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Constrained Density Functional Theory Plus the Hubbard $U$ Correction Approach for the Electronic Polaron Mobility: A Case Study of TiO$_2$†

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The formation and migration of polarons have important influences on physical and chemical properties of transition metal oxides. Density functional theory plus the Hubbard $U$ correction (DFT+$U$) and constrained density functional theory (cDFT) are often used to obtain the transfer properties for small polarons. In this work we have implemented the cDFT plus the Hubbard $U$ correction method in the projector augmented wave (PAW) framework, and applied it to study polaron transfer in the bulk phases of TiO$_2$. We have confirmed that the parameter $U$ can have significant impact on theoretical prediction of polaronic properties. It was found that using the Hubbard $U$ calculated by the cDFT method with the same orbital projection as used in DFT+$U$, one can obtain theoretical prediction of polaronic properties of rutile and anatase phases of TiO$_2$ in good agreement with experiment. This work indicates that the cDFT+$U$ method with consistently evaluated $U$ is a promising first-principles approach to polaronic properties of transition metal oxides without empirical input.

Key words: Small polaron, Constrained density functional theory, Density functional theory, the Hubbard $U$ correction

I. INTRODUCTION

Small polarons, excess electrons or holes locally stabilized by surrounding structural distortion, play important roles in determining electronic properties of insulating transition metal oxides [1–3]. Although the basic physical features of small polarons have already been well understood since seminal works by Landau [4], Pekar [5], and Holstein [6], realistic and first-principles-based modeling of small polarons in real materials remains a great challenge [1, 3]. Three issues are particularly crucial for first-principles treatment of small polarons: (i) the formation of small polarons, i.e. the relative stability of the charge localized and structurally distorted polaronic state with respect to the charge delocalized state, (ii) the mobility of small polarons, and (iii) the interactions between small polarons, and between the small polaron and other defects or surface adsorbed species. In this work we are mainly concerned with the first two issues, and recent developments regarding the third issue can be found in Ref.[3]. For the formation of small polarons, widely used treatments based on local density approximation (LDA) or generalized gradient approximation (GGA) of density-functional theory (DFT) suffer from severe difficulty due to the well-known strong correlation error prob-

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lems of LDA/GGA [7, 8], which leads to qualitative failure in describing the formation of small polarons in many cases [3]. Currently this problem is mainly circumvented by using DFT plus the Hubbard $U$ correction (DFT+$U$) [9] or hybrid functionals [10], which can correctly predict the formation of small polarons in many transition metal oxides (see Ref.[3] and references therein), but the quantitative results from them can strongly depend on the values of the Hubbard $U$ or the fraction of the Hartree-Fock exact exchange. For the mobility of small polarons, three types of approaches have been used in recent theoretical studies [3]. Firstly, important information can be obtained by calculating the polaron hopping barrier via the nudged elastic band (NEB) [11] calculation of the transition state [12], or by simplistic linear interpolation scheme [13, 14]. Secondly, one can also model the mobility of small polarons by performing first-principles molecular dynamics [15, 16]. It should be pointed out that these two approaches are under the assumption that the small polaron hopping is an adiabatic process, which is, however, not true in general [13]. The hopping of small polarons can be alternatively considered as electron transfer (ET) from one polaronic site to the neighboring one, and it has been well established that ET processes can be adiabatic or non-adiabatic depending on the strength of electronic coupling between neighboring polaronic sites [17, 18]. The third approach that has been widely used in theoretical study of charge transfer in molecular and biological systems (see, e.g. Ref.[18] for a comprehensive review), and recently intensively explored for polaron dynamics in oxides [13, 19–25], is to combine first-principles calculations with Marcus [17] and Emin-Holstein-Austin-Mott [2] formalisms of charge transfer. This approach has the advantages that the qualitative nature of the polaron dynamics can be discerned based on calculated parameters, and one can obtain quantitatively the charge mobility to be directly compared to experiment. On the other hand, it requires defining diabatic (or charge-localized) states and the coupling between them that characterizes the electron transfer process accompanying the polaron hopping, in which a certain conceptual ambiguity is necessarily involved [18].

In this work, we mainly address the issue of polaron transfer in transition metal oxides by combining DFT+$U$ and the Marcus-Emin-Holstein-Austin-Mott (MEHAM) polaron hopping model. We use the constrained DFT (cDFT) formalism [26, 27] to obtain diabatic states and the coupling parameter between them, which was originally developed for molecular systems [28, 29], and recently also used for extended systems [20, 22, 24, 30]. We use the Hubbard $U$ correction in cDFT to overcome the strong correlation error of LDA/GGA, and the Hubbard $U$ is determined by the cDFT method itself. We have implemented cDFT+$U$ in the projector augmented-wave (PAW) method [31] in the VASP code [32, 33]. As a validation of our implementation, we have investigated the mobility of small polarons in the rutile and anatase phase of TiO$_2$, which has become the most studied prototypical polaronic material (see Ref.[3] for a comprehensive review).

