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Ab initio procedure for constructing effective models of correlated materials with entangled band structure

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In a previous work [Phys. Rev. B **77**, 085122 (2008)], a procedure for constructing low-energy models of electrons in solids was proposed. The procedure starts with dividing the Hilbert space into two subspaces: the low-energy part ("d space") and the rest of the space ("r space"). The low-energy model is constructed for the d space by eliminating the degrees of freedom of the r space. The thus derived model contains the strength of electron correlation expressed by a partially screened Coulomb interaction, calculated in the constrained random-phase approximation (cRPA), where screening channels within the d space, P_d, are subtracted. One conceptual problem of this established downfolding method is that for entangled bands it is not clear how to cut out the d space and how to distinguish P_d from the total polarization. Here, we propose a simple procedure to overcome this difficulty. The d space is defined to be an isolated set of bands generated from a set of maximally localized Wannier basis, which consequently defines P_d. The r subspace is constructed as the complementary space orthogonal to the d subspace, resulting in two sets of completely disentangled bands. Using these disentangled bands, the effective parameters of the d space are uniquely determined by the cRPA method. The method is successfully applied to $3d$ transition metals.

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I. INTRODUCTION

In the last several decades many new materials with intriguing properties were discovered and synthesized. These materials range from the high-temperature superconductors to magnetic materials, and the latter have already found real applications in electronic industry. Typically, most of these materials contain elements from the $3d$ or $4f$ rows and their electronic structure is characterized by the presence of a partially filled narrow band crossing the Fermi level. The fact that the narrow band is partially filled implies that there are many configurations with comparable weight rendering a one-particle description of the electronic structure problematic. Indeed, it has been recognized for a long time that many of the intriguing properties of these materials originate from correlations among the electrons residing in the partially filled narrow band. The electrons are neither fully localized, like core electrons, nor itinerant, like s or p electrons in alkalis or conventional semiconductors such as silicon or diamond. This hybrid property poses a tremendous theoretical difficulty for an accurate description of the electronic structure because due to the electrons' partially itinerant character the problem can neither be treated as a purely atomic problem nor within a pure band picture. Moreover, the interaction with other electrons can be very important.

A large amount of work has been directed to solving the correlation problem of the above materials. The usual approach is to consider only the narrow bands near the Fermi level and eliminate the degrees of freedom of the rest of the bands by the downfolding procedure, resulting in the well-known Hubbard model which contains an effective on-site Coulomb interaction, the Hubbard U. In general, the models represent multiband systems containing the interorbital as well as the long-range part of the Coulomb interaction. The models can then be solved with various sophisticated low-energy solvers such as dynamical mean-field theory[1] or solvers for lattice models.[2]

An important issue in mapping the real system to a model Hamiltonian is how to determine the one-particle kinetic energy term and the effective interaction or the Hubbard U in the model. Unlike the one-particle parameters that can be downfolded from the band structure, the Hubbard U is much more elusive to determine and it is often treated as an adjustable parameter. A widely used scheme to calculate the Hubbard U from first principles is the constrained local density approximation (cLDA) method.[3–5] The cLDA method, however, is known from early on to yield values of U, which are too large in some cases (e.g., late transition metals). It has been argued that this arises from technical difficulty in including transitions of electrons between the d and r space contributing to the screening processes. Here the d space is the low-energy part of the Hilbert space, for which an effective model is constructed, and the r space is the rest of the space. This oversight leads in some cases to a larger value of U.[6] Recent extensions of the cLDA method may be found in Refs. 7 and 8. Another method for determining the effective interaction is a scheme based on the random-phase approximation (RPA). Early attempts along this direction can be found in Refs. 9 and 10.

