Physisorption of CO and N₂O on ceria surfaces

CARSTEN MÜLLER
Dissertation presented at Uppsala University to be publicly examined in Angström 2001, Lägerhyddsvägen 1, Uppsala, Friday, June 5, 2009 at 13:15 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

Physisorption of CO and N₂O on surfaces of ceria (CeO₂) was investigated by means of high-level quantum-mechanical embedded cluster calculations. Both systems have high relevance in the field of environmental chemistry and heterogeneous catalysis. The CO/CeO₂ system, has been investigated in a couple of both experimental and theoretical studies, but for the N₂O/CeO₂ system, this is the first study in the literature, experimental or theoretical.

In physisorption, the interaction relies entirely on classical electrostatic interactions and electron dispersion forces. No covalent bond is formed between the molecule and the surface. A proper description of the dispersion requires some of the most accurate quantum-mechanical methods available, such as MP2 or CCSD(T). Moreover, even the most sophisticated methods cannot heal errors anywhere else in the theoretical treatment. Standard periodic models cannot be used with methods such as CCSD(T), but embedded cluster models can, and have been thoroughly explored in this thesis.

In this thesis, embedded cluster models were constructed for the CeO₂(110) and (111) surfaces. Using a range of assessment tests, it was verified that the electronic structure of the central region of a large and fully embedded surface cluster agrees well with the corresponding region in a periodic system. CO physisorption was investigated at the CCSD(T) level. Due to the prohibitively large expenses (in computer time) for standard CCSD(T) calculations, the method of increments, previously used in the literature for bulk systems, was extended to adsorption problems. It was found that, electron correlation contributes by 30 - 80% to the molecule-surface interaction and that the contribution depends on the topology of the surface. The calculated CO-ceria interaction energy is 20 kJ/mol for the (111) surface and 27 kJ/mol for the (110) surface.

In low temperature TPD experiments for the N₂O/CeO₂(111) system, one surface species was found with an adsorption energy of about 29 kJ/mol. IR measurements showed stretching frequencies that are typically assigned to N₂O adsorption with the O-end directed towards surface cations. However, theoretical calculations up to the MP2 level predicted two equally favorable adsorption species. Improvements in the structural model (larger clusters, consideration of molecule-induced relaxation) or the computational method (larger basis sets) did not affect this result. Only at the CCSD(T) level was one dominating surface species found, namely N₂O adsorbed over a Ce ion, with the O-end of the molecule directed towards the surface. The calculated stretching vibrational frequency shifts (with respect to the gas phase) for this adsorbed species agree well with the measured IR spectra.

Keywords: ceria, carbon monoxide, nitrous oxide, embedded cluster, physisorption, method of increments, CCSD(T), vibrational frequencies

Carsten Müller, Department of Materials Chemistry, Structural Chemistry, Box 538, Uppsala University, SE-75121 Uppsala, Sweden

© Carsten Müller 2009

ISSN 1651-6214
urn:nbn:se:uu:diva-101271 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-101271)
Ich habe dich so lieb

Ich habe dich so lieb!
Ich würde dir ohne Bedenken
Eine Kachel aus meinem Ofen
Schenken.

Ich habe dir nichts getan.
Nun ist mir traurig zu Mut.
An den Hängen der Eisenbahn
Leuchtet der Ginster so gut.

Vorbei – verjährt –
Doch nimmer vergessen.
Ich reise.
Alles, was lange währt,
Ist leise.

Die Zeit entstellt
Alle Lebewesen.
Ein Hund bellt.
Er kann nicht lesen.
Er kann nicht schreiben.
Wir können nicht bleiben.

Ich lache.
Die Löcher sind die Hauptsache
An einem Sieb.

Ich habe dich so lieb.

Joachim Ringelnatz

für Suse
This thesis is based on the following papers, which are referred to in the text by their Roman numerals I–V.


## Contents

1 Introduction .......................................... 11
   1.1 The role of physisorption in surface science .............. 12
   1.2 The role of theoretical investigations in surface science .. 13
   1.3 The importance of CO and N₂O adsorption on ceria surfaces . 14

2 Surface models ....................................... 17
   2.1 The embedded cluster model .......................... 18
   2.2 Our embedding scheme ................................ 20
   2.3 Quality assessment ................................... 21

3 Electron correlation calculations for adsorption problems .... 23
   3.1 Conventional electron correlation methods ............... 23
      3.1.1 Size extensivity ................................ 24
   3.2 Local correlation methods ............................. 25
      3.2.1 The method of increments in detail ............... 26

4 Applications .......................................... 31
   4.1 Embedded clusters of ceria ........................... 31
   4.2 Adsorption of CO on ceria surfaces .................... 36
   4.3 Adsorption of N₂O on ceria(111) ....................... 40
      4.3.1 Experimental results and interpretation ............ 41
      4.3.2 Periodic slab calculations and coverage dependence . 43
      4.3.3 Embedded cluster calculations ..................... 45
      4.3.4 The nature of the molecule-surface interaction .... 47
      4.3.5 Synopsis of the N₂O/CeO₂(111) results ............ 52
   4.4 Interpretation of the $\eta^{\text{int}}$ terms ............. 52
   4.5 Electron correlation localization and basis set vs. cluster size . 54

5 Conclusion ........................................... 57
   5.1 Future development and improvements ................... 59

Bibliography ............................................ 63
Adsorption av olika gaser som tex kolmonoxid (CO) och lustgas (N₂O) på ytor används inom ytvetenskap för att ge information om ytan ras karaktär eller för att mäta ytan area. I katalytiska reaktioner på ytor är adsorptionsprocesser de första stegen och ofta bestämmande för reaktionshastigheten. Experimentella metoder som undersöker adsorptionsprocesser är ofta beroende av teoretiska modeller för att tolka resultaten. Exempelvis är det inte möjligt att mäta direkt hur starkt en viss molekyl är bunden till ett visst ställe på ytan oftast vet man inte ens vilka denna platser är. Genom att använda teoretiska modeller och beräkningsmetoder är det möjligt att förutsäga var och hur stark en molekyl-yt växelverkan är och hur molekylens egenskaper kommer att förändras på grund av adsorptionen. Kombinerat med experimentella resultat kan detta leda till en mycket tydlig bild av adsorptionsprocesser på ytor.

Det är viktigt för trovärdigheten av teoretiska resultat att de modeller och metoder som används är tillräckligt noggranna. Svaga adsorptionsprocesser, så kallad fysisorption, är en stor ytmaning. Vid fysisorption bildas eller bryts inga kovalenta bindningar, men därmed kommer ett stort bidrag till molekyl- yt-växelverkan från van der Waals krafter av olika slag. Hela växelverkansenergien är mindre än ca. 0.4 eV. Små fel i beskrivningen av ytan med en teoretisk modell eller i beskrivningen av molekyl-yt växelverkan med en teoretisk metod kan leda till väldigt stora konsekvenser. Antag att man har fått experimentella resultat för fysisorption av en molekyl vid en temperatur om ca 100 K och att man med hjälp av beräkningar hittar två eller fler olika ställen på ytan där molekylen kan adsorbera med ungefär samma bindningsenergi. Ett fel om 0.03 eV i beräkningar av växelverkansenergier betyder då att bara 1% av molekylerna vill adsorbera vid stället som är mindre fördelaktig. Altså kan små fel i beskrivningen av systemen leda till stora felbedömningar.

Periodiska modeller är mycket effektiva för att beskriva perfekta och ren ytor som på tunna filer i experiment, men om man vill använda en s.k. kvantmekanisk beräkningsmetod kan de tyvärr bara användas tillsammans med metoder som HF eller DFT, som inte är lämpliga för beskrivning av svaga växelverkningar eftersom de använder väldig grova approximationer för elektron- elektron repulsion. Å andra sidan, i en s.k. klustermodell beskrivs bara en liten del av en yta kvantmekaniskt medan resten av systemet beskrivs med mycket enklare modeller. Med klustermodeller kan man, till skillnad från i periodiska modeller, använda många metoder som är noggrannare än HF eller DFT såsom tex MP2 och CCSD(T), men man måste konstruera strukturmodellen.
med mer omsorg. En så kallad inbäddning (”embedding”) ser till att atomer i mitten av kluistret har samma elektroniska struktur som de skulle ha i en periodisk yta. Problemet är oftast att hitta en bra inbäddning för ett visst system som ser till att stora avvikelser i elektronstrukturen är begränsade till de yttre delarna av kluistret.


I denna avhandling har fysisorption av CO (artikel II och III) och N₂O (artikel IV och V) på CeO₂(110) och (111) undersökt. I artikel I diskuteras hur man bäst skapar inbäddade kluster för bulk CeO₂ och för CeO₂(110) och (111) och hur deras kvalitet testades med många olika metoder. Artikel IV innebärl resultat från båda experiment och beräkningar (med inbäddade kluster och periodiska modeller) för N₂O/CeO₂(111) systemet. Beräkningarna i den uppsats är gjorda på s.k. Hartree-Fock, B3LYP och MP2 nivå. En slutsats från denna undersökning är att elektronkorrelation ger ett mycket stort bidrag till molekyl-yt växelverkningen för N₂O på ceria. På grund av detta föll valet på att använda den s.k. inkrementmetoden i artikel V, för att kunna beskriva elektron korrelation med den mycket mycket noggranna metoden CCSD(T) för N₂O/ceria. I artikel II och III används samm hög-nivå-metod för att beskriva elektronkorrelationsbidraget till fysisorptionen av CO på CeO₂(110) och CO/CeO₂(111) systemen. För CO/CeO₂ systemen visas hur strukturen av CeO₂(111) ytan leder till ett betydligt större växelverkning med CO än CeO₂(110) ytan. För N₂O/CeO₂(111) systemet överensstämmer inte bara växelverkningsenergin bra med experiment på CCSD(T) nivå, utan beräkningar ger också rätt inbördes ordning för två olika adsorptionsstrukturer och förklrar varför bara en av dem syns i experiment.
1. Introduction

Adsorption processes of molecules on surfaces occur in many different contexts. Using the strength of the molecule-molecule interaction as the criterion, two types of adsorption processes are distinguished: physisorption and chemisorption.

**Physisorption** (also called physical adsorption or molecular adsorption) is characterized by interaction energies below $-0.4 \text{ eV} \ (\approx -10 \text{ kcal/mol} \text{ or } -40 \text{ kJ/mol})$. The name originates from the lack of a “chemical bond” between the molecule and the surface. Thus only “physical forces” are responsible for the interaction. Such forces are either classical electrostatic interactions (for example the interaction of static and induced dipole moments) or dispersion forces. Since the interaction is very weak, neither the atomic positions nor the electronic structure of the molecule and the surface are much affected, and the properties of the molecule (e.g. vibrational frequencies) differ little from the corresponding gas-phase values.

If a molecule forms covalent bonds with a surface, the adsorption process is called **chemisorption** (or chemical adsorption). In this case, interaction energies are much larger and the atomic positions and electronic structure undergo larger changes. Both types of adsorption often occur simultaneously or sequentially in the same system. For example, on a surface that offers both chemisorption and physisorption sites, a molecule can first physisorb, then migrate on the surface, and eventually chemisorb.

The purpose of this thesis is to combine sophisticated embedded cluster models with very accurate ab initio methods to obtain reliable theoretical data for adsorption processes. First, experimental measurements were performed for the N$_2$O/ceria(111) system (Paper IV). State of the art density functional theory (DFT) calculations were performed using periodic slab models for ceria(111) but failed to reproduce the experimental interaction energies for N$_2$O/ceria(111). So as an alternative, embedded clusters were constructed and carefully tested (Paper I). A good embedding quality was reached. Then the N$_2$O/ceria(111) system was investigated with standard Hartree-Fock (HF) and DFT ab initio calculations using these embedded clusters (Paper IV), but it was found that more accurate ab initio calculations were needed to obtain interaction energies of the same quality as those derived from experiment. MP2 calculations were performed and gave interaction energies in the range of the

---

1In this thesis and in all related papers, a negative adsorption/interaction energy stands for a stabilization.
experimental values, but could still not explain why only one of two possible adsorption structures was observed in experiment, since they came out equally favourable in the MP2 calculations. After extensive tests of cluster size effects, basis set dependence and effects due to molecule-induced relaxation (Paper IV), I concluded that even more accurate calculations such as coupled cluster [CCSD(T)] were required. Since CCSD(T) is very time consuming these calculations were in principle not feasible for the large embedded clusters used. Therefore, the CCSD(T) calculations had to be performed within a special scheme, the method of increments, which also had to be extended for adsorption problems. This was first tested for the CO/ceria(110) system (Paper II) and then applied to the N₂O/ceria(111) system (Paper V). In an additional study CCSD(T) calculations were performed for the CO/ceria(111) system and results were compared to the two previously investigated systems (Paper III).

1.1 The role of physisorption in surface science

Physisorption processes are in focus in this thesis and their role for surface characterization and heterogeneous catalysis is discussed here as with the help of two examples to highlight the importance of physisorption.

One widely used method for surface characterization is the determination of the surface area of, e.g., a porous material. The sample is exposed to a gas stream, and the amount of uptake of this gas by the sample can be correlated to the available area of the material. In total area measurements, nitrogen gas (N₂) is typically used, but to obtain more specific information, more reactive molecules such as carbon monoxide (CO) or nitrous oxide (N₂O) can be used. Sequential adsorption of two different gases is a way to first block certain sites by chemisorption and then measure the area of the remaining surface by physisorption. More information about the surface layer is obtained by reflection absorption infra-red spectroscopy (RAIRS). In this method an infrared (IR) spectrum of the adsorbed molecules is measured and analyzed. Frequency shifts, with respect to the frequencies of the free gas-phase molecule, can be related to the interaction energy between the molecule and the surface, which is considered as a measure of the acid or base strength of the adsorption site (see the review by Knözinger and Huber [1] and references therein). A number of criteria for the probe molecule to fulfill have been proposed, such as selectivity of the molecule-surface interaction and low reactivity. Thus weakly interacting molecules can often give more specific information about a surface than strongly interacting molecules. Small and highly symmetric molecules have the advantage that they can reach sites in narrow places and that their IR-spectra can more easily be interpreted. Additionally, and not unimportant for my thesis, small molecules permit accurate ab initio calculations for comparison with experiment. The calculations add valuable information about
bonding and structure to the experimental interpretation, and the experiments constitute a valuable testbed against which to test and improve the theoretical methods.

