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CHITEL/QUITEL

August 25 – 30, 2019
Montréal, Canada

Program and eBook of Abstracts

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Université Concordia University

Concordia University Research and Graduate Studies

CATC
Canadian Association of Theoretical Chemists
Association canadienne des chimistes théoriciens

Université Concordia University
Faculty of Arts and Science
Department of Chemistry and Biochemistry

CERMM
Centre for Research in Molecular Modeling
Centre de recherche en modélisation moléculaire

Mount Saint Vincent University

www.q-chem.org International Journal of Quantum Chemistry
Journal of Computational Chemistry www.c-chem.org

Physical, Theoretical and Computational Chemistry Division

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16:00 Paula Homem-de-Mello — *Design of dyes based on density functional theory and molecular dynamics descriptors*

16:20 Eliel Carvajal — *Crystal structure and mechanical properties of* Sr_2FeNbO_6 *under high pressure*

Tuesday, August 27

Density Functional Theory II

9:00 Paul W. Ayers — *Flexible wavefunction ansatze for N-electron systems*

9:40 Matthias Ernzerhof — *Analyzing and approximating the exchange-correlation hole through the factorization approach*

10:00 Paul Geerlings — *New avenues in conceptual density functional theory*

Biochemistry & Biophysics I

10:40 E. Laura Coitiño — Testing the redox switch for oligomerization hypothesis in human peroxiredoxin 6: structure, dynamics and reactivity over different oligomeric and redox states

11:20 Daniel P. Vercauteren — *Investigation of cyclic ligands inhibiting CD2-CD58 interactions using molecular dynamics and molecular docking approaches*

11:40 Céline Toubin — *Toward a molecular level understanding of heterogeneous processes relevant for the atmosphere or the interstellar medium*

12:00 Maria Rossano-Tapia — *Multiphoton absorption studies of fluorescent proteins and fluorescent protein chromophores*

Theory & Applications II

15:20 António J. C. Varandas — *Optimal low-cost basis sets & global potentials*

15:40 Gustavo A. Arteca — *Shape transitions in geometrically-confined grafted polymers*

16:00 Sergei Manzhos — *Advances in rectangular collocation for solution of the Schrödinger equation*

16:20 Lázaro. A. Monteserín Castanedo — *Could thermodynamics have driven the selection of present day nucleosides/nucleotides in early evolutionary times?*

Wednesday, August 28

Biochemistry & Biophysics II

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9:40 Ann M. English — *Insights from MD simulations on NO diffusion in hemoglobin*

10:00 Stéphanie Baud — *Structural bioinformatics: a tool to improve ECM understanding and description*

Electron Densities & Bonding I

10:40 Jesús Hernández-Trujillo — *The role of H...H bonding in the biphenyl crystal*

11:00 Fernando Cortés-Guzmán — *Spin and energetic contributions to the valence shell*

11:20 Michael Hilke — *Using machine learning to determine molecular properties from electron densities.*

11:40 Alain Rochefort — *Tracking weak interactions and ghost atoms in adsorbed layers*

12:00 Pablo Carpio-Martínez **—** *Mixed quantum-classical simulations of nonequilibrium heat transport in a model molecular junction*

Theory & Applications III

13:40 Lou Massa — *Density matrix expression of Quantum Crystallography (QCr)*

14:20 Alfonso Hernández-Laguna — *The compressibility of micas: muscovite-phlogopite series minerals*

14:40 Benoît Champagne — *Thermochromism in crystals and co-crystals – a quantum chemistry investigation*

Electron Densities & Bonding I

15:20 Jean-Michel Gillet — *Possible quantum crystallography solutions for N-representable one- electron reduced density matrices reconstruction*

16:00 Armand Soldera — *A Chemical Perspective of the Glass Transition thanks to MD*

16:20 François Légaré — *Probing the insulator to metal phase transition in VO_2 using high harmonicspectroscopy*

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Electron Densities & Bonding II

9:00 Carlo Gatti — *Novel paths for the study of spin polarized systems and phase change materials*