Some years ago a scheme for calculating the Hubbard U, called the constrained RPA (cRPA) scheme,[11] was proposed. Subsequently a combined cLDA and cRPA method was also proposed.[12] The main merit of the cRPA method over currently available methods is that it allows for a precise elimination of screening channels, which are instead to be included in a more sophisticated treatment of the model

Hamiltonian. This is a controlled approximation without any ambiguity, expected to become asymptotically exact if the r space becomes well separated from the d space. Moreover, the effective screened interaction can be calculated as a function of $\mathbf{r}$ and $\mathbf{r}'$, i.e., $U(\mathbf{r},\mathbf{r}')$, independent of the basis functions. This allows easy access to obtaining not only on-site matrix elements but also off-site matrix elements as well as screened-exchange matrix elements, which are usually taken to be the atomic value. Another merit is the possibility of obtaining the frequency-dependent Hubbard U, which may prove to be important. The cRPA method has now been applied to a number of systems with success.[6,13–15]

Although the cRPA method is rather general, its applications to real systems have revealed a serious technical problem. The problem arises when the narrow band is entangled with other bands, i.e., it is not completely isolated from the rest of the bands, which is the case in many materials. Even in simple materials such as the 3d transition metals, the 3d bands mix with the 4s and 4p bands. Similarly, the 4f bands of the 4f metals hybridize with the more extended s and p bands. For such cases, it is not clear anymore which part of the polarization should be eliminated when calculating the Hubbard U using the cRPA method.

Some procedures to overcome the problem of determining U for entangled bands have been attempted. One of these is to choose a set of band indices and define the bands of the Hubbard model as those bands corresponding to the chosen indices. Another alternative is to introduce an energy window and define the Hubbard bands to be those that have energy within the energy window. Yet another alternative is to have a combination of energy window and band indices. These procedures, however, suffer from a number of difficulties. When choosing band indices it is inevitable that some of the states will have a character very different from that of the intended model. For example, in the case of 3d transition metals, choosing five "3d" bands will include at some **k**-points states which have little 3d character, with a considerable 4s component instead. Moreover, the chosen bands will be awkward to model since they do not form smoothly connected bands. A similar problem is encountered when choosing an energy window. A combination of band indices and energy window proposed in Ref. 6 partially solves the problem but it suffers from arbitrariness. Another procedure is, as we will discuss in detail later, to project the polarization to the orbitals of interest, e.g., 3d orbitals, but this procedure has been found to yield an unphysical result of negative static U. In this work, we offer a solution to the problem of determining the Hubbard U for entangled bands. The basic idea is to disentangle the narrow bands of interest from the rest and carry out the cRPA calculation for the disentangled band structure, not using the original band structure. The disentangling procedure is described in Sec. II. We apply the method to 3d transition metals in Sec. III and show that the method is numerically stable and yields reasonable values of U. Finally the paper is summarized in Sec. IV.

II. METHOD

In the cRPA method we first choose a one-particle subspace $\{\psi_d\}$, which defines the model Hamiltonian, and label the rest of the Hilbert space by $\{\psi_r\}$. We define P_d to be the polarization within the d subspace and the total polarization is written as P. It is important to realize that the rest of the polarization $P_r = P - P_d$ is *not* the same as the polarization of the r subspace alone because it contains polarization arising from transitions between the d and r subspaces. Since P_d is the polarization of the model Hamiltonian, this polarization should be subtracted out from the total polarization when the effective parameter of the model is determined. The effective Coulomb interaction W_r should be calculated with the rest of the polarization P_r,

$$W_r(\omega) = [1 - vP_r(\omega)]^{-1}v, \tag{1}$$

where v is the bare Coulomb interaction. It can indeed be shown[11] that the fully screened interaction is given by

$$W = [1 - W_r P_d]^{-1} W_r. \tag{2}$$

This mathematical identity ensures that W_r can be interpreted as the effective interaction among the electrons residing in the d subspace since the screening of W_r by P_d leads to the fully screened interaction. The matrix elements of W_r in some localized functions can then be regarded as the frequency-dependent Hubbard U. It has been shown that the formula in Eq. (1) is formally exact, provided P_r is the difference between the exact polarization P and the exact polarization of the d subspace P_d.[16] In the cRPA method, P_r is calculated within the random-phase approximation.

If the d subspace forms an isolated set of bands, as for example in the case of the t_{2g} bands in SrVO$_3$, the cRPA method can be straightforwardly applied. However, in practical applications, the d subspace may not always be readily identified. An example of these is provided by the 3d transition metal series where the 3d bands, which are usually taken to be the d subspace, do not form an isolated set of bands but rather they are entangled with the 4s band. To handle these cases we propose the following procedure.

