

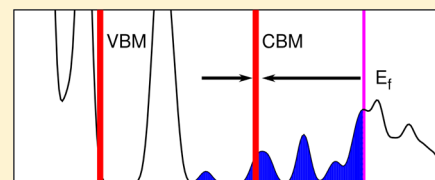
Band-Filling Correction Method for Accurate Adsorption Energy Calculations: A Cu/ZnO Case Study

Matti Hellström, Daniel Spångberg, Kersti Hermansson, and Peter Broqvist*

Department of Chemistry, The Ångström Laboratory, Uppsala University, P.O. Box 538, SE-751 21 Uppsala, Sweden

S Supporting Information

ABSTRACT: We present a simple method, the “band-filling correction”, to calculate accurate adsorption energies (E_{ads}) in the low coverage limit from finite-size supercell slab calculations using DFT. We show that it is necessary to use such a correction if charge transfer takes place between the adsorbate and the substrate, resulting in the substrate bands either filling up or becoming depleted. With this correction scheme, we calculate E_{ads} of an isolated Cu atom adsorbed on the ZnO(10 $\bar{1}$ 0) surface. Without the correction, the calculated E_{ads} is highly coverage-dependent, even for surface supercells that would typically be considered very large (in the range from 1 nm \times 1 nm to 2.5 nm \times 2.5 nm). The correction scheme works very well for semilocal functionals, where the corrected E_{ads} is converged within 0.01 eV for all coverages. The correction scheme also works well for hybrid functionals if a large supercell is used and the exact exchange interaction is screened.



I. INTRODUCTION

In *ab initio* calculations of the supercell type for defects in a bulk host material, several types of total-energy corrections are often needed in order to extrapolate any calculated quantities (such as the defect formation energy) to the dilute limit. In the case of charged defects, for example, there are various schemes that correct for the interactions between defects in neighboring supercells.^{1–4} Recently, such a scheme was proposed also for charged defects at surfaces and interfaces.⁵

Another type of correction that may be necessary even for charge-neutral defects is the *band-filling correction*,^{1,6–8} if for example the defect band hybridizes with the host conduction band and the host conduction band *fills up* as a result of the finite supercell. Such a correction has been used to study intrinsic defects in, for example, ZnO,^{1,8–10} In₂O₃,⁸ and Cu₂ZnSnS₄.¹¹

Here, we show for the first time that such a correction can also easily and practically be applied to adsorbate/surface systems in periodic slab calculations for the calculation of accurate adsorption energies in the dilute coverage limit. The correction is applicable in all cases where the substrate bands either fill up or become depleted as a result of charge transfer between the adsorbate and the substrate.

Our model system consists of Cu atom adsorption on ZnO(10 $\bar{1}$ 0). The Cu/ZnO system has attracted a lot of attention because it forms a rather versatile catalyst that can catalyze methanol synthesis, the water–gas shift reaction, and methanol steam reforming.¹² We have previously shown that the Cu atom, depending on the adsorption site, can either remain neutral or donate an electron to the ZnO conduction band.¹³ Upon population of the conduction band, we noted a significant coverage dependence of the calculated Cu atom adsorption energy. Such a coverage dependence has also been reported for Cu/ZnO(0001).¹⁴ In the present work, we

propose a practical method to extrapolate these adsorption energies to the dilute coverage limit, by means of a band-filling correction. We also evaluate the performance of the correction in conjunction with semilocal, nonscreened hybrid, and screened hybrid DFT functionals.

II. COMPUTATIONAL METHOD

Spin-polarized DFT calculations were performed using four different functionals: (i) the semilocal PBE functional,¹⁵ (ii) the hybrid PBE0 functional,^{16,17} where 25% of semilocal exchange energy is replaced by exact exchange, (iii) the hybrid HSE06 functional,^{18,19} where the exact exchange interaction is screened at long distances by dividing the total exchange energy into a short-range and a long-range part, and 25% of the short-range exchange is replaced by exact exchange, and (iv) what we call the HSE06' functional, which is constructed in the same way as the HSE06 functional but with 37.5% exact exchange. The amount of exact exchange in the HSE06' functional is commonly used^{9,20} to get the correct ZnO band gap and Zn 3d energies relative to the valence band maximum. The core electrons were described by PAW^{21,22} pseudopotentials. The number of valence electrons explicitly treated in the calculations were 6, 11, and 12 for O, Cu, and Zn, respectively. The one-electron orbitals were described by a plane-wave basis set with energy cutoff 500 eV, and a Gaussian broadening of width $\sigma = 0.05$ eV was applied to the electronic states. All calculations were performed using the VASP^{23–25} package.

