Localized 4f Electrons in Ceria: Interplay between DFT and Experiment

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Abstract

Heterogeneous catalysis drives industrial reactions of extreme importance to our current welfare. From food industry to transportation, more and more of our necessities depend on costly catalysts utilising rare metals, such as platinum and rhodium. The race for cheaper and more active alternatives is underway and ceria is emerging as one of the favourites, its applications ranging from fluid catalytic cracking to fuel cell technology.

In order to improve the current ceria based catalysts, we have to have a thorough understanding of the electronic structure of ceria. Typically, a combination of density functional theory (DFT) calculations and photoelectron spectroscopy (PS) is employed for this purpose. However, ceria presents an unusual obstacle in the form of atom-like localized 4f orbitals, the occupation of which changes during the reactions ceria is employed in. Accurate description of such a system calls for either a DFT+U approach or a use of hybrid functionals.

In this work the justifications for the above mentioned modifications to DFT and the necessity of comparison with experimental data are discussed. Moreover, it is argued that the interplay between theory and experiment is bidirectional. The need for detailed experimental studies for assessing the correctness of the theoretical approach is stressed and the requirement of theoretical calculations for interpretation of experimental data is shown on the case of high resolution angle resolved photoelectron spectroscopy (ARPES) on ceria.

Introduction

Catalysis is an effective tool allowing us to cope with the ever increasing production demand dictated by rising population. Its significance is perhaps best illustrated by the importance of the Haber-Bosch process, without which the population boom of the 20th century would turn into a worldwide famine. The same bleak picture would be painted by the absence of public and personal transportation that made the increased population somehow sustainable —
there the connection with catalysis lies in a complete dependence of the automotive industry on fluid catalytic cracking for fuel production and on three-way (formerly two-way) catalysis for detoxication of exhaust fumes. In the 21st century catalysis is posed to power the fuel cell technology, even on the micro level with on-chip fuel cells, and strives in multitude of other industrial branches. However, the illustrious role of catalysis is tainted by its consumption of irreplaceable materials, which are slowly running out. This makes platinum and other rare metals materials of extreme strategic importance, especially considering localization of their distribution throughout the world. The search for alternatives is thus not only required by noble reasons of self-preservation and sustainability, but initiated by a lowly political currents, too.

Most of the crucial industrial catalytic reactions employ the use of heterogeneous catalysts — typically, a solid catalysts composed of a combination of reducible oxides and rare metals are used with the reactants in either a liquid or a gas phase. The importance of incorporating reducible oxides lies in their ability to store or release oxygen depending on the reaction conditions and thus acting as an oxygen supply or sink during the reaction. Moreover, such catalysts usually exhibit a much higher specific power with respect to the content of the rare metal. Unfortunately, the reactions over reducible oxides are typically realized on complex phase diagrams due to the changes of their stoichiometry during the reactions, which makes understanding the underlying principles determining their activity much more complicated as the phase transitions are accompanied by changes of local coordination, long range ordering and surface termination. In order to gain insight into the chemistry over reducible oxides, careful model studies isolating the aforementioned changes individually over the whole phase space have to be conducted to provide input for deployment of theoretical methods and vice versa the theoretical results have to be confronted with the experimental data.

Particularly in the case of ceria the catalytic activity is greatly influenced by the presence of oxygen vacancies. The ability to adjust the concentration and the distribution of oxygen vacancies allows for the control over the reactivity and the selectivity of ceria-based catalysts.
The reason for the effect oxygen vacancies have on the catalytic activity are the accompanying changes of electronic structure. Upon the creation of an oxygen vacancy two excess electrons are left to localize on empty f states of surrounding cerium atoms, effectively changing their stoichiometry from Ce$^{4+}$ to Ce$^{3+}$. Here, fundamental questions arise. Are the f states in Ce$^{4+}$ really empty? Where exactly do the excess electrons localize and are they really localized? How does the electronic structure of reduced ceria look like?

While all of the answers are not known, the combination of experimental (ARPES) and theoretical (DFT) probes of electronic structure we have access to provides sufficient hints to form an educated guess. But only having one piece of the puzzle — either the experimental or the theoretical one — is not enough and conclusions based on such partial information have been and still are being shown wrong.

