

## European Master in Theoretical Chemistry and Computational Modelling

XII<sup>th</sup> International Intensive Course

VALENCIA  
4th - 28th  
September  
2017



With the support of the Erasmus Mundus programme of the European Union.

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## Foreword

“I could have done it in a much more complicated way, said the red Queen, immensely proud”

Attributed to Lewis Carroll

Providing the theoretical framework for the understanding of the chemical reaction and the properties of chemical entities under the most varied conditions is the great defy that endeavours the Theoretical and Computational Chemistry. TCC has reached a grade of maturity and efficiency that allows it to play, currently, a key role in modern Chemistry and some parts of Physics, but also in interdisciplinary sciences such as Materials Science, Biochemistry, Nanotechnology, and many others. Well founded in sound physical theories and with the invaluable help of continuously increasing computational power and numerical efficiency, Theoretical Chemistry and Computational Modelling (TCCM) offers an attracting and broad subject to students and scientist interested in a consistently wide variety of projects.



A number of European superior education institutions have recognized the interest of offering Master studies in the TCCM field. In particular, a consortium of seven universities acted as pivot institutions to promote the European Master in Theoretical Chemistry and Computational Modelling, EMTCCM, that was awarded in 2009 with an Erasmus Mundus action by the Education, Audiovisual and Culture Executive Agency, (EACEA) of the EU. After a Mid-Term Quality review, the award was renewed for a second period of three editions starting in the 2015–17 edition. Up to 47 High Education institutions have joined the training program provided by the EMTCCM and this large consortium has obtained the recognition of the “Euromaster Label” by the European Chemistry Thematic Network Association (ECTNA). The Universidad Autónoma de Madrid, UAM, is the coordinating institution in all these initiatives, which started in 2005 with the launching of the EMTCCM project.

The EMTCCM is structured in two years, and comprises 120 ECTS credits. A key piece of the academic activity of the Master is the International Intensive Course (IIC) that is common to all the participants. The IIC, placed at the beginning of the second academic year of each two-years Master Course edition, provides the core of common classroom lecturing and workshop hands-on sessions for no less than 24 ECTS credits. Eleven IIC course editions have taken place in previous years, the last ones held at the Universities of Perugia (Italy, 2012), Madrid (Spain, 2013), Toulouse (France, 2014), Groningen/Leuven (The Netherlands/Belgium, 2015) and Oporto (Portugal, 2016).

The present edition, the 12<sup>th</sup> International Intensive Course in TCCM, will be held at the University of Valencia (Spain) from September 4<sup>th</sup> to 28<sup>th</sup>, 2017. Forty five students have registered to the course, coming from more than twelve countries, ten of them being Erasmus Mundus grant holders. On the other hand, twenty scientists (two of them granted as Erasmus Mundus Scholar), coming from six countries and from twelve Higher Education and Research Institutions, have joined this course as lecturers and teachers eager to share their knowledge and experience, to afford case examples and to teach on the wide fan of subjects covered by the course. To all of them, both students and lecturers, I express here the deepest gratitude, on behalf of the organizing committee.

José Sánchez Marín  
Prof. of Physical Chemistry  
Chairman of the organizing committee

## Acknowledgements and sponsoring

It would not have been possible to organize this 12<sup>th</sup> International Intensive Course of the European Master in Theoretical Chemistry and Computational Modelling without the collaborative help provided by the Universitat de València, and by some of its centres and services. In particular, the organizers must acknowledge the directive team and staff of the *Servei de Formació Permanent* and the *Centre de la Formació i la Qualitat "Sanchis Guarner"* for allowing us to use their academic facilities and for all the help provided. Thanks are also due to Martin Córdoba from the ICMol for technical support about the workshop sessions. We also recognize here the technical and scientific help from the Asociación para la Promoción de la Química Teórica y Computacional (APQTC) and from all the people in the "TCCM team" at Universidad Autonoma de Madrid (UAM), notably the people at the emtccm secretary. The organizers acknowledge also the UAM that is the Coordinating Institution of this European Master.

The organizers are specially recognized to the *Vice-rectorat de Postgrau* of the Universitat de Valencia for its financial and academic support.

Many other people have contributed in some degree to the organization of this course. Thanks to all them-



*With the support of the Erasmus Mundus programme of the European Union.*



## Organizing and local scientific committee

José Sánchez-Marín (Chairman, Director of the EMTCCM at the UV)

Ignacio J. Nebot-Gil (Member of the International Committee of the EMTCCM)

Ignacio N. Tuñón García de Vicuña

Inmaculada García Cuesta

Alfredo M.J. Sánchez de Merás

Enrique Ortí Guillén

Remedios Gonzalez Luque

Mercedes Rubio Más

Martín Córdoba Martínez

## Time Table

All sessions: Classroom 1.1 at Servei de Formació Permanent (SFP) in the Centre de Formació i Qualitat « Sanchis Guarner »

FIRST WEEK					
	04-sep	05-sep	06-sep	07-sep	08-sep
Time	Monday	Tuesday	Wednesday	Thursday	Friday
09:00-10:30	FREE	ACT 1	AES 1	AES 2	AES 4
		Planelles	Koch	De Graaf	Yánez
BREAK					10:45-12:15
11:00-12:30	FREE	ACT 1	AES 1	AES 2	AES 4
		Planelles	Koch	De graaf	Yánez
LUNCH					12:30-14:00
15:00-16:30	REGISTRATION	Workshop ACT 1	AES 3	Workshop AES 2	Workshop AES 4
	Technical issues	Planelles	Roca	De Graaf	Yánez
BREAK					14:00 onwards
17:00-18:30	REGISTRATION	AES 3	Workshop AES 3	Workshop AES1	FREE
	Technical issues	Roca	Roca	Koch	FREE

SECOND WEEK					
	11-sep	12-sep	13-sep	14-sep	15-sep
Ttime	Monday	Tuesday	Wednesday	Thursday	Friday
09:00– 10:30	EVALUATION	AES 6	AES 6	AES 7	MSD 1
		Broer	Broer	Havenith	Faraji
BREAK					
11:00– 12:30	AES 5	CONFERENCE 2	AES 6	AES 7	MSD 1
	Sancho	ACC	Broer	Havenith	Faraji
LUNCH					
15:00– 16:30	AES 5	Ethics	Workshop AES 6	AES 7	MSD1
	Sancho	Broer	Havenith	Havenith	Faraji
BREAK					
17:00– 18:30	Workshop AES 5	FREE	FREE	Workshop AES 7	Workshop MSD 1
	Sancho			Havenith	Faraji



THIRD WEEK						
	18-sep	19-sep	20-sep	21-sep	22-sep	
Ttime	Monday	Tuesday	Wednesday	Thursday	Friday	
09:00– 10:30	EVALUATION	ACC 1	MDS 3	MDS 6	MSD 6	
		Sánchez	Faginas	Worth	Worth	
BREAK						
11:00– 12:30	MDS 2	ACC 1	MDS 5	MDS 3	Workshop MSD 6	
	González	Sánchez	Moliner	Faginas	Worth	
LUNCH						
15:00– 16:30	MDS 2	Workshop ACC 1	MDS 5	MDS 4	Workshop MDS 3	
	González	Sánchez	Moliner	Lombardi	Faginas	
BREAK						
17:00– 18:30	Workshop MDS 2	CONFERENCE	Workshop MDS 5	MDS 4	Workshop MDS 4	
	González	MDS – Worth	Moliner	Lombardi	Lombardi	

FOURTH WEEK					
	25-sep	26-sep	27-sep	28-sep	29-sep
Ttime	Monday	Tuesday	Wednesday	Thursday	Friday
09:00– 10:30	EVALUATION	ACC 2	CS	CS	FREE
		Gierschner	Gaita	Gaita	
BREAK					
11:00– 12:30	ACT 2	ACC 2	CS	CS	EVALUATION
	Gervasi	Gierschner	Gaita	Gaita	
LUNCH					
15:00– 16:30	ACT 2	ACC 2	Workshop ACC 3	Workshop ACT 3	colloquium ACC 4
	Gervasi	Gierschner	Milian	Clemente	Gaita
BREAK					
17:00– 18:30	Workshop ACT 2	ACT 3	ACT 3	FREE	FREE
	Gervasi	Clemente	Clemente		

Courses legend: Main subjects

AES	Advanced Electronic Structure and Condensed Matter
MCD	Molecular and Chemical Dynamics and Computer Modelling
ACT	Advanced Computational Techniques
ACC	Applied Computational Chemistry
ES	Ethics in Science
CS	Communication Skills

## •• AES (Advanced Electronic Structure and Condensed Matter)

### *AES 1 –Multilevel Coupled Cluster Theory (H. Koch)*

Henrik Koch  
U. Trondheim (Norway)

Course on coupled cluster and multilevel coupled cluster theory

#### Session I

1. Mathematical background and second quantization
2. Coupled cluster wave function and projection equations
3. Excited states in coupled cluster theory
4. Molecular properties and response theory

#### Session II

1. General idea behind QM/QM multilevel models
2. Partitioning of the molecular system
3. Hierarchy of coupled cluster models.
4. Some technical aspects
5. Example applications to valence and core excited states

#### Session III

1. Introduction to DALTON and LSDALTON
2. Applications of coupled cluster implementation for excited states
3. Practical exercises

## ***AES 2 – Electron correlation with multiconfigurational wave function methods (C. de Graaf)***

Coen De Graaf

Universitat Rovira I Virgili (Tarragona) / University of Gröningen

Outline:

- 1) - Identification of situations where a monoconfigurational approach may fail.
- 2) - Multiconfigurational SCF; wave function ansatz, orbital and CI optimization
- 3) - Complete Active Space SCF; choice of the active space
- 4) - Beyond CASSCF; RASSCF, ORMAS, DMRG, Split-CAS
- 5) - Dynamic correlation; multiconfigurational reference perturbation theory (MRPT) and configuration interaction (MRCI)
- 6) - Hands-on session with ORCA

\* Abstract:

An accurate treatment of the electron correlation effects is indispensable to obtain the correct answer for the correct reason in a computational study. In many cases, density functional theory can be used to obtain a sufficiently accurate description of the electronic structure, but this methodology can become problematic when it comes to systems with (many) unpaired electrons. In these cases, the assumption of one dominant electronic configuration may not be useful anymore and one has to take into account the multiconfigurational character of the electronic structure from the start. In this course, we will shortly review the most commonly used approaches to treat multiconfigurational situations. Not only will we pay attention to the theoretical and technical aspects of the methods, but also give extensive practical insights in their (dis)advantages and how to avoid common pitfalls. Starting with an outline of multiconfigurational self-consistent field theory, we will continue with the complete active space SCF (the working horse of multiconfigurational quantum chemistry) and how to choose the active space. Currently, it is very hard to treat active spaces with more than 16 orbitals and 16 electrons. However, there are several approaches to go further and the basics of some of these new developments will be exposed. Although CASSCF gives typically a rather accurate account of the electron distribution, it often badly fails in the prediction of relative energies of different electronic states. The course will review some methods that account for the remaining dynamic correlation such as CASPT2, NEVPT2, DDCI, among others. If time permits, a hands-on session will be organized to illustrate some concepts of the course.

## ***AES 3 – Electronic Excited States and Computational Photochemistry (D. Roca)***

Electronic Excited States and Computational Photochemistry

Daniel Roca-Sanjuán

Institut de Ciència Molecular, Universitat de València, P.O.Box 22085, ES 46071 València, Spain

[Daniel.Roca@uv.es](mailto:Daniel.Roca@uv.es)

Outline:

Chapters:

1. Quantum chemistry of the excited state (theory)
2. Photophysics and photochemistry: theory and applications (theory)
3. Environmental effects (theory)
4. An introduction to excited-state dynamics (theory)

MOLCAS: Excited-state computations and an introduction to computational photochemistry (workshop)

Abstract:

Computational Photochemistry can be defined as the study by means of computer simulations using specialized software tools and strategies of what happens to a molecule after the absorption of a photon. In the last decades, the establishment of the Photochemical Reaction Path Approach (PRPA), along with the implementation in the quantum-chemical packages of software of algorithms capable to compute Minimum Energy Paths (MEPs) and Conical Intersections (CIs), which are the most important features in the approach, and the improvements of the multiconfigurational methodologies caused a revolution in the field of Theoretical Photochemistry. Accurate determinations of the energy-decay mechanism after light-absorption were possible from that point and many scientists began intensive works to study photochemical processes of biological and technological relevance, such as the photoestable properties of DNA components against UV radiation, the photoproduction of lesions in the genetic code, which can result in mutations, the process of vision in the retinal chromophore, the design of molecular devices with movements controlled by light, etc.

