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Abstract

The spinel cobalt oxide Co$_3$O$_4$ is a magnetic semiconductor containing cobalt ions in Co$^{2+}$ and Co$^{3+}$ oxidation states. We have studied the electronic, magnetic and bonding properties of Co$_3$O$_4$ using density functional theory (DFT) at the Generalized Gradient Approximation (GGA), GGA+U, and PBE0 hybrid functional levels.

(110) is a frequently exposed surface in Co$_3$O$_4$ nanomaterials. We employed DFT+U to study the atomic structures, energetics, magnetic and electronic properties of the two possible terminations, A and B, of this surface. These calculations predict A as the stable termination in a wide range of oxygen chemical potentials, consistent with recent experimental observations. The Co$^{3+}$ ions do not have a magnetic moment in the bulk, but become magnetic at the surface, which leads to surface magnetic orderings different from the one in the bulk. Surface electronic states are present in the lower half of the bulk band gap and cause partial metallization of both surface terminations. These states are responsible for the charge compensation mechanism stabilizing both polar terminations.

We also carried out DFT+U to study the interaction of water with the (110) surface of Co$_3$O$_4$, a widely used oxidation catalyst. Dissociative water adsorption is preferred from low coverage up to one monolayer on the A termination and up to one-half monolayer coverage on the B termination. On the latter, a mixed molecular and dissociated monolayer is more stable at full coverage. The computed structures are used to investigate the free energy changes during water oxidation on both surface terminations.

Using first-principles density functional theory (DFT) calculations we determine the relative Gibbs free energies of CoO, Co(OH)$_2$, Co$_3$O$_4$, CoO(OH) and CoO$_2$ in electrochemical environment. We find that CoO(OH) and CoO$_2$ are the stable phases under oxidation conditions. These results, combined with surface structure studies of CoO(OH) (0001), show that a CoO$_2^{x^-}$ (x=0~0.5) layer is present when the surface is
exposed to solution under oxidation conditions. Study of the oxygen evolution reaction (OER) reveals however that natural surface of a CoO$_2$ layer has a high overpotential, due to the difficulty of first deprotonation to form a surface OH species. Taken previous study of CoO(OH) (0112) surface into consideration, the OER reactivity of CoO(OH) could come from surface step-edge and defects.

As a promising candidate electrode material for photoelectrochemical water splitting, TiO$_2$ is perhaps the most studied oxide semiconductor in photocatalysis. Recent computational studies of the oxygen evolution reaction (OER) have shown that the first proton-coupled electron transfer is responsible for the high overpotential of the OER on TiO$_2$ surfaces. Here, we report a study of the chemical dynamics of the first proton and electron transfers across the TiO$_2$-water interface. Using a periodic model that includes an anatase slab and explicit water molecules, we sample the solvent configurations by ab-initio molecular dynamics and determine the energy profiles of the two electronic states involved in the electron transfer by the hybrid PBE0 functional. Our calculated energy profiles suggest that the first proton and electron transfers are sequential, with the electron transfer (ET) following the proton transfer (PT). The ET is facilitated by a shared-hole state, and there is no significant solvent reorganization barrier during the ET.
Acknowledgement

This thesis is dedicated to my mother
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Chapter 1

1 Introduction

Electrochemical and photochemical water splitting reactions provide possibilities for new energy storage and conversion technologies by turning water into oxygen and hydrogen gas: \(^1\)

\[
2H_2O(l) \rightarrow 2H_2(g) + O_2(g)
\]

Overall, water splitting consists of two reactions on separate electrodes, the hydrogen evolution reaction (HER) on the cathode and the oxygen evolution reaction (OER) on the anode. As the rate limiting step of the whole process, the OER is a process of both fundamental and technological interest. In particular, an area of intense activity concerns the search for more efficient anode materials. Besides acting as electrodes, anode materials serve also as OER catalysts, which control the rate of the reaction.

Among the promising candidate materials, much attention has been recently focused on the spinel cobalt oxide Co\(_3\)O\(_4\), which has an OER activity only slightly lower than that of the noble metal oxides RuO\(_2\), IrO\(_2\) and PtO\(_2\), with the advantage that cobalt is an earth-abundant element. \(^2\) Recent efforts at developing catalysts based on Co\(_3\)O\(_4\) include the synthesis of nanomaterials with various morphologies, \(^3,4\) the use of active supporting materials, \(^5,6\) the growth of thin films containing Co\(_3\)O\(_4\) and other metal oxides. \(^7\)
Another advance has been the development of an efficient amorphous cobalt-phosphate catalyst.⁸ Crystalline Co₃O₄ thin film catalysts have also been prepared,⁹ which could be used for detailed model catalyst studies of the OER. In this dissertation, we present a systematic study of spinel Co₃O₄ as an anode material for the OER. In chapter 3, we shall present our work on the bulk properties of Co₃O₄, and in chapter 4 we discuss the properties of the Co₃O₄(110) surface. Water adsorption and oxidation on Co₃O₄(110) will be the topic of chapter 5.

In addition to the efforts aimed at preparing better anode materials, several studies have focused on the atomic-scale mechanisms of the OER. With regard to spinel Co₃O₄, a recent in-situ Raman spectroscopy study found that Co₃O₄ actually transforms into cobalt oxyhydroxide, CoO(OH), during the OER.⁶ On the other hand, ex-situ XPS measurements showed that the transformation of the spinel Co₃O₄ to layered oxyhydroxide is incomplete, which suggests that the in-situ transformation from the spinel structure to the layered structure is actually inhibited.⁷

The above observations give rise to several interesting questions, e.g. which is the thermodynamic ground state structure of cobalt oxide under OER conditions, what is the role of the kinetics of the structural transformation, and, more importantly, which component is mainly responsible for the catalyst’s OER activity. Focusing on crystalline materials, in this dissertation, we will address these questions in chapter 6.

The OER is a very complicated process, because of the four electron and proton transfers involved to produce one oxygen molecule.
For heterogeneous catalytic OER, the mechanism is largely unknown due to the many possible intermediates and the complex structure of liquid-solid interfaces. Nevertheless, significant advances have been made. In particular, Nørskov and co-workers developed a method to compute the OER overpotential based on adsorption energies of intermediates obtained from density functional theory (DFT) calculations. This method is very useful when comparing the OER activity of different materials; moreover, it can provide information about the rate limiting step in the OER. Nørskov’s method has been applied to study the OER on both the rutile and anatase polymorphs of TiO₂, the most widely used water splitting photocatalyst. One consistent conclusion from those studies is that the rate-limiting step is the initial removal of one proton and one electron from an adsorbed water molecule to form an adsorbed OH* species

\[ H_2O(l) \rightarrow HO^* + H^+ + e^- \]

where * (on the left) denotes an empty surface site. However, the chemical dynamics of the first proton and electron transfer is missing in those studies. Therefore important questions are still unanswered, e.g. whether the proton and electron transfers are coupled, and whether there are additional contributions from reaction barriers to the overpotential. We will try to answer these questions in chapter 7, where we present a study of the chemical dynamics of first proton and electron transfer on the TiO₂ surface.
Bibliography


Chapter 2

2 Theoretical Methods

2.1 Kohn-Sham Density Functional Theory

Electrochemical oxygen evolution is a complex process which involves physical changes and chemical reactions. To obtain an overall understanding, we studied both the material properties of the electrodes, including electronic, magnetic, and structural properties and thermodynamics, and the chemical reactions taking place on the electrode surfaces. Our basic theoretical tool is Density functional theory (DFT) in the Kohn-Sham (KS) scheme. The KS Hamiltonian for a single electron state contains electron kinetic energy, electron-ion interaction, electron-electron Hartree interaction and exchange-correlation interaction among electrons.

\[ H_{KS} = -\frac{1}{2} \nabla^2 + v(r) + \int r' \frac{\rho(r')}{|r - r'|} + \frac{\delta E_{XC}(\rho)}{\delta \rho(r)} \]

In our work, we consistently employed the exchange-correlation functional PBE at the general gradient approximation (GGA) level, which usually provides a qualitatively correct description of the properties of solids and molecules.
2.2 DFT+U and hybrid functionals

For transition metal oxides, standard DFT calculations within the local density approximation (LDA) or the generalized gradient approximation (GGA) often severely underestimate the band gaps, or even predict insulators as metals. This is an effect of the delocalization error which originates from the incomplete cancellation of the Coulomb self-interaction. Among the schemes proposed to overcome this problem, the DFT+U method and hybrid functionals have been applied with some success to a number of solid-state materials. The idea behind the DFT+U method is to add another term in the KS Hamiltonian as a penalty of the d state partial occupation, which is a result of electron delocalization.

\[
H_{DFT+U} = H_{KS} + \frac{U_{\text{eff}}}{2} \sum_{l,\sigma} Tr[n^{l,\sigma}(n^{l,\sigma} - 1)]
\]

The hybrid functional approach partially cancels the self-interaction error by mixing some exact exchange into the exchange-correlation functional

\[
E_{xc}^{\text{hyb}} = bE_{x}^{\text{exact}} + (1 - b)E_{x}^{\text{app}} + E_{c}^{\text{app}}
\]

where the superscript “app” indicates the approximate DFT exchange-correlation functional. In our studies, we used the PBE0 hybrid functional, where the fraction of exact exchange is \( b=0.25 \) and “app” indicates the PBE functional.
2.3 Maximally-Localized Wannier Function

As an alternative representation of the electronic states of periodic systems, Wannier functions are unitary transformations of the extended Bloch orbitals.\(^\text{13}\)

\[
|R_n\rangle = \frac{V}{(2\pi)^3} \int dk \, e^{-i \mathbf{k} \cdot \mathbf{r}} \sum_m U^{(k)}_{mn} |\varphi_m\rangle
\]

To uniquely define this unitary transformation \(U^{(k)}_{mn}\), Marzari and Vanderbilt introduced Maximally-Localized Wannier Functions (MLWFs) by adding a constraint to minimize the sum of each Wannier function’s spread.\(^\text{14}\)

\[
\Omega = \sum_n \langle \mathbf{r}^2 \rangle_n - \langle \mathbf{r} \rangle_n^2
\]

Since MLWFs are usually localized, they can provide information on the positions of the electrons. In fact MLWFs are widely used to study local phenomena like electronic polarization and orbital magnetization.\(^\text{15}\) In our work, we extensively used MLWFs to analyze the occupations of local orbitals and the nature of the chemical bonding. Moreover, hybrid functional studies in our work are based on an order-N implementation based on MLWFs.\(^\text{16}\) Hybrid functional calculations in extended systems are expensive because of the large amount of two-body integrations. Since MLWFs are exponentially localized, the amplitude of the exchange integrals of two MLWFs decreases very quickly with increasing distance between their centers. Usually, only a few neighboring pairs are necessary, and the number is independent of the system size.\(^\text{15}\)
Bibliography:


Chapter 3

3 Bulk Properties of Co$_3$O$_4$

3.1 Introduction and Experimental Information

Co$_3$O$_4$ crystallizes in the cubic normal spinel structure (space group $Fd\overline{3}m$), which contains cobalt ions in two different oxidation states, Co$^{2+}$ and Co$^{3+}$. These are located at the interstitial tetrahedral (8$a$) and octahedral (16$d$) sites, respectively, of the close-packed face centered cubic (fcc) lattice formed by the oxygen ions (see Fig. 3.1). In a simplified picture, the crystal fields at the 8$a$ and 16$d$ sites split the five degenerate atomic d orbitals into two groups, leading to three unpaired d electrons on Co$^{2+}$, while all the d electrons of Co$^{3+}$ are paired (see Fig. 3.2). As a result, the Co$^{3+}$ ions are not magnetic, whereas the Co$^{2+}$ ions carry a magnetic moment. Experimentally, Co$_3$O$_4$ is a paramagnetic semiconductor at room temperature. It becomes antiferromagnetic below $T_N \sim 40$ K, where the antiferromagnetism is mainly due to the weak coupling between nearest neighbor Co$^{2+}$ ions. The conductivity is usually p-type at low temperature and intrinsic at high temperature; measured values of the band gap are around 1.6 eV.\textsuperscript{3,4}
3.2 Structural Properties

Our results for the structural properties of Co$_3$O$_4$ are summarized in Table 3.1. The lattice constant was determined by fitting computed total energies to Murnaghan’s equation of state,$^5$ with all internal degrees of freedom fully relaxed. Comparison to experiment shows that the GGA-PBE lattice constant and bond distances are overestimated by about 1.5 percent. With PBE+U, the overestimate increases to about 2 percent, as found also in other GGA+U studies of oxide materials.$^6,^7$
<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>PBE+U</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant</td>
<td>8.19</td>
<td>8.27</td>
<td>8.08</td>
</tr>
<tr>
<td>Bulk Modulus</td>
<td>199</td>
<td>192</td>
<td>---</td>
</tr>
<tr>
<td>Distance Co^{2+}-O^{2-}</td>
<td>1.95</td>
<td>1.99</td>
<td>1.93</td>
</tr>
<tr>
<td>Distance Co^{3+}-O^{2-}</td>
<td>1.93</td>
<td>1.95</td>
<td>1.92</td>
</tr>
</tbody>
</table>

**TABLE 3.1** Lattice constant (Å), bulk modulus (GPa), and bond distances (Å) of Co$_3$O$_4$ from PBE and PBE+U calculations using the primitive 14-atom unit cell and an 8×8×8 k-point mesh.

For the fully optimized structure, we determined the heat of formation (ΔH) at T=298 K relative to metallic, ferromagnetic Co in the hcp structure and gas phase O$_2$. For Co, the PBE+U reference was obtained by combining the ground state energies at U=4.4 and 6.7 eV in a 1:2 ratio; Co was computed to be metallic and ferromagnetic at both values of U. We found ΔH = -683 and -815 kJ/mol at the PBE and PBE+U levels, respectively, whereas experimentally values of -891$^8$ and -910$^9$ kJ/mol have been reported. To avoid the difficulties associated with having two different U values for Co, we also performed calculations for Co$_3$O$_4$ using a single value of U for both Co$^{2+}$ and Co$^{3+}$, namely U = 4.4, 5.9 and 6.7 eV, the value U= 5.9 eV being a 1:2 average of 4.4. and 6.7 eV. From these calculations, we obtained ΔH= -803, -852, and -884 kJ/mol, respectively, indicating that the dependence of the computed ΔH on the value of U is moderate, a 10% variation for a variation of U of more than 2eV. Comparison between the value of ΔH obtained using the average U value, U=5.9 eV, and experiment shows a deviation on the order of 6%.

It has been suggested that the difference between theoretical and experimental values of ΔH may be often attributed to the overestimate of the O$_2$ binding energy (E_b) given
by GGA calculations.\textsuperscript{10} Using the experimental value of $E_b$, we find $\Delta H_{\text{corr}} = -878$ kJ/mol at the PBE level, in reasonable agreement with the experiment. Instead, using PBE+U with $U=5.9$ eV for both Co\textsuperscript{2+} and Co\textsuperscript{3+}, we obtain $\Delta H_{\text{corr}} = -1047$ kJ/mol, which is significantly overestimated in comparison to experiment.