The paper is organized as follows. In Section II we present the theory about constrained-DFT and the MEHAM model for small polaron transfer, and the implementation of cDFT in the PAW framework. In Section III we present the results of polaron formation and transfer in TiO$_2$ from DFT+$U$ and cDFT+$U$ calculations, and make some comparison with previously published results. In Section IV we summarizes main findings of this work.

II. METHOD AND TECHNICAL DETAILS

A. Marcus-Emin-Holstein-Austin-Mott model for small polaron transfer

The key parameters involved in a symmetric polaron transfer process are illustrated in FIG.1, including the diabatic barrier $\Delta E^*$, the reorganization energy $\lambda$, the adiabatic barrier $E_a$, and the electronic coupling term.

![FIG. 1 General feature of the symmetric polaron transfer along one dimensional reaction path. $q_A$ and $q_B$ are the polaron structure at site A and one of its adjacent site B. $q_T$ is the transition structure. Blue and red curves stand for two diabatic potential surfaces with electronic configuration $\Psi_A$ and $\Psi_B$ respectively. Two green curves are ground and excited adiabatic potential surfaces. $\Delta E^*$ is the diabatic barrier, $E_a$ is the adiabatic barrier, $V_{AB}$ is the electronic coupling parameter and $\lambda$ is the reorganization energy.](https://example.com/fig1.png)
V_{AB}. Assuming the parabolic diabatic surfaces, \( \lambda \) equals 4\( \Delta E^* \). Neglecting the nuclear quantum tunneling effect, the rate constant for polaronic charge transfer can be calculated in the terms of semi-classical transition state theory as follows [18, 34, 35],

\[
k_{AB} = \nu_n \kappa_{el} \exp \left( - \frac{E_a}{k_B T} \right) \tag{1}
\]

In Eq.(1), \( \nu_n \) is the effective vibration frequency along the reaction coordinate of the charge transfer, and \( \kappa_{el} \) is the electronic transmission coefficient, which can be evaluated in terms of the Landau-Zener semiclassical model [36–38]:

\[
\kappa_{el} = \frac{2P_{LZ}}{1 + P_{LZ}} \tag{2}
\]

with

\[
P_{LZ} = 1 - \exp \left( - \frac{\pi^{3/2} |V_{AB}|^2}{\hbar \nu_n \sqrt{\lambda k_B T}} \right) \tag{3}
\]

Depending on the strength of the electronic coupling, the kinetics of polaron transfer can be roughly categorized into different regimes. In the adiabatic limit, in which \( V_{AB} \) is large and \( \kappa_{el} \approx 1.0 \), the charge transfer rate constant is given by the well-known transition state theory

\[
k^{(a)}_{AB} = \nu_n \exp \left( - \frac{E_a}{k_B T} \right) \tag{4}
\]

In the nonadiabatic limit, in which \( V_{AB} \) is small and \( \kappa_{el} \ll 1.0 \), corresponding to the non-adiabatic regime, one obtains

\[
k^{(na)}_{AB} = \frac{2\pi}{\hbar} \frac{|V_{AB}|^2}{\sqrt{4\pi \lambda k_B T}} \exp \left( - \frac{\Delta E^*}{k_B T} \right) \tag{5}
\]

which is the well-known Marcus rate equation of electron transfer [17, 34, 39]. Marcus’s ET theory is essentially equivalent to the Emin-Holstein-Austin-Mott (EHAM) model of small polarons in the literature of condensed matter physics [2, 40, 41], and therefore we term the formalism presented above as the MEHAM polaronic model.

In general the adiabatic barrier \( E_a \) is related to the diabatic barrier \( \Delta E^* \) by

\[
E_a = \Delta E^* - |V_{AB}| + \left( \sqrt{\frac{\lambda^2}{4} + |V_{AB}|^2} - \frac{\lambda}{2} \right) \tag{6}
\]

The last bracketed term in Eq.(6) is a correction arising from the fact that the finite electronic coupling \( V_{AB} \), which is assumed to be constant as a function of \( q \) (Condon approximation [42]), can stabilize the adiabatic state energy at the initial structure (i.e. \( q_A \) in FIG.1) [18]. In the case of vanishingly small \( V_{AB} \), one obtains the well-known relation between the adiabatic and diabatic barrier,

\[
E_a = \Delta E^* - V_{AB} \tag{7}
\]

The adiabatic rate constant depends on \( \nu_n \) and \( E_a \) only, and both of them can be readily obtained from first-principles calculation. In particular, the adiabatic transition state can be determined by standard techniques like NEB [11], and \( \nu_n \) can be calculated in terms of transition state theory [24],

\[
\nu_n = \frac{k_B T Q_{TS}}{\hbar} \frac{Q_A}{Q_A} \tag{8}
\]

where \( Q_{TS} \) and \( Q_A \) are partition function corresponding to the adiabatic transition state and the initial ground state, respectively. The calculation of the non-adiabatic rate constant is more challenging since it depends on the reorganization energy \( \lambda \), the diabatic barrier \( \Delta E^* \) and the electronic coupling parameter \( V_{AB} \), all of which depend on the charge localized diabatic states that are not uniquely defined [18]. A lot of efforts have been invested in methodological developments for the modeling of nonadiabatic charge transport in solution, biological systems and molecular materials, which have been comprehensively reviewed recently [18, 35].