The first step towards accurate and complete theoretical studies on photochemistry implies the comprehension of the electronic structure of the excited state. In contrast to ground state, excited states have a much more complex nature, and flexible enough basis sets and multiconfigurational methods are most of the times required. Different types of processes can take place upon light-absorption: adiabatic and non-adiabatic, radiative and non-radiative events, etc. The determination of some singular points in the Potential Energy Hypersurfaces (PEHs) of the ground and lowest-lying excited states of the chromophore, such as minima, saddle-points, CIs, and singlet-triplet crossings, and the mapping between these structures can help to understand the photoreactivity of the molecule. Nevertheless, the number of singular points on the PEHs increases dramatically with the molecular size, and in addition not all these structures and paths between them contribute equally to the photochemistry of the system. Therefore, in order to describe the most relevant energy-decay paths, the PRPA approach must be followed. In a subsequent step and

taking into account that the chromophores under study are usually solvated or embedded in a biologic environment, an appropriate strategy must be selected to analyze the effect of the surroundings on the properties of the molecule. Finally, once the topography of the hypersurfaces is obtained by solving the time-independent Schrödinger equation, the evolution of the nuclei on that potential (dynamic model) must be described to provide with rate constants, state lifetimes. All these concepts and computational strategies will be analyzed in detail in this course and illustrated with some examples.

One of the most successful quantum-chemical packages of software to perform photochemical studies is MOLCAS. This program was developed by Björn O. Roos in the 70s and nowadays contains codes for several quantum-chemical methods and strategies appropriate to carry out accurate photochemical studies. An introduction to the computation of excited states and computational tools useful for photochemical analyses will be provided here.

This course is organized in two parts. First, state-of-art computational strategies in photochemistry will be described, based on the expertise in the field of the group Quantum Chemistry of the Excited State University of Valencia (QCEXVAL) and the collaborations of QCEXVAL with other photochemical groups. Next, the use of the MOLCAS program will be introduced, focusing in the computation of excited states and subsequent photochemical calculations. In particular, the following topics will be explained:

## ***AES 4-Wavefunction and Bonding Analysis (M. Yáñez)***

Manuel Yáñez

Departamento de Química, Facultad de Ciencias, Módulo 13.

Universidad Autónoma de Madrid. Cantoblanco. 28049-Madrid. Spain

### Outline

1. Molecular Electrostatic potentials
2. Quantum Theory of Atoms in Molecules (QTAIM)
3. Electron Localization Function (ELF)
4. Natural Bond Orbitals (NBO)
5. Non-Covalent Interactions (NCI)

### Summary

The relevant information that can be obtained by solving the Schroedinger equation (approximately in most cases) is not only a good approximation to the exact energy of the system investigated, but also how the electrons are distributed in the physical space surrounding the nuclei of the molecule. This information is directly related with the square of the wavefunction, which according to one of the postulates of quantum chemistry has a probabilistic interpretation. Accordingly the square of the wavefunction provides direct information of the so-called electron density distribution of the system under investigation. The obvious result is that with this information it is possible to predict in which regions of the molecular space the electrons are more likely to be found and in this way it is possible to have an idea of the electric multipoles of the system.

The aim of this course is to present the currently available methods that permit to analyze the electron density distribution function which, as mentioned above, differently from the wavefunction itself has a well defined physical interpretation.

We will start our survey by considering very simple models, which in spite of its simplicity provide qualitative useful information on reactivity trends or allow to predict which is the most reactive site of a molecular system. This is the case of the molecular electrostatic potentials,<sup>1</sup> defined as the potential (attractive or repulsive) that a unit positive charge experiences in the surroundings of a molecular system. From its definition it is obvious that this approach permits to locate the most active site of the neutral reactant in electrophilic or nucleophilic additions, in which one of the reactants is an ionic species. This approach is particularly useful when the reactant has several active sites susceptible of undergoing an electrophilic or nucleophilic attack. We will discuss different examples. The limitation of these models and others based exclusively in a static description of the reactants will be also analyzed.<sup>2</sup>

The information that can be obtained through the analysis of the electron density is of high relevance because, after all, chemical processes are the result of breaking and making bonds, which unavoidably leads to a significant rearrangement of the electron density of the systems participating in the reaction. One of the most popular approaches in this respect is the Atoms In Molecules theory (AIM)<sup>3</sup>. This approach is based on a topological analysis of the electron density function,  $\rho(\mathbf{r})$ , and its Laplacian,  $\nabla^2\rho(\mathbf{r})$ . This topological analysis leads to the definition of the molecular graph as the ensemble of stationary points of  $\rho(\mathbf{r})$ , maxima (nuclei), minima (cage points) and saddle points (ring and bond critical points), and the paths connecting them. The values of



the electron density and the Laplacian of the density at the bond critical points provide relevant information about the strength and the nature (covalent or ionic) of the interaction between two (bonded) atoms.

Alternatively, the electron density of a chemical system can also be analyzed by the so-called electron localization function (ELF)<sup>4-6</sup> theory. The ELF theory was originally conceived as a local measure of the Fermi hole curvature around a reference point within the Hartree-Fock approximation,<sup>4</sup> and therefore it measures the probability of finding an electron in the neighborhood space of a reference electron located at a given point and with a different spin. This implies that the value of the ELF function should be large in those regions of the space where the probability of finding an electron pair is maximum. This analysis leads to the partition of the molecular space into electronic domains, or basins. There are two types of basins: polysynaptic basins (generally disynaptic), which are formed by the contribution of two or more atomic valence shells, accommodating bonding pairs, and monosynaptic basins, to which only one atomic valence shell contributes, and which therefore describe either lone-pairs or core-electrons.

A third complementary procedure to analyze chemical bonding, but not related with a direct analysis of the electron density is the natural bond orbital (NBO) method.<sup>7</sup> The NBO approach<sup>7</sup> recovers somehow the Lewis description of a chemical systems by describing the bonding in terms of localized hybrids and lone pairs obtained as local block eigenvectors of the one-particle density matrix. This method also permits to carry out a second-order perturbation analysis of the Fock matrix to quantify the interactions between occupied MOs of the system acting as an electron donor and unoccupied MOs of the molecule or fragment behaving as an electron acceptor.


We will show how these different techniques are complementary by discussing some critical cases in which not all the available techniques offer an unambiguous description of the bonding pattern of systems. A particularly interesting and challenging case is that of the non-covalent interactions, which in most cases are weak or very weak and difficult to describe accurately by the aforementioned approaches. Hence, the last part of the course will be devoted to present the so-called Non-Covalent Interaction (NCI) method specifically designed to describe these kinds of interactions.<sup>8</sup>

#### References

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XII<sup>th</sup>-IIC-EMTCCM

 Postgraduate studies in  
Theoretical Chemistry  
and Computational  
Modelling

  
European Commission  
ERASMUS  
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## **AES 5-Advanced Density Functional Theory (J.C. Sancho)**

Juan Carlos Sancho



### Advanced DFT (Outline)

\* Lecture 1: The electronic density is the key. Definitions, theorems & models.

#### 1.a General comments

1.a.1 Could it be considered  $\rho(\mathbf{r})$  a state variable?

1.a.2 Some mathematical aspects

1.a.3 Probabilistic interpretation of  $|\Psi|^2$

#### 1.b Density matrices

1.b.1 Reduced density matrices

1.b.2 The electronic density and its properties

#### 1.c Hohenberg-Kohn theorems

1.c.1 First Hohenberg-Kohn theorem: existence

1.c.2 Second Hohenberg-Kohn theorem: variational principle

#### 1.d The Kohn-Sham orbitalic approach

1.d.1 The Kohn-Sham hypothesis

1.d.2 Basic equations of the Kohn-Sham model

\* Lecture 2: Modern expressions for the exchange-correlation functional.

#### 2.a Exchange-correlation modeling

2.a.1 LDA, GGA and meta-GGA approximations

2.a.2 The adiabatic connection functionals

2.a.3 Variety of forms: real or not?

#### 2.b Precautions to be taken

2.b.1 Accuracy and validity domain

2.b.2 The self-interaction-error

2.b.3 Some successful stories: DFT-D and beyond

2.b.4 Density fitting (RI) and numerical quadrature

\* Lecture 3: Chemical concepts and reactivity.

## 3.a The chemical potential

## 3.a.1 Definition and derivation

## 3.a.2 Related concepts

## 3.b Hardness and Fukui functions

## 3.b.1 Curvature, frontier orbital energies and band gaps

## 3.c Size-extensivity

## \* Lecture 4: Extensions to excited-states: TD-DFT

## 4.a Extension to excited-states

## 4.a.1 Runge-Gross-Kohn-Sham exact formalism

## 4.a.2 Lineal response regime: escape from TD-KS equations

## 4.a.3 The importance of the exchange-correlation potential

## 4.a.4 Charge transfer and related issues

## Advanced DFT (Abstract)

In 1964, P. Hohenberg and W. Kohn published a pair of theorems constituting the basis for Density Functional Theory (DFT). Only one year later, the development of the Kohn-Sham (KS) scheme allowed to make the DFT a practical theory for all kind of (intended) calculations, as it is known today (KS-DFT). These authors showed that there always exists a one-to-one relation (correspondence) between the energy and the electron density of a system, i.e. it is in principle possible to obtain directly the exact energy from this density through an universal functional. The key is thus to model or mimic the subtle effects dominating matter at the quantum scale by means of a functional of the electronic density. The machinery should accurately include exchange and correlation effects, in order to address structure and bonding of molecules, and it should be more advantageous than the *ab initio* methods, either by reducing the computational cost associated to any calculation or by introducing theoretical concepts able to rationalise chemical reactivity, morphologies, extensions to excited-states, etc.

The development of accurate mathematical expressions (the density functionals) is normally a hard and painstaking work, and often underestimated by the community. Apart from the older Local Density Approximation (LDA), which is, however, still appreciated in some fields of Physics, the extension coined as Generalized Gradient Approximation (GGA), the hybrid functionals containing a portion of exact-like (Hartree-Fock) exchange, but calculated with the KS orbitals, the meta-GGA functionals, the double hybrid functionals also containing a portion of a perturbative correlation, local hybrid functionals, and the range-separated hybrid functionals are available today for running any calculation. The (admittedly) proliferation of functionals have provoked two (apparently contradictory) effects: (i) routine calculations plague nowadays almost all existing fields; and (ii) cautions must be taken and experience in use is needed more than ever. Furthermore, one always needs to calibrate first the methodology before next tackling the

interested systems. Also note that the results are sometimes system-dependent and/or property-dependent, which implies to analyse carefully how the results evolve or compare with closely related data before concluding anything, and that comparison with experimental data may need to model solvent effects or nanostructured systems, which complicate the task further. We will try to briefly outline how this can be done in practice through recent examples.

## ***AES 6-Electronic Structure of Solids and Surfaces (R. Bröer & R. Havenith)***

Ria Broer and Remco Havenith  
Theoretical Chemistry, University of Groningen

Important subjects of study in chemistry and physics are solids and their surfaces. This has for a large part to do with the ability to tune their properties for improved functionality. For example, chemical doping of manganite crystals can drastically affect their magnetic properties. Organic charge transfer salts show controllable transitions from diamagnetic to magnetic phases and from semiconducting to conducting phases. Surfaces of solids are at least as interesting for chemists as the bulk, since much physics and most of chemistry happens at a surface. Think, for example, of heterogeneous catalysis, chemisorption, dissociation at surfaces. Transition metal oxide surfaces can undergo controlled adsorption/desorption.

This course considers the theoretical treatment of the geometrical and electronic structure of solids and surfaces and of molecule-surface interactions. For molecules a much-used approximation is molecular orbital (MO) theory, similarly, for crystalline solids and surfaces a widely used approximation is band theory. For molecules point group symmetry can be used to make the computations easier and also to label the MOs in their energies. In band theory the use of translational symmetry is essential to make the computations feasible and to label the crystal orbitals and their energies. Band theory focuses mainly on ground state properties. Embedded cluster models, where a small part of the solid or surface is considered quantum mechanically, can be used for the study of local excitations. Embedded cluster models are also better suited for the study of solids and surfaces where strong electron correlation plays a role, since for such systems the one-electron band models are too crude.

The course starts with a short introduction into molecular and crystal symmetry. Concepts like Bloch orbitals, energy bands and densities of states, will be introduced and explained. We will discuss the bulk properties of some interesting materials, like graphene, diamond and rock salt in the frameworks of Hartree-Fock and density functional band theory. Chemisorption on surfaces will also be considered. Finally, theoretical descriptions based on embedded cluster models will be explained.

The concepts presented will be illustrated with hands-on calculations, using periodic band theory as well as embedded cluster models.

The following books have been used:

- [1] Molecular Quantum Mechanics, by P.W. Atkins and R. Friedman
- [2] Solid State Physics, by N.W. Ashcroft and N. D. Mermin
- [3] Solids and Surfaces: A Chemist's View on Bonding in Extended Structures, by R. Hoffmann
- [4] Atomic and Electronic Structure of Solids, by E. Kaxiras

## ***AES 7-Introduction to Valence Bond Theory (R. Havenith)***

Remco W.A. Havenith

Theoretical Chemistry. University of Groningen

### Contents

- The valence bond wavefunction
  - Special flavour: the block-localised wavefunction
- Calculation of the matrix elements
  - One-electron part
  - Two-electron part
- Valence Bond Self Consistent Field – Orbital optimisation
- Applications
  - H<sub>2</sub> description
  - Ionisation of methane (CH<sub>4</sub>)
  - Bent benzene
  - Valence bond theory and the (delocalized) chemical bond
  - Valence Bond calculations on pyrene
  - Meaning of VB structures
- Hands-on session
  - Exercise 1) Valence Bond calculations on benzene (C<sub>6</sub>H<sub>6</sub>).
  - Exercise 2) Valence Bond calculations on borazine (an inorganic benzene, B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>)

### Abstract:

In this course an introduction to Valence Bond (VB) theory will be given. In the first part of the course the theory will be explained: the form of the VB wavefunction will be explained, with the definition of structures and spinfunctions. Then the general way to calculate matrix elements between determinants with nonorthogonal orbitals will be presented. After that, orbital optimisation together with the application of orbital restrictions will be discussed. In the second part of the course, some applications of VB theory will be shown. The calculation of the ionisation potential of methane will be discussed and the applicability of VB theory to deduce the aromaticity of conjugated molecules will be demonstrated. In the hands-on session, you will do some VB calculations on benzene and borazine to learn how to interpret the results of different VB calculations using different orbital models.

## •• MDS (Molecular and Chemical Dynamics and Computer Modelling)

### *MDS 1 –Excited-State Dynamics and Photochemistry (S. Faraji)*

*Shirin S. Faraji*

*Theoretical Chemistry – University of Groningen*

#### **Outline:**

- Born-Oppenheimer approximation and its breakdown
- Diabatic vs. Adiabatic electronic state
- Vibronic coupling model
- Time-dependent Schrödinger equation for nuclei
  1. Standard methods
  2. Time-dependent Hartree
  3. Multi-configuration time-dependent Hartree
- Representation of Hamiltonian
- Multi-layer formalism
- POTFIT algorithm
- Dynamical observables
  1. Spectra
  2. Electronic population
  3. Probability density
- Examples

#### **Abstract:**

Photo-induced processes lie at the heart of numerous natural phenomena, such as photosynthesis, human vitamin D production, circadian rhythm, and visual response. Nuclear motion in electronically excited molecules is often not confined to a single potential energy surface, but rather proceeds on several, coupled potential energy surfaces



simultaneously. Conical intersections lead to strongly coupled electronic and nuclear motions such that the familiar adiabatic (or Born-Oppenheimer) approximation fails severely, giving rise to what is called nonadiabatic chemistry. The singularities in the non-adiabatic couplings that occur in the proximity of conical intersections are a blister for the computational treatment of the nuclear dynamics. To circumvent the singularity problem the concept of complementary diabatic electronic representation was introduced. In this representation, the diverging kinetic energy couplings are transformed into smooth potential energy couplings through a unitary transformation of the adiabatic electronic states within a suitable subspace. The well-known vibronic coupling approach that has been successfully used in the field of nonadiabatic chemistry, relies on the use of a diabatic electronic basis, where the potential energy coupling matrix is expanded in a Taylor series in suitable displacement coordinates and linear or quadratic terms are retained.

The time-dependent theoretical framework is the most natural way to describe molecular dynamics events. This is particularly true for short-time processes such as photoelectron or dissociation spectra, fragmentation dynamics, as well as fluorescence. Multiconfigurational time-dependent Hartree (MCTDH) method and its extension towards multi-layer formulation is an efficient algorithm to solve the time-dependent Schrödinger equation for nuclei in multidimensional systems. Time-dependent quantities of interest are often electronic populations in the interacting manifold of states. Strong nonadiabatic couplings manifest themselves typically in diffuse (under low resolution) or very irregular (under high resolution) spectral structures and in a femtosecond electronic population dynamics, thus signaling internal conversion processes proceeding on the same time scale as the nuclear motion.

## **MDS 2- Reaction Dynamics: Variational Transition State Theory (M. À. González)**

*Maria Àngels Gonzalez Lafont*  
*Universitat autònoma de Barcelona*

### **Outline:**

#### REACTION DYNAMICS: VARIATIONAL TRANSITION STATE THEORY

- I. Variational Transition State Theory
  - a) Dynamical formulation of Transition State Theory (TST).
  - b) TST main problem: Non-recrossing hypothesis.
  - c) Classical formulation of the Canonical Variational Theory rate constant

$$(k_C^{CVT}(T)),$$

- d) Variational effects in chemical reactions.
- II. General methodology to calculate  $k^{CVT/MT}(T)$ 
    - a) Direct Dynamics calculations: Computational protocol.
    - b) Quantum corrections: Generalized frequencies along the reaction path.
    - c) Quantum corrections: Multidimensional Tunneling (MT) transmission coefficient.
    - d) Kinetically equivalent pathways.
  - III. Application to atmospheric chemical reactions
    - a) Arrhenius parameters: Activation energies and preexponential factors.
    - b) Kinetic isotope effects.
    - c) Multiwell reactions.

#### **Abstract:**

In this lecture the physical basis of Variational Transition State Theory (VTST), including Multidimensional Tunneling (MT) corrections, will be explained. The computational protocol for the calculation of rate constants in the gas-phase as a function of temperature will also be outlined. Finally, the application of VTST/MT will be illustrated by the comparison with experimental kinetic data of some atmospheric reactions.

**MDS 3- Introduction to Classical Molecular Dynamics (N. Faginas)**

*Dr. Faginas-Lago, Noelia*

*Dipartimento di Chimica, Biologia e Biotecnologie*

[noelia.faginaslago@unipg.it](mailto:noelia.faginaslago@unipg.it)

## Outline:

- Introduction to Classical Molecular Dynamics
- The Mechanics of Molecular Dynamics.
- Statistical Mechanics
- Integration Algorithms
- The Calculation of Forces and Torques.
- A portable intermolecular potential for molecular dynamics studies
- Coulombic Forces
- Calculating the Pressure
- Molecular Dynamics Methodology
- Applications and visualization development—hands on (test cases)

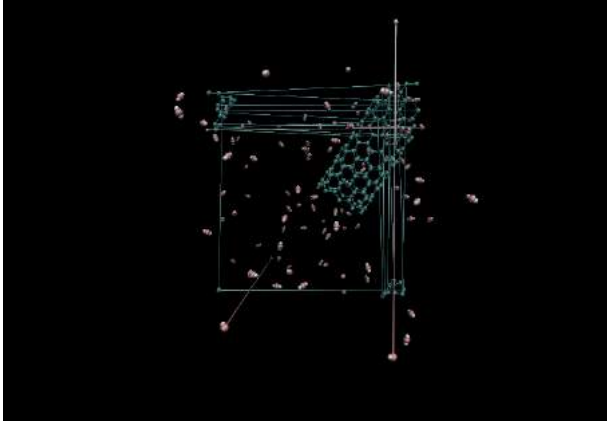
## Abstract:

The molecular dynamics describes the time evolution of molecular systems using classical mechanics. Molecular dynamics is, a computational method and its application represents a simulation of the system of interest. It is necessarily computational because an analytical solution for the dynamics of many interacting particles is mathematically impossible. Thus the solution offered by molecular dynamics is inevitably numerical in nature.

At heart molecular dynamics is an attempt to solve the classical equations of motion for a system composed of atoms and molecules with the aim of obtaining the time evolution of the system. The method is most often applied to condensed phase systems i.e. systems in the solid or liquid state, where the objective is to learn something about how the bulk properties of the system arise from the molecular basis. The time evolution aspect of molecular dynamics distinguishes it from the Monte Carlo method, in which the molecular system evolves through a stochastic or random-walk process rather than a true dynamical process.

This gives molecular dynamics a handle on time dependent properties, which means it is particularly useful for exploring transport properties, such as diffusion, thermal conductivity and

viscosity, or aspects of spectroscopy, such as solvation induced spectral shifts, or the kinetics of chemical processes – all areas in which the dependence on time is the key factor.



**Illustration of the Periodic Boundary Conditions using DL\_POLY package[1] for a SWCNT simulation.**

[1] [http://www.ccp5.ac.uk/DL\\_POLY/](http://www.ccp5.ac.uk/DL_POLY/)

## ***MDS 4- Introduction to Classical Molecular Dynamics-(II) (A. Lombardi)***

Molecular dynamics modeling: from few- to many-body systems

Andrea Lombardi

*Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8,  
06123 Perugia, Italy*

### **Outline**

-Background theory

-Building molecular models

*Representation and choice of coordinates*

*Modeling of the interactions: intra- and intermolecular forces*

-Intermolecular forces

*Construction of potential energy surfaces and link to experimental measurements*

*Weak interactions in large molecules*

*Case study: simulations of molecular energy transfer (hands on)*

-Reduced dimension models

*Case studies: Berry pseudorotation, chirality changing pathways (hands on)*

### **Abstract:**

The study of many striking problems of chemistry and biochemistry requires theoretical modeling based on classical dynamics simulations, which can be highly demanding in terms of computing resources. To proceed brute force, simplified representations are usually adopted for the simulations to be feasible, relying on the tacit assumption that an exhaustive statistics generated by massive computation would replace the missing accuracy. The obvious drawback in such practice is that a simple model may miss essential features of the system under concern. To obtain more realistic and physically meaningful simulations, theoretical chemists are therefore at the continuous search for new more accurate models, through the comparison with experiments and the practice of alternative approaches.

In these lectures we consider a bottom-up approach to the design of realistic models and simulations, ideally starting from few-body systems and moving to larger ones, such as mid-size organic molecules, clusters and prototypical biological molecules. We will consider the most sensitive points and concerns, such as the dimensionality of the model and the choice of coordinates (reduced-dimension models), the description of the interactions, especially intermolecular interactions, the search for global variables, indicators and pathways in phase

space to efficiently describe complex dynamics behavior and phenomena involving many atoms at once (e.g. folding and phase transitions).

## ***MDS 5- Modelling Chemical Reactivity by Hybrid QM/MM MD Simulations (V. Moliner)***

Molecular Dynamics Simulations in Modeling Biochemical Processes.

Vicent Moliner  
Departament de Química Física i Analítica.  
Universitat Jaume I  
12071 Castellón, Spain

### **Outline:**

#### Overview – Lectures

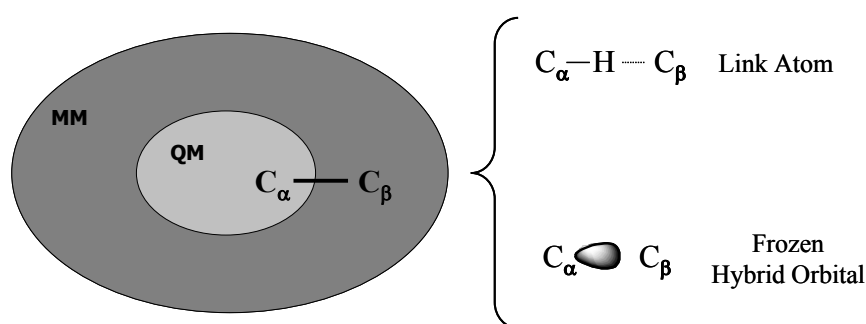
- I. From Quantum Mechanics (QM) and Molecular Mechanics (MM) to the QM/MM schemes.
- II. Exploring Potential Energy Surface (PES)
- III. Statistical Simulations: Exploring Free Energy Surface (FES)
- IV. Examples
- V. Year 2017: The State of the Art

### Summary:

Historically, first theoretical insights into large biological systems such as enzymes, DNA or RNA were obtained through gas phase calculations, using standard programs of quantum chemistry, assuming the invariance of the transition structures. However, the properties of stationary structures of reactions taking place in biological processes can be different from those obtained in the gas phase and, obviously, the interaction energy with the environment is not considered in these calculations. A better understanding was obtained including a small part of the active centre into the calculations. The problem is that in this case the optimised structures did not always fit into the enzyme active site. An approximate solution was obtained anchoring some key atoms of the enzyme to their crystallographic positions and optimising the rest of the coordinates of the model. The computational cost of these calculations rapidly increases as more atoms of the environment are explicitly included. Linear-scaling quantum methods can be used to partially avoid this bottleneck.

In the aforementioned strategies the enzyme flexibility and long-range effects on the nuclear and electronic polarisation of the chemical system by the environment are not easily incorporated. Shortly after those first gas phase calculations, there was a major breakthrough that included the enzyme in the calculations.<sup>1</sup> Although this approach was ignored for long time, now it is the most popular computational methodology to study enzymatic reactions, which is based on the

combination of quantum mechanics and molecular mechanics. In these methods the quantum mechanical (QM) description is reserved to a small portion of the system, the region where the most important chemical changes (i.e. bond breaking and forming processes) take place. The rest of the system can be described by means of molecular mechanics (MM) potentials. In this way a very large number of atoms can be explicitly considered in the calculations. The division of the full system in two subsystems may require cutting a covalent bond. Different techniques<sup>2</sup> have been developed to treat this problem, fulfilling the valence of the quantum atom placed in the boundary with hydrogen atoms or frozen orbitals (see Figure 1). The combination of these two levels, by means of the appropriated coupling terms, is generically known as hybrid QM/MM methods<sup>1,3</sup>. In this way the wave function of the quantum subsystem, and thus any related property, can be obtained under the influence of the environment.