### 3.3 Electronic Properties

Results of PBE and PBE+U calculations of the electronic band structure along various symmetry directions in the Brillouin zone are presented in Fig. 3.3. Computed direct and indirect gaps at a few symmetry points are reported in Table 3.2. Both PBE and PBE+U predict the valence band maximum and the conduction band minimum to occur at the high symmetry point X along the [100] direction, thus resulting in a direct minimum band gap at X. The GGA-PBE approach successfully predicts Co\textsubscript{3}O\textsubscript{4} to be a semiconductor but the minimum band gap, 0.3 eV, is severely underestimated with respect to the experimental value of 1.6 eV (obtained from measurements on films and nanocrystalline samples).\textsuperscript{3,4} The PBE+U method gives a minimum gap of 1.96 eV, in satisfactory agreement with the experiment. To test the sentivity of the gap to the use of two different U values for Co\textsuperscript{2+} and Co\textsuperscript{3+}, we also performed calculations with a single U for both Co\textsuperscript{2+} and Co\textsuperscript{3+}. We found a gap of 1.67, 2.02, and 2.16 eV using $U = 4.4$, 5.9 and 6.7 eV, respectively. The band gap with the average $U=5.9$ eV value is thus very similar to that obtained using two different values of U for the Co\textsuperscript{2+} and Co\textsuperscript{3+} ions. Both PBE and PBE+U approaches predict a larger dispersion near the conduction band minimum than
at the valence band maximum, and therefore a smaller effective mass for electron than for hole states.

FIGURE 3.3 Band structure of Co$_3$O$_4$ obtained by PBE (left) and PBE+U (right) approach. The Fermi energy is set to 0.

Fig. 3.4 displays the GGA-PBE and PBE+U partial densities of states (PDOS) obtained by projecting the Kohn-Sham states onto atomic orbitals centered on the various cobalt and oxygen ions. The GGA-PBE results show a splitting of the valence band in two sub-bands. The sub-band at lower energies is dominated by O 2p states, while the upper one originates primarily from Co$^{3+}$ d states, especially in proximity of the valence band edge. In the upper valence band, smaller contributions from oxygen states and Co$^{2+}$ d states are also present, with a Co$^{2+}$ peak around -2.5 eV. These features are in qualitative
agreement with results of photoemission experiment performed on a Co$_3$O$_4$ film epitaxially grown on CoO(100). The bottom of the conduction band shows contributions of both Co$^{2+}$ and Co$^{3+}$ d states, with a similar weight.

**FIGURE 3.4** Total and projected density of states from PBE (top) and PBE+U (bottom) calculations. The Fermi energy is set to 0.

In the PBE+U results, the total valence bandwidth, 8.33 eV, is similar to that given by GGA-PBE, 8.20 eV. At variance with the pure PBE case, however, no clear splitting of the valence band is present. The contributions from O 2p, Co$^{3+}$ d and Co$^{2+}$ d states in the PDOS are spread with similar weights throughout the valence band, indicating a stronger hybridization with respect to the PBE case. This can be attributed to a
stabilization of the cobalt d orbitals relative to the O 2p and 2s states. The band gap is much wider than in GGA-PBE, and at the bottom of the conduction band the largest contribution originates from the Co$^{3+}$ d states.

<table>
<thead>
<tr>
<th>Band gap</th>
<th>PBE</th>
<th>PBE+U</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$$\rightarrow$$\Gamma$</td>
<td>1.39</td>
<td>3.25</td>
</tr>
<tr>
<td>X$\rightarrow$$\Gamma$</td>
<td>0.94</td>
<td>2.81</td>
</tr>
<tr>
<td>$\Gamma$$\rightarrow$$X$</td>
<td>0.75</td>
<td>2.41</td>
</tr>
<tr>
<td>X$\rightarrow$$X$</td>
<td>0.30</td>
<td>1.96</td>
</tr>
</tbody>
</table>

**TABLE 3.2** Direct and indirect band gaps (in eV) at various symmetry k-points, from PBE and PBE+U calculations. As a comparison, the minimum gap obtained from PBE0 calculations is 3.42 eV, while experiments found 1.60 (Ref. 7) and 1.65 eV (Ref. 8).

Calculations based on the PBE0 hybrid functional were performed at the $\Gamma$ point of a tetragonal supercell containing 112 atoms, which includes the X point of the primitive cell. The experimental lattice constant and geometry were employed. For a more direct comparison, calculations using the same setup were performed also at the PBE and PBE+U levels. Both the valence bandwidth (9.48 eV) and the band gap (3.42 eV) obtained with the PBE0 functional are larger than those given by PBE (8.41 and 0.33 eV, respectively) and PBE+U (8.35 and 1.94 eV), a trend observed for other oxide semiconductors as well, see, e.g., Refs. 12 and 13. This trend, however, appears to be amplified in the present case, resulting in a substantial overestimate of the computed band gap with respect to the experiment.
3.4 Bonding Properties

Numerous studies have shown the effectiveness of maximally-localized Wannier functions (MLWFs) for the analysis of the electronic and bonding properties of crystalline materials.\textsuperscript{14,15} In particular, the Wannier centers and the shapes of MLWFs have been found to provide useful insights into the nature of chemical bonds in a variety of compounds. To investigate the bonding properties of \( \text{Co}_3\text{O}_4 \), we determined the MLWFs at the PBE, PBE+U and PBE0 levels, using the algorithm developed by Sharma et al.\textsuperscript{16} We considered the conventional 56-atom cubic supercell and restricted k-space integration to \( \Gamma \) only. Our results are summarized in Table 3.3.

Independent of the approach used to describe the electronic structure; we found 6 and 7 singly occupied d-type Wannier functions whose centers are very close to each cobalt ion at an octahedral and tetrahedral site, respectively. Since with our pseudopotential a neutral Co should have 9 valence electrons, this means that the charge states of the cobalt ions at octahedral and tetrahedral sites are \( \text{Co}^{3+} \) and \( \text{Co}^{2+} \), respectively, in full agreement with their expected oxidation states. Similarly, we found four pairs of Wannier centers (WCs) in proximity of each oxygen ion (see Fig. 3.5), indicating an \( \text{O}^{2-} \) charge state, in agreement with the formal oxidation state of oxygen ions. The simple connection between Wannier centers and ionic oxidation states is quite remarkable. Standard computational approaches for characterizing oxidation states are based on electron population analyses, in which the occupied electronic states are projected onto atom-centered orbitals. It is known, however, that these methods depend significantly on the basis set chosen and often yield charges that cannot be directly related to the
oxidation states. In fact, if we integrate the occupied PDOS for Co$^{3+}$ and Co$^{2+}$ (e.g. the DOS computed at the PBE level in Fig. 3.4), we find more electrons on Co$^{3+}$ (7.98) than on Co$^{2+}$ (7.70), in obvious contrast with the expected oxidation states, simply because the Co$^{3+}$ ions are coordinated to a larger number of oxygens, and therefore more electrons from Co-O bonds are around them. This clearly shows that projections onto atomic-like states are inadequate for the identification of oxidation states. It was recently pointed out that optimally-localized orbitals, such as MLWFs in the case of crystalline systems, can instead provide a reliable estimate of oxidation states. This is confirmed by our results for Co$_3$O$_4$, for which the analysis of Wannier centers unambiguously identifies cobalt ions in +2 and +3 oxidation states.

*FIGURE 3.5* Wannier centers of Co$_3$O$_4$. Light cyan, navy blue and red balls indicate Co$^{2+}$, Co$^{3+}$ and O$^{2-}$ ions, respectively. Green small balls indicate Wannier centers near O$^{2-}$ ions. Wannier centers very close to Co ions are almost overlapped with Co ions so that they can not been seen in this figure.
<table>
<thead>
<tr>
<th>MLWF type</th>
<th>No.</th>
<th>PBE</th>
<th>PBE+U</th>
<th>PBE0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ω</td>
<td>E_MLWF</td>
<td>Ω</td>
</tr>
<tr>
<td>Co(^{3+}) t(_{2g})</td>
<td>6</td>
<td>0.66</td>
<td>1.1</td>
<td>0.47</td>
</tr>
<tr>
<td>Co(^{2+}) t(_{2g}) majority spin</td>
<td>3</td>
<td>0.76</td>
<td>\textbf{0.0}</td>
<td>0.51</td>
</tr>
<tr>
<td>Co(^{2+}) e(_{g}) majority spin</td>
<td>2</td>
<td>0.53</td>
<td>0.6</td>
<td>0.45</td>
</tr>
<tr>
<td>Co(^{2+}) e(_{g}) minority spin</td>
<td>2</td>
<td>0.71</td>
<td>1.9</td>
<td>0.51</td>
</tr>
<tr>
<td>Co(^{3+})-O sp(^3)d</td>
<td>6</td>
<td>0.66</td>
<td>-5.9</td>
<td>0.64</td>
</tr>
<tr>
<td>Co(^{2+})-O sp(^3)d</td>
<td>2</td>
<td>0.64</td>
<td>-6.8</td>
<td>0.61</td>
</tr>
</tbody>
</table>

**TABLE 3.3** Type and number of Wannier functions for each ion, spreads Ω of MLWFs (in \(a_0^2\)), average energy \(E\_\text{MLWF}\) of MLWFs (in eV) relative to the energy of Co\(^{2+}\) t\(_{2g}\). Results of PBE, PBE+U and PBE0 calculations are listed.

The Wannier centers of Co\(_3\)O\(_4\) are shown in Fig. 3.5. The oxygen WCs are located along the directions connecting each oxygen ion to its four nearest neighbors, so as to form a somewhat distorted tetrahedron, suggesting that the bonding has a partially covalent character. This is confirmed by the explicit form of the Wannier functions. From Table 3.3 and Fig. 3.6, we can see that the Wannier functions can be classified in 6 different types. These include d states of t\(_{2g}\) symmetry localized on Co\(^{3+}\) and Co\(^{2+}\) ions, d e\(_{g}\) states for majority and minority spins on Co\(^{2+}\) ions, and Wannier functions with the character of sp\(^3\)d bonds both between Co\(^{3+}\) and O\(^{2-}\) and between Co\(^{2+}\) and O\(^{2-}\) ions. These MLWFs show that the bonding character of Co\(_3\)O\(_4\), although mainly ionic, has also a small covalent component. This is in agreement with earlier work indicating that covalent bonds are essential to cation ordering in the spinel structure.\(^{21}\)
FIGURE 3.6 Isosurfaces of charge density of 6 types of MLWFs. Values of the isosurfaces are 1% of maximal values. Co and O ions are denoted by blue and red balls respectively.

It is interesting to examine the MLWFs’ spreads in Table 3.4. The d-type and sp$^3$d bonding MLWFs have similar spreads at the PBE level, whereas the PBE+U and PBE0 calculations predict that the spreads of the d-type MLWFs are smaller than those of the sp$^3$d bonding orbitals. For the latter, the spreads obtained from PBE and PBE+U calculations are rather similar, whereas those given by PBE0 are smaller. Altogether, PBE0 leads to a stronger localization of all orbitals relative to PBE, whereas the main differences between PBE+U and PBE concern the localization of the d orbitals. We also notice that at all electronic structure levels the average spread of the Co$^{2+}$ d orbitals is larger than the d orbital spread for the Co$^{3+}$ ions. This is consistent with the larger value of U found for Co$^{3+}$ in comparison to that for Co$^2$. 
In Table 3.3 we also report the average energies $E_{\text{MLWF}}$ of the various MLWFs relative to the energy of Co$^{2+} t_{2g}$. $E_{\text{MLWF}}$ is defined as

$$E_{\text{MLWF}}^i = \sum_l A_{ij} E_{KS}^j$$

where $A$ is the unitary transformation matrix between MLWFs and Kohn-Sham states, defined as

$$\psi_{\text{MLWF}}^i = \sum_j A_{ij} \psi_{KS}^j$$

As shown in Fig. 3.2, crystal field theory predicts doubly occupied $e_g$ orbitals for Co$^{2+}$ ions. Instead, we find that the Co$^{2+} e_g$ orbitals are split into different spin-orbitals due to the exchange interaction between $e_g$ and singly occupied $t_{2g}$ states (see Fig. 3.7). PBE0 gives the largest splitting, 2.2eV, whereas PBE and PBE+U give splittings of 1.3 and 1.2 eV, respectively. Also different from crystal field theory, the Co$^{2+} e_g$ orbitals are higher in energy than the Co$^{2+} t_{2g}$ orbitals. For the minority $e_g$ spin-orbitals, the higher energy can be attributed to the lack of exchange interaction with the $t_{2g}$ orbitals. For the majority $e_g$ spin-orbitals, the higher energy is likely caused by the Hartree repulsion with the minority spin $e_g$ orbitals. As shown in Fig. 3.6, there is indeed a strong overlap between majority and minority spin $e_g$ orbitals. Thus the main contribution to the Co$^{2+}$ atomic magnetic moment comes from the three singly occupied $t_{2g}$ orbitals and the resulting moment is close to three.
3.5 Magnetic Properties

The magnetic properties of Co$_3$O$_4$ originate from the atomic magnetic moments of Co$^{2+}$ ions ($\mu_{Co^{2+}}$). Experimentally $\mu_{Co^{2+}} = 3.26\mu_B$, where the part in excess of 3.00 is due to the spin-orbit coupling.$^1$ Computed values of $\mu_{Co^{2+}}$ are listed in Table 3.4. PBE+U and PBE0 predict larger values of $\mu_{Co^{2+}}$ with respect to PBE, in better agreement with the experiment. Since the Co$^{2+}$ magnetic moment is associated with localized d electrons, this improvement comes from the partial correction of the PBE delocalization error within PBE+U and PBE0.

Couplings between atomic magnetic moments are weak in Co$_3$O$_4$, as implied by its low Neel temperature, and may not have a strong impact on the material properties at room temperature. We estimated the coupling parameter $J_1$ between nearest neighbor Co$^{2+}$
ions from the total energy difference between the anti-ferromagnetic and ferromagnetic solutions in the primitive cell using the Heisenberg spin Hamiltonian

$$H = -\sum_{ij} J_1 S_i \cdot S_j$$

where sites i and j denote nearest neighbor sites. There are four nearest neighbor pairs in a primitive cell, and therefore $J_1$ can be expressed as

$$J_1 = \frac{11}{24} S^2 (E_{AFM} - E_{FM})$$

where $S = \frac{3}{2}$. Computed values of $J_1$ are reported in Table 3.4. PBE and PBE0 calculations correctly predict the antiferromagnetic phase to be more stable than the ferromagnetic one; however the absolute value of the computed $J_1$ is much larger than the experimental one. By contrast, we found that PBE+U favors the ferromagnetic solution; therefore the computed $J_1$ has opposite sign with respect to the experiment.

