Polaronic hole localization and multiple hole binding of acceptors in oxide wide-gap semiconductors

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Acceptor-bound holes in oxides often localize asymmetrically at one out of several equivalent oxygen ligands. Whereas Hartree-Fock (HF) theory overly favors such symmetry-broken polaronic hole localization in oxides, standard local-density (LD) calculations suffer from spurious delocalization among several oxygen sites. These opposite biases originate from the opposite curvatures of the energy as a function of the fractional occupation number n, i.e., $d^2E/dn^2 < 0$ in HF and $d^2E/dn^2 > 0$ in LD. We recover the correct linear behavior, $d^2E/dn^2 = 0$, that removes the (de)localization bias by formulating a generalized Koopmans condition. The correct description of oxygen hole localization reveals that the cation-site nominal single acceptors in ZnO, In_2O_3, and SnO_2 can bind multiple holes.

I. INTRODUCTION

Experimental evidence for cation-site acceptors in wide-gap oxides demonstrates that holes often lock into individual oxygen ligands instead of being distributed over all symmetry-equivalent oxygen sites, e.g., in case of Al_{Si} in SiO_2 or Li_{Zn} in ZnO.[1–4] Formally, the hole binding can be described by the change in the oxidation state of individual O atoms from the normal O^{-II} in to an O^{-I} state. A systematically consistent theoretical description of such acceptor states remains, however, challenging as common density-functional theory (DFT) calculations in the local density approximation (LDA) or generalized gradient approximation (GGA) fail to reveal the correct hole localization on just one O atom and the associated lattice relaxation effects. This failure has been traced back to a residual self-interaction present within the O p shell in LDA or GGA.[5–7] Hartree-Fock (HF) theory, on the other hand, is known to overestimate the tendency toward hole localization on individual lattice sites.[4] The correct description of the balance between competing tendencies toward single-site localization vs delocalization among equivalent sites bears great importance for physical phenomena such as hyperfine interactions,[6] magnetism without d elements,[7–10] and p-type doping in wide-gap oxides.[11,12]

A number of electronic structure methods are able to restore the qualitative picture of single-site localization, e.g., self-interaction correction,[6,7] DFT$+U$,[8,9,13] and hybrid DFT.[14,15] However, a guiding principle as to how to select free parameters (e.g., U in DFT$+U$ or the fraction of HF exchange in hybrid DFT) has been missing. In order to achieve a systematical quantitative description of hole localization, we first formulate the condition that assures that the energies of the unoccupied hole states (hs) are correctly placed relative to the spectrum of occupied states. Second, we define an on-site occupation-dependent potential that serves to increase, relative to DFT, the energy splitting between occupied and unoccupied states. By determining the strength of this potential such that the general condition of the first step is fulfilled, we achieve a consistent description of localization vs delocalization without relying on empirical

parameters. Applying the present method to the case of cation-vacancies along the series of Zn-chalcogenide semiconductors, we have recently[10] demonstrated that the correct description of the energy splitting between occupied and unoccupied anion-p orbitals is decisive for the structural, electronic, and magnetic properties of the vacancies. Interestingly, the creation of an energy separation between the occupied and unoccupied anion-p states, and the resulting localization of the holes, is observed not only for first-row anions elements like O, for which such correlation effects have been discussed before,[7–9] but also for much heavier anions including Te.[10] In the present work, we employ this method to quantitatively predict the acceptor transition energies for the cation-site acceptors in ZnO, In_2O_3, and SnO_2. In all studied cases, we find that these acceptors introduce states at rather deep energies inside the band gap and can bind even multiple holes despite the fact that from their position in the periodic table they are expected to be single acceptors. Thus the correct description of the energy splitting between occupied and unoccupied anion-p states and the respective localization of the acceptor-holes has important ramifications for the prediction of p-type doping of oxides.