**Figure 1.** In QM/MM methods the subsystem is divided into a QM part and a MM part. The QM subsystem must include all those atoms directly involved in the bond breaking and forming process. This partition may require cutting a covalent bond (between a QM atom  $\alpha$  and a MM atom  $\beta$ ) in the boundary and thus special techniques should be applied to fulfil the valence of the QM atom ( $\alpha$ ).

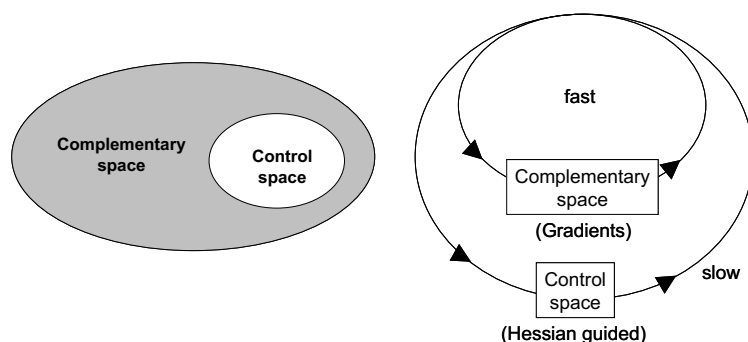
#### Exploring Potential Energy Surfaces

The existence of this QM/MM potential energy function, which combines reliability and computational efficiency, is not the only requirement to deal with chemical reactions. To describe such a process we should be able to locate and characterize the set of stationary structures (reactants, products, transition state and possible intermediates) that defines a particular reaction mechanism. This is complicated by the large dimensionality of the Potential Energy Surface (PES) when the environment is explicitly included. Most of the programs using hybrid calculations contain algorithms to locate energy minima. Several approximate strategies have been proposed to locate these structures. In the simplest one only the positions of the QM atoms are varied while the MM part remains frozen at some particular positions obtained from x-ray data or previous optimisations. A more accurate way of optimising the relevant structures is to allow also the relaxation of the environment coupled with the chemical system. However, this simulation is computationally taxing.

In a first approximation to follow a chemical process a distinguished geometrical coordinate can



be chosen and energy minimisations would be carried out for different values of this coordinate. Obviously, this procedure can not be always convenient as far as the true reaction coordinate can be different from the selected distinguished one. The direct location of transition structures is even more difficult and is not included in all commercial programs. The high dimensionality of the surface prevents the calculation of the full Hessian matrix and thus the proper location and characterization of saddle points of index one. Recently some algorithms have been proposed to calculate approximate Hessians for chemical processes in very large systems<sup>4</sup>. For example, a reduced Hessian matrix can be defined containing only the relevant coordinates for the chemical process under study. The difference is that the Hessian matrix now guides the geometrical search and thus second derivative based optimisation methods can be employed to explore the selected coordinates while the rest is minimised at each step of this search. The procedure is schematically shown in Figure 2. The stationary structure obtained in this way can be characterized as a true stationary structure (all the first derivatives are equal to zero) and having the correct number of imaginary frequencies in the approximate Hessian matrix (i.e zero for minima and only one for transition state). From this structure the transition vector and reaction paths can be defined and used to get relevant knowledge about the reaction mechanism.



**Figure 2.** Stationary structures in very large systems can be located and characterized using a partition of the coordinates space into the control space (all the geometrical variables with a significant contribution to the reaction coordinate) and the complementary space (the rest of coordinates). A reduced Hessian matrix is calculated for the control space and used to guide the search of the stationary structure. At each step of the search the complementary space is minimised using only gradients. The obtained structure is thus a stationary point on the PES (all gradients are zero) and it contains the correct number of imaginary frequencies) in the control space.

#### Statistical Simulations: Exploring Free Energy Surfaces

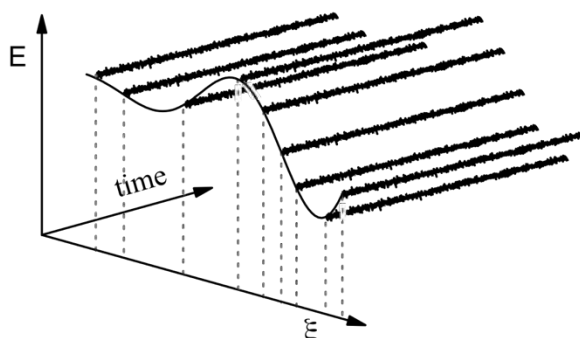
One substantial difference between gas phase and condensed media reactions is that in the former, the reactant, the product and the transition state usually correspond to well-defined single structures. Thus thermodynamic properties can be obtained applying standard formulae to the different energy levels of these structures. In solution or enzymatic environments exploration of the PES is not enough to get magnitudes directly comparable to experiment. The PES contains a myriad of stationary structures mainly due to the great number of possible conformations accessible to the enzyme and the solvent molecules. Thus, a statistical ensemble of minima and transition structures must be explored to properly define the reactant, product and transition

states. Simulations can be carried out using Monte Carlo or Molecular Dynamics methods obtaining detailed information from which averaged and thermodynamical properties can be derived.<sup>5</sup> In particular, free energies associated to the transformation from the reactant state to the transition state (the activation free energy) and to the product state (the reaction free energy) can be extracted using different techniques applied to molecular simulations.<sup>6</sup>

One of the most popular techniques to get reaction free energy profiles for enzymatic reactions is the quantum mechanics-free energy perturbation (QM-FEP) method developed by Kollman and coworkers<sup>7</sup>. In this approach the reaction path is obtained for a gas phase model of the active site. Coordinates and charges of the chemical system are afterwards used into purely classical simulations where only the changes in the environment are sampled. Free Energy Perturbation (FEP) is then used to get the reaction and activation free energies as the sum of the gas phase reaction energy and environment free energy contributions. The main advantage of this approach is that high-level quantum methods can be used for the gas phase calculations. The main drawbacks are: i) the lack of the chemical system flexibility contribution to the free energy and ii) during the simulation of the reaction path, the environment is not incorporated in the calculation. A similar but more coupled scheme is obtained if the reaction path is determined in the active site by means of QM/MM iterative optimisations along a distinguished coordinate<sup>8</sup>.

Free energies profiles can be also obtained as a Potential of Mean Force (PMF) appearing along a particular reaction coordinate<sup>5</sup>. Selection of this reaction coordinate should be based on the exploration of the PES including the environment, or even better, on IRCs traced down to the corresponding products and reactants valleys from transition structures located and characterized in the enzyme active site. The umbrella sampling method is used to place the chemical system at different values of the reaction coordinate that cannot be enough frequently sampled by thermal fluctuations. This is done by adding an adequate parabolic energy function centred at the value of the reaction coordinate that is to be explored. Simulations are then carried out sampling all the degrees of freedom of the system except for the reaction coordinate (see Figure 3).

Once the reaction coordinate has been fully explored from reactants to products, the total probability distribution function is obtained and thus the free energy profile is calculated. Furthermore, averaged properties can be derived from the dynamics obtained on the maximum and the minima regions of the PMF profile, characterizing in this way the transition and reactant and product states, respectively. The main advantage of this technique is then the inclusion of all contributions to the free energy but this require a very large number of energy evaluations. These calculation are expensive and nowadays restricted to semiempirical hamiltonians<sup>3</sup> or empirical valence bond (EVB)<sup>9,10</sup> methods. This latter can be fitted to gas phase ab-initio surfaces and charges and then transfer this information in a consistent coupled way to FEP calculations in solution or enzymes.



**Figure 3.** The PMF is obtained by means of a series of molecular dynamic simulations where all the degrees of freedom but a distinguished reaction coordinates are sampled. Umbrella sampling is used to place the system at an adequate value of the reaction coordinate ( $\zeta_0$ ) and then Monte Carlo or Molecular Dynamics simulations are run. The fluctuations of the reaction coordinate are finally pieced together obtaining the full distribution function and thus the free energy profile.

### Examples

After presenting the different computational methodologies used to simulate enzymatic processes, we have selected an example of an enzyme reaction that has been used by most of the previous cited authors to explain the origin of the enzyme catalysis.

### Year 2017: The State of the Art

The unit will be closed with an overview of alternative methods used to study reactivity in large systems, with special attention to those methods that are based on the use of a collective reaction coordinate involving not only the reaction system but also the solvent degrees of freedom. This work was pioneered by Marcus, who used a generalized coordinate to measure the electric field generated by the solvent coordinates as a reaction coordinate to drive an electron transfer.<sup>11</sup> The electric field contributes to the energy difference or gap between two different states of the solute that differ in their charge distribution. The energy gap between the reactants and the product states of a given reaction can be also used as a collective coordinate, involving solute and solvent degrees of freedom, to drive a particular reaction and then to obtain the corresponding free energy profile. Latest methods employed in this sense will be presented to close the unit.<sup>12</sup>

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## ***MDS 6 - Quantum and Classical Molecular Dynamics (G. Worth)***

Graham Worth  
University College of London

### Outline:

Molecular dynamics (MD) simulations have become an essential tool to help interpret experimental data in terms of the underlying molecular motion. In these lectures we will look at the basic theory of MD and how it is applied to fundamental processes.

The following topics will be covered in the 4 sessions:

1. Introduction to chemical physics (elementary processes, spectroscopy and electronic transitions, molecular collisions and chemical reactivity)
2. Born–Oppenheimer approximation and beyond
3. Quantum methods using wavepacket propagation
4. Classical methods based on swarms of trajectories
5. Examples of application

### Abstract:

The introduction will give an overview of fundamental chemical processes and how information on these can be obtained by experiment. The following parts will develop the theory.

The starting point for a description of a molecular system is the time-dependent Schrödinger equation (TDSE). Using the Born–Oppenheimer approximation we are able to integrate out the electronic motion and focus on the nuclei. The validity of this approximation and what to do when it breaks down will be discussed in part 2. In part 3 methods will be developed to solve the TDSE directly. These are known as wavepacket dynamics and in addition to standard methods, a particularly powerful algorithm, the multi-configurational time-dependent Hartree (MCTDH) method.

Unfortunately wavepacket dynamics can only treat very small systems (typically 3–4 atoms). For this reason approximate methods based on classical trajectories have been developed. In part 4 it will be shown how trajectory simulations relate to the full quantum mechanical solution.

Throughout the lectures examples will be given of calculations to show problems and limitations. In the associated workshops there will be a chance to run some simple simulations.

While there are many textbooks on classical mechanics and on quantum mechanics, few books are based on the TDSE. Ref. [1, 2] are 2 general textbooks that do just that. Ref. [3] details the MCTDH method with applications of wavepacket dynamics calculations. Ref. [4] is a review article which covers the swarm of trajectory approach. Ref. [5] is a recent book on describing reactivity.

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## •• ACT (Advanced Computational Techniques)

### ***ACT 1- Modelling the energy spectra of some nanosystems under different conditions (J. Planelles)***

J. Planelles

Departament de Química Física i Analítica

Universitat Jaume I

Castelló de la Plana, E12080, Spain

#### **Outline:**

Quantum dots: periodicity, spatial confinement and external fields

T1: Quantum dots

1. What is a quantum dot (QD)?
2. Translational symmetry. Bloch functions. Energy Bands.
3. The  $k \cdot p$  model.
4. Heterostructures: envelope function approximation (EFA).
5. Numerical integration (finite differences) of the  $kp$ -EFA eigensystem of an excess electron (or hole) in a QD.
6. Stochastic methods to solve eigenvalue equations in a variational manner.

T2: Quantum dots in a magnetic field

1. The Hamiltonian. Where does it come from?
2. Lagrange equations with velocity-dependent potentials.
3. A quantum disk in a magnetic field.
4. Multiple-connected quantum systems: Aharonov-Bohm effect.
5. Case study: effects on the energy spectrum of a beam of magnetic flux restricted to a small area inside, outside and piercing the ring.

T3: Hands on: Simulating the Energy Spectrum of Quantum Dots

1. A single-excess electron (or hole) in a QD.
2. A single-excess electron (or hole) in a QD pierced by a magnetic field.
3. Many-particles in a QD. Introduction to stochastic variational Monte Carlo (VQMC) method.