The ZnO(10 $\bar{1}$ 0) surface was built from the PBE-optimized bulk wurtzite ZnO structure ($a = 3.288$ Å, $c = 5.305$ Å, $u = 0.3792$, which compare well to the experimental room-temperature values of $a = 3.250$ Å, $c = 5.207$ Å, $u =$

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0.3825).²⁶ It was modeled as a four double-layer thick slab, periodic in the x ([1 $\bar{2}$ 10]) and y ([0001]) directions. The surface (lateral) dimensions were 3×2 , 4×3 , 6×4 and 8×5 surface unit cells, corresponding to $9.9 \text{ \AA} \times 10.6 \text{ \AA}$, $13.2 \text{ \AA} \times 15.9 \text{ \AA}$, $19.7 \text{ \AA} \times 21.2 \text{ \AA}$, and $26.3 \text{ \AA} \times 26.5 \text{ \AA}$, respectively. The Cu adsorbates were adsorbed onto both sides of the slab, at sites a and b (see Figure 1), which we have previously reported

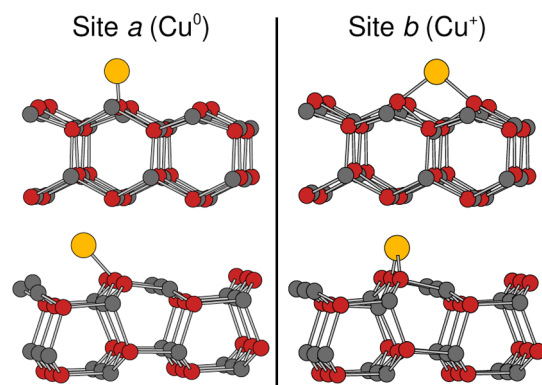


Figure 1. Structural depictions of adsorption sites a and b for Cu/ZnO(10 $\bar{1}$ 0), with Zn in gray, O in red, and Cu in yellow. Two ZnO double-layers are shown. Side views are shown from two different angles for each adsorption site. The structures were optimized with HSE06' in the 3×2 cell.

to be the most stable adsorption sites.¹³ Three-dimensional periodic boundary conditions were employed, with a 15 \AA vacuum gap between neighboring slabs in the surface normal direction. In the PBE calculations, we used a $4 \times 4 \times 1$ k-point grid in the 3×2 and 4×3 supercells, and a $2 \times 2 \times 1$ grid for the 6×4 and 8×5 supercells. Because of the significant computational resources required for the hybrid DFT calculations, they were performed only in the 3×2 and 4×3 supercells at the Γ -point in the geometry optimizations and with a $2 \times 2 \times 1$ grid for the total energy calculations in the 3×2 cell. Geometry optimizations were carried out using the conjugate gradient algorithm with a force convergence criterion of 0.03 eV/ \AA . Test calculations we performed with the PBE functional with tighter force convergence criteria (0.01 eV/ \AA) showed that the calculated adsorption energies are converged within 1 meV.

III. RESULTS AND DISCUSSION

Band-Filling Correction Applied to Bulk ZnO. In Table 1, we give the calculated band gaps for ZnO (at the PBE-optimized lattice parameters) using different methods. A particularly good agreement with experiment is obtained for the HSE06' method. The somewhat larger band gaps reported for the slab compared to the bulk can be explained by quantum confinement effects, as well as some relaxation along the surface

Table 1. Calculated Bulk ZnO Band Gaps (in eV) with Different Methods

method	bulk gap	slab gap
PBE	0.73	0.90
PBE0	3.07	3.20
HSE06	2.41	2.51
HSE06'	3.30	3.38
expt.	3.37	

normal. The band gaps reported correspond to the gap in Kohn–Sham eigenvalues, that is, $e_{\text{CBM}}^{\text{unocc}} - e_{\text{VBM}}$.

In this work, we will show that Cu atoms can donate electrons to the ZnO upon adsorption. As the ZnO conduction band becomes populated, the conduction band energies change relative to the valence band energies, compared to the unoccupied case. These band energy changes depend both on the extent of the occupation, that is, the number of electrons per ZnO formula unit, as well as the computational method. We will first illustrate these points for bulk ZnO and then consider the combined Cu/ZnO system.

In Figure 2(a), we plot the electronic DOS for a ZnO bulk supercell containing 48 formula units, with and without an

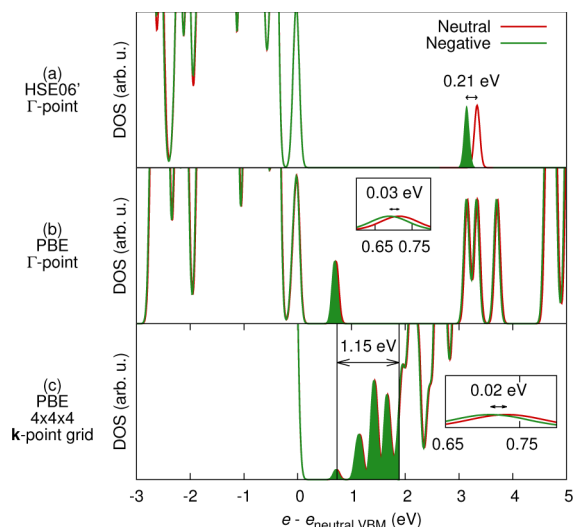


Figure 2. Electronic DOS for bulk ZnO with (green lines) and without (red lines) an extra electron per 48 ZnO formula units. The filled green areas mark the states that are occupied by the extra electron.

excess electron. For the negative system with an excess electron, the excess charge is compensated by a neutralizing jellium background. The calculations were performed at the Γ -point with the HSE06' functional. As the excess electron populates the ZnO conduction band, the CBM becomes *down-shifted* by 0.21 eV, while the valence bands of the neutral and negative systems line up almost perfectly.

In Table 2, we give the energy down-shifts $\Delta e_{\text{Zn}3d}$ and Δe_{CBM} for various excess electron densities and computational methods, for calculations performed for bulk ZnO at the Γ -point. The quantity $\Delta e_{\text{Zn}3d}$ corresponds to the average energy shift of the electronic states with primarily Zn 3d character, located at the bottom of the valence band (in a region not shown in Figure 2). This shift appears to be practically independent of the computational method, and decreases to become 0.00 eV in the large supercell. The Zn 3d shift can be regarded as arising from the effective interaction with the neutralizing jellium background and the conduction band electron. Because of the delocalized nature of the conduction band electron, $\Delta e_{\text{Zn}3d}$ is very small, as the effects of the jellium background and the conduction band electron effectively cancel each other.

The magnitude of the down-shift of the conduction band upon population, Δe_{CBM} , is much greater than $\Delta e_{\text{Zn}3d}$. We would thus expect the CBM down-shift to be present also for the charge-neutral Cu/ZnO system.

Table 2. Bulk Down-Shifts $\Delta e_{\text{Zn}3d}$ and Δe_{CBM} and the Band-Filling Correction Error BFCE (all in eV) for Various Excess Electron Densities (One Excess Electron per n ZnO Formula Units)^a

method	n	$\Delta e_{\text{Zn}3d}$	Δe_{CBM}	BFCE
PBE	16	−0.03	−0.08	0.02
PBE	48	−0.01	−0.03	0.00
PBE	180	0.00	−0.01	−0.01
PBE0	16	−0.03	−0.65	0.31
PBE0	48	−0.01	−0.51	0.24
PBE0	180	0.00	−0.32	0.14
HSE06	16	−0.03	−0.30	0.14
HSE06	48	−0.01	−0.15	0.06
HSE06	180	0.00	−0.04	0.01
HSE06′	16	−0.04	−0.41	0.19
HSE06′	48	−0.01	−0.20	0.09
HSE06′	180	0.00	−0.06	0.01

^aThe calculations were performed at the Γ -point. For these calculations, the band-filling correction $\Delta E_{\text{bf}} = -\Delta e_{\text{CBM}}$.

It is clear from Table 2, by comparing the PBE values to the PBE0 values, that the introduction of exact exchange results in a significant increase for the CBM down-shift (from −0.08 to −0.65 eV for 16 ZnO formula units). When increasing the supercell size, the down-shift also decreases much more slowly with PBE0 than with PBE. This phenomenon has previously been explained as arising from exchange self-interaction associated to the extra charge.²⁷ The increase in down-shift can in part be counteracted by screening the exact exchange interaction, as in HSE06. By adding even more exact exchange in HSE06′, the down-shift increases again. However, for all methods, the down-shift decreases when increasing the number of ZnO formula units. We would thus expect the down-shift to be zero for all methods for sufficiently large supercells.