We first construct a set of localized Wannier orbitals from a given set of bands defined within a certain energy window. These Wannier orbitals may be generated by following the postprocessing procedure of Souza, Marzari, and Vanderbilt[17,18] or other methods, such as the preprocessing scheme proposed by Andersen *et al.* within the Nth-order muffin-tin orbital (NMTO) method.[19] We then choose this set of Wannier orbitals as the generator of the d subspace and use them as a basis for diagonalizing the one-particle Hamiltonian, which is usually the Kohn-Sham Hamiltonian in the local density approximation (LDA) or generalized gradient approximation (GGA). The so obtained set of bands, which equivalently define the d subspace, may be slightly different from the original bands defined within the chosen energy window, because hybridization effects between the d and r spaces are neglected. It is therefore important to confirm that the dispersions near the Fermi level well reproduces the original Kohn-Sham bands. From these bands we calculate the polarization $\tilde{P}_d$ as

$$\tilde{P}_d(\mathbf{r},\mathbf{r}';\omega)=\sum_i^{\text{occ}}\sum_j^{\text{unocc}}\left[\frac{\tilde{\psi}_i^*(\mathbf{r})\tilde{\psi}_j(\mathbf{r})\tilde{\psi}_j^*(\mathbf{r}')\tilde{\psi}_i(\mathbf{r}')}{\omega-\tilde{\varepsilon}_j+\tilde{\varepsilon}_i+i\eta} - \frac{\tilde{\psi}_i(\mathbf{r})\tilde{\psi}_j^*(\mathbf{r})\tilde{\psi}_j(\mathbf{r}')\tilde{\psi}_i^*(\mathbf{r}')}{\omega+\tilde{\varepsilon}_j-\tilde{\varepsilon}_i-i\eta}\right], \tag{3}$$

where $\{\tilde{\psi}_i\}$, $\{\tilde{\varepsilon}_i\}$ $(i=1,\cdots N_d)$ are the wave functions and eigenvalues obtained from diagonalizing the one-particle Hamiltonian in the Wannier basis.

It would seem sensible to define the rest of the polarization as $P_r=P-\tilde{P}_d$, where P is the full polarization calculated using the *original* (Kohn-Sham) wave functions and eigenvalues $\{\psi_i\}$, $\{\varepsilon_i\}$ $(i=1,\cdots N)$, and calculate W_r according to Eq. (1). We have found, however, that this procedure is numerically very unstable, resulting in some cases to unphysically negative static U and a large oscillation as a function of frequency. This is understandable given that P and $\tilde{P}_d$ are obtained from two different band structures, so that low-energy screening channels associated with the *d*-*d* transitions are not excluded from P_r completely. Due to the singular nature of the expression in Eq. (1) these low-energy excitations can cause a large fluctuation in W_r.

Another way of calculating P_r is to project the wave functions to the *d* space,

$$|\bar{\psi}_i\rangle=\hat{\mathcal{P}}|\psi_i\rangle, \tag{4}$$

where the projection operator $\hat{\mathcal{P}}$ is defined as

$$\hat{\mathcal{P}}=\sum_{j=1}^{N_d}|\tilde{\psi}_j\rangle\langle\tilde{\psi}_j|. \tag{5}$$

The effective *d* polarization may be expressed as

$$\bar{P}_d(\mathbf{r},\mathbf{r}';\omega)=\sum_i^{\text{occ}}\sum_j^{\text{unocc}}\left[\frac{\bar{\psi}_i^*(\mathbf{r})\bar{\psi}_j(\mathbf{r})\bar{\psi}_j^*(\mathbf{r}')\bar{\psi}_i(\mathbf{r}')}{\omega-\varepsilon_j+\varepsilon_i+i\eta} - \frac{\bar{\psi}_i(\mathbf{r})\bar{\psi}_j^*(\mathbf{r})\bar{\psi}_j(\mathbf{r}')\bar{\psi}_i^*(\mathbf{r}')}{\omega+\varepsilon_j-\varepsilon_i-i\eta}\right], \tag{6}$$

and $P_r=P-\bar{P}_d$ can be used to calculate W_r. We found that this procedure does not work either and is again unstable. This problem may be related to the fact that $\bar{\psi}_i$'s are not orthogonal with each other and transitions between the states do not correspond to single particle-hole excitations.