**Localization of 4f electrons in ceria**

In order to begin to understand the process of excess electron localization in ceria we have to have as accurate description of the electronic structure of ceria as is possible. To achieve that we have to start the description from first principles and thus make use of the tools of quantum mechanics. Unfortunately, the apparently simple problem of solving the Schrödinger equation of the system we have in mind is inherently complicated by its many-body nature. Finding ourselves unable to reach an analytical solution, we have to make do with numerical simulations. Through several approximations we can arrive at a rigorous methodology for description of electronic structure — the Density Functional Theory. However, one should be mindful of the aforementioned approximations while making conclusions or comparisons based on the results of DFT. We will thus briefly discuss these approximations.

We are first concerned with reducing the dimensions of the proposed problem to make it numerically solvable. The first step towards this goal is the neglection of the motion of nuclei on the basis of the mass difference between electrons and nuclei (the so called Born-
Further simplification of the now reduced N-particle problem is achieved through the use of the Hohenberg-Kohn theorem: *To each given stationary charge density* \( \eta(r) \) *corresponds exactly one outer potential* \( V(r) \). This simplifies the N-particle problem to searching for the 3-dimensional function \( \eta(r) \).

As has been proven by Kohn and Sham the problem can be reformulated in a following manner: *Let us map the system of interacting electrons on an auxiliary system of non-interacting electrons with an identical stationary charge density* \( \eta(r) \). This further simplifies the problem leaving only three terms contributing towards the energy of stationary states — the kinetic energy of electrons, the mean field interaction representing the Coulombic interaction and the exchange correlation energy consisting of all the remaining interactions.

Unfortunately, the exchange correlation energy generally has complex behavior and necessitates further approximations. The first of these being the Local Density Approximation (LDA), which approximates the exchange correlation energy by a function of a local charge density with the dependence on density in the form of a homogeneous electron gas. Owing to this approximation the applicability of the LDA is limited to systems with a smooth and continuous electron charge density, such as simple metals and intrinsic semiconductors. Sufficiently good results might be produced even for some non-homegeneous systems (certain transition metals). While good agreement between theoretical calculations using LDA and experimental measurements is obtained in regards to the structural parameters, the binding energies are often overestimated and consequently the length of bonds for systems in equilibrium are predicted shorter.

The mentioned shortcomings of LDA can be mostly overcome by introducing gradient corrections of the charge density — Generalized Gradient Approximation. Making the exchange correlation energy depend on local charge density and its gradient corrects for the influence of local inhomogeneities of charge density that were neglected in LDA.

The final reduction of the problem discussed here is the pseudopotential method. This method is based on the statement that all the physical and chemical properties of the stud-
ied system are determined by the behaviour of electrons localized in the valence band. The suitability of this approach is determined by the possibility of considering the electron localized near nuclei as frozen in their atomic configuration. Thus they form an object called an ionic nucleus, which induces effective external field for the valence electrons to move in. The pseudopotential method tries to simulate this external field and further simplifies the problem by carrying on the calculations only with valence electrons.

Even with all the discussed approximations description of a real system is complicated by its size — the sheer number of equations would make the computation time practically infinite. Of course, we can leverage a periodicity of symmetrical systems (for example single crystals) through the use of the Bloch theorem, but many systems do not posses the necessary periodicity. In those cases we have to create it artificially by periodically reproducing a certain part of the system, using an approach called the supercell method. Such cell has to be large enough to neglect irregularities tampering the periodicity, meaning that any irregularities will not influence the same irregularity in a next cell. The danger here lies in considering too small a cell and thus arriving at wrong results. However, the benefits of this approach far outweighs the problems as it allows us to simulate surfaces (as a kind of irregularity), which are an integral part of materials science.