In Figure 2(b) we show the DOS for the ZnO with and without an excess electron calculated using PBE at the Γ -point. Compared to the HSE06′ case (Figure 2(a)), both the band gap and the CBM down-shift are considerably smaller. If the calculation is performed with more k-points, the situation becomes a little more complicated. In Figure 2(c), we show the DOS calculated with PBE using a $4 \times 4 \times 4$ k-point grid. Now the band energy range spanned by this excess electron is 1.15 eV. In the limit of a very large supercell, this range would decrease in size until the band energy would be the same for all k-points. This band energy would correspond to the band energy of the *unoccupied* CBM. In this particular case, the difference between the occupied and unoccupied CBM is not very large (0.02 eV, see inset in Figure 2), although with other methods and/or supercell sizes the difference can be larger (see Table 2).

The basic underlying idea to the *band-filling correction*^{1,7} is to correct for the “filling-up” of the conduction band shown in Figure 2(c), by shifting all eigenvalues above a certain energy to a reference energy, with consideration of k-point weights and band occupation numbers. Thus, the 1.15 eV range spanned by the conduction band electron “collapses” to a single value, and the corresponding change to the total energy of the system becomes ΔE_{bf} .

$$\Delta E_{\text{bf}} = - \sum_{n,k} \Theta(e_{n,k} - e_{\text{CBM}}^{\text{occ}}) w_k \eta_{n,k} (e_{n,k} - e_{\text{CBM}}^{\text{unocc}}) \quad (1)$$

where the sum runs over all k-points and bands, Θ is the Heaviside step function, $e_{n,k}$ is the energy of band n , $e_{\text{CBM}}^{\text{occ}}$ is the occupied CBM energy, $e_{\text{CBM}}^{\text{unocc}}$ is the unoccupied CBM energy, w_k is the weight of the k-point, and $\eta_{n,k}$ is the band occupation. Thus, all eigenvalues $e_{n,k} \geq e_{\text{CBM}}^{\text{occ}}$ will effectively become the reference value $e_{\text{CBM}}^{\text{unocc}}$. This will give an estimation to the energy in the dilute limit, where both the down-shift and the “filling-up” of the band disappears. The CBM down-shift, using the notation in eq 1, is defined as $\Delta e_{\text{CBM}} = e_{\text{CBM}}^{\text{occ}} - e_{\text{CBM}}^{\text{unocc}}$. For a Γ -point calculation with one electron in the conduction band, $\Delta E_{\text{bf}} = -\Delta e_{\text{CBM}}$.

Equation 1 differs subtly from the previous implementations of the band-filling correction^{1,6–8} in that in our study the correction shifts all eigenvalues greater than or equal to one value ($e_{\text{CBM}}^{\text{occ}}$) to a *different* value ($e_{\text{CBM}}^{\text{unocc}}$). This approach is necessary when there is a non-negligible down-shift (as was the case particularly for the hybrid DFT functionals, see Table 2).

We now illustrate the use of the band-filling correction for the bulk with the excess electron. In the limit of an *infinite* supercell, where the excess electron becomes infinitely diluted, the following equality holds for the delocalized conduction band state:^{7,28}

$$e_{\text{CBM}}^{\text{unocc}} = E_{N+1} - E_N \quad (2)$$

where E_{N+1} and E_N are the total energies for the negative and neutral systems, respectively. In practical calculations, finite supercells are used, in which case the energy of the negative system, E_{N+1} , can be corrected with the band-filling correction:

$$E_{N+1}^{\text{corr}} = E_{N+1} + \Delta E_{\text{bf}} \quad (3)$$

If the band-filling correction works perfectly, then the equality in eq 2 will hold when E_{N+1}^{corr} is substituted for E_{N+1} . However, the band-filling correction only corrects for the contribution to the Hamiltonian coming from the band eigenvalues, while changes to any other contributions (e.g., the double-counting term) when approaching the dilute limit are neglected. This may be particularly relevant for hybrid functionals, where any change to the exact exchange energy is not considered. In order to evaluate the band-filling correction, we define the *band-filling correction error*, BFCE, as

$$\text{BFCE} = E_{N+1}^{\text{corr}} - E_N - e_{\text{CBM}}^{\text{unocc}} \quad (4)$$

