Time-dependent density functional theory applied to clusters and molecules in contact with an environment

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THÈSE pour l'obtention de l'

Habilitation à Diriger des Recherches
Spécialité : Physique Théorique

présentée par

Phuong Mai DINH

Time-dependent Density Functional Theory applied to Molecules and Clusters in contact with an Environment

Théorie de la fonctionnelle de la densité dépendante du temps appliquée à des molécules et des agrégats en contact avec un environnement

soutenue le 7 décembre 2009 à Toulouse
devant la Commission d'examen :

Monsieur	Julio A. Alonso	Rapporteur
Monsieur	Xavier Blase	Rapporteur
Monsieur	Jean-Paul Crocombette	Président du jury
Monsieur	Karl-Heinz Meiwes-Broer	Examinateur
Monsieur	Paul-Gerhard Reinhard	Examinateur
Monsieur	Eric Suraud	Examinateur

To my father.

Abstract

We present recent theoretical and methodological explorations on the dynamics of sodium clusters in the framework of Time-Dependent Density Functional Theory (TDDFT), coupled non-adiabatically to Molecular-Dynamics (MD). In particular, a hierarchical approach, in the spirit of Quantum-Mechanical/Molecular-Mechanical methods, has been developed for the description of metal clusters in interaction with a dynamically polarizable substrate, as rare gases or MgO. Numerous examples of application of this approach (Na clusters in or on Ar substrate, Na clusters deposited on MgO; optical response, dynamical deposition, laser irradiation, ...) are reviewed.

We also briefly discuss complementing research activities. Formal developments on the Self-Interaction Correction issue in DFT and TDDFT are discussed in a word. We have furthermore extended our TDDFT-MD theory to the case of organic (C, N, O, H made) systems and a few examples of investigated dynamical processes are presented. Recent calculations of photoelectron angular distributions of free metal clusters are reported as well. We finally sketch with some perspectives for the years to come.

Résumé

Nous présentons des développements théoriques et méthodologiques sur la dynamique d'agrégats de sodium dans le cadre de la théorie de la fonctionnelle de la densité dépendante du temps (TDDFT), couplée non adiabatiquement à de la dynamique moléculaire (MD). En particulier, une approche hiérarchique, s'inspirant des méthodes Mécanique-Quantique/Mécanique-Moléculaire, a été élaborée afin de décrire des agrégats métalliques au contact avec un substrat de polarisabilité dynamique. De nombreux exemples d'applications de cette approche (agrégats de Na dans ou sur un substrat d'Ar, agrégats de Na déposés sur MgO; réponse optique, dynamique de dépôt, irradiation laser, ...) sont passés en revue.

Nous exposons aussi brièvement quelques activités de recherche complémentaires. Des développements formels sur le problème de la correction de l'auto-interaction en DFT et en TDDFT sont rapidement discutés. De plus, nous avons étendu notre théorie de TDDFT-MD au cas de systèmes organiques (composés de C, N, O, H) et quelques exemples d'études de processus dynamiques sont présentés. De récents calculs de distributions angulaires de photoélectrons sont également exposés. Enfin nous donnons quelques perspectives pour les années à venir.

Acknowlegements

First I have been honored that Prof. Karl-Heinz Meiwes-Broer has accepted a member of my habilitation jury, and I greatly thank him for that. When we collaborated for the writing of a Review of Modern Physics, I already appreciated and benefited from his deep knowledge and understanding in cluster physics, especially when they are deposited on or embedded in an environment.

I also thank Prof. Julio A. Alonso to have accepted to be one of the referees of my habilitation thesis. He is one of the worldwide experts of DFT and TDDFT, and I hope that my habilitation thesis will be an opportunity for future collaborations.

My friendship with M. Xavier Blase goes back more than (already!) ten years ago; I deeply thank him to have been one of the referees of my thesis, and thus to have taken the heavy responsibility for judging my scientific activities. His expertise on ab initio simulations, especially on nanotubes and semiconductors, allows to appreciate my work in a different light.

I thank Prof. Paul-Antoine Hervieux who has been chosen as the third referee of my thesis. Some theoretical tools that he has developped during the past years are very close, if not identical, to those used in Toulouse. He is probably one of the physicists in France who possesses the deepest expertise on the theory we develop in Toulouse. I regretted his absence at my habilitation defense.

M. Jean-Paul Crocombette has a long experience in ab initio simulations of defects in insulators, and in oxydes in particular. The link with the hierarchical method we developed in Toulouse is thus obvious. I thank him to have assumed the (heavy!) role of the president of my jury.

I thank Sylvain Vidal to have accepted the hard task to be my very first Ph.D. student. I also thank Matthias Baer, Gaspard Bousquet, Bernhard Faber, Frank Fehrer, Jérémie Messud, Uguette Ndongmouo, Zhiping Wang, and Philipp Wopperer for their work in our group and for their friendship.

I thank colleagues in the Laboratory for Theoretical Physics in Toulouse, for their friendship, their collaboration in teaching, and their company during lunchtime. I would like to thank in particular Olivier Giraud, former classmate at the École polytechnique and at the D.E.A. for Theoretical Physics. I will regret our many discussions on physics or on other subjects (that I will not detail for sake of privacy!).

Of course, I express my sincere gratitude to Prof. Eric Suraud, who believed in me, when I was finishing my Ph.D. and when I arrived in Toulouse in 2002. The numerous discussions I have with Prof. Suraud, on scientific topics as well as on children, music, teaching, cooking, well whatever the subject, are always interesting and very instructive. I really take a great pleasure to work with him and our now longstanding collaboration is very promising for the years to come. He has also constantly in mind my scientific carrier and relentlessly suggests me proposals in that sense. I thus deeply thank him for all this.

Inevitably joined with Prof. Suraud comes Prof. Paul-Gerhard Reinhard, who I heartily thank for his precious help and collaboration during all these years. Prof. Reinhard's expertise in nuclear and cluster physics, and on numerics, has always impressed me. His numerous visits

in Toulouse are always fruitful, while they probably represent for him a unique opportunity to practise his love for trains and subways. His availability on emails has also been constant all over the years, allowing me to receive emails from him on a Dec. 23th. I hope his close retirement will not prevent him to keep an eye on physics and to allow further collaboration with our group.

Last but not least, I would like to warmly thank my husband Philippe, who has constantly given me his support for my work. His help and his unique understanding has certainly played a determinant role in my carrier.

Finally I dedicate this thesis to my father who recently passed away. Without doubt, his love for science, history, philosophy and culture has strongly surrounded my childhood. If I chose to enter upon an academic carrier, this is probably due thanks to his influence. He would have been for sure very proud to attend to my habilitation defense.

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Chapter I

Bibliographical note

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I.1 Curriculum Vitae

Phuong Mai DINH, spouse SÈVE
Born 8 June 1974 in Paris (France)
French
Married, 2 children

Laboratory for Theorical Physics of Toulouse
IRSAMC, University Paul Sabatier, and CNRS
118 Route de Narbonne Bât. 3R1B4
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email : dinh@irsamc.ups-tlse.fr

Education and Degrees

- 1999-2002 Ph.D. in Theoretical Physics, École polytechnique (June 2002, Palaiseau, France)
- 1998-1999 Graduate studies in Theoretical Physics,
  École Normale Supérieure of Paris / École polytechnique
- 1995-1998 École polytechnique in Palaiseau, France

Scientific Carrier

- Since 2003 : Assistant Professor, Univ. Paul Sabatier, Toulouse 3, France
- 2002-2003 : Post-doctoral fellow at the Laboratory for Theoretical Physics, Univ. Paul Sabatier, Toulouse, France

Scientific Activities

- Since 2002 : Microscopic theories for the dynamics of finite fermionic systems
  - Time-dependent density functional theory (TDDFT) non-adiabatically coupled with molecular dynamics (MD) for the description of the dynamics of strongly irradiated alkaline clusters
  - Hierarchical approach of metal clusters in contact with an inert substrate (rare gas, MgO) with explicit dynamical polarizability
  - Extension of our TDDFT-MD to small organic molecules under irradiation
  - Formal developments of DFT and TDDFT on the self-interaction correction
- 1998 – 2003 : Collective effects in ultrarelativistic heavy ion collisions
  - Theories of signatures of the quark-gluon plasma creation in ultrarelativistic heavy ion collisions
  - Phenomenological model of the J/ψ suppression in ultrarelativistic heavy ion collisions observed at the CERN facility
  - Elaboration of an analysis method, based on a cumulant expansion, for the extraction of the collective flow observed in ultrarelativistic heavy ion collisions observed at the CERN facility