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>PBE+U</th>
<th>PBE0</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{Co^{2+}}$</td>
<td>2.64</td>
<td>2.84</td>
<td>2.90</td>
<td>3.26 (Ref. 1)</td>
</tr>
<tr>
<td>$J_1$</td>
<td>$-2.5 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$-5.0 \times 10^{-3}$</td>
<td>$-6.26 \times 10^{-4}$ (Ref. 22)</td>
</tr>
</tbody>
</table>

**TABLE 3.4** Atomic magnetic moment of Co$^{2+}$, $\mu_{Co^{2+}}$ (in $\mu_B$), and exchange coupling between nearest neighbors, $J_1$ (in eV), as given by PBE, PBE+U and PBE0 calculations.
3.6 Summary and Conclusion

In this work, we have studied the bulk properties of the spinel cobalt oxide \( \text{Co}_3\text{O}_4 \) using density functional theory at the PBE, PBE+U and PBE0 levels. The U parameters for the PBE+U calculations were determined from first principles,\(^{15}\) resulting in 4.4 and 6.7 eV for \( \text{Co}^{2+} \) and \( \text{Co}^{3+} \), respectively. The PBE0 calculations were carried out using an order-N method based on Maximally Localized Wannier Functions (MLWFs).\(^{23}\) The GGA-PBE correctly predicts \( \text{Co}_3\text{O}_4 \) to be a semiconductor, but severely underestimates the band gap. The PBE+U band gap (1.96 eV) agrees well with the available experimental value (\(~1.6\) eV), whereas the band gap obtained using the PBE0 hybrid functional (3.42 eV) is strongly overestimated with respect to the available experimental data. While there is in principle no reason why the PBE0 functional should give a band gap in agreement

\( \text{FIGURE 3.8} \) Antiferromagnetic configuration and coupling coefficients of \( \text{Co}_3\text{O}_4 \). \( J_1 \) corresponds to magnetic coupling between nearest \( \text{Co}^{2+} \) neighbors and \( J_2 \) corresponds to second nearest neighbors.
with the experiment, the present result for Co$_3$O$_4$ is somewhat disappointing, as this functional has been found to yield satisfactory band gaps in several cases.$^{24,25}$

MLWFs were used also to investigate the bonding properties of Co$_3$O$_4$. Independent of the electronic structure approach, we found 7 and 6 singly occupied d-type Wannier functions whose centers are very close to each cobalt ion at a tetrahedral and octahedral site, respectively. This is a clear indication that these ions have Co$^{2+}$ and Co$^{3+}$ oxidation states, in agreement with the formal oxidation states derived from simple chemical arguments. Besides d-type MLWFs on the cobalt ions, there are also Wannier functions with the character of sp$^3$d bonds between cobalt and oxygen ions. Such hybridized bonding states imply the presence of a covalent component in the primarily ionic bonding character of Co$_3$O$_4$.

In agreement with experiment and consistent with crystal field theory (Fig. 3.2), the computed magnetic structure is characterized by three unpaired spins on the Co$^{2+}$ ions and a weak coupling between the atomic magnetic moments. Due to the inclusion of exchange and correlation interactions in our calculations, however, the spin energy level distribution derived from the average energies of the d-type MLWFs (Fig. 3.7) is quite different from the one given by simple crystal field theory. Both the PBE+U method and the hybrid PBE0 functional yield values of the magnetic moments which agree well with experiment. This is an indication that these approaches provide a satisfactory description of the cobalt localized d states and, more generally, of the ground state properties of Co$_3$O$_4$. 

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Bibliography


4 Surface Properties of the Co₃O₄ (110) Surface

4.1 Introduction and Experimental Information

Surfaces have a key role in applications of Co₃O₄ in catalysis, and a detailed understanding of the physical and chemical properties of Co₃O₄ surfaces is important for the design of Co₃O₄-based functional materials with improved performance. Experimental atomic-scale investigations of Co₃O₄ surfaces are relatively scarce. To help obtaining a better fundamental understanding of the surface properties of Co₃O₄, in this chapter, we present a first-principles Density Functional Theory (DFT) study of the Co₃O₄(110) surface, which is the predominant one on Co₃O₄ nano-rods,¹ and is believed to be mainly responsible for the oxidation reactivity² of this material.

Co₃O₄ crystallizes in the cubic normal spinel structure with magnetic Co²⁺ ions in tetrahedral sites and non-magnetic Co³⁺ ions in octahedral sites. The (110) surface is a Type III polar surface according to Tasker’s criterion.³ It has two different terminations, usually denoted as the A and B terminations (see Fig. 4.1): the (110)-A termination exposes both Co²⁺ and Co³⁺ ions, whereas the (110)-B termination has only Co³⁺ ions. As Co₃O₄ is basically ionic,⁴ the unit cell of the (110)-A termination – exposing two Co²⁺, two Co³⁺, and four O²⁻ ions – has formal charge +2, whereas the same unit cell on the (110)-B termination exposes two Co³⁺ and four O²⁻ ions, and therefore has formal charge -2. Thus a (110) slab can be viewed as a stack of charged layers as sketched in Fig. 4.2.
While in principle such a system has a polarization which increases linearly with slab thickness and eventually diverges, in reality polarity compensation mechanisms exist which prevent the “polar catastrophe” and stabilize the surface.\(^5\) (also see Fig. 4.2)

\[\text{Figure 4.1 Ball and stick models of the A (top) and B (bottom) terminations of Co}_3\text{O}_4(110). \text{ Left: side views. Right: top views (surface layer only). Superexchange interactions between surface Co ions are indicated. Dashed lines denote a rectangular cell which is the primitive surface cell for the (110)-A terminations and a surface cell twice the primitive cell for the B-(110) termination; the solid line indicates the primitive cell of the B termination. Light cyan and navy blue balls indicate Co}^{2+} \text{ and Co}^{3+} \text{ ions, red ones indicate O}^{2-} \text{ ions.}\]

\[\text{Figure 4.2 Sketch of a Co}_3\text{O}_4(110) \text{ slab model as a stack of charged layers.}\]
Experimental studies on Co$_3$O$_4$(110) epitaxial films grown on MgAl$_2$O$_4$(110) single crystal substrates found that the surfaces of the as-grown films are relatively disordered and have an oblique low-energy electron diffraction (LEED) pattern characteristic of the (110)-B termination, whereas the annealed surfaces show a sharp rectangular LEED pattern indicating a well ordered (110)-A termination. These findings indicate that the (110)-A termination is more stable than the B one under ultrahigh vacuum (UHV) conditions. However, the occurrence of the (110)-B termination on the as-grown films suggests the existence of kinetic limitations, so that the actual exposed termination may depend on the synthetic method and the post-treatment of the samples.

A number of first principles studies of Co$_3$O$_4$(110) have been already reported, but some basic properties, including the polarity compensation mechanism, have not been examined in detail and/or are not yet well understood. An objective of this work is thus to investigate how polarity is compensated on the two different surface terminations of Co$_3$O$_4$(110). Since experiments do not show evidence of surface reconstruction on either termination, we will restrict ourselves to undefected and unreconstructed (110)-A and (110)-B terminations obtained by simply relaxing the bulk truncated structures, and will study the compensation mechanism by focusing on the surface electronic structure. We will also examine the surface magnetic structure as recent experiments on Co$_3$O$_4$ nanostructures have revealed interesting features which cannot be fully explained simply on the basis of the magnetic properties of bulk Co$_3$O$_4$. 
4.2 Methods and Models

Calculations were performed within the plane wave-pseudopotential scheme as implemented in the Quantum Espresso package. Spin polarization was always included and exchange and correlation were described using the gradient corrected Perdew-Burke-Ernzerhof (PBE) functional with on-site Coulomb repulsion U term on the Co 3d states. As mentioned in the Introduction, we used a single U value for all Co ions, namely $U = 5.9 \text{ eV}$, which corresponds to the weighted average of the two computed U values for the bulk. For comparison, pure PBE calculations have been also performed; however, unless otherwise specified, only PBE+U results are reported in the following. Ultrasoft pseudopotentials were used and the valence electrons included O 2s, 2p and Co 3d, 4s states. Plane wave energy cutoffs of 35 Ry for the smooth part of the wavefunction and 350 Ry for the augmented density were found sufficient to ensure a good convergence of the computed properties.

Surfaces were modeled using a periodic slab geometry, with consecutive slabs separated by a vacuum layer 15 Å wide. We adopted the PBE+U lattice constant from our previous work which is 2% larger than the experimental one. (Pure PBE calculations were performed with the corresponding optimized lattice constant.) To study the properties of a single A or B termination, we considered symmetric slabs with odd number of layers, for which the total dipole moment is zero. Although nonstoichiometric, these models provide useful information in the thick sample limit, when the effect of the nonstoichiometry becomes negligible. We performed tests on slabs with different number of layers, from 5 up to 11 layers, and found that a well converged
description could be achieved with 9-layer models. On the other hand, to achieve perfect stoichiometry, one should consider slabs with even number of layers, which expose the A and B terminations on the two different sides, and have a dipole moment perpendicular to the slab. We also performed tests to compare the results obtained with symmetric and non-symmetric slabs and found that the surface properties (e.g. the surface electronic structures of the different terminations, see Sect. 3C) obtained with 9-layer models agree well with those from symmetric slabs of 8 or 10 layers. Results reported in the following thus refer to calculations on 9-layer models, unless otherwise specified. Structural optimizations were carried out by relaxing all atomic positions until all forces were smaller than $1 \times 10^{-3}$ a.u.

For most calculations the rectangular surface cell depicted in Fig. 4.1 was used, and the sampling of the surface Brillouin zone was performed using a $3 \times 4$ k-point grid. Comparisons to calculations using a $4 \times 6$ k-point grid show surface energy differences of $\sim 1 \text{meV/Å}^2$. Maximally-localized Wannier functions (MLWFs)\cite{21} were obtained using the $\Gamma$ point only on models with a surface supercell twice the size of the rectangular cell in Fig. 4.1. Test calculations showed that the results for the two setups were in satisfactory agreement. The MLWFs were calculated with the algorithm developed by Sharma et al.\cite{22}

### 4.3 Surface Energies

In order to study the properties of a single termination, it is convenient to consider symmetric, non-stoichiometric slabs, and express their surface formation energies in
terms of the chemical potentials of Co ($\mu_{\text{Co}}$) and oxygen ($\mu_O$). Since $3\mu_{\text{Co}} + 4\mu_O = \mu_{\text{Co}_3\text{O}_4}$ under equilibrium conditions, $\mu_{\text{Co}_3\text{O}_4}$ being the chemical potential of bulk Co$_3$O$_4$, it is possible to eliminate the dependence on $\mu_{\text{Co}}$, and express the surface energy only in terms of the oxygen chemical potential $\mu_O$ or, equivalently, $\mu_O' \equiv \mu_O - \frac{1}{2} E_{\text{tot}}(\text{O}_2)$, where $E_{\text{tot}}(\text{O}_2)$ is the total energy of an O$_2$ molecule. The oxygen potential $\mu_O'$ satisfies the condition $\frac{1}{4} H_f \leq \mu_O' \leq 0$, where $H_f$ is the heat of formation of bulk Co$_3$O$_4$ and the lower and upper limits correspond to O-poor and O-rich conditions, respectively. Values for $H_f$ are given in Ref. 4.

The computed surface energies for slab models with 5, 7 and 9 layers in the O-rich limit ($\mu_O' = 0$) are listed in Table 4.1, whereas Fig. 4.3 shows the surface energies in the full range of $\mu_O'$ for the 9-layer slabs. For the sake of comparison with previous GGA calculations, in Fig. 4.3 results obtained at both the pure PBE and PBE+U levels are presented. We can see a significant difference between the results of the two approaches. According to the pure PBE calculations the (110)-B termination has lower surface energy except at very low $\mu_O'$, in agreement with previous published results. By contrast, the PBE+U calculations predict the (110)-A termination to be more stable in a wide range of the oxygen chemical potential, consistent with the experimental results of Ref. 6. This difference between the PBE and PBE+U results can be understood on the basis of the computed surface electronic structures, reported later. Briefly, the B termination is found to have delocalized metallic surface states, for which the energy penalty from the Hubbard U term is larger, thus making the surface energy of the B termination higher. The PBE functional is known to overestimate the O$_2$ binding energy.
our computed value is 130 Kcal/mol, against 118 kcal/mol from experiment. This
error affects the chemical potential of the oxygen rich limit as indicated in Fig. 4.3.

<table>
<thead>
<tr>
<th>Surface Energy (eV/Å²)</th>
<th>A termination</th>
<th>B termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-layer</td>
<td>0.081</td>
<td>0.080</td>
</tr>
<tr>
<td>7-layer</td>
<td>0.085</td>
<td>0.081</td>
</tr>
<tr>
<td>9-layer</td>
<td>0.082</td>
<td>0.080</td>
</tr>
</tbody>
</table>

Table 4.1 Surface energies of Co₃O₄(110), computed at the PBE+U level and in the O-rich limit, for symmetric slabs of different thicknesses.

Figure 4.3 Surface energies of the (110)-A and (110)-B surfaces from PBE and PBE+U calculations. Vertical lines define the allowed range of the oxygen chemical potential \( \mu'_O \equiv \mu_O - \frac{1}{2} E_{\text{tot}}(O_2) \): the leftmost line indicates the oxygen-poor limit, while the lines on the right indicate the oxygen rich limit determined using the computed (\( \mu'_O = 0 \) line) and experimental (rightmost line) \( O_2 \) binding energy, respectively.
4.4 Surface Relaxation

The A-terminated Co$_3$O$_4$(110) surface exposes all types of ions present in the bulk, namely Co$^{2+}$, Co$^{3+}$ and O$^{2-}$ ions. (We identify the surface ions with the oxidation state they have in the bulk, even though their actual oxidation state may be different at the surface.) The Co$^{2+}$ (Co$^{3+}$) ions are 3-fold (4-fold) coordinated and form bonds with two surface oxygen ions and one (two) oxygen(s) in the second layer; they will be denoted Co-3f (Co-4f) in the following. All surface oxygens are equivalent and 3-fold coordinated to one Co-3f and one Co-4f surface ion as well as to one 6-fold Co$^{3+}$ in the second layer (see Fig. 4.1). Calculated atomic relaxations on the (110)-A termination are listed in Table 4.2. While all surface atoms undergo an inward relaxation, this relaxation is larger for the Co than for the oxygen ions, and therefore the surface becomes slightly buckled. The reflection symmetry of the surface remains during relaxation, so that on the relaxed (110)-A surface there is one type of 3-fold and one type of 4-fold Co ion as well as one type of oxygen ion. As shown in Table 4.2, all surface Co-O bonds are shorter after relaxation.
### Table 4.2 Atomic displacements from bulk-like positions on the relaxed (110)-A surface.

Displacements along the [001], [110] and [110] directions are denoted as (Δx, Δy, Δz). Atoms are labeled as in Fig. 4.1.