In Table 2, we compare the band-filling correction errors for different methods and supercell sizes. Although the BFCE values in Table 2 were computed at the Γ -point, similar results are obtained with more converged k-point sampling (Supporting Information (SI) Table S1). With PBE, the BFCE is very small even for the smallest supercell, but with the hybrid functionals, the error is non-negligible even in the $n = 48$ supercell. It appears that for the hybrid functionals, simply shifting the occupied CB eigenvalues consistently results in an *overcorrection* to the total energy.²⁹ However, in the largest supercell with $n = 180$, the BFCE for the screened hybrid functionals is only 0.01 eV, while the BFCE with PBE0 is still as large as 0.14 eV. The small error for the screened hybrid functionals in the $n = 180$ supercell is related to the supercell size (average cell axis length 16.5 Å) and the screening parameter $\mu = 0.2 \text{ Å}^{-1}$, which gives a characteristic screening length of $2/\mu = 10 \text{ Å}$. Thus, the exact exchange interaction is almost completely screened between neighboring supercells. In

calculations that we performed with a shorter screening length ($\mu = 0.4 \text{ \AA}^{-1}$), we obtained a BFCE of 0.01 eV already in the $n = 48$ supercell (see SI Table S1). Since the exact exchange interaction is not screened at all in PBE0, prohibitively large supercells are needed for the band-filling correction to be accurate using this functional (of course, if such a large supercell is used, the band-filling correction will be very small and is not needed).

In summary, the band-filling correction, which consists of simply shifting the calculated eigenvalues for the occupied ZnO conduction band while neglecting changes to, for example, the double-counting term when approaching the dilute limit, works well provided the supercell is large enough. For hybrid functionals, larger supercells are needed than for semilocal functionals because of the long-range exact exchange interaction. The band-filling correction thus works best for semilocal functionals and for hybrid functionals where the exact exchange interaction is screened, such as with HSE06.

Band-Filling Correction Applied to Cu/ZnO. We now turn our attention to the adsorbate/substrate system Cu/ZnO, where we are interested in applying the band-filling correction in order to calculate accurate adsorption energies in the dilute limit for the cases where Cu transfers an electron to the ZnO. Since both the unoccupied and occupied CBM energies are needed for the band-filling correction, the band energies for the clean (relaxed) slab and for the Cu-adsorbed (relaxed) slab are aligned *via* the average electrostatic potential in the center of the slabs. All the band energies (eigenvalues) that enter into eq 1 are thus the differences between the “raw” band energies and the average electrostatic potential in the center of the slabs (the clean slab for $e_{\text{CBM}}^{\text{unocc}}$, and the adsorbed slab for $e_{n,k}$ and $e_{\text{CBM}}^{\text{occ}}$). This procedure is valid since the band energies are defined with respect to the electrostatic potential (if nothing but the potential changes when a Cu atom is adsorbed, all ZnO band eigenvalues should change by the same amount as the potential). The assumption behind the alignment procedure is that the centers of the slabs in the two different calculations are similar in all respects but the potential. Any errors resulting from this alignment should become progressively smaller as the size of the slab increases, because of the smaller contribution from Cu. The definition of the region “center of the slab” is somewhat arbitrary, but as long as the *same* region is used in the calculations with and without adsorbate, we have found that the choice of region does not influence the calculated band-filling corrections by more than 0.02 eV (provided the region does not approach the vicinity of the surface atoms).

In Figure 3, we show the electronic DOS calculated with HSE06' for the two slab systems with Cu adsorbed either at site *a* or site *b*, as well as for the clean slab. We additionally show the partial DOS projected onto the surface normal direction, which allows for a simple way to characterize the highest occupied state. In the case of site *a*, the highest occupied state is projected mainly onto the Cu atoms at either side of the slab (together with nearby surface atoms), while in the case of site *b*, the state is almost equally projected onto all atoms in the system, which is very similar to the projection of the ZnO conduction band for the clean slab. Sites *a* and *b* illustrated in Figure 3 thus correspond to Cu^0 and Cu^+ species, respectively.

