Hubbard-$U$ calculations for Cu from first-principle Wannier functions

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We present first-principles calculations of optimally localized Wannier functions for Cu and use these for an ab-initio determination of Hubbard (Coulomb) matrix elements. We use a standard linearized muffin-tin orbital calculation in the atomic-sphere approximation (LMTO-ASA) to calculate Bloch functions, and from these determine maximally localized Wannier functions using a method proposed by Marzari and Vanderbilt. The resulting functions were highly localized, with greater than 89% of the norm of the function within the central site for the occupied Wannier states. Two methods for calculating Coulomb matrix elements from Wannier functions are presented and applied to fcc Cu. For the unscreened onsite Hubbard $U$ for the Cu 3d-bands we have obtained about 25eV. These results are also compared with results obtained from a constrained local-density approximation (LDA) calculation.

I. INTRODUCTION

During the past few decades powerful numerical methods have been developed for the ab-initio (first-principles) calculation of the electronic ground-state properties of solids. In most of these methods density-functional theory (DFT) has been used to treat the electron-electron Coulomb repulsion, and a local-density approximation (LDA) (or a local spin-density approximation, LSDA, for magnetic systems) has been used for the exchange-correlation potential. This procedure has been very successful for many materials and ground-state properties (e.g., crystal structure, lattice constant, binding energy, and ionization energy), but it has its limitations; the band gap of semiconductors is not properly reproduced, for instance. Furthermore, for systems such as high-temperature superconductors, heavy fermion materials, transition-metal oxides, and $3d$ itinerant magnets, i.e., for systems in which the Fermi level falls into a region of narrow energy bands, the LDA is usually not sufficient. It is generally accepted that the problem for these materials is the strong electronic correlations that are responsible for their electronic properties. For a description of such strongly correlated systems one usually instead uses as a starting point model Hamiltonians like the Hubbard model and its multi-band generalizations. But in these models the Coulomb (interaction) matrix elements and also the one-particle (hopping) matrix elements that determine the unperturbed band structure are usually treated as free, adjustable parameters, i.e., they are not known from "first principles" for the given material; on the other hand, Coulomb correlations can be studied within reliable many-body approximations that go beyond the Hartree-Fock approximation.

Both the ab-initio LDA and the many-body model-Hamiltonian methods based on Hubbard-like models have their merits, but until rather recently they have been almost separate and complementary approaches. But, in view of the power of each, a combination of these methods is desirable; and, in fact, during the last few years there have been some attempts in this direction. All of these recent developments add local, screened Coulomb (Hubbard) correlations $U$ between localized orbitals to the one-particle part of the Hamiltonian obtained from an ab-initio LDA band-structure calculation, but differ in how they handle the correlation part. In the earliest attempts, the LDA+$U$ method used essentially a static mean-field-like (or Hubbard-I-like) approximation for the correlation. The simplest approximation beyond Hartree-Fock, second-order perturbation theory (SOPT) in $U$, was used to study the electronic properties of $3d$-systems (like Fe and Ni) and heavy fermion systems (like UPt$_3$). The LDA++ approach has a similar strategy, but uses other many-body approximations to treat the correlation problem, namely, either the fluctuation exchange approximation (FLEX) or the dynamical mean field theory (DMFT). Some of the other many-body treatments have also used DMFT, which is based on the limit of large-dimension ($N \rightarrow \infty$) approximation for correlated lattice electrons. Within DMFT the selfenergy becomes local, i.e., independent of momentum $k$, which allows a mapping of the lattice problem onto an effective impurity model. The LDA+DMFT treatments mentioned above differ in the many-body method they used for the effective impurity problem, namely, Quantum Monte Carlo (QMC), the non-crossing approximation (NCA) or (iterated) perturbation theory (IPT). But all these approaches, including the LDA+$U$, have in common that they have to introduce a Hubbard $U$ as an additional parameter, and hence are not real first-principles (ab-initio) treatments. Although they use an LDA ab-initio method to obtain a realistic band structure, i.e., single-particle properties, Coulomb matrix elements for...
any particular material are not known, and the Hubbard U remains an adjustable parameter.

One can obtain estimates on the magnitude of $U$ either from experiment (high-energy spectroscopy) or from the constrained LDA method. In the latter method one adds the constraint that the electron occupation number for the correlated bands is fixed to a given number through a Lagrange parameter. One can then use LDA to calculate the ground-state energy for different occupations of the correlated states, and the difference between the energy for double and single occupation is an estimate for the Hubbard U. This method has the advantage that effects of screening are already somehow included. On the other hand there are usually several bands and many interaction matrix elements (on-site, density-density, intra-band, inter-band, exchange, intersite, etc.) that have different magnitudes, and the constrained LDA can only give some average value for these various Coulomb matrix elements and not the individual ab-initio parameters (Coulobm matrix elements). This approach is intuitive and contains some type of screening within a one-electron LDA approach. It is difficult to sort out the actual approximation involved.

In this paper we suggest a different approach, namely, the direct ab-initio calculation of the one-particle (tight-binding) and two-particle (Coulomb) matrix elements. Our starting point is a standard electronic band-structure calculation, for which we have used the linearized muffin-tin orbital (LMTO) method within the atomic sphere approximation (ASA). The LDA band-structure calculation yields not only one-particle energies but also their eigenstates, the Bloch wavefunctions, which form a proper basis of a one-particle Hilbert space. To determine the local (on- and inter-site) Coulomb matrix elements it is necessary to construct Wannier functions, which are closely related to the Bloch functions via a unitary transformation, but which are not unique since the phases of the Bloch functions are undetermined.

As first suggested by Marzari and Vanderbilt, this gauge freedom can be used to construct “maximally localized Wannier functions.” Those are just Wannier functions with a special gauge that makes them optimally localized according to some criterion. A proper localization of the Wannier functions is important in our opinion, because only then do the standard assumptions of the model treatments hold such that only a few (on-site, nearest, and next-nearest neighbor) one-particle (hopping) and two-particle (Coulomb) matrix elements have to be considered explicitly. These matrix elements can then be calculated from the Wannier functions.

We use two different methods to calculate Coulomb matrix elements from Wannier functions. The first method uses the fact that the LMTO-method provides Bloch functions in the basis of linear muffin-tin orbitals. Therefore the Wannier functions are given as linear combinations of such muffin-tin orbitals as well, and can be used to evaluate the Coulomb integrals efficiently, similarly to what was done in Ref. 28. The second method uses a fast Fourier transformation (FFT). It does not rely on the property of the wave functions being linear and is therefore more general. It is also very quick and efficient.

The paper is organized as follows. In Sec. II we present some of the computational details: we describe the form of the Bloch functions in the LMTO method, how to obtain the Wannier functions from them, and how to optimize the choice of the Wannier functions by using the Marzari-Vanderbilt method. Then we describe how the one-particle (hopping) matrix elements are obtained from these localized Wannier functions, and we present the two methods to calculate the Coulomb matrix elements. To illustrate the method we have performed actual calculations for a well understood system, namely for Cu. Although this material is not a strongly correlated system, it has almost completely filled, narrow, 3d-bands, for which (well localized) Wannier functions and one- and two-particle matrix elements can be calculated. Results for Cu are presented in Sec. III, where we show some of the Wannier functions, demonstrate how well localized they are and that the one-particle (tight-binding) matrix elements obtained from them allow for a reconstruction of the band structure. The direct Coulomb matrix elements obtained are rather large, between 20 and 25 eV for Wannier states with mainly 3d-character, and are about 5 eV for nearest neighbors, and about 1 eV for exchange interactions. In Sec. IV we describe constrained LDA calculations, which yield somewhat smaller values (about 18 eV) for the Hubbard U of Cu, and in the final section (V) we discuss how to extend and further apply the current approach.