Publications and conferences

- 31 publications in international peer reviewed journals, including 2 review articles
- 17 proceedings and articles in books
- 12 participations in international conferences, including 6 on invitation
- 9 seminars in laboratories, including 7 on invitation

Scientific administration

- Member of the Physics Dept Committee at the University Paul Sabatier (Toulouse 3)
- Member of the Recruitment Committee for Theoretical Physics at the University Paul Sabatier (Toulouse 3)
- Correspondent at the University Paul Sabatier of the European project STEPS (Stakeholders Tune European Physics Studies), held by EUPEN (EUropean Physics Education Networks)
- Former representative of non-permanent fellows at the IRSAMC (Institute for Research on Complexe Atomic and Molecular Systems) Comittee (2002-2003)

Other responsabilities and achievements

- Co-author of *Océans et gouttelettes quantiques*, P. M. Dinh, J. Navarro, É. Suraud, CNRS Éditions, Paris (2007)
- Member of the organization committee of the 27th edition of the international conference on Condensed Matter Theories (Sep 3th–8th 2002, Toulouse); and co-editor with M. Belkacem of the proceedings, *Condensed Matter Theories, Vol. 19*, Nova Science (2005)

Awards

- "Daniel Guinier Jeune Chercheur" prize of the French Society of Physics (SFP), 2002
  http://sfp.in2p3.fr/Prix/prix.html
- Ph.D. prize of the École polytechnique, 2003
  http://www.ecoledoctorale.polytechnique.fr/WEBFrancais/PrixThese.html

I.2 Scientific production

I.2.1 List of publications

[1] *Modeling of the deposition of Na Clusters on MgO(001)*
M. Bär, P. M. Dinh, L. V. Moskaleva, P.-G. Reinhard, N. Rösch, and E. Suraud,
Phys. Rev. B **80** (2009) 195404

[2] *Time-dependent Generalized SIC-OEP formalism and Generalized SIC-Slater approximation*,
J. Messud, P. M. Dinh, P.-G. Reinhard, and E. Suraud,
Phys. Rev. A **80** (2009) 04450

[3] *Signatures from laser-driven non-linear cluster dynamics*,
Th. Fennel, K.-H. Meiwes-Broer, J. Tiggesbaumker, P.-G. Reinhard, P. M. Dinh, and E. Suraud,
accepted in Rev. Mod. Phys. (2009), preprint arXiv:0904.2706

[4] *Generalized Slater and static polarizabilities*
J. Messud, P. M. Dinh, P.-G. Reinhard, and E. Suraud,
Chem. Phys. Lett. **479** (2009) 300

[5] *Dynamics of clusters and molecules in contact with an environment*
P. M. Dinh, P.-G. Reinhard, and E. Suraud,
Physics Reports (2009) in press, preprint arXiv:0903.1004

[6] *Microscopic studies of atom-water collisions*
Z. P. Wang, P. M. Dinh, P.-G. Reinhard, E. Suraud, G. Bruny, C. Montano, S. Feil, S. Eden, H. Abdoul-Carime, B. Farizon, M. Farizon, S. Ouaskit, and T. D. Maerk,
Intern. J. Mass Spectr. **285** (2009) 143

[7] *Dipole excitations of Ar substrate in contact with Na clusters*
P. M. Dinh, F. Fehrer, P.-G. Reinhard, and E. Suraud,
Surf. Sci. **603** (2009) 400

[8] *On the exact treatment of Time Dependent Self-Interaction Correction*
J. Messud, P. M. Dinh, P.-G. Reinhard, and E. Suraud,
Annals of Physics (NY) **324** (2008) 955

[9] *Time-Dependent Density-Functional Theory with a Self-Interaction Correction*
J. Messud, P. M. Dinh, P.-G. Reinhard, and E. Suraud,
Phys. Rev. Lett. **101** (2008) 096404

[10] *Deposition dynamics of Na monomers and dimers on an Ar(001) substrate*
P. M. Dinh, F. Fehrer, P.-G. Reinhard, and E. Suraud,
Surf. Sci. **602** (2008) 2699

[11] *Improved Slater approximation to SIC-OEP*
J. Messud, P. M. Dinh, P.-G. Reinhard, and E. Suraud,
Chem. Phys. Lett. **461** (2008) 316

[12] *Self-interaction correction in a simple model*
P. M. Dinh, J. Messud, P.-G. Reinhard, and E. Suraud,
Phys. Lett. A **372** (2008) 5598

[13] *Embedded metal cluster in strong laser fields*
F. Fehrer, P. M. Dinh, P.-G. Reinhard, and E. Suraud,
Comp. Mat. Sci. **42** (2008) 203

[14] *Dynamics of cluster deposition on Ar surface*
P. M. Dinh, F. Fehrer, P.-G. Reinhard, and E. Suraud,
Eur. Phys. J. D **45** (2007) 415

[15] *Dynamics of metal clusters in rare gas clusters*
M. Baer, G. Bousquet, P. M. Dinh, F. Fehrer, P.-G. Reinhard, and E. Suraud,
Intern. J. Mod. Phys. B **21** (2007) 2439

[16] *Size and charge effects on the deposition of Na on Ar*
P. M. Dinh, F. Fehrer, P.-G. Reinhard, and E. Suraud,
Intern. J. Quant. Chem. **107** (2007) 2828

[17] *Structural properties and optical response of Na clusters in Ne, Ar, and Kr matrices*
F. Fehrer, P. M. Dinh, P.-G. Reinhard, and E. Suraud,
Phys. Rev. B **75** (2007) 235418

[18] *Hindered Coulomb explosion of embedded Na clusters – stopping, shape dynamics and energy transport*
F. Fehrer, P. M. Dinh, M. Baer, P.-G. Reinhard, and E. Suraud,
Eur. Phys. J. D **45** (2007) 447

[19] *Shape dynamics during deposit of simple metal clusters on rare gas matrices*
P. M. Dinh, F. Fehrer, G. Bousquet, P.-G. Reinhard, and E. Suraud,
Phys. Rev. A **76** (2007) 043201

[20] *Pump and probe analysis of metal cluster dynamics*
K. Andrae, P. M. Dinh, P.-G. Reinhard and E. Suraud,
Comp. Mat. Sci. **35** (2006) 169

[21] *Time resolved fission in metal clusters*
P. M. Dinh, P.-G. Reinhard and E.Suraud,
J. Phys. B **38** (2005) 1637

[22] *Analysis of cluster dynamics*
K. Andrae, M. Belkacem, P. M. Dinh, E. Giglio, M. Ma, A. Pohl, P.-G. Reinhard and E. Suraud,
Lecture Notes in Physics, Formation of correlations (Nonequilibrium at short time scales)
Springer, Berlin 2003.

[23] *Directed and elliptic flow of charged pions and protons in Pb + Pb collisions at 40-A-GeV and 158-A-GeV*
C. Alt et al. [NA49 Collaboration],
Phys. Rev. C **68** (2003) 034903

[24] *J/psi suppression in central Pb Pb collisions*
P. M. Dinh, J. P. Blaizot and J. Y. Ollitrault,
Nucl. Phys. A **698** (2002) 579

[25] *Effects of momentum conservation on the analysis of anisotropic flow*
N. Borghini, P. M. Dinh, J. Y. Ollitrault, A. M. Poskanzer and S. A. Voloshin,
Phys. Rev. C **66** (2002) 014901

[26] *Analysis of directed flow from elliptic flow*
N. Borghini, P. M. Dinh and J. Y. Ollitrault,
Phys. Rev. C **66** (2002) 014905

[27] *Flow analysis from multiparticle azimuthal correlations*
N. Borghini, P. M. Dinh and J. Y. Ollitrault,
Phys. Rev. C **64** (2001) 054901

[28] *A new method for measuring azimuthal distributions in nucleus-nucleus collisions*
N. Borghini, P. M. Dinh and J. Y. Ollitrault,
Phys. Rev. C **63** (2001) 054906

[29] *Transverse energy fluctuations and the pattern of J/psi suppression in Pb Pb collisions*
J. P. Blaizot, P. M. Dinh and J. Y. Ollitrault,
Phys. Rev. Lett. **85** (2000) 4012

[30] *Are flow measurements at SPS reliable ?*
N. Borghini, P. M. Dinh and J. Y. Ollitrault,
Phys. Rev. C **62** (2000) 034902

[31] *Effects of HBT correlations on flow measurements*
P. M. Dinh, N. Borghini and J. Y. Ollitrault,
Phys. Lett. B **477** (2000) 51

[32] *DFT studies of ethylene in femtosecond laser pulses*,
Z. P. Wang, P. M. Dinh, P.-G. Reinhard, E. Suraud, and F. S. Zhang,
submitted to Phys. Rev. A (2009)

[33] *High-order harmonic generation and multi-photon ionization of ethylene in laser*,
Z. P. Wang, P. M. Dinh, P.-G. Reinhard, E. Suraud, and F. S. Zhang,
submitted to THEOCHEM (2009)

[34] *Angular distributions of electrons emitted from free and deposited Na_8 clusters*
M. Bär, P. M. Dinh, L. V. Moskaleva, P.-G. Reinhard, N. Rösch, and E. Suraud,
submitted to Eur. Phys. J. D

I.2.2 Oral communications leading to conference proceedings

P1) *Metal cluster fission : A dynamical study by a pump-probe analysis*
International workshop on Off-shell Effects in Quantum Transport
Dresden, Germany, May 4-16 2003 (invited)

P2) *Transverse energy fluctuations : The pattern of J/ψ suppression in Pb-Pb collisions*
15th International Conference on Ultra-Relativistic Nucleus-Nucleus Collisions (QM 2001)
Stony Brook, NY, USA, Jan. 15-20 2001

I.2.3 Oral communications not leading to conference proceedings

C1) *Dynamics of metal clusters in contact with an environment : A hierarchical approach*
International workshop on Theoretical Developments for Radiation Damage
Fréjus, France, Sep. 21-22 2007 (invited)

C2) *Time-dependent density functional theory in metal clusters*
International workshop on Mean Field Dynamics and Beyond for Nuclear Reactions
ENST/CEA Saclay, France, Jan 23-27 2006 (invited)

C3) *Dynamique de la fission d'un agrégat : Analyse pompe-sonde*
Annual general meeting of the French theoreticians in nuclear physics
Lyon, France, April 1st 2003

C4) *Collisions d'ions lourds ultrarelativistes : Effets collectifs*
Annual general meeting of the French Society of Physics
Paris, France, Feb. 1st 2003 (invited)

C5) *Directed and elliptic flow from multiparticle cumulants at 160 AGeV*
NA49 Collaboration Meeting
GSI, Darmstadt, Germany, April 8-12 2002 (invited)

C6) *Collisions d'ions lourds ultrarelativistes : Le flot elliptique et les corrélations azimutales*
7th Meeting of Young Researchers in Nuclear Physics
Aussois, France, Dec. 10-14 2001

C7) *Collective flow analysis : A cumulant expansion of multiparticle azimuthal correlations*
NA49 Collaboration Meeting
CERN, Genève, Switzerland, Oct. 21-25 2001 (invited)

C8) *Collisions d'ions lourds ultrarelativistes : La suppression du J/ψ*
Annual general meeting of the French theoreticians in nuclear physics
Orsay, France, March 22th 2001

C9) *Plasma de quarks et de gluons : Le flot dans les collisions d'ions lourds ultrarelativistes*
7th Meeting of Young Researchers in Nuclear Physics
Aussois, France, Dec. 3-8 2001

C10) *Ultrarelativistic heavy ion collisions : Flow analysis*
12th Summer School in Nuclear Physics
Santa Cruz, CA, USA, July 3-14 2000

I.2.4 Seminars in laboratories

S1) *L'argon : un matériau inerte?*
Joined seminar of the Laboratory for Theoretical Physics and the Laboratory for Quantum Chemistry and Physics
Toulouse, France, 19 juin 2008 (invited)

S2) *Collisions d'ions lourds ultrarelativistes : Analyse des effets collectifs par l'étude de corrélations azimutales multiples*
GANIL seminar
Caen, France, June 23th 2003 (invited)

S3) *Dynamique de la fission d'un agrégat métallique : Analyse pompe-sonde*
IRSAMC seminar
Toulouse, France, March 14th 2003 (invited)

S4) *Effets collectifs dans les collisions d'ions lourds ultrarelativistes*
Seminar of the Group for Theoretical Physics, Laboratory for Quantum Physics
Toulouse, France, April 30th 2002 (invited)

S5) *Collisions d'ions lourds ultrarelativistes : Le flot elliptique et les corrélations azimutales*
Ph.D. day, Service for Theoretical Physics of CEA/Saclay
Saclay, France, Nov. 13th 2001

S6) *Charmonium suppression in central nucleus-nucleus collisions at SPS and RHIC*
GSI Theory Seminar
Darmstadt, Germany, May 21st 2001 (invited)

S7) *Collective flow analysis : Multiparticle azimuthal correlations*
Institut für Kernphysik Seminar
Frankfurt, Germany, May 14th 2001 (invited)

S8) *Deux observables dans les collisions d'ions lourds ultrarelativistes : La suppression du J/ψ et le flot*
Ph.D. day, Service for Theoretical Physics of CEA/Saclay
Saclay, France, Oct. 20th 2000

S9) *Collisions d'ions lourds ultrarelativistes : Le flot existe-t-il?*
Young researcher seminar of the Service for Theoretical Physics of CEA/Saclay
Saclay, France, Jan. 20th 2000 (invited)

I.3 Supervision and teaching activities

I.3.1 Supervision

1) Oct 2008 – ... 2010 : Ph.D. thesis, S. Vidal, *Méthodes hiérarchiques pour la dynamique d'agrégats en contact avec un environnement*

2) Mar – Jun 2008 : Graduate internship (Physics of Matter), S. Vidal, *Méthodes hiérarchiques pour la dynamique d'agrégats en contact avec un environnement*

3) June 2008 : Undergraduate internship, S. Garcia (École Normale Supérieure of Cachan) and O. Chabiron (Fundamental Physics, University of Toulouse 3), *Simulation de l'irradiation d'agrégats de sodium par un laser à électrons libres*

4) May – June 2004 : Master training (Fundamental Physics), A. Bail, *Modélisation numérique d'un agrégat d'argon*

I.3.2 Teaching

- In charge since 2007 of the course *Tools for Statistical Physics*, L3 Physique Fondamentale, Univ. Paul Sabatier, Toulouse

- In charge since 2007 of both courses *Analytical methods for physicists* et *Computer modelling and solutions of problems in physics*, L2 Physique, Chimie et Applications, option Physique, Univ. Paul Sabatier, Toulouse

- In charge from 2003 to 2007 of the course *Analytical methods for physicists*, L2 Physique, Chimie et Applications, option Physique, Univ. Paul Sabatier, Toulouse

- 2008–2009 : Computer tutorials of *Numerical recipies*, M1 Physique Fondamentale, M1 Astrophysique et M1 Atmosphère-Océans-Continents, Univ. Paul Sabatier, Toulouse

- Since 2002 : Tutorials of *Non-linear physics*, M1 Physique Fondamentale, M1 astrophysique et M1 Atmosphère-Océans-Continents, Univ. Paul Sabatier, Toulouse
- Since 2002 : Computer tutorials of *Non-linear physics*, M1 Physique Fondamentale, M1 astrophysique et M1 Atmosphère-Océans-Continents, Univ. Paul Sabatier, Toulouse

- Since 2007: Course of *Tools for Statistical Physics*, L3 Physique Fondamentale, Univ. Paul Sabatier, Toulouse
- Since 2002 : Tutorials of *Tools for Statistical Physics*, L3 Physique Fondamentale, Univ. Paul Sabatier, Toulouse
- 2002 – 2006 : Computer tutorials of *Statistical Physics*, L3 Physique Fondamentale, Univ. Paul Sabatier, Toulouse

- Since 2002 : Tutorials of *Analytical methods for physicists*, L2 Physique, Chimie et Applications, option Physique, Univ. Paul Sabatier, Toulouse
- 2002 – 2006 : Computer tutorials of *Scientific Calculus*, L2 Physique, Chimie et Applications, option Chimie, Univ. Paul Sabatier, Toulouse
- 2002 – 2003 : Tutorials of *Solid mechanics*, DEUG SM, Univ. Paul Sabatier, Toulouse

- 2007–2008 : Tutorials of thermodynamics, L1 Chimie-Biologie-Physique-Santé, Univ. Paul Sabatier, Toulouse
- 2003 – 2006 : Tutorials of *General Physics*, L1 Chimie-Informatique-Mathématique-Physique, Univ. Paul Sabatier, Toulouse
- 1999 – 2002 : Tutorials of *General physics*, 1st year of medecine studies, Univ. Paris-Sud, Orsay

Chapter II
Thesis

Contents

This chapter summarizes my scientific activities during the last seven years. A particular focus lies on the development of a hierarchical method to describe the interaction of metal clusters with a substrate with dynamical polarizability (see Sec. II.1 and Appendix A). In a second section, I briefly present complementary research activities, especially since 2005. Finally I give some perspectives in the last section.

Nota Bene : The citations in arabic figures (as for instance [16]) correspond to my articles, listed in Sec. I.2.1, while those in latin alphabet and two arabic figures (as [Koh 99]) refer to published articles from the bibliography at the end of the manuscript.

II.1 Dynamics of clusters in contact with an environment

II.1.1 Starting scientific context

I arrived in 2002 in Prof. E. Suraud's group, in the Laboratory for Theoretical Physics of Toulouse, University Paul Sabatier (Toulouse 3) and got a permanent position as an assistant professor in 2003. The "Finite Fermionic Systems" group consisted in Prof. E. Suraud and Prof. M. Belkacem, and had already at that time a rich experience on the dynamics of free metal clusters under irradiation. However Prof. M. Belkacem's departure in Sep. 2005 strongly weakened the group. Nevertheless, the longstanding and active collaboration with Prof. P.-G. Reinhard from Erlangen University (Germany) allowed our group to maintain a high level of scientific production.

The core activity of our group concerns the microscopic description of the dynamics of clusters and molecules subject to violent electromagnetic perturbations, such as delivered by short and intense laser pulses or highly charged ionic projectiles. From the formal point of view, density functional theory (DFT) [Hoh 64, Par 89, Dre 90, Koh 99] has evolved over the last decades to a standard theoretical tool for the description of electronic properties in many physical and chemical systems, especially in systems with sizeable numbers of electrons. Its time-dependent version (TDDFT) [Run 84, Gro 90, Mar 04] is a more recent achievement and still motivating many investigations, both for formal and practical aspects [Mar 06]. TDDFT offers a unique and versatile tool for the development of several theories in the realm of violent dynamical scenarios in irradiated free metal clusters, from fully quantum to mostly classical approaches [Rei 03]. In particular, the treatment of the valence electrons of the cluster by TDDFT, coupled non-adiabatically to molecular dynamics (MD) for the cluster ions, allows us to explore many possible scenarios of irradiated clusters and molecules, from the linear to the highly non-linear regime. Our group has meanwhile worked out a platform of very robust and flexible homemade numerical tools developed over the years [Cal 00]. Only few groups in the world can actually compete with such a microscopic description of non-linear processes.

II.1.2 Hierarchical approaches for the description of clusters in contact with an environment

In 2002, these methods were already well validated in the case of free metal clusters [Cal 00]. This scientific context was thus favorable for new methodological developments, as the construction of dynamical hierarchical approaches to describe the coupled response of a cluster in contact with an environment. This topic has been the core of my research activities during the last years. The physical motivation of our investigations was the understanding of the dynamics of clusters and molecules in contact with a substrate, a situation which occurs in numerous physical contexts, ranging from surface physics to water-embedded biological systems. While environments may help controlling experimental conditions, such as for example on surfaces, they also make the description of the system much more involved, precisely due to the presence of the environment which may play a non-negligible role in the response of the system to an external perturbation such as an irradiation. Nevertheless, standard approaches do not take into account the dynamical polarizability of the environment. We have thus been led to develop a more sophisticated model accounting for such degrees of freedom.

We first developed since 2003 a hierarchical modeling of metal cluster in contact with an argon substrate (surface or matrix) [Feh 05, Feh 06a, Feh 06b]. While the cluster is treated in TDDFT-MD as before, the environment is described at a lower level of sophistication in the spirit of QM/MM (Quantum Mechanics/Molecular Mechanics) approaches of quantum chemistry, hence the term "hierarchical". The idea is to treat atoms of the environment as classical particles. However, at variance with earlier approaches, we complement the descrip-

tion by attributing dynamical dipoles to each atom of the environment. These new degrees of freedom turn out to be a key issue for the description of irradiation processes, especially when charges are involved, either because of dealing with charged species or as a result of an irradiation process. The many results obtained demonstrated a posteriori the key importance of this aspect, whatever the dynamical regime under consideration. We later extended our hierarchical method to other rare gases (Ne, Kr) [18], and to a mechanically harder insulator, that is MgO [Bar 07a, Bae 08].

The results of our hierarchical methods applied to various scenarios (neutral or charged cluster deposition on a surface, Coulomb explosion of embedded clusters after irradiation by an intense laser, photoelectron spectroscopy of deposited clusters, ...) represent 11 published articles including 1 review [1, 5, 7, 10, 13–19], 1 submitted article [34] and 2 in preparation. The review article [5] can be found in the Appendix A. For the sake of briefness, we refer the reader to this appendix for an exhaustive report of our models and results on this topic.

II.2 Complementary research activities

Since 2005, we also developed new activities along three complementing lines : *i)* Formal developments for the correct description of ionization dynamics in the framework of TDDFT; *ii)* Technical and numerical extension of the non-adiabatic description of electron dynamics to the case of organic systems; *iii)* Elaborated study of the dynamics of free clusters under extreme light irradiation. All three aspects have been successfully worked out over the last few years. They are briefly discussed below and illustrated by a few typical results.

II.2.1 Dynamical self-interaction correction

A correct treatment of ionization processes in TDDFT is still raising sizeable difficulties, especially from the formal side. Indeed, standard DFT approaches rely on the local density approximation (LDA) which is plagued by the well known self-interaction problem, that is the self-interaction of an electron with itself through the total density from which the electron potential is built. There is thus a crucial need to overcome this problem in order to recover properly ionization properties, especially when considering explicit time-dependent processes. A key point thus concerns a clean formulation of the self-interaction correction (SIC) method on top of the standard LDA of TDDFT, see [Mar 06, Kue 08] and references therein, for recent reviews on the topic. While the problem is well studied in the static domain, time-dependent versions of the theory have only been developed in the framework of further approximations, especially within the optimized effective potential (OEP) strategy. The first task was thus a clean reformulation of time-dependent SIC (TDSIC) in which an explicit account of orthonormalization was included in the theory [8, 9]. The TDSIC equations are rather involved and in order to be able to have a proper time propagation, we have been led to introduce two sets of single electron orbitals. Such a strategy amounts to exploit the usually left-over degree of freedom of unitary transform amongst electronic orbitals in time propagation, an idea which had never been put forward. The result led, to the best of our knowledge, to the first complete calculation of full TDSIC, which is thus providing a benchmark for the development of further approximations.

This double set strategy also turned out to be extremely useful for the stationary limit as it provided the basic idea for developing efficient and simple approximations of the OEP methods built on top of SIC. This allowed to propose a new, efficient SIC-OEP scheme which turns out to provide remarkably accurate results from a rather simple treatment [4, 11]. The double set scheme furthermore shed some light on the longstanding difficulties associated to the more or less localized nature of electronic orbitals. Indeed, one set provides rather localized

orbitals (which allow to properly ensure orthonormalization), while the second one leads to more delocalized orbitals typical of bonding orbitals. An illustration of our simplified SIC-OEP with the double set strategy (Generalized SIC-Slater) is given in Fig. II.1 and applied to the cluster Na_5 in a dynamical situation [2]. The initial excitation is a small boost of

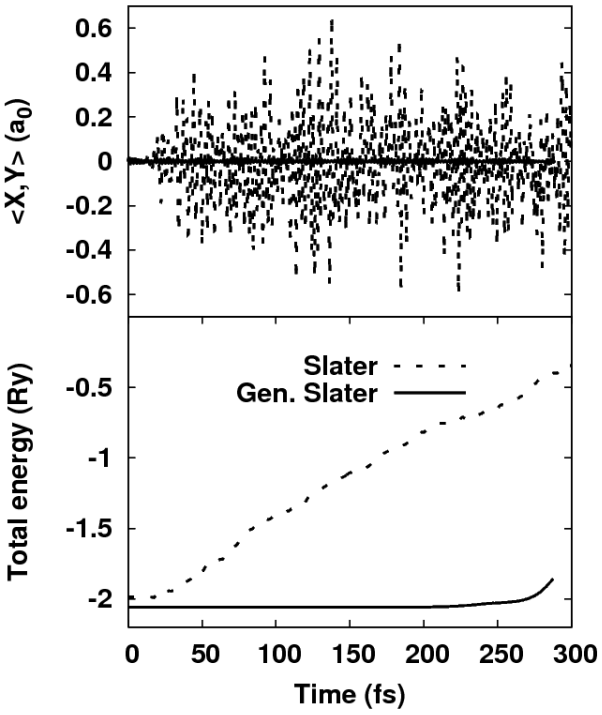

Figure II.1: Total energy and dipole moments, $\langle x \rangle$ and $\langle y \rangle$, as a function of time, after an initial small boost of groud-state electronic distributions of Na_5. Are compared standard (one-set) SIC-Slater and our simplified two-set SIC-OEP, Generalized SIC-Slater [2].

the initial (ground state) electronic distributions of Na_5. This simulates a very short laser pulse and still allows to check energy conservation in time. Time evolutions of the total energy and the dipole moments are plotted and compared with standard (one-set) SIC-Slater approximation. It is well known that this approximation suffers from inconsistencies in the time domain, as it can strongly violate energy conservation and zero force theorem [Mun 07]. As it is obviously visible in Fig. II.1, the range of stability (that is, time of energy-stable propagation) is dramatically enhanced by Generalized SIC-Slater, while standard SIC-Slater diverges at very short times.

The full TDSIC and its simplified SIC-OEP version have been applied with success to various physical systems including metal clusters, organic molecules and quantum dots, and led to 6 publications [2,4,8,9,11,12], and 2 in preparation. The next step to come is to develop a simplified and robust version of the theory to be used in large scale calculations, since our schemes, even in their simplified version, are still highly time-consuming.

II.2.2 Extension to organic molecules and clusters

While we continued to investigate our model in the case of cluster/substrate combinations, we also started in 2005 to consider its extension to the case of organic molecules in contact with polar molecules. The description of water is a well explored field and we have identified a few

approaches compatible with our strategy. Still, discussions with several colleagues working on the irradiation of small organic/biomolecules led us to postpone the implementation of this extension of our hierarchical modeling to the benefit of more detailed studies of very small systems, which were more urgently interesting experimental colleagues. Indeed this turns out to provide valuable prototype cases for irradiation studies even when very small. In such cases, the system is fully treated at a TDLDA-MD level. SIC is still handled, however in a simplified way (Average Density SIC, ADSIC [Leg 02]). This SIC allows to properly treat electronic dynamics but fails at describing molecular dissociation quantitatively. Such calculations, in addition to their intrinsic physical interest, will furthermore serve as benchmarks for hierarchical approaches to come.

The extension of our TDLDA-MD method to organic molecules is in principle straightforward but requires some technical fine-tuning. Surprisingly enough, such fully non-adiabatic calculations allowing to cover any dynamical regimes had not been realized before. Only simplified situations in which either ions are kept fixed (linear processes or very energetic collisions) [Yab 99, Hei 00, Var 06] or electrons "follow" ions at Born-Oppenheimer level were available for such systems. The major effort to be done in our approach concerned the validation of pseudopotentials especially designed for our grid representation of electronic wave functions. Pseudopotentials imply a minimum length scale associated to the atomic core size which, in turn, determines a minimum grid spacing. As long as only one material is present, any well behaved (smooth enough) pseudopotential is applicable. In the case of mixed systems (as typical organic molecules), one has to retune pseudopotentials to a common (and sufficiently large) minimum length. Such a fine-tuning was successfully done for the standard organic elements (C, N, O, and H) to be used in our target molecules. Of course, the retuning implies some compromises. But these are beneficial to attain representations which allow robust calculations over long times and in the non-linear domain.

The new set of pseudopotentials was then used to study the dynamics of small organic systems especially under laser irradiation and collisions with charged or neutral projectiles. We studied the laser irradiation of the ethylene molecule extensively; two articles reporting our findings have been submitted [32, 33]. In close collaboration with Prof. M. Farizon's experimental group at the Institute for Nuclear Physics of Lyon (IPNL), with which we have a joined contract from the French National Agency for Research (ANR), we have also focused on the irradiation of simplest water molecules clusters. A common article on collision of a molecule water with a proton at low velocity or a neutral carbon atom at high velocity has been published recently [6]. The full non-adiabatic coupling between electrons and ions is here crucial as it allows to cover any dynamical regime in the field, namely charged or neutral projectiles at low or high velocity, a possibility which, to the best of our knowledge, is a "premiere" in the field [Gai 07, Koh 08].

Further results on irradiation of small charged water cluster are currently available and are being prepared for 2 publications. As an illustration, we present in Fig. II.2 the dynamics of $(H_2O)H_3O^+$ irradiated by lasers with intensity $I = 2 - 7 \times 10^{14}$ W/cm^2, full width at half maximum (FWHM) of 20 fs, and three different frequencies (far IR, optical, XUV). In the optical domain, the electronic dipole nicely follows the laser pulse, and electronic excitation ends as soon as the laser is switched off. This pattern is very similar to what is observed in metal clusters when irradiated by an optical laser with frequency off the plasmon resonance. As expected, no electronic emission is observed, since water is an electronic insulator with a gap of about 10 eV. Only a slight cluster rotation is induced. Similar behaviors are observed with UV frequencies (not shown). For XUV frequencies, which lie in the optical absorption regime of $(H_2O)H_3O^+$, significant ionization occurs (~ 1 electron) and the charge instability provokes a Coulomb explosion of the cluster. Note also the unusual dipole response pattern, very different from the previous case. Highly non-linear dynamics obviously takes place as

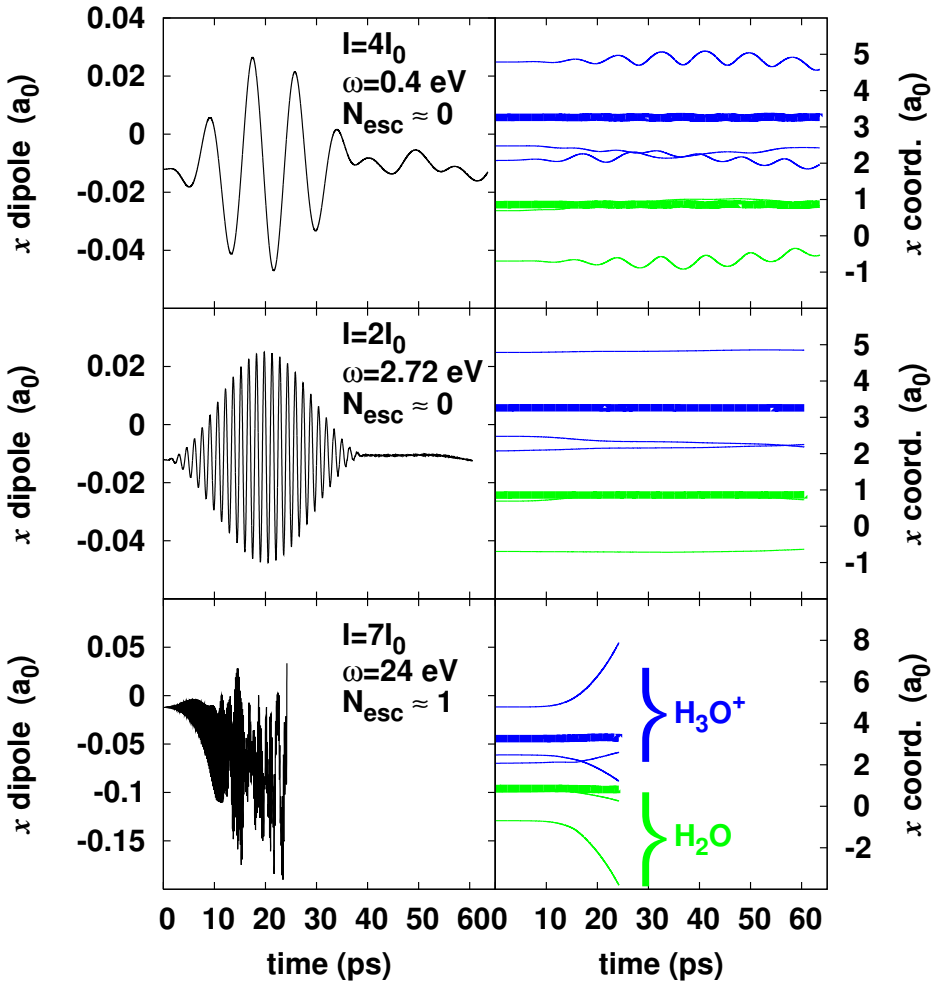

Figure II.2: Irradiation of $(H_2O)H_3O^+$ by lasers with polarization along x axis, FWHM of 20 fs, intensities of about $I_0 = 10^{14}$ W/cm^2, and three frequencies as indicated. The number of escaped electrons $N_{\rm esc}$ is also reported for each case. As a function of time : Electronic dipole moment in x direction (left column), and ionic x coordinates (right column). The dark (blue) lines correspond to the ionic positions of H_3O^+, while the light (green) ones show that of H_2O. The thick curves stand for the position of the oxygen atoms.

soon as electrons are emitted. In the far IR domain instead, the water cluster is stable but ionic vibrations show up after 30 fs, while still no electronic emission is observed. This frequency scan thus nicely presents the various dynamical couplings between a laser and a water cluster. A systematic study on larger water clusters is in progress. The case of irradiation by a charged projectile is also currently investigated.

II.2.3 Detailed analysis of the dynamics of free irradiated clusters

In parallel to these (sometimes heavy) theoretical developments, we have continued to analyze some detailed aspects of coupled electron and ion dynamics in free irradiated metal clusters, motivated by new challenging experimental developments. Indeed, the new developments in laser technology allow growing availability of light under extreme conditions : Attosecond pulses, and high photon frequencies delivered by free electron lasers (FEL). Moreover new experimental detailed data on properties of distributions of emitted electrons (high-order harmonic generations, angular-resolved photoelectron spectra, time-resolved photoelectron spectra) call us for pursuing our studies on free irradiated clusters [Sur 05,Rei 05,Nes 06,20,21].

In particular, non-linear interactions between an intense laser field and a dense cluster matter constitute a topic of high current interest in which many investigations have been carried over the past years (for a recent review, see e.g. [3]). For instance, these interactions can produce an enhanced high-order harmonic generation (HHG), compared with the case of irradiation of atomic jets. HHG have been observed in a few experiments on rare gas clusters [Don 96,Tis 97,Vel 01,Pai 06]. It has also been observed in organic molecules [Lev 01, Ita 04]. However the theoretical exploration of a such a phenomenon for multielectron systems is still a developing domain, since computations in full time-dependent Schrödinger equation are very time-consuming. Thus TDLDA-MD appears as a powerful tool to elucidate this issue in large systems.

As an example, we simulated molecular HHG (MHHG) obtained after irradiation of an ethylene molecule by a one-color laser (frequency of $\omega_1 = 2.72$ eV, intensity of $I_1 = 10^{14}$ W/cm^2, ramp profile with whole duration of 30 fs, polarization along C-C double bond direction) and a two-color laser (same ω_1 and I_1 for the first color, but $\omega_2 = 2\omega_1$ and $I_2 = I_1/4$ for the second color, and no relative phase; same time profile and polarization) [33]. The MHHG spectrum of C_2H_4, obtained after interaction with the one-color laser, is more or less similar to that of an atom. At variance, after the two-frequency laser irradiation, the MHHG pattern strongly differs. To get a deeper insight of these discrepancies, we performed a Gabor trans-

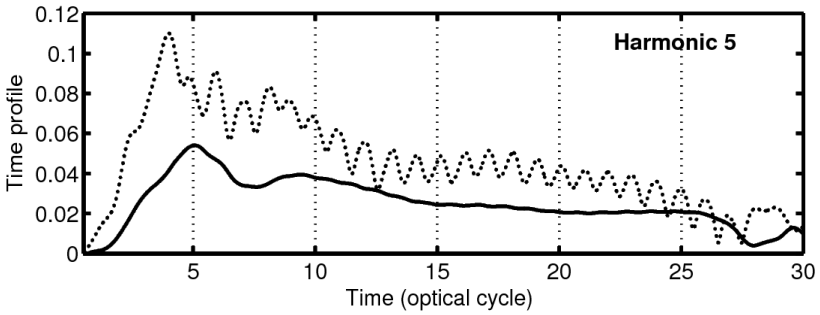

Figure II.3: Time profile of the 5th harmonic obtained by Gabor transform of the dipole moment of C_2H_4 along the laser polarization direction (same as the C-C double bond one), after irradiation by a one-color laser ($\omega_1 = 2.72$ eV, $I_1 = 10^{14}$ W/cm^2, solid line), and a two-color laser (same ω_1 and I_1, and $\omega_2 = 2\omega_1$, $I_2 = I_1/4$, dots). From [33].

form of the dipole moment $\mathbf{D}(t)$. The latter is dominated by the response along the laser polarization, denoted in the following as $D_{\rm pol}$. The Gabor transform consists in a Fourier transform where the function to transform is multiplied by a Gaussian, viewed as a time window. More precisely, we compute the function $D_G(\nu,\tau) = \int {\rm d}t\, D_{\rm pol}(t)\, e^{2\pi i\nu t} e^{-(t-\tau)^2/2\sigma^2}$, where σ is chosen as one-tenth of the laser optical period. This time-frequency analysis thus provides time profiles of the different harmonics ν. As an illustration, we plot $D_G(5,\tau)$ in Fig. II.3. The 5th harmonic, in the one-color case, smoothly evolves in time, indicating a multiphoton mechanism. When the two-color laser is used instead, the yield is higher and exhibits nice oscillations in phase with the laser optical cycles. One can explain this behavior by recollisions of the electronic wave packet with the ionic cores.

