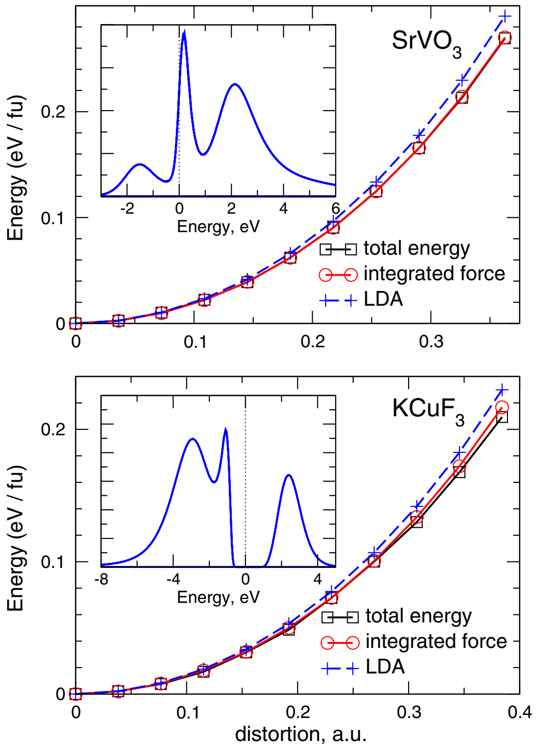

FIG. 3 (color online). Comparison of the total energies of paramagnetic SrVO$_3$ (top) and KCuF$_3$ (bottom) computed by LDA + DMFT with (i) the results obtained by numerical integration of the corresponding forces with respect to the oxygen and fluorine displacement, and (ii) with the LDA results.

an ideal test material to benchmark our computation of forces and, thereby, the prediction of the atomic positions. In our calculations, we use the experimental cubic structure with lattice constant $a = 3.838$ Å and take the Coulomb interaction $\bar{U} = 3.55$ eV and exchange coupling $J = 1.0$ eV from previous constrained LDA calculations [7]. For the partially filled V t_{2g} orbitals, a basis of atomic-centered symmetry constrained t_{2g} Wannier functions is constructed. In Fig. 3 (upper panel), we present our results for the spectral function of paramagnetic SrVO$_3$ obtained by LDA + DMFT for $T = 0.125$ eV. Overall, our results qualitatively agree with previous calculations.

In order to model the internal lattice distortions, we displace the apical oxygen atom O $(00\frac{1}{2})$ by δ in the z direction, thereby introducing a polar mode. In Fig. 3 (upper panel), we present our results for the total energy obtained by LDA + DMFT as a function of δ. These results are found to be about 9% lower in energy than those calculated with the LDA (i.e., the corresponding phonon mode is softer by about 4%). Our calculations predict the polar mode to be unstable, implying the internal stability of the cubic perovskite structure of SrVO$_3$. We evaluate the LDA + DMFT forces acting on that particular oxygen atom as a function of δ. By integrating the force, the accuracy of our method in predicting the correct atomic positions can be checked. We find excellent agreement (within 1 meV/fu) between the force and the total energy calculations. Our results clearly show that our method is able to treat atomic displacements for a realistic correlated electron metal such as SrVO$_3$.

Finally, we turn to KCuF$_3$, a prototypical Mott-Hubbard insulator with a single hole (Cu $3d^9$ electronic configuration) in the Cu e_g states. For simplicity, a hypothetical cubic perovskite lattice is assumed, with $a = 4.066$ Å; i.e., the Jahn-Teller distortion and tetragonal compression of the unit cell are neglected. Constructing a basis of atomic-centered symmetry constrained e_g Wannier functions for the partially filled Cu e_g orbitals, we calculate the electronic structure of paramagnetic KCuF$_3$ within the LDA + DMFT approach for $T = 0.125$ eV, using the interaction parameters $\bar{U} = 5.2$ eV and $J = 0.9$ eV from previous calculations [12]. The obtained spectral function is shown in Fig. 3 (bottom panel). Similar to SrVO$_3$, we introduce a polar mode by shifting an apical fluorine atom F $(00\frac{1}{2})$ in the z direction. By integrating the resulting force, our results can be compared with the total energy calculations. We find an overall good quantitative agreement, implying internal consistency and numerical stability of the proposed linear-response approach. Our results for both materials, the correlated metal SrVO$_3$ and the correlated Mott-Hubbard insulator KCuF$_3$, demonstrate that the linear-response method presented here provides a robust computational tool for the study atomic displacements caused by electronic correlations. In particular, it allows one to determine the structural phase stability of both metallic and insulating correlated materials.

In conclusion, by implementing LDA + DMFT with the linear-response formalism regarding atomic displacements, we constructed a robust computational scheme for the investigation of the electronic structure and lattice properties of correlated electron materials. The approach allows one to calculate forces and, thereby, explore lattice transformations induced by electronic correlations. In particular, it is now possible to study lattice instabilities observed at correlation induced metal-insulator transitions. Furthermore, lattice dynamical properties of correlated electron materials can be calculated by implementing the approach with, for example, the so-called small displacements method [27].

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[22] We assume here that the Wannier basis is complete, i.e., there is no contribution caused by the change of the projectors $\delta_s\langle\phi_n|\psi_{i\mathbf{k}}\rangle$. In general, $\delta_s\langle\phi_n|\psi_{i\mathbf{k}}\rangle$ can be evaluated using the orthonormality conditions $\sum_{i=N_1}^{N_2}\langle\phi_n|\psi_{i\mathbf{k}}\rangle\langle\psi_{i\mathbf{k}}|\phi_m\rangle = \delta_{nm}$.

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