All of the simplifications introduced above stay valid until we consider a case where electrons tend to localize nearer to nuclei and to strongly interact, such as the case in reduced ceria, where the atom-like localized 4f orbitals are populated. The reason for the failure lies in the self-interaction error (SIE) intrinsic to LDA and GGA approaches. The error arises due to incomplete cancellation of the self-interaction Coulomb term for the electrons localized near nuclei, which is caused by the approximate nature of the correction of exchange interaction in LDA and GDA. As a result the electrons tend to be overdelocalized. In the case of excess electrons left behind after creation of an oxygen vacancy in CeO$_2$, the electrons would not populate the 4f orbitals with integer occupation numbers due to SIE and instead spread out over all the cerium atoms leading to a fractional occupation of the 4f orbitals. The error
further underestimates band gaps to such an extent that it might even artificially metallize semiconductors. It is apparent that a remedy to SIE has to be found in order to accurately describe ceria. Fortunately, three such remedies are currently available — SIC, DFT+U and hybrid functionals.

SIC (meaning Self-Interaction Corrections) starts from the approximate functionals, typically GGA, and attempts to correct the unphysical self-interaction in exchange correlation functionals by subtracting certain self-terms. Regrettably, only a very few applications of SIC to the case of ceria have been reported to date.

More commonly used approach to remedy the problem of SIE is the DFT+U, named so as it adds a correction term called Hubbard-U term to the used functionals. Generally, the Hubbard model leverages the tight-binding approximation from solid state physics, where electrons are viewed as occupying the standard orbitals of their constituent atoms and the conduction is viewed as *hopping* (tunneling) of these electrons between atoms of the system. Practically, there is a competition between the *hopping* and on-site Coulomb repulsion between electrons on the same atomic orbital. The dominance of these terms describes the transition between metal and insulator in the Hubbard model. DFT+U thus presents an extension to DFT that considers the on-site interaction from the Hubbard model in the form of U-term, that describes the behaviour of a system of electrons based on their localization as an additional correcting interaction. Here, an important issue arises — the value of the U is principally material dependent and the correct value is generally not known. This makes the DFT+U approach nonuniversal as the obtained results (band gap, lattice constant, etc.) strongly depend on the U parameter. The possible way out of this problem lies in the availability of good experimental data, that can serve as a reference in finding the correct U parameter. This highlights the necessity for complementing experimental and theoretical studies.

It is in the nature of the DFT+U approach that the U-term is applied to orbitals of a certain angular momentum of a particular atomic species only. To achieve a proper de-
scription it is necessary to apply the corrections to all atomic species of the system as well as to all orbitals. Such approach is incorporated into the most computationally demanding remedy to SIE — the hybrid functionals. Hybrid functionals add a certain fraction of Fock exchange energy to the gradient corrected DFT exchange energy. However, this advanced method incorporates an erroneous description of metals by Hartree-Fock and so its applicability to systems with very small or vanishing band gaps is limited. Lastly, the hybrid functional approach still shares the nonuniversality of DFT+U through parameters that fix the amount of Fock exchange and thus influence the results.

At last, possessing the introduced theoretical tools and carefully combining them with experimental data due to the issues discussed above, we can attempt to answer the questions posed at the beginning, starting with the occupancy of f states in Ce$^{4+}$.

The ground state of CeO$_2$ (where cerium atoms are in Ce$^{4+}$ state) has been ambiguous since 1980s. Several authors assigned the state to 4f$^0$ configuration, while others to a mixture of 4f$^0$ and 4f$^1$L$^{-1}$ configurations (where L$^{-1}$ denotes a hole in the valence band). It has not been until 1994 when the advances of experimental techniques, namely the synchrotron radiation excited photoelectron spectroscopy (SRPES), that a decision between the two assignments based on theory has been made. The SRPES experiments clearly illustrated the presence of the 4f$^1$L$^{-1}$ states in the ground state of CeO$_2$ through resonant photoemission in the Ce 4d$\rightarrow$4f photoadsorption region. With the experimental proof of the mixed valence ground state the mixture of 4f$^0$ and 4f$^1$L$^{-1}$ configurations was used to interpret the complicated Ce 3d core level spectra observed in XPS — the three spin-orbitally splitted features were explained by screening effect of 4f electrons. Thus, the feature at the highest binding energy corresponds to 4f$^0$ configuration, the middle feature to 4f$^1$ configuration and the feature at the lowest binding energy to 4f$^2$ configuration. This classical interpretation is held to this day, partially due to its seductive simplicity — the 4f electrons screen the core hole more effectively the more of them occupy the 4f level. However, while the Occam’s razor calls for simplicity, the interpretation might not be as straightforward. Recently, the
previous theoretical results have been questioned by Nelin et al.\textsuperscript{1} Their results show that charge transfer from O 2p to the Ce 4f levels contributes to the Ce 3d features at higher binding energy, completely reversing the accepted interpretation. While the nature of the Ce 3d core level features is still ambiguous, this whole scientific endeavour again illustrates the need for complementing theoretical studies with experimental data. The one thing we are now sure about is that the ground state of CeO\textsubscript{2} is a mixture of 4f\textsuperscript{0} and 4f\textsuperscript{1}L\textsuperscript{−1} (arising through a charge transfer from O 2p) configurations and thus the 4f level in CeO\textsubscript{2} is fractionally occupied (about 0.5 electrons).