Physically the electronic coupling between different polaronic states in transition metal oxides can be weak, and it is difficult to know a prior whether the polaron transfer falls in the adiabatic or non-adiabatic regime. In this work we evaluate the key parameters in the MEHAM polaronic model based on the constrained DFT method, which has been developed by several groups [20, 22, 30] since the seminal work by Wu et al. for molecular systems [28, 29].

**B. Orbital-projector based constrained density-functional theory plus the Hubbard \( U \) correction**

We give a brief introduction to the constrained DFT method implemented in this work following the similar formalism used by Wu et al. [28, 29, 43]. We drop the spin index to simplify the notation. As first proposed
by Dederichs et al. [26], the essence of the cDFT is to introduce a physically motivated constraint to the ground state DFT to obtain electronic states with certain physical characters that can not be accessed by conventional DFT. In the previous cDFT formalism of electron transfer, the constraint is defined in terms of the number of electrons in a predefined region, often by some weight function \( w_c(r) \)

\[
\int w_c(r)\rho(r)dr = N_c
\]

where \( \rho(r) \) is the electron density, and \( N_c \) is the target number of electrons related to the particular constraint denoted by \( c \), which will be further elaborated soon. The constraint can be more generally represented as the trace of the product between a constraining projector \( \hat{P}_c \) and the one-electron Kohn-Sham density operator

\[
\hat{\rho} \equiv \sum_{i\in\text{occ}} |\psi_i\rangle\langle\psi_i|
\]

with \( \psi_i \) being Kohn-Sham orbitals,

\[
\text{Tr} \left( \hat{P}_c \hat{\rho} \right) \equiv \int P_c(r,r')\rho(r',r)drdr' = N_c
\]

where \( \rho(r, r') \) is one-electron density matrix,

\[
\rho(r, r') = \sum_{i\in\text{occ}} \psi_i(r)\psi_i^*(r')
\]

To be more specific, the constraining projector is often defined in terms of a set of ortho-normal local orbitals \( \phi_m \) with given physical characters as

\[
\hat{P}_c = \sum_m |\phi_m\rangle\langle\phi_m|
\]

and its real-space representation, termed as the projection function henceforth, is therefore

\[
P_c(r, r') \equiv \sum_m \phi_m(r)\phi_m^*(r')
\]

Introducing the Lagrange multiplier \( \mu_c \) related to the constraint \( c \), the cDFT method can be formulated as the following variational problem [43],

\[
E(N_c) = \min_{\rho} \max_{\mu_c} \left[ E_{\text{DFT}}(\rho) + \sum_c \mu_c \left( \text{Tr} \hat{P}_c \hat{\rho} - N_c \right) \right]
\]

where \( E_{\text{DFT}} \) is the total energy functional with a certain density functional approximation to the exchange-correlation energy. The corresponding Kohn-Sham equation with the constraint can be written as (atomic units are used through the paper)

\[
\left( -\frac{1}{2} \nabla^2 + V_{\text{KS}} + \sum_c \mu_c \hat{P}_c \right) |\psi_i\rangle = \varepsilon_i |\psi_i\rangle
\]

where \( V_{\text{KS}} \) is the Kohn-Sham effective potential in a certain density-functional approximation (DFA), which is local in the local density approximation (LDA) or generalized gradient approximation (GGA) method, and non-local when using hybrid functionals.

In practice, the cDFT equations are often solved in a dual-loop scheme: in the inner loop, the Kohn-Sham equation (Eq.(16)) with a fixed constraining parameter \( \mu_c \) is solved self-consistently; and in the outer loop, the value of \( \mu_c \) is adjusted such that the constraint as represented by Eq.(11) is satisfied. Alternatively, one can also treat the determination of the \( \mu_c \) as the internal loop and update the Kohn-Sham potential as the outer loop. It has been proved in terms of first-order perturbation theory that the solution of these nonlinear equations always exists [29].