Based on these observations we propose the following procedure. We define the *r* subspace by

$$|\phi_i\rangle=(1-\hat{\mathcal{P}})|\psi_i\rangle, \tag{7}$$

which is orthogonal to the *d* subspace constructed from the Wannier orbitals. In practice it is convenient to orthonormalize $\{\phi_i\}$ and prepare $N-N_d$ basis functions. By diagonalizing the Hamiltonian in this subspace a new set of wave functions $\{\tilde{\phi}_i\}$ and eigenvalues $\{\tilde{e}_i\}$ $(i=1,\cdots,N-N_d)$ are obtained. Namely, the Kohn-Sham Hamiltonian is diagonalized in the *d* space and *r* space separately, and the hybridization effects between them are neglected,

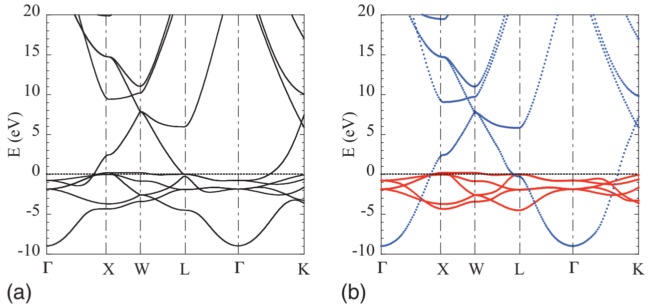

FIG. 1. (Color) (a) Kohn-Sham band structure of nickel in the LDA. (b) Disentangled band structure with *d*-*r* hybridization switched off. The red lines show the *d* states obtained by the maximally localized Wannier scheme, while the blue lines are disentangled *r* states. Energy is measured from the Fermi level.

$$H=\begin{pmatrix} d\ \text{space} & 0 \\ 0 & r\ \text{space}\end{pmatrix}. \tag{8}$$

As a consequence of orthogonalizing $\{\tilde{\phi}_i\}$ and $\{\tilde{\psi}_j\}$, the set of *r* bands $\{\tilde{e}_i\}$ are completely disentangled from those of the *d* space $\{\tilde{\varepsilon}_j\}$, and they are slightly different from the original band structure $\{\varepsilon_i\}$. As we will see later, however, the numerical tests show that the disentangled band structure is close to the original one.

The Hubbard U is calculated according to Eq. (1) with $P_r=\tilde{P}-\tilde{P}_d$, where $\tilde{P}$ is the full polarization calculated for the *disentangled* band structure. It is important to realize that the screening processes between the *d* space and the *r* space are included in U, although the *d*-*r* coupling is cut off in the construction of the wave functions and eigenvalues.

III. RESULTS AND DISCUSSIONS

As an illustration we apply the method to 3*d* transition metals. The electronic structure calculations are done in the LDA (Ref. 20) of density-functional theory[21] with the full-potential linear muffin-tin orbital implementation.[22] The wave functions are expanded in the basis of *spdf*+*spd* MTOs and a $8\times8\times8$ **k** mesh is used for the Brillouin zone summation. As an illustrative purpose, spin polarization is neglected, but this can be easily included. More technical details are found elsewhere.[13,23]

Figure 1(a) shows the Kohn-Sham band structure of nickel. There are five orbitals having strong 3*d* character at [−5 eV:1 eV], crossed by a dispersive state which is mainly of 4*s* character. Using the maximally localized Wannier function prescription with the energy window of [−7 eV:3 eV], interpolated “*d*“ bands are obtained. The subsequent disentangling procedure gives the associated “*r*“ bands. Comparing Fig. 1(b) with Fig. 1(a) we can see that there is no anticrossing between the *d* bands and the *r* bands in Fig. 1(b). Otherwise the two band structures are nearly identical.