II. COMPUTATIONAL DETAILS

We restrict ourself to the case where there is only one atom per unit cell and where we can neglect spin (non-spin-polarized calculations). For a given material the only input to an ab-initio LDA calculation is the atomic number. In the density-functional approach a local-density approximation is normally used for the exchange and correlation interactions between the electrons; we have used the von Barth-Hedin exchange-correlation potential and a frozen-core approximation. Within DFT the total energy of the ground state could be calculated as a function of volume for a given crystal structure and used to determine the equilibrium lattice constant; it is usually in good agreement with experiment. However, since our focus is on the determination of Coulomb matrix elements in a Wannier basis, we have simply used the experimental lattice parameters.

A. LMTO wave functions

For our band-structure results we have used the LMTO method within the atomic sphere approximation.
(ASA). The combined correction term was not included. The muffin-tin spheres are overlapping and their radius (the Wigner-Seitz radius $S$) is determined by the condition that the sphere volume equals the volume of the unit cell. Within the muffin-tin spheres the potential and wave functions are expanded in spherical harmonics with a cutoff $l_{\text{max}} = 3$, i.e., s, p, d, and f-orbitals are included. Furthermore the Bloch wave functions are given in terms of the solution to the radial Schrödinger equation $\phi_{nl}(r)$ to some fixed energies $E_{nl}$ and its energy derivative $\dot{\phi}_{nl}(r)$:

$$\Psi_{nk}(r) = \sum_{L} \left( \phi_{nl}(r) A_{nL}^{k} + \dot{\phi}_{nl}(r) B_{nL}^{k} \right) Y_{L}^{}(\hat{r}) ,$$

where we use complex spherical harmonics in all of our calculations. This expansion is valid in one muffin-tin sphere. Here, as usual, $L = \{l, m\}$ is understood and $n$ is the band index and $k$ is the wave vector. We define $n$ by the condition that $E_{n}(k) < E_{n+1}(k)$. The virtue of using this method for Wannier functions is the simplification that only integrals over spheres are needed; no real-space integrations over complicated Wigner-Seitz (unit) cells are required.

The Bloch functions obey

$$\Psi_{nk}(r + R) = e^{ikR} \Psi_{nk}(r) .$$

Therefore, the knowledge of a Bloch function in a single muffin-tin sphere is sufficient for the knowledge of the function in the whole crystal. This situation is different when we consider Wannier functions, which can be centered on different sites. It is useful to introduce a notation that holds for both Bloch and Wannier functions. To do this we perform an expansion like Eq. (1) in each muffin-tin sphere, which we label by its site vector $R$. The complete wave function (either Bloch or Wannier) is then given by:

$$\Phi_{\alpha}(r) = \sum_{i} \Phi_{\alpha}(R_{i}; r - R_{i})$$

In this equation we have used the general notation for the wave function expansion $\Phi_{\alpha}(R_{i}; r - R_{i})$ such that: (i) $\Phi$ is any kind of wave function. (ii) The $\alpha$ stands for quantum numbers (Bloch: $\alpha = \{n, k\}$; Wannier: $\alpha = \{R, n\}$). (iii) The first argument in the parenthesis indicates the muffin-tin sphere about which we are expanding and is labeled by its site vector. (iv) The second argument in the parenthesis is the position inside this muffin-tin sphere described by its relative vector. This means that this vector has zero length in the center of the muffin-tin sphere described by the first argument. (v) Note that, for every $R_{i}$,

$$\Phi_{\alpha}(R_{i}; r) = 0 \quad \text{if} \quad |r| > S .$$

In the case where $\Phi$ is a Bloch function we find

$$\Psi_{nk}(R; r) = e^{ikR} \Psi_{nk}(r) .$$

It is easy to see that Eq. (2) inserted in Eq. (3) obeys Eq. (2).

Also note that Eq. (3) disregards the effects of overlapping muffin-tin spheres. Within the ASA approximation, all derivations are done as though non-overlapping muffin-tins are being used, and then these formulas are used with expanded muffin-tins, whose volumes sum to equal the unit cell volume (where the muffin-tin radius is expanded to a Wigner-Seitz radius for one atom per unit cell). In addition, this approximate eliminates the necessity to handle interstitial regions, and hence the ASA formalism is mathematically much simpler than a full-potential electronic-structure calculation would require.

### B. Wannier functions

In this section we show how to calculate Wannier functions from the LMTO type of Bloch functions of Eq. (4). The Wannier functions are defined by

$$w_{R_{n}}(r) \equiv \langle r | R_{n} \rangle = \frac{1}{N} \sum_{k} e^{-ikR} \Psi_{nk}(r) .$$

Here, $N$ is the number of $k$-mesh points in the Brillouin zone or, equivalently, the number of unit cells in the real space supercell that is used to discretize the $k$-mesh. As mentioned above, Wannier functions are not unique. Consider, for example, a single band $n$ with Bloch functions $|\Psi_{nk}\rangle$; a transformation of the kind

$$|\Psi_{nk}\rangle \rightarrow e^{i\phi_{n}^{(k)}} |\Psi_{nk}\rangle , \quad \phi_{n}^{(k)} \quad \text{real} ,$$

will still lead to Bloch functions. We shall call this a gauge transformation of the first kind. In the case of a composite set of bands this uniqueness corresponds to the freedom to choose the phases and “band-index labeling” at each $k$ point of the Bloch functions:

$$|\Psi_{nk}\rangle \rightarrow \sum_{m} U_{mn}^{(k)} |\Psi_{mk}\rangle$$

We shall call this a gauge transformation of the second kind. Here $U_{mn}^{(k)}$ is a unitary matrix. From all the arbitrary choices of Wannier functions we will pick out that particular set that minimizes the total spread given by

$$\Omega = \sum_{n} \left[ \langle \phi_{n}^{\dagger} \rangle \langle \phi_{n} \rangle - \langle \phi_{n}^{\dagger} \phi_{n} \rangle \right] .$$

For any operator $A$, $\langle A \rangle_{\alpha}$ denotes the expectation value $\langle R_{n} | A | R_{n} \rangle$. A method for minimizing $\Omega$ has been developed by Marzari and Vanderbilt and its application to the ASA wave functions does not pose any particular problems (details will be given below).

Before minimizing $\Omega$ according to this procedure, it is useful to prepare the Bloch orbitals to make the starting Wannier functions somewhat localized. This has two
advantages: (i) the minimization procedure converges faster, and (ii) this helps avoid getting trapped in local minima. Marzari and Vanderbilt suggest several possible preparations. We have found our own method, which seems to work well. This involves a simple gauge transformation for each band, which is given by

$$\Psi_{nk}(r) \rightarrow \exp(-i\text{Im} \ln \Psi_{nk}(r_0)) \Psi_{nk}(r). \quad (10)$$

This gauge transformation has the property that Im ln $\Psi_{nk}(r_0)$ transforms to zero. So at the point $r_0$ all the Bloch functions will have the same phase (in this case just $1 + i0$) and $(r_0|0n)$ will take a large value. We thus expect the Wannier function to be fairly localized at $r_0$. To make the method work well one should choose $r_0$ where the Wannier functions are expected to be reasonably large. In our calculations we have chosen the direction of this vector to be well away from the expected zeroes of the spherical harmonics and with an absolute value far enough away from the origin to be in a place where the Wannier functions should have a significant magnitude. We found an $r_0$ of $(0.8, 1.0, 0.3)a_0$ to work well for fcc Cu.

We shall now derive expressions of the form of Eq. (3) for Wannier functions. From Eqs. (3) and (4) we have

$$w_{Rn}(R';r) = \frac{1}{N} \sum_k e^{-i\mathbf{k}R} \Psi_{nk}(R';r)$$

$$\quad = \frac{1}{N} \sum_k e^{i\mathbf{k}(R' - R)} \Psi_{nk}(r). \quad (11)$$

Because Wannier functions on different sites have the same form (shape) of their wave functions and differ only by a translation of their origin, it is useful to use a notation that indicates values of a wave function relative to a Wannier function centered at the origin:

$$w_{Rn}(R';r) = w_{0n}(R' - R; r) \equiv w_n(R' - R; r), \quad (12)$$

where we have introduced the notation $w_{0n} \equiv w_n$ (i.e., if the subscript contains only a wave function label without a spatial vector $\mathbf{R}$, then we use a relative notation that refers to a Wannier function centered at the origin). We can use the Bloch condition (cf. Eq. (11)) to calculate the parts of the Wannier function on other sites $\mathbf{R}$:

$$w_n(\mathbf{R}; r) = \frac{1}{N} \sum_k e^{i\mathbf{k}\mathbf{R}} \Psi_{nk}(r). \quad (13)$$

Note that $|r| < S$. For this notation to work in our numerical calculations, it is essential to force the Wannier center, i.e., the muffin-tin sphere where $(\mathbf{r}|0n)$ is largest, to be at the muffin-tin sphere around the lattice site $0$; we achieve this by setting $|r_0| < S$ in Eq. (10). In most of the rest of the paper, we will almost always use the relative notation that refers to Wannier states centered at the origin, and will perform whatever translations are necessary to be able to use these states.

In the method of Marzari and Vanderbilt the starting point for the calculations are a set of reference matrices defined by

$$M_{mn}^{(0)}(\mathbf{k}, \mathbf{b}) = \langle \Psi_{nk}|e^{-ibr}|\Psi_{n,k+b} \rangle. \quad (14)$$

Here $\mathbf{b}$ denotes a nearest-neighbor vector on the discretized mesh in $k$-space (in this method, the set of $\mathbf{b}$-vectors are needed for numerical derivatives). We calculated the action of $e^{-ibr}$ on the ket by using Eqs. (A4) and (A5) and solved the remaining integral by using Eq. (22). We used a uniform (cubic) discrete $k$-mesh with a spacing $\Delta k$ of 0.2$(2\pi/a)$. In such a mesh there are 6 nearest-neighbors for the $\mathbf{b}$ vectors needed for the numerical derivatives. We were careful not to double count vectors in the $k$-mesh (those equivalent to each other by a reciprocal lattice vector) within the Brillouin zone (which has 500 $\mathbf{k}$ points in the full zone).

We then used the steepest-descent method and relevant equations in Sec. IV of Ref. [27] to iterate a series of small steps where a set of $\Delta W^{\mathbf{k}}$ were calculated and used to update the unitary matrices $U^\mathbf{k}$ and the $M^{\mathbf{k},\mathbf{b}}$. After each iteration, where we update all the relevant $\mathbf{k}$ matrices, we calculated the spread function $\Omega$, and continued iterating until this converged.

In these calculations the initial matrices $M^{(0)}(\mathbf{k}, \mathbf{b})$ are by far the most time consuming computationally (it requires storing $6 \cdot 500 \cdot 16^2 = 768,000$ complex numbers). The iterations of the steepest descent method were much faster. For this reason we used many iterations (about 1500 steps) and converged $\Omega$ to about 0.01%. For the step size (cf. Eq. (57) of Ref. [27]) we used an $\alpha$ of 0.2.

The final result can be written in a form similar to the LMTO wave functions, Eq. (1).

$$w_n(\mathbf{R}; r) = \sum_L \left( \phi_{nl}(r)A^\mathbf{L}_n + \phi_{nl}(r)B^\mathbf{L}_n \right) Y_L(\hat{r}), \quad (15)$$

where the $A$ and $B$ matrices originally come from the LMTO wave functions, but are then updated from the relevant phase information, unitary matrix, and other integrations and transformations of the method.

Because of the normalization of the starting LMTO Bloch wave functions (which are normalized to unity within a single unit cell), each Wannier function is naturally normalized to unity when integrated over all space.

**C. One particle matrix elements**

The Wannier function basis can be viewed as an orthogonal tight-binding basis. For this reason it is useful to calculate one-particle matrix elements of the Hamiltonian in the Wannier basis. As we shall see, these matrix elements are (for a gauge transformation of the first kind only) equivalent to the Fourier components of the band structure; this equivalence is useful for checking some of the numerical aspects of the calculations.
Because the Hamiltonian has the property that $H(r) = H(r + R)$, it is sufficient to consider the matrix elements:

$$t_{Rnm} = \langle Rn | H | 0m \rangle$$  \hfill (16)

Inserting Eq. (11) and using $H|\Psi_{nk}\rangle = E_n(k)|\Psi_{nk}\rangle$ we find

$$t_{Rnm} = \frac{\delta_{nm}}{N} \sum_{k} e^{i k R} E_n(k) \ ,$$  \hfill (17)

which are just the Fourier components of the band structure. The Bloch states $|\Psi_{nk}\rangle$ continue to be eigenstates of $H$ under a gauge transformation of the first kind and one can also easily show that the $t_{Rnm}$ are invariant under this type of gauge transformation. The $t_{Rnm}$ from Eq. (17) can be directly calculated from the band structure $E_n(k)$.

A gauge transformation of the second kind leads to states $|\Psi_{nk}\rangle$ that are no longer eigenstates of $H$ with eigenvalue $E_n(k)$. Therefore $t_{Rnm}$ are not invariant under a gauge transformation of the second kind. However, generally we can always calculate

$$H_{nm}^k = \langle \Psi_{nk} | H | \Psi_{mk} \rangle = \sum_{R} e^{-i k R} t_{Rnm}$$  \hfill (18)

and use its diagonalized eigenvalues as the band structure for any set of Wannier functions. The matrix $H_{nm}^k$ is Hermitian; it is, of course, already diagonal for a gauge transformation of the first kind, with the energy levels as the diagonal matrix elements.

To calculate $t_{Rnm}$ from Eq. (11), i.e., using Wannier functions, we can use Eqs. (6) and (12) to find

$$t_{Rnm} = \sum_{R} \int d^3 r \ w_n^*(R_i - R; r) H w_m(R_i; r) \ ,$$  \hfill (19)

where the integral is over a single sphere only. The effect of $H$ on the second wave function can be carried out easily because we are working in a linear basis. We only note that $(H - E_{nl}) \phi_l(r) = 0$ and $(H - E_{nl}) \phi_l(r) = \phi_l(r)$, for details see Ref. [23]. In order to calculate Eq. (19), we must evaluate integrals of the form

$$I = \int d^3 r f_1(r) f_2(r) \ ,$$  \hfill (20)

where the functions $f_i(r)$ are given by the expansion

$$f_i(r) = \sum_{L} R_{iL}(r) Y_{L}(\hat{r}) \ .$$  \hfill (21)

Inserting Eq. (21) into Eq. (20) and using the orthonormality of the spherical harmonics yields:

$$I = \sum_{L} \int dr \ r^2 R_{iL}^*(r) R_{2L}(r)$$  \hfill (22)

Because Eq. (11) was our starting point, the radial functions $R(r)$ will always be given in terms of $\phi_l(r)$ and $\phi_l(r)$, i.e.,

$$R_{iL}(r) = A_{iL} \phi_l(r) + B_{iL} \phi_l(r) \ .$$  \hfill (23)

We will use this form to calculate the integral $I$ very efficiently. It is clear that any integral can be reduced to a linear combination of “basic” integrals. Those basic integrals consist of the (very limited) combinations of the $\phi_l(r)$’s and $\phi_l(r)$’s. We will label them by

$$b_{L;p_1p_2} = \int dr \ r^2 [\delta_{p_1,0} \phi_l(r) + \delta_{p_1,1} \phi_l(r)] \times [\delta_{p_2,0} \phi_l(r) + \delta_{p_2,1} \phi_l(r)] \ ,$$  \hfill (24)

where $p_1$ and $p_2$ can take the values 0 and 1. So it must be possible to write the integral $I$ as:

$$I = \sum_{L} \sum_{p_1=0}^{1} \sum_{p_2=0}^{1} a_{L; p_1 p_2} b_{L; p_1 p_2}$$  \hfill (25)

It follows that the coefficients $a_{L; p_1 p_2}$ are given by

$$a_{L; p_1 p_2} = \left[ \delta_{p_1,0} A_{iL}^* + \delta_{p_1,1} B_{iL}^* \right] \times \left[ \delta_{p_2,0} A_{2L} + \delta_{p_2,1} B_{2L} \right] \ .$$  \hfill (26)

We are now in a position to calculate Eq. (19) with the aid of Eq. (25).

D. Wannier-Function Projected Density of States

The density of states (DOS) per spin is defined by

$$N(E) = \frac{V}{(2\pi)^3} \sum_n \int_{BZ} d^3 k \ \delta(E - E_n(k)) \ ,$$  \hfill (27)

where $V$ is the volume of the unit cell. In the same way that the DOS is often projected in terms of the $l$-character of the states, one can do a similar treatment for a projection onto the Wannier states. We can define a projected DOS for Wannier states, by inserting the projection operator onto the Wannier states $|0j\rangle\langle0j|$ into Eq. (27):

$$N_j(E) = \frac{V}{(2\pi)^3} \sum_n \int_{BZ} d^3 k \ |\langle \psi_{nk} | 0j \rangle|^2 \delta(E - E_n(k)) \ .$$  \hfill (28)

Note that the $\psi_{nk}$ in this formula have to be the Bloch states before the gauge transformation, since the band structure $E_n(k)$ is related to the untransformed states. The Bloch wave functions are normalized to a single unit cell and each Wannier function over all space. We can calculate $N_j(E)$ by using the tetrahedron method [3].
the \(\mathbf{k}\)-points that form the tetrahedras we need to calculate \(|\langle \psi_{nk} | \mathbf{0} \rangle|^2\), which we have done using the scheme described in section [II]. In these calculations it is important to be aware that \(|\mathbf{0}\rangle\) has parts of its wavefunction on other sites than the central site where it is centered. In our calculations, we included parts of the Wannier function out to 17 near-neighbor shells of sites.

Note that the exact projection operator is a sum over all \(\mathbf{R}\), since

\[
\sum_{\mathbf{R}_j} |\langle \mathbf{R}_j | \mathbf{0} \rangle| = 1 .
\]

(29)

However, it is sufficient to only consider the Wannier states \(|\mathbf{0}\rangle\) in our projection (and not all the \(|\mathbf{R}_j\rangle\)), since

\[
|\langle \psi_{nk} | \mathbf{R}_j \rangle| = |\langle \psi_{nk} | \mathbf{0} \rangle| .
\]

(30)

We can check the correctness of our projection by comparing \(N_{\alpha}(E) = \sum_j N_j(E)\) with the \(N(E)\) that is calculated directly from the LMTO energy eigenvalues. We find that our projected sum is accurate to within 0.2% of the LMTO value.

E. Coulomb matrix elements

The matrix elements we wish to calculate are

\[
W_{12,34} = \int \frac{d^3r d^3r'}{ |r - r'|} \frac{e^2}{2} w_1^*(r) w_2^*(r') w_3(r) w_4(r') .
\]

(31)

where \(1, 2, 3, 4 = i = \{\mathbf{R}, \mathbf{n}_i\}\) is a Wannier state, and \(W\) denotes the Coulomb interaction. The spatial integrals over \(r\) and \(r'\) extend over all space. Using Eqs. (3) and (23), we can use translations to rewrite this expression so that the integrals are only over the muffin-tin sphere at the origin:

\[
W_{12,34} = \sum_{i,j} W(12, 34; \mathbf{R}_i, \mathbf{R}_j) ,
\]

(32)

where the expression \(W(12, 34; \mathbf{R}, \mathbf{R}')\) is defined by:

\[
\int \frac{d^3r d^3r'}{ |r - r' + \mathbf{R} - \mathbf{R}'|} \frac{e^2}{2} w_1^*(r) w_2^*(r') w_3(r - \mathbf{R}_3; \mathbf{r}) w_4(r' - \mathbf{R}_4; \mathbf{r}')
\]

(33)

Since most applications of the Hubbard model use only two orbitals instead of all four, it is useful to define the limiting subset of the \(W\) functions as direct Coulomb \(U_{ij}\) and exchange \(J_{ij}\) integrals:

\[
U_{12} = W_{12,12}
\]

(34)

\[
J_{12} = W_{12,21} ,
\]

and the obvious generalizations for:

\[
U(12; \mathbf{R}, \mathbf{R}') = W(12, 12; \mathbf{R}, \mathbf{R}')
\]

(35)

\[
J(12; \mathbf{R}, \mathbf{R}') = W(12, 21; \mathbf{R}, \mathbf{R}')
\]

1. Spherical harmonics expansion

We will now only consider matrix elements between Wannier functions centered on the origin (i.e., where the \(\mathbf{R}_i = \mathbf{0}\) in Eq. (21)). Because we are using maximally localized Wannier functions, most of the Wannier functions have their largest component in the center cell (see section [II]). As a first approximation, we will therefore neglect all other muffin-tin spheres. This approximation allows us to calculate on-site inter-band matrix elements. We are thus looking for

\[
W_{n_1 n_2 n_3 n_4} = W(12, 34; \mathbf{0}, \mathbf{0})
\]

\[
= \int d^3r d^3r' w_{n_1}^*(\mathbf{0}; \mathbf{r}) w_{n_2}^*(\mathbf{0}; \mathbf{r}')
\]

\[
\times \frac{e^2}{|r - r'|} w_{n_3}(\mathbf{0}; \mathbf{r}) w_{n_4}(\mathbf{0}; \mathbf{r}') ,
\]

(36)

where the integral over \(\mathbf{r}\) is only over the central site. Inserting the expansion Eq. (21) for the Wannier functions and making use of the well-known expansion (see for example Ref. [32])

\[
\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l=0}^{\infty} \frac{4\pi}{2l + 1} r^l \sum_{m=-l}^{l} Y_l^m(\hat{\mathbf{r}}) Y_l^m(\hat{\mathbf{r}}'),
\]

(37)

where \(r_>(r_<)\) is the length of the greater (smaller) of the two vectors \(\mathbf{r}\) and \(\mathbf{r}'\), we find

\[
I = \sum_l \frac{4\pi}{2l + 1} \sum_{l_1} \int d\mathbf{r} d\mathbf{r}' R_{1L_1}(\mathbf{r}) R_{3L_1}(\mathbf{r}) \int d\mathbf{r}' d\mathbf{r}^2 \times
\]

\[
x R_{2L_2}(\mathbf{r}') R_{4L_2}(\mathbf{r}') \sum_{m=-l}^{l} C_{L_3 L_1 L} C_{L_2 L_1 L} .
\]