The detailed study of photoelectron angular distributions (PAD) can also shed some light on the dynamics of photoemission, in particular regarding the symmetry of the electronic wave functions and the degree of thermalization. A few highly detailed experimental results start to be available in the optical domain [Kos 07, Bar 09]. An example of such an analysis on Na_{58}^- is presented in Fig. II.4. Comparison with our calculations is drawn and fair agreement

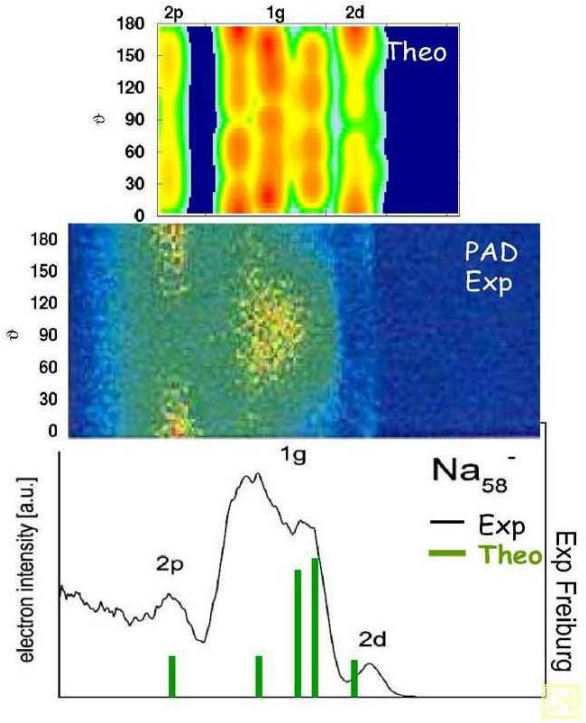

Figure II.4: Experimental photoelectron angular distributions (PAD) of Na_{58}^- after irradiation by a laser of intensity less than 10^{10} W/cm^2, and a frequency of 4.02 eV (bottom) or 2.48 eV (middle) [Kos 07]. Experimental results are compared with a theoretical PAD (top) obtained with a laser frequency of $\omega = 2.48$ eV. The vertical lines in the lower panel indicate the static single-particle energies, with an additional contribution from ω (unpublished).

is found between theory and experiment. A complete investigation will be reported in a paper in preparation.

It is also interesting to explore PAD for the case of irradiated deposited clusters. Such calculations are underway in the case of simple metal clusters deposited on either an Ar or a MgO surface (in preparation).

Interaction of clusters with lasers in the FEL frequency domain finally constitute challenging and exciting issues, since ionization mechanisms strongly differ from that in the optical

domain. We have thus started to compute the response of (organic and metal) clusters and molecules to very high laser frequencies, focusing on the detailed analysis of the properties of emitted electrons, and PAD in particular.

II.3 Scientific project

As exemplified in Secs. II.1 and II.2, the elaborated TDDFT-MD codes developed in our group over the years offer a unique numerical tool to explore many non-linear scenarios in clusters and molecules under extreme conditions, processes that are usually not accessible by other techniques. They also constitute a great opportunity to test in truly realistic situations the applicability of formal developments from a numerical standpoint. We also have long-standing contacts with experimental groups working in related fields, for instance in Rostock (Germany) and Lyon (France). This provides promising opportunities for the applications of the developed formalisms. Following these considerations, we have identified several complementary axes of work. Three of them rely on the hierarchical methods developed during the last years. The fourth one focuses on free cluster dynamics irradiated by extreme light. The last topic concerns numerical and formal developments of our codes. We shortly present all of them in the following sections.

II.3.1 Metal clusters adsorbed at defects on MgO(001)

Whereas the dynamics of Na atom/clusters in contact with a rare gas environment (deposited or embedded) has been extensively explored [5, 7, 10, 13–19], the case of MgO(001) still offers many interesting dynamical scenarios to explore. Indeed, metal oxides are of great technological importance in surface science and engineering, especially for their applications in catalysis processes, protective coatings, and microelectronics [Hei 94, Woo 01]. It has been moreover demonstrated experimentally that defects at the MgO surface can act as strong nucleation and diffusion sites [Als 88, Meu 94, Haa 00]. This has also been investigated theoretically but only in static calculations [Yan 02, Vit 05, Inn 06, Hon 07, Bar 07b]. Within our hierarchical model, we can easily explore dynamical deposition/diffusion of Na clusters on neutral or charged oxygen vacancies, and fully appreciate the effect of the dynamical polarizabitility of the oxygen atoms in these processes.

II.3.2 Helium surrounding

Chemical physics of ultra-cold atoms and molecules represents nowadays a growing field for the exploration of a large variety of phenomena, e.g., formation of metastable molecular complexes or chemical reactions under extremely well-defined conditions (temperature, orientation, distributions of populated states). Superfluid helium nanodroplet beams now provide a powerful tool for chemical and physical investigations at very low temperatures for a wide range of embedded molecules and clusters.

In the ANR contract MIRRAMO, joined with Prof. Farizon's experimental group in Lyon, we aim at elucidating at the microscopic level the damage on water-coated biomolecules when interacting with a high-energy projectile. The next step in this experiment is to use embedding in rare-gas (helium or argon) droplets to control the external conditions under which irradiation takes place. From the theoretical point of view, the simplest assumption is that the rare gas mostly provides a low temperature heat (cold) bath. But a high precision description has also to account for the side-effects due to the embedment. This thus calls for an extension of our hierarchical model to the case of a helium environment. We have then identified two complementing directions, relying on the energy scale involved there.

Electronic spectroscopy in helium droplets We have already performed detailed studies of low energy observables (structures, optical response) for simple metal clusters in contact with rare gas environments (Ar, Kr, Ne) and found that, in spite of their inert character, rare gases do contribute [17]. However there is only a weak influence on the optical response of the embedded cluster and on electronic transport, in agreement with experimental findings [Die 02].

Still many experimental and theoretical works exist for electronic spectroscopy of doped helium droplets (see [Sti 01, Sti 06] for recent experimental reviews). For instance, excited states of benzene [Log 07] or Ag atoms [Evg 08] embedded in helium droplets have been explored experimentally, and measurements of metastable states have been reported. In the same spirit, it has been observed very recently by means of pump-probe techniques that the interaction of Mg with He can lead to metastable Mg complexes, with a delayed collapse when irradiated by a laser [Prz 08]. These findings have been confirmed theoretically by DFT calculations [Her 08].

Hence, regarding the numerous works using helium surrounding for the study of electronic properties, the calibration of the potentials between Na and He in our hierarchical method will definitely add versatility to our model. The basis of modeling will remain the same as before, that is the description of helium by classical atoms dressed with (classical) dynamical polarizabilities. There exist, in addition, recent detailed experimental measurements on Na-doped helium droplets [Log 08], which will allow the fine-tuning of the parameters of our model.

High energy excitations in helium droplets At the other limit, we aim at describing the microscopic mechanisms involved in the irradiation of molecules embedded in helium droplets in the non-linear regime, more closely to Prof. Farizon's experiment. The strategy here is to describe the interaction of an organic system with a He environment, and thereafter the time evolution after collision with an energetic proton. New developments and calibration in detail will be needed here and will probably ask for more effort, since one has to define model potentials for the various combinations of C, N, O, H and rare gases. We will rely on benchmark computations from the literature, especially from ab-initio quantum chemistry, if available. We also have the capability to perform our own ab-initio calculations and will do that if necessary. Final re-tuning of model parameters allows in the end of the process to fit available experimental results on such mixed systems.

II.3.3 Chromophore effects in irradiated water clusters

When, in 2005, we aimed at extending our hierarchical method of sodium clusters in contact with an insulator substrate to the case of organic systems in contact with a polar environment, we started in the same spirit a few studies of Na and Na_2 embedded in water clusters. Indeed some experimental and theoretical investigations are available (see e.g. [Sch 03,Bao 07,Cwi 08, Kry 09]). Note that, at variance with the exothermic reaction between alkali metals and water, single Na atoms do not react with H_2O molecules or clusters.

However, as mentioned in Sec. II.2.2, we postponed the calibration of such a theory and preferred to describe the water molecules at the same level of refinement as the embedded molecule. Indeed in Prof. Farizon's experiments, the number of coating water molecules will be precisely controlled (from 2 to about 30). Hence water will not act as a macroscopic environment but rather as a finite system in contact with the biomolecule under study.

The exploration of a Na atom embedded in a water cluster recently gained a high interest from our point of view. Indeed, Prof. L. Sanche's group in Sherbrooke (Canada) has, since the eighties, a longstanding expertise on the damage on biomolecules caused by low-energy

electrons (LEE). The latter are primary produced by an irradiation, as the interaction with fast projectiles during radiotherapy [San 05]. The understanding and the control of the chemistry induced by LEE produced in biological cells is thus of utmost importance. Very recently, L. Sanche *et al.* reported that in the presence of gold nanoparticles, the amount of LEE created by a high energy radiation near DNA considerably increases and thus causes much more damage [San 09]. What is observed here is a chromophore effect of the gold cluster. Indeed the gold cluster, constituting an electron reservoir, can easily couple with an external electromagnetic field, and thus can be highly ionized.