<table>
<thead>
<tr>
<th>Label</th>
<th>Δx</th>
<th>Δy</th>
<th>Δz</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co3f1</td>
<td>0.17</td>
<td>0.00</td>
<td>-0.22</td>
<td>Co3f2-O1, -5.9%</td>
</tr>
<tr>
<td>Co3f2</td>
<td>-0.17</td>
<td>0.00</td>
<td>-0.22</td>
<td>Co4f1-O1, -0.2%</td>
</tr>
<tr>
<td>Co4f1</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.19</td>
<td>Co4f1-O3, -0.2%</td>
</tr>
<tr>
<td>Co4f2</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.19</td>
<td>Co3f1-O3, -5.9%</td>
</tr>
<tr>
<td>O1</td>
<td>0.00</td>
<td>-0.06</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>0.00</td>
<td>0.06</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>0.00</td>
<td>0.08</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>0.00</td>
<td>-0.08</td>
<td>-0.05</td>
<td></td>
</tr>
</tbody>
</table>

The less dense (110)-B surface exposes only Co$^{3+}$ and O$^{2-}$ ions. All Co ions are equivalent and 4-fold coordinated to two surface and two second layer oxygens. There are two different types of surface oxygen ions: one is 2-fold (O-2f) coordinated to one surface Co ion and one 4-fold Co$^{2+}$ ion in the second layer; the other is 3-fold (O-3f) coordinated to one surface Co and two Co$^{3+}$ ions in the second layer (see Fig. 4.1). Table 4.3 shows the computed atomic relaxations for the (110)-B termination. The surface 2-fold and 3-fold oxygen ions behave differently upon relaxation: O-2f ions relax outwards and the bond with Co ions weakens, whereas O-3f ions relax inwards and their bonds to Co ion become stronger upon relaxation.
<table>
<thead>
<tr>
<th>Label</th>
<th>$\Delta x$</th>
<th>$\Delta y$</th>
<th>$\Delta z$</th>
<th>Bond expansion</th>
</tr>
</thead>
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<tr>
<td>Co4f</td>
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<td>-0.08</td>
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</tr>
<tr>
<td>O2f</td>
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<td>-0.04</td>
<td>0.08</td>
<td>Co1-O3f</td>
</tr>
<tr>
<td>O3f</td>
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<td>-0.14</td>
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</tr>
</tbody>
</table>

**Table 4.3** Atomic displacements from bulk-like positions on the relaxed (110)-B surface. Displacements along the [001], [110] and [110] directions are denoted as ($\Delta x$, $\Delta y$, $\Delta z$). Atoms are labeled as in Fig. 1.

### 4.5 Surface magnetization

In bulk Co$_3$O$_4$, only the Co$^{2+}$ ions at tetrahedral sites have a magnetic moment, whereas the Co$^{3+}$ ions at octahedral sites are non-magnetic. At the surface, the bulk symmetry is broken and the ionic coordinations are reduced, and therefore the magnetic properties of the surface cobalt ions can differ from those in the bulk. We computed the magnetic moments of the different surface ions on the (110)-A and (110)-B surfaces using a Löwdin charge analysis. The results, reported in Table 4.4, show that the surface Co$^{3+}$ ions are indeed magnetic on both terminations. Moreover, all surface Co ions have similar magnetic moments, which are also similar to the computed magnetic moment, 2.59$\mu_B$, of the Co$^{2+}$ ions in bulk Co$_3$O$_4$. Contour plots of the surface spin density for both terminations are shown in Fig. 4.4. We can see that on the (110)-A surface the oxygen ions are essentially non-magnetic, whereas on the (110)-B termination a slight spin polarization is present on the O-2f ions. The ionic magnetic moments in the second layer are already the same as in the bulk.
To determine the ground state surface magnetic configuration, we need to analyze the couplings between the different magnetic moments. In contrast to the bulk, where magnetic couplings are due to weak superexchange interactions (two metal ions separated by two oxygen ions), on the surface the presence of magnetic $\text{Co}^{3+}$ ions gives rise to normal superexchange interactions (two metal ions separated by one oxygen ion). There are normal superexchange interactions between surface Co ions, as well as between surface ions and the magnetic $\text{Co}^{2+}$ ions in the next layer (Fig. 4.1). For the A termination, there are three different superexchange interactions. The coupling between surface neighboring Co-4f ions (J1 in Fig. 4.1) is via an intermediary oxygen ion in the second layer, with a Co-O-Co angle of 90°. According to the Goodenough-Kanamori-Anderson (GKA) rules, the exchange interaction between them is ferromagnetic. The other two superexchange interactions are associated with angles of about 120°, for which the GKA rules do not make well defined predictions. The ground state ordering obtained by calculating the surface energies of different magnetic configurations is given in Table 4.5.

<table>
<thead>
<tr>
<th>Ion type</th>
<th>Magnetic moment</th>
<th>Ion type</th>
<th>Magnetic moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co3f ($\text{Co}^{2+}$ in bulk)</td>
<td>2.64</td>
<td>Co4f ($\text{Co}^{3+}$ in bulk)</td>
<td>2.56</td>
</tr>
<tr>
<td>Co4f ($\text{Co}^{3+}$ in bulk)</td>
<td>2.52</td>
<td>O2f</td>
<td>0.08</td>
</tr>
<tr>
<td>O</td>
<td>0.02</td>
<td>O3f</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4.4 Magnetic moments ($\mu_B$) of surface ions determined through Lowdin charge analysis.
**Figure 4.4** Contour plots of the surface spin density on the (110)-A (left) and (110)-B (right) surfaces. The scale in the bottom has units of $\mu_B$. The positions of the Co ions are indicated by white circles and those of the oxygen ions by red circles.

<table>
<thead>
<tr>
<th></th>
<th>A Termination</th>
<th>B Termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑↑↑↑</td>
<td>0.0</td>
<td>↑↑</td>
</tr>
<tr>
<td>↓↓</td>
<td></td>
<td>↓↓</td>
</tr>
<tr>
<td>↑↑↑↑</td>
<td>2.8</td>
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</tr>
<tr>
<td>↓↑↓↑</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>↑↑</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.5** Surface energies (meV/Å$^2$) of various magnetic configurations relative to the lowest energy state, taken as zero. Co-4f ions are schematically indicated by underlined arrows, Co-3f ions and $\text{Co}^{2+}$ ions in the second layer are indicated by arrows without underlines.

On the (110)-B termination, the distance between the surface magnetic Co-4f ions is quite large, and therefore the coupling between them can be considered weak. The only normal superexchange interaction is the one between surface Co-4f and $\text{Co}^{2+}$ ions in the second layer, which is also associated with a Co-O-Co angle of about 120°. From total
energy differences between different magnetic configurations, it appears that this coupling is antiferromagnetic (see Table 4.5).

Based on the results in Table 4.5, the expected surface ground state magnetic configurations for the A and B terminations are schematically illustrated in Fig. 4.5. The surface region comprises the first and second layers, and is characterized by normal superexchange couplings, whereas below the second layer only weak antiferromagnetic superexchange interactions are present, as in bulk Co$_3$O$_4$. The presence of a ferrimagnetic surface region on the A termination is interesting. It can provide the mechanism to understand a number of experimental observations on Co$_3$O$_4$ nanostructures, notably: (i) the decoupling of magnetic core and shell contributions$^{12}$; (ii) the ferrimagnetic behavior of porous nanostructures$^{13}$; (iii) the exchange anisotropy phenomena observed in Co$_3$O$_4$ nanowires.$^{16}$

![Figure 4.5](image.png)

**Figure 4.5** Magnetic ground state configurations of the (110)-A (left) and (110)-B (right) surfaces, as inferred from the surface energies in Table 5. Red arrows refer to Co-4f and blue arrows refer to Co-3f and Co$^{2+}$ in second layer.
4.6 Surface Electronic Structure

Surface electronic states in the bulk band gap are of great interest because they can strongly influence the physical and chemical properties of semiconductor materials. For Co$_3$O$_4$, evidence of surface states in the band gap has been recently found in STM and STS studies on nanowires. In this section we characterize the surface states on both Co$_3$O$_4$(110) terminations, by studying their energies and spatial distributions, i.e. on what ions these states are primarily localized, and how fast they decay when moving from the surface toward the bulk. The calculations were performed on symmetric slab models of 9 layers, for which spin densities are also symmetric, and spin up and spin down states are degenerate in energy. For this reason, we do not distinguish between spin up and spin down in the following; instead, all results include the sum over the two spin directions.

Fig. 4.6 shows the computed band structures along various directions of the surface Brillouin zone. By comparison with the projected bulk structure (shaded area in Fig. 4.6), it is evident that on both surface terminations several surface state bands are present in the lower half of the bulk band gap. Partially occupied bands are present, indicating a metallic state. In Fig 4.7, we plot the Layer-Resolved Density of States (LRDOS) for surface models of A, B termination and a 4-layer bulk model. The DOS curves for the inner layers have a clear bulk-like character, as shown by the similarity between the bulk DOS and the DOS for the 4$^{th}$ and 5$^{th}$ layers of both surface models. At the surface new states appear close to the top of the valence band, while in the second layer, just below
the surface, the tail of these states is still present, more prominent for the B termination, but starting from the third layer the DOS is already bulk-like.

![Band structures for symmetric slabs of 9 layers terminated by (110)-A (top) and (110)-B (bottom) surfaces. Spin up and spin down states are degenerate in energy (see text). The shaded area represents the projected bulk bands. The energy zero corresponds to the Fermi energy. For both terminations partially occupied bands are present, indicating that the surfaces are metallic.](image)

**Figure 4.6.** Band structures for symmetric slabs of 9 layers terminated by (110)-A (top) and (110)-B (bottom) surfaces. Spin up and spin down states are degenerate in energy (see text). The shaded area represents the projected bulk bands. The energy zero corresponds to the Fermi energy. For both terminations partially occupied bands are present, indicating that the surfaces are metallic.

To clarify the character of the surface states, in Fig. 4.8 we show the partial densities of states, obtained by projecting the surface LRDOS onto the different surface oxygen and cobalt ions separately. On the (110)-A termination, surface states originate predominantly from surface O 2p states, and may be described as oxygen dangling bond-like states. On the (110)-B termination, both Co and oxygen contribute to the surface states which look more delocalized and metallic-like in character in comparison to those on the A termination. Partially metallic surface states are known to occur on
other transition-metal oxide polar surfaces as well, notably on the Zn-terminated ZnO (0001) surface, suggesting that partial metallization may be a quite common phenomenon on surfaces of transition metal oxides.

![Figure 4.7](Image)

Figure 4.7 Spin-averaged layer-resolved Density of States (DOS) for the (110)-A (left), (110)-B (middle) surfaces and bulk (right) of Co₃O₄. Surface states in the surface layer are highlighted. The energy zero corresponds to the Fermi energy. The DOS curves for the inner layers in the slab calculations have a clear bulk-like character, as shown by the similarity between the bulk DOS and the DOS for the 4th and 5th layers of both surface models.

Work functions for the two surface terminations were computed at both PBE and PBE+U levels. The results, reported in Table 4.6, clearly show a larger work function for the B termination relative to the A case, which can be attributed to the different surface dipoles on the two surfaces. We can also notice that PBE+U predicts a larger value of
the work function in comparison to PBE, which may be attributed to the stabilization of the Co d states at the Fermi energy caused by the U term.

![Projected Density of States](image)

**Figure 4.8** Spin-averaged projected density of states on the (110)-A (top) and (110)-B (bottom) surfaces. The energy zero corresponds to the Fermi energy.

<table>
<thead>
<tr>
<th></th>
<th>A Termination</th>
<th>B Termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>3.96</td>
<td>4.59</td>
</tr>
<tr>
<td>PBE+U</td>
<td>5.28</td>
<td>5.97</td>
</tr>
</tbody>
</table>

**Table 4.6** Computed work functions (eV) from PBE and PBE+U calculations

### 4.7 Compensating Charges and Bonding Properties

A simple way to determine the value of the compensating charge for each termination is by calculating the total charge $Q_i$ in each layer of the slab. This can be done very effectively...
and precisely by counting the number of Wannier centers (WCs) associated with each ion in that layer.\(^4\) For the (110)-A termination, we find that the surface unit cell of the outermost layer has a total charge \(Q_4 = +1\), instead of the value +2 found for the same layer in the bulk (see Fig. 4.2). Similarly, for the (110)-B termination, the total charge of the top layer is \(Q_4 = -1\), instead of the value -2 for the same layer in the bulk. Below the second layer, the charge of each layer is the same, +2 or -2, as in the bulk (Fig. 4.2). As expected,\(^5\) the compensating charges are \(\Delta Q = -1\) and +1/cell for the A and B termination, respectively.

The same result can be also obtained by using a result of the modern theory of polarization\(^{27,28}\) which shows that the compensating (or external) surface charge density \(\sigma_{\text{ext}}\) is equal to the component of the bulk polarization, \(P_{\text{bulk}}\), normal to the surface.\(^{27,28}\)

\[
\sigma_{\text{ext}} = P_{\text{bulk}} \cdot \hat{n}
\]

We determine \(P_{\text{bulk}}\) from our previously calculated MLWFs and WCs for bulk Co\(_3\)O\(_4\).\(^4\) Eq. (1) then gives the surface charges on the A and B terminations simply using the frozen bulk ionic positions and ionic charges, without the necessity of slab calculations.

For bulk Co\(_3\)O\(_4\) different types of Wannier functions are present, namely \(d\) states of \(t_{2g}\) and \(e_g\) symmetries localized on the cobalt ions, and Wannier functions with the character of \(sp^3d\) bonds both between the cobalt and \(O^2-\) ions.\(^4\) These MLWFs show that the bonding character of Co\(_3\)O\(_4\), although mainly ionic, has also a small covalent component.
As for the (110) surface, the MLWFs show that the surface is more covalent than the bulk, a result valid for both the A and B terminations. For instance, on the outermost surface layer there are several Wannier centers in mid position between different ions, see Fig. 4.9. The MLWF analysis also indicates that on the A termination the compensating excess electron is shared among two different Co$^{3+}$ ions, which are thus partially reduced. This compensating charge cannot be described by a single Wannier function or Kohn-Sham state. Similarly, on the B termination the compensating hole is shared between two Co$^{3+}$ ions which are thus partially oxidized. On the B termination, one MLWF has relatively large spread, indicating that this termination has a metallic character.

**Figure 4.9** Charge densities of typical covalent MLWFs on the (110)-A (left) and (110)-B (right) termination.

So far, our results were obtained from calculations on symmetric, non-stoichiometric slab models appropriate for the study of the surface properties of thick samples, on
which charge compensation occurs naturally. In the case of thin films and nanostructures, however, the polarity may remain uncompensated below a critical thickness and possibly affect the properties and reactivity of these systems. It is therefore interesting to determine what is this critical thickness for Co$_3$O$_4$(110). To this end we considered non-symmetric, stoichiometric slab models with different (even) number of layers and calculated the formation energy $E_{\text{form}}$ (total energy difference between the slab and an equal number of bulk Co$_3$O$_4$ units) and the electrostatic potential energy drop along the slab $\Delta V$ as a function of the number of layers. The results (Fig. 4.10) show that both $E_{\text{form}}$ and $\Delta V$ become approximately constant when the number of layers is larger than 4, implying that the critical thickness is 4 layers.

![Figure 4.10](image.png)  

**Figure 4.10** Formation energy and electrostatic potential energy drop (eV) for stoichiometric slab models as a function of the number of layers in the slab.
4.8 Summary and Conclusion

We have presented an accurate and comprehensive computational study of the structural, electronic and magnetic properties of the polar Co$_3$O$_4$ (110) surface by the GGA+U method. We found the atomic relaxations give rise to a surface buckling of $\sim 0.2$ Å on both surface terminations. Surface energy calculations indicate that the (110)-A termination is more stable in a wide range of the oxygen chemical potential, in agreement with surface science experiments. The Co$^{3+}$ ions do not have a magnetic moment in the bulk but become magnetic at the surface which leads to interesting surface magnetic properties, as found also in recent experiments on Co$_3$O$_4$ nanostructures. From band structure and density of states calculations, we found that surface electronic states are present in the bulk band gap for both terminations, consistent with STM experiments on Co$_3$O$_4$ nanowires. The B termination is found to have a more pronounced metallic character compared to the (110)-A surface. It has also a larger work function, which could play an important role in the study of surface redox reactions. Maximally localized Wannier functions clearly show that charge compensation takes place on the top layer of both terminations. They also reveal that the surface is more covalent with respect to the bulk. Calculations on asymmetric models predict a critical thickness for polarity compensation of four layers. We hope that these predictions can be tested experimentally in the near future.
Bibliography


(14) Serrano, A.; Pinel, E. F.; Quesada, A.; Lorite, I.; Plaza, M.; P&eacute;rez, L.; Jim&eacute;nez-Villacorta, F.; De la Venta, J.; Martínez-González, M.