In heterogeneous catalysis, physisorption is considered to be the initial step of the catalytic cycle, after a molecule has approached the surface\(^2\). Figure 1.1 is a simple model of the steps involved in the catalytic cycle for the oxidation of CO to carbon dioxide (CO\(_2\)) on a surface. The molecule first weakly adsorbs on the surface, then it migrates to an active site where it chemisorbs and dissociates\(^3\). Dissociated atoms migrate on the surface and can react with other adsorbed CO molecules to form CO\(_2\), which is finally desorbed. If molecules are (only) physisorbed, it is much easier for them to migrate on the surface and meet other reactants. On the other hand, the strong interactions due to chemisorption lead to a better activation of molecules, e.g. by weakening covalent bonds.

![Figure 1.1: Catalytic cycle: (1) physisorption, (2) surface migration, (3) chemisorption, (4) dissociation, (5) surface migration, (6) surface reaction, (7) desorption.](image)

1.2 The role of theoretical investigations in surface science

The interpretation of experimental results often relies on theoretical concepts. For example, RAIRS measurements show only that a probe absorbs IR-radiation of a certain wavelength, but they do not tell where a molecule binds on the surface or how strong the bond is. To obtain this information, it is necessary to apply a theoretical model. The model could, for example,

\(^2\)On a gas/solid interface, the rates of catalytic reactions are known to be less dependent on the reactants’ diffusion rate to the surface than, e.g. in a fluid/solid system.

\(^3\)In fact on many surface systems CO does not dissociates but reacts with oxygen that dissociates into atoms on the surface.
be that, the intramolecular bond of a CO molecule that binds to a cation site is weakened and it absorbs IR-radiation of a longer wavelength. Theoretical calculations can help to test this hypothesis by calculating the frequency shifts of a molecule which is bound to different sites on that surface.

In the framework of heterogeneous catalysis, processes are often investigated with multi-scale modeling techniques such as the kinetic Monte Carlo (KMC) method e.g. based on ab initio calculations (see e.g. [2]). When KMC is applied to catalysis, a number of basic processes with their rates are chosen, for instance steps 1–7 in Figure 1.1, and the time evolution of the system then yields information about the overall kinetics. In this way it is possible to test if the proposed catalytic cycle is correct or how a certain surface reaction affects the overall reaction rate.

In fact theoretical calculations have been applied successfully to a large number of molecule/surface systems and helped with the interpretation and prediction of experimental results by providing information about the electronic structure or vibrational frequencies of adsorbed molecules [3–5]. In all applications, it is essential to use accurate methods and reliable structure models, or the theoretical results will not be of much use. For example, the rate of a reaction on a surface depends exponentially on the heat of adsorption. At a temperature of about 100 K, an error of only 20 meV (2 kJ/mol) in the adsorption energy will change the calculated overall reaction rate by a factor of 10, which can give the wrong impression that adsorption is no longer the rate-determining step.

The purpose of this thesis-work was to investigate physisorption processes with very accurate theoretical methods, that capture most of the interaction correctly, and accurate structure models for the surface. Naturally, this attempt was limited by the available computer resources. Some of these obstacles, e.g. the large computer times required for accurate electron correlation treatment, were removed by applying new types of methods (the method of increments), and in other cases (cluster size dependence, relaxation of the surface) it was at least possible to estimate the effects that certain approximations have on the molecule-surface interaction.

### 1.3 The importance of CO and N$_2$O adsorption on ceria surfaces

In this thesis physisorption processes of CO and N$_2$O on the two most stable ceria surfaces (111) and (110) have been studied. These systems are of a special interest in the context of catalytic converters in cars. CO is produced directly in the car’s engine and is oxidized in the catalytic converter to CO$_2$. Modern three-way catalytic converters are very effective in removing CO. The addition of ceria has improved their performance at sub-optimal conditions when the partial oxygen pressure is too high or too low. N$_2$O together with
other nitrogen oxide species (NO\textsubscript{x}) is formed in the engine as well, and also in the catalytic converter, by the reaction of N\textsubscript{2} with adsorbed oxygen atoms. It has been found that cars equipped with three-way catalytic converters emit up to 10 times more N\textsubscript{2}O than those without any catalytic converter [6]. Both CO and N\textsubscript{2}O are toxic, and N\textsubscript{2}O is also a greenhouse gas with a 300 times higher global warming potential than CO\textsubscript{2} [6, 7]. N\textsubscript{2}O also participates in the depletion of the ozone layer via photochemical reactions [8, 9]. Therefore, N\textsubscript{2}O emission remains a problem which in fact increases today due to the extended use of biodiesel [10, 11].

In experiment, CO adsorption has been investigated on ceria(111) thin films [12, 13] and on powder samples [14–24] (often in combination with platinum). Different attempts to investigate CO adsorption on thin films of the less stable (110) surface have failed. It is believed that crystallites in catalytic converters partly expose (110) surfaces, since theoretical calculations have suggested these to be more active. For example, carbonate species have been observed in experiments on powder samples but theoretical calculations indicate that they do not occur on the most stable (111) surface but only on the less stable (110) surface [25–30], which indicates that (110) surface facets might be exposed in powder samples. For the N\textsubscript{2}O/ceria(111) system no experiments were published previously.
In this thesis two strategies were used for the construction of models for ceria, periodic models and finite cluster models. **Periodic models** are constructed from a small building block (the *unit cell*), which is periodically repeated in one (chains), two (surfaces) or three (bulk) directions. Since these periodic boundary conditions are also enforced on the electronic structure, the calculation of the infinitely large system collapses to the calculation of just a few atoms in the unit cell. Periodic models are easy to construct and are implemented in many computational codes. However, there are some restrictions concerning which computational methods can be applied in combination with periodic models. Cluster models, on the other hand, are, so to speak, large molecules that were cut out from a periodic system. In the most simple case this means one atom with its nearest neighbors. In practice, much larger models may be needed. Since clusters are, from a computational point of view, just molecules, all methods that are available for molecular calculations can also be applied to the calculation of clusters.

The best choice of model for a particular problem depends on the nature of the system and the properties to be investigated. Periodic models are always favorable for systems in which electronic delocalization plays an important role, e.g. extended metals. Electronic band structure or phonons are then reasonably well investigated. Cluster models, however, are preferable for the investigation of local phenomena e.g. adsorption of molecules on a surface or localized defects. In periodic models the investigation of local effects require large unit cells to prevent interactions of, e.g., a defect with its mirror images. All in all, it can be beneficial to combine both periodic and cluster models in order to exploit their individual strengths.

A challenge with cluster models is that the electronic structure is disturbed when clusters of atoms are cut out from their environment. In periodic models this is not a problem since all systems are forced to be periodic, but for cluster models special schemes have to be designed in order to mimic long and short-range effects induced by the environment on the QM cluster region. These schemes are called *embedding schemes* and the resulting cluster models are named *embedded clusters*.
2.1 The embedded cluster model

CeO$_2$ is a very ionic solid. Therefore, only embedding schemes for ionic materials will be discussed in this section.

A large number of embedding schemes have been developed over the years, one of the first being the model by Watson [31] proposed in 1958, and later called, after its inventor, the *Watson sphere*. In this model, atoms were surrounded by a uniform charge distribution on the surface of a sphere, and as simple as this model may seem, it made it possible to estimate how atoms would change their properties in extended systems like crystals. Almlöf et al. developed this concept further. They investigated water molecules in solid hydrates [32], and modeled the water environments by a set of some 50 point charges, the positions and values of which were fitted in order to reproduce the electrostatic potential of the environment within the van der Waals surface of the central water molecule. For the calculation of the Madelung potential generated by the infinite crystal Almlöf et al. assumed Mulliken charges. Hermansson and Lunell investigated the Li$_2$(OH)$_2$(H$_2$O) supermolecule in the LiOH·H$_2$O crystal and modeled all nearest neighbors of the complex by a set of point charges that were first derived from Mulliken population analysis and then optimized self-consistently [33].

A more common procedure, since it is much simpler, truncates the point charge array (PCA). Typically, clusters are embedded in large arrays of point charges located on the positions of the atoms in a crystal. These charges could be either formal charges (e.g. $-2.0$ for O) [34–37] or charges derived from some sort of population analysis. For example Becker et al. embedded a PbS surface cluster into an array of point charges derived from Mulliken population analysis [38]. Additionally, they calculated the electrostatic potential above the surface of the embedded cluster and a periodic PbS slab and included optimized charges in the embedded cluster model to minimize the difference in the potentials. Neyman and Rösch found that the frequency shift of CO physisorbed on the (001) surface of MgO was overestimated when clusters were embedded in charges of $\pm 2.0$ and instead suggested charges of $\pm 1.5$ for MgO [39]. At the end of the 1990s, Stefanovich and Truong came back to the ideas from Almlöf et al. and invented the so called SCREEP model (Surface Charge Representation of the Electronic Embedding Potential) [40]. In their scheme, a cluster is embedded in a infinitely large array of point charges. However, the electrostatic potential of this infinite system is modeled by charges on a surface around the cluster. While Stefanovich and Truong assumed formal point charges, Batista and Friesner improved an approach by Derenzo et al. [41] and developed a scheme in which the charges are self-consistently optimized [42]. It is important to remember that all these models rely on the assumption that the environment is well described by PCAs, even when the way to represent the potential from the PCA is more sophisticated than a truncated PCA. One drawback of this assumption is that it prevents
any structure optimization of regions larger than the QM-cluster region, since point charges interact only via Coulomb forces between themselves and the cluster atoms.

A more advanced model was first developed by Harding et al. [43]. Instead of point charges, their clusters were embedded in arrays of shell model atoms that can interact with the atoms in the cluster and with each other via classical force fields (Coulomb and Buckingham potentials). Shell model charges are two point charges, representing the core and the electron shell of an atom, connected by a classical spring potential. Grimes et al. investigated how the classical Mott-Littleton method [44], which uses inter-atomic shell-model potentials to describe defects in ionic crystals, could be combined with quantum mechanical cluster methods [35], and implemented an interface in the ICECAP program [43,45]. The advantage of this model is that it made it possible to perform structure optimizations for the cluster and even for parts of the surrounding environment. Their ideas have been refined and are now implemented in a number of different programs e.g. by Shluger et al. [46–50], Donnerberg and Bartram [51], Eichler et al. [52], Watson et al. [53], Nasluzov et al. [54] and French et al. [55].

Still, one problem that remained with embedding schemes that use point charges or shell-model atoms for the long-range interaction was that the atoms on the borders of the cluster, in the interface region, experiences an artificially large polarization due to the environment. In other words, point (or shell-model) charges fail to describe short range interactions correctly. These effects were intended to be reduced by applying more sophisticated models of the environment-cluster interactions in another school of embedding procedures. Krijn and Feil investigated \( \alpha \)-oxalic acid dihydrate [56]. In their model they first calculated the electron density of a single \( \alpha \)-oxalic acid dihydrate complex. They then created an embedding by transforming this electron density to all neighboring complexes within a sphere of radius \( \approx 6 \) Å. Outside this sphere, up to a radius of \( \approx 18 \) Å, molecules were modelled by multipoles up to the quadrupole moment derived from a calculation for the isolated molecule, and the potential from both regions was added to the one-electron Hamiltonian. Later Orlando et al. embedded their clusters of MgO in infinite arrays of multipoles calculated directly from periodic model calculations [57]. (A similar approach was used by Kaplan et al. [58]) A very simple, yet nowadays popular way of improving the interface region is to replace the positive point charges around the cluster up to a certain distance by effective large core potentials with no associated basis set. This approach requires no special software and appears to work well for many systems (for a systematic investigation of MgO and CeO\(_2\) see [59] and Paper I). More advanced potentials for the same purpose were developed by Huzinaga et al. in their AIMP method [60]. Even more sophisticated schemes couple the electronic structure of the cluster atoms directly to the electronic structure of periodic models e.g. Pisani et al. in their EMBED program [61]. Other schemes following the same
philosophy are the approaches by Kunz and Klein [62], Meijias and Sanz [63], Shidlovskaya [64], Bredow et al. [65], Andriotis [66] and, Shukla et al. [67]. Different solvent models, e.g. effective fragment potentials (EFP) by Day et al. [68], are very closely related.

2.2 Our embedding scheme

The embedding scheme that was used in this thesis was initially developed by Herschend et al. [59] and can be seen as a variation of the SCREEP method. The environment of the QM cluster region is modeled by an infinite array of formal point charges (+4.0 for Ce and −2.0 for O). However, this array is truncated at a distance of about 20 Å from the center of the cluster and the remaining long range contribution is fitted by a set of a couple of thousand point charges at the surface of a sphere with the same radius of 20 Å. This sphere of charges reproduces the exact Madelung potential of the infinite PCA up to an accuracy of $\approx 10^{-5}$ V within the QM cluster region. Close to the cluster, all positive point charges are replaced by large core Ce pseudopotentials [69] without any associated basis set. The scheme for the creation of the embedded cluster model was implemented for 3D and 2D systems in the PC $\equiv$ Ψ (point charge embedded cluster package) program package.

Figure 2.1: Embedded ceria(111) surface cluster. A cluster of QM atoms is embedded in an array of formal point charges at the crystallographic positions of Ce and O up to a radius of about 20 Å. At this radius, point charges on the surface of a sphere reproduce the electrostatic potential from the remainder of an infinite PCA in the cluster region.
The advantage of this embedding scheme is that it only relies on point charges and effective core potentials, both available in most quantum chemistry codes, and after the creation of the cluster model no additional software is required.

2.3 Quality assessment

All embedding schemes rely on a number of assumptions. In our model (as in many other models in the literature), one important assumption is that long range effects of the ceria crystal are well described by a periodic array of (+4.0/−2.0) point charges. This assumption is well suited for ceria which is a highly ionic material. However, in principle, it is necessary to validate for each system, or even for each embedded cluster, if the assumptions that were made in the embedding scheme lead to an adequate model of the solid.

In view of the large number of publications about different embedding schemes that exist in literature, surprisingly few studies have performed a rigorous quality assessment for the embedded cluster models used. Most authors choose to focus on the results obtained from their embedded-cluster calculations in comparison with experimental data as a method to evaluate the quality of the embedding. However, there exist several attempts to make more systematic and detailed assessments of the embedding model used. Four such studies, all dealing with embedded MgO surface clusters, will be discussed (more examples are found in Paper I). Neyman and Rösch investigated CO adsorption on a number of small stoichiometric and non-stoichiometric embedded MgO clusters\(^1\) and compared shifts of the CO stretching frequency to experimental data [39]. They came to the conclusion that “...extended stoichiometric [...] cluster models are adequate to describe rather sensitive properties of weakly bound molecular complexes on the surface of magnesium oxide...”, but that non-stoichiometric clusters gave results that “...agree worse or even disagree with the available experimental data for the CO-frequency shift...”. Ferrari and Pachhioni investigated the electrostatic potential above stoichiometric and non-stoichiometric embedded MgO(001) clusters\(^2\) and could observe large differences in the potential, which also affected the interaction energy of a CO\(_2\) molecule with the surface [70]. Pascual and Petterson applied the more sophisticated AIMP scheme to the embedding of stoichiometric and non-stoichiometric MgO(001) clusters\(^3\) and, again, investigated the electrostatic potential above the surface [71]. However, in contrast to Ferrari and Pachhioni they found that “...once the cluster is [properly] embedded both stoichiometric and non-stoichiometric clusters show similar electrostatic potentials and properties.” Recently, Florez et al. used the electron localization

\(^{1}\)8 to 18 atoms in arrays of up to 1700 point charges
\(^{2}\)6 to 42 atoms in arrays of about 700 point charges
\(^{3}\)6 to 18 atoms
function (ELF) to show that replacing point charges by total ion model potentials (TIMP) around a MgO(001) cluster reduces spurious polarizations of the atoms at the edge of the cluster [72].

These four studies demonstrate very well how the quality of embedded clusters can effect computational results. Non-stoichiometric MgO clusters embedded in point charge arrays lead to spurious electrostatic potentials above the cluster which affect the interaction energy of MgO with CO or CO₂ [39, 70]. However, with more advanced embedding schemes, such as AIMP or TIMP, these errors are reduced and stoichiometric and non-stoichiometric clusters become more similar [71, 72].

In Paper I, I have presented a number of tests that can be used to assess the quality of embedded clusters by comparing properties from embedded clusters with those from periodic models. In all tests, a periodic slab model and an embedded cluster model were treated on the same level of theory (atomic structure, computational method, basis set) so that disagreements in any property can only be related to the construction of the structure model itself. The properties we selected to study were the atomic (Mulliken) charges, the electron density, the (projected) electronic density of states, and the electrostatic potential above a surface. These properties are characteristic for the structure model itself and are evaluated independent from any application of the embedded cluster model. Other interesting properties in this context that could be evaluated are, e.g., the forces on atoms, electron localization functions (ELF) or ionization potentials.
3. Electron correlation calculations for adsorption problems

The character of physisorption was discussed above. Thus two types of interactions are important, namely dispersion and/or classical electrostatics. The dispersion part is often referred to as long-range, or non-local, electron correlation, and is by definition not included in the HF formalism. DFT has been proved to yield the exact ground-state energy and electron density if the correct density functional is found. This functional has not yet been found but instead a large number of approximations to this functional are used and give quite good agreement with experiment for a large variety of systems. Both methods are mean field approaches that avoid the calculation of many-body wavefunctions. Therefore, even in DFT (with commonly available functionals) electron-electron repulsion is not treated explicitly. Instead, each electron interacts with a potential that is created by all other electrons, and even by the electron itself (self-interaction).

The other part of physisorption, classical electrostatic interactions, is not directly related to electron correlation, but very much so in an indirect way. In principle, HF and DFT can describe the interaction of multipole moments correctly, but electron correlation can be necessary to obtain the correct multipole moments. As an example the dipole moment of N₂O is considered (for more details see Table 4.7 in section 4.3.4.2). The experimental value is $-0.161$ D\(^1\). At the HF level $\mu$ is $+0.687$ D and with different DFT functionals it varies between $-0.076$ D (B3LYP) and $+0.196$ D (LDA). Good agreement is reached first when electron correlation is considered in a more accurate way; at the CCSD(T) level $\mu$ is $-0.143$ D.

Hence, I believe that for an accurate treatment of physisorption processes, electron correlation has to be considered at a very high level of accuracy.

3.1 Conventional electron correlation methods

For molecules (and thus embedded clusters) a number of wavefunction based electron correlation methods (also called post-Hartree-Fock methods) exist, that can capture a large portion of electron correlation. The most popular of

\(^1\)For all dipole moments of N₂O in this thesis, a negative sign means that the O-end is negative.
these are in principle divided into two groups\(^2\): methods that add configurations with excited electrons to the ground-state wavefunction [e.g. the configuration interaction (CI) and coupled cluster (CC) method] and methods that have a perturbation theory ansatz [Møller-Plesset perturbation theory (MP)].

In CI, the correlated wave function \( \Psi \) is expressed as a linear combination of the Hartree-Fock ground-state wave function \( \Psi_{\text{HF}} \) and excited states of \( \Psi_{\text{HF}} \). Thus

\[
|\Psi\rangle = \left(1 + \sum_{P}^{\text{occ}} \sum_{R}^{\text{virt}} c_{P}^{R} \xi_{R}^{P} \xi_{P} + \frac{1}{2} \sum_{P,Q,R,S}^{\text{occ vrr}} c_{PQ}^{RS} \xi_{S}^{QR} \xi_{PQ} + \cdots \right) |\Psi_{\text{HF}}\rangle. \tag{3.1}
\]

[I refer to standard textbooks for the explanation of these terms. Expressions (3.1) and (3.2) are included in this chapter only to give a flavor of these methods.]

If all possible configurations are included, this approach is called full CI and gives the correct ground state energy for a system. However, in practice this is only possible for small molecules with few electrons. Therefore, the expansion is often terminated after the double excitations, giving the CISD method. This method gives very accurate ground state energies for small systems but lacks a desirable feature for the application of the method to extended systems, namely size extensivity.

### 3.1.1 Size extensivity

Size extensivity is the ability of a computational method to give a total energy for a number of systems with different numbers of electrons, that scales linearly with the number of electrons [74]. If a method is size extensive it means that one part of a system can be calculated with the same accuracy as any other part of the system. (A very closely related, yet different, concept is size consistency. In the past, a method was called size consistent if it gave the same energy for two molecules separated at a very large distance, as for the two molecules calculated separately. Nowadays, it is even required, that the whole potential energy curve with respect to the molecules’ separation is qualitatively correct. While full CI is size extensive, any truncated CI is not\(^3\), which makes these methods inappropriate for the investigation of extended systems. However, size extensivity can be achieved if the correlated wave function is developed in products of excitations instead of sums, which gives

---

\(^2\)Other, less commonly used, methods are for example the Jastrow-type ansatz in Quantum Monte Carlo [73] and, for multi-referent systems, the multi-configurational self-consistent field (MCSCF) method or the complete active space perturbation theory of second order (CASPT2).

\(^3\)Obviously, CISD will be size extensive in a 2-electron system, since in this system it is identical to full CI.
the coupled cluster approach.

\[
|\Psi\rangle = \prod_{\mu} \left( 1 + c_{\mu} \tau_{\mu} \right) |\Psi_{\text{HF}}\rangle.
\]  

(3.2)

Here \( \mu \) refers to an excitation of any order with amplitude \( c_{\mu} \) and the excitation operator \( \tau_{\mu} \). If all possible excitations are included, this approach is called full CC, but as for full CI this is not often the case. Instead the expansion is usually terminated after the inclusion of all double excitations (CCSD), and higher excitations are included approximately \{e.g. CCSD(T) or CCSD[T]\}. In contrast to CISD also all higher excitations that can be formulated as products of single and double excitations are included, which is the reason why CCSD is size extensive and CISD not.

Another size extensive method is the perturbation theory according to Rayleigh and Schrödinger where the correlated wave function is expanded in a Taylor series. If this is done in a post-Hartree-Fock fashion assuming \( \Psi_{\text{HF}} \) as the unperturbed wavefunction, this method is known as Møller-Plesset perturbation theory (MP). It is mostly used up to the second order (MP2) but also to some higher orders (e.g. MP4).

### 3.2 Local correlation methods

The greatest disadvantage with electron correlation methods is their computational demands. While the computational time of a Hartree-Fock calculation formally scales as \( O(N^4) \) (where \( N \) is the number of electrons), conventional MP2 scales as \( O(N^5) \), CCSD as \( O(N^6) \) and, CCSD(T) as \( O(N^7) \). This makes conventional post-Hartree-Fock methods unfeasible for larger systems than a few atoms. It is characteristic for all these methods that they rely on the canonical Hartree-Fock orbitals, which are spread over the whole system. However, electron correlation effects are usually very confined. For example, van der Waals forces decay with \( 1/r^6 \), where \( r \) is the distance between the atoms. So called local correlation methods rely on localized orbitals and therefore require much lower computational resources.

In this thesis a local correlation method was used for the calculation of physisorption, namely the method of increments (MoI), first set up by Stoll [75–77]. Other methods in the literature are the local ansatz (LA) method by Stollhoff and Fulde [78–80], and the local correlation treatment originally proposed by Pulay and Saebø [81–84] and implemented in the MOLPRO program by Werner and Schütz [85–87]. In all local correlation methods, a system with a large number of electrons is reduced to several smaller systems, each with considerably fewer electrons. For this purpose, the space of virtual and/or occupied orbitals is reduced to smaller local sub-spaces. In the method of increments, only the occupied canonical orbitals are localized and all excitations into the delocalized canonical virtual orbitals are taken into account.
In the LA method, non-orthogonal occupied and virtual orbitals are created by projection of the canonical orbitals onto the atomic basis functions. Thus only “local” excitations from the occupied orbitals into virtual orbitals on the same atom are considered. In the method of Pulay and Sæbo, again the occupied canonical orbitals are localized, but for the virtual space a set of non-orthogonal orbitals is generated from atomic basis functions by projecting out the occupied space. In that method, each electron receives its individual “domain” of virtual orbitals, and pairs of occupied orbitals can be correlated with different methods, depending on their minimum distance.

The efficiency of all local correlation methods depends very much on how well the canonical Hartree-Fock orbitals can be localized. This depends on the localization method used (usually either Foster-Boys [88] or Pipek-Mezey [89]) but also on how the centers for the localization are chosen, and on the chemical system at hand, of course. In ionic systems, localization on atomic centers is preferable. In molecular or metallic systems this is often not successful if the orbitals are constrained to be orthogonal. However, in the literature metals and molecules have been investigated with MoI, for example, either by applying non-orthogonal sets of localized orbitals or by localizing some orbitals on different centers, such as the middle of a covalent bond (see [90] and references therein).

3.2.1 The method of increments in detail

![Figure 3.1](image-url)

*Figure 3.1:* In the method of increments the canonical HF orbitals are localized to the atomic positions. All localized orbitals at one atomic position constitute an *atom-group*, all localized orbitals at the position of a molecule form a *molecular-group*.

This section describes the method of increments in more detail. As explained above, a system is divided into a number of sub-systems. In Papers
II, V and III, a sub-system was always either an O or a Ce ion, or a whole molecule. Each of these sub-systems (in MoI called centers) is associated with a group of localized orbitals (Figure 3.1). Analogously to the definition of electron correlation energy in for example the MP2 method, where it is defined as $E_{\text{corr}}^{\text{MP2}} = E_{\text{MP2}} - E_{\text{HF}}$, the 1-center increment $\varepsilon_i^{\text{MP2}}$ (sometimes also called 1-body increment) is defined as the electron correlation energy for all orbitals in the group $i$,

$$\varepsilon_i^{\text{MP2}} = E_i^{\text{MP2}} - E_{\text{HF}}.$$  (3.3)

Here, $E_i^{\text{MP2}}$ is the total energy (in this example at the MP2 level) of a system with only the orbitals in the group $i$ being correlated and all other orbitals being frozen at the Hartree-Fock level (Figure 3.2). The sum over all 1-center increments gives the first approximation to the correlation energy of the whole system.

As a correction, one includes the non-additive part of the correlation energy of two centers, the 2-center increment $\Delta\varepsilon_{ij}^{\text{MP2}}$, defined as

$$\Delta\varepsilon_{ij}^{\text{MP2}} = E_{ij}^{\text{MP2}} - E_{\text{HF}} - \varepsilon_i^{\text{MP2}} - \varepsilon_j^{\text{MP2}}.$$  (3.4)

Higher order increments are defined accordingly, e.g. the 3-center increments $\Delta\varepsilon_{ijk}^{\text{MP2}}$, as

$$\Delta\varepsilon_{ijk}^{\text{MP2}} = E_{ijk}^{\text{MP2}} - E_{\text{HF}} - \varepsilon_i^{\text{MP2}} - \varepsilon_j^{\text{MP2}} - \varepsilon_k^{\text{MP2}} - \Delta\varepsilon_{ij}^{\text{MP2}} - \Delta\varepsilon_{ik}^{\text{MP2}} - \Delta\varepsilon_{jk}^{\text{MP2}}.$$  (3.5)

Figure 3.2: In the calculation of 2-center increments $\Delta\varepsilon_{ij}$, only electrons in two groups are correlated, all other orbitals are frozen at the Hartree-Fock state.

In an extended system, $i$ always refers to a group within a reference unit cell, but $j$, $k$, ... refer to groups in the whole system. However, due to the use
of localized orbitals, the size of the energy increments decreases rapidly with the separation of the groups. The same is true for the order of the increments: experience shows that most of the correlation energy is usually covered by the sum over the 1- and 2-center increments, and higher order increments contribute little.

If all increments are included, the MoI is an exact method that recovers 100% of the correlation energy at a given level of theory. It can be applied to weakly correlated systems, were a single determinant dominates the ground state as well as to multi-referent systems, as long as the applied level of theory is size extensive (and size consistent if atomic positions are changed, for example in structure optimizations).

### 3.2.1.1 Scaling with the number of electrons

The large decrease in computational time for the method of increments compared to conventional implementations of correlation methods involving all the canonical Hartree-Fock orbitals simultaneously, is due to the reduction of the $2N$-electron system into a number of smaller $2n$-electron ($n \ll N$) systems. The computational time of a conventional method will scale as $O(N^k)$. For the 1-center increments, the computational time will scale as $O(Nnk^{-1})$. For the 2-center increments, it will in principal scale as $O(N^2nk^{-2})$. However, due to the use of localized orbitals, the number of non-zero 2-center increments will decay as $\approx 1/r^4$ with the distance between the groups$^4$.

Depending on how small $n$ is compared to $N$ the result is essentially a linear scaling in $N$ for the whole method of increments. However, one should remember that the method of increments does not, contrary to the LA method or the method by Puley and Saebø, reduce the number of virtual orbitals (see above). MP2 which is known to scale as $O(N^5)$, actually scales as $O(KV^4)$, where $K$ is the number of occupied and $V$ the number of virtual orbitals [91]. Therefore, the MP2 method is not expected to become any faster with the method of increment scheme. For CCSD(T), the scaling is $O(K^3V^4)$ which can be reduced to almost $O(KV^4)$.

For the CO/CeO$_2$(110) system, we have performed some tests to compare the computational times for calculations with and without the incremental scheme. For an embedded Ce$_{12}$O$_{24}$ surface cluster with 350 electrons and 698 basis functions, a single point calculation with the conventional CCSD(T) method would take about 35 years on a single processor$^5$. With the method of increments, the same total energy is obtained in 39 calculations that altogether take about 23 days of computer time on the same computer. All 39 calcula-

---

$^4$The number of 2-center increments will increase with $r^2$ but van der Waals interaction will decrease with $1/r^6$.

$^5$In this best case scenario it is assumed that this computer has an unlimited amount of memory and disk space.
tions are independent and can be run in parallel, which reduces the actual wall clock time\(^6\) further.

### 3.2.1.2 Extension to adsorption problems

In this thesis the method of increments was used to calculate binding energies of adsorbed molecules and to analyze the electron correlation contributions from the atoms on the surface to the binding. In Paper II we demonstrated how to extend the method of increments to adsorption problems and in Paper V we formulated the new formalism of interaction energy increments \(\eta^{\text{int}}\).

The interaction energy \(E_{\text{int}}\) between a molecule and a surface is defined as

\[
E_{\text{int}} = E(\text{molecule/surface}) - E(\text{molecule}) - E(\text{surface}). \tag{3.6}
\]

We can divide this interaction into a Hartree-Fock contribution, \(E_{\text{int}}^{\text{HF}}\), and a contribution due to electron correlation, \(E_{\text{int}}^{\text{corr}}\),

\[
E_{\text{int}} = E_{\text{int}}^{\text{HF}}(\text{molecule/surface}) - E_{\text{int}}^{\text{HF}}(\text{molecule}) - E_{\text{int}}^{\text{HF}}(\text{surface})
+ E_{\text{int}}^{\text{corr}}(\text{molecule/surface}) - E_{\text{int}}^{\text{corr}}(\text{molecule}) - E_{\text{int}}^{\text{corr}}(\text{surface})
= E_{\text{int}}^{\text{HF}} + E_{\text{int}}^{\text{corr}}. \tag{3.7}
\]

For the calculation of \(E_{\text{int}}^{\text{corr}}\) we have to evaluate all increments that emerge or change due to the adsorption process. The first class contains all increments that contain groups from both the molecule \((M)\) and the surface \((i, j, \ldots)\), e.g. \(\Delta \epsilon_M\). The second class contains all other increments, e.g.

\[
\delta \Delta \epsilon_{ij} = \Delta \epsilon_{ij}(\text{molecule/surface}) - \Delta \epsilon_{ij}(\text{surface}). \tag{3.8}
\]

In order to simplify this notation we have defined the emerging increments \((\Delta \epsilon_M, \Delta \epsilon_{Mi}, \ldots)\) and the changes of increments due to adsorption \((\delta \epsilon_M, \delta \epsilon_i, \delta \Delta \epsilon_{ij}, \ldots)\) as interaction energy increments \(\eta^{\text{int}}\). Thus equation 3.7 becomes

\[
E_{\text{int}} = E_{\text{int}}^{\text{HF}} + \eta^{\text{int}}_M + \sum_i \eta^{\text{int}}_i + \sum_{i<j} \eta^{\text{int}}_{ij} + \sum_i \eta^{\text{int}}_{Mi} + \cdots \tag{3.9}
\]

The sum in (3.9) converges quite fast. We found that already 3-body terms including the molecule, such as \(\eta_{Mi}^{\text{int}}\), contribute very little to the interaction energy, and could in principle be neglected. The individual sums in (3.9) converge quickly with respect to the distance of the involved groups from the adsorption site, which is the reason why cluster models can be used successfully in these calculations.

---

\(^6\)Wall clock time is a measure of how much real time elapses from the start of a calculation to the end.
4. Applications

4.1 Embedded clusters of ceria

The great advantage of using embedded clusters (instead of periodic models) for the physisorption studies in this thesis is that the model allows the use of very high-level wavefunction based QM methods. Paper I describes the embedding scheme used for all clusters in this thesis. Tests were made to assure the quality of the embedded clusters, i.e. their ability to faithfully reproduce the surface-induced influence on a molecule adsorbed on an infinite periodic slab, calculated with the same QM model. A hierarchy of properties with different sensitivity to the environment outside the QM cluster (i.e. the embedding) was found. At the lower end of the sensitivity scale are the charge values for the atoms in a QM cluster. As stated in Paper I, atomic charges require no extra calculations and can be used as “a negative test”: if the agreement is bad between the charges calculated for the atoms at the center of the QM cluster and those in the periodic model, then the embedding is insufficient. However, even for naked QM clusters of ceria, the agreement can be quite good in the middle of the cluster. Charges at the edges of a QM cluster will not be good probes for the embedding quality since they will always deviate from the periodic model values, no matter how good the embedding is. At the cluster borders, both the proximity of polarizing point charges (or, to a less extent, ECPs) and the lack of a full QM “coordination shell” bias the electronic density. At the cluster border, the cations cannot give away as many electrons as they would in a periodic system, and anions cannot take up the appropriate amount of electron density [26]. Similar effects occur on ionic surface compared to the bulk. Good embedding schemes can limit these deviations to a relatively small region at the edge of the cluster, and leave the middle of the cluster unaffected.

In the Mulliken population analysis, the number of electrons $N_A$ for atom $A$ is determined by partitioning the electron density $\rho(r)$ among the atoms in the system.

$$N_A = 2 \left[ \sum_{\mu \in A} \sum_i c_{\mu i}^2 + \sum_{\mu \in A \neq \mu} \sum_{\nu \in A} \sum_i c_{\mu i} c_{\nu i} S_{\mu \nu} \right]$$

(4.1)

Here, $c_{\mu i}$ is a density matrix element for the basis function $\mu$ and the molecular orbital (MO) $i$, and $S_{\mu \nu}$ is the overlap matrix element for the basis functions $\mu$ and $\nu$ (closed-shell system with $N$ electrons occupying $N/2$ basis functions.)
If the summation over all occupied orbitals in (4.1) is not performed, the number of electrons as a function of the MO energy is obtained. This function is the density of states projected on the basis functions of an atom (pDOS). Again it is only reasonable to compare the pDOSs of atoms in the best embedded region of the cluster with those in the slab model. However, just as for the Mulliken charges, we found in Paper I the pDOS is not particularly sensitive to the embedding quality.

Next, the electron density $\rho$ in the cluster region is considered. Electron density difference maps $\Delta \rho = \rho_{\text{Cluster}} - \rho_{\text{Slab}}$ (all terms using the same structure) are quite sensitive to the environment of the QM cluster [59]. Figure 4.2
shows $\Delta \rho$ maps for four different embedding scheme used in this thesis for Cluster 2 (Figure 4.1).

![Electron difference density maps](image)

Figure 4.2: Electron difference density maps, $\Delta \rho = \rho_{\text{Cluster}} - \rho_{\text{Slab}}$, in a (110) plane perpendicular to the surface of Cluster 2 (Figure 4.1). Solid and dashed lines indicate positive (electron excess) and negative (electron deficiency) values for $\Delta \rho$. The dashed-dotted line is the zero-contour. The contour level interval is $5.0 \cdot 10^{-4}$ e/bohr$^3$ and the contour level cutoffs are set to $\pm 0.02$ e/bohr$^3$. All calculations were performed at the B3LYP level using the basis set described in Paper I.

The four different embeddings schemes are defined as follows. A **naked cluster** is a QM cluster without any sort of embedding. A **truncated PCA** means that the cluster is embedded in a point charge array of formal ($+4/-2$ a.u.) charges, which is truncated at a radius of 20 Å from the middle of the cluster (about 1400 point charges). In the **PCS** (point charge sphere) scheme, a sphere of point charges is added to the truncated PCA in order to reproduce the remainder of the Madelung potential, i.e. the potential from an infinitely large point charge array. The **full embedding** scheme is as the PCS
scheme, except that all point charges residing at the border of the QM cluster, close to an O ion in the cluster, are replaced by large core pseudopotentials. Figure 4.2 displays the gradual improvement of the embedding as the description of the environment is made more sophisticated. For the *naked cluster*, large features close to the Ce ion in the middle of the naked cluster show that this ion has a very different electronic structure than its counterpart in the periodic slab. For the other three embedding schemes the features are much reduced, for Ce ions almost to zero, although for the nearest-neighbor O ions, large features remain close to the nuclei but not further out.

Figure 4.3 shows the electrostatic potential above the surfaces in the same planes as the $\Delta \rho$ maps. The three embedding schemes, *truncated PCA*, *PCS*, and *full embedding*, give similar $\Delta \rho$ maps, but large differences are seen in the electrostatic potential maps. These differences also show up in the interaction of the embedded clusters with molecules. In Paper I the interaction energy was calculated for the CO$_2$/ceria(111) system with different embedded clusters. The result is also given in Figure 4.3. The electrostatic map for the *truncated PCA* is seen to deviate significantly from that of the periodic slab, from which we predict that the CO$_2$ adsorption energy (being a consequence of electrostatic and electron correlation interactions) for this embedding scheme will be in error. Indeed it deviates by almost 50% from the value calculated for the cluster with the *full embedding*. Also a too small molecule-surface distance is observed in Paper I. (The intramolecular bond distances and the stretching frequencies of CO$_2$ turn out to be less affected, however.)

In our embedded ceria clusters, the point charges surrounding the QM cluster out to infinity (as described by the PCS construction) have the nominal charges $+4/−2$ a.u., which represents a fully ionic system. The Mulliken charges of bulk ceria are $+3.55$ and $−1.775$ a.u. (HF calculations with the basis set described in Paper I), suggesting less ionicity for ceria. It has been attempted in the literature to account for the reduced ionicity by scaling the charges in the embedding model, e.g. in the work by Melle-Franco and Pacchioni for SnO$_2$ [92] or Pykavy et al. for Cr$_2$O$_3$ [93]. In the present thesis-work, two schemes were explored in an attempt to obtain useful and reasonable reduced charges to employ for the PC part (and the PCS) of our embedded ceria clusters, i.e. charges different from $+4/−2$ a.u. In the first scheme, the electrostatic potential above a periodic CeO$_2$ slab was calculated using periodic ab initio calculations with the CRYSTAL06 program [94], just as in the last picture of Figure 4.3. Then charges were placed at the positions of the atoms in the unit cell, repeated periodically and, optimized in order to reproduce this potential. In the second scheme, embedded surface clusters were constructed for a certain point charge model (starting with $+4$ and $−2$ a.u.), and then the difference electron density or difference electrostatic potential with respect to a periodic slab was calculated, and the charges were optimized in order to minimize these differences.
The first scheme was successful, giving charges of $+2.46$ and $-1.32$ a.u. (at the B3LYP level with the basis set as described in Paper I). However, an embedded cluster with the $+2.46/-1.32$ a.u. charge model was found to give no better agreement with a periodic slab model than the nominal charges, according to the tests demonstrated in Paper I. In the second scheme, charges of $+3.98$ and $-1.99$ a.u. were obtained, i.e. no difference from the purely ionic...
case. This is consistent with the results obtained in Paper I, $\Delta \rho$ and electrostatic potential maps were calculated for four different charge models in the range from $+4.0/−2.0$ a.u. to $+3.0/−1.5$ a.u. The best agreement is observed for the fully ionic charge model.

I conclude that with the embedding scheme used in this thesis I was able to construct embedded surface clusters of CeO$_2$ that, according to the quality assessment carried out, are good models of CeO$_2$(111) and CeO$_2$(110). For CeO$_2$(111), the Ce$_{22}$O$_{44}$ cluster (Cluster 2, see Figure 4.1), shows an electrostatic potential that is in good agreement with the potential above the equivalent periodic slab. For the smaller Ce$_{13}$O$_{26}$ cluster (Cluster 1) the agreement is suboptimal and an overestimation of interaction energies is expected. This is indeed what was observed when CO$_2$ was adsorbed (Paper I).

4.2 Adsorption of CO on ceria surfaces

In Papers II and III, adsorption of CO on the two most stable ceria surfaces, (110) and (111), was investigated. The CO molecule is a very common probe molecule for the investigation of surfaces and the CO/CeO$_2$ system has been studied extensively in both experiment [12–24] and quantum mechanical calculations [25–30].

For the CO/CeO$_2$ system, experiments have been reported in the literature for either (calcinated) powder samples or (111) thin films and they give a wide span of adsorption energies ranging from about $−0.2$ to $−2.0$ eV. In IR spectroscopic experiments, large adsorption-induced down-shifts of the stretching vibrational frequency of the CO molecule were seen [13, 14, 16–22], suggesting that carbonate species form on the CeO$_2$ surface. Other species were found with only small frequency down-shifts compared to the gas-phase CO frequency [14, 18, 21, 22]. This corresponds to physisorbed CO.

The theoretical calculations for CO on ceria surfaces in the literature have been performed for two different surface models, periodic slabs and embedded clusters, and at a range of different computational levels (see Table 4.1). Two main results emerge from these studies. (1) On the CeO$_2$(111) surface only physisorption occurs with an adsorption energy of about $−0.2$ eV [25,27,30], and, (2) on the CeO$_2$(110) surface, CO can chemisorb, forming carbonate species with an adsorption energy of about $−2.0$ eV [25, 27, 29, 30] or physisorb with an adsorption energy of about $−0.2$ eV [25–27,29,30].

From the list of quantum mechanical studies in literature, those with the highest level of accuracy are the MP2 calculations performed by Herschend et al. [29]. In Ref. [29], a significant difference between the adsorption energies calculated at the B3LYP and MP2 levels was found, suggesting that electron correlation effects play a significant role in the CO/ceria(110) system.

In this thesis, I set out to elucidate this hypothesis. Thus MP4 and CCSD(T) calculations were performed for the physisorbed CO/ceria(110) system with
Table 4.1: Theoretical results from the literature and this thesis for CO adsorption on CeO$_2$(111) and (110) (energies in eV). Different adsorption sites are listed, labelled according to Ref. [25].