Considering the fact that LDA/GGA cannot describe the formation of electronic small polarons in transition metal oxides, we use the DFT+\( U \) in the cDFT calculation implemented in the projector-augmented wave (PAW) framework. In particular, we use the isotropic form of the DFT+\( U \) [44, 45], and the Hubbard \( U \) correction term is defined in terms of the same set of projection functions as those used in cDFT. The working equation for the cDFT+\( U \) reads

\[
\left( -\frac{1}{2} \nabla^2 + V_{\text{KS}} + \delta \hat{V}_U + \sum_c \mu_c \hat{P}_c \right) |\psi_i\rangle = \varepsilon_i |\psi_i\rangle
\]

with [46]

\[
\delta \hat{V}_U = U \sum_{m,m'} \left( \frac{1}{2} \delta_{mm'} - n_{mm'} \right) |\phi_m\rangle\langle\phi_{m'}|
\]

One of the key issues in DFT+\( U \)-based calculations is how to choose the value of the Hubbard \( U \), which has a significant influence on the results of DFT+\( U \). DFT+\( U \) has been widely used in polaronic properties in TiO\(_2\), and a wide range of \( U \) values, from 2.5 eV to 10 eV [13, 16, 21, 47, 48], has been used based on different considerations. In this work we evaluate the
Hubbard $U$ by using the cDFT, similar to the linear response approach [49],
\begin{equation}
U = \frac{\Delta \mu_c}{\Delta N^0} - \frac{\Delta \mu_c}{\Delta N_c}
\end{equation}
where $\Delta \mu_c$ is a slight variation of the constraining parameter $\mu_c$ in Eq.(16), and $\Delta N_c$ is the induced change in the number of the constrained electrons as a response to $\Delta \mu_c$. $\Delta N^0_c$ is the variation of the constrained electron number caused by changing $\mu_c$ but fixing $V_{KS}(r)$ in Eq.(16) [49].

C. Evaluation of electronic coupling by cDFT

By imposing different constraints, we can use cDFT to obtain electronic states of different characters for a given structure. For the polaron transfer process as illustrated in FIG. 1 in particular, we can obtain Kohn-Sham determinant wave-functions $\Phi_A(q)$ and $\Phi_B(q)$ that represent the polaronic states A and B, respectively, along the reaction coordinate $q$. This is in contrast to the direct (i.e. without constraints) treatment by DFT+$U$ or the hybrid functional approach, in which for a given structure, only one state, usually interpreted as the adiabatic ground state, can be obtained. On the other hand, since these states are not orthogonal, they can not be directly identified as diabatic states as required by the MEHAM model. As a common practice in the construction of diabatic states, one can first use $\Phi_A(q)$ and $\Phi_B(q)$ as the basis to build the Hamiltonian matrix,
\begin{equation}
\hat{H} = \begin{bmatrix}
\hat{H}_{AA} & \hat{H}_{AB} \\
\hat{H}_{BA} & \hat{H}_{BB}
\end{bmatrix}
\end{equation}
with
\begin{equation}
\hat{H}_{IJ} = \langle \Phi_I | \hat{H} | \Phi_J \rangle, \quad I, J = A \text{ or } B
\end{equation}

One can use the full many-electron Hamiltonian to evaluate the matrix elements in Eq.(21), as it is often done in the framework of the Hartree-Fock theory. In the DFT framework, however, it is more common to obtain these matrix elements from the Kohn-Sham total energies,
\begin{equation}
\hat{H}_{II} = E^{(KS)}_I, \quad I = A \text{ or } B
\end{equation}
\begin{equation}
\hat{H}_{AB} = \frac{F_A + F_B}{2} S_{AB} - \sum_c \frac{\mu^A_c + \mu^B_c}{2} P_{c,AB}
\end{equation}
where $E^{(KS)}_I$ are the total energy from the cDFT calculation excluding the contribution of the constrain potentials,
\begin{equation}
F_I = E^{(KS)}_I + \sum_c N^I_c \mu^I_c
\end{equation}
\begin{equation}
S_{AB} = \langle \Phi_A | \Phi_B \rangle
\end{equation}
\begin{equation}
P_{c,AB} \equiv \langle \Phi_A | \sum_i \hat{P}_c(i) | \Phi_B \rangle
\end{equation}

Conceptually the treatment above can be justified by considering that the Kohn-Sham determinant wave function is not expected to be a good approximation to the true many-electron wave function, while the Kohn-Sham total energy within a certain density-functional approximation can be regarded as a good approximation to the true total energy.

The Hamiltonian matrix corresponding to orthogonal diabatic states can be obtained by introducing a certain orthogonalization transform to $\hat{H}$, which is non-unique. Different orthogonalization schemes are used in the literature. In the original work of Wu et al. [43], $\hat{H}$ is orthogonalized by the requirements that the constraining potential is diagonal after orthogonalization. A more straightforward one is the Löwdin (symmetric) orthogonalization [20],
\begin{equation}
\hat{H} \equiv \begin{bmatrix}
H_{AB} & V_{AB} \\
V_{AB} & H_{BB}
\end{bmatrix} = S^{-1/2} \hat{H} S^{-1/2}
\end{equation}
\begin{equation}
S = \begin{bmatrix}
1 & S_{AB} \\
S_{BA} & 1
\end{bmatrix}
\end{equation}