(38)

The coefficients \(C_{L_1 L' L''}\) are called Gaunt coefficients [see Eq. (A3) in the appendix]. If we define

\[
C_{L_1 L_2 L_3 L_4} = \sum_{m=-l}^{l} C_{L_3 L_1 L} C_{L_2 L_4 L} ,
\]

(39)

and

\[
I_{L_1 L_2 L_3 L_4} = \int d\mathbf{r} d\mathbf{r}' R_{1L_1}(\mathbf{r}) R_{3L_1}(\mathbf{r}) \times
\]

\[
x \int d\mathbf{r}' d\mathbf{r}^2 R_{2L_2}(\mathbf{r}') R_{4L_2}(\mathbf{r}') \sum_{m=-l}^{l} C_{L_3 L_1 L} C_{L_2 L_4 L} ,
\]

(40)

the integral takes the form

\[
I = \sum_{l, L_1} \frac{4\pi}{2l + 1} C_{L_1 L_2 L_3 L_4} I_{L_1 L_2 L_3 L_4} .
\]

(41)

The task is now to determine \(I_{L_1 L_4}\) (we use the shorthand notation \(L_i\) for the \(L_1 L_2 L_3 L_4\). To do this, we will use the formalism developed in the last section. In complete analogy to Eqs. (24–26) we now find
\[ I_{l;L_i} = \sum_{p_i} a_{L,p_i} b_{l;L_i} , \]  
\text{where} 
\[ a_{L,p_i} = \prod_{i=1}^{2} (\delta_{p_i,0} A_{iL_i}^* + \delta_{p_i,1} B_{iL_i}^*) \times \prod_{i=3}^{4} (\delta_{p_i,0} A_{iL_i} + \delta_{p_i,1} B_{iL_i}) \]  
\text{and} 
\[ b_{l;L_i} = \int dr \; r^2 [\delta_{p_i,0} \phi_{l_i}(r) + \delta_{p_i,1} \dot{\phi}_{l_i}(r)] \times [\delta_{p_2,0} \phi_{l_3}(r) + \delta_{p_2,1} \dot{\phi}_{l_3}(r)] \times \int dr' \; r'^2 [\delta_{p_2,0} \phi_{l_4}(r') + \delta_{p_2,1} \dot{\phi}_{l_4}(r')] \times [\delta_{p_4,0} \phi_{l_4}(r') + \delta_{p_4,1} \dot{\phi}_{l_4}(r')] \frac{r'^2}{r^2} . \]  

It should be noted that these basic integrals are symmetric with respect to some of their indices. If we introduce the joined index \( n_i = \{ l_i, p_i \} \) then: 
\[ b_{l_1; n_1 n_2 n_3 n_4} = b_{l_2; n_2 n_3 n_1 n_4} = b_{l_3; n_3 n_1 n_2 n_4} = b_{l_4; n_1 n_4 n_3 n_2} = \]  
\[ b_{l_1; n_2 n_3 n_4 n_1} = b_{l_2; n_3 n_1 n_4 n_2} = b_{l_3; n_3 n_4 n_1 n_2} = b_{l_4; n_1 n_2 n_3 n_4} = \]  
\[ b_{l_1; n_2 n_3 n_4 n_1} = b_{l_2; n_3 n_1 n_4 n_2} = b_{l_3; n_3 n_4 n_1 n_2} = b_{l_4; n_1 n_2 n_3 n_4} = \]  

If we consider the numerical aspects for the case where \( s, p, d, \) and \( f \) orbitals are included in the wave function expansion, we find that we need to use a cutoff of \( l_{\text{max}} = 6 \) in Eqs. (42) and (43). Using the symmetries in Eq. (45), we then find 9072 basic integrals that have to be calculated and stored. The sum in Eq. (47) however involves \( 7 \cdot 16^4 = 458,752 \) elements. Fortunately, only 6778 combinations of the \( l, L_1, L_2, L_3, L_4 \) coefficients in Eq. (42) have to be calculated; the others vanish. Each of these coefficients involves a sum over 16 elements, and each of these elements is a product of 5 numbers.

2. Fast Fourier Transformation (FFT) approach

The method we have just described works well, but requires a lot of Gaunt functions and other complications. As written, it also only involves integrals over the central site and ignores parts of the Wannier functions on nearby neighbors. We have therefore found a different approach to the problem.

To calculate \( W(12, 34; \mathbf{R}, \mathbf{R}') \) for any lattice sites \( \mathbf{R} \) and \( \mathbf{R}' \), we make use of the Fourier transform
\[ \int d^3 \mathbf{q} \; e^{i \mathbf{q} \mathbf{r}} = \frac{2\pi^2}{|r|} \]  
and find for Eq. (43):
\[ W(12, 34; \mathbf{R}, \mathbf{R}') = \frac{e^2}{2\pi^2} \int d^3 \mathbf{q} \; e^{i \mathbf{q} (\mathbf{R}-\mathbf{R}')} f_{13}(\mathbf{q}) f_{24}(-\mathbf{q}) \]  
where \( f_{ij}(\mathbf{q}) \equiv \int d^3 \mathbf{r} \; e^{i \mathbf{q} \mathbf{r}} w_{ij}(\mathbf{R}-\mathbf{R}_i; \mathbf{r}) w_{nj}(\mathbf{R}-\mathbf{R}_j; \mathbf{r}) \)  

The \( f_{ij} \) functions are just the Fourier transforms of a product of some Wannier functions in a sphere. These can be calculated very efficiently by calculating the Wannier functions on a cubic mesh in real space and then applying a standard FFT algorithm. To do this, we have used the routine “fourn” (cf. Ref. [33]). For details on how to apply the FFT to continuous functions, Ref. [24] is very useful. The result of the Fourier transform is \( f_{ij}(\mathbf{q}) \) on a cubic mesh in \( q \)-space with some \( \Delta q \) (the distance between the mesh points). We perform the remaining \( q \)-integral in the following way. Let us call the integrand without the \( q^{-2} \) term
\[ F(q) = e^{i \mathbf{q} (\mathbf{R}-\mathbf{R}')} f_{13}(\mathbf{q}) f_{24}(-\mathbf{q}) , \]  
which is smooth function at \( q = 0 \). In order to treat the divergence arising from \( q^{-2} \), we split the integral in the following way:
\[ \int d^3 q \; \frac{F(q)}{q^2} = \int d^3 q \; \frac{F(q) - F(0)}{q^2} + F(0) \int d^3 q \; \frac{1}{q^2} \]  

All integrals are over a cube with length \( N \Delta q \). The last integral is just half of this length times \( C \), which we define as
\[ C \equiv \int_{-1}^{+1} dx \int_{-1}^{+1} dy \int_{-1}^{+1} dz \; \frac{1}{r^2} \approx 15.34825 . \]  

The remaining integral in Eq. (47) is transformed into a sum over little cubes with volume \((\Delta q)^3\). For \( q = 0 \) the value of integrand is calculated via the second derivative of \( F(q) \) at \( q = 0 \) numerically (the second derivative is needed to cancel the \( q^2 \) in a power-law expansion of \( F \)).

The cubic grid in real space that we used to calculate the Wannier functions in Eq. (17) had \( N = 64^3 \) points in the real space grid with a spacing \( \Delta x = 0.17 \). The \( \Delta q \) spacing of the \( q \)-mesh is determined by \( N \) and \( \Delta x \). Using the FFT for continuous Fourier transformations one has to be very careful about the choice of these values because the FFT is a discrete Fourier transform. It is important to make sure that the results of a FFT calculation do not depend on the values \( N \) and \( \Delta x \).