#### **Abstract:**

A quantum dot is a small crystal of nanometric size. It is built of a huge amount of electrons and nuclei. As in macroscopic crystals, atoms inside quantum dots are arranged according to an ordered pattern, displaying microscopic periodicity. However, nanocrystals and macroscopic

crystals display quite different behaviour and properties. In a macroscopic crystal, despite its finite size, most of the properties are bulk-like. At the electronic scale, macroscopic crystal is so huge that electrons see the crystal border as if located at infinity. This allows to fully exploiting translational symmetry, drastically simplifying its quantum mechanical description. If we now introduce a heterojunction (or consider a nanocrystal) we still have local periodicity. However, the border is no longer felt at infinity. Instead, we may consider the border effect as a potential superimposed to the crystalline periodic potential. This extra potential is extremely smooth at the scale of a lattice constant. Physically, it behaves as a confining potential which renders a discrete character to the electron energy structure. The possibility to precisely control the size of a quantum dot enables to determine the wavelength of the absorption and emission, which in turn determines the colour of light the human eye perceives. Quantum dots can therefore be tuned during production to emit any desired colour light. The smaller the dot, the closer it is to the blue end of the spectrum, and the larger the dot, the closer to the red end. Quantum dots can even be tuned beyond visible light, into the infra-red or into the ultra-violet. In addition to this potential, hereafter referred to as spatial confining potential, externally applied fields or just the presence of interfaces may bring about additional sources of confinement, as the magnetic confinement. We can therefore understand why quantum dots are called artificial atoms, as the manufacturer can tune its properties in the fabrication process or/and by means of appropriate external sources of confinement. Along two lectures, we will provide a bird's eye view on periodicity and spatial and magnetic confinements on quantum dots. The aim of these talks, more than introducing the world of nanosystems is to revisit some basic knowledge viewed from and used for solid state and nanoscience oriented to the hands on session where some toy-models will be studied.



## 1. QUANTUM DOTS

## 1.1. Crystal structure: Translation symmetry

The periodicity of a crystal, i.e., the existence of a lattice, is related to the translation symmetry and has profound consequences in the physical behaviour and the electronic structure of solids. For example, the observable electronic density  $\rho(\mathbf{r})$  is periodic ( $\rho(\mathbf{r}) = \rho(\mathbf{r}+\mathbf{t})$ , with  $\mathbf{t}$  a translation vector). The square of the modulus of the wave function then is periodic, and therefore the wave function is periodic up to a phase. These phases are precisely the characters of the irreducible representations (irreps) of the translation group (since translations commute, the translation group is commutative, so all its irreps are one-dimensional). The linear momentum is the generator of translations ( $\hat{T}_n = e^{i a n \hat{p}}$ ). Then, its eigenfunctions  $\{e^{i k x}\}$  can be used as basis of the irreps, the calculation of their characters and the associated quantum number  $k$  as label for these irreps. However, while  $k$  can assume the value of all possible finite real numbers, the number of non-equivalent irreducible representations of the translation group is much smaller because  $e^{i k a} = 1$ , where  $a$  is a point of the Lattice, that means  $e^{i k x} = e^{i k(x+a)}$ , i.e.,  $k$  and  $(k+a)$  are the same irrep as they have the same set of characters. We see then that for each point of the direct Lattice ( $a$ ) there is a point  $k$  in the so-called reciprocal space (units 1/length). The full set of  $k$  points form a lattice whose unit cell is known as the first Brillouin zone. The reciprocal lattice is extremely useful in the study of crystals.

## 1.2. Translations in 3D: Bloch functions

The extension to three dimensions implies replacing  $x$  by  $\mathbf{r}$  and  $k$  by  $\mathbf{k}$ . Now the label of the three-dimensional translation group is not a number  $k$  but a vector  $\mathbf{k}$ . The most general basis of the irreps are the so-called Bloch functions:  $\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} u(\mathbf{r})$ ;  $u(\mathbf{r} + \mathbf{a}) = u(\mathbf{r})$ . We also can define in 3D the reciprocal lattice and identify the labels of all non-equivalent irreps within the 3D first Brillouin zone.

## 1.3. Solving the Schrödinger equation

In order to solve the Schrödinger equation of a crystal we use translational symmetry and the characters of the irreducible representation to set the required boundary conditions: since  $\hat{T}_a \Psi(\mathbf{r}) = e^{i k a} \Psi(\mathbf{r})$  then,  $\Psi_{\mathbf{k}}(-a/2) = e^{i \phi} \Psi_{\mathbf{k}}(a/2)$ ,  $\phi \in [-\pi, \pi]$ . We solve the Schrödinger equation for each  $k$  value and find a set of low-lying eigenvalues. The plot vs.  $k$  of the  $n$ -th eigenvalue,  $E_n(k)$ , represents an energy band.

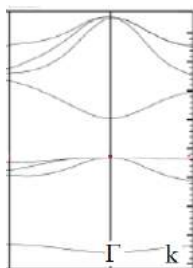


Figure 1.1: energy bands

## 1.4 Energy band structures

As a starting point to study the energetics of crystal solids, we consider an electron travelling along the crystal. The quasi-free electron feels the Coulomb potential exerted by the lattice ions as a perturbation. This kind of carriers is responsible for most of the solid's collective properties. Let us first assume that the kinetic energy of the electron greatly exceeds the potential,  $\epsilon \gg V$  (empty lattice). The Hamiltonian describing the system and its solutions are given by:

$$\frac{p^2}{2m} \Psi(\vec{r}) = \epsilon_k \Psi(\vec{r}), \quad \Psi(\vec{r}) = N e^{i\vec{k}\vec{r}}, \quad \epsilon_k = \frac{\hbar^2 k^2}{2m}.$$

With  $p = \hbar k$  the linear momentum and  $N$  the normalization constant. Such a wave function is known as plane wave, and its energy structure vs  $k$  is shown in figure 1.3a. At zero temperature, the electrons in a solid will occupy the lowest orbitals allowed by the Pauli's exclusion principle, from  $k=0$  till  $k=k_F$ . We then define the Fermi energy as  $\epsilon_F = \hbar^2 k_F^2 / 2m$ .

Let us next include the lattice as a weak perturbation. It can be shown that electrons will not feel the lattice unless  $k \sim \pi/a$ , where  $a$  is the lattice constant. If,  $k \sim \pi/a$ , the plane wave experiences Bragg reflection. This leads to forbidden values of  $k$ , where energy gaps appear (figure 1.2b). Depending on the magnitude of the gap and the position of the Fermi energy, we classify solids as insulators, semiconductors and conductors (metals) –figure 1.2c–.

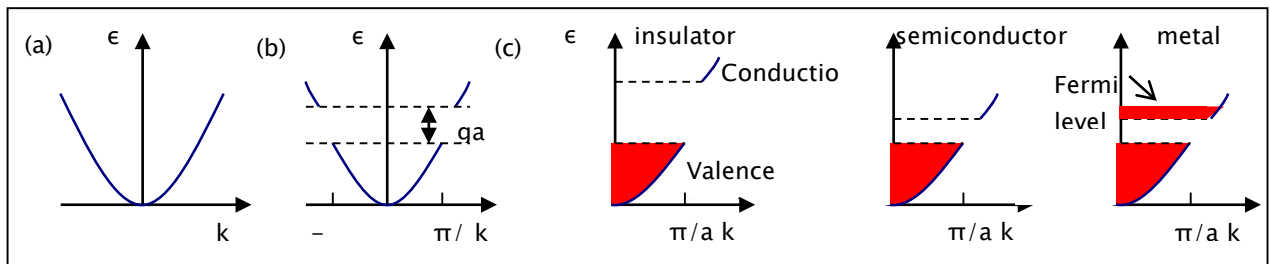


Figure 1.2.

## 1.5 The $k \cdot p$ model. Effective mass.

A computationally affordable yet reliable description of many semiconductor crystal is obtained using the  $k \cdot p$  method. The idea is to project the crystal Hamiltonian,  $H = p^2/2m + V_{cr}(\mathbf{r})$ , onto a general Bloch function  $\psi(\mathbf{r}) = N e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ . After operating and left-multiplying by  $e^{-i\mathbf{k}\mathbf{r}}$ , one gets the  $k \cdot p$  Hamiltonian:

$$\left( \frac{p^2}{2m} + V_{cr}(\vec{r}) + \frac{\hbar^2 k^2}{2m} + \hbar \mathbf{k} \cdot \mathbf{p} \right) u_{nk} = \epsilon_{nk} u_{nk}$$

If we have some information about  $u_{nk}$  at a given point  $k=0$  ( $\Gamma$  point, at the centre of the Brillouin zone), we can solve the Hamiltonian perturbationally for  $k$  near  $k=0$ . To this end, we expand the Hamiltonian in terms of a basis of functions  $u_{nk}(\mathbf{r}) = \sum_n c_{nk} u_{n0}(\mathbf{r})$ . A general matrix element is of the form:

$$\langle u_{n0} | \hat{H}_{kp} | u_{l0} \rangle = \left( \epsilon_{n0} + \frac{\hbar^2 k^2}{2m} \right) \delta_{nl} + \frac{1}{m} \vec{k} \cdot \vec{P}_{nl}$$

Where  $\epsilon_{n0}$  is the energy gap and  $\vec{P}_{nl} = \langle u_{n0} | \mathbf{p} | u_{l0} \rangle$  is the Kane parameter. Both magnitudes can be inferred from spectroscopy experiments. Depending on the number  $n$  of functions in our basis, we speak about  $n$ -band  $k \cdot p$  models. Typical models employed to describe zinc-blende semiconductors are the 1-band model for conduction electrons, 4-band model for valence holes

and 8-band model to include coupling between conduction and valence bands.

The 1-band model (all models indeed) is usually solved up to second-order perturbation theory, leading to energies:

$$\varepsilon_{nk} = \varepsilon_{n0} + \sum_{\alpha=x,y,z} \frac{k_{\alpha}^2}{2} \left( \frac{1}{m} + \frac{2}{m} \sum_l \frac{P_{nl}^{(\alpha)2}}{(\varepsilon_{n0} - \varepsilon_{nl})} \right) = \varepsilon_{n0} + \sum_{\alpha=x,y,z} \frac{k_{\alpha}^2}{2m_{\alpha}^*}$$

Note that the energy is simply that of a free electron but with an effective mass  $m^*$ , which depends on the coupling with other bands. The effective mass can have small and even negative values, which leads to lots of interesting physics in semiconductors.

### 1.6 Heterostructures. Quantum wells, wires and dots.

So far, we have considered homogeneous crystals. However, current semiconductor research is largely focused on semiconductors made of different materials. How do we model a system with two semiconductor crystals A and B (figure 1.4a)? If both materials have the same crystal structure and similar lattice constant, one usually employs the envelope function approximation. We replace the usual Bloch function by:  $\psi(\mathbf{r}) = N e^{i\mathbf{k}\cdot\mathbf{r}} \chi(z) u_{\mathbf{k}}(\mathbf{r})$ , where  $\chi(z)$  is an unknown function in the direction where the translational symmetry has been broken. Noteworthy,  $f(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \chi(z)$ , varies slowly as compared to the unit cell function  $u_{\mathbf{k}}(\mathbf{r})$ . Thus, it is often referred to as the envelope function, which is modulated inside each unit cell by  $u_{\mathbf{k}}$ . Next, one proceeds as in the homogeneous case, with the additional consideration that the integral  $\int_{\Omega} f(\mathbf{r})u(\mathbf{r}) d\mathbf{r}^3 \approx 1/\Omega (\int_{\Omega} u(\mathbf{r}) d\mathbf{r}^3) (\int_{\Omega} f(\mathbf{r}) d\mathbf{r}^3)$ , with  $\Omega$  standing for the crystal volume. For a one-band model, eventually this leads to the eigenvalue equation:

$$\left( \frac{p_z^2}{2m} + V(z) + \frac{\hbar^2 k_{\perp}^2}{2m} + \varepsilon_0^A \right) \chi(z) = \varepsilon \chi(z),$$

where  $V(z)$  is the spatial confinement potential defined by the alignment between the band gaps of materials A ( $\varepsilon^A$ ) and B ( $\varepsilon^B$ ). As shown in figure 1.4b, for a B/A/B heterostructure the potential can be that of a quantum well, and the eigenstates  $\chi(z)$  the solutions particle in the box. Thus, semiconductor heterostructures provide the experimental realization of fundamental systems which had hitherto been but theoretical idealizations. It is also possible to fabricate heterostructures where translational symmetry is broken in two and three directions of the space, which gives rise to quantum wires and quantum dots, respectively. Of particular interest are quantum dots, where a strong spatial confinement in the three directions leads to discrete energy levels, very much as in atoms. Because of this quantum dots are often referred to as artificial atoms or macroatoms. Unlike natural atoms, however, quantum dots can be built with different sizes, shapes and composition, so that the energy spectrum is designed at will. This has opened great prospects for fundamental research and technological developments over the last decades.