Chapter 5

5 Water Adsorption and Oxidation at the Co$_3$O$_4$ (110) Surface

5.1 Introduction

Understanding the interaction of Co$_3$O$_4$ surfaces with water is an essential step to shed light on the atomic scale reaction mechanisms of OER on Co$_3$O$_4$ anodes. More generally, the interaction of water with oxide surfaces is important because water is always present on these surfaces, and has thus a significant influence on their catalytic activity. In this chapter, we investigate the interaction of water with both A and B terminations of Co$_3$O$_4$ (110) surface using density-functional theory (DFT) calculations with on-site Coulomb repulsion U term.$^1$ As shown in earlier chapters of bulk Co$_3$O$_4$ and the clean Co$_3$O$_4$(110) surface$^{2,3}$, the DFT+U method provides a quite satisfactory description of the electronic structure of Co$_3$O$_4$. For instance, the computed bulk band gap is 1.92 eV, against an experimental value of $\sim$ 1.6 eV.$^{4,5}$ Moreover, for the polar Co$_3$O$_4$(110) surface, DFT+U predicts the cationic A-terminated surface to be more stable than the anionic B-terminated one in a wide range of oxygen partial pressure,$^3$ in good agreement with the experimental observations.$^6,7$
Only a few experimental surface science and theoretical investigations of water on the Co$_3$O$_4$(110) surface are available. Here we present a comprehensive investigation of the structure and energetics of adsorbed water monolayers at different coverages and determine the surface phase diagram as a function of the water chemical potential (or water vapor pressure). Based on these results, we investigate plausible intermediates of the OER and determine the energetic profile of the reaction. Through analysis of the electronic structure, we explain why the A termination is more active for the OER than the B-terminated surface.

5.2 Methods and Models

The electronic structure methods used in this chapter are the same as in the last chapter. Surfaces were modeled by periodic slabs separated by a vacuum layer 12 Å wide, and symmetric non-stoichiometric slabs with 7 layers were used for both A and B terminations. The effect of non-stoichiometry is known to become negligible for sufficiently thick slabs, as those used in this work, and we find it thus more convenient to consider such symmetric slabs instead of stoichiometric asymmetric slabs requiring the use of dipole correction methods. We considered 1×1 surface models with a rectangular (8.08 × 5.72 Å$^2$) surface cell (Fig. 5.1), which corresponds to the surface primitive cell for the A termination. For the B termination, this rectangular cell is twice the size of the rhombic primitive cell. We sampled the surface Brillouin zone using a 2×3 k-point grid; tests with denser 3×4 k-point grid gave adsorption energy differences smaller than 0.05 eV. Similarly, test calculations with a 9-layer slab gave differences in water adsorption energy of less than 0.1 eV. We used lattice parameters optimized at
the DFT+U level, which are 2% larger than the experimental ones.\textsuperscript{2} Ionic structures were relaxed until all forces were smaller than $1\times10^{-3}$ a.u. As discussed in Ref. \textsuperscript{3}, the Co$_3$O$_4$(110) surface shows a delicate surface magnetic ordering. While the magnetic ordering is not expected to have a significant impact on water adsorption, all calculations were consistently performed on the ground magnetic state of the corresponding surface model in order to avoid possible errors from different magnetic orderings.

Adsorption calculations were performed using asymmetric surface models with adsorbates on one side only. Since this asymmetric model gives rise to an artificial dipole moment which may affect the computed adsorption energies, we performed additional calculations on symmetric models with identical adsorbates on both sides of the slab. As shown in Table 5.1 and Table 5.2, the two (symmetric and asymmetric) models give very similar adsorption energies indicating that the effect of the artificial dipole moments is essentially negligible. In all cases, positive values of the adsorption energy indicate that the adsorption is favorable. Water dissociation barriers were calculated by the nudged elastic band (NEB) method\textsuperscript{15}.

Surface formation energies as a function of the water chemical potential ($\mu_{H2O}$) were determined using the ab-initio thermodynamic approach.\textsuperscript{16} We used for Co the value of the chemical potential in bulk Co$_3$O$_4$, and assumed for oxygen the value of the chemical potential at 298 K and 0.21 atm (the partial pressure of oxygen gas in air at room temperature). Entropy contributions to the chemical potential were evaluated from experimental data listed in the NIST-JANAF Thermochemical Tables.\textsuperscript{17} Zero point
energies were calculated using experimental vibrational frequencies for oxygen and molecular water; \( h\nu = 460 \text{ meV} \) was used for the vibrational frequency of surface O-H bonds.\(^{16}\) The chemical potential of liquid water (\( \mu_{\text{liq}} \)) relative to water vapor was estimated from the experimental value of the Gibbs free energy change in the phase transition; in this way we find that \( \mu_{\text{liq}} \) varies between -0.55 and -0.63 eV in the temperature range 273 - 373K.

### 5.3 Structure and Energetics of Adsorbed Water

The geometries of the A- and B-terminated surfaces are shown in Fig. 5.1. The A termination exposes both types of bulk Co ions. The bulk \( \text{Co}^{2+} \) (tetrahedral) and \( \text{Co}^{3+} \) (octahedral) ions become 3-fold (\( \text{Co}_{3f} \)) and 4-fold (\( \text{Co}_{4f} \)) coordinated at the surface, respectively, while all surface oxygens are equivalent and 3-fold coordinated. There are two \( \text{Co}_{3f} \), two \( \text{Co}_{4f} \) and four oxygen ions per surface unit cell. On this surface water is found to adsorb preferentially at bridge sites between either two \( \text{Co}_{3f} \) or two \( \text{Co}_{4f} \) ions, the \( \text{Co}_{3f}-\text{Co}_{3f} \) and \( \text{Co}_{4f}-\text{Co}_{4f} \) distances being 3.10 and 2.85 Å, respectively. The B-\((110)\) surface exposes oxygen anions and cobalt ions that are octahedrally coordinated in the bulk. All Co ions are equivalent and 4-fold coordinated at the surface, whereas there are two different types of surface oxygen ions, one 2-fold (\( \text{O}_{2f} \)) and the other 3-fold (\( \text{O}_{3f} \)) coordinated. There are two cobalt, two \( \text{O}_{2f} \) and two \( \text{O}_{3f} \) ions per surface unit cell. The distance between Co ions is quite large, 5.72 Å, on the B termination, and bridge sites are not favorable for water adsorption. We found instead that each surface Co ion can bind two water molecules. Altogether, there are four adsorption sites per cell for both terminations in our surface models (Fig. 5.1), so the smallest water coverage in our
calculations is 0.25 of a monolayer (ML), whereas full coverage (1 ML) corresponds to four water molecules per cell.

Figure 5.1 Ball and stick model of the Co$_3$O$_4$ (110) surface structure. Top (a1 and b1) and side (a2 and b2) views of A (left) and B (right) terminations. In the top views, empty blue circles indicate water and hydroxyl group adsorption sites. Dark and pale blue spheres indicate Co cations which in the bulk are octahedrally and tetrahedrally coordinated, respectively. Red spheres indicate oxygen anions.

For a surface with n adsorbed waters, we define the adsorption energy per molecule ($E_{ads}$) as the total energy difference $E_{ads} = [E_{tot}(0) + nE_{tot}(H_2O) - E_{tot}(n)]/n$, where the various terms represent the total energies of the clean surface ($E_{tot}(0)$), n gas-phase water molecules ($nE_{tot}(H_2O)$), and the surface with n adsorbed waters ($E_{tot}(n)$), respectively. Computed adsorption energies and dissociation barriers at 0.25 ML are listed in Table 5.1, while adsorption geometries and minimum energy pathways (MEPs) are shown in the Supporting Information (SI), Fig. 5.2 and Fig. 5.3. These results clearly...
show that on both surface terminations dissociative adsorption of water is energetically favored. Moreover dissociation barriers are very low, indicating that the $\text{Co}_3\text{O}_4$ (110) surface is easily hydroxylated, in agreement with the experiment. On the A-(110) surface, dissociation at the Co$_{4f}$ bridge site is preferred. On the B termination, adsorption of the dissociated H at the O$_{2f}$ oxygen is more favorable than at O$_{3f}$.

*Figure 5.2* Molecular and dissociative adsorption configurations of water on the $\text{Co}_3\text{O}_4$ (110) surface at 0.25 ML coverage. Selected adsorption distances (in Å) are indicated.
Figure 5.3: Minimum energy pathways for water dissociation on the Co$_3$O$_4$ (110) surface at 0.25 ML coverage.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$E_{\text{ads}}$</th>
<th>$E_{\text{barrier}}$</th>
<th>Configuration</th>
<th>$E_{\text{ads}}$</th>
<th>$E_{\text{barrier}}$</th>
</tr>
</thead>
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<tr>
<td>A:M@Co4f</td>
<td>0.62</td>
<td></td>
<td>B:M</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>A:M@Co3f</td>
<td>1.02</td>
<td></td>
<td>B:D-H@O3f</td>
<td>1.05</td>
<td>0.16</td>
</tr>
<tr>
<td>A:D@Co4f</td>
<td>$1.55$ ($1.52$)</td>
<td>0.14</td>
<td>B:D-H@O2f</td>
<td>$1.50$ ($1.44$)</td>
<td>0.12</td>
</tr>
<tr>
<td>A:D@Co3f</td>
<td>1.27</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1 Water adsorption energies and dissociation barriers (all in eV) for different configurations at 0.25 ML coverage. M and D denote molecular and dissociated adsorption configurations, respectively. Values in parentheses are results of calculations on symmetric slab models with identical adsorbates on both sides of the slab. Bold characters highlight the most stable structures.

Water adsorption energies at half and full monolayer coverage are reported in Table 5.2.

We notice a decrease of the adsorption energies at a full monolayer, corresponding to effective repulsive interactions between the adsorbates. The most stable adsorption
geometries for all different investigated coverages are summarized in Fig. 5.4. For the A termination, the lowest energy configuration at 0.5 ML coverage has one hydroxyl at a bridging Co$_{3f}$ and another hydroxyl at a bridging Co$_{4f}$ site (denoted A:D@Co$_{3f}$+D@Co$_{4f}$ in Table 5.2). At 1 ML coverage, all bridge sites are occupied by hydroxyl groups and surface oxygen ions are bound to hydrogens. Interestingly, the computed Co$_{4f}$-OH bond lengths for the two Co$_{4f}$ ions in the surface unit cell result to be different, 1.94 and 2.04 Å (Fig 5.5). We find that this structural difference is related to different oxidation states of the two Co$_{4f}$. On the B termination, the most stable configuration at 0.5 ML is formed by two dissociated waters with the hydrogens adsorbed at O$_{2f}$ ions (denoted B:2D-2H@O$_{2f}$ in Table 5.2). At full coverage, a mixed molecular-dissociated adsorption mode is favored, with one hydroxyl and one intact water molecule bound to each surface Co ion (denoted B:2M+2D-2H@O$_{2f}$ in Table 5.2).
**Figure 5.4** Structure of the most stable configurations of adsorbed water at different coverages on the A (left) and B (right) terminations.

**Figure 5.5** Bond lengths (in Å) and oxidation states of Co ions on fully hydrated A and B termination.
We used the results in Tables 1 and 2 to compute the surface stability diagram as a function of the water chemical potential, see Fig. 5.6. We find that the surface is partially (0.25-0.5 ML) hydroxylated under most temperature and pressure conditions. The surface is predicted to be fully covered by adsorbed water in the range of $\mu_{\text{H}_2\text{O}}$ values corresponding to liquid water.
5.4 Oxygen Evolution Reaction

Co$_3$O$_4$ is a promising anode material for the oxygen evolution reaction (OER) in electrochemical water splitting cells.$^{18-20}$ While the atomic scale mechanisms of the OER are complicated and not fully established, insights into the thermodynamics of the reaction can be obtained using the scheme developed by Nørskov and co-workers$^{11-13}$. In this scheme the OER is assumed to consist of four elementary reaction steps, each involving the coupled transfer of an electron to the electrode and a proton to water:

\begin{align*}
  H_2O(l) &\rightarrow HO^* + H^+ + e^- \quad (1) \\
  HO^* &\rightarrow O^* + H^+ + e^- \quad (2) \\
  O^* + H_2O(l) &\rightarrow HOO^* + H^+ + e^- \quad (3) \\
  HOO^* &\rightarrow O_2(g) + H^+ + e^- \quad (4)
\end{align*}
where * denotes a surface site and X* an adsorbed X species; H2O(l) is a water molecule in the liquid phase.

We determined the free energy changes of reactions (1) ~ (4) based on DFT+U calculations of adsorbed intermediates on the A and B terminations at different (0.25 and 1 ML) coverages. In agreement with previous studies,\textsuperscript{11–13} we find approximately linear scaling relations between the adsorption energies of O*, HO*, and HOO* at various adsorption sites, terminations and coverages (see Fig. 5.7). The dependences on pH and external bias potential were included as additional terms to the free energy changes,\textsuperscript{13} and contributions from zero point energy and entropy at 298K were taken as in Ref. \textsuperscript{13}. For simplicity, here we restrict ourselves to pH=0. Computed free energy changes at external potentials V = 0 and 1.23 V with respect to the standard hydrogen electrode (SHE) are plotted in Fig. 5.8. In all investigated cases, the step with the largest free energy change is the oxidation of HO* to O*, Eq. (2). The overpotential can be calculated from the difference between the voltage at which all free energy steps become down-hill and the minimum voltage required for OER, 1.23V. As shown by the results in Fig. 5.8, the overpotential depends on the reaction site, surface termination and coverage (0.39 - 0.72 V). In general, high coverage surfaces – as expected to occur in the liquid water environment of an electrochemical cell – have smaller overpotential (0.39 - 0.57 V) than low coverage surfaces (0.46 - 0.72 V), and the A termination has always a smaller overpotential (0.39 V at 1 ML) than the B-terminated surface (0.57 V at 1 ML).
Figure 5.7 Scaling relations between the adsorption energies of atomic oxygen ($\Delta E_O$) and HO (left), and O and HOO (right).

Figure 5.8 Free energy diagram at pH=0 and T = 298 K for the four steps of the OER at zero potential ($V=0$) and the equilibrium potential for oxygen evolution ($V=1.23$ V). Results for the A and B terminations at 0.25 and 1 ML water coverage are shown; for the A termination, results for both the Co-3f and Co-4f sites are given. In each case, the highest free energy change is indicated. Values in parentheses are the overpotentials, given by the difference between the highest free energy change and the minimum energy of 1.23 eV required for the OER. All energies are in eV.
To evaluate the importance of the proton transfer barriers for the second deprotonation reaction, Eq. (2), we considered the alternative process:

$$OH^* \rightarrow O^* + H^* \quad (2')$$

where the proton, instead of being transferred to liquid water, gives rise to an adsorbed H species on the Co$_3$O$_4$ surface. The barrier of (2') does not include the entropic effect of proton diffusion in liquid water and thus represents an upper bound for the free energy barrier of (2). The structures of the final states of (2'), is the fully dissociated O*+H* + H* states. We can notice that the O* adatom shows no tendency to bind to a surface oxygen so as to form an adsorbed O$_2$ species, as found in a recent study of water oxidation on anatase (101)$_{25}$, thus suggesting that O$_2$ production with formation of a surface O-vacancy is unlikely. Potential energy profiles along the MEPs for the reaction (2') are reported in Fig. 5.9. Resulting barriers are in the range 0.5-1.4 eV, i.e. about a factor of 10 higher than the barriers of first deprotonation in Fig. 5.3. Still, these barriers are typically only 0.2-0.3 eV higher than the corresponding final states, suggesting that their effect on the estimated overpotential should be relatively small.
5.5 Discussion and Conclusion

It is interesting that the A-(110) surface, which is found to be more stable than the B-(110) surface under a wide range of temperature and oxygen pressure conditions,\(^3\) is predicted to be also more active for the OER, as indicated by the smaller value of its overpotential. To understand why this is so, we have analyzed the surface electronic structure with and without adsorbed water. Projected densities of states (PDOS) for the surface top layer and the adsorbed water at different coverages are shown in Fig. 5.10. For comparison, the PDOS of A- and B-type layers in bulk Co\(_3\)O\(_4\) are also reported (right panel). On both clean surface terminations, a band of surface states is present in the bulk band gap near the valence band edge. The Fermi level is in the middle of this band,
so the surface is metallic. As discussed in Ref.²³, these states provide the charge compensation mechanism necessary to stabilize the polar (110) surface. Upon water adsorption, a gap opens at the Fermi level pushing part of the surface states at higher energy in the gap. When full water coverage is reached, empty surface states are still present in the bulk band gap, as seen by comparing the surface to the bulk PDOS.

Interestingly, the surface gap is larger on the B termination, ~1 eV vs. only 0.3 eV on the A termination, where the empty gap states become more localized on the subsurface layer (see Fig. 5.11). Even more significantly, the cobalt contribution to the surface PDOS is more prominent on the A termination, especially near the Fermi level.

In the OER, this leads to a greater stability of the O* species on the A-(110) surface relative to the B-(110) one. Since the stability of the O* species is what determines the overpotential of both Co₃O₄(110) terminations, this difference can explain the lower overpotential of the A-terminated surface.

Another remarkable feature of the PDOS curves in Fig. 5.10 is the strong energy overlap between the electronic states of the Co₃O₄ surface and those of adsorbed water. At one monolayer coverage (as present on the surface in contact with liquid water, see Fig. 5.5), this feature is more pronounced on the A termination, where the highest occupied water states are well aligned with the surface valence band maximum, as indicated also by the HOMO and LUMO (Fig. 5.10). This result is very different from what was found for TiO₂, where the highest occupied water levels are well below the surface valence band edge,²¹ despite the fact that the computed TiO₂ work function is ~2 eV larger than that of the A-(110) termination of Co₃O₄.²³ This suggests that, upon light absorption,
transfer of the photoexcited carriers in Co$_3$O$_4$ to adsorbed water should be quite easy, especially on the A-(110) surface.

**Figure 5.10** Projected density of states (PDOS) for the surface and water layers at 0.25, 0.5 and 1 ML coverage. As a reference, the PDOS curves for A- and B-type layers in bulk Co$_3$O$_4$ are also shown (right panels). The energy zero is set at the Fermi energy for the clean surfaces, which are metallic, and at the top of the valence band for all other systems, which have an energy gap.
In conclusion, using accurate DFT+U calculations we have shown that water adsorbs
dissociatively on Co$_3$O$_4$ (110) and the surface is partially to fully hydroxylated under a
wide range of conditions. Based on these results, we have investigated the energetics of
the oxygen evolution reaction using a simplified approach in which only neutral species
are considered and the liquid water environment is not included. While solvent
effects are generally expected to be small for neutral species, the neglect of the water
environment is a rather drastic approximation, for which the main justifications are
that it provides a qualitative description of experimentally observed trends, and it is
the first step toward more complete treatments which include the solvent. From the

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**Figure 5.11** Isosurfaces of charge density (0.01 a.u.) for the HOMO and LUMO on the
fully hydrated A- and B-(110) surfaces. The HOMO and LUMO energies are -0.20 eV
and +0.14 eV for the A termination and -0.30 eV and +0.27 eV for the B termination,
where the energy zero corresponds to the Fermi energy. On the B termination, the
HOMO and LUMO are mainly localized on a surface Co$_4$f with smaller contributions
from subsurface Co ions. The HOMO and LUMO are mainly localized on the surface Co-
4f ions and their nearest oxygens on the A termination, which shows also a significant
contribution of the oxygens from dissociated water.
computed free energy changes along the OER, we found that the A termination is more active for the OER than the B-terminated surface and in all cases the rate limiting step of the reaction is the second water deprotonation. For the latter we also provided an upper bound estimate of the proton transfer barrier, which indicates that its effect on the overpotential is small. Our computed overpotential for the A termination is similar to the result of a recent DFT-GGA study. As discussed in that study, comparison with experiment is difficult because the measurement is influenced by many factors, such as pH, effective surface area, and particle size. However, comparison to overpotential values calculated for other widely used anode materials such as RuO$_2$ and TiO$_2$ shows that our results for Co$_3$O$_4$ are consistent both with the experimental observation that the Co$_3$O$_4$ overpotential is slightly higher than that of RuO$_2$ (by ~ 0.2 eV) and with the established fact that Co$_3$O$_4$ is a better catalyst for the OER than TiO$_2$. 
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(17) Technology, N. I. of S. and JANAF Thermochemical Tables (on line).


Chapter 6

6 Composition, Structure and Oxygen Evolution Activity of Cobalt (Hydr)Oxide under Electrochemical Conditions

6.1 Introduction

Recently, numerous studies aimed at understanding the atomic scale mechanisms of the OER on cobalt oxide catalysts have been carried out. By in-situ Raman spectroscopy, Yeo and Bell showed that Co$_3$O$_4$ undergoes progressive oxidation to CoO(OH) under reaction conditions, suggesting that the Co electrode is largely covered by CoO(OH) during the OER $^1$. However, ex-situ XPS analysis on thin film catalysts revealed that the transformation of the spinel Co$_3$O$_4$ to a layered hydroxide/oxyhydroxide is incomplete, suggesting that in-situ transformation to the layered structure is allowed from the rock salt structure whereas it is inhibited from the spinel structure $^2$.

The above observations give rise to several interesting questions, e.g. which is the thermodynamic ground state structure of cobalt oxide under OER conditions, what is the role of the kinetics of the structural transformation, and, more importantly, which component is mainly responsible for the catalyst’s OER activity. Focusing on crystalline materials, in this chapter, we address these questions by first principles DFT calculations.
of the bulk and surface stabilities of CoO, Co(OH)$_2$, Co$_3$O$_4$, CoO(OH) and CoO$_2$ as a function of pH and applied voltage in an electrochemical environment.

6.2 Bulk Properties and Validation of the Computational Approach

Calculations were performed within the plane-wave-pseudopotential scheme as implemented in the QUANTUM ESPRESSO package \(^3\), including spin polarization, and using the Perdew-Burke-Ernzerhof (PBE)\(^4\) exchange-correlation functional with on-site Coulomb repulsion U term \(^5\). U= 3 eV was used, which provides a satisfactory description of all the different cobalt oxide and hydroxide phases investigated in this work (see below). Electron-ion interactions were described by ultrasoft pseudopotentials \(^6\), with O (2s, 2p) and Co (3d, 4s) electrons treated explicitly. Plane wave kinetic energy cutoffs were set at 35 and 350 Ry for the wave functions and augmented densities, respectively. k-point samplings varied from system to system; their convergences with respect to computed quantities were carefully tested. Surfaces were modeled using symmetric slabs with vacuum widths of 12-15 Å. Adsorption calculations were performed using symmetric surface models with adsorbates on one side only. Experimental values of the lattice parameters were used for all systems.

We carefully assessed the validity of our computational approach by calculating the bulk properties of CoO, Co(OH)$_2$, Co$_3$O$_4$, CoO(OH) and CoO$_2$.

6.2.1 Cobalt Oxide CoO

CoO is antiferromagnetic with a Néel temperature $T_N \sim 289$ K.\(^7\) Above $T_N$, it has rock salt cubic structure, space group Fm3m, with lattice constant $a= 4.258$ Å.\(^8\) Below $T_N$, it
becomes tetragonal due to a Jahn-Teller distortion. The magnetic wave vector is along the [111] direction with a complicated non-collinear pattern. Ignoring the non-collinear part, we accommodate the AFM ordering using a (2×2×2) super cell of the high T structure, with a 8×8×8 mesh of k-points. The resulting spin density is shown in Fig. 6.1.

![Figure 6.1](image)

**Figure 6.1** Structure of CoO. (a) Rock salt cubic conventional cell, with blue and red spheres denoting cobalt ions and oxygens, respectively. (b) AFM spin density of (2×2×2) super cell. Isosurfaces of spin density are 10% of maximum values.

The electronic structure of CoO indicates the presence of strong correlation effects among the d electrons. The band gap is about 2.5 eV. The atomic magnetic moment is > 3 μB, which implies some contribution from orbital magnetization. With U=3.0 eV, the computed band gap is 2.0 eV and the spin magnetic moment of each cobalt ion is 2.68 μB. The computed density of states is shown in Fig. 6.2.
Figure 6.2 Density of states of CoO from PBE+U calculations with U=3.0 eV. The zero of energy is set at the top of the valence band.

6.2.2 Cobalt hydroxide, Co(OH)$_2$

Cobalt hydroxide can crystallize in two different forms, $\alpha$ and $\beta$, named after a common electrode material with similar structures: $\alpha$- and $\beta$-Ni(OH)$_2$ $^{12}$. $\beta$-Co(OH)$_2$ is the better known form of cobalt hydroxide $^{13}$, and is available commercially$^{14}$. $\beta$-Co(OH)$_2$ is isostructural with the mineral brucite Mg(OH)$_2$ which is in the hexagonal crystal family, trigonal crystal system, and point group P3m1. This is a layered structure, with OH$^-$ anions between cobalt ions, and layers held together by hydrogen bonds, see Fig. 6.3. In our calculations, we adopted the experimental lattice parameters, $a = 3.18$ Å and $c = 4.65$ Å $^{14}$, with a 10×10×8 k-point mesh.

![Image of primitive cell and layer structure of $\beta$-Co(OH)$_2$.](image)

Figure 6.3 Primitive cell (a), and layer structure (b) of $\beta$-Co(OH)$_2$.

With 7 electrons in the 3d shell, the Co(II) ions of $\beta$-Co(OH)$_2$ have non-zero atomic moments. In particular, Co(II) ions prefer a high spin configuration according to our calculations, see Fig. S4. However, the in-plane ferromagnetic interactions have been shown to be very small, $J=9.2K$ ($7.9\times10^{-4}$ eV) $^{15}$, and inter-plane interactions are even
smaller because of the larger separations. Therefore, the magnetic ordering should not be important in the study of thermodynamic properties.

![High Spin Configuration E=0.0eV](image1) ![Low Spin Configuration E=0.97eV](image2)

**Figure 6.4** High and low spin configurations of Co(II) ions of β-Co(OH)$_2$, according to PBE+U calculations with $U=3.0$ eV.

As for the electronic structure, PBE calculations predict that the ground state of β-Co(OH)$_2$ is slightly metallic, with some spin down states at the Fermi level. PBE+U with $U=3.0$ eV predicts instead an insulating ground state with a band gap of about 2.0 eV; the corresponding projected density of states is shown in Fig. 6.5. The spin up valence band edge includes both cobalt and oxygen states, whereas the spin down valence band edge contains only cobalt d bands.
6.2.3 Cobalt oxyhydroxide CoO(OH)

CoO(OH) is an example of a metastable phase which can be very hard to isolate and very active\(^\text{16}\). The mineral of CoO(OH) is called heterogenite. The most common form of heterogenite is heterogenite-3R, which belongs to the hexagonal crystal family, trigonal crystal system, rhombohedral crystal class and space group is R3m\(^\text{17}\) (see Fig. S6).

Another form is heterogenite-H with space group P63/mmc\(^\text{18}\). In our study we considered only the more common heterogenite-3R form, whose primitive cell contains one CoO(OH) unit, with \(a= 4.6922\, \text{Å}\), and \(\alpha= 35.4503°\)^\text{18}. Our calculations were carried out using this cell and a 12×12×12 mesh of k-points. With \(U=3.0\, \text{eV}\), we found a band gap of 2.16 eV, which is slightly higher than experimental value 1.7 eV\(^\text{16}\). The density of states of CoO(OH) is shown in Fig. 6.7.

![Figure 6.5](image)

**Figure 6.5** Density of states of Co(OH)\(_2\) from PBE+U calculations with \(U=3.0\) eV. The energy zero is set at the top of the valence band.

![Figure 6.6](image)

**Figure 6.6** - Primitive cell (a), and hexagonal unit cell (b) of CoO(OH). Blue: cobalt; red: oxygen; pink: hydrogen.
6.2.4 Cobalt (IV) oxide CoO$_2$

CoO$_2$ is the x=0 end member of Li$_x$CoO$_2$ and Na$_x$CoO$_2$ family. CoO$_2$ has a layer structure similar to Co(OH)$_2$ and CoO(OH), with space group $P3m$ (see Fig. 6.10). The lattice parameters are $a=2.820\text{Å}$ and $c=4.238\text{Å}$ $^{19}$. Calculations were performed using a 12x12x12 mesh of k points.

CoO$_2$ is a Pauli-paramagnetic metal with itinerant electrons, according to recent experimental studies $^{19-21}$. Instead, our calculations yield a ferromagnetic metallic state slightly more stable than the paramagnetic metallic state (by 0.2 eV/cell with U=3.0 eV) in a wide range of U values, which is in good agreement with published results $^{22}$. As discussed in Ref. $^{22}$, it may require a higher level electronic structure method to capture the correct magnetic structure. We used the computed ferromagnetic ground state for our stability diagrams. Densities of states of ferromagnetic and paramagnetic CoO$_2$ are shown in Figs. 6.8, 6.9.
Figure 6.8 Density of states for the ferromagnetic state of CoO$_2$, from PBE+U calculations with $U=3.0$ eV. The energy zero is set at the Fermi level.

Figure 6.9 Density of states for the paramagnetic state of CoO$_2$ from PBE+U calculations with $U=3.0$ eV. The energy zero is set at the Fermi level.

From these present results, we can conclude that PBE+U calculations with $U=3.0$ eV provide qualitatively good descriptions of the electronic and magnetic structure for all cobalt (hydr)oxides of interest in our study. This computational approach is thus used to study bulk and surface phase diagrams.

6.3 Bulk Phase Diagram in Electrochemical Environments
We determined the relative stabilities of CoO, Co(OH)$_2$, Co$_3$O$_4$, CoO(OH) and CoO$_2$ under electrochemical conditions by calculating the Gibbs free energy changes $\Delta G$ for the following reactions:

\[
\begin{align*}
CoO(s) + H_2O(l) &\rightarrow Co(OH)_2(s) \quad (1) \\
Co(OH)_2(s) &\rightarrow CoO(OH)(s) + H^+ + e^- \quad (2) \\
Co_3O_4(s) + 2H_2O(l) &\rightarrow 3CoO(OH)(s) + H^+ + e^- \quad (3) \\
CoO(OH)(s) &\rightarrow CoO_2(s) + H^+ + e^- \quad (4)
\end{align*}
\]

where the symbols (s) and (l) indicate a solid and liquid system, respectively. The chemical potentials of the proton and electron depend on the pH and the external voltage $V$ according to

\[
\mu_{H^+} + \mu_{e^-} = \mu_{H^+}^0 + \mu_{e^-}^0 + k_B T \ln a_{H^+} - eV
\]

where $a_{H^+}$ denotes the activity of the proton in water solution, $\mu_{H^+}^0$ and $\mu_{e^-}^0$ represent the chemical potential of electron and proton in standard conditions ($T=298$ K, $p_{H_2}=1$ bar).

To evaluate the vibrational contributions to the free energies, we determined the vibrational frequencies of the different materials at the $\Gamma$ point using density functional perturbation theory $^{23}$. The only exception was the vibration of the proton along the O-H-O direction in CoO(OH). The almost symmetric O-H-O bond structure present in CoO(OH) (Fig. 6.10) is similar to that found in high-pressure ice $^{24}$, where significant quantum effects in the motion of the proton are observed. To investigate the possible role of nuclear quantum effects in CoO(OH), we determined the potential energy surface for a proton moving along the O-H-O direction, and then solved the Schrödinger
equation for the proton numerically. The computed potential energy surface is a double-well potential (Fig. 6.11), and solution of the Schrödinger equation shows that the proton is delocalized across the two wells, an indication that at low temperatures quantum effects should be indeed relevant. We thus determined the zero point energy for the proton vibration along O-H-O from the proton ground state energy in the double well of Figure 3. Finally, to complete our free energy calculations, we also evaluated the free energy change associated with the magnetic phase transition of CoO at 289 K using experimental thermodynamic data at 298 K and standard conditions. In this way, the free energy change for reaction (1) is

$$\Delta_f G = \Delta_f G^0_{Co(OH)\text{$_2$}} - \Delta_f G^0_{CoO} - \Delta_f G^0_{H$_2$O} = -1.24 eV/Mol$$

indicating that CoO in contact with liquid water actually transforms to Co(OH)$_2$.

![Figure 6.10](image)

**Figure 6.10.** Layer structure of: (a) Co(OH)$_2$, (b) CoO(OH), and (c) CoO$_2$. The main difference among these structures is the number of protons between CoO$_2$ layers.
Figure 6.11 Potential energy (blue) and probability density (black) for a proton moving along the O-H-O direction between two adjacent CoO₂ layers in bulk CoO(OH).

The phase diagram for bulk cobalt (hydr)oxides in electrochemical environments is shown in Fig. 6.12. Similarly to CoO, also Co₃O₄ is not present in this phase diagram. Co(OH)₂ is the thermodynamic ground state under reduction conditions, i.e. at negative voltages in acidic solution, whereas CoO(OH) and CoO₂ are stable under oxidation conditions, i.e. at external voltage larger than 1.23 eV in basic solution. Interestingly, all three compounds in our phase diagram, Co(OH)₂, CoO(OH) and CoO₂, share a similar CoO₂ₓ⁻ (x=0-2) layered structure (Fig. 6.10).

6.4 Surface phase diagram in electrochemical environments

We determined the surface structures of CoO₂ and CoO(OH), the compounds which are stable under electrochemical oxidation conditions, using the same approach outlined above for the bulk phases. For both materials, the natural stable surface is the (0001), but for CoO(OH) different terminations are possible corresponding to different proton
concentrations on the surface. We modeled the (0001) surface of CoO(OH) using 7-layer symmetric slabs with different terminations, (Fig. 6.13) one with no protons on top (O-terminated), one fully covered by protons (H-terminated), and one half-covered by protons, and calculated their surface energies as a function of pH and applied voltage. The resulting surface phase diagram (Fig. 6.12) shows that the O- and H-terminated surfaces are stable under oxidizing and reducing conditions, respectively. The stability of the surface with one-half H-coverage in a large part of the phase diagram suggests that the surface H coverage may vary during electrochemical experiments.

Figure 6.12 Phase diagram for: (a) bulk cobalt (hydr)oxide, and (b) the CoO(OH) (0001) surface (right) in electrochemical environments, from PBE+U calculations with U=3.0 eV. The value of the external voltage is referred to the standard hydrogen electrode (SHE).
Figure 6.13 Seven-layer symmetric slab used to model the CoO(OH) (0001) surface.

6.5 OER activity of layered CoO$_2^{x-}$ and crystalline Co$_3$O$_4$

PBE+U calculations with different values of U show that the electronic structure of the O-terminated CoO(OH)(0001) surface, which is stable under oxidation conditions, changes from metallic to insulating at $U \sim 3.5$ eV. Since no experimental information is available on the character, insulating vs. metallic, of this surface, we examined the OER for both the metallic ($U=3.0$ eV) and insulating ($U=5.0$ eV) cases. In addition, we studied the OER also on an isolated CoO$_2$ layer meant to represent the CoO$_2$(0001) surface. We used the simplified scheme developed by Nørskov et al. $^{26-28}$ in which the OER is assumed to consist of the following four steps:

- $H_2O(l) + * \rightarrow HO^* + H^+ + e^-$  \hspace{1cm} (5)
- $HO^* \rightarrow O^* + H^+ + e^-$  \hspace{1cm} (6)
- $O^* + H_2O(l) \rightarrow HOO^* + H^+ + e^-$  \hspace{1cm} (7)
- $HOO^* \rightarrow O_2(g) + H^+ + e^-$  \hspace{1cm} (8)
and calculated the Gibbs free energy changes for these reactions. Our results are presented in Fig. 6.14. We can see that the first deprotonation is rate limiting and gives rise to a substantial overpotential on all layered structures, indicating that layered \( \text{CoO}_2^{x-} \) is not active for the OER. This can be attributed to the fact that \( \text{CoO}_2^{x-} \) layers have a very stable and closed structure, and therefore their interactions with the OER intermediates are rather weak, see Fig. 6.15.

**Figure 6.14** Free energy diagrams at \( T = 298 \text{ K}, \text{pH}=0 \) for the four steps of the OER at \( V=0 \) (full line) and at the equilibrium potential for the OER, \( V=1.23 \text{ V} \) (dashed line), on different surfaces: (a) metallic O-terminated \( \text{CoO(OH)} \) (0001) (\( U=3 \text{ eV}, \frac{1}{2} \text{ ML coverage} \)); (b) insulating O-terminated \( \text{CoO(OH)} \) (0001) (\( U=5 \text{ eV}, \frac{1}{2} \text{ ML coverage} \)); (c) \( \text{CoO}_2 \) (0001) (\( U=3 \text{ eV}, \frac{1}{2} \text{ ML coverage} \)); (d) O-4f site on the A-terminated (Ref. 19) \( \text{Co}_3\text{O}_4 \) (110) surface (\( U=3 \text{ eV}, \frac{1}{4} \text{ ML coverage} \)). Overpotential values are in parentheses, 1 ML coverage is defined as one adsorbate per cobalt site.
6.6 Conclusion and Discussion

Our work indicates that the $\text{CoO}_2^{x-}$ structures are thermodynamically stable in electrochemical environments. However, natural (0001) surface of this layered structure is poorly active for the OER, which is consistent with various experimental observations. For instance, LiCoO$_2$, which consists of $\text{CoO}_2^{1-}$ layers, was reported to be not catalytically active$^{29}$. Other studies also pointed out that CoO$_2$ layers are resistant to water oxidation$^{30}$. On the other hand, recent computational work by us$^{31}$ and others$^{32}$ indicates that $\text{Co}_3\text{O}_4$ has a rather small overpotential and is thus an active catalyst for the OER, see Fig. 6.14. Concerning the in-situ transformation of $\text{Co}_3\text{O}_4$, kinetic stability of the spinel structure could be helpful to preserve the activity of catalysts, since complete surface of layered $\text{CoO}_2^{x-}$ is not active anymore.
Bibliography


Chapter 7

7 Chemical Dynamics of the First Proton and Electron Transfer in Oxygen Evolution on TiO₂ Anatase

7.1 Introduction

The development of new technologies for energy conversion and storage has been a challenge for the scientific community. Photo-electrochemical water splitting provides a way of making use of solar and electric energy to produce chemical fuels. Since being reported in the early 1970s, TiO₂ probably has been the most important and studied electrode material for this purpose. Overall, water splitting consists of two reactions on separated electrodes, hydrogen evolution reaction (HER) on the cathode and oxygen evolution reaction (OER) on the anode. Being the rate limiting reaction of water splitting, OER is more complicated because of 4 electron and proton transfers involved to produce one oxygen molecule. Understanding the mechanism of OER may open up the possibility to achieve more efficient water splitting cells through engineering the materials of OER catalysts.

For heterogeneous catalytic OER, the mechanism is, in general, difficult because of the complex structure of liquid-solid interfaces and the presence of many possible intermediates. Nevertheless, people have made significant progresses. Especially, Nørskov and his co-workers developed a method to compute OER overpotential.
on energetics of intermediates from density functional theory (DFT) calculations.\textsuperscript{11,12} This method is very useful when comparing OER activity of different materials and can provide information about the rate limiting step in OER.\textsuperscript{13} Applications of this approach to investigate of OER on rutile\textsuperscript{14} and anatase\textsuperscript{15} show that the initial step removes a proton and electron from an adsorbed water molecule to form a surface OH\textsuperscript{*} species.

\[
H_2O(l) + \cdots \rightarrow HO^* + H^+ + e^-
\]

The calculated overpotential due to this step is around 0.7 eV, a value that does not depend on specific surface structures.\textsuperscript{14,15} However, the chemical dynamics of the first proton and electron transfer is missing in those studies. Therefore, several important questions are still unsolved, in particular whether the barriers of proton and electron transfer can also contribute to the overpotential.

Many catalytic and biological reactions involve proton and electron transfer. Proton-coupled electron transfer (PCET) has been well studied and reviewed\textsuperscript{33-35}. In the electrochemistry of metal electrodes, PCET theory has also been formulated\textsuperscript{36,37}. In general, proton transfer and electron transfer can be concerted or sequential. In this work, we would like to build a qualitative understanding of chemical dynamics of the first PCET of OER at the TiO\textsubscript{2}/water interface (See Fig. 7.1), by first-principle calculations at an atomic level.

Charge carriers in TiO\textsubscript{2} have been observed by electron paramagnetic resonance (EPR)\textsuperscript{16-20}, photoluminescence (PL)\textsuperscript{21-24}, and O\textsubscript{2} photodesorption\textsuperscript{25}. All experimental evidence indicates localized trap states for both electrons and holes. Since we are
mostly interested in OER, which needs the oxidation power of holes, we are going to focus on the hole states in TiO\textsubscript{2}. Theoretically, density-functional theory at the generalized gradient approximation (GGA) level is not able to capture the polaronic character of the hole because of self-interaction error\textsuperscript{26}. Higher level theory, like DFT+U\textsuperscript{27–29} or hybrid functional\textsuperscript{30–32} are needed when studying localized holes explicitly. On surfaces, previous studies found surface oxygen ions are good trapping sites for holes, and the hole is mostly localized on one oxygen ion\textsuperscript{27,31}. Our work used a surface trapped hole, which is closest to adsorbed water, as our starting configuration.

\section*{Figure 7.1} Schematic illustration of proton and electron transfer with a hole on a surface. Blue isosurfaces are spin densities at 0.01 atomic units.

\subsection*{7.2 Models and Methods}

The model we used for the surface is a 3×1×2 anatase (101) surface model of 72 atoms. Lattice constants X and Y were optimized at the PBE level and they are 10.273 Å and 11.136 Å. Z of the model was chosen to be 18.600 Å, so that the density for 48 water molecules is 0.996 g/cm\textsuperscript{3}. (See Fig. 2) In this study, we employed two different models
to study two processes. For proton transfer, we had 48 water molecules in our model.

We also studied the possibility that electron transfer occurred after proton transfer, for which we used a model of 47 water molecules and one OH group on surface, assuming the proton had already left the surface region. Concerning the computational method, we employed density functional theory with a plane-wave basis set and norm-conserving pseudopotentials. For titanium, the pseudopotential includes a semi-core of 3s and 3p electrons, and so 12 valence electrons in total. The wavefunction cutoff was 70 Ry and we tested its convergence by calculating the adsorption energy of a single water molecule. When sampling solvation configurations by ab-initio molecular dynamics, Perdew-Burke-Ernzerhof (PBE) \(^{38}\) was used as the exchange-correlation functional, and when studying proton and electron transfer explicitly by structure relaxation, the hybrid functional PBE0 was used \(^{39}\). Since the system in this work is large, 215 or 216 atoms and 959 electron states to be specific, we utilized a recently introduced order-N implementation \(^{40}\) based on Maximally-Localized Wannier Functions (MLWFs) \(^{41}\) to perform hybrid functional calculations.
7.3 System preparation

In order to have reasonable solvation structures, we utilized molecular dynamics \(^{42}\) to sample configurations of water molecules in our model. However, molecular dynamics simulations with a hybrid functional for our models are still too expensive. Our strategy is to use a much less computationally demanding GGA functional, PBE, to run molecular dynamics, then use a hybrid functional, PBE0, to do structure relaxations of snapshots from molecular dynamics. Car-Parrinello molecular dynamics (CPMD) \(^{42}\) with a time step of 0.0725 fs and a Nosé-Hoover thermostat \(^{43}\) at 330 K was used. We ran simulations for two models for about 10 ps. (see Fig. 7.3) In the whole set of simulations, we didn’t find surface adsorption/desorption, or O-H bond breaking. We sampled two snapshots as

\[\text{Figure 7.2 Side (left) and front view (right) of the model.}\]
starting point to do hybrid functional relaxations, and they were chosen to be about 4 ps apart from each other, so they are not correlated.

Figure 7.3 Total potential energy of two models during 10 ps of CPMD. Red circles indicate snapshots we used in hybrid functional calculations.

7.4 Proton Transfer

Starting from the selected CPMD snapshot, we removed an electron and studied the transfer of a proton from an adsorbed water molecule on the anatase (101) surface to a nearby water in the solvent using the hybrid PBE0 functional (due to the presence of the hole, the whole system was positively charged). To determine the energy profile, we performed constrained minimizations using the difference between the proton distances from the two water oxygens as the reaction coordinate. The transfer was studied in the two electronic states relevant for the ET, notably the state with the hole
localized mainly on a surface $O_{3c}$ atom (surface-hole state, $O^{-}_{3c}$), and the one with the hole localized on an adsorbed water molecule (water-hole state), see Fig. 7.4. Since the water-hole state is an unstable excited state (see below), we constrained two O-H bonds at the lengths given by the CPMD simulation, and then gradually increased one O-H bond length until proton transfer to a neighboring water molecule was complete, i.e. a hydronium cation, $H_3O^+$ was formed. To make the energetics comparable, we used the same constraints of the O-H bond lengths also in the surface-hole states. Note all constraints are on atomic coordinates, and no constraints on the electronic degrees of freedom were used in our calculations.