Note that each integral in Eq. (47) could be calculated from the spherical-harmonic expansions. However, many such integrals would be required and the method would be extremely computationally expensive. The FFT method generates all the \( q \) values needed with a single calculation and is much more efficient. However, because of finite mesh sizes and compromises between real and \( q \) space integrals, it is not as accurate as the spherical-harmonic expansion method of Sec. 1.1 when the latter is applicable.
III. RESULTS AND DISCUSSION

We have tested our methods on Cu, which has the following properties: (i) It has a simple close-packed fcc crystal structure for which the ASA should be a reasonable approximation. (ii) Cu is a simple metal that belongs to the 3d transition metals, so one can determine Coulomb matrix elements for the 3d states which are interesting and of relevance for the really correlated 3d-systems. (iii) Since Cu is non-magnetic, we do not have to worry about spin-polarized or magnetic calculations. We have used the experimental lattice constant \(a=3.614\text{Å}\) as given in Ref. [3]. As usual we use atomic Rydberg units and \(a_0 = \hbar^2/mec^2\) is the Bohr radius.

\[
\ln\langle w_2|w_2\rangle_R = \int d^3r|w_2(R; r)|^2, \quad (51)
\]

which is the relative weight the Wannier function localized at the site 0 has in the muffin-tin sphere centered around \(R\). In Fig. 1 we have plotted for \(n=2\) the function \(\ln\langle w_2|w_2\rangle_R\) as a function of \(|R|\). Although the contribution to \(w_2\) appears to decrease exponentially with increasing distance from the central sphere when plotted in this way, i.e., our Wannier functions are exponentially localized, we actually get just as good a fit through the scatter of the data with a power-law dependence with a power of about -7. It is not easy to numerically decide whether the decay is an exponential or a power-law dependence, since our Wannier functions are ultimately periodic in a supercell determined by the \(\Delta k\) spacing of the discrete \(k\) mesh used to construct them. In either case, the Wannier function is highly localized. The grey dots and line in the figure show the result when only the phase has been adjusted according to Eq. (10); then the Wannier functions have a relatively smaller decay constant of \(\gamma = 0.38a_0^{-1}\). The black dots and line show the result after the full localization (minimization) procedure of Ref. [2] has been applied by minimizing the full set of all 16 bands considered; clearly a much better localization with a larger decay constant \(\gamma = 1.14a_0^{-1}\) has been achieved. When we tried to minimize a smaller subset of bands (5 bands instead of the full 16) the decay factor was in between the other two values, with \(\gamma \approx 0.71a_0^{-1}\) (not shown in the figure).

| \(n\) | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| \(\gamma\) | \(0.102\) | \(0.131\) | \(0.000\) | \(0.091\) | \(0.151\) | \(0.373\) |
| \(R\) | \(0.012\) | \(0.131\) | \(0.058\) | \(0.042\) | \(0.151\) | \(0.373\) |
| \(\gamma\) | \(0.407\) | \(0.663\) | \(0.895\) | \(0.886\) | \(0.716\) | \(0.323\) |
| \(\gamma\) | \(0.096\) | \(0.140\) | \(0.024\) | \(0.039\) | \(0.064\) | \(0.069\) |
| \(\sum\) | \(0.902\) | \(0.947\) | \(0.977\) | \(0.975\) | \(0.956\) | \(0.899\) |

Here we should note that the Wannier functions are not pure in terms of their \(l\)-character. Table I shows the angular character in the center muffin-tin (MT) and the first shell for the first 7 Wannier states. We see that for the states with \(n=0\) to \(n=4\) the \(d\)-character is largest which suggests to call these states \(d\)-like states yielding 5 \(d\)-states per spin direction as expected. But among these states the \(d\)-character is highest (nearly 90 %) for the states \(n=2\) and 3. Table I also tells us how much of the state is found in the center muffin-tin. We see that the state \(n=2\) has 97.7% in the center MT and only 2.1% in the next shell demonstrating how well localized this Wannier function is. The Wannier functions corresponding to \(n=0\), \(n=5\), and \(n=6\) have considerable \(4s\)- and \(4p\)-character, and \(n=5\) and \(n=6\) have the smallest \(3d\)-character. But they are very well localized as well, having at least 88% of their total weight already within the central muffin-tin sphere. On the other hand, all Wannier states are mixed with respect to their \(l\)-character, since the minimization procedure mixes all the \(l\) characters.

Figure 2 shows a few radial averaged Wannier functions in their center MT. We should note that the peak of the states \(n=0\) and 6 for \(r\rightarrow0\) does not contribute very much to matrix elements because of the \(r^2\) in Eq. (22). Figure 2 may also be qualitatively compared with the Wannier function of Cu in Ref. [2].
From these Wannier functions we have calculated the hopping matrix elements $t_{Rnm}$ according to Eq. (19). These can be inserted into Eq. (18) in order to determine an effective orthogonalized (diagonal $S$-matrix) tight-binding representation. The matrices $H^k$ are not diagonal because the unitary matrix which was used in the minimization of the Wannier functions scrambled the different bands. However, we can still diagonalize $H^k$ for each $k$-point and compare the eigenvalues with the original LDA band structure. The results are shown in Fig. 3, where we have cutoff the $R$-sum in Eq. (18) to include only 0 and the 3 nearest shells, i.e., 43 sites. We have found that the decay of $t_{Rnm}$ as a function of $|R|$ is a lot faster than that of the Fourier components of the band structure, Eq. (17). If we just take Eq. (17) and recalculate the band structure according to Eq. (18), the agreement is a lot worse (for the same number of sites in $t_{Rnm}$). This can be understood in the following way: Labeling the bands according to $E_n(k) < E_{n+1}(k)$ is not “natural”, therefore at points in $k$-space where two bands cross each other $E_n(k)$ has a kink. Those kinks have non-negligible Fourier components with large $|R|$, which our cutoff sets to zero.

Next, consider the projected DOS (PDOS). In these calculations we have used the tetrahedron method (see also Ref. 23) with 200 $k$-points and 691 tetrahedras in the irreducible part of the Brillouin zone. In Fig. 5 we have plotted the total DOS which can also be found in the literature (see Ref. 37).
It is interesting that states to Eq. (28) for the Wannier functions 0 through 7. It emphasize different parts of the character (cf. Table I) but a very different projected DOS of the DOS in different states) and the projected number of states at the Fermi energy, i.e., $N(E_F)$

\[ n_j(E_F) = \int_{E_F}^{E_F} dE N_j(E). \]  

(52)

This is just the number of electrons in the $j$th state. Every state could maximally be occupied with 2 electrons (one for each spin direction).

FIG. 6. Projected DOS for Wannier states 0 through 3.

FIG. 7. Projected DOS for Wannier states 4 through 7.

Figures 6 and 7 show the projected DOS according to Eq. (28) for the Wannier functions 0 through 7. It is interesting that states $j = 2$ and 3 have very similar $\ell$ character (cf. Table I) but a very different projected DOS in Fig. 6, i.e., they are peaked at different energies, and emphasize different parts of the $d$ band. Table I shows the projected density of states (actually the percentage of the DOS at different states) and the projected number of states evaluated at the Fermi level, where the $j$th projected number of states is defined as

\[ n_j(E_F) = \int_{E_F}^{E_F} dE N_j(E). \]

(52)

This is just the number of electrons in the $j$th state. Every state could maximally be occupied with 2 electrons (one for each spin direction).