9:40 M. Esmaïl Alikhani — *To π or not to π? The topography of non-covalent interactions*

10:00 Frédéric Guégan — *Exploring chemical reactivity through excitability and polarizability*

Theory & Applications V

10:40 Michael Adán Martínez Sánchez — *Testing one-parameter hybrid exchange functionals in confined atoms*

11:00 Kalil Bernardino — *Dimer free energy surfaces as a probe for ionic liquids structure*

11:20 Gabriel L. C. de Souza — *Electron scattering cross sections for $C_2H_6O_2$ isomers*

11:40 Cecile Malardier-Jugroot — *Nanomaterials at the interface: link between computation and experiment*

12:00 Kevin M. Lefrancois-Gagnon — *Transferability of substituent properties from atoms in molecules*

Theory & Applications VI

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14:20 Joaquín Barroso-Flores — *Singlet fission as a viable exciton transference mechanism through photosynthetic pigments.*

14:40 Alberto Vela — *Robust prediction of spin-crossover in transition metal complexes*

Theory & Applications VII

15:20 René Fournier — *Melting-like transitions in silver clusters with 8 to 20 atoms*

15:40 Jacques K. Desmarais — *Self-consistent treatment of spin-orbit coupling in periodic systems from a two-component approach: implementation in the CRYSTAL code and lessons learned along the way*

16:00 Roberto Rivelino — *Electronic properties of low-dimensional materials*

16:20 Miguel A. San-Miguel — *Computational Modelling of Metallic Nanoestructures Growth from Electron-Beam/Laser-Radiation on Metal Oxides*

Friday, August 30

Reaction Dynamics

9:00 Pascal Larregaray – *Scattering dynamics of N_2 off W(100) at low collision energies: reconciling theory and experiments.*

9:20 Marius Lewerenz — *Spectroscopie et dynamique théorique de dopants moléculaires dans des agrégats d'hélium liquide*

9:40 Patrick Ayotte — *Separation of ortho-H_2O using magnetic focusing in a molecular beam*

10:00 Nadine Halberstadt — *Real time dynamics and He-induced electronic transitions in doped helium nanodroplets at 0.4 K*

Organic & Organometallic Chemistry and Catalysis I

10:40 Ana Martínez — *Agonists and antagonists of dopamine: a theoretical study*

11:20 Philippe Archambault — *Structure électronique des thionitrates et effets de la protonation sur leurréactivité*

11:40 Liliana Mammino — *Intramolecular hydrogen bonds and mutual orientations of the monomers in the stabilization of trimeric acylphloroglucinols*

12:00 Walid Lamine — Exploring the reactivity of cellulose under non-thermal atmospheric plasma conditions

Solid State, Extended Systems & Materials

13:40 Piero Ugliengo — From astrochemistry to prebiotic chemistry through the eyes of computer molecular modeling

14:20 Bartolomeo Civalleri — *Extending and assessing composite electronic structure methods to the solid state*

14:40 Irina Paci — *Optical and dielectric properties of nanocomposite materials*

Organic & Organometallic Chemistry and Catalysis II

15:20 Julien Pilmé — *Quantum chemical topology analysis of heavy elements*

15:40 Claude Y. Legault — CYLview: a free molecular analysis and representation program for chemists.

16:00 Ricardo A. Matute — *Insights into the competition between E1cb and E1cb/E2 borderline mechanisms of the 1,2-elimination of β-phenylmercaptoethyl phenolate*

Poster Session, Tuesday, August 27, 12:20 — 15:20

C1 Philippe Archambault — *Electronic structure analysis of solvent effects on nucleobase pairing*

C2 Ritu Arora — *Structure of the death complex between glyceraldehyde-3-phosphate dehydrogenase and seven-in-absentia homolog 1 (GAPDH-Siah1)*

C3 Pablo Carpio-Martínez — *Laplacian of the Hamiltonian kinetic energy density as an indicator of molecular interactions*

C4 Eliel Carvajal — *Si/LaTiO*$_3$ *heterojunction: a theoretical study*

C5 Miguel Cruz-Irisson — *Electronic properties of hydