First-principles Calculation of Effective Onsite Coulomb Interactions of 3d Transition Metals: Constrained Local Density Functional Approach with Maximally Localized Wannier Function

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We present a new ab initio method for calculating effective onsite Coulomb interactions of itinerant and strongly correlated electron systems. The method is based on constrained local density functional theory formulated in terms of maximally localized Wannier functions. This scheme can be implemented with any basis, and thus allows us to perform the constrained calculation with plane-wave-based electronic-structure codes. We apply the developed method to the evaluation of the onsite interaction of 3d transition-metal series. The results are discussed using a heuristic formula for screened Coulomb interactions.

Properties of itinerant and strongly correlated electron systems are widely discussed with phenomenological Hamiltonians such as Anderson-impurity [1] and Hubbard models [2]. These models embody essential aspects of correlated electrons, and can be solved numerically or sometimes analytically for special cases. However, parameters in the models are often determined empirically so that the employed model should reproduce experimental results of interest.

Recently, there has been growing interest in constructing model Hamiltonians from first principles [3]. The principal motivation for such a study is a so-called long-standing “beyond LDA” problem. One of recent major approaches toward correlated electrons from first principles is combining density-functional theory within local density approximation (LDA) with dynamical mean-field theory (DMFT) [4]. The main idea of this method is to map a first-principles Hamiltonian onto a lattice-fermion model to which the DMFT method is applicable, so developments of tractable but rational mapping techniques are highly needed.

An important notice in constructing ab initio model Hamiltonians lies in an evaluation of an onsite interaction parameter known as the Hubbard $U$. Transfer parameters can be easily obtained by representing a one-body ab initio Hamiltonian with a spatially localized (or atomic) orbital, while the $U$ parameter evaluated with a one-center Coulomb integral of the atomic orbital gives a rather large value relative to that deduced from experiments [5,6]. This is because a screening effect of surrounding valence electrons is completely neglected in the evaluation of the value. A representative treatment for calculating $U$ including the screening effect is a constrained approach [7,8]. It gives an optimally screened $U$, because, in that calculation, the $U$ value is obtained from a response of the system to a change in a local charge density, thus incorporating the valence-electron-screening effect statically into the $U$ calculation.

An important point in performing the constrained calculation is a choice of basis functions to define the charge density of localized electrons. The use of an atom-centered localized basis set like a linear muffin-tin orbital (LMTO) [9] facilitates this definition, so constrained calculations to date have been performed with LMTO-based electronic-structure codes. The method has been widely applied to investigations of effective Hubbard $U$’s of various correlated materials [10,11], while it is known that the calculated effective onsite Coulomb interaction includes an error [11] arising from the atomic sphere approximation employed in the conventional LMTO calculations [12].

In this Letter, we present a new method for calculating an effective $U$; that is, a constrained local density functional approach based on “maximally localized” Wannier functions (WF’s) [13]. The maximally localized WF, obtained by minimizing a spatial spread of WF’s in real space, has a practical advantage that it can be computed with any basis functions. This property enables us to implement the constrained scheme in the plane-wave-based electronic-structure codes. In addition, the maximally localized WF is regarded as a reasonable basis for constructing model Hamiltonians; the property of the WF being well-localized spatially ensures that the Hamiltonian matrix represented by this basis is sparse and short-ranged. In the present study, we apply the developed method to the systematic analysis for effective onsite Coulomb interactions of 3d transition metals [13].

An electronic structure of a transition metal consists of localized $d$ electrons forming a narrow band and itinerant $sp$ electrons associated with a wider band. There are $n$ localized electrons per atom for the ground state. An effective Coulomb interaction $U_{\text{eff}}$ between two $d$ electrons in an atom is defined as an energy cost in the electron transfer process, $2d^n \rightarrow d^{n-1} + d^{n+1}$, which is written in terms of total energies as

$$U_{\text{eff}} = E(n + 1) + E(n - 1) - 2E(n),$$  \hspace{1cm} (1)

where $E(n)$ is the ground-state energy of the system, while $E(n \pm 1)$ correspond to total energies for cases where there are $n \pm 1$ localized electrons in a specific atom. It should be noted here that the number of onsite $d$ electrons is regarded as an adiabatic parameter for the electronic state of the system; i.e., for the total-energy calculation, the charge density of the system is relaxed in the constraint that the occupation number of localized $d$ orbitals of the specific atom is kept at a given
value. The $U_{\text{eff}}$ value thus obtained includes a screening effect due to the relaxation of the valence-electron density around the specific atom.

The total energies can be basically calculated in density-functional formalism [15], but an important point is how to impose the constraint mentioned above. To this end, we first define the $d$ occupation number of the atom $I$ as

$$N_{1d} = \sum_\mu \sum_k \sum_\alpha f_{\alpha k} \langle w_{1\mu} | \phi_{\alpha k} \rangle^2,$$

where $\phi_{\alpha k}$ is a Bloch orbital of a band $\alpha$ with a wave vector $k$, $f_{\alpha k}$ is its occupation number, $\{w_{1\mu}\}$ are $d$-type maximally localized Wannier functions centered at the atom $I$, and the index $\mu$ specifies the five types of the $d$ orbital. With the definition of the $N_{1d}$ above, we may write a constrained density functional as

$$E(N_{1d}) = \min_\rho \left\{ F[\rho(r)] - \lambda \left[ \sum_\mu \sum_k \sum_\alpha f_{\alpha k} \langle w_{1\mu} | \phi_{\alpha k} \rangle^2 - N_{1d} \right] \right\}. \tag{3}$$

Here, $F[\rho]$ is a usual density functional with a total charge density $\rho(r) = \sum_k |\phi_{\alpha k}(r)|^2$, and $\lambda$ is a Lagrange multiplier. A functional derivative of $E(N_{1d})$ with respect to the Bloch orbital $\phi_{\alpha k}$ leads to the following constrained Kohn-Sham (KS) equation,

$$[H_{KS} + \lambda \sum_\mu |w_{1\mu}| \langle w_{1\mu} | w_{1\mu} \rangle] \phi_{\alpha k} = \epsilon_{\alpha k} \phi_{\alpha k}, \tag{4}$$

where $H_{KS}$ is a one-body KS Hamiltonian, and the second term in the brackets is an additional potential due to the constraint.

The calculation for the effective onsite Coulomb interaction $U_{\text{eff}}$ proceeds as follows: We first perform a total-energy density-functional calculation with no constraint ($\lambda = 0$) to obtain the ground-state energy $E(n)$. Then, we transform the resulting Bloch functions $\{\phi_{\alpha k}^{\lambda=0}\}$ into the maximally localized WFs $\{w_{\lambda=0}\}$ used as the input of the subsequent constrained calculations. We then solve the constrained KS equation [Eq. (4)] with a non-zero $\lambda$, and calculate the occupation number $N_{1d}$ in Eq. (2) using the resulting Bloch functions $\{\phi_{\alpha k}^{\lambda\neq0}\}$ and the WFs above $\{w_{\lambda=0}\}$. The $\lambda$ parameter is adjusted so that $N_{1d}$ should be a desired number; i.e., $n - 1$ or $n + 1$. Finally, we calculate $U_{\text{eff}}$ of Eq. (1) with the total energies thus obtained, $E(n)$, $E(n - 1)$, and $E(n + 1)$.

We implemented the scheme presented here in *Tokyo Ab initio Program Package* [16] developed by the condensed-matter-theory group in the University of Tokyo. With this program, calculations were performed within the generalized gradient approximation [17] to density-functional theory, using a plane-wave basis set and the Troullier-Martins norm-conserving pseudopotentials [18] in the Kleinman-Bylander representation [19]. The energy cutoff was set to 64 Ry, and a $9 \times 9 \times 9$ $k$-point sampling was employed to represent electronic structures of transition metals [20]. A spin polarization effect was neglected in the present calculations, and this effect seems to be negligible for the evaluation of $U_{\text{eff}}$ [11]. The $d$-type WF’s were constructed with the algorithm of Souza, Marzari, and Vanderbilt [15]. To show the validity of representing $d$ bands by the resulting WF’s, we compare in Fig. 1 original bands of Fe (solid line) with interpolated bands (dotted line) obtained by diagonalizing $k$-space Hamiltonian matrix represented by the five $d$-type WF’s. We see that the calculated interpolated bands reproduce reasonably the original narrow $d$ bands, except when $sp$ bands cross the $d$ bands. Constrained calculations were performed for a supercell containing 8 transition-metal atoms to consider a full relaxation of a screening charge density to a local charge perturbation. It was found that the size of the supercell is sufficient for obtaining a converged $U_{\text{eff}}$ value.

*FIG. 1: Solid line: Calculated band structure of Fe. Dotted line: Interpolated bands obtained from the five $d$-type Wannier functions. Energy window [13] used to compute the Wannier functions was set to $[−9.0, +8.5]$ eV. The zero of the energy scale is at the Fermi energy.*

We show in Fig. 2 the calculated effective onsite Coulomb interaction $U_{\text{eff}}$ (solid line) of the 3$d$ metals. An importance of a screening effect is clear from a comparison between the $U_{\text{eff}}$ value and a bare Coulomb integral averaged over five $d$-type WFs,

$$U_{\text{bare}} = \frac{1}{5} \sum_\mu \int \int \frac{|w_{1\mu}(r)|^2 |w_{1\mu}(r')|^2}{|r - r'|} dr'dr'. \tag{5}$$

As expected, an unscreened value $U_{\text{bare}}$ (dotted line) is rather large relative to $U_{\text{eff}}$. The screening effect makes a significant reduction of the value, thus leading the theoretical values to the same energy order as experimental values (dashed [5] and dotted-dashed [6] lines) deduced from a combined use of Auger and x-ray photoemission spectroscopy. A more detailed comparison with the $U_{\text{expt}}$’s requires to calculate ab ini-
tio Auger and photoemission spectra, but this is not the scope of the present study.

An interesting behavior seen in the figure is that $U_{\text{eff}}$ increases gradually as an atomic number increases, and this trend agrees with the experiments. To our knowledge, there is no explanation for the chemical trend observed in $U_{\text{eff}}$, so we focus on understanding this behavior. If the screening effect is neglected, $U_{\text{eff}}$ is $U_{\text{bare}}$, for which it is apparent from Eq. (5) that the value of $U_{\text{bare}}$ reflects a feature of the WF itself. More specifically, the observed increasing behavior of $U_{\text{bare}}$ results from the trend that the WF shrinks as an early metal goes to a late one, which will be also stated in terms of the Wannier spread; namely, $U_{\text{bare}}$ is inversely scaled by a localization length describing a spatial extent of WF

$$\Omega = \frac{1}{5} \sum_{\mu} \sqrt{\langle r^2 \rangle_\mu - \langle r \rangle^2_\mu},$$

where $r$ is electron coordinates and $\langle r \rangle_\mu = \int r |w_{I\mu}(r)|^2 dr$, etc.

In contrast to $U_{\text{bare}}$, the analysis for $U_{\text{eff}}$ itself is rather intractable, because, in that case, in addition to the shrinking effect above, a difference in the screening in the metals also contributes to the trend in $U_{\text{eff}}$. In the transition metal, the screening results mainly from itinerant $sp$ electrons behaving as a free electron, so the effective Coulomb interaction between two $d$ electrons is to a first approximation written as an interaction between test charges placed in a homogeneous electron gas, i.e., as the Yukawa-type interaction $e^{-(r/\sigma_0)/r}$ with $\sigma_0$ being the Thomas-Fermi screening length [23]. From this viewpoint, we give a heuristic formula for $U_{\text{eff}}$, which is assumed to be a one-center integral of the Yukawa potential

$$\tilde{U}_{\text{eff}} = \frac{1}{5} \sum_{\mu} \int \int |w_{I\mu}(r)|^2 \exp(-|r - r'|/\sigma) \frac{dr dr'}{|r - r'|} \times |w_{I\mu}(r')|^2 dr',$$

where $\sigma$ in the integral is an adjustable parameter to specify a characteristic length of the screening in the system. As the value of $\sigma$ becomes larger (i.e., the screening is weakened), $\tilde{U}_{\text{eff}}$ approaches to $U_{\text{bare}}$ (unscreened value), so this parameter is regarded as a measure of the screening strength. We determined the $\sigma$ parameter so that the integral value $\tilde{U}_{\text{eff}}$ should coincide with the $U_{\text{eff}}$ obtained from $ab$ initio calculations. By plotting $\sigma$ for all the $3d$ species, we can discuss the trend in the screening strength of the transition metals.

We display in Fig. 3 the resulting dependence of $\sigma$ on atomic species (dashed line), together with that of $\Omega$ (dotted line). The figure clearly shows that the increasing behavior of $U_{\text{eff}}$ (solid line) results from the orbital shrink (i.e., the decrease of $\Omega$). In contrast, the effective screening length $\sigma$ is almost the same for the listed metals, although there is a small jump of $\sigma$ between Ni and Cu, which reflects the fact that Ni has two screening channels of $sp$ and $d$ electrons, while Cu has no latter channel because the Cu $d$ bands are fully occupied. We note that the calculated $\sigma$ agrees reasonably well with the Thomas-Fermi screening length $\sigma_0$ (dotted-dashed line) of a free electron gas with the same density as the $sp$-electron density of the system [23], which indicates a validity of our $\sigma$ estimation based on Eq. (7). The small difference between $\sigma$ and $\sigma_0$ ($\sim 0.1 \text{ Å}$) reflects the presence or absence of a screening contribution from intersite $d$ electron transfers.

![Fig. 2: $U_{\text{eff}}$ (solid line), $U_{\text{bare}}$ (dotted line), and two experimental onsite Coulomb interactions (dashed and dotted-dashed lines). The experimental values are taken from Ref. [5] for $U_{\text{exp}}^{(1)}$, and Ref. [6] for $U_{\text{exp}}^{(2)}$.](image)

![Fig. 3: $U_{\text{eff}}$ (solid line), Wannier spread $\Omega$ (dotted line), effective screening length $\sigma$ (dashed line), and Thomas-Fermi screening length $\sigma_0$ (dotted-dashed line).](image)
functions, and applied it to the systematic study of the effective onsite Coulomb interaction of 3d transition metals. This scheme is of practical significance because it is free from a limitation on a choice of basis functions, and thus allows us to perform the constrained calculations with plane-wave-based electronic-structure codes. This property will be particularly helpful in a situation where one’s interest is in molecular solids such as BEDT-TTF and solid C60, for which the plane-wave basis is suitable for calculating their electronic structures. To see whether the present scheme can be indeed exploited in constructing ab initio model Hamiltonians and/or in discussing experimental U’s for the above mentioned systems, however, needs future studies.

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