II. REMOVAL OF THE NONLINEARITY OF $E(N)$

The key for the correct description of localized oxygen hole states, as present in the case of acceptor-bound small polarons in oxides,[3] lies in the observation that LDA/GGA and HF theory produce errors of opposite sign in the energy E between adjacent integer occupation numbers n_i of the highest occupied state i.[16,17] As illustrated schematically in Fig. 1(a), in HF theory the energy is a *concave* function of the (continuous) occupation number, $d^2E/dn_i^2 < 0$, but it is generally a *convex* function, $d^2E/dn_i^2 > 0$, in LDA or GGA. The correct behavior, however, would be linear,[16–18] i.e.,

$$d^2E/dn_i^2 = 0. \tag{1}$$

On the other hand, the electron addition energy (under fixed atomic positions) can be expressed as[19]
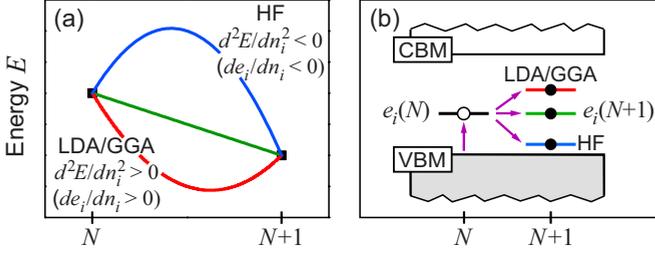
FIG. 1. (Color online) (a) In HF theory (blue) the energy is a concave function of the continuous occupation number n_i but a convex one in LDA or GGA (red). The correct behavior (green) is linear. (b) The corresponding shift of the eigenvalue e_i upon electron addition into a localized hole state in an oxide (the vertical arrow indicates optical excitation from the VBM into the hole state).

$$E(N+1) - E(N) = e_i(N) + \Pi_i + \Sigma_i, \qquad (2)$$

where $e_i(N)$ is the energy eigenvalue before electron addition, Π_i is the self-interaction energy after electron addition to the orbital i under the constraint of the wave functions being fixed at the initial state, and Σ_i is the energy contribution arising due to wave-function relaxation. In the case of the correct linear behavior [Eq. (1)], the integration of Janak's theorem, $dE(n_i)/dn_i = e_i(n_i)$, leads to the condition

$$E(N+1) - E(N) = e_i(N) \quad \text{or}$$

$$\Pi_i + \Sigma_i = 0. \qquad (3)$$

While resembling Koopmans theorem[20] in Hartree-Fock theory, Eq. (3) formulates a *condition* to be fulfilled, whereas the original Koopmans theorem states an *approximate equality*. Indeed, in HF theory, where $\Pi_i \equiv 0$, condition (3) is generally not fulfilled since $\Sigma_i < 0$ is not negligible for localized defect or impurity states in semiconductors. Consequently, the initially unoccupied eigenvalue e_i is lowered upon electron addition in HF [see Fig. 1(b)]. In contrast, in LDA or GGA, where $\Pi_i > 0$ and generally also $\Pi_i + \Sigma_i > 0$, the energy of the eigenvalue e_i increases following the electron addition [Fig. 1(b)] as a result of residual self-interaction.

III. HOW TO MAKE THE GENERALIZED KOOPMANS CONDITION SATISFIED

Due to the opposite behavior of LDA/GGA and HF (Fig. 1), methods that introduce HF-like interactions into the DFT Hamiltonian, such as hybrid DFT or DFT+U, are conceptually justified to correct the spurious delocalization and their parameters could in principle be adjusted to make Eq. (1) satisfied. Indeed, LDA+U was applied in Ref. 21 in a related approach. However, the parameters that are suited to remove the shift of the energy of the hole state upon occupation [Fig. 1(b)] are in general not simultaneously appropriate for the description of the host matrix. For example, the fraction of 42% HF (exact) exchange used in Ref. 14 for the case of SiO_2:Al largely exceeds the fraction of 25% that is generally more suitable for the band structure of wide-gap semiconductors.[22] A similar concern exists for DFT+U,

which creates an additional potential of the form[23]

$$V_U = (U - J)(0.5 - n_{m,\sigma}), \qquad (4)$$

where $n_{m,\sigma}$ is the fractional occupancy (partial charge) $0 \leq n_{m,\sigma} \leq 1$ of the m sublevel of spin σ (diagonal representation). Since, the occupancy of O p orbitals in the oxides considered here depends strongly on the projection radius,[24] the application of DFT+U to O p orbitals distorts the band structure of the defect-free oxide host in a rather uncontrolled way.