For site *b*, where the ZnO conduction band is populated, the adsorption energy obtained from the calculation is only valid for the actual coverage used in the calculation. We will demonstrate that the band-filling correction (eq 1) is necessary to get the adsorption energy in the dilute limit. In the case of

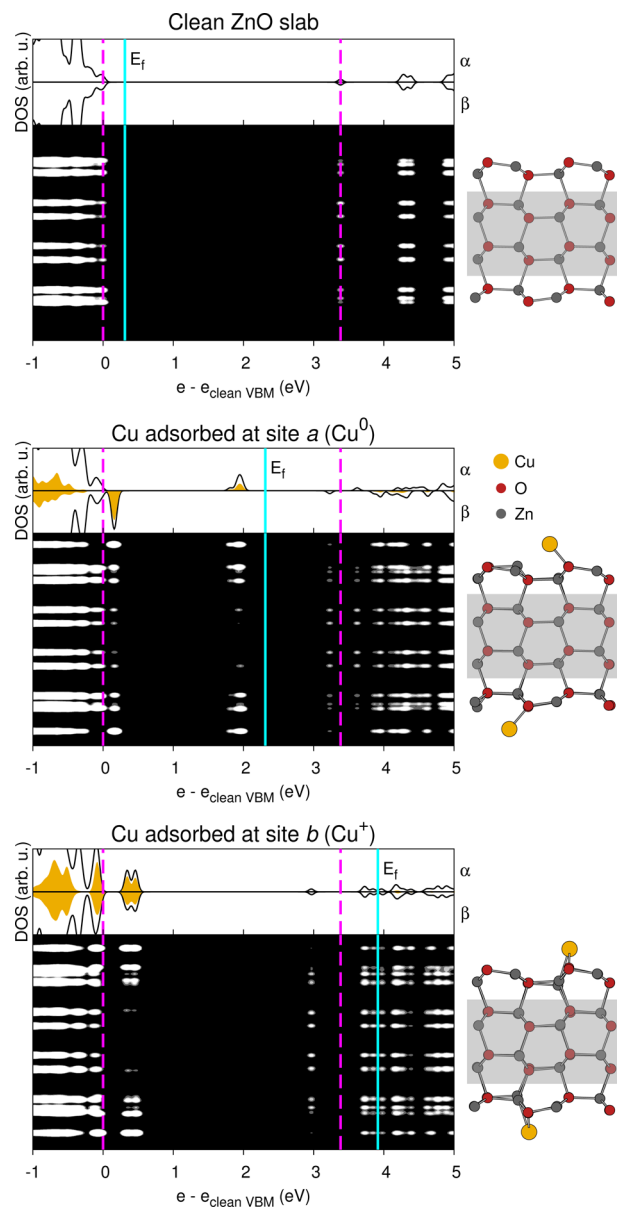


Figure 3. Electronic DOS for the clean slab, and for a Cu atom adsorbed at sites *a* and *b*, respectively, calculated with HSE06' in the 3×2 supercell. The energies are aligned with respect to the average electrostatic potentials in the centers of the slabs (indicated by the grayed regions in the structural representations to the right), and have been shifted so that the clean slab VBM lies at 0 eV. The dashed purple lines mark the positions of the clean slab band edges. The light blue lines mark the positions of the Fermi levels E_f . For each of the three cases in the figure, in the upper panel the filled yellow area is the Cu-projected DOS. In the lower panels, the DOS at different depths in the slabs is shown, and the figures to the right illustrate where the various atomic layers are projected.

site *a*, the band-filling correction is *not* needed, since the ZnO conduction band does not fill up (i.e., there is no charge transfer).

In order to evaluate the band-filling correction scheme for the adsorbate/slab system, we first performed a detailed coverage analysis using PBE. For site *a*, the adsorption energy is simply $E_{\text{ads}} = 1/2[E(\text{Cu/ZnO}) - 2E(\text{Cu}) - E(\text{ZnO})]$, while for site *b*, this would correspond to the uncorrected adsorption energy $E_{\text{ads}}^{\text{uncorr}}$. The corrected adsorption energy is $E_{\text{ads}}^{\text{corr}} = E_{\text{ads}}^{\text{uncorr}}$.