In order to see the impact of the disentanglement on the screening effects, we perform the full RPA calculation using the disentangled band structure. The fully screened Coulomb interaction is compared with that for the original band struc-

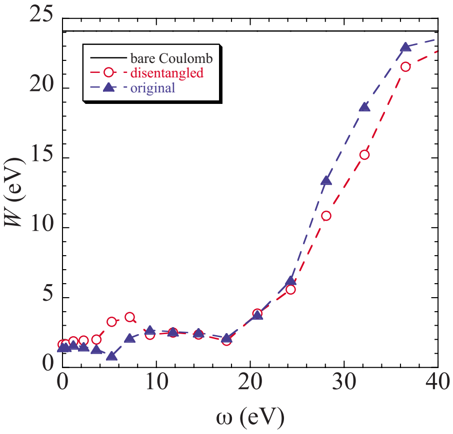

FIG. 2. (Color online) Fully screened Coulomb interaction of nickel as a function of frequency. The average of the diagonal terms in the Wannier basis is plotted. The present scheme using the disentangled bands is compared to the results obtained from the original band structure.

ture in Fig. 2, where the average of the five diagonal terms in the Wannier basis φ_i is plotted,

$$W(\omega) = \frac{1}{5}\sum_{i=1}^{5}\int d\mathbf{r}d\mathbf{r}'\,\varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r})W(\mathbf{r},\mathbf{r}';\omega)\varphi_i^*(\mathbf{r}')\varphi_i(\mathbf{r}'). \tag{9}$$

The two methods yield similar results The static values agree with each other within 0.2 eV, and the frequency dependence is weak at low frequencies. As frequency increases there is a sharp increase at ~20 eV, where screening by plasmons becomes ineffective. These results assure that screening effects can be treated accurately with the disentangled band structure.

The Hubbard U is calculated by the constrained RPA, namely, by replacing W in Eq. (9) with W_r. The results are shown in Fig. 3. There is no large fluctuation against frequency, in contrast to the methods described in Sec. II, and $U(\omega)$ shows a stable behavior. As is expected, U is significantly larger than W at low frequencies. This implies proper elimination of d-d screening processes is crucial. Comparing with the previous results using a combined energy and band window,[13] the agreement is reasonably good. A small difference between these two results at low frequency may be due to a small portion of d-d screening presumably contained in the previous method, although it should be excluded from the cRPA calculations.

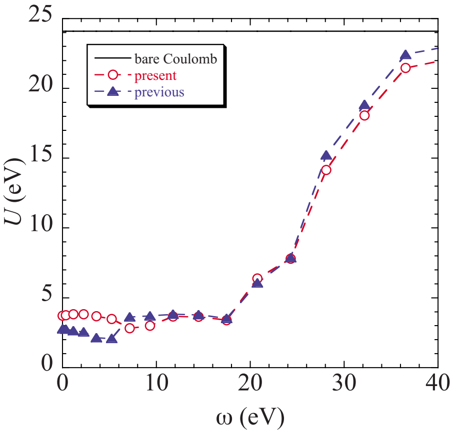

FIG. 3. (Color online) Hubbard U of nickel as a function of frequency. The diagonal term of the partially screened interaction in the Wannier basis is calculated by the present method and compared with the published data of Ref. 13.

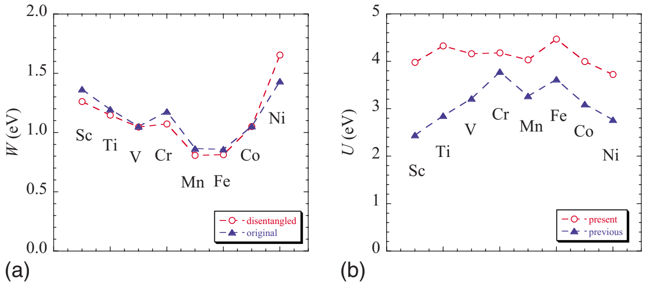

FIG. 4. (Color online) Static values of (a) fully screened Coulomb interaction W and (b) Hubbard U for 3d metals. We emphasize that there is no contradiction between the present and previous results. The difference arises from the choice of energy windows or the choice of bands defining the model Hamiltonian.

We carried out the calculations for a series of other 3d metals as well and found in all the cases that (i) the present scheme is numerically stable and does not result in unphysical frequency dependence of U, and (ii) the value of $W(\omega)$ is close to that from the original band structure. The latter is confirmed in Fig. 4 where the static values ($\omega \to 0$ limit) are summarized. Concerning U, the present method gives larger values compared to the previous results,[13] particularly for early transition metals. Since W is nearly equal to each other in the two methods, the discrepancy is ascribed to the different treatment between P_d and $\tilde{P}_d$. We emphasize that there is no contradiction between the previous and present results. We should note that P_d in the previous method depends on the choice of the window ("window 2" in Ref. 13): The wider the window, the larger the value of U because P_r becomes smaller. Also, some states have a mixed character of 3d and 4s near the anticrossing points. This makes elimination of the screening process within the 3d states only difficult. The present scheme, on the other hand, enables us to determine U without ambiguity. The d bands are disentangled from the r bands. Consequently, the polarization in the d space is well defined and can be removed completely in $P_r = \tilde{P} - \tilde{P}_d$.

Although the present method does not introduce an energy window explicitly to define P_r, there is still one energy window in calculating U. As described above, the Wannier functions are a linear combination of the Kohn-Sham states inside a certain energy window ("window 1" in Ref. 13). The window 1 must be wider than the target d band. When the window 1 is too wide, however, the contribution of Kohn-Sham states away from the target band to the Wannier orbitals becomes non-negligible. In such a case, the transfer integrals get so small that the interpolated d band deviates from the original band structure and the bands outside the target

TABLE I. The values of U in nickel as a function of energy window for the Wannier functions. The bare Coulomb interaction v and total spread of the five Wannier orbitals is also presented.

Window 1	U (eV)	v (eV)	Spread (Å^2)
[−5 eV:3 eV]	3.97	24.05	4.457
[−7 eV:3 eV]	3.72	24.10	3.466
[−10 eV:3 eV]	3.71	24.08	3.434
[−7 eV:2 eV]	3.40	23.73	3.799
[−7 eV:3 eV]	3.72	24.10	3.466
[−7 eV:4 eV]	4.05	24.38	3.257

have to be simultaneously considered. On the other hand, when the window is too small, optimization of the Wannier orbitals becomes numerically unstable. In practice we set the energy window 1 slightly wider than the d band. Table I shows the value of U in nickel for different energy windows. As the lower limit of the window is raised, the total spread of the Wannier functions decreases because this quantity is minimized using more degrees of freedom. However, the value of U, as well as the bare Coulomb interaction v, is not sensitive to the lower limit. This is because the lowest band is mainly of 4s character, which at low energy does not mix much with the 3d band. The change in the Wannier functions alters the disentangled band structure, which in turn changes the strength of the screening in $W_r(\mathbf{r},\mathbf{r}')$. This would be the cause of slight decrease in U for a wider window. Concerning the upper limit, the upper bands hybridize more with the 3d band. As the window is widen, U increases gradually, reflecting reduction in the Wannier spread. Even within some appropriate interval of the window width, the spread of the Wannier orbitals as well as transfer and interaction parameters slightly depend on the choice of the window width, and the resultant effective model parameters may depend on this choice as we see in Table I. However, if one correctly solves the models, physical quantities should not depend on these variations.

In the present formulation, in order to obtain a separate set of bands, small off-diagonal matrix elements of the Kohn-Sham Hamiltonian between the d space wave function $|\psi_i\rangle$ constructed from the Wannier orbitals and the r space $|\phi_j\rangle$ are neglected. This is the reason why the anticrossing is avoided. If the energy of this hybridization point in the band dispersion is smaller than the energy scale of interest, one has to keep all of these hybridizing bands in the effective model, because the hybridization effect changes the band dispersion and character of the wave function significantly in the vicinity of the anticrossing points. Also, the d-r excitation energies lie within the energy range of interest, which may affect the response properties of the model. In many correlated materials with d or f electrons, the energy scale is typically of the order of 100 K or lower, which is smaller than the energy crossing points. Therefore, the low-energy models constructed only from the d or f Wannier orbitals may give at least qualitatively reasonable description of the low-energy physics.

IV. SUMMARY

We have proposed a method to calculate the effective interaction parameters for the effective low-energy models of real materials when the bands are entangled. The key point is to first properly orthogonalize the low-energy subspace contained in the model and the complementary high-energy subspace to each other. This orthogonalization by the projection technique enables the disentanglement of the bands. Although physical properties may not sensitively depend, there is still some arbitrariness in the definition of the d space depending on the choice of the energy window in constructing the Wannier functions. However, once the disentangled band structure is obtained, the constraint RPA method can be used to determine the partially screened Coulomb interaction uniquely. Numerical tests for 3d metals show that the method is stable and yields reasonable results. The method is applicable to any system, and applications to more complicated systems, such as interfaces of transition metal oxides are now under way.

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