In the case when $\Phi_A$ and $\Phi_B$ are real wavefunctions, one can explicitly have
\begin{equation}
V_{AB} = \frac{1}{1 - S_{AB}^2} \left( \hat{H}_{AB} - \frac{\hat{H}_{AA} + \hat{H}_{BB}}{2} S_{AB} \right)
\end{equation}
\begin{equation}
H_{AA} = \frac{1 + \sqrt{1 - S_{AB}^2}}{2(1 - S_{AB}^2)} \hat{H}_{AA} + \frac{2S_{AB}}{2(1 - S_{AB}^2)} \hat{H}_{AB}
\end{equation}
\begin{equation}
H_{BB} = \frac{1 + \sqrt{1 - S_{AB}^2}}{2(1 - S_{AB}^2)} \hat{H}_{BB} + \frac{2S_{AB}}{2(1 - S_{AB}^2)} \hat{H}_{AB}
\end{equation}

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In practice, $S_{AB}$ and the matrix element of constraining operator $\hat{P}$ between non-orthogonal cDFT KS determinant wave functions $\Phi_A$ and $\Phi_B$ can be calculated by using the general rules for the matrix elements between determinants made of non-orthogonal orbitals [50]. In particular, $S_{AB}$ is equal to the determinant of the following matrix,

$$
S_{AB} = \begin{bmatrix}
S_{11}^{AB} & S_{12}^{AB} & \cdots & S_{1N}^{AB} \\
S_{21}^{AB} & S_{22}^{AB} & \cdots & S_{2N}^{AB} \\
\vdots & \vdots & \ddots & \vdots \\
S_{N1}^{AB} & S_{N2}^{AB} & \cdots & S_{NN}^{AB}
\end{bmatrix}
$$

(32)

with

$$
S_{ij}^{AB} = \langle \psi_i^A | \psi_j^B \rangle
$$

(33)

$$
P_{c,AB} = \sum_{i,j} P_{cij} S_{ij}^{AB}
$$

(34)

$$
P_{cij} = \langle \psi_i^A | \hat{P}_c | \psi_j^B \rangle
$$

(35)

In Eq.(34), $S_{ij}^{AB}$ denotes the cofactor corresponding to $S_{ij}$, i.e. $(-1)^{i+j}$ times the determinant of the matrix obtained by removing the $i$-th row and $j$-th column of $S_{AB}$.

D. Implementation in the PAW framework

One of the most important ingredients for the implementation of cDFT is the local projector that defines the constraining subspace. In this work we implement the cDFT in the PAW framework, in which the local projection operator takes a more complicated form than Eq.(13). Again we drop the spin index to simplify the notation. In the PAW approach, the whole space is divided into the augmentation region, denoted as $\Omega$ henceforth, which are the areas around atomic centers within certain spherical radii, and the interstitial region, denoted as $\bar{\Omega}$. All-electron (AE) Kohn-Sham orbitals $|\psi_i\rangle$ are related to pseudo(PS)-orbitals $|\tilde{\psi}_i\rangle$ by a set of PAW projectors in terms of [31, 51]

$$
|\psi_i\rangle = |\tilde{\psi}_i\rangle + \sum_\lambda \left( |\phi_\lambda\rangle - |\tilde{\phi}_\lambda\rangle \right) \langle p_\lambda | \psi_i \rangle
$$

(36)

$|\phi_\lambda\rangle$ and $|\tilde{\phi}_\lambda\rangle$ with $\lambda=(I, \nu, l, m)$ are AE and PS partial waves that are defined on a particular atom indexed by $I$ with angular quantum numbers $l$ and $m$ at certain reference energy $\epsilon_{rl}$. $|p_\lambda\rangle$ are the PAW projector functions that satisfy the following completeness relation,

$$
\sum_\lambda |\tilde{\phi}_\lambda\rangle \langle p_\lambda | = \hat{I}_\bar{\Omega}
$$

(37)

where $\hat{I}_\bar{\Omega}$ denotes the identity operator in the augmentation region $\Omega$. Using the completeness relation above, Eq.(36) can also be written as

$$
|\psi_i\rangle = \hat{I}_\bar{\Omega} |\tilde{\psi}_i\rangle + \sum_\lambda |\phi_\lambda\rangle \langle \tilde{\phi}_\lambda | \psi_i \rangle
$$

(38)

where $\hat{I}_\Omega$ indicates the identity operator in the interstitial region. Obviously the first term in Eq.(38) vanishes in the augmentation region, and the second term vanishes in the interstitial region.

Assuming the Hubbard $U$ correction is applied to the states with the characters of angular quantum number $l$ on the target atom $t$, collectively denoted as $c\equiv(t,l)$, the projection function used to calculate local density matrix can be written as [52, 53]

$$
P_{tl}^{\nu_1
u_2}(r, r') = \frac{1}{r} \delta_\Omega(r) \delta(r-r') Y_{lm_1}^* (\hat{r}) Y_{lm_2}(\hat{r'})
$$

(39)

where $\delta_\Omega(r)$ is equal to 1 for $r$ falling in the augmentation sphere corresponding to the target orbitals $c$. The local density matrix in the PAW framework can then be calculated from the pseudo-wavefunctions $|\tilde{\psi}_i\rangle$ as [52]

$$
n_{m_1m_2}^{tl} = \sum_{\nu_1\nu_2} \rho_{\nu_1\nu_2} Y_{lm_1}^{*}_{\nu_1} \rho_{\nu_2} Y_{lm_2}(\nu_2) O_{\nu_1\nu_2}^{tl}
$$