Answering the question about the occupancy of the 4f level in CeO\textsubscript{2}, we now turn to the localization of excess electrons left behind after a creation of an oxygen vacancy. The oxygen vacancy defect is defined by three points in the structure — the missing oxygen site and two Ce sites where the excess electrons localize. Experimental observations show further structural changes connected with the creation of the oxygen vacancy. For example an oxygen defect on the surface makes the six closest oxygen anions move outwards and laterally away from the vacancy. Similar structural modifications are connected with the creation of a subsurface vacancy. The importance of the structural changes is highlighted by the fact, that when DFT+U calculations are carried on an unrelaxed structure, the excess electrons are delocalized over all the three nearest neighbour Ce ions (or four for the subsurface vacancy).

When accounting for the relaxation of the structure, the excess electrons have been found to localize on the two nearest neighbour Ce ions. This interpretation explained high resolution STM images of single oxygen vacancies, which clearly showed the accompanying structural relaxations. However, a 2 × 2 reconstruction of single oxygen subsurface vacancies observed in STM and NC-AFM revealed a hole in the calculations connected with the relaxations. Murgida et al.\textsuperscript{2} carried out DFT+U calculations on larger supercells in order to explain the 2×2 reconstructions and revealed the fact that previously used supercells were too small with regards to the resulting relaxations. The new results show at least one of the excess electrons to localize at next nearest neighbouring Ce ion or even further away and explain well the
$2 \times 2$ reconstruction. One has to be careful to recognize the effects of the approximations and limitations of the DFT approach and constantly check with the experimental data, but this case shows that an agreement can occur even without the correct parameters and thus provide incorrect results — one should always be mindful of this issue. Anyway, a conclusion can be reached that the localization of the excess electrons is governed by the accompanying structural changes and thus depends on the density of the oxygen defects. Moreover, the issue of SIE is highly important in this case as one would not reach the localized solutions without correcting for it and thus not reach the agreement with the experimental observations at all.

Alas, one must not get distracted from the ultimate purpose for the study of the electron localization in ceria, that being the role of the localized electrons in promoting the activity of ceria based catalysts through creation of Ce$^{3+}$ sites. Here, a fundamental question arises — is one able to extrapolate the knowledge gained through the theoretical and experimental studies mentioned above over the so called pressure gap? Meaning, does the knowledge gained in vacuum carry through to the atmospheric conditions of real catalytical reactions? Unfortunately, it is necessary to carry on the theoretical calculations in vacuum conditions as otherwise the problem would be as yet too complicated to solve. Likewise, the vacuum conditions are fundamental to most of the experimental techniques of surface and materials science as one typically studies electrons or ionized/neutral atoms interacting with the sample and conservation of their momentum while they propagate towards the detector is ensured by the high inelastic mean free path in the ultra high vacuum conditions. It might thus seem that we are not able to answer the question of the pressure gap with the tools available. Fortunately, the development of near ambient pressure experimental techniques (such as near ambient pressure scanning tunneling microscopy and near ambient pressure photoelectron spectroscopy) in the recent years gradually bridges the gap between model studies and real catalysts. In a recent paper Cafun et al. studied the catalytic activity of ceria nanoparticles during decomposition of hydrogen peroxide in situ. No presence of Ce$^{3+}$ was found during the reaction. The compensation of the excess charge was proposed to be
achieved through tuning the $4f^0$ and $4f^1L^{-1}$ configurations ratio, while the excess electrons are believed to be delocalized over the whole nanoparticles. These findings contradict those obtained in ultra high vacuum. This is not to say that all the previous studies are not relevant to catalytic applications, but rather that gaining fundamental knowledge about a certain catalytic reactions can not be done through extrapolation of data obtained under slightly different conditions. One thus has to be careful about generalizing his conclusions.