TABLE II. Projected number of states at the Fermi energy, i.e., $n_j(E_F)$. For $j > 8$ (the numbers not given) $n_j(E_F) < 0.25$. The second line shows the percentage of the DOS at Fermi energy, i.e., $100 \cdot n_j(E_F)/N(E_F)$.

| $j$ | 0  | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  |
|-----|----|----|----|----|----|----|----|----|----|
| $n_j(E_F)$ | 1.17 | 1.31 | 1.59 | 1.80 | 1.34 | .66 | .90 | .51 | .78 |
| % DOS  | 4.7 | 2.1 | 11.1 | 7.1 | 15.4 | 13.0 | 4.6 | 3.2 | 27.3 |

We next consider a calculation of the direct Coulomb integral $U_{ii}$ for a $d$-like orbital with itself. As discussed above, the Wannier function for $n = 2$ has nearly perfect $d$-character and to a good approximation we can consider only its contribution in the central MT, i.e., at site 0. What we then calculate is the on-site Coulomb matrix element between two electrons (with different spin because of the Pauli principle) at the same site in the same Wannier state, i.e., essentially the Hubbard-U in its original sense. The method described in Sec. [1E1] yields $U(\text{dd};0,0) = 25.26$ eV while the method from Sec. [1E2] yields 25.16 eV for this quantity. But with the second method we are able to calculate all the elements involving tails of the Wannier functions in other muffin-tins in the double sum in Eq. (23). When we do this and include sites where $R_i$ and $R_j$ are nearest neighbors, we get $U_{dd} = 25.51$ eV, which shows that including the portions of the Wannier function on neighboring sites is a rather small correction on $U$ for such a strongly localized function. Table III show these quantities for the Wannier functions $n = 0$ through 6. Going beyond nearest neighbors would have even a smaller effect. Therefore, one can truncate the sums over higher neighbor shells for the Coulomb matrix elements, which converge faster than for the hopping matrix elements. The reason for this is that the Coulomb integral involves a product of four wave functions, whereas the hopping matrix elements involve only two wave functions.

TABLE III. Onsite FFT $U$'s. In the first line (onsite-U) we have only included $R_i = R_j = 0$ in Eq. (23), i.e., $U_{jj}(0,0)$. The second line (NN-U) shows the same quantity, where we have included nearest neighbors for $R_i$ and $R_j$.

| $j$ | 0 | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  |
|-----|---|----|----|----|----|----|----|----|----|
| onsite-U | 14.82 | 19.05 | 25.16 | 25.49 | 20.79 | 13.81 | 13.22 |
| NN-U  | 16.29 | 19.81 | 25.51 | 25.86 | 21.44 | 15.32 | 14.97 |

The FFT approach allows us to calculate Coulomb matrix elements for Wannier functions centered on different sites. We have done this for the states $a = \{0,2\}$ and $b = \{R,2\}$ where $R$ is a nearest neighbor of 0. Both are $d$-like states. In Eq. (23) we have again included nearest neighbors for $R_i$ and $R_j$. The result is $U_{ab} = 5.87$ eV. The largest contribution in the sum is $U(ab;R,R) = 5.66$ eV, which is the contribution arising from the two center spheres of states $a$ and $b$.

Our first method is most useful for calculating interband (on-site) Coulomb matrix elements when the states are so well localized that we can neglect the contribution from neighboring spheres. We have calculated both the direct Coulomb matrix elements $U_{nm}$ and the exchange integrals $J_{nm}$ for all $n$ and $m$. Here the $n,m$ just indicates the band and all Wannier states are centered at site 0. The results are given in Tables IV and V for the first 7 bands. We see that the on-site intra-band Coulomb matrix elements are largest for the Wannier states $n=2$ and 3, which have almost pure $d$-character. We also note that all the direct Coulomb matrix elements $U_{nm}$ are rather large, while the exchange Coulomb matrix elements $J_{nm}$ with $n \neq m$ are rather small (note that the diagonal terms for both $U_{ii}$ and $J_{ii}$ are identical.
by definition, cf. Eq. (34). When we compare the diagonal elements $U_{nn}(= J_{nn})$ from Tables II and III with the first line of Table II we note relatively large differences for the states $n=0$, 5, and 6, which have large $s$ and $p$ character, as can be seen from Table I (e.g. 0.52eV for $n=0$). This leads to a peak in their charge density near $r = 0$ as we can see from Fig. 3 for $n=0$ and 6. For those states our FFT calculations had a numerical problem because our real-space grid was too large (with $\Delta x = 0.17a_0$). But for $n=2$, we do not have a peak at $r = 0$, and the FFT approach does an excellent job.

TABLE IV. Inter-band on-site matrix elements: $U_{nn}$ in eV.

| $n$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|-----|---|---|---|---|---|---|---|
| $m=0$ | 14.30 | 15.86 | 17.86 | 17.45 | 16.31 | 13.24 | 12.77 |
| 1   | 15.86 | 19.02 | 21.36 | 20.98 | 19.33 | 15.25 | 14.42 |
| 2   | 17.86 | 21.36 | 25.26 | 24.13 | 22.30 | 17.09 | 15.86 |
| 3   | 17.45 | 20.98 | 24.13 | 25.26 | 21.88 | 16.69 | 16.12 |
| 4   | 16.31 | 19.33 | 22.30 | 21.88 | 20.70 | 15.76 | 14.78 |
| 5   | 13.24 | 15.25 | 17.09 | 16.69 | 15.76 | 13.23 | 12.32 |
| 6   | 12.77 | 14.42 | 15.86 | 16.12 | 14.78 | 12.32 | 12.43 |

TABLE V. Inter-band on-site matrix elements: $J_{nn}$ in eV.

| $n$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|-----|---|---|---|---|---|---|---|
| $m=0$ | 14.30 | 0.91 | 0.73 | 0.76 | 0.92 | 0.98 | 1.34 |
| 1   | 0.91 | 19.02 | 1.22 | 1.22 | 0.84 | 0.91 | 1.43 | 0.69 |
| 2   | 0.73 | 2.22 | 25.26 | 0.92 | 1.14 | 1.95 | 0.58 |
| 3   | 0.76 | 0.84 | 0.92 | 25.26 | 0.99 | 0.71 | 0.62 |
| 4   | 0.92 | 0.91 | 1.14 | 0.99 | 20.70 | 1.20 | 0.79 |
| 5   | 0.98 | 1.43 | 0.95 | 0.71 | 1.20 | 13.23 | 1.22 |
| 6   | 1.34 | 0.69 | 0.58 | 0.62 | 0.79 | 1.22 | 12.43 |

IV. CONSTRAINED LDA

Finally, we have done a constrained LDA calculation to obtain an estimate for the Hubbard $U$. In this method the Hubbard $U$ is defined as the Coulomb energy cost to place two (in our case $d$) electrons at the same site. This is

$$U = E(N_d + 1) + E(N_d - 1) - 2E(N_d).$$

(53)

Here $E(N_d)$ is the ground-state energy with $N_d$ $d$-electrons. If we consider this energy as a continuous function of $N_d$, where we constrain the value of $N_d$ to be away from its minimized value, then the Hubbard $U$ is given by:

$$U_{dd} = \frac{\delta^2 E(N_d)}{\delta N_d^2}$$

(54)

This constraint, which fixes the total number of $d$-electrons to be $N_d$, can be taken into account by adding a Lagrange parameter $v_d$ to the total energy; i.e., the energy of the constrained system is given by

$$E(N_d) = \min\{E(n(r)) + v_d\int d^3r n_d(r) - N_d\}.$$  

(55)