+ $\Delta E_{\text{bf}}/2$. The calculated adsorption energies as well as the size of the band-filling corrections are given in Table 3, where we

Table 3. Calculated Adsorption Energies and Band-Filling Corrections for Various Coverages of Cu/ZnO for Sites *a* and *b*^a

cell	method	site <i>a</i>		site <i>b</i>		
		E_{ads}	$E_{\text{ads}}^{\text{uncorr}}$	Δe_{CBM}	$\Delta E_{\text{bf}}/2$	$E_{\text{ads}}^{\text{corr}}$
3 × 2	PBE	−1.61	−1.60	−0.29	−0.31	−1.91
4 × 3	PBE	−1.61	−1.72	−0.17	−0.19	−1.91
6 × 4	PBE	−1.62	−1.79	−0.10	−0.12	−1.91
8 × 5	PBE	−1.61	−1.83	−0.07	−0.07	−1.90
3 × 2	PBE0	−1.28	−0.88	−1.01	0.26	−0.62*
4 × 3	PBE0	−1.28	−1.36	−0.85	0.85	−0.52*
3 × 2	HSE06	−1.31	−0.99	−0.40	−0.23	−1.23
4 × 3	HSE06	−1.31	−1.45	−0.28	0.28	−1.17
3 × 2	HSE06'	−1.21	−0.76	−0.42	−0.19	−0.94
4 × 3	HSE06'	−1.20	−1.21	−0.31	0.31	−0.90

^aAll energies are given in eV. Because of the large band-filling correction errors obtained with PBE0, the corrected adsorption energies for site *b* (marked with an asterisk) may contain considerable errors.

see that the adsorption energy for site *a* is largely coverage independent (−1.61 eV), while the uncorrected adsorption energy for site *b* is highly coverage dependent. One contributing factor to the observed coverage dependence may be electrostatic repulsion between adsorbed Cu⁺ species in neighboring supercells, although the *major* contributing factor is the extent of the band-filling, which decreases as the supercell size is increased. In the Supporting Information, we discuss the coverage dependence as a function of k-point sampling to further elucidate this point. The adsorption energy for site *b* corrected for the band-filling ($E_{\text{ads}}^{\text{corr}}$) has converged to −1.91 eV (within 0.01 eV), which shows that the band-filling correction works very well for this adsorbate/slab system when the PBE functional is used. The well-converged corrected adsorption energies also indicate that the determination of the reference clean slab CBM by aligning the potentials in the centers of the clean and adsorbed slabs is reliable, even for the small 3 × 2 cell.

Our PBE-calculated CBM down-shifts for site *b* in Table 3 are all considerably larger than the CBM down-shifts for the bulk; see Table 2 (the *n* = 48 bulk supercell has the same dimensions as the 3 × 2 slab supercell, but without the vacuum gap). There are a number of reasons for this: (i) Because of the presence of the Cu atom, the conduction band is really a “perturbed host state”¹ that invariably has some Cu character (this also explains the small “down-shift” for the *unoccupied* conduction band for site *a* in Figure 3), (ii) in the slab calculations, as opposed to the bulk calculations, we allow for atomic relaxation that can help stabilize the conduction band electron, and (iii) since the slabs are double-sided, two electrons populate the conduction band as opposed to just one in the bulk calculations. However, the CBM down-shift approaches zero when the supercell size is increased, as was the case for the bulk.

Now, let us turn our attention to the hybrid DFT results. For site *a*, where no population of the ZnO conduction band

occurs, the calculated adsorption energies for PBE0 ($E_{\text{ads}} = -1.28$ eV) and HSE06 ($E_{\text{ads}} = -1.31$ eV) are similar, while increasing the amount of exact exchange with HSE06' gives a little less stable adsorption ($E_{\text{ads}} = -1.20$ eV). The adsorption energy appears to be independent of the coverage, as was the case for PBE.

Next, we applied the band-filling correction to the hybrid DFT results for site *b* in the 3 × 2 and 4 × 3 cells, where the calculations were performed with a 2 × 2 × 1 k-point grid in the 3 × 2 cell and at the Γ -point in the 4 × 3 cell. In the 4 × 3 cell, all values for the band-filling correction ΔE_{bf} are positive as a result of the Γ -point sampling. In the 3 × 2 cell, ΔE_{bf} is negative for the screened hybrid functionals, while it is positive for PBE0. This is because of the very large down-shift obtained with PBE0.