In order to satisfy the generalized Koopmans condition, Eq. (3), without such adverse side effects, we define a potential operator that acts on empty hole states but vanishes for the normally occupied states of the oxide host,

$$V_{hs} = \lambda_{hs}(1 - n_{m,\sigma}/n_{host}). \qquad (5)$$

The quantity n_{host} is the occupancy of the respective lm channel in the unperturbed host (e.g., O p) and λ_{hs} is a parameter for the strength of the potential that is determined through the condition (3). The technical implementation of the potential operator V_{hs} is achieved through a combination of the occupation-dependent DFT+U potential, Eq. (4), and our (occupation-independent) nonlocal external potential V_{nlep} of Ref. 25, both being implemented through the projector augmented wave (PAW) method of the VASP code.[26] The hole-state potential V_{hs}, Eq. (5), retains the conceptual justification of DFT+U but eliminates, by construction, the effect on the host band structure. Thus, applying V_{hs} to the O p orbitals in an otherwise standard GGA calculation allows us to stabilize the localized hole states for acceptor-bound polarons by avoiding their spurious occupation. By satisfying the required straight line behavior of $E(N)$ between integer N, the actual magnitude of the discontinuity of the slope of $E(N)$ at integers is restored, i.e., the correct energy difference $e_i(N+\delta) - e_i(N-\delta)$ between the unoccupied and the occupied O-p states is recovered (with an infinitesimal positive δ). Since self-interaction errors that cause the convexity of $E(N)$ in standard DFT functionals are associated mainly with localized atomiclike states, the PAW atomic-orbital projectors used to implement the potential Eq. (5) can be expected to form a good basis for the correction of such errors. We emphasize that the value of the parameter λ_{hs} is defined through the general condition (3) and does not rely on any empirical data. Therefore, the *first-principles* character of the GGA Hamiltonian is not compromised.

All results in the present work are based on the GGA of Ref. 27. Supercell size effects have been treated as described in Ref. 28, where, in particular, we showed that finite-size effects for charged defects are effectively eliminated when the third-order image charge interaction[29] and potential alignment effects are taken into account simultaneously.

IV. APPLICATION OF V_{hs} TO ZnO:Li

Figure 2(a) shows the structural and magnetic properties around the Li_{Zn} impurity in ZnO as a function of λ_{hs}. Whereas in a standard LDA or GGA calculation the wave function of the unoccupied state has a practically equal amplitude at all four O neighbors and decays only very slowly
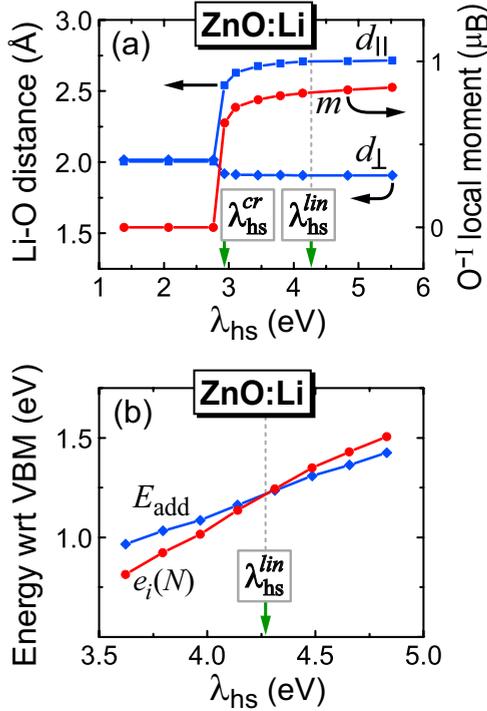
FIG. 2. (Color online) (a) Structural and magnetic properties of the Li_{Zn} impurity in ZnO, as a function of the hole-state potential strength λ_{hs}. The polaronic state is stable above a critical value $\lambda_{hs} > \lambda_{hs}^{cr}$. $d_\parallel$:Li-O^{-I} distance; $d_\perp$:Li-O^{-II} distance [cf. Fig. 3(a)]; and m: local magnetic moment of O^{-I} (integration radius R=1 Å). (b) The electron addition energy $E_{add}=E(N+1)-E(N)$ and the energy eigenvalue $e_i(N)$ of the initially unoccupied acceptor state of Li. λ_{hs}^{lin} marks the value of λ_{hs} for which Eq. (3) is satisfied.

with the distance from the Li_{Zn} site, the hole locks into a single O p orbital, as shown in Fig. 3(a), when λ_{hs} exceeds a critical (cr) value $\lambda_{hs}^{cr} \approx 3$ eV. As seen in Fig. 2(a), this transition entails the spontaneous breaking of the approximate tetrahedral symmetry in GGA and the emergence of a local magnetic moment at the O^{-I} ion that traps the hole. Figure 2(b) shows the energy eigenvalue $e_i(N)$ of the initially unoccupied state [cf. Fig. 1(b)] and the electron addition energy $E_{add}=E(N+1)-E(N)$ as a function of λ_{hs}. We see that the condition (3) is fulfilled for λ_{hs}^{lin}=4.3 eV, at which point the correct linear (lin) behavior [Eq. (1)] of $E(N)$ is recovered. Since, $\lambda_{hs}^{lin} > \lambda_{hs}^{cr}$ lies well above the critical value required to stabilize the polaronic state [see Fig. 2(a)], this symmetry-broken localized state is predicted to be the physically correct state, in agreement with experiment.[2,3] We further confirmed that our method correctly predicts a delocalized hole state in cases where this is the physical reality, e.g., in the defect-free ZnO host (i.e., no hole self-trapping is predicted) and in case of the shallow Li acceptor in ZnTe. In both cases, the localized polaronic state exists only as a local minimum above the energy of the delocalized state.

As seen in Fig. 2(b), the electron addition energy increases continuously with the strength λ_{hs} of the hole-state potential in the vicinity of the correct strength λ_{hs}^{lin}, whereas the structural properties and the local magnetic moment at the O^{-I} ion are rather insensitive to the value of λ_{hs}, once the threshold $\lambda_{hs}^{cr} \approx 3$ eV [Fig. 2(a)] for the stabilization of the
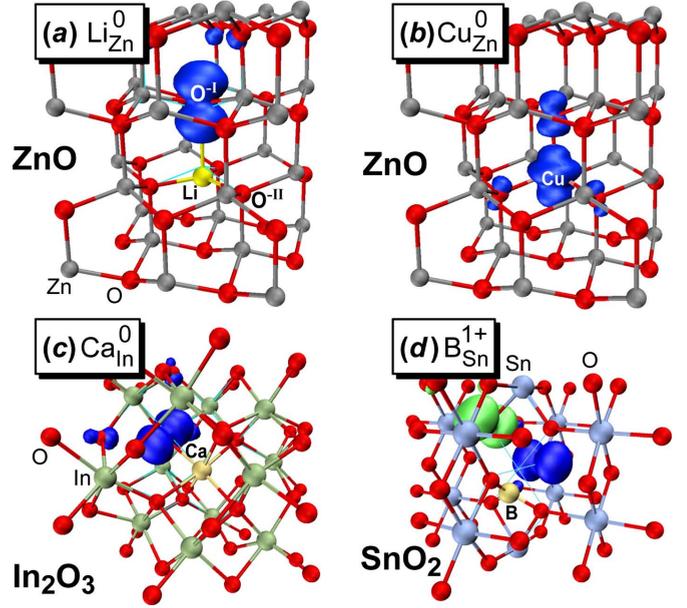
FIG. 3. (Color online) The calculated atomic structures and the one-particle-hole densities for different cation-site acceptors in ZnO, In_2O_3, and SnO_2 (isosurface density: 0.03 $e/Å^3$). For B_{Sn}^+ in SnO_2, binding two holes, the low-spin singlet state (S=0; blue =spin down and green=spin up) is shown, so to illustrate the localization of the individual one-particle densities. The underlying wire grid (light blue) shows the host lattice before atomic relaxation.

polaronic state is exceeded. Thus, properties such as the lattice distortion, hyperfine parameters,[6] or magnetic interactions[7–10] can generally be expected to be relatively insensitive to the question how well the condition (3) is fulfilled, if only the applied method stabilizes the polaronic state. In contrast, the accurate prediction of quantities which are based on the energy difference between occupied and unoccupied states, e.g., the acceptor binding energies that are addressed next, requires that the fundamental condition [Eq. (3)] for the energy splitting between occupied and unoccupied states be fulfilled rather accurately.