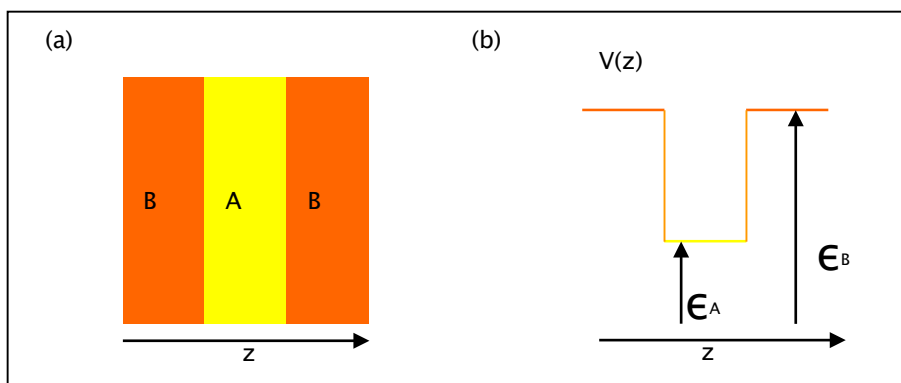


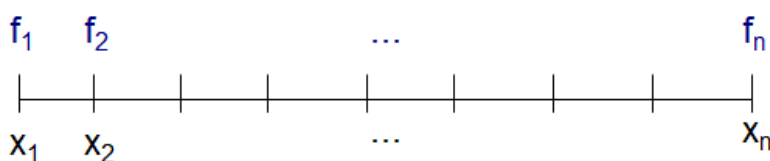
Figure 1.3.

## 1.7. A toy-case: solving a differential eigenvalue equation with finite differences

We will present here a toy example. We will address cases more sophisticated in the hands on session. Let us consider by now the simple case of stationary states of a particle in a box with finite walls defined by the equation:

$$\left[-\frac{1}{2m} \frac{d^2}{dx^2} + V(x)\right]f(x) = E f(x)$$

Then, we define grid in the coordinate domain:



and approximate the analytical  $f(x)$  by a numerical list  $\{f_i\}$  defined on the grid. The goal of finding the analytical  $f(x)$  function solving the differential equation turns into the search of the numerical list  $\{f_i\}$  of  $f$ -values defined on the grid. The differential equation in a given node of the grid reads:

$$-\frac{f_i''}{2m} + V_i f = E f_i$$

Next, we approximate derivatives by finite differences:

$$f'(x_i) = f'_i = \frac{f_{i+1} - f_{i-1}}{2h} = \frac{f_{i+1/2} - f_{i-1/2}}{h}$$

where  $h$  is the grid step. The first definition allows defining the derivative on the grid nodes. The second one will be useful to find second derivatives, as follows:

$$f''(x_i) = f''_i = \frac{f'_{i+1/2} - f'_{i-1/2}}{h} = \frac{f_{i+1} + f_{i-1} - 2f_i}{h^2}$$

These expressions replace derivatives on node  $i$  by the values of the function on it and the nearest neighbor nodes. We can achieve better accuracy by employing information from further nodes. For example, the coefficients of the five-points second derivative,

$$f''_i = \frac{1}{h^2} (a f_{i+2} + b f_{i-1} + c f_i + d f_{i-1} + e f_{i-2})$$

can be determined by imposing that this derivative must be exact if  $f(x)$  is a polynomial of degree four. It is not difficult to find out the coefficient values:  $a = e = -1/12$ ,  $b = d = 4/3$  and  $c = -5/2$ . For the sake of easiness, we will employ 3-points finite differences in this example, thus yielding:

$$-\frac{1}{2mh^2}[f_{i+1} - 2f_i + f_{i-1}] + V_i f_i = E f_i$$

By grouping coefficients we have:  $b f_{i-1} + a_i f_i + b f_{i+1} = E f_i$ , a set of equations with  $i=2, n-1$  involving the function on the  $n$  nodes of the grid. The two boundary conditions ( $f_1 = f_n = 0$  in this case) close the system of equations:

$$\begin{array}{l} i=2 \rightarrow b \overset{0}{f_1} + a_2 f_2 + b f_3 = E f_2 \\ \vdots \\ i=n-1 \rightarrow b f_{n-2} + a_{n-1} f_{n-1} + b \underset{0}{f_n} = E f_{n-1} \end{array}$$

What remains is just solving this homogeneous system of equations that turns into the diagonalization of a tridiagonal matrix:

$$\begin{bmatrix} a_2 & b & & & \\ b & a_3 & b & & \\ & \ddots & \ddots & \ddots & \\ & & b & a_{n-2} & b \\ & & & b & a_{n-1} \end{bmatrix} \cdot \begin{bmatrix} f_2 \\ f_3 \\ \vdots \\ f_{n-2} \\ f_{n-1} \end{bmatrix} = E \begin{bmatrix} f_2 \\ f_3 \\ \vdots \\ f_{n-2} \\ f_{n-1} \end{bmatrix}$$

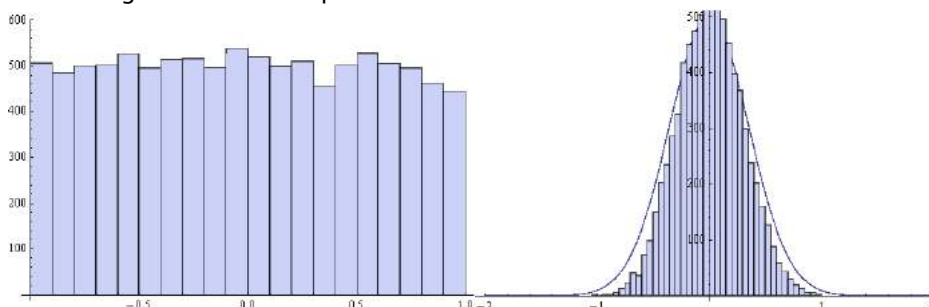
## 1.8. Stochastic methods to solve eigenvalue equations in a variational manner.

The energy spectrum of multiexcitations in a QD is a many-body problem. Among the several methods employed to address the study of multiexcitations, we can say that, like in atoms and small molecules, the use of rather simple variational functions may provide accurate results. Solving a variational problem with a many-variable many-parameter wave function is a huge task that can be made feasible with the use of stochastic methods. We present an outline of the Variational Quantum Monte Carlo (VQMC) method applied to some toy-models. In VQMC one should carefully choose a trial wave function which depends on a set of variational parameters and then, evaluate the expectation value of the energy  $\langle E \rangle$  (a multi-dimensional integral).

$$\langle E \rangle = \frac{\int dR \Psi_{T,\alpha}^* H \Psi_{T,\alpha}}{\int dR |\Psi_{T,\alpha}|^2}$$

The technical problem is that this multi-dimensional integral must be evaluated many times as the program searches the position in the parameter space where the energy  $\langle E \rangle$  has a minimum. Stochastic methods build a sample of random numbers in the  $R$  domain of coordinates. Then, averages the integrand on the sample and estimates the energy accuracy by means of the associated variance. It should be said that by using random numbers uniformly distributed across the  $R$  domain of coordinates, information is spread all over  $R$  so that regions of very high and very low probability are treated on equal foot. A simple transformation allows Monte Carlo to generate far better results: drawing random numbers from non-uniform density  $|\Theta|^2$ . How to do it? By using a Metropolis-like algorithm. This algorithm generates a random walk in the  $R$  domain

modulated by the transition probability  $w(r_i \rightarrow r_j)$  whose asymptotic probability approaches  $|\Theta|^2$  after a large number of steps.

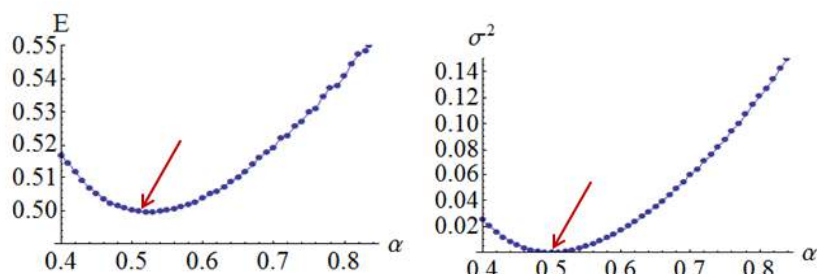


On the left of the above figure we show a histogram of 10.000 calculated random numbers uniformly distributed in the domain  $(-1,1)$ . The histogram on the right shows 10.000 random numbers distributed according to a non-uniform density  $|\Theta|^2$  in the domain  $(-1,1)$ , calculated using the Metropolis algorithm.

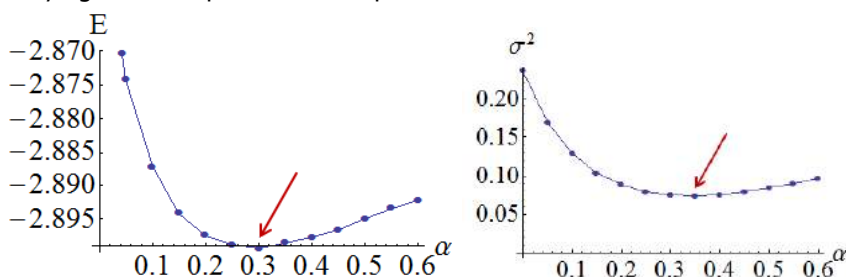
We will introduce VQMC using the toy models of one-dimensional harmonic oscillator and the helium atom. In the former case, the form of the trial function will be a Gaussian with an unknown exponent. In the second, we will employ the following function,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-Zr_1} e^{-Zr_2} e^{\frac{\beta r_{12}}{(1+\alpha r_{12})}}$$

which depends on three variational parameters. To assure a high-quality wave function it is particularly important that the wave function satisfy the cusp conditions (R. T. Pack and W. B. Brown, J. Chem. Phys. 45 (1966) 556), representing the behavior of the exact wave function at the coalescence of two particles. It is achieved in the above function by setting  $Z=2$  and  $\beta=1/2$ .



On the left/right of the above figure, we show the profile energy/variance vs. the Gaussian exponent of the harmonic oscillator variational wave function calculated by means of 300 random walks with 10.000 steps. The next one corresponds to the He atom taking  $Z=2$  and  $\beta=1/2$  and varying  $\alpha$ . These profiles correspond to 500 random walks of 300.000 steps.



## 2. QUANTUM DOTS IN A MAGNETIC FIELD

### 2.1. Lagrange equations with velocity-dependent potentials

The concept of a Lagrangian  $L$  is introduced in order to reformulate classical Newton mechanics. In the case of conservative systems, the Lagrangian is defined as the velocity-dependent kinetic energy  $T$  of the system minus its coordinate-dependent potential energy  $V$ ,  $L=T-V$ , and the Lagrange equation,

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{x}} \right) - \left( \frac{\partial L}{\partial x} \right) = 0,$$

can be seen as a rewriting of the Newton law  $\frac{d}{dt}(p) - F = 0$ , as can be easily checked. When the potential does not depend on the velocity, kinetic momentum (velocity-derivative of the kinetic energy) and canonic momentum (velocity-derivative of the Lagrangian) coincide. In this case, the Hamiltonian (Lagrange transformation of the Lagrangian function) is just the total energy  $H=T+V$ .

When the potentials also dependent on velocity,  $U(x, v)$ , kinetic  $\pi$  and canonic  $P$  momenta are different and the Hamiltonian coincides with the kinetic energy. It can be check in the case of a particle in a magnetic field, described by the potential  $U = -e(v \cdot A)$ , with  $A$  being the potential vector, related to the magnetic field by the equation  $B = \nabla \wedge A$ . One can easily find

$$H = \frac{1}{2m} (p - eA)^2.$$

that  $p = \pi + eA$ , and that the Hamiltonian can be written as

### 2.2. Coulomb gauge and quantification

We can realize that, as far as  $\chi(x)$  is a scalar potential, two vector functions,  $A(x)$  and  $A(x) + \nabla\chi(x)$ , yield the same magnetic field (since  $\nabla \wedge \nabla\chi(x) = 0$ ). This means that we have some freedom to select the potential vector. Having in mind the transition to quantum mechanics, where momentum ( $-i\hbar\nabla$ ) and coordinate do not commute, it is customary to select  $\chi(x)$  such that it yields a null the divergence of  $A$  ( $\nabla \cdot A = 0$ ). This is called the Coulomb gauge. Assuming this gauge, the quantification ( $p \rightarrow -i\hbar\nabla$ ,  $x \rightarrow x$ ) of the Hamilton function yields

$$H = \frac{\hat{p}^2}{2m} - \frac{e}{m} A \cdot \hat{p} + \frac{e^2}{2m} A^2$$

In the case of a uniform axial magnetic field,  $B = B_0 \vec{k}$ , we can select a potential vector  $A = [-yB_0/2, xB_0/2, 0]$  and this equation turns into:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{e^2 B_0^2}{8m} \rho^2 - \frac{eB_0}{2m} \hat{L}_z, \text{ with } \rho = \sqrt{x^2 + y^2}.$$

### 2.3. Magnetic Confinement: Landau levels

By introducing the notation  $\omega = -eB_0/2m$ , the above equation can be rewritten as:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega^2\rho^2 + \omega\hat{L}_z = \frac{\hat{p}_z^2}{2m} + H_{HO}^{2D} + \omega\hat{L}_z$$

Since the two-dimensional harmonic oscillator Hamiltonian,  $\hat{H}_{2D}^{HO}$ , commutes with the z-component of the angular momentum,  $\hat{L}_z$ , in addition to the kinetic energy along z, the energy of the system is just  $E(m, M) = (2n + |M| + M + 1)\omega$ , where  $\omega$  is proportional to the magnetic field. These are the so-called Landau levels of a free electron in a uniform magnetic field. As we see, the energy levels grow linearly without crossings as the magnetic field increases.