<table>
<thead>
<tr>
<th>Reference</th>
<th>$E_{ads}$ for CO/CeO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(111)</td>
</tr>
<tr>
<td>Yang et al. [25]</td>
<td></td>
</tr>
<tr>
<td>periodic slab/GGA</td>
<td>$-0.17$</td>
</tr>
<tr>
<td>Müller et al. [26]</td>
<td></td>
</tr>
<tr>
<td>embedded cluster/HF</td>
<td>$-0.12$</td>
</tr>
<tr>
<td>Herschend et al. [29]</td>
<td></td>
</tr>
<tr>
<td>embedded cluster/MP2</td>
<td>$-0.22$</td>
</tr>
<tr>
<td>Nolan et al. [27]</td>
<td></td>
</tr>
<tr>
<td>periodic slab/GGA + U(5.0)</td>
<td>$-0.26$</td>
</tr>
<tr>
<td>Huang et al. [30]</td>
<td></td>
</tr>
<tr>
<td>periodic slab/GGA + U(2.0)</td>
<td>$-0.17$</td>
</tr>
<tr>
<td>Müller et al. Paper II</td>
<td></td>
</tr>
<tr>
<td>embedded cluster/CCSD(T)</td>
<td>$-0.21$</td>
</tr>
<tr>
<td>Müller et al. Paper III</td>
<td></td>
</tr>
<tr>
<td>embedded cluster/CCSD(T)</td>
<td>$-0.28$</td>
</tr>
</tbody>
</table>

Cluster 4 (Figure 4.4) and, for comparison, also for the CO/ceria(111) system with Cluster 1 (Figure 4.1), in both cases using the method of increments. The key results, summarized in Table 4.2 are as follows: (1) electron correlation plays an important role in the adsorption phenomenon for both systems, and (2) MP2 is a clear improvement over B3LYP but overestimates the interaction of CO with ceria by 10–20% compared to CCSD(T). A comparison of our results with theoretical calculations in the literature shows that DFT in general underestimates the molecule-surface interaction in the CO/CeO$_2$(110) and (111) systems. The GGA+U adsorption energies from Nolan et al. [27] seem to agree well with our CCSD(T) results, but, Huang and Fabris showed recently that the CO/CeO$_2$ interaction energy is very sensitive to the U value [30] in the Hubbard model. Huang and Fabris claim that Nolan et al. applied too large U values, which overestimates the interaction energy of the CO/CeO$_2$ system. A closer look at the optimized structures of CO on the two surfaces, reveals that the main difference is the closest distance between the carbon atom of CO and the O ions on the surface, $r(C-O_{surface})$. On the CeO$_2$(110) surface there
Figure 4.4: A $\text{Ce}_12\text{O}_{24}$ surface cluster used for my calculations on the CO/\text{CeO}_2(110) system.

Table 4.2: Adsorption structure and interaction energies for CO adsorption on a Ce ion on the (110) and (111) surfaces of ceria. CO adsorbes perpendicularly with the C atom down. For the isolated CO molecule $r = 1.126\,\text{Å}$. All distances are given in Å, all energies in meV.

<table>
<thead>
<tr>
<th>Structure and energies</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r(\text{C-O})_{\text{B3LYP}}$</td>
<td>1.125</td>
<td>1.123</td>
</tr>
<tr>
<td>$r(\text{C-Ce}<em>{\text{surface}})</em>{\text{B3LYP}}$</td>
<td>2.959</td>
<td>2.856</td>
</tr>
<tr>
<td>$r(\text{C-O}<em>{\text{surface}})</em>{\text{B3LYP}}$</td>
<td>3.810</td>
<td>3.058</td>
</tr>
<tr>
<td>$E_{\text{int}}^{\text{B3LYP}}$ (optimized)</td>
<td>$-104$</td>
<td>$-110$</td>
</tr>
<tr>
<td>$E_{\text{int}}^{\text{RHF}}$ (single point)</td>
<td>$-149$</td>
<td>$-48$</td>
</tr>
<tr>
<td>$E_{\text{int}}^{\text{MP2}}$ (single point)</td>
<td>$-244$</td>
<td>$-323$</td>
</tr>
<tr>
<td>$E_{\text{int}}^{\text{MP4(SDTQ)}}$ (single point)</td>
<td>$-215$</td>
<td>$-$</td>
</tr>
<tr>
<td>$E_{\text{int}}^{\text{CCSD(T)}}$ (single point)</td>
<td>$-206$</td>
<td>$-283$</td>
</tr>
</tbody>
</table>

are four O ions at an $r(\text{C} - \text{O}_{\text{surface}})$ distance of about 3.8 Å, but on the (111) surface there are three O ions with an $r(\text{C} - \text{O}_{\text{surface}})$ distance of about 3.1 Å (see Figure 4.5).
Paper III (and Tables 4.3 and 4.8, discussed in another context later) gives the correlation contributions to the interaction energy for CO on CeO$_2$(111) in terms of its various 2-body ($\eta_{\text{int}}^{\text{CO},i}$), and higher order contributions. In particular the values for the $\eta_{\text{int}}^{\text{CO},O_1}$ term on the two CeO$_2$ surfaces were compared because this is the term which gives the largest correlation contribution to the interaction energy. On the CeO$_2$(110) surface, this term is about $-30$ meV per O$_1$ ion, and on the CeO$_2$(111) surface, it is almost $-90$ meV per O$_1$ ion [all values at the CCSD(T) level]. Some of this difference might be related to the different oxygen basis sets used in the two studies. However, calculations for the CO/CeO$_2$(110) system with a larger basis set on the oxygen ions did not change $\eta_{\text{int}}^{\text{CO},O_1}$ by more than 5%. Therefore, most of the difference appears to be a “real” effect and is probably related to the different $r(C-O_{\text{surface}})$ distances for the two surfaces, which in turn is a consequence of the different topologies of these two surfaces.

The second largest correlation contribution to the interaction energy originates from the $\eta_{\text{int}}^{\text{CO},Ce_1}$ term. On CeO$_2$(110), this term is about $-90$ meV and on CeO$_2$(111), about $-110$ meV. These values follow the same trend as the $r(C-Ce_{\text{surface}})$ distance.

In Paper II, additional calculations were performed for the Ar/CeO$_2$(110) system to find out how the $\eta_{\text{int}}$ terms behave with an adsorbate without a static dipole moment (Ar). Table 4.3 shows the results at the CCSD(T) level. Most of the $\eta_{\text{int}}$ terms are astonishingly similar to those for the CO adsorbate although differences occur for $\eta_{\text{int}}^{\text{CO}}$ and $\eta_{\text{int}}^{\text{Ar}}$ and for 2-body increments including O$_1$. The comparison indicates that the CO molecule is polarized more than Ar by the surface ($\eta_{\text{int}}^{\text{CO}} > \eta_{\text{int}}^{\text{Ar}}$).
CO and Ar adsorption on CeO\(_2\)(111)

<table>
<thead>
<tr>
<th>Increments</th>
<th>Contributions to (E_{\text{corr}}^{\text{ads}}) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
</tr>
<tr>
<td>1-body Adsorbate</td>
<td>29</td>
</tr>
<tr>
<td>Ce1</td>
<td>0</td>
</tr>
<tr>
<td>Ce2</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>26</td>
</tr>
<tr>
<td>O2</td>
<td>11</td>
</tr>
<tr>
<td>O3</td>
<td>3</td>
</tr>
<tr>
<td>2-body Ads-Ce1</td>
<td>(2.96 Å)</td>
</tr>
<tr>
<td>Ads-Ce2</td>
<td>(4.91 Å)</td>
</tr>
<tr>
<td>Ads-O1</td>
<td>(3.81 Å)</td>
</tr>
<tr>
<td>Ads-O2</td>
<td>(5.11 Å)</td>
</tr>
<tr>
<td>Ads-O3</td>
<td>(5.47 Å)</td>
</tr>
<tr>
<td>2-body Ce1-O1</td>
<td>(2.40 Å)</td>
</tr>
<tr>
<td>Ce1-O2</td>
<td>(2.40 Å)</td>
</tr>
<tr>
<td>Ce2-O1</td>
<td>(2.40 Å)</td>
</tr>
<tr>
<td>O1a-O1b</td>
<td>(2.77 Å)</td>
</tr>
<tr>
<td>O1a-O1c</td>
<td>(4.80 Å)</td>
</tr>
<tr>
<td>O1a-O1d</td>
<td>(3.92 Å)</td>
</tr>
<tr>
<td>O1a-O2a</td>
<td>(2.77 Å)</td>
</tr>
<tr>
<td>O1a-O2b</td>
<td>(3.92 Å)</td>
</tr>
<tr>
<td>O2a-O2b</td>
<td>(2.77 Å)</td>
</tr>
<tr>
<td>3-body Ads-Ce1-O1</td>
<td></td>
</tr>
<tr>
<td>Ads-Ce1-O2</td>
<td></td>
</tr>
<tr>
<td>Sum</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3: Contributions (in meV) from the various increments (at the CCSD(T) level) to \(E_{\text{corr}}^{\text{ads}}\) for CO and Ar adsorbed on CeO\(_2\)(110). All increments are BSSE corrected. A positive sign means repulsion. The values in parentheses are the distances (in Å) between the orbital groups.

4.3 Adsorption of N\(_2\)O on ceria(111)

In Papers IV and V, the N\(_2\)O/CeO\(_2\)(111) system was investigated. This system has high relevance in many environmental related contexts (see the Introduction), just as the CO/CeO\(_2\) systems have, and the first experimental and theoretical study of this system in the literature are presented in Papers IV.
and V. The main focus in our N₂O studies was the interpretation of the experimental vibrational spectra in terms of the N₂O bonding to the CeO₂(111) surface.

4.3.1 Experimental results and interpretation

The experiments were carried out in the laboratory of Professor R. M. Nix at Queen Mary, University of London. The sample was a (111)-oriented epitaxial film of ceria, grown on a Cu(111) substrate. Low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) measurements seemed to confirm that the ceria film was well-ordered and fully oxidized. At temperatures of 85 – 95 K, molecular beam scattering (MBS) and XPS measurements showed an extensive uptake of N₂O with near unity sticking probability, suggesting the formation of monolayers on the surface. Infrared spectra showed down-shifts of 15 to 30 cm⁻¹ for the symmetric stretching mode of N₂O and up-shifts of 5 to 20 cm⁻¹ for the anti-symmetric stretching mode, compared to the free gas-phase values of 1285 cm⁻¹ and 2225 cm⁻¹ (see Figure 4.6).

\[
\begin{align*}
\text{transmittance} & \quad \text{wave number (cm}^{-1}\text{)} \\
0.14 \text{ L} & \quad 1220 \quad 1240 \quad 1260 \quad 1280 \quad 1300 \\
1.00 \text{ L} & \quad 1280 \quad 1300 \\
2.20 \text{ L} & \quad 2200 \quad 2220 \quad 2240 \quad 2260 \quad 2280 \\
3.70 \text{ L} & \quad 2200 \quad 2220 \quad 2240 \quad 2260 \quad 2280 \\
9.20 \text{ L} & \quad 2200 \quad 2220 \quad 2240 \quad 2260 \quad 2280 \\
\end{align*}
\]

\(\text{Figure 4.6: IR-spectrum for different exposure of N}_2\text{O on ceria}(111)\text{ thin films}\)

Temperature programmed desorption (TPD) experiments showed that the majority of N₂O was desorbed at \(\approx 125\) K and that further desorption of the small remaining amount of N₂O took place at about 140 K. From the IR and TPD results two conclusions were drawn: (1) Using the Redhead equation [95] and assuming a pre-exponential factor of \(10^{13}\) s⁻¹, the adsorption energy
for the majority of the N2O molecules must be around \(-0.30\) eV, and (2) a negative frequency shift of the symmetric mode suggests that N2O is adsorbed with the oxygen-end towards a cation on the surface. The second conclusion is based on a “rule of thumb” prevailing in the literature. This rule of thumb is based on some simple considerations relating to the Lewis model for the electronic structure of N2O. In the Lewis model, N2O is best described by a combination of two resonance structures,

\[
\begin{align*}
\delta^- & \quad \delta^+ \\
\vdots \quad \vdots \\
O - N & \equiv N \\
\vdots \quad \vdots
\end{align*}
\]

\[
\begin{align*}
\delta^+ & \quad \delta^- \\
\vdots \quad \vdots \\
O = N = N & \equiv
\end{align*}
\]

(a) (b)

Considering only electrostatic molecule-surface interactions we then have that if N2O adsorbs with the O-end towards a surface cation (O-down), the contribution of structure (a) increases. This would entail an increase in the N-O bond length and a decrease in the N-N bond length. On the other hand, if N2O adsorbs with the N-end towards a cation (N-down), the contribution of structure (b) increases and, the N-O bond length decreases while the N-N bond length increases.

In experiments on two other systems, namely N2O/\(\alpha\)-Cr2O3 [96] and N2O/TiO2 [97], it was concluded that two adsorption species were present on the surface, one with \(\Delta\omega\)\text{symm} < 0 and \(\Delta\omega\)\text{anti-symm} > 0, and one with \(\Delta\omega\)\text{symm} > 0 and \(\Delta\omega\)\text{anti-symm} > 0. The authors assigned the former to O-down adsorption based on the widespread presumption that the symmetric stretching mode is associated with the N-O bond and the anti-symmetric stretching mode with the N-N bond. Following this reasoning and the reasoning above concerning Lewis structures, O-down adsorption will strengthen N-N and weaken N-O, and this would lead to \(\Delta\omega\)\text{symm} < 0 and \(\Delta\omega\)\text{anti-symm} > 0. Indeed, that is the frequency shift pattern that was observed for the species in Ref. [96] and [97]. A similar chain of argumentation for the species with \(\Delta\omega\)\text{symm} > 0 and \(\Delta\omega\)\text{anti-symm} > 0 suggests that it corresponds to an N-down mode.

In our theoretical calculations for N2O/CeO2(111) (Paper IV) it was found that the normal mode coordinates of the two stretching modes are more complex than the names “N-O-stretching mode” and “N-N-stretching mode” imply, and predictions of the frequency shifts from the changes in the intramolecular bonds are not so straightforward. The calculations also show that N2O adsorption in the N-down mode on Ce\(^{4+}\) does not display the \(\Delta\omega\)\text{symm} > 0 and \(\Delta\omega\)\text{anti-symm} < 0 pattern. This demonstrates the limitations of the simple model discussed above, and the importance of performing ab initio calculations to actually explore the pattern in a particular case.

Calculations of the N2O/ceria(111) system were performed with different surface models (periodic slabs and embedded surface clusters) and at different
levels of sophistication [HF, DFT, MP2 and CCSD(T)]. In Paper IV, interaction energies and vibrational frequencies were calculated and it was tested how the results are affected by different cluster sizes, basis sets, models for molecule-induced surface relaxation, and coverage. In the same paper the electrostatic contributions to the molecule-surface interaction were investigated and in Paper V an analysis of the electron correlation part of the interaction was performed.

4.3.2 Periodic slab calculations and coverage dependence

Plane wave calculations at the PAW-PW91 level were performed with periodic slab models for three different coverages for N$_2$O. The results from these calculations are summarized in Table 4.4.

In these periodic calculations, the N$_2$O molecule was found to adsorb both N-down or O-down on a Ce cation. At low coverage, O-down adsorption was found to be more favorable. At full coverage the difference between O-down and N-down adsorption is very small (the N-down adsorption mode is more favorable by only 4 meV). While recognizing that the systematic errors in my calculations are much larger than 4 meV (although this does not necessarily apply to the relative error in $E_{\text{int}}$ for the N-down and O-down modes), it may be illustrative to make a back-of-the-envelope calculation of the consequence of such a small difference. Applying Boltzmann statistics at the temperature where the experiments were performed, about 100 K, an energy difference of 4 meV leads to a population of 60% for the N-down structure and 40% for the O-down structure. This is inconsistent with our experimental results, which suggest mainly one type of adsorbed species.

The obvious conclusion from these results is that PAW-PW91 fails to describe the N$_2$O/CeO$_2$(111) system well enough to draw any specific conclusions. To the best of my knowledge, my periodic calculations were converged with respect to the basis set, the Brillouin zone integration scheme and other computational parameters. In principle the result is not surprising, since PW91 (and other DFT methods) are known to underestimate the interaction also in other van der Waals bound systems, e.g. the water dimer which is a common text book example. Keeping this weakness in mind, we can still discuss some qualitative results from the periodic DFT calculations, but clearly additional calculations with more sophisticated methods are required to obtain more reliable results that stand for comparison with experiment.

One of the qualitative results that the periodic calculations reveal is that there is a large attractive interaction between the N$_2$O molecules in the overlayer on ceria(111). At 25% coverage, this effect is very small and stabilizes the adsorption energy by only a few meV. At 50% coverage, the adsorption energy per N$_2$O molecule is stabilized by about 40 meV due to molecule-molecule interaction. At 100% coverage, the difference between the O-down and N-down overlayer structures becomes important. A molecule in the N-
<table>
<thead>
<tr>
<th></th>
<th>25%</th>
<th>50%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-down</td>
<td>O-down</td>
<td>O-down</td>
</tr>
<tr>
<td>$R_{CeO}$</td>
<td>3.075</td>
<td>3.275</td>
<td>3.595 / 3.527</td>
</tr>
<tr>
<td>$r_{NN}$</td>
<td>1.139</td>
<td>1.140</td>
<td>1.140</td>
</tr>
<tr>
<td>$r_{NO}$</td>
<td>1.201</td>
<td>1.199</td>
<td>1.198</td>
</tr>
<tr>
<td>Tilt</td>
<td>59°</td>
<td>69°</td>
<td>55° / 50°</td>
</tr>
<tr>
<td>$E_{ads}$</td>
<td>−105</td>
<td>−120</td>
<td>−93</td>
</tr>
<tr>
<td></td>
<td>N-down</td>
<td>N-down</td>
<td>N-down</td>
</tr>
<tr>
<td>$R_{CeN}$</td>
<td>3.202</td>
<td>3.186</td>
<td>3.297</td>
</tr>
<tr>
<td>$r_{NN}$</td>
<td>1.141</td>
<td>1.140</td>
<td>1.141</td>
</tr>
<tr>
<td>$r_{NO}$</td>
<td>1.195</td>
<td>1.196</td>
<td>1.198</td>
</tr>
<tr>
<td>Tilt</td>
<td>83°</td>
<td>64°</td>
<td>32°</td>
</tr>
<tr>
<td>$E_{ads}$</td>
<td>−89</td>
<td>−105</td>
<td>−97</td>
</tr>
</tbody>
</table>

Table 4.4: Optimized structures for adsorption of N$_2$O on periodic slabs of ceria(111). For the free N$_2$O molecule, structure optimization gives $r_{NN} = 1.121$ Å and $r_{NO} = 1.184$ Å.

down overlayer is stabilized by about 50 meV due to molecule-molecule interactions, one in the O-down overlayer by about 30 meV.

Although I pointed out that PW91 results lack somewhat in credibility for van der Waals systems, the large molecule-molecule interaction is an important result, since it indicates that embedded cluster calculations for isolated molecules would not be sufficient either for the N$_2$O/CeO$_2$(111) system. It was therefore necessary to find a strategy that either combines results from periodic calculations and embedded cluster calculations, or to estimate coverage effects in embedded cluster calculations with large clusters. The latter was done in Paper IV and the results are summarized in section 4.3.4.2 of this thesis.

44
4.3.3 Embedded cluster calculations

For the N$_2$O/CeO$_2$(111) system, RHF, B3LYP, MP2 and CCSD(T) calculations were performed with Cluster 1 and Cluster 2 (Figure 4.1). Table 4.5 shows the results for adsorption of a single N$_2$O molecule on a Ce cation. The quality of the embedded clusters was investigated in Paper I, and found to be good.

<table>
<thead>
<tr>
<th>N$_2$O adsorption on CeO$_2$(111)</th>
<th>Cluster 1</th>
<th>Cluster 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce$<em>{13}$O$</em>{26}$</td>
<td>Ce$<em>{22}$O$</em>{44}$</td>
</tr>
<tr>
<td>N-down adsorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{\text{CeN}}$</td>
<td>2.837</td>
<td>2.924</td>
</tr>
<tr>
<td>$r_{NN}$</td>
<td>1.120</td>
<td>1.120</td>
</tr>
<tr>
<td>$r_{NO}$</td>
<td>1.175</td>
<td>1.176</td>
</tr>
<tr>
<td>Tilt</td>
<td>$0^\circ$</td>
<td>$0^\circ$</td>
</tr>
<tr>
<td>$E_{\text{int}}$(HF)</td>
<td>+2</td>
<td>+17</td>
</tr>
<tr>
<td>$E_{\text{int}}$(B3LYP)</td>
<td>$-144$</td>
<td>$-67$</td>
</tr>
<tr>
<td>$E_{\text{int}}$(MP2)</td>
<td>$-280$</td>
<td>$-242$</td>
</tr>
<tr>
<td>$\omega_{\text{symmetric}}$</td>
<td>1364 (+40)</td>
<td>—</td>
</tr>
<tr>
<td>$\omega_{\text{anti-symmetric}}$</td>
<td>2385 (+46)</td>
<td>—</td>
</tr>
<tr>
<td>O-down adsorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{\text{CeO}}$</td>
<td>2.805</td>
<td>2.896</td>
</tr>
<tr>
<td>$r_{NN}$</td>
<td>1.115</td>
<td>1.117</td>
</tr>
<tr>
<td>$r_{NO}$</td>
<td>1.193</td>
<td>1.191</td>
</tr>
<tr>
<td>Tilt</td>
<td>$53^\circ$</td>
<td>$60^\circ$</td>
</tr>
<tr>
<td>$E_{\text{int}}$(HF)</td>
<td>$-141$</td>
<td>$-113$</td>
</tr>
<tr>
<td>$E_{\text{int}}$(B3LYP)</td>
<td>$-141$</td>
<td>$-79$</td>
</tr>
<tr>
<td>$E_{\text{int}}$(MP2)</td>
<td>$-266$</td>
<td>$-261$</td>
</tr>
<tr>
<td>$\omega_{\text{symmetric}}$</td>
<td>1299 ($-25$)</td>
<td>—</td>
</tr>
<tr>
<td>$\omega_{\text{anti-symmetric}}$</td>
<td>2363 (+24)</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 4.5: Adsorption of a single N$_2$O molecule on CeO$_2$(111) calculated with two different embedded clusters (see Figure 4.1). The structures and frequencies were obtained at the B3LYP level. The bond distances for the free N$_2$O molecule are $r_{NN} = 1.121$ Å and $r_{NO} = 1.184$ Å. Frequency shifts are given with respect to the free gas-phase molecule.
There are several differences between the results from the periodic slab and the embedded cluster calculations. (1) of all, the interaction energies\(^1\) are much smaller in the periodic slab calculations. At the PAW-PW91 level for 25% coverage, the energies are of the order of those calculated at the B3LYP level (about \(-0.1\) eV), but much smaller than the MP2 energies, which are close to what was observed in experiment (about \(-0.3\) eV). (2) the molecule-surface distance is about 0.2–0.3 Å larger in the periodic slab calculations than in the embedded cluster calculations. And (3) the N-down adsorption structure is perpendicular to the surface in the embedded cluster calculations but at all coverages tilted in the periodic calculations. The \(\text{N}_2\text{O}\) stretching frequencies were calculated for the cluster model only (at the B3LYP level) and the shift-pattern was found to agree well with those observed by Borello et al. \([96]\) and Rusu et al. \([97]\).

4.3.3.1 Methodological aspects of the \(\text{N}_2\text{O}/\text{ceria}\) cluster calculations

Some considerable effort was spent on investigating the reliability of the results from the embedded cluster calculations. The tests that were performed in Paper \(\text{IV}\) include calculations with different cluster sizes but also calculations with a larger basis set for some of the O ions in the cluster as well as calculations with different models for molecule-induced surface relaxation.

In Paper \(\text{I}\), differences were observed between the electrostatic potential above the two CeO\(_2\)(111) clusters \(\text{Cluster 1 (Ce}_{13}\text{O}_{26})\) and \(\text{Cluster 2 (Ce}_{22}\text{O}_{44})\), leading to a difference of about 30% in the interaction energy between the surface and CO\(_2\) (B3LYP values). Also the \(\text{N}_2\text{O}/\text{CeO}_2\)(111) system shows a significant cluster size dependence of the molecule-surface interaction energy. At the Hartree-Fock and MP2 levels, the dependence is quite small, but at the B3LYP level \(E_{\text{int}}\) with the larger cluster is a factor of 2 smaller than with the smallest cluster.

As expected, when the \((14s,6p)/[3s,2p]\) basis set was extended to \((11s,6p,d)/[5s,3p,d]\) for the O ions closest to the adsorbed molecule, the largest effect was observed at the MP2 level. At the RHF and B3LYP levels, the smaller oxygen basis set is already sufficient to yield converged results for \(E_{\text{int}}\). At the MP2 level, \(E_{\text{int}}\) increases by about 20%, but the relative difference between the interaction energies of the O-down and N-down mode remains the same.

Molecule induced surface relaxation was studied using three different models. In most of the calculations only the \(\text{N}_2\text{O}\) structure was optimized, while the positions of the ions in the surface were fixed to their optimized bulk values. This is a good approximation for the \(\text{N}_2\text{O}/\text{ceria(111)}\) system, since the interaction is very weak and the ceria(111) surface is known to deviate only little from the bulk structure (see the discussion in Paper \(\text{IV}\) or \([98–103]\)).

\(^1\)In Paper \(\text{IV}\) the difference between adsorption energy \(E_{\text{ads}}\) and interaction energy \(E_{\text{int}}\) was discussed in detail. Since \(\text{N}_2\text{O}\) is weakly bound to the surface the difference between the two kinds of energy is small and can be neglected.
For systems where higher relaxation effects are expected, other embedding schemes, e.g. of the force-field-embedding type are more suitable. Still, even with our type of embedding, it is possible to consider relaxation effects that are confined to a small area in the middle of the cluster. In two sets of calculations, we also allowed part of the surface to relax along the surface normal. Either only the Ce ion beneath the adsorbed molecule, or the Ce ion and its 6 nearest neighbor O ions, were then optimized together with the positions of the atoms in the molecule. It so happens that the bulk parameter used in the construction of the embedded clusters was optimized with a smaller Ce basis set than that used later in the embedded cluster calculations\(^2\), two effects were observed in these calculations. First of all, the atoms in the cluster moved to minimize the strain due to the “wrong” bulk parameter and, second, they respond to the adsorbed molecule. The first effect is relatively large, leading to a displacement of the topmost O ions by about 0.18 Å. But as expected, the second effect is very small. The largest molecule-induced displacement is found for the Ce ion, which moves about 0.03 Å in the direction perpendicular to the surface. The consequence of the O-displacement of 0.18 Å is all in all quite modest. The N\(_2\)O-surface interaction energy increases by about 10% compared to adsorption on the bulk terminated surface. Most of the energy difference is from the mismatch in cell parameter and by allowing for the adjustment (relaxation) due to that effect one introduces an unwanted error, since it is only the molecule-induced relaxation we are after. Nevertheless, the 10% might serve as an estimate of the surface relaxation effects on the interaction energy. These effects are significant but an error of 10% (probably less) does not justify the higher computational costs of calculations where the molecule and the surface are relaxed simultaneously.

### 4.3.4 The nature of the molecule-surface interaction

The N-down and O-down adsorption modes have similar interaction energies at the B3LYP and MP2 levels, but at the Hartree-Fock level, only the O-down mode is stable. This indicates that electron correlation effects contribute more to the interaction in the N-down mode. But the tilted structure of the O-down mode suggests that the total dipole or quadrupole moment (static + induced) of the molecule plays an important role as well. In Paper IV, simple model calculations were performed to elucidate the role of the surface-induced dipole moment of N\(_2\)O. In Paper V the electron correlation contribution to the molecule-surface interaction was examined in more detail using incremental calculations.

\(^2\)Diffuse basis functions and \(f\)-functions cause linear dependencies or convergence problems in the CRYSTAL03 program, which was used for the bulk optimizations. Therefore it was not possible to use the large basis set of our cluster calculations for the periodic calculations.
4.3.4.1 Electrostatic contribution

The purpose of the investigation summarized here and presented in Paper IV was to estimate the electrostatic contributions to the N₂O-ceria interaction from the interaction of the molecule’s dipole moment with the electrostatic potential generated by the surface. It is not straightforward to evaluate multipole moments of an atom or a molecule while it is bound. Therefore, in this study a simple test system was created. First the electrostatic potential was calculated above a clean CeO₂(111) surface cluster at the RHF, B3LYP or MP2 levels. As it turned out, the field over the N₂O molecule was almost constant. The electrostatic fields values “along the molecule” were determined for the molecule in the equilibrium structure of the N₂O/ceria(111) system and the average field was calculated from the values at the N-end and O-end. Thus, a single molecule with the same intramolecular structure as in the adsorption structures was immersed in a homogeneous field of the same magnitude and direction as this “average field” and molecular calculations were performed at the same levels of theory, producing our estimate of the electrostatic interaction energy. In Table 4.6, the electrostatic interaction energy between the field and the molecule is compared with the total $E_{\text{int}}$ for a N₂O molecule on the CeO₂(111) surface (within parenthesis in Table 4.6). The N₂O dipole moment was recorded in this mimicked surface field, to get a handle on the magnitude of the induced dipole moment.

The most important result from these calculations is that, due to the field above the cation site on the surface, a large dipole moment is induced in the N₂O molecule. In the O-down case, the permanent and induced dipole moments have the same direction, so that the total dipole moment is enlarged. In the N-down case, the induced dipole moment is opposite to the static and the resulting $\mu_{\text{tot}}$ is smaller than in the O-down case at the B3LYP and MP2 level, and almost zero at the RHF level.

The electrostatic interaction energies for the molecule in the field (Table 4.6) are correlated to the differences in the total dipole moment. At the B3LYP and MP2 levels, the induced dipole moments are large and, the electrostatic interaction energies of both adsorption modes are stabilizing. At the RHF level, the N-down mode is destabilized because the permanent and induced dipole moment almost cancel, but the O-down mode, where $\mu^0$ and $\mu^\text{ind}$ reinforce each other, is strongly stabilized. The RHF values are discussed here just to show a principle. From a chemical point of view, the RHF values themselves provide little insight into the physisorption phenomenon. A comparison of the electrostatic interaction energies calculated in the homogeneous field model with the total interaction energies for N₂O/CeO₂(111) (in parenthesis) show that the neglect of all the non-electrostatic effects (charge transfer, electron correlation, Pauli repulsion) results in interaction energies much lower than the full interaction energy of N₂O with the ceria surface.
<table>
<thead>
<tr>
<th></th>
<th>N\textsubscript{2}O in electric field</th>
<th>free N\textsubscript{2}O</th>
<th>N-down</th>
<th>O-down</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{int}} )</td>
<td>RHF</td>
<td>——</td>
<td>+22 (+2)</td>
<td>−105 (−141)</td>
</tr>
<tr>
<td></td>
<td>B3LYP</td>
<td>——</td>
<td>−41 (−144)</td>
<td>−64 (−141)</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>——</td>
<td>−36 (−280)</td>
<td>−38 (−266)</td>
</tr>
<tr>
<td>( \mu^0 )</td>
<td>RHF</td>
<td>−0.69</td>
<td>−0.57</td>
<td>−0.75</td>
</tr>
<tr>
<td></td>
<td>B3LYP</td>
<td>−0.08</td>
<td>−0.02</td>
<td>−0.16</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>+0.16</td>
<td>+0.08</td>
<td>−0.05</td>
</tr>
<tr>
<td>( \mu^{\text{tot}} )</td>
<td>RHF</td>
<td>——</td>
<td>+0.05</td>
<td>−1.43</td>
</tr>
<tr>
<td></td>
<td>B3LYP</td>
<td>——</td>
<td>+0.80</td>
<td>−0.99</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>——</td>
<td>+0.75</td>
<td>−0.77</td>
</tr>
</tbody>
</table>

Table 4.6: Permanent (\( \mu^0 \)) and total (\( \mu^{\text{tot}} \)) dipole moments of an N\textsubscript{2}O molecule exposed to a uniform electric field of the same magnitude as the average (non-uniform) field over the molecule in the N-down and O-down adsorption structures on ceria(111). Surface Cluster 1 (Figure 4.1) and three methods were used. The different values for \( \mu^0 \) for a certain computational level originate from the different intramolecular structure of N\textsubscript{2}O in the two adsorption modes. Negative dipole moments mean that the O-end is negatively charged. For comparison also the dipole moments for the isolated molecules without an external field are given. The electrostatic interaction in the uniform field is also given as \( E_{\text{int}} \). The values in parenthesis are \( E_{\text{int}} \) for the N\textsubscript{2}O/CeO\textsubscript{2}(111) system. All energies are given in meV, all dipole moments in D.
4.3.4.2 Electron correlation contribution

In this section, the electron correlation part of the N₂O/ceria(111) interaction is in focus. As discussed in the Introduction, electron correlation effects will improve the multipole moments of N₂O and of ceria and thus improve the description of the electrostatic N₂O/ceria interaction, and it will add dispersion interactions. By definition the electron correlation effects are given using the HF method as a reference. Since HF is a mean-field approach, it does not capture any dispersion. DFT methods can in principle be made to capture electron dispersion, but the most commonly used functionals do not perform well for weakly bound systems. The other group of interactions important for weakly bound systems are those between multipole moments. Table 4.7 shows how N₂O’s dipole moment varies with the computational level; the list can help in finding an adequate computational method. The table shows that HF and DFT methods either predict the wrong sign for μ or underestimate it compared to experiment. The most accurate description is given by CCSD(T), which is probably the most suitable method for an accurate description of the weakly bound N₂O/CeO₂(111) system. Other electrostatic properties (e.g. the quadrupole moment and the isotropic polarizability; not shown here) vary less with the computational level, but are also well reproduced at the CCSD(T) level.

<table>
<thead>
<tr>
<th>Free N₂O</th>
<th>Method</th>
<th>μ / D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>−0.161</td>
<td></td>
</tr>
<tr>
<td>RHF</td>
<td>−0.687</td>
<td></td>
</tr>
<tr>
<td>LDA</td>
<td>+0.196</td>
<td></td>
</tr>
<tr>
<td>PW91</td>
<td>+0.122</td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>−0.076</td>
<td></td>
</tr>
<tr>
<td>MP2</td>
<td>+0.164</td>
<td></td>
</tr>
<tr>
<td>MP4</td>
<td>−0.085</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td>−0.327</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>−0.143</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7: Static dipole moment for the free gas phase N₂O molecule calculated at different levels with the aug-cc-pVTZ basis set. A negative value indicates a negatively charged oxygen in N₂O.

To elucidate the role of all these electron correlation effects, incremental coupled cluster calculations were performed for the two adsorption modes of N₂O on ceria(111) at the CCSD(T) level. In the O-down case, electron correlation effects contribute with about 60% to the total interaction energy, and
in the N-down case, the entire interaction with the surface is due to electron correlation effects.

A comparison of the increments for N-down and O-down adsorption (Paper V), shows large differences for the $\eta^{\text{int}}_{N,O}$ term, which indicates larger changes of N$_2$O’s electronic structure in the O-down case than in the N-down case. Smaller differences are seen in the $\eta^{\text{int}}_{N_2O,Ce}$ and $\eta^{\text{int}}_{N_2O,O}$ terms. As a consequence, electron correlation changes the order of stability of the various adsorption modes. At the MP2 level, the N-down mode was found to be 23 meV more stable than the O-down mode, but at the CCSD(T) level, the O-down mode is 34 meV more stable than the N-down mode. Applying Boltzmann statistics, such a difference would mean that, at 100 K, about 98% of the N$_2$O molecules will adsorb O-down. This is now more consistent with experiment.

Co-adsorption of 2 N$_2$O on Cluster 3

![Co-adsorption diagram](image)

Figure 4.7: Ce$_{22}$O$_{44}$ cluster used in the co-adsorption calculations of the N$_2$O/CeO$_2$(111) system

At the MP2 level, calculations with two N$_2$O molecules adsorbed on Cluster 3 (see Figure 4.7) were performed. While for adsorption of a single N$_2$O molecule the N-down and O-down modes are about equally stable, the O-
down adsorption mode is slightly more stable for co-adsorption of two N\textsubscript{2}O molecules. Thus two effects, the change of the stability order at the CCSD(T) level (compared to less sophisticated methods) and the effect of co-adsorption of two N\textsubscript{2}O molecules, suggest that no N-down adsorption would be observed in experiments.

4.3.5 Synopsis of the N\textsubscript{2}O/CeO\textsubscript{2}(111) results

Let us now combine all the theoretical results obtained for the N\textsubscript{2}O/ceria(111) system to get an overall picture. N\textsubscript{2}O was found to adsorb only to the Ce ions, either in a perpendicular structure towards the surface with the N-end pointing towards the Ce cation, or in a tilted structure with the O-end pointing towards the surface. Vibrational frequency shifts with respect to the free gas-phase for the N\textsubscript{2}O stretching modes were calculated for these two orientations and show a $\Delta \omega_{\text{symm}} > 0$ and $\Delta \omega_{\text{anti-symm}} > 0$ pattern for N-down and a $\Delta \omega_{\text{symm}} < 0$ and $\Delta \omega_{\text{anti-symm}} > 0$ pattern for O-down. Only the latter pattern was observed in experiment. At the RHF level only the O-down mode is binding. With the electron correlation methods, both modes give almost equal interaction energies. $E_{\text{int}}$ values of about $-0.23$ eV for the N-down mode and $-0.27$ eV for the O-down mode are obtained by adding the CCSD(T) correlation contributions (from $E_{\text{int}}$ calculations with Cluster 1) to the RHF $E_{\text{int}}$ values (obtained with Cluster 2). Concerning basis size effects and surface relaxation, we will assume that such model improvements affect the B3LYP, MP2 and CCSD(T) results in similar ways (20% stabilization due to larger O basis set and 10% due to relaxation). Co-adsorption calculations at the MP2 level show that the N-down mode is less affected (stabilized by $\approx 5\%$) by the molecule-molecule interaction than the O-down mode (stabilized by $\approx 10\%$). Assuming a similar trend at the CCSD(T) level, we obtain our most sophisticated estimates of the interaction energies to be about $-0.32$ eV for the N-down mode and $-0.39$ eV for the O-down mode. The values for O-down adsorption is consistent with the experimental adsorption energy. Moreover, at the temperature of our experiments, $\approx 100$ K, this energy difference is sufficient to favour only O-down adsorption. Altogether, three quantities from my calculations corroborate that it is the O-down mode which is present in our experiments: the absolute value of $E_{\text{int}}$, the energy difference between the N-down and O-down modes, and the pattern of the vibrational frequency shifts.

4.4 Interpretation of the $\eta^{\text{int}}$ terms

A side-benefit of the method of increments is that the individual interaction energy increments can be interpreted to obtain some chemical information. Since this interpretation is not straightforward, it is helpful to explore the mechanisms that affect the size of an $\eta^{\text{int}}$ term. As an example, the $\eta_{\text{N}_2\text{O}}^{\text{int}}$
increment for the N\textsubscript{2}O/CeO\textsubscript{2} system at the MP2 level will be discussed. Note that the “true” dispersion energy contribution will show up in the higher-order terms. The \( \eta_{\text{N}_2\text{O}} \) energy term expresses how much the electron correlation amongst the localized orbitals on the N\textsubscript{2}O molecule change when the molecules is adsorbed on the surface.

The major effect of chemical significance that contributes to \( \eta_{\text{N}_2\text{O}} \) is the polarization of the N\textsubscript{2}O molecule by the surface. \( \eta_{\text{N}_2\text{O}} \) is calculated as the difference between the 1-body electron correlation energy increments \( \varepsilon_{\text{N}_2\text{O}}(\text{N}_2\text{O/ceeria}) \) and \( \varepsilon_{\text{N}_2\text{O}}(\text{N}_2\text{O/ghosts}) \), and in the former, N\textsubscript{2}O is polarized by the electrostatic field from the surface atoms. Since all localized orbitals on surface atoms are frozen during the calculation of \( \varepsilon_{\text{N}_2\text{O}}(\text{N}_2\text{O/ceeria}) \), N\textsubscript{2}O actually experiences the field of the surface ions at the RHF level. This “flaw” is “corrected” when the 2-body terms are added but it affects the interpretation of the 1-body terms. In the same way, the N\textsubscript{2}O molecule (at the RHF level) polarizes the surface ions; this is contained in the \( \eta_{\text{i}} \) terms.

The other major effect that contributes to \( \eta_{\text{N}_2\text{O}} \) originates from the different descriptions of the N\textsubscript{2}O molecule at the RHF and MP2 levels. Since \( \eta_{\text{N}_2\text{O}} \) at the MP2 level is a difference between two electron correlation energy increments at the MP2 level, the difference between \( \mu^{\text{HF}} \) (\(-0.69 \) D) and \( \mu^{\text{MP2}} \) (\(-0.16 \) D) does not directly affect \( \eta_{\text{N}_2\text{O}} \). However, the surface interacts with the molecule’s dipole moment and this interaction contributes to \( \eta_{\text{N}_2\text{O}} \). To clarify this we decompose \( \eta_{\text{N}_2\text{O}} \) at the MP2 level:

\[
\begin{align*}
\eta_{\text{N}_2\text{O}} &= \varepsilon^{\text{MP2}}_{\text{N}_2\text{O}}(\text{N}_2\text{O/ceeria}) - \varepsilon^{\text{MP2}}_{\text{N}_2\text{O}}(\text{N}_2\text{O/ghosts}) \\
&= E^{\text{MP2}}_{\text{N}_2\text{O}}(\text{N}_2\text{O/ceeria}) - E^{\text{RHF}}_{\text{N}_2\text{O}}(\text{N}_2\text{O/ceeria}) \\
&\quad - E^{\text{MP2}}_{\text{N}_2\text{O}}(\text{N}_2\text{O/ghosts}) + E^{\text{RHF}}_{\text{N}_2\text{O}}(\text{N}_2\text{O/ghosts}).
\end{align*}
\]  

Focusing only on \( \mu_{\text{N}_2\text{O}} \), one sees in (4.3) that the effects of the permanent dipole moments (at the RHF and MP2 level) will cancel, but the induced dipole moments or interactions with the dipole moments will not. Thus some part of the \( \eta_{\text{i}} \) terms will always depend on how badly RHF performs for a system compared with the post-Hartree-Fock method used.

A third effect contributing to \( \eta_{\text{N}_2\text{O}} \) is worth mentioning but is rather small. In the definition of the \( \eta_{\text{i}} \) terms, the BSSE is avoided by applying the counterpoise scheme from Boys and Bernardi [104]. However, another finite basis set error emerges when occupied orbitals are emptied and become available for excitations. This effect always leads to small destabilizing contributions to the \( \eta_{\text{i}} \) terms, which should, however, converge to zero for large basis sets.

It is difficult, if not impossible, to predict to what amount these three terms will contribute to the interaction energy increments; for the first two effects it is not even possible to predict the sign. The dissection of other n-body increments is similarly difficult. Therefore, we have been very careful in Papers
II, III and V, not to read too much into the adsorption energy increments. Nevertheless, some trends were found that will be summarized briefly.

- The 1-body increments are usually small and positive.
- The 2-body terms that include the molecule are large and negative, but decay rapidly with the distance between the involved surface ions and the molecule.
- Other 2-body terms are small and either positive or negative. They are largest if they include those ions that have large 1-body terms.
- The 3-body terms are very small and their size decays very rapidly with the distance from the adsorption site. This is very good because it will save us computer time if we ignore them. Again, 3-body terms are largest if they include groups with large 1-body terms.

4.5 Electron correlation localization and basis set vs. cluster size

The basis sets used for the investigations in Papers II, III and V are as large as we could reasonably afford but they might nevertheless be too small to expect converged results at the MP2 or CCSD(T) levels, even though at the RHF and B3LYP level, the interaction energies are already converged. Our tests in Papers II and V showed that the results were almost, but not fully, converged with respect to the basis sets at the MP2 and CCSD(T) levels. The practical problem is that although the computational time is tremendously much reduced by applying the method of increments (or any other linear correlation method), the calculations are still extremely costly and it was not possible to increase the size of the basis set further, with the current (quite large) computer resources. It has been argued that due to the local nature of electron correlation effects, small QM clusters are sufficient for accurate calculations (see e.g. [90]), but on the other hand, in Paper I it was seen that the central region in small QM clusters suffers from edge effects even when the embedding is very good. For the CO/ceria(110) system, we tried to make some more elaborate investigation of to what extent the size of the QM cluster affects the $E_{\text{int}}$.

For this purpose, a very small embedded Ce3O6(110) surface cluster (Figure 4.8) was created and interaction energy increments were calculated for this cluster and compared with the larger Ce12O24 cluster (Cluster 4), for two basis sets: the basis set used in Paper II, and a larger basis set for the four O ions at the surface, namely the TZVP basis set by Schäfer et al. [105]. The same CO/ceria structure, optimized for Cluster 4, was used for CO above the two clusters. The results of these calculations at the CCSD(T) level are shown in Table 4.8.

A comparison of the interaction energy increments calculated with the large and the small cluster says something about the transferability of the increments between different cluster sizes. Both clusters overall give similar re-
results, although, some sizeable deviations in the $\eta_{O1}^{int}$ and $\eta_{Ce2,O1}^{int}$ terms lead to a difference of about 30% for the electron correlation contribution to the interaction energy. At the MP2 and MP4 levels (not shown), $E_{int}^{corr}$ is much more similar for the two different clusters. An increase of the basis set size gives the same trend.

Based on the CCSD(T) results, I suggest that the cluster size does affect $E_{int}^{corr}$. In principle, this is no contradiction to the local nature of electron correlation effects. Apparently, in a very small cluster, edge effects spread far enough into the cluster to disturb the electronic structure so much that also electron correlation becomes affected. Therefore, for an accurate treatment of electron correlation effects in physisorption problems it is necessary to find a balance between cluster size and basis set size.
Table 4.8: Contributions (in meV) from the various increments [at the CCSD(T) level] to $E_{\text{corr}}^{\text{ads}}$ for CO adsorbed on CeO$_2$(110). All increments are BSSE corrected. A positive sign means repulsion.
5. Conclusion

In this thesis embedded surface clusters were constructed to investigate physisorption of CO and N$_2$O on ceria (CeO$_2$), by means of quantum-mechanical (QM) calculations. The quality of the embedded cluster model was assessed by comparing atomic charges, the projected electronic density of states (pDOS), the electron density and the electrostatic potential of the clean embedded QM clusters to the same properties calculated using a clean periodic surface model for the QM calculations. It was found that the electron density within the cluster and the electrostatic potential above it are very sensitive to the embedding scheme and are therefore useful tools in the quality assessment of the cluster model. It was shown that with the full embedding scheme described in this thesis, the central region of the embedded QM clusters are well described, both concerning short- and long-range interactions.

Three general conclusions from this thesis work are as follows.

- **Periodic slab and embedded cluster calculations complement each other.** Most quantum-mechanical studies of surface science problems use periodic models, some use finite cluster models. In my opinion, it is often beneficial to investigate a system with both types of models and benefit from the advantages of each model. I found that, in the N$_2$O/CeO$_2$(111) system, the periodic DFT calculations underestimated the molecule-surface interaction but were able to give useful qualitative information concerning the importance of molecule-molecule interactions, which made me construct larger clusters and investigate the co-adsorption of two N$_2$O molecules. The advantage of the embedded cluster approach on the other hand, is clusters made it possible to use high level QM methods.

- **Credibility of embedded cluster results relies on a careful quality assessment.** Even the most accurate calculation methods cannot heal errors anywhere else in the theoretical treatment. I have devoted a large amount of my time on the assessment of different embedded clusters and embedding schemes, to find really well behaving models for CeO$_2$ surfaces. Still I believe that these extended tests kept me from wasting even more time on unreliable surface models. Bad embedding does not only produce wrong results, but also increases computer time, due to bad convergence of electronic structure calculations. For the CO/CeO$_2$(110) system too small cluster resulted in errors of 30% for the interaction energy.
Advanced electron correlation calculations (with an embedded-cluster model) are necessary for physisorption problems. In the literature, physisorption has often been studied with DFT, although it is well known from many van der Waals systems, that DFT often underestimates van der Waals forces. Post-Hartree-Fock methods such as MP2 and CCSD(T) are needed, but their computational demands are often prohibitively large. With local electron correlation schemes they can become feasible but are still very costly. Even so, this is the price that is necessary for an accurate treatment of weakly bound systems! For example, my investigations of the N₂O/CeO₂(111) system required more than 1.700.000 CPU-hours (almost 200 years) of computer time (so some calculations were run in parallel on 128 CPUs), and some of the computers had to be equipped with up to 30 GB RAM or 10 TB hard disks. With these efforts I was able to investigate physisorption of CO and N₂O on CeO₂(110) and (111) at the CCSD(T) level, which to my knowledge is the first time, ever, such a high-level method was used for physisorbed molecules.

More specific conclusions for the individual chemical systems follow:

Below I summarize some specific results that I have found for CO and N₂O physisorbed on CeO₂(111) and CeO₂(110). Electron correlation was found to play an important role in the molecule-surface interaction for CO on ceria. On the (110) surface, electron correlation effects, calculated at the CCSD(T) level, make up 30% of the interaction, on the (111) surface it is 80%. The B3LYP method underestimates the interaction energies by 40 to 50%, MP2 overestimates the interaction energy by about 20%.

For the N₂O/CeO₂(111) system theoretical calculations were performed to guide the interpretation of IR-measurements. In the experiments most of the N₂O had desorbed at about 125 K, which corresponds to a stabilizing adsorption energy of about −0.30 eV. The frequency of the N₂O symmetric stretching mode (at ≈1280 cm⁻¹), was found to down-shift due to the interaction with the surface, while the anti-symmetric mode (at ≈2230 cm⁻¹) up-shifted. In my theoretical embedded cluster calculations this shift-pattern was reproduced when N₂O adsorbes “O-down” above a Ce ion. For this structure the frequencies of both stretching modes are up-shifted, i.e. not consistent with experiment. At the B3LYP level the interaction energies for the two adsorption structures are almost similar (about −0.06 eV) and at the MP2 level too (about −0.24 eV). Incremental CCSD(T) calculations revealed a small difference between the two adsorption modes: −0.23 eV for N-down and −0.26 eV for O-down. Such a difference means that at about 125 K only 2% of the adsorbed N₂O molecules would be adsorbed N-down, i.e. electron correlation effects could explain, why only O-down adsorption is observed in the experiment. Co-adsorption of two N₂O molecules (at the MP2 level) also stabilizes O-down adsorption compared to N-down, which may be another contributing reason for the experimental observation. Periodic slab calculations at the
PAW-PW91 level gave small interaction energies (about $-0.10$ eV) and long molecule-surface distances.

### 5.1 Future development and improvements

The methodology for accurate embedded cluster calculations of physisorption energies can be improved in several ways. First of all, a more advanced surface model can be invoked. In our current embedded cluster model, optimization of the surface structure is limited to a small surface region at the center of the cluster and the remainder of the surface (modeled by formal point charges) cannot adapt to the structural changes. Several models exist that apply a more sophisticated embedding scheme which allows for surface relaxation. Such models are particularly suitable when the surface structure is more perturbed, e.g. in chemisorption or with structural defects.

As for the incremental calculations, the basis set can be improved. So far, we used moderately large basis sets that probably do not yield fully converged results at the CCSD(T) level. This is a consequence of the situation that we have to find a compromise between cluster size (which is important for a good embedding quality) and basis set size (which is important for the accuracy of the calculations) and the available computer resources. Up to now, we have calculated CCSD(T) interaction energies based on B3LYP-optimized structures. A more consistent approach with the optimization performed at the CCSD(T) level is far beyond realistic dreams. Until such calculations become possible, very time-consuming, but feasible approach would be to sample selected points along the potential-energy curve of the adsorption. If the equilibrium molecule-surface distance is shorter at the CCSD(T) level than at the B3LYP level, the correlation energy contribution to $E_{\text{int}}$ would probably increase.

I have tried to use the method of increments not only for the calculation of electron correlation contributions to the interaction energy, but also as a tool for the interpretation of molecule-surface interaction. So far we lack enough experience in this field. In the future more incremental data will be required from a wider range of systems to make the $\eta_{\text{int}}$ terms more useful for interpretation.

It would be useful to have access to additional data, experimental as well as theoretical, for the N$_2$O/ceria system. Low energy electron diffraction (LEED) would be helpful to establish if the N$_2$O-overlayer structure predicted from my theoretical calculations is correct or not. I found that electron correlation plays a large role in the molecule-surface interaction, but was not able to explore their role in the molecule-molecule interaction. Such a study requires CCSD(T) calculations for larger embedded surface clusters which requires more computational resources than we have right now. Alternative methods for the analysis of molecule-surface or molecule-molecule interac-
tions are the Morokuma method [106] or the symmetry adapted perturbation theory (SAPT) [107]. Commonly available implementations of these methods (in the GAMESS [108] and SAPT06 [107] programs) were found to be incompatible with our embedding scheme. A related question is why only O-down adsorption of N₂O was observed in the experiments on CeO₂(111) in contrast to the N₂O/α-Cr₂O₃ [96] and N₂O/TiO₂ [97] systems were both adsorption modes are present.

An interesting field that was not explored in this thesis is the role of defects in the N₂O/CeO₂(111) system. XPS measurements on thin films used in our experiments suggest a rather low concentration of surface defects. On the other hand, we also observe N₂O adsorption on some sites with slightly larger adsorption energies, which could be related to surface defects. In further studies the interaction of N₂O with a few selected defects should be investigated, where the most important candidate probably being the oxygen vacancy. However, as recent investigations of Kullgren et al. have shown, these studies will require a much larger basis set for the Ce ions [109].
Acknowledgments

I would like to thank my supervisor Kersti Hermansson for sharing her scientific knowledge and experience, and for the support and enthusiasm she has shown for my work.

I thank Beate Paulus (Freie Universität Berlin and Max-Planck-Institute for Physics of Complex Systems MPI-PKS, Dresden) for introducing me to the method of increments and for all the discussions we had about it. Elena Voloshina and Nicola Gaston I thank for their help with setting up the incremental calculations in the beginning of my collaboration with Beate Paulus. Peter Fulde is thanked for allowing us to run a large part of the calculations on the facilities of the MPI-PKS and Hubert Scherrer-Paulus for his support with computer problems.

From the members of my research group I thank Björn Herschend for introducing me to his embedding scheme and encouraging me to leave common ways and try new strategies. Daniel Spångberg for his friendship and all the discussions we had in the past five years about theoretical chemistry and the world beyond. Pavlin (Awk-Master) Mitev I thank for his friendship and all his help with small computer issues that would take me hours and hours to solve without him. Christopher M.W. Castleton I thank for all the stimulating discussions about chemists’ and physicists’ view on condensed materials.

Roger M. Nix and Jörn Erichsen (both Queen Mary University London), I thank for the nice time in London and for introducing me to the experimental techniques used in surface characterization. Helmut Weiss and Jochen Vogt (both Otto-von-Guericke-Universität Magdeburg) I thank for inviting me to Magdeburg and for the valuable discussions about the interpretation of experimental results for the $\mathrm{N_2O/CeO_2(111)}$ system.

David Muñoz Ramo and Peter V. Sushko (University Collage London) I thank for introducing me to the GUESS scheme and for all the discussions we had about different embedding schemes, Ljupčo Pejov (Ss. Cyril and Methodius University, Skopje) for valuable discussions about multipole models and Steffen Börm (Christian-Albrechts-Universität, Kiel) for his patient attempts to explain mathematical algorithms to me.

Computational resources were provided by the Swedish National Infrastructure for Computing and special thanks goes to Leif Nixon, Pär Andersson and Torben Rasmussen (all three from the National Supercomputer Center in Linköping) for their support.
Gunilla Lindh, Eva Larsson and Katarina Israelsson are thanked for keeping the Department running and thinking about accounting while I fool around with molecules.

I am very grateful for all the people that spend so much time and energy to teach young researchers like me. In particular I want to thank Henrik Ottoson (Uppsala University) for taking out the horror from coupled cluster theory and Keith Refson (Rutherford Appleton Laboratory) for teaching me how to perform good plane-wave DFT calculations. Further, I want to thank the teams from the MSSC summer school in London (e.g. Roberto Dovesi, Carla Roetti, Nicholas Harrison), the ESQC in Palermo (e.g. Peter R. Taylor, Trygve Helgaker, Jeppe Olsen) and, the summer school on "Electronic Structure Calculations and Correlated Materials" 2006 in Les Houches (e.g. Silke Biermann).
Bibliography


Acta Universitatis Upsaliensis

Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 644

Editor: The Dean of the Faculty of Science and Technology

A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)

Distribution: publications.uu.se
urn:nbn:se:uu:diva-101271