(40)

where $\rho_{\nu_1\nu_2} Y_{lm}(\nu_2)$ is the PAW occupation matrix generally defined as [51]

$$
\rho_{\lambda_1\lambda_2} = \sum_{I\in\text{occ}} \langle \tilde{\phi}_{\lambda_1} | \hat{P}_{\lambda_2} | \tilde{\phi}_{\lambda_2} \rangle
$$

(41)

and

$$
O_{\nu_1\nu_2}^{tl} \equiv \langle R_{\nu_1l} | R_{\nu_2l} \rangle
$$

(42)

with $R_{\nu l}$ being the radial part of the AE partial wave $\phi_\lambda$. The number of electrons with spin $\sigma$ occupying the target orbitals $c\equiv(t, l)$ can be calculated as

$$
n_{tl} = \sum_m n_{c,m\sigma}
$$

(43)

$$
= \sum_m \sum_{\nu_1\nu_2} \langle \tilde{p}_{\nu_1\nu_2} | \hat{p} | p_{\nu_1\nu_2} \rangle O_{\nu_1\nu_2}
$$

(43)

from which we can obtain the expression for the local
projection operator corresponding to the target orbitals $c$ as
\[ \tilde{P}_c = \sum_{m} \sum_{\nu, \nu'} O_{\nu, \nu'}^c |p_{\nu,lm}\rangle \langle p_{\nu',lm}| \] (44)

Using Eq.(36), and assuming that the PS orbitals are expanded by plane-waves, denoted as $|\phi_G\rangle$,
\[ |\tilde{\psi}_i\rangle = \sum_G c_{G,i} |\phi_G\rangle \] (45)

$S_{i,j}^{AB}$ defined in Eq.(33) can be calculated as
\[ S_{i,j}^{AB} = \sum_G A_{G,i}^{A} B_{G,j}^{B} + \sum_{l,l',m,m',\nu\nu'} p_{l,lm,i}^{A} p_{l',lm',j}^{B} Q_{\nu\nu'}^{ll'} \] (46)

where
\[ Q_{\nu\nu'}^{ll'} = \langle R_{l\nu} | R_{l'\nu'} \rangle - \langle R_{l\nu} | R_{l'\nu'} \rangle \] (47)

and
\[ p_{X,i}^{X} = \langle \tilde{p}_X | \psi_i^{X} \rangle, \quad X = A \text{ or } B \] (48)

Using $\tilde{P}_c$ given in Eq.(44), the evaluation of $P_{ij}^{AB}$ defined in Eq.35 is straightforward,
\[ P_{c,ij}^{AB} = \sum_{\nu\nu'} O_{\nu\nu'}^{c} \sum_{m} p_{l\nu,lm,i}^{A} p_{l'\nu',lm',j}^{B} Q_{\nu\nu'}^{ll'} \] (49)

### III. CASE STUDY: POLARON TRANSFER IN TiO$_2$

In this work, we apply the method presented in the preceding section to investigate polaron hopping dynamics in the rutile and anatase phase of TiO$_2$, the prototypical polaronic transition metal oxide that has attracted tremendous interest because of the ubiquitous importance of TiO$_2$ in photovoltaics, photocatalysis and photoelectrochemistry. Recent experimental and theoretical studies of properties of excess electrons in TiO$_2$ have been comprehensively reviewed in Refs.[3, 54]. There have been a series of works devoted to theoretical understanding of polaronic properties in bulk phases [13, 14, 16, 21, 55-63] and surfaces [15, 47, 64-67] of TiO$_2$.

All cDFT+$U$ calculations in this work are performed by using a locally modified version of the VASP package (version 5.4) [32, 33]. We use the PBEsol [68] functional plus the Hubbard $U$ correction in the isotropic scheme [44]. The energy cutoff for the plane wave expansion is set to 400 eV. The core-valence interaction is treated by the PAW approach in which 3p electrons of Ti are treated as valence. For the calculation of the Hubbard $U$ in terms of Eq.(19), using $\Delta E_c$ of 0.05 eV and 0.001 eV leads to $U$ equal to 3.9 eV and 4.1 eV, respectively. Therefore we use $U=4.0$ eV in all subsequent calculations unless stated otherwise. We note that this Hubbard $U$ value is close to the values used in the literature that were evaluated by the linear response approach [69] or constrained random phase approximation [55].