Here $E\{n(r)\}$ is the usual band-structure energy and $n_d(r)$ is the $d$-electron density. On minimization the extra term in Eq. (55) leads to an additional constant potential, $v_d$, in the Kohn-Sham equations, which acts only on the $l = 2$ angular momentum components of the wave function. Within the LMTO method, this is accomplished by adding a constant potential, $v_d$, when solving the radial Schrödinger equation for $l = 2$, and then calculating the total energy as a function of $v_d$. Since each value of $v_d$ changes the $d$ occupation number, the final result can be written as $E(N_d)$. This dependence is shown in Fig. 8 and can be accurately fitted by a parabola, $\delta E = \frac{1}{2}U_{dd}N_d^2$, with $U_{dd} = 18.2$ eV. This is of the same magnitude as the result obtained from the direct calculation of the Coulomb matrix elements, even though one might expect a smaller value because of the orthogonalization properties and mixing necessary for localizing our Wannier functions scramble the $l$-character of the resulting orbitals. Hence, our effective $U$’s do not have a pure $d$ or $f$ character (or $s$ or $p$). Also, since we calculate $U$’s for all of the orbitals, we are implicitly including correlation effects for all orbital ($s$ and $p$ as well as $d$ and $f$), and however the $U$’s in our treatment are ultimately screened in some many-body treatment, this screening may be different from that assumed in the model Hamiltonians. We may ultimately be forced to use some kind of projection of our orbitals onto pure $l$-character states in order to make appropriate identification between our types of states and more conventional model Hamiltonians.

The Hubbard-$U$ clearly depends on the specific shape of the Wannier functions. Intuitively, one expects bigger $U$’s for more localized orbitals. As an example of this, we have calculated a less localized Wannier state (by doing fewer steps in the minimization procedure). In this case, the highest $d$-character state, which is almost pure $d$-like, has only 58.5% of its charge density in the center muffin- tin, and 95.4% within the first 3 shells. For those three shells we have used the FFT method to calculate all 432 terms (34). We find a $U = 13.8$eV for this less localized $d$-state.

We should also note that most model calculations assume very localized, pure (in $l$-character) Wannier functions. In particular, they often assume that LDA or some one-electron-like treatment is adequate for non-$d$ and non-$f$ electron states, and that the only explicit correlations that need to be included are related to onsite (or sometimes also nearest-neighbor) Coulomb $U$’s for the $d$ (or $f$) states. It is also often implicitly assumed that the non-$d$ and non-$f$ states have some screening contribution to the effective $U$’s in the model Hamiltonian. These types of assumptions raise some difficulties for us to connect our treatment to the model Hamiltonians, since the
screening effects that are believed to be included in this calculation. In our calculations we have only used a one-atom unit cell. If a larger unit cell is chosen, one could do a variety of additional constraints (e.g., changing the d-occupation separately on two different atoms). Such calculations could attempt to sort out more details of effective Hamiltonians (perhaps even two-particle parameters). However, such calculations would take our work in a different direction from what we are interested. Also, given the intuitive nature of the constrained method and the difficulties in fitting such a large parameter space, it is not clear how useful the resulting parameters would be or their uniqueness.

\[ \delta E_{\text{tot}}/\text{eV} \]

\[ U_d = 18.2 \text{eV} \]

FIG. 8. The total energy as a function of the effective change in d charge. The line is a quadratic fit.

V. CONCLUSIONS

We have shown in this paper that ab-initio band-structure methods can be used for a first-principles calculation of well localized Wannier functions, which is achieved by using a method proposed by Marzari and Vanderbilt. From these localized Wannier functions the on-site and inter-site one-particle matrix elements of the Hamiltonian can be calculated. A good localization of the Wannier functions is needed to keep tight-binding (hopping) matrix elements restricted to a small number of near neighbors. The Coulomb matrix elements within these localized Wannier states can also be calculated and are similarly only important between on-site and nearest-neighbor Wannier functions. The result is thus an electronic multi band Hamiltonian in second quantization with first-principles one- and two-particle matrix elements. The Hamiltonian is of the form of an extended multi-band Hubbard model but without adjustable parameters; the parameters are directly calculated for a given material. The only approximations still involved are the ones inherent to the ab-initio band structure method used (e.g., the muffin-tin assumption, the ASA approximation, the choice of linearized orbitals in the LMTO, and the "frozen-core" approximation), and the truncation in the number of bands (states) per site that is explicitly taken into account (truncation of the \( l \)-sum). The resulting multi-band Hamiltonian that includes the Hubbard-\( U \) terms, of course, still has to be studied within a reliable many-body method or approximation, e.g., a multi-band version of the DMFT as in Refs. \( \text{Ref.} \) 7, 10, 12, and 14.

Our Cu calculations yield on-site direct Coulomb matrix elements ("Hubbard-\( U \)’s") of the magnitude of 20 eV for 3d-Wannier-states and inter-site (Hubbard-\( U \)’s between nearest-neighbors) values of 5 eV. This is the magnitude discussed already earlier and similar to those for atomic 3d-states. These U-values are much larger than commonly expected or used in model studies. Although our calculated Coulomb matrix elements are unscreened, the constrained LDA, which includes some screening effects, gives comparable magnitudes for \( U \). Since dynamic screening due to the mobile electrons in the outer shells (bands) is taken into account automatically when using an appropriate many-body method, e.g., a generalized random phase approximation (RPA), the only screening that should be included in a better theory is a static, short range screening by the inner core electrons. However, the (atomic like) electronic states representing the inner ("frozen") core are well known, and it should be possible to calculate their screening contribution from a (generalized) static Lindhard theory. In future work we plan to examine the static screening due to the inner core states, an application of appropriate (multi-band) many-body methods, and the application to more strongly correlated 3-d materials such as iron, cobalt, and nickel. Any treatment of screening will, of course, have to be very careful that screening effects are not double counted (once in the explicit screening and then a second time when the many-body Hamiltonian is solved). Finally, although any localized orbitals could be used as the basis for a many-body treatment, the approach we have used (of constructing localized orbitals from LDA band states) has the advantage that these orbitals are a good basis set for any states without strong electron-electron correlations, since LDA is believed to be an accurate approximation in this limit. We can hope that an additional more explicit treatment of the strong correlations by a many-body theory will correct and improve on the LDA starting point.

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APPENDIX A: SPHERICAL HARMONICS EXPANSIONS

Any function \( A(r) \) within a (muffin-tin) sphere may be expanded in terms of spherical harmonics:

\[
A(r) = \sum_L A_L(r)Y_L(\hat{r}) \tag{A1}
\]

If two functions \( A(r) \) and \( B(r) \) are given via their coefficients \( A_L(r) \) and \( B_L(r) \), then the corresponding coefficients \( F_L(r) \) of the function \( F(r) = A(r)B(r) \) are given by:

\[
F_L(r) = \sum_{L_1, L_2} A_{L_1}(r)B_{L_2}(r)C_{L_1, L_2} \tag{A2}
\]

The Gaunt coefficients \( C_{L_1 L_2 L'} \) are defined by

\[
C_{L_1 L_2 L'} = \int d^3\Omega \ Y_{L_1}(\Omega) \ Y_{L_2}^*(\Omega) \ Y_{L'}(\Omega)
= \delta_{m''m'} \sqrt{\frac{2l' + 1}{4\pi}} \ c_l''(L', L) \tag{A3}
\]

and the \( c_l''(L', L) \) are tabulated in Ref. 68. We may use Eq. (A2) to multiply a function with a plane wave \( \epsilon_k^L(r) \equiv e^{-ikr} \) whose coefficients are given by (see Ref. 32):

\[
\epsilon_k^L(r) = 4\pi j_{l}(kr) \left[ ijY_{L}(\hat{k}) \right]^* \tag{A4}
\]

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