With PBE0, the corrected adsorption energies $E_{\text{ads}}^{\text{corr}}$ in the 3 × 2 and 4 × 3 cells differ by as much as 0.1 eV. This could be expected, since we, in the previous section, showed that the band-filling correction does not work very well for PBE0. The band-filling correction performs better with the screened hybrid functionals, where the corrected adsorption energies differ by roughly 0.05 eV (which is quite striking considering the 0.5 eV difference for the uncorrected adsorption energies). This difference is still considerably larger than the PBE-calculated differences, where the corrected adsorption energy was converged to within 0.01 eV. The greater difference obtained with the hybrid functionals can be ascribed not only to the larger band-filling correction errors (Table 2) but also to our use of much more limited k-point sampling (especially in the 4 × 3 cell where just the Γ -point was used). In the PBE calculations, we used well-converged 4 × 4 × 1 k-point grids for the 3 × 2 and 4 × 3 cells.

In order to verify the reliability of our calculated Γ -point results for the cell with the hybrid functionals, we additionally performed nonspin-polarized calculations for site *b* using HSE06 with a 2 × 2 × 1 k-point grid. We then obtained an uncorrected adsorption energy $E_{\text{ads}}^{\text{uncorr}} = -1.10$ eV and a corrected adsorption energy $E_{\text{ads}}^{\text{corr}} = -1.19$ eV, in good agreement with the Γ -point calculated value of $E_{\text{ads}}^{\text{corr}} = -1.17$ eV, but this still shows that even in the large supercell, the k-point sampling may influence the results by a few hundredths of an eV.

We note that with PBE, site *b* is more stable than site *a*, but with all of the hybrid methods, the opposite picture emerges. This is related to the greater ZnO band gaps obtained with the hybrid methods, so that it is energetically less favorable to donate electrons into for example the HSE06-calculated conduction band than the PBE-calculated conduction band. For the kind of adsorbate/substrate system studied here, where charge transfer between the adsorbate and the substrate can take place, it is therefore very important to use a functional that describes the substrate band gap correctly.

Of the hybrid methods, HSE06' gives the band gap closest to the experimental value and is the method that we expect to be most accurate in this case. With HSE06', the corrected adsorption energy $E_{\text{ads}}^{\text{corr}} \approx -0.90$ eV for site *b* (Cu⁺), while $E_{\text{ads}} = -1.20$ eV for site *a* (Cu⁰). Thus, although we argued in ref 13 based on an extrapolation scheme for the PBE0 results that sites *a* and *b* should be similarly stable at low coverage, we here feel inclined to revise this statement and conclude that site *a* is more stable than site *b* at all coverages. The key to this statement is that although PBE0 and HSE06' give rather similar band gaps, the PBE0-calculated eigenenergies for the

conduction band become heavily down-shifted when the conduction band is populated, for all practical supercell sizes.

IV. CONCLUSIONS

We have successfully applied a simple band-filling correction scheme (eq 1) to an adsorbate/substrate system consisting of Cu/ZnO(10 $\bar{1}$ 0) in order to extrapolate the calculated adsorption energies to the dilute limit. In the Cu/ZnO(10 $\bar{1}$ 0) system, the Cu atom can transfer an electron to the ZnO conduction band, which necessitates the use of the band-filling correction. The band-filling correction corrects both for the down-shift of the eigenvalues that occurs as result of band population and the “filling-up” of the band that occurs as a result of the finite supercell. No calculations other than those for the clean surface and the adsorbed surface are needed in order to apply the correction. The correction works very well for semilocal density functionals such as PBE. For hybrid density functionals, the band-filling correction is accurate if the exact exchange contribution is screened and a large supercell, with dimensions that are at least of the order of the screening length, is used.

■ ASSOCIATED CONTENT

Supporting Information

Calculated band-filling correction errors for ZnO bulk with better k-point sampling, and with hybrid functionals with shorter screening length. Discussion of coverage dependence of uncorrected adsorption energies for site *b* for different k-point samplings. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: peter.broqvist@kemi.uu.se.

Notes

The authors declare no competing financial interest.

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- (29) The BFCE values for ZnO bulk with hybrid functionals correspond very well to half the $G = 0$ singularity correction (normalized for the supercell volume) at the Γ -point for the calculation of the exact exchange (see ref 27 for details). The latter values are for the $n = 16, 48, 180$ supercells 0.28 eV, 0.24 eV, 0.15 eV with PBE0; 0.11 eV, 0.06 eV, 0.02 eV with HSE06; 0.16 eV, 0.09 eV, 0.02 eV with HSE06'.