We take the following procedures to calculate the polaron transfer properties of TiO$_2$: (1) Using a super-cell of certain size, the initial state structure ($q_A$ in FIG. 1) with an excess electron is relaxed by DFT+$U$ to obtain the geometric structure with the small polaron stabilized on the initial site, and the final state structure ($q_B$ in FIG. 1) is obtained in a similar way; (2) The structure of the transition state ($q_T$ in FIG. 1) is obtained by a linear interpolation between $q_A$ and $q_B$ structures, $q_T=0.5q_A+0.5q_B$; (3) The cDFT calculations at $q_T$ with charge distribution constrained to that of the initial and final polaron state respectively are carried out, from which the diabatic energy barrier $\Delta E^*$ and the wave functions $\Phi_A$ and $\Phi_B$ are obtained; (4) The electronic coupling parameter $V_{AB}$ at $q_T$ is then calculated in terms of the formalism presented in the preceding section. The supercells of $2\times2\times3$ and $3\times3\times1$ are used for rutile and anatase, respectively. We use a $k$-mesh of $4\times4\times4$ for Brillouin zone sampling. For the directions of polaron transfer, we consider (001) and (111) for rutile, and (100) and (201) for anatase, as illustrated in FIG. 2. Only Kohn-Sham orbitals on the $\Gamma$ ($k=0$) point are used in the calculation of electronic couplings. We have found that using a larger super-cell leads to similar results, which verifies the validity of our treatment.

We first characterize the formation of small polaron in the rutile and anatase phase of TiO$_2$ by checking the density of states (DOS) calculated with two different Hubbard $U$ parameters ($U=4.0$ and 6.0 eV), as shown in FIG. 3. The most distinctive feature of small polarons in terms of DOS is the presence of a narrow peak with mainly Ti-d characters within the band gap [3], which is well reproduced in our DFT+$U$ calculations. In both rutile and anatase, increasing the Hubbard $U$ value pushes the energy of polaronic peak towards lower energy, which is consistent with the general effect of the
Hubbard $U$ correction. On the other hand, rutile and anatase show significantly different polaronic features. With $U=4.0$ eV, the polaronic peak in rutile is about 0.8 eV below the conduction band minimum (CBM); in contrast, the polaronic peak is very close to the CBM edge in anatase, indicating that the small polaron is not stable in anatase, which is consistent with the findings of previous theoretical studies and recent experimental measurements [3, 16]. Using $U=6.0$ eV would predict the small polaron in anatase is also stable, which clearly indicates the crucial importance of using the physical $U$ to obtain correct physics.

To further investigate the effects of Hubbard $U$ on the key parameters of small polaron transfer, FIG. 4 shows the dependence of the diabatic barrier $\Delta E^*$, the adiabatic barrier $E_a$, the electronic coupling $V_{AB}$ and the overlap integral $S_{AB}$ along different crystalline directions in rutile and anatase as a function of the Hubbard $U$. For rutile, we consider $U$ in the range from 3.0 eV to 6.0 eV, and for anatase, we consider $U$ from 4.0 eV to 6.0 eV, since stable polaronic structure can not be formed with a smaller $U$ value. All these parameters exhibit strong dependence on the value of the Hubbard $U$. For example, in rutile, the diabatic barriers along (001) and (111) increase by about 0.15 and 0.1 eV, respectively, when $U$ increases from 3.0 eV to 6.0 eV. The overlap integrals $S_{AB}$ and electronic coupling parameter $V_{AB}$ decrease significantly as $U$ increases, especially for rutile (001), anatase (100) and (201), which is consistent with the general trend that increasing $U$ enhances the localization of polaronic states.

We can see that the results along different crystalline directions differ significantly. For rutile, the diabatic barrier ($\Delta E^*$) along (001) is about 0.08 eV lower than that along (111) at $U=3$ eV, and the difference decreases for larger $U$, but remains to be about 0.03 eV with $U=6.0$ eV. The values of $S_{AB}$ and $V_{AB}$ along the (001) direction are considerably larger than those along (111), which, combined with the difference in $\Delta E^*$, results in even more significant difference in the adiabatic barrier, which is larger than 0.1 eV with $U=4.0$ eV. The dependence on the crystalline direction is significantly weaker in anatase, as indicated by nearly identical $\Delta E^*$ along the direction (100) and (201). There are some difference in $S_{AB}$ and $V_{AB}$, such that the adiabatic barrier differs by about 0.02 eV. We note that such anisotropy in migration parameters were also reported in previous studies [13, 21, 60].

From the results of the overlap integral and the electronic coupling, one can see that the coupling between the adjacent polaronic sites in anatase is much stronger than that in rutile, which leads to much lower adiabatic barrier for the polaron transfer in anatase. With $U=4.0$ eV, the adiabatic barrier in anatase essentially disappears, which indicates that small polaron is not stable in anatase, consistent with the features observed.
FIG. 4 The results of diabatic barrier $\Delta E^*$, adiabatic barrier $E_a$, electron coupling $V_{AB}$ and overlap integral $S_{AB}$ of rutile and anatase in different $U$ value.

TABLE I The results of diabatic barrier $\Delta E^*$, adiabatic barrier $E_a$, electronic coupling $V_{AB}$, reorganization energy $\lambda$, the transmission probability $\kappa$ and the transfer rate constant $k$ (using Eq.(1)) calculated at $T=300$ K with $U=4.0$ eV. For comparison the transfer rates from other works are shown.

