Variations on a QM/MM approach to cluster dynamics

P M Dinh\textsuperscript{1}, D Berger\textsuperscript{2}, B Faber\textsuperscript{2}, P-G Reinhard\textsuperscript{2}, E Suraud\textsuperscript{1}

\textsuperscript{1}Laboratoire de Physique Théorique, Université P. Sabatier, 118 Rte de Narbonne, F-31062 Toulouse cedex, France
\textsuperscript{2}Institut für Theoretische Physik II, Universität Erlangen-Nürnberg, Staudstr. 7, D-91058 Erlangen, Germany

E-mail: suraud@irsamc.ups-tlse.fr

Abstract.

We discuss two extensions of a hierarchical QM/MM approach developed to describe clusters embedded into a polarizable environment. The first extension consists in considering the presence of a supporting metal. More specifically we consider the structure and dynamics of Na clusters on a surface built from Ar layers grown on a metal support. We study the effect of the Ar substrate and of the metal support. We find a faint binding on the surface and the effect of the dielectric response of the metal (DRM) turns out to be negligible. Deposit of small Na clusters is crucially influenced by the mechanical hardness of the metal support and the number of Ar layers, while the DRM makes little effect. The second extension consists in using the QM/MM approach to study color centers at an MgO surface. The particular efficiency of the QM/MM approach allows to consider large system’s sizes and thus test the impact of the (necessarily) finite (surface) sample. We find that our results compare favorably with ab-initio approaches as well as with available experimental results.

1. Introduction

Cluster physics has been a lively research field over the last decades, see e.g. [1, 2]. The case of clusters in contact with a substrate is more involved and covers an extremely rich range of physical and chemical situations. Indeed many experiments can better be performed for non-isolated systems but new phenomena also appear which could possibly lead to practical applications as, for example, chromophore effects to induce well localized heating of a substrate [3, 4]. The field is still much a fast evolving one, see e.g. the collections [5, 6, 7, 8, 9].

Substrates carry an enormous amount of degrees of freedom and a fully detailed quantum mechanical description of such systems is thus beyond today’s possibilities. A good way out is attained by considering Quantum Mechanical/Molecular Mechanical (QM/MM) approaches, which rely on a hierarchy of importance from the active zone of interest down to the farther outskirts of the system. These QM/MM approaches couple a quantum description of the active piece to a classical description of the outer environment. These methods were first developed in bio-chemistry [10] and surface chemistry [11]. The QM/MM approach is the method of choice for active electron systems (molecules, clusters, color centers...) in contact with an environment as there is a clear distinction between the electrons and the environment. The applications we plan to consider, however, require a careful modeling of the dynamical response of the substrate.
We have thus built an extension of the usual QM/MM methods which includes the dynamical polarizability of the substrate [12, 13, 14]. This is perfectly adapted for a cluster deposited on an insulating surface. But we will now apply this approach to 2 slightly different scenarios.

We will concentrate first on the particular combination of a Na$_N$ cluster deposited on a few Ar layers themselves deposited on a metal support, following typical experimental setups [15, 16, 17]. This indeed allows gentle deposition of a metal cluster on a hard surface [15, 18]. But the structural and spectral properties of such systems are also very interesting [17], as they combine an optically active metal cluster with an inert and insulating raregas material, itself coupled to bulk metal. We will thus mostly focus here on structural aspects and explore how deposition dynamics proceeds in the presence of the hard underlying metal.

As a second extension of our approach we shall explore the case of color centers by considering an oxygen vacancy near MgO(001) surfaces, as color centers in solids have attracted attention since long [20]. Studies in MgO have also a long history, see the book [21] for a summary of the early stages. Reliable theoretical descriptions of color centers in MgO have come up only recently, because of the high computational effort required [22, 23, 24, 25, 26, 27, 28, 29].

These calculations employ an embedded cluster approach which imposes to treat only a very small fraction of the system, so that there is a demand for simplifications. Again one can simplify the picture by realizing that the most active pieces are the electrons in the vacancy while the MgO surroundings are only slightly perturbed, which again justifies the use a hierarchical approach such as our QM/MM approach. The idea is now to apply our modeling to the electrons confined in a color center of MgO. This is not as detailed as the full ab-initio methods, but it allows to proceed to larger samples in and at the MgO substrate, and also to account for a pertinent description of the long-range tail of the electron cloud and of the optical response. In that respect our simplified QM/MM approach is to say complementary to ab-initio ones.

We concentrate here on a so called $F$-center, produced from an O vacancy in the MgO substrate. For that we replace an O-site in MgO by 2 electrons, thus ensuring proper neutrality. This configuration produces large optical activity stemming from the two vacancy electrons. We shall only consider such an $F$-center on the surface, and not in the bulk, although the principle is the same in the latter case.

2. An extended QM/MM approach for dynamics of molecules and clusters in contact with an environment

2.1. Basics of the QM/MM approach

The QM/MM model for metal clusters in contact with a rare gas substrate has been developed in [30, 13]. A detailed description of the model is provided, e.g., in the review [31]. The such developed QM/MM approach provides a good basis for exploring the case of clusters deposited on a rare gas layer itself topping a metal surface. Similarly the case of color centers (obtained by creating a vacancy) can be attacked by omitting the cluster itself and simply replacing it by electrons. These are the two extensions we explore in this paper. Figure 1 provides a schematic picture of both setups: O vacancy and Ar covered metal environments. More details can be found in [32, 33]. We give here only a short summary.

The (cluster or vacancy) electrons are described by the time-dependent local-density approximation (TDLDA) augmented by an averaged self-interaction correction [34]. The cluster ions, when present, are propagated by means of molecular dynamics (MD), while the electron-ion interaction is described by soft, local pseudo-potentials [35]. This forms together the TDLDA-MD approach, an approach which was well validated for linear and non-linear dynamics of free metal clusters [36, 37]. The substrate atoms (Ar or Mg, O) are described as purely classical particles, but (for Ar and O) dressed by a classical time dependent dipole, which in particular allows to account for charge effects [31]. These time dependent dipoles may play a very important role for example in deposition scenarios. They constitute a specific feature of
The hierarchical QM/MM model has been detailed in [24].

...MgO. All dynamical degrees-of-freedom (zone II in the figure). This accounts by a time-independent shell-model potential [28]; the ac-

The modeling is continued further far outward by Mg...ions frozen at crystalline positions and accounts for the long-range Madelung potential.

Right panel: the separation in 3 zones is similar in Ar as in MgO but is now complemented by the hard metal surface. The vacancy is replaced by a small Na cluster.

2.2. The case of color centers: O vacancy on MgO surface

The substrate is composed of two species: Mg$^{2+}$ cations and O$^{2-}$ anions. While the cations are electrically inert and can thus be treated as charged point particles the anions are easily polarizable, an aspect which is accounted for by the associated dynamical dipole. The combined system is sorted in several stages of decreasing activity as sketched in figure 1. The (quantum) vacancy electrons are represented in a large numerical simulation box. The Mg$^{2+}$ and O$^{2-}$ ions of the substrate are arranged in the fcc crystalline order of bulk MgO. All dynamical degrees-of-freedom for Mg$^{2+}$ and O$^{2-}$, are taken into account in an active cell of the MgO(001) surface region near the vacancy (zone I in the figure). This fully active area is continued by an outer region of bulk MgO material with fixed MgO and O ionic centers but active O dipoles (zone II in the figure), thus accounting for long range polarization effects. Zone III contains Mg and O ions frozen at crystalline configuration in order to obtain the correct Madelung potential for the whole system [41, 42].
2.3. Extension to account for a dielectric: Na cluster deposited on Ar and metal

Each Ar atom is associated with two classical degrees of freedom: center-of-mass and electrical dipole moment, allowing polarizability effects via polarization potentials [41]. A local pseudopotential is added for the electron-Ar short-range repulsion following [43]. The Na-Ar Vander-Waals interaction is absorbed here for simplicity in the Ar-Na coupling parameters, while the atom-atom interactions are described by a standard Lennard-Jones potential. The Ar-Na$^+$ subsystem is treated by means of known effective potentials [44].

The underlying metal support interacts with the Na-Ar system in two ways. It delivers a strong coupling with the lowest layer of Ar atoms directly in contact with the metal. This is modeled by fixing the atomic position in the bottom layer: in parallel direction to their crystal equilibrium positions and in perpendicular direction at a fixed distance of $3.5 \times 10^{-10} \text{m}$ from the metal surface. Furthermore the dielectric response of the metal (DRM) establishes a long range interaction with all charges in the Na-Ar system. This is described in standard textbook manner by the method of image charges [45], assuming the metal to be an ideal conductor.

3. Some illustrative examples

3.1. Structure of a sodium clusters deposited on Ar coated metal

As a first example we consider in figure 2 a small sodium cluster (Na$_6$) deposited on an Ar surface (actually three layers of Ar, here represented by an Ar$_{192}$ system) topping a metal surface. The lower panel visualizes the areas of mobile atoms (open symbols) surrounded by fixed atoms (full symbols). It turns out that the deposited structure (which integrates the DRM) very little differs from the case in which the DRM is omitted. Switching on/off the DRM changes the
distance between the cluster and the top Ar layer by 0.15 \(a_0\), i.e. by 2.5\%, which is negligible as the binding pocket has a rather flat bottom (whence some uncertainty in the binding distance at negligible energetic cost). Still, the robustness of the ionic/atomic configuration is a bit surprising as the Ar dipoles are modified substantially by the DRM. The equilibrium distance thus emerges from a subtle balance of counter-acting effects (dipole attraction, core repulsion, tail of the electronic wavefunction, metal polarization), the net result being here in stabilizing the positions. The resulting small impact of the metal on the structure has also been noted in other explored cases. This a posteriori validates approaches avoiding the account of the metal, at least what concerns the actual structures. It is then interesting to check how the metal affects the deposition process itself, a situation which corresponds to many experimental cases.

3.2. Dynamics of deposit

![Figure 3. Time evolution of ionic kinetic energy for the deposition dynamics of Na\(_6\) on Ar\(_{192}\) at \(E_{\text{kin}} = 0.014\) eV impact kinetic energy, with DRM ("with DRM") and without ("no DRM").](image)

We now want to explore the dynamics of deposition for Na\(_6\) impinging on Ar layers grown on a metal support. We handle here the electronic potentials approximately, in axial symmetry (cylindrical averaged pseudo-potential method [39]), which is acceptable as discussed in [14, 46]. We initially place a free Na\(_N\) cluster at a large distance from a free surface (typically 17–20 \(a_0\)) with the cluster symmetry axis perpendicular to the surface. Then the cluster is boosted instantaneously with the velocity along the symmetry axis towards the substrate. There are different possible choices for the position of the collision axis on the substrate but this plays a minor role for the Na\(_6\) we consider here, for which the cluster symmetry does not match the surface geometry anyway. The collision axis is on a top site, i.e. it hits an Ar atom in the uppermost layer.

In figure 3 we illustrate this deposition process. The most important effect of the metal support, namely the mechanical stability, fixes the lowest Ar layer, thus stops the propagation of absorbed energy. This leads to cluster reflection in the more energetic cases. The DRM had not been considered here but one can check that the differences are extremely small, except maybe for very slow initialization. This holds particularly for the impact phase where the metal dipole attraction produces slightly more initial acceleration. The differences for the dynamics after impact remain smaller and not significant at the level of our modeling. The dominant role of the mechanical hardness makes the number of Ar layers a key ingredient for energy absorption. We have systematically varied the number of Ar layers and found that energy absorption levels off from six layers on, so that an Ar surface with at least six layers behaves like a bulk Ar surface. Energy absorption from the impinging cluster is then almost complete.
3.3. Optical response
A usually well accessible and crucial observable in electronic systems is the optical absorption. For systems without symmetry it is most efficient to compute these spectra directly from real time electronic evolution and subsequent spectral analysis. The present QM/MM model is well suited for such a purpose as electrons are propagated with time-dependent LDA (with self-interaction correction) [47, 31]. The optical absorption spectra were thus computed in the usual manner by starting from the stationary ground state, and by initializing dynamics by an instantaneous small dipole boost. The emerging time-evolution of the dipole moment $D(t)$ is finally Fourier transformed to the frequency domain [48, 37] and the imaginary part of the Fourier transform $\Im\{\tilde{D}(\omega)\}$ becomes the optical absorption strength.

Fig. 4 shows an example of dipole strength in all three principal directions for an O vacancy in MgO. There is a strong resonance mode at about 2.2 eV for the $z$ mode which has some resemblance with the collective Mie resonance seen in metal clusters [1]. This resonance is determined by global features and thus insensitive to details. The spots of smaller strength above that dominant peak depend very sensitively on the active area chosen around the vacancy. The modes in $x$- and $y$-direction have much less strength as compared to $z$ direction, which is plausible as the motion parallel to the surface is much more restricted. They furthermore exhibit no prominent resonance peak. The numerous small structures can be attributed to single-electron excitations.

It is interesting to compare our results to available experimental ones and to the ones from ab-initio methods. The experimental analysis is difficult, as one cannot easily associate observed peaks to the configurations as calculated here. Still, one can claim that a peak for a surface site has been observed at 2.05–2.3 eV [21]. The ab-initio calculations of [25] yield the “same” peak for optical response of the surface vacancy at 3.24 eV, namely about 30% higher than our results and than the experimental values. Still the matter is debated, especially what concerns the interpretation of experimental results and one should thus not overconclude here. The situation is thus mixed and experiments might very well reside in between the two different approaches.

3.4. Conclusion
We have discussed some extensions of a hierarchical QM/MM approach developed to study the dynamics of clusters in contact with a polarizable environment. In this approach the optically active electrons are treated fully quantum-mechanically at the level of time-dependent local-density approximation (TDLDA) while cluster ions, atoms and dipole moments are described by classical molecular mechanics.
We have first considered the case of a compound consisting out of a Na cluster in contact with the surface of an Ar systems of several layers resting on a metal support. The latter provides a hard mechanical boundary for the motion of the lowest Ar layer and its dielectric response is also accounted for. We have seen that equilibrium structure of deposited Na\textsuperscript{6} is fairly insensitive to the dielectric response of the metal support (DRM). We also studied the dynamics of cluster deposition. It turns out that the dominant effect of the metal support is its mechanical hardness which limits energy absorption from the impinging Na cluster by the Ar layers. Above typically 6 Ar layers one reaches full energy absorption and thus cluster stopping.

As a second extension we have presented a study of color centers in MgO, again on the basis of our hierarchical approach, which allows to treat rather large samples as compared to standard ab-initio approaches, still at an acceptable degree of accuracy. A direct comparison between both theoretical approaches and experiments is possible for the optical response of the surface F center. It shows a good qualitative agreement between theory and experiments, similar between the QM/MM and ab-initio methods, what concerns the differences with experiments.

Acknowledgment: This work was supported by the Deutsche Forschungsgemeinschaft, project RE 322/10-1. Institut Universitaire de France and Agence Nationale de la Recherche are also acknowledged for support.

References
[1] Kreibig U, Vollmer M, Optical Properties of Metal Clusters, Vol. 25 (Springer Series in Materials Science, 1993)
[2] Haberland H, ed., Clusters of Atoms and Molecules 1- Theory, Experiment, and Clusters of Atoms, Vol. 52 (Springer Series in Chemical Physics, Berlin, 1994)
[3] Richardson H H et al, Nano Lett. 6 (2006)
[4] Khlebtsov B et al Nanotechnology 17, 5167 (2006)
[5] Haberland H, ed., Clusters of Atoms and Molecules 2- Solvation and Chemistry of Free Clusters, and Embedded, Supported and Compressed Clusters, Vol. 56 (Springer Series in Chemical Physics, Berlin, 1994)
[6] Meiwes-Broer K-H, ed., Metal clusters at surfaces (Springer, Berlin, 2000)
[7] Meiwes-Broer K-H, ed., Clusters at Surfaces: Electronic Properties and Magnetism, Vol. 82 (2006), Applied Phys. A, special issue
[8] Meiwes-Broer K-H, Berndt R, eds., Atomic Clusters at Surfaces and in Thin Films, Vol. 45 (2007), Eur. Phys. J. D, topical issue
[9] Meiwes-Broer K-H, ed., Clusters at surfaces, Phys. Stat. Sol. B 247, No. 5 (2010)
[10] Warshel A, Levitt M, J. Mol. Biol. 103, 227 (1976)
[11] Matveev A V et al, Chem. Phys. Lett. 299, 603 (1999)
[12] Gervais B et al, Phys. Rev. A 71, 015201 (2005)
[13] Fehrer F et al, Ann. Phys. (Leipzig) 14, 411 (2005)
[14] Fehrer F et al, Appl. Phys. A 82, 151 (2006)
[15] Bromann K et al, Surf. Sci. 377, 1051 (1997)
[16] Schaub R et al, Phys. Rev. Lett. 86, 3590 (2001)
[17] Irawan T et al, Appl. Phys. A 82, 81 (2005)
[18] Schlipper R et al, Appl. Phys. A 72, 255 (2001)
[19] Gresh N et al, THEOCHEM 458, 27 (1999)
[20] Schulman J H, Compton W D, Color Centers in Solids (Pergamon, Oxford, 1962)
[21] Henrich V E, Cox P, The surface science of metal oxides (Cambridge University Press, Cambridge, 1994)
[22] Pandey R, Vail J M, J.Phys.: Condens. Matter 1, 2801 (1989)
[23] Ferrari A-M, Pacchioni G, J.Phys.Chem. 99, 17010 (1995)
[24] Scorza E, Birkenheuer U, Pisani C, J. Chem. Phys. 107, 22 (1997)
[25] Francesc Illas G-P, Journal of Chemical Physics 108, 18 (1998)
[26] Sousa C, Pacchioni G, Illas F, Surface Science 429, 217 (1999)
[27] Sushko P V, Shluger A L, Catlow C R A, Surface Science 456, 153 (2000)
[28] Suhsko P V, Gavartin J L, Shluger A L, J. Phys. Chem. B (2002)
[29] Tobita M, Ho S, J.Chem.Theory Comput. 4, 1057 (2008)
[30] Gervais B et al, J. Chem. Phys. 121, 8466 (2004)
[31] Dinh P M et al, Phys. Rep. 485, 43 (2009)
[32] Faber B et al, Euro. Phys. J. D 66, 194 (2012)
[33] Berger D et al, Euro. Phys. J. D 66, 164 (2012)
[34] Legrand C et al, J. Phys. B 35, 1115 (2002)
[35] Kümmel S et al, Euro. Phys. J. D 9, 149 (1999)
[36] Reinhard P-G, Suraud E, *Introduction to Cluster Dynamics* (Wiley, New York, 2003)
[37] Calvayrac F et al, Phys. Rep. 337, 493 (2000)
[38] Feit M D et al, J. Comp. Phys. 47, 412 (1982)
[39] Montag B, Reinhard P-G, Phys. Lett. A 193, 380 (1994)
[40] Montag B, Reinhard P-G, Z. f. Physik D 33, 265 (1995)
[41] Dick B G, Overhauser A W, Phys. Rev. 112, 90 (1958)
[42] Nasluzov A et al, J. Chem. Phys. 115, 17 (2001)
[43] Duplía F, Spiegelmann F, J. Chem. Phys. 105, 1492 (1996)
[44] Ahmadi G R et al, Chem. Phys. 199, 33 (1995)
[45] Jackson J D, *Classical Electrodynamics* (Wiley, New York, 1962)
[46] Dinh P M et al, Euro. Phys. J. D 45, 415 (2007)
[47] Bär M et al, Euro. Phys. J. D 45, 507 (2007)
[48] Calvayrac C et al, Ann. Phys. (NY) 255, 125 (1997)
[49] Blum V et al, J. Comp. Phys 100, 364 (1992)