The theoretical description of such a phenomenon is not possible nowadays for such a large system (gold cluster-DNA complex), since electronic emission is involved and thus calls for a detailed description of the ionization. However, within TDDFT-MD, we can explore the underlying mechanisms by investigating the irradiation by an optical laser of a simpler atom embedded in a water cluster. The idea here is to gently deposit a small amount of energy in an organic system, by means of a (cheap) optical laser, via the preferrential coupling of a metal atom with the laser field. LEE can hopefully be emitted from the metal atom, and provoke a fragmentation of the water cluster, in line with the dissociative electron attachment observed by Sanche *et al.*. Work in that direction is under way.

II.3.4 Irradiation of clusters by laser light under extreme conditions

High-intensity X-ray/XUV Free Electron Lasers (FEL) are now available and will allow new, possibly time-resolved (TR), spectroscopies for imaging the electronic motion on its natural time-scale and at the length-scale of a molecule. Furthermore, the availability of attosecond pulses will even reduce the time scale at which dynamics will be resolved. While there was for years no urgent need for theoretical studies in that regime, the recent new experiments in these fields open exciting areas in cluster and molecular physics. However, accurate theoretical descriptions are still missing. Indeed, intense fields as provided by these lasers inevitably excite complex dynamics. The success of imaging techniques depends on our understanding of these largely unknown dynamics, creating demand for the theory of complex polyatomic systems in non-perturbative and ultrashort external fields.

Some contact with Dr. F. Lépine's experimental group at the LASIM in Lyon (France) have been established this year and scientific collaborations are expected to come. This group aims at developing an experiment on C_{60} combining attosecond pulses and modern imaging detection techniques, to investigate ultrafast multi-electron dynamics in complex isolated systems. From the experimental standpoint, C_{60} is a welcome test case since it can be easily produced with no need for mass selection. At the side of theory, it appears as a good candidate for theoretical investigations because of its high symmetry, still keeping the complexity of a large multielectron system. Up to now, no experiment has explored extreme light excitations in the highly non-linear dynamical regime in C_{60}, and furthermore on a sub-fs timescale.

Production of experimental time-resolved photoelectron spectra of C_{60} is extremely promising for us. Our previously developed theoretical and numerical tools are ideally suited to tackle the opening issues of the dynamics of clusters and molecules in extreme light. The simulation of the dynamics of irradiated C_{60} is actually essentially a matter of computing time. One of our goals here will be to establish time-resolved photoelectron spectra and angular distributions of electrons emitted after the interaction of C_{60} (or another cluster/molecule) with an extremely short-pulse and/or a high-frequency laser. This will allow us to explore the mechanism of light absorption and electronic emission in such new processes.

II.3.5 Development of softwares

Our platform of TDDFT-MD codes allow us to explore in principle many different types of dynamical situations which are sketched in Fig. II.5. However, our numerical tools has been

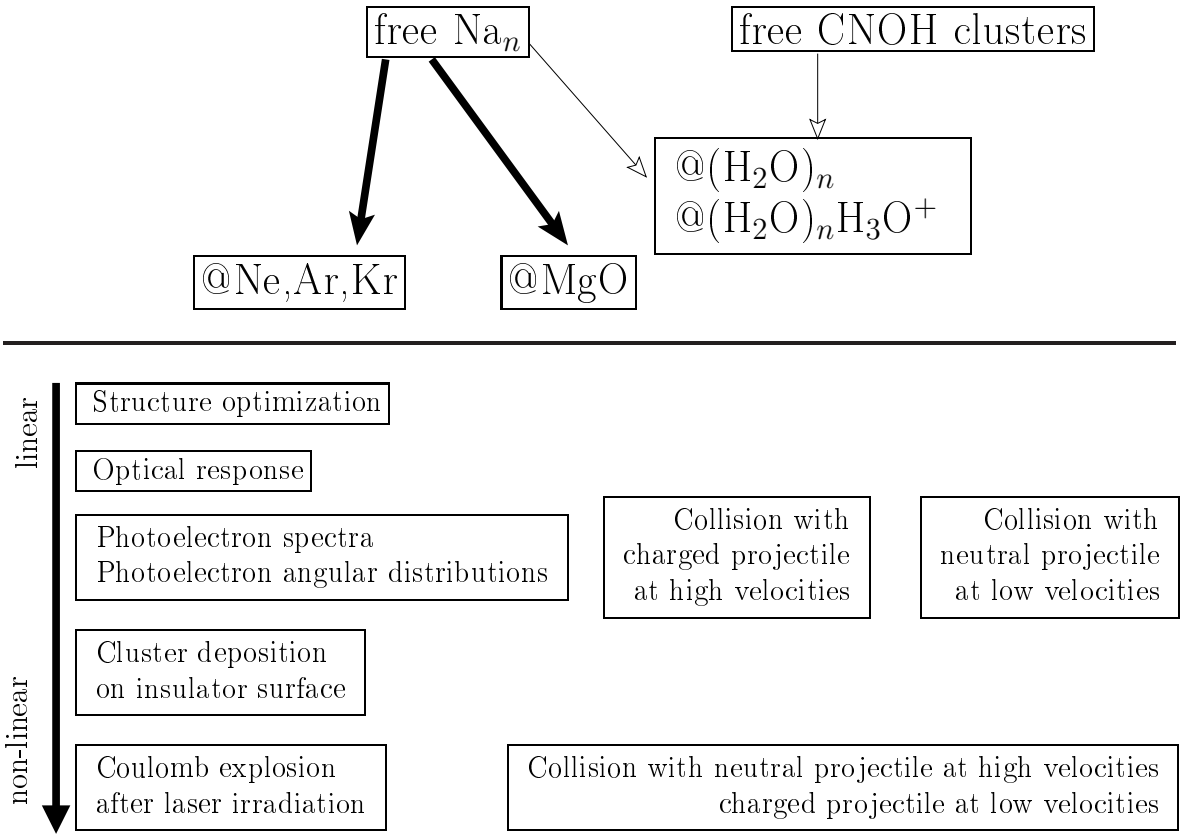

Figure II.5: Top : Various cluster/environment combinations that can be studied by our TDDFT-MD codes. The thick arrows indicated the cases described within our hierarchical method. Bottom : Dynamical processes that can be simulated with our TDDFT-MD codes, from statics and the linear regime downto the highly non-linear domain.

developed over the years in the groups of Profs. Reinhard and Suraud, with clear purposes on simulations of physical processes, and not on with ultimate numerical optimization as a first task. This makes them hard to handle for users from outside. It is time for a clean-up of the code and possibly some further optimization, particularly with respect to parallel execution.

Regarding the numerous possible calculations that our codes can offer, and the potential audience that may be interested to use them, we aim at improving the interface and the optimization of our codes, so that we can propose them as open sources, similarly to what have been achieved with the Octopus code. To that end, we will start during this fall a close collaboration on this topic with Prof. Reinhard, Prof. F. Calvayrac from the University of Maine (Le Mans, France), who actually developed the three-dimension version of our TDDFT-MD code during his Ph.D. thesis with Prof. Suraud at the end of the nineties [Cal 00], and Prof. S. Contassot-Vivier from the University Poincaré (Nancy, France), who is a professor in computer science. This will also probably ease the test and the implementation of formal developments in TDDFT, as TDSIC or SIC-TDOEP. Indeed, although formal problems have been clarified in the SIC issue, the techniques developed up to now (see Sec. II.2.1) are very costly numerically and almost prevent any practical use of such a correction in realistic cases.

However, the implementation of more sophisticated TDSIC than ADSIC, as it is currently used in almost all presented results, will allow to upgrade the treatment from qualitative to quantitative description of dissociation of systems, especially organic ones.

By combining our various expertises, we are quite confident that we will be able to offer versatile TDDFT-MD softwares with a competitive computing speed in the years to come.

Appendix A

Review article: P. M. Dinh et al., Phys. Rep. (2009) in press

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