<table>
<thead>
<tr>
<th>Direction</th>
<th>$\Delta E^*/eV$</th>
<th>$\Delta E_a/eV$</th>
<th>$V_{AB}/eV$</th>
<th>$\lambda/eV$</th>
<th>$\kappa/eV$</th>
<th>$k_{AB}/s^{-1}$</th>
<th>$k/s^{-1}$ in other work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile</td>
<td>(001) 0.200 0.090 0.131 0.796 1.000 7.4$\times$10$^{11}$</td>
<td>7.7$\times$10$^{13}$</td>
<td>5.6$\times$10$^{13}$</td>
<td>5.6$\times$10$^{13}$</td>
<td>5.6$\times$10$^{13}$</td>
<td>5.6$\times$10$^{13}$</td>
<td>5.6$\times$10$^{13}$</td>
</tr>
<tr>
<td>Anatase</td>
<td>(111) 0.325 0.228 0.007 0.920 0.034 1.2$\times$10$^8$</td>
<td>3.7$\times$10$^6$</td>
<td>8.1$\times$10$^{10}$</td>
<td>8.1$\times$10$^{10}$</td>
<td>8.1$\times$10$^{10}$</td>
<td>8.1$\times$10$^{10}$</td>
<td>8.1$\times$10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>(201) 0.109 0.011 0.100 0.427 0.997 1.6$\times$10$^{12}$</td>
<td>1.7$\times$10$^8$</td>
<td>5.4$\times$10$^7$</td>
<td>5.4$\times$10$^7$</td>
<td>5.4$\times$10$^7$</td>
<td>5.4$\times$10$^7$</td>
<td>5.4$\times$10$^7$</td>
</tr>
</tbody>
</table>

in the DOS discussed above. If $U=4.0$ eV is the proper choice for TiO$_2$ as suggested from our cDFT calculations and previous theoretical study [55, 69], the polaronic state in anatase falls in the large polaron regime, which agrees well with the conclusions in recent experimental and theoretical works [16, 19, 62].

In Table I, we show the key parameters relevant to the small polaron transfer in the rutile and anatase of TiO$_2$ calculated by cDFT+U with $U=4.0$ eV. The ratio of $\lambda$ to $\Delta E^*$ is very close to 4, indicating that the diabatic potential curves obtained from cDFT are close to parabola, verifying the validity of the MEHAM model. The calculated transmission probability $\kappa_{ad}$ along the (001) direction in rutile is close to 1.0, while that along the (111) direction is much smaller than 1.0, which implies that the transfer along (001) is an adiabatic process while the one along (111) is non-adiabatic and mainly through quantum tunneling. As a result, the rate constant of the former is about four order of magnitude larger than that of the latter. Overall the rate constants calculated in this work are in reasonable agreement with the results from previous works [13, 60]. For anatase, as we have discussed above, small polarons are not stable with $U=4.0$ eV, and therefore rigorously speaking the rate constant for charge transport cannot be evaluated in the same way as in rutile. Theoretical approaches for large polaron dynamics (e.g. Ref.[70]) should be used for charge mobility in anatase. Nevertheless, the transfer rate constant in anatase in terms of Eq.(1), which, of course, should be taken with caution for the reason stated above, is about two order of magnitude larger than that in rutile, qualitatively consistent with the experimental findings that anatase has a larger electron mobility than rutile [3]. In contrast, the transition rate constant of anatase given by previous works [13, 21] is smaller than that in rutile, inconsistent with...
experiment. In Ref. [13], the polaronic structure and the diabatic barrier was obtained by using DFT+U with \( U = 10.0 \) eV, and the electronic coupling parameter was then obtained by a Hartree-Fock calculation based on a cluster model. One can expect that with such a large \( U \), it is very likely that the transition barrier is overestimated, and the electronic coupling from Hartree-Fock wavefunctions, which tend to be over-localized [7], is underestimated.

IV. CONCLUSIONS

To summarize, we have implemented the constrained density functional theory and the procedure of calculating the electronic coupling parameter in the PAW framework based on the VASP code [32, 33]. Transfer of polarons in rutile and anatase phase of TiO\(_2\) is exploited as a prototypical example to investigate the performance of combining cDFT and the Hubbard \( U \) correction approach in studying polaron transfer properties. We find that all key properties relevant to polaron transfer are strongly affected by the Hubbard \( U \) value. With increasing \( U \), the small polaron becomes more stabilized, the energy barrier increases and the electronic coupling parameter decreases significantly, which can change the microscopic mechanism of charge transfer from adiabatic to non-diabatic. We proposed that the physical Hubbard \( U \) evaluated based on first principle calculations (e.g. cDFT) should be used in the simulation of small polaron cDFT, which, in the case of TiO\(_2\), leads to polaronic properties of rutile and anatase consistent with experiment.

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