V. ACCEPTOR IONIZATION ENERGIES IN ZnO, In_2O_3, AND SnO_2

When we apply the hole-state potential to an otherwise standard GGA calculation, we obtain the acceptor transition of Li_{Zn} at $\varepsilon(0/-)=E_V+0.36$ eV above the valence-band maximum (VBM), considerably deeper than in an uncorrected GGA calculation with a delocalized acceptor state ($E_V+0.16$ eV). While the hole-state operator, Eq. (5), allows to correctly place the energy of the hole-state relative to the occupied host bands in a nonempirical way, it does not correct the strong band-gap underestimation of GGA (E_g =0.7 eV). In order to avoid an ambiguity of the position of the acceptor level inside the true band gap, we present in Table I results for metal-site acceptors in ZnO, In_2O_3, and SnO_2 that are obtained with an additional empirical band-gap correction via the nonlocal external potentials.[30] The λ_{hs} pa-

TABLE I. The calculated acceptor (ε_A) and deep donor (ε_D) levels of nominal single acceptors in ZnO, In$_2$O$_3$, and SnO$_2$ (in eV relative to the VBM). For Cu and Ag, the values in parenthesis include an additional hole-state correction for their d states.

ZnO	Li	Na	Cu	Ag
$\varepsilon_A(0/-)=E_V+$	0.86	0.79	2.32 (3.46)	1.18 (1.54)
$\varepsilon_D(+/0)=E_V+$	0.15	0.25	0.37 (0.14)	0.56 (0.35)
In$_2$O$_3$	Be	Mg	Ca	Zn
$\varepsilon_A(0/-)=E_V+$	1.27	0.86	0.68	1.04
$\varepsilon_D(+/0)=E_V+$	0.97	0.41	0.37	0.63
SnO$_2$	B	Al	Ga	In
$\varepsilon_A(0/-)=E_V+$	1.57	0.85	0.76	0.58
$\varepsilon_D(+/0)=E_V+$	1.39	0.47	0.44	0.30

rameters for the band-gap corrected calculations are determined via Eq. (1) as 4.8, 4.3, and 4.1 eV for ZnO, In$_2$O$_3$, and SnO$_2$, respectively. Thus, the values found for λ_{hs} are comparable among the three oxides studied here. We further tested for several cases the variations between different impurities in the same oxide and found them to be even smaller, introducing uncertainties in the calculated acceptor levels of less than 0.1 eV.

We see in Table I that the acceptor level of Li at 0.9 eV above the VBM is now closer to the experimental value of 0.8 eV (Ref. [31]) compared to the calculation without the band-gap correction. The latter underestimates the acceptor binding energy mainly because of overestimated p-d repulsion between the valence-band states and the Zn d shell, placing the VBM too high[28] relative to the Li acceptor state. In the band-gap corrected calculation, the Zn d energies are corrected by GGA$+U$.[25] We find that all acceptor states are localized in a single O p orbital (see Fig. 3) and that the ionization energies are relatively deep, $\varepsilon_A \geq 0.6$ eV (Table I), thereby strongly questioning the suitability of cation-site acceptors in ZnO, In$_2$O$_3$, and SnO$_2$ for the purpose to achieve p-type transparent conductive oxides.[11,12] In addition to the $\varepsilon(0/-)$ acceptor level, we observe also a very deep $\varepsilon(+/0)$ donor level closer to the VBM, which results from the binding of a second hole. When two holes are bound in the positive charge state, the two individual one-particle states are each localized on only a single O p orbital, as shown for B$_{Sn}^+$ in SnO$_2$ [Fig. 3(d)]. In case of the strongly size-mismatched impurities Be$_{In}$ in In$_2$O$_3$ and for B$_{Sn}$ in SnO$_2$, we further observe a large lattice relaxation that breaks three Be-O or B-O bonds and leads to threefold coordination [Fig. 3(d)], even in the ionized Be$_{In}^-$ and B$_{Sn}^-$ states. The breaking of three bonds with O neighbors facilitates the binding of yet another hole leading to a deep (double) donor transition at $\varepsilon_D(2+/+)=E_V+0.21$ eV for Be$_{In}$ in In$_2$O$_3$ and at $E_V+0.62$ eV for B$_{Sn}$ in SnO$_2$.