#### 2.4. Spatial and magnetic confinement in quantum dots

When an additional, spatial confining potential co-exists with the magnetic confinement, the above Landau levels mix and we find out a competition between linear and the quadratic terms of the magnetic field. For example, the case of a spherical quantum dot in a homogeneous magnetic field is described by the following eigenvalue equation

$$\left( -\frac{\hbar^2}{2m_e}\nabla^2 + \frac{e^2 B^2 \rho^2}{8m_e} + \frac{eBM}{2m_e} + V_e(\rho, z) \right) \Phi_{n,M} = E_{n,M} \Phi_{n,M}$$

We find a very different behaviour for short/large radius, owing to the  $\rho^2$  factor appearing in the second term of the above equation. As a result, for small radius the response to the magnetic field is atomic-like (just an energy splitting due to  $W = -\mu B$ , see figure 2.1 a) while for larger systems one may envisage the formation of Landau levels for extremely large magnetic fields, where the magnetic confinement overpasses the spatial one -figure 2.1b-.

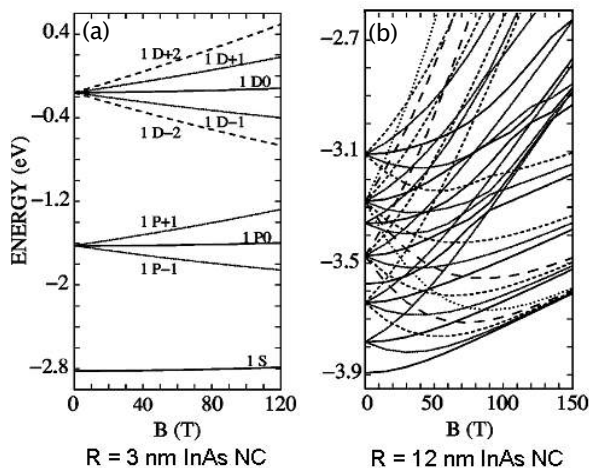


Figure 2.1

#### 2.5. Multiple-connected quantum systems: Aharonov-Bohm effect

The response of a system with a multiply connected topology, as for example a quantum ring, is even more complex, showing level crossings as the magnetic field increases. This is related to the so-called Aharonov-Bohm effect. In figure 3.2 (from J. Planelles, W. Jaskólski, and I. Aliaga, Phys.



Rev. B 65 (2001) 033306) we show the two low-lying bands of a prototypical InAs quantum ring.

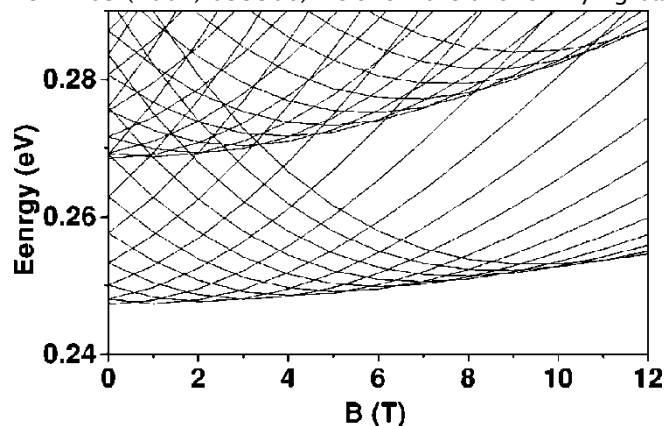
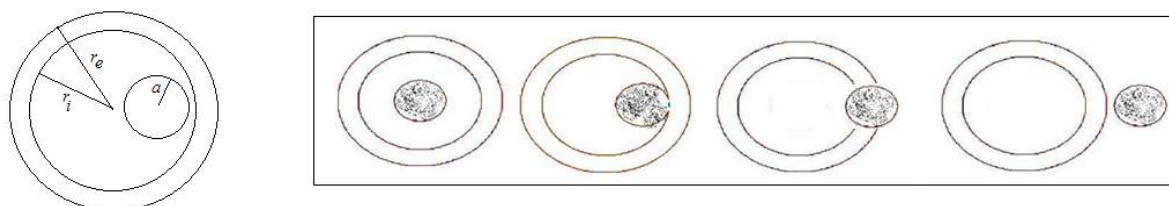


Figure 2.2

The most intriguing aspect of the Aharonov-Bhm effect is that these crossings can be predicted even in the case that the magnetic field pierces the inner hole of the ring only, i.e. no magnetic field acts on the ring section, the region where the electron is located. The mathematical reason comes from the fact that it is the potential vector and not the magnetic field itself that comes into the Hamiltonian, so that an electron can be influenced by the potentials even if no fields act upon it. The physical counterpart is a set of experimental observations that can only be understood as coming from this purely quantum effect without a classical correspondence.

2.6. Case study: effects on the energy spectrum of a beam of magnetic flux restricted to a small area inside, outside and piercing the ring.

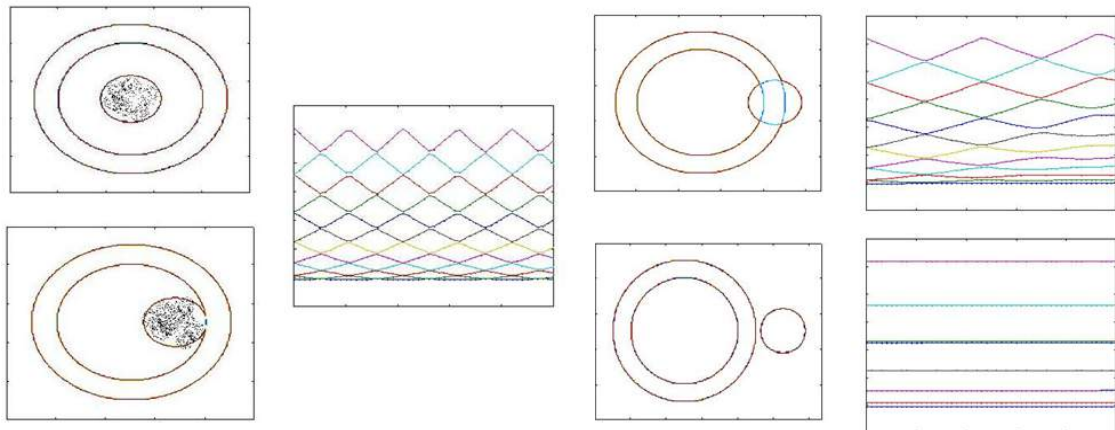


We consider a 2D quantum ring pierced by a magnetic field derived from the potential vector:

$$A = \begin{cases} \frac{1}{2} B_0 \rho \vec{u}_\phi & ; \quad 0 < \rho < a \\ \frac{1}{2\rho} B_0 a^2 \vec{u}_\phi & ; \quad a < \rho < \infty \end{cases}$$

It produces an axial uniform magnetic field crossing a circle of radius  $a$ , and zero everywhere else. We will consider the disk off-centered by an amount  $x_0$  from the center of a quantum ring. This destroys the axial symmetry we need two coordinates on equal foot to describe the system. For the sake of easiness we chose Cartesian coordinates. The eigenvalue equation of a particle in this ring is a two-coordinate homogenous partial differential equation. We assume that  $a < r_i$ , where  $r_i$  is the internal ring radius. We proceed to numerically integrate the eigenvalues differential equation for different values of  $x_0$ , from  $x_0 = 0$  up to  $x_0 > r_e + a$ , where  $r_e$  is the external ring radius. The results will show that the effect of the magnetic field (the Aharonov-Bhm effects) is independent of the off-centering of the magnetic disk if it is confined within the ring hole. The magnetic field does not affect the system if the magnetic disk is external to the ring and has a changing effect depending on how much the field pierces the region where the particle is confined (the ring). We will discuss the origin of this non-classical response of the particle in a ring to the

magnetic field.



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### 3. HANDS ON SESSION

The aim of this session is to introduce the students to the task of identifying a system, the Hamiltonian describing its physical behaviour and, then translate it into a differential equation, numerically integrate it and plot the results. To this end we propose a set of elementary examples of increasing difficulty. The first and most simple case of determining the bottom of the bands in a quantum well (or equivalently, the energy spectrum of a 1D QD) is fully developed and used to introduce some key matlab/octave commands that will be used in the later examples. Also, some basic on differences finites to numerically integrate differential equations, choice of appropriate boundary conditions, building up appropriate matrix representation and further diagonalization are outlined. Then the rest of examples are sketched with some hints.

**Exercise 1.** Write a code to calculate the electron energy spectrum of a 1D GaAs/AlGaAs QD as a function of the size. Consider GaAs effective mass,  $m^*=0.05$ , all over the structure. Justify the assumed simplification. The GaAs/AlGaAs band off set amounts 0.25 eV. Assume a well width  $L=25\text{nm}$ . Repeat the calculations for  $L$  ranging in  $[5, 50]$  nm and plot a few low-lying energies vs.  $L$ . Discuss the obtained results.

**Exercise 2.** Write a code to calculate the electron energy spectrum of two coupled GaAs/AlGaAs QDs as a function of their separation  $S$ .

**Exercise 3.** Write a code to calculate the electron energy spectrum of  $N=20$  coupled GaAs/AlGaAs QDs as a function of their separation  $S$ .

**Exercise 4.** Write a code to calculate the energies of an electron in a 2D GaAs/AlGaAs cylindrical quantum disk/ring with inner radius  $R_{in}$  and outer radius  $R_{out}$ , subject to an axial magnetic field  $B$ . The system (disk/ring) is made of GaAs. The surrounding matrix and inner hole of the ring is made of AlGaAs. Consider a finite width  $L_b$  for the surrounding AlGaAs matrix,  $L_b=10$  nm, (i.e., assume that beyond of this distance the wave function is zero). Calculate the energies as a function of  $B$  in the range 0–20 T, both, for a structure with  $(R_{in}, R_{out})=(0, 30)$  nm –i.e. a quantum disk– and for  $(3, 30)$  nm –a quantum ring–. Discuss the role of the linear and quadratic magnetic terms in each case.

**Exercise 5.** Write a code to calculate the energies of an electron in a 2D GaAs/AlGaAs quantum ring under the influence of a beam of magnetic flux restricted to a small area inside, outside and piercing the ring. Now since the system has no polar symmetry, no analytical partial integrations are possible so that the differential equation will be discretized in a two-dimensional grid.

**Exercise 6.** In general, the differential equation describing interacting carriers in a QD cannot be integrated numerically. Then a configuration interaction (CI) after the single-particle calculation is called for. Alternatively, for excitons and multiexcitons in a QD, appropriate variational functions may provide accurate results. The goal of this exercise is to write a variational Quantum Monte Carlo VQMC code to solve some toy-problems.

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## **ACT 2- Modern trends and challenges in high performance/high-throughput computing (O. Gervasi)**

Dr. Osvaldo Gervasi

Department of Mathematics and Computer Science, University of Perugia

Via Vanvitelli, 1/A 06123 Perugia, Italy.

email: [osvaldo.gervasi@unipg.it](mailto:osvaldo.gervasi@unipg.it)

*personal email:* [osvaldo.gervasi@gmail.com](mailto:osvaldo.gervasi@gmail.com)

The purpose of this group of lectures is to provide to the students an updated view about the available solutions for high performance/high throughput computing for scientist active in Molecular Science and Computational Chemistry domains.

The lectures will cover three main aspects:

1. Grid Computing
2. Cloud Computing
3. General Purpose GPU Computing

### **Grid Computing**

We will present the main aspects related to the Grid Computing Platform[1], in particular the European Grid Infrastructure (EGI) and the Virtual Organization CompChem[2], devoted to the Computational Chemistry Community.

The Grid Computing Infrastructure served several computational campaigns and showed very interesting properties for the disciplines having a strong need of computational resources.

Unfortunately the budget constraints and the management issues introduced severe limitations in the future of the Grid.

#### Cloud Computing

In the recent years the Cloud Computing paradigm provided to scientist new models for gaining computational resources at low price. The major IT companies are trying to acquire customers profiting of their data centers and making available several computational resources and services. Scientists may take advantage of the virtualization of resources which enables the researchers to access private, public and hybrid Cloud environments.[3,4]

#### General Purpose GPU (GPGPU) Computing

The development of GPUs, which are not only used for the 3D rendering but also as a powerful Single Instruction Multiple Data (SIMD) architecture for executing general purpose programs, made available to researchers new computing resources. To this end the OpenCL language, a standard, cross-vendor, programming language, made available heterogeneous resources composed by the GPU cores and the CPU cores.[5]

All programs executing the same instruction set on multiple data are candidate to explore such an innovative architecture.

Several research papers are investigating the possibility of interoperate the various available

computational platforms in order to provide the users with a flexible and optimized infrastructure[6].