While discussing the nature of 4f electrons in ceria we have so far been highlighting the importance of experimental data for interpretation of theoretical results. Let us now briefly concentrate on the reverse issue of interpretation of experimental data, while pondering the last question posed at the beginning — the electronic structure of reduced ceria. We have recently published a paper\textsuperscript{4} regarding the preparation of ordered phases of reduced ceria. Such systems are ideal for the purpose of studying the electronic structure of reduced ceria using experimental tools, most prominent of these being angle resolved photoelectron spectroscopy, which provides a direct probe of the band structure through measuring the momentum of photoelectrons. However, the interpretation of ARPES data is not as straightforward as the interpretation of the conventional photoelectron spectroscopy data and the cooperation with theory is of utmost importance. Let us explore this issue on the case of the dispersion of the 4f level in \textit{c-Ce}_2\textit{O}_3 measured by our group at the Hiroshima Synchrotron Radiation Center.

We have employed the 4d→4f resonance in order to gain intensity and measure the 4f level with as high resolution as possible. Figure 1 a) shows the 4f level over 15° around Γ point with the direction towards positive angles being Γ − $K$. Changes are clearly visible along the angular axis. One might be tempted to quickly jump to a conclusion that the observed photocurrent modulation indeed arises from the band structure, but a deliberate examination has to be conducted before asserting such conclusion. The most obvious mistake would be disregarding diffraction effects without previous analysis as such effects might modulate the photocurrent at the employed excitation energy. Here, theoretical calculations of multiple scattering in a cluster of the studied material can be employed, such as the
ones used for interpretation of photoelectron diffraction data. Fortunately in this case, our previous calculations show no significant contribution of the diffraction effects to the photocurrent modulation. Another modulation that has to be carefully regarded might come from matrix elements describing the probability of transition from state $i$ to state $f$ and related to the direction of the incoming polarized light. Theoretical calculations can again supply these matrix elements and the magnitude of this effect can be guessed at through careful experimentation with the angular rotation of the sample. We can thus have a basic estimation of this influence even before the computationally demanding calculations are finished. In our case, the observed dispersion is indeed related to the band structure. Knowing this, we can proceed with the analysis. Figure 1 b) shows the first derivative of the measured data and Figure 1 d) shows the second derivative. One can see that the observed dispersion of 4f level is very subtle and indeed the first approximation shows changes in the range of 20 meV. That puts us at the limit of the resolution of the used apparatus. In order to gain as much information as possible from such data, we have to carefully fit the measured energy dispersion curves of the 4f level. Because we are not able to resolve the spin orbit splitting of the Ce 4f level as is apparent from the energy dispersion curves in Figure 1 c), we have to again turn to theory to get input parameters such as the splitting distance and ratio. Finally, a comparison of the measured dispersion with calculated band structure has to be done. Owing to the small changes, the calculations have to be carried out with extremely high precision and over curved paths in the k-space simulating the experimentally probed paths.

Although we do not have the results available at the moment, the indicated analysis of ARPES data clearly illustrates the intertwining between experiment and theory in unraveling the electronic structure of the studied material and shows that using one without the other would be comparable to blundering in the dark.
Figure 1: ARPES of c-Ce$_2$O$_3$ measured at the Hiroshima Synchrotron Radiation Center (HiSOR). a) dispersion of f states of c-Ce$_2$O$_3$ measured at 4d→4f resonance. b) the first derivative of a). c) several energy dispersion curves from a). d) the second derivative of a).
Conclusions

One hopes that the purpose of this elaboration on the topic of 4f electrons in ceria is not lost in the amount of details discussed. The purpose being highlighting the bidirectional interplay between theory and experiment and the utmost care that has to be employed in interpreting their results and making conclusions based on those interpretations. However bleak the situation is described here, with the amount of hardships in the process seeming unsurmountable, the treasured rewards of such endeavour are the nature of physics — it works.

References