VI. GROUP Ib ACCEPTORS IN ZnO

In case of the group Ib elements Cu and Ag, the hole-wave function has mainly the d character of the impurity atom [see Fig. 3(b)] and not O p character like in case of the main group acceptors. Thus, the hole-state potential for O p has little effect and is not sufficient to satisfy the condition (1). Therefore, we apply GGA$+U$ with $(U-J)=5$ and 4 eV for Cu d and for Ag d, respectively. These parameters have been established before and were chosen so to reproduce photoemission spectra, e.g., for Cu$_2$O, i.e., to correctly place the energies of the occupied d-shell electrons.[28] Despite the application of GGA$+U$, the condition (3) is not fulfilled satisfactorily yet, which indicates that the energy splitting between occupied and unoccupied d symmetries is still underestimated.[32] Therefore, we apply an additional hole-state potential V_{hs} on Cu d and Ag d so that condition (3) is satisfied. In Table I, we give the transition energies for Cu$_{Zn}$ and Ag$_{Zn}$ with and without this additional correction. In either case, we find very deep acceptor states which are not conducive to p-type doping, in contrast to much more optimistic conclusion for Ag derived from standard LDA calculations.[11] Like all other acceptors, Cu and Ag can bind a second hole, giving rise to a deep donor transition (Table I). In contrast to the other cases, however, where both holes are bound in a O p orbital [Fig. 3(d)], here only one hole is located in a O p orbital while the other is in the Cu d or Ag d shell, e.g., forming a Cu$^{+II}(d^9)+$O^{-1} configuration.

VII. HOLE BINDING AND MAGNETISM OF V_{Zn} IN ZnO

Previous DFT calculations of V_{Zn} predicted acceptor levels close above the VBM, which, however, could not be reconciled with magnetic-resonance data.[33] Nevertheless, as we have shown in Ref. [34], the O p dangling bonds lie inside the band gap in a standard GGA calculation, which suggests that V_{Zn} could bind up to four holes, one at each O neighbor, if the delocalization due to the self-interaction error is avoided. Indeed, applying the present method to V_{Zn} we find that all charge states from $+2,\ldots,-2$ lie within the gap, with the respective transition levels being located at 0.45, 0.99, 1.46, and 1.91 eV above the VBM. Notably, the binding of up to four holes at V_{Zn} is also supported by a recent hybrid-DFT calculation.[15]

As discussed in Ref. [10] the strong wave-function localization impedes the magnetic interaction between pairs of V_{Zn} compared to the prediction of standard DFT calculations,[35] as it diminishes the exchange interaction between the holes. Indeed, the calculated energy of the high-spin state ($S=1$) of V_{Zn}^0 is only 1 meV lower in energy than the singlet state ($S=0$), indicating that the cation vacancy does not have a robust magnetic moment to support ferromagnetism. Further, the magnetic coupling energies between pairs of V_{Zn} in their high-spin state are practically negligible for pairs that do not share a common anion.[10] Thus, supporting the conclusion of Ref. [7], we find that the incorrect delocalization of the hole-wave-function in LDA and GGA can create a false prediction of hole-mediated magnetism due to p-orbitals.

VIII. CONCLUSIONS

We introduced a hole-state potential operator that, within the DFT framework, serves to place the O p bound hole

states of acceptors in oxides at their correct energies relative to the spectrum of occupied states without adversely affecting the underlying host band structure. Quantitative predictions of acceptor binding energies were attained by nonempirical determination of the parameter for the potential strength through a generalized Koopmans condition. In all studied oxides, the metal-site acceptors introduce deep and localized states, whereas standard DFT predicts shallow and delocalized levels.

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