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### ***ACT 3- Parallelization and magnetism. Localized and delocalized magnetic systems (J. M. Clemente)***

Juan M. Clemente-Juan  
Instituto de Ciencia Molecular, Universidad de Valencia,  
c/Catedrático José Beltrán, 2,  
46980 Paterna, Spain

Molecular magnetism is a comparatively new research area aimed at the design and the study of molecule-based magnetic materials which are interesting both from the point of view of their unusual physical properties and their importance for applications including high-density information storage and quantum computing. These compounds provide ideal opportunities to study basic concepts of magnetism and explore the new physical phenomena, such as quantum tunneling of magnetization, etc.

In this lecture, polyoxometalate chemistry compounds are going to be present in order to illustrate with examples of spin clusters, single-molecule magnets and mixed-valence clusters. Polyoxometalates (POMs) form a class of inorganic compounds that can incorporate a large number of magnetic centers at specific sites of the diamagnetic POM framework. In addition, they can be reversibly reduced to mixed-valence (MV) species (heteropoly 'blues' and 'browns') by injection of variable numbers of electrons. In the heteropoly blues these extra electrons are delocalized over a significantly large number of centers of the heteropoly framework. The high symmetry of these metal-oxide clusters framework facilitates the development of exact quantum-mechanical models from which a clear picture of the relevant parameters involved in the magnetic properties can be extracted.

As far as the spin clusters are concerned, we discuss that these systems constitute ideal models for studying the exchange interactions at the molecular level, allowing for the study of the exchange anisotropy in orbitally-degenerate metal ions (like Co(II)) using non conventional spectroscopic techniques as the inelastic neutron scattering.

Finally, as far as mixed-valence clusters are concerned, we discuss that POMs constitute one of the few chemical examples in which it is possible to quantitatively model the magnetic and electronic properties of these complex magnetic systems. Thus, exact solutions have been developed in some cases that provide important hints on the role played by the electron transfer processes on the magnetic properties of these clusters. For example, it has been shown that in these structures, electron delocalization can result in a strong antiferromagnetic coupling between widely separated blue electrons. On the other hand, we have shown that MV POMs can also have an important impact in molecular electronics, as they can provide examples of magnetic molecules in which an electric control of the spin-spin coupling might be possible.

At the same time with the examples, we present two powerful and efficient computational approaches to solve the exchange problem in high nuclearity spin clusters with all kind of exchange interactions (isotropic and anisotropic), including the single-ion anisotropic effects and

to solve the double exchange problem for high-nuclearity MV clusters containing arbitrary number of localized spins and itinerant electrons, respectively. This approach is based on the use of the irreducible tensor operators (ITO) technique. It allows evaluation of both eigenvalues and eigenvectors of the system, and then, calculation of the magnetic susceptibility, magnetization, or heat capacity, and also the inelastic neutron scattering spectra.



## ●● ACC (Applied Computational Chemistry)

### ***ACC 1 – Quantum and Statistical Methods to Model Solution Chemistry (E. Sanchez)***

Enrique Sánchez Marcos  
Departamento de Química Física  
Universidad de Sevilla  
e-mail:sanchez@us.es

#### Outline (CONTENTS: )

1. Introduction
  - 1.1 Basic Concepts
  - 1.2 Solvation Models
  - 1.3 Quantum Mechanical Definition of a Solution
2. Continuum Solvation Models
  - 2.1 Principles of Electric Polarization
  - 2.2 Quantum Mechanical Continuum Solvation Models
  - 2.3 Non-electrostatic Contributions to Continuum Solvation Models
  - 2.4 Molecular Properties of Solvated Systems
3. Discrete Solvation Models: the Inclusion of the Molecular Description of the Solvent
  - 3.1 General Approaches
  - 3.2 Classical and Quantum Models
  - 3.3 Solute-Solvent and Solvent-Solvent Interaction Potentials
  - 3.4 Quantum and Semiclassical Computer Simulations
  - 3.5 Molecular and Macroscopic Properties of Solvated Systems
  - 3.6 Free Energy Calculations
4. Applications of Solvation Models to Chemical Problems

#### Abstract:

Solution Chemistry is of great importance in Physics, Chemistry, Biology and Chemical Engineering. Most of chemical reactions or molecular structure determinations take place in a condensed phase, mostly in the liquid state. The large body of chemical knowledge is implicitly associated with the assumption that it is valid if an in-solution scenario is defined. Even more, Nature, Life and water are three intimately joined concepts since water acts as the solvent in which essentially all biochemical reactions take place. The term solvation refers to the surroundings of each dissolved molecule or ion by a shell of more or less tightly bound solvent molecules. More generally this term compasses the set of factors which allows the stabilization of a given minor component in

the bulk of another major component. When the solvent is water the term used is hydration. A molecular view of this type of system leads to the recognition that a huge number of molecules is involved in it, as soon as one realizes that solvation and solvent effects are a consequence of condensed medium effects.

The theoretical modeling of this type of system from first principles is not possible, since a huge number of degrees of freedom must be included in the total Hamiltonian of the solution. The system size needs the use of statistical concepts in solvent effect theories. At the molecular level, two extreme models of the phenomena can be distinguished.

In the first model, the solute molecule is described quantum-mechanically whereas the ensemble of solvent molecules is represented by a simplified uniform medium structure possessing dielectric properties, a polarizable dielectric continuum. It is through the dielectric behavior of the continuum that statistically averaged results are included in the model. A cavity, fitted to host the solute molecule, is created in the solvent, the charge distribution of the solute creates an electric field in its surroundings such as to polarize the continuum. As a consequence of the dielectric polarization, an electrostatic field appears inside the cavity. This is called the Solvent Reaction Field. This electrostatic field interacts with the charge distribution of the solute molecule and the total free energy change corresponding to this interaction could be called the solute-solvent purely electrostatic contribution. Apart from the electrostatic contribution to the solvation energy, non-electrostatic solute-solvent interactions must be included to complete the continuum model. The dispersion, cavitation and repulsion terms are relevant contributions. The analysis of the polarized wavefunction of the solute and the application of quantum-mechanical operators allow the determination of molecular properties for the solvated molecule-in-solution, and via comparison with gas-phase results, theoretical estimations of solvent effects can be computed.

In the second extreme model, the solvent is represented as a collection of molecules because: (i) specific solute-solvent interactions are mainly responsible for the solvent effects on the solute or other properties of the solution; (ii) an understanding of solvent structure or other collective properties is required. This approach leads to a massive increase in the number of freedom degrees of the system. Classical, quantal or hybrid models, sometimes in conjunction with statistical techniques have been developed to give answers to these problems. A compromise between a reasonably simple description of the interactions present in solution and inclusion of a significant number of solvent molecules explicitly considered in the simulation has to be achieved. This is feasible by combining classical statistical simulations and appropriate interaction potentials, either derived from first-principles or empirically. In this context, the development of solute-solvent and solvent-solvent interaction potentials based on quantum-mechanical interaction energies, and its use in Monte Carlo or Molecular Dynamics simulations are useful strategies. Beyond this point, simulation methods where periodic updating of the solute and solvent wavefunctions may be considered in the course of the statistical simulation have been developed recently, supported by extensive use of computer resources. Explicit solvation models where a statistical trajectory has been computed provide a large number of snapshots (structural arrangements along the trajectory) which can be used to obtain average properties of the solute molecule, as well as other solution properties.

Ab initio Molecular Dynamics has become an affordable technique with the current increase of the computer resources and is giving access to an on-the-fly quantum-mechanical description of the statistical trajectory.

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## ***ACC 2 - Excited States in Conjugated Organic Materials (J. Gierschner)***

Johannes Gierschner

Madrid Institute for Advanced Studies, IMDEA Nanoscience  
Ciudad Universitaria de Cantoblanco, 28049, Madrid, SPAIN  
johannes.gierschner@imdea.org

### Outline

#### Excited States in Conjugated Organic Molecules & Materials

1. Light-Matter Interaction
2. Electronic Transitions
3. Chemical Constitution & Absorption
4. Molecular Spectra
5. Excited State Deactivation
6. Optical and Photophysical Properties of Interacting Molecules
7. Dimers in the PDA Regime and beyond
8. Weakly Interacting 3D Chromophore Assemblies
9. Crystals, Films and Nanoparticles

### Abstract

Chromophores, based on  $\pi$ -conjugated organic molecules, are of eminent importance in chemistry, materials science, biology and pharmacy as dyes, pigments and functional components in opto-electronic devices, such as optical switches, sensors, lasers, organic LEDs and solar cells. Analysis of the working principles and design of novel compounds requires however a deep understanding of structure-property relationships in solution and – more challenging – in the solid state, ideally at a predictive level. The lecture will give a thorough introduction to this subject, combining spectroscopy, photophysics, quantum chemistry, (physical) chemistry, and materials science.

## ***ACC 3 - Excited States in Conjugated Organic Materials (II) (B. Milian)***

Physical-Chemistry Department  
Faculty of Chemistry  
University of Valencia  
c/ Dr. Moliner 50  
46100 Burjassot - (Valencia) – Spain  
B.Milian.Medina@uv.es

### Contents:

Practical examples on Computational Design of Conjugated Organic Materials  
For details and additional info, refer to the ACC 2 chapter.

## **ACC 4 -Quantum computation(colloquium) (A. Gaita)**

Alejandro Gaita-Ariño

Institute of Molecular Science

*Universidad de Valencia*

Edificios Institutos de Paterna

Catedrático José Beltrán Martínez nº 2, 46980 Paterna – Spain

email/phone: gaita@uv.es / 963544421

### Outline:

Interactive colloquium on the current state of magnetic molecules as hardware for quantum technologies.

Be ready not only to listen but also to talk, ask and discuss.

IMPORTANT: Voluntary activity: come only if you're interested!

### Abstract:

While quantum technologies are attracting more attention lately, as demonstrated by the European QT Flagship (10<sup>9</sup> € over a period of 10 years for research in the field), the ultimate quantum hardware has not been determined yet, and competitors abound.

Chemistry and molecules may play a role, and are at least useful for fundamental studies of important physical phenomena like quantum decoherence.

Depending on the current level of understanding of the audience, we will start from (and remain near) the very basics or move on to discuss the current state of the art about molecular spin qubits.

## ●● ES (Ethics in Science)

### *ES 1- Ethics in Science (R. Bröer)*

Ria Bröer  
Theoretical Chemistry  
University of Groningen

#### Abstract:

This short course is concerned with ethics and integrity in science, in the planning, conducting and reporting of research. An important issue is how to recognize (and avoid) scientific misconduct. In the planning of research conflicts of interest can easily occur. In the conduction of research it is important to have a clear distinction between the responsibilities of trainee, mentors and collaborators.

Proper data collection, selection, storage and sharing will also be discussed. With regards to reporting and publication of research, authorship, ownership and (fair) reviewing are important issues.

## ●● CS (Communication Skills)

### **CS 1 - Writing skills (A. Gaita)**

*Alejandro Gaita-Ariño*

*Institute of Molecular Science*

*Universidad de Valencia*

*Edificios Institutos de Paterna*

*Catedrático José Beltrán Martínez n° 2, 46980 Paterna – Spain*

*email/phone: gaita@uv.es / 963544421*

Outline:

Session 1: You should be writing

1: Don't bore the reader

Reading, motivation, discussion

2: You get better at writing... by writing

Writing exercises, discussion

3: Writing is re-writing

Reading, rewriting, again and again

4: Writing group

Exchanging texts, reading, discussion

Session 2: On Wikipedia and writing well

1: Wikipedia: Featured article criteria

Reading, motivation, discussion

2: Wikipedia: basic setup

Get an account, do a valid edit

3: Wikipedia: advanced setup

Slightly more ambitious achievements

4: Organising homework

Discuss, organise, start

Abstract:

Writing is one of the key skills in science. As a scientist, if you perform brilliant research work but your writing is clumsy or boring, you will have to publish in lesser journals and your career will



suffer. Also, it will be less useful for Humanity because fewer people will understand the awesome work you did.

Later on, if you have excellent ideas for research projects but your writing is not up to the same level of quality, you will not be able to get grants, which is also dramatic for a research career. And again this is bad for everyone, since it's a waste of good ideas!

So, we will dedicate some time to talk about writing and reading, and to a few practical writing exercises to get a couple of points across. We will read a little bit, write what probably will feel like way too much, and discuss in small groups.

As a practical approximation to writing well, we will use Wikipedia. We'll start by setting up accounts for everyone and doing simple things, if needed. Eventually, you will be editing articles in either the category "Quantum chemistry software" or in the category "Quantum information science". This part will be a little more technical, and it will also constitute the preparation for the homework.

As preparation for session 1, read a good book before you come to class.

As preparation for session 2, read a featured Wikipedia article.

If you have already written a good book and/or a featured Wikipedia article before class, let me know beforehand! You can either help me with the teaching or have some free time for yourself.

Recommended bibliography:

Derrick Jensen's "Walking on water: Reading, Writing and the Revolution"

Ursula K. Leguin's "Steering the craft: a 21st century guide to sailing the sea of story"