To check different solvent configurations, we repeated our calculations starting from a different snapshot of the CPMD simulation. Results are shown in Fig. 7.5. Although the shapes of the curves are somewhat different from those in Fig. 7.4, the key messages are the same. First of all, the hole prefers to be localized on a surface oxygen (initially the water-hole state is about 1.4 eV higher in energy than the surface-hole state), and a small energy barrier (0.2-0.4 eV from calculated snapshots) must be overcome for proton transfer. Second, a localized hole on a surface adsorbed water molecule is not stable, because proton transfer is downhill energetically all the way. Moreover, the two energy profiles only cross when the proton transfer is almost complete (Fig. 7.4), or do not intersect at all (Fig. 7.5), which indicates that the proton and electron transfers are likely to be decoupled, and the electron transfer is likely to occur after the proton transfer.
Figure 7.4 (Above) Energy profiles of diabatic water-hole and surface-hole state with respect to proton transfer. (Below) Isosurfaces of spin density (0.01 atomic unit) of two states before and after proton transfer reaction. (snapshot I)
Figure 7.5 Energy profiles of diabatic water-hole and surface-hole states with respect to proton transfer. (snapshot II)

7.5 Electron Transfer after Proton Transfer

Based on above results, we next studied the electron transfer at the TiO$_2$-water interface assuming hydronium ion H$_3$O$^+$ has left the interface region and a hydroxide anion is on the surface (with a hole on the TiO$_2$ surface, the whole model system is charge neutral). This model is realistic in basic environment. Since the point of zero charge of the TiO$_2$ surface is about pH 6.5,$^{44}$ meaning that negatively charged hydroxide anions are predominant on the TiO$_2$ surface at pH > 6.5, our model should be appropriate mostly in basic environments.

Electron transfer in solutions is usually described by Marcus theory,$^{45-48}$ in which charge transfer is instantaneous compared to nuclear motions and energy barriers come from solvent reorganization. Here the two electronic states involved in ET are the state with the hole localized on the adsorbed hydroxyl radical and that with the hole localized on
the surface O$_{3c}$ atom closest to the adsorbed hydroxyl. To study this ET, we performed PBE0 constrained minimizations using the O-O distance between the oxygen of the adsorbed hydroxyl and the nearest surface O$_{3c}$ as the reaction coordinate. We carried out such calculations for two distinct solvent configurations generated during the CPMD simulation (Fig. 7.3) as our starting points. The results for the two configurations are reported in Fig. 7.6 and 7.7. Interestingly, we observed the occurrence of a “shared-hole” electronic state, which can facilitate charge transfer by reducing or eliminating the solvent reorganization barrier during charge transfer. When a hole is localized on a surface oxygen ion beside a surface hydronium anion, ((D) state in Fig. 6) this hydronium anion would like to lean towards the surface oxygen ion with the hole to form a shared-hole state, as (A) and (C) states in Fig. 7.6. This process is spontaneous because it is exothermic, as shown in the energy profile. Then, the shared-hole state could turn into a surface hydroxyl radical state when vibrations increase the distance between the surface oxygen ion and surface OH group. The energy profile shows that a hydroxyl radical state ((B) in Fig. 7.6) is a global minimum in the whole charge transfer process, by a small margin compared to shared-hole state. There may be a very small barrier between the shared-hole state and hydroxyl radical state, (less than 0.1eV from our calculations) but it should not be important at room temperature.
**Figure 7.6** (Above) Energy profiles and water-hole and surface-hole state with respect to distance between the surface OH group and oxygen ion on the surface. (Below) Isosurfaces of spin density (0.01 atomic unit) of states. (snapshot III)
Based on relative energetics of the different states, we suggest a mechanism for charge transfer between the surface hole and an adsorbed hydronium anion, as illustrated in Fig. 7.8. The hole smears from the surface oxygen ion to the hydroxide anion when the two oxygens come close, and then localizes to form a surface hydroxyl radical as the two oxygens move away from each other.
In the shared-hole state, the hole is almost evenly distributed on the two oxygens. For the local energy minimum shared-hole state, the O-O distance is about 2.2 Å, which is much larger than a typical O-O single bond at about 1.5 Å. So, we don’t think this is the O-O single bond observed in in-situ FTIR. Due to the presence of shared-hole states, the charge transfer process is more like a charge-flow rather than a charge-hopping process. During the charge transfer the solvent should thus rearrange more easily than in the case of charge hopping, suggesting that no significant energy barrier due to solvent reorganization should occur in this charge transfer process.

7.6 Conclusion

In this chapter we have studied the detailed mechanism of the first proton-coupled-electron transfer of the OER at the interface between anatase TiO₂ and water. Using a periodic model of the anatase (101) surface and explicit water molecules, we first sampled the solvent configurations by ab-initio molecular dynamics, and next studied the energy profiles of two electronic manifolds of proton and electron transfer by the PBE0 hybrid functional. From the calculated energy profiles, we suggest: (i) the first proton transfer (PT) and electron transfer (ET) are sequential; (ii) electron transfer follows proton transfer; (iii) electron transfer is facilitated by a shared-hole state in which the hole is evenly distributed on two oxygens. Due to the existence of this state, we expect that the solvent reorganization barrier in this ET should not be significant. With a surface hole in the system, PT requires overcoming a small energy barrier, whereas the subsequent ET is likely to be barrierless. As a result, when the population of
hydroxyl anions on the TiO$_2$ surface is significant, as in basic solution, transfer of the hole across the TiO$_2$/water interface may occur without an additional barrier.
Bibliography


Appendix A: Chemical Potential of Liquid Water on a DFT Scale

When using ab initio thermodynamics to study formation energies of various configurations, it is important to have a range of chemical potential of a particular species according to the real environments we are interested in. In studies of water-solid interfaces, assuming interactions between adsorbates or first monolayer and bulk water are weak, ab initio thermodynamics still can give us some information about the interface structure, provided we know the chemical potential of liquid water on a DFT scale.

DFT calculations of an isolated H$_2$O molecule can model gas phase water well, because interactions between gas phase molecules are rather weak. But liquid phase calculations are not as good as gas phase calculations, because weak interactions like hydrogen bonds and van der Waals interactions are not well described in DFT at LDA or GGA level. So, we prefer to calculate the chemical potential of liquid water based on the chemical potential of gas-phase water together with experimental data. The formula used extensively to determine gas phase chemical potential is:

$$\mu_{gas}(T, P) = E_{molecule}^{DFT} + ZPE + \Delta \mu(T, p^0) + k_B T \ln \left( \frac{P}{p^0} \right)$$

The third term on right hand side $\Delta \mu(T, p^0)$ can be calculated based on $H - H^0$ and $S(T)$ from NIST-JANAF Thermochemical Tables which are available online. Using this method, chemical potentials of oxygen gas and critical point of water in REF 1 and REF 2
can be reproduced perfectly. In order to calculate the chemical potential difference
between gas phase and liquid phase water, one possibility is to use the formation Gibbs
free energies of gas phase and liquid phase water which are also available from NIST-
JANAF Thermochemical Tables. So, at 1 atm, we can use

\[ \mu_{\text{liquid}}(T, p^0) = E_{\text{molecule}}^{\text{DFT}} + ZPE + \Delta \mu(T, p^0) + \Delta_f G^0_{\text{liquid}}(T) - \Delta_f G^0_{\text{gas}}(T) \quad * \]

Alternatively, the method used in REF.3 (supporting information) is to use the vapor
pressure of water in equilibrium. Because water liquid is in equilibrium with water vapor
with a certain vapor pressure at certain temperature, the chemical potential of liquid
water is equal to the chemical potential of gas water at that pressure. The formula
authors used in REF 3. Is

\[ \mu_{\text{liquid}} = \mu_{\text{gas}} = E_{\text{molecule}}^{\text{DFT}} + ZPE - TS(p = 0.035 \text{ bar}) \quad ** \]

And 0.035bars is the vapor pressure of water at 298.15K. According to theory of an ideal
gas, entropy at different temperatures can be connected by

\[ S(p_2) - S(p_1) = R \ln \left( \frac{p_1}{p_2} \right) \]

And entropy at 1atm can also be found from NIST-JANAF Thermochemical Tables, so
this method can be used to calculate chemical potential of liquid water.

The chemical potential with respect to \( E_{\text{molecule}}^{\text{DFT}} + ZPE \) at 1 atm were calculated and
listed in following table. Thermodynamic data at 273K and 373K are from linear
interpolations of JANAF data.
<table>
<thead>
<tr>
<th></th>
<th>H$_2$O (gas)</th>
<th>Vapor Pressure</th>
<th>H$_2$O (liquid) by *</th>
<th>H$_2$O (liquid) by **</th>
</tr>
</thead>
<tbody>
<tr>
<td>273K</td>
<td>-0.43eV</td>
<td>0.006 atm</td>
<td>-0.55eV</td>
<td>-0.40eV</td>
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<td>298K</td>
<td>-0.48eV</td>
<td>0.031 atm</td>
<td>-0.57eV</td>
<td>-0.49eV</td>
</tr>
<tr>
<td>300K</td>
<td>-0.49eV</td>
<td>0.035 atm</td>
<td>-0.58eV</td>
<td>-0.50eV</td>
</tr>
<tr>
<td>373K</td>
<td>-0.63eV</td>
<td>1.00 atm</td>
<td>-0.63eV</td>
<td>-0.76eV</td>
</tr>
</tbody>
</table>

From the above table we can see that method * and ** give similar results and the reasonable range of liquid water chemical potential at room temperature is (-0.5eV, -0.6eV).

**Reference**


Appendix B: Proton Wave Function in Cobalt Oxyhydroxide

In order to obtain a general solution to this problem, instead of assuming a certain form of the trial wave function, we solved the Schrödinger equation of the proton by expanding the wavefunction on a basis set. A polynomial basis set is a convenient choice because the Hamiltonian matrix elements can be calculated analytically. Also, we expect protons wave function is confined between two oxygen ions, it is reasonable to assume they go to zero on the oxygen ions. We thus used the polynomial basis

\[ \varphi_n(x) = x^n(x - a)(x + a), \ n = 0, 1, 2 \ldots \]

This basis set is not orthogonal, but the overlap matrix is easy to calculate,

\[ S_{mn} = \langle \varphi_m | \varphi_n \rangle = \int_{-a}^{+a} \varphi_m(x) \varphi_n(x) dx \]

\[ S_{mn} = a^{n+m+5} \left( \frac{2}{n + m + 5} - \frac{4}{n + m + 3} + \frac{2}{n + m + 1} \right) \]

The Hamiltonian of the proton can be written as:

\[ H = -\frac{1}{2m} \frac{d^2}{dx^2} + ax^2 + \beta x^4 + \epsilon x + \gamma \]

Quartic, quadratic and constant terms are used to fit double-well potential, the linear term is the electric field (see below). Due to the simplicity of polynomial basis set, the matrix elements of each term in this Hamiltonian can be calculated,

\[ T_{mn} = \left( \varphi_m \left| \frac{d^2}{dx^2} \varphi_n \right| \right) = -8a^{n+m+3} \frac{1-m-n-2mn}{(n+m+3)(n+m+1)(n+m-1)} \]

if \(n+m\) is even

\[ = 0 \quad \text{if otherwise} \]
\[ A_{mn} = \langle \varphi_m | x^2 | \varphi_n \rangle = a^{n+m+7} \left[ \frac{2}{m+n+7} - \frac{4}{n+m+5} + \frac{2}{n+m+3} \right] \quad \text{if } n+m \text{ is even} \]
\[ = 0 \quad \text{if otherwise} \]
\[ B_{mn} = \langle \varphi_m | x^4 | \varphi_n \rangle = a^{n+m+9} \left[ \frac{2}{m+n+9} - \frac{4}{n+m+7} + \frac{2}{n+m+5} \right] \quad \text{if } n+m \text{ is even} \]
\[ = 0 \quad \text{if otherwise} \]
\[ E_{mn} = \langle \varphi_m | x | \varphi_n \rangle = a^{n+m+6} \left[ \frac{2}{m+n+6} - \frac{4}{n+m+4} + \frac{2}{n+m+2} \right] \quad \text{if } n+m \text{ is even} \]
\[ = 0 \quad \text{if otherwise} \]

Eigenvalues and eigenvectors can be solved in a generalized eigenvalue equation and calculations can be systematically improved by including more basis set functions.

\[ HC = ESC \]

First of all, we need to obtain parameters in Hamiltonian by fitting DFT calculations. Because the experimental information about this material is limited besides crystal structure, I fixed the lattice parameters and the atomic positions at the experimental values, then moved the proton along the O-H-O direction and calculated the total energy change as a function of the proton position. Because I only used one primitive cell as super-cell in the DFT calculations, the system is in a ferroelectric state. The fitted double well potential from calculations is shown in Fig. B.1 and parameters from fitting (in atomic units) are: \( \alpha = -6.107 \times 10^{-3}, \beta = 7.775 \times 10^{-3}, \gamma = 1.195 \times 10^{-3} \).

With fitted potential, we can calculate eigenvalues and eigenvectors by solving the generalized eigenvalue problem. Moreover, I checked the convergence by increasing the number of basis set functions. The results are listed in Table B.1. As we can see, the eigenvalues are well converged when the number of basis functions reaches 20.
The polarizability of this structure can be calculated from the definition:

\[ P = \varepsilon_0 \alpha E \]

The electric susceptibility and relative permittivity are given by:

\[ \chi_e = N \alpha \]

\[ \varepsilon_r = \chi_e - 1 \]

<table>
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<th>Number</th>
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<td>0.2053</td>
<td>0.2051</td>
<td>0.2051</td>
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</tbody>
</table>

**Table B.1** First four eigenvalues (eV) for calculations with different number of basis set functions

<table>
<thead>
<tr>
<th>H</th>
<th>He</th>
<th>Li</th>
<th>Ne</th>
<th>K</th>
<th>Cs</th>
<th>OHO</th>
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</thead>
<tbody>
<tr>
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<td>43.4</td>
<td>59.6</td>
<td>60.1</td>
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</table>

**Table B.2** Polarizability from calculation and comparison with experimental values of atoms (cm³); OHO represents the proton in cobalt oxyhydroxide

<table>
<thead>
<tr>
<th>Salt</th>
<th>Diamond</th>
<th>Silicon</th>
<th>OHO</th>
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<tr>
<td>3</td>
<td>5.5</td>
<td>11.68</td>
<td>23.48</td>
</tr>
</tbody>
</table>

**Table B.3** Relative permittivity of solids; OHO represents the proton in cobalt oxyhydroxide
**Figure B.1** Potential energy surface of proton, probability density of ground and first excited state

**Figure B.2** Polarization due to proton as function of external electric field
Figure B.3 Probability density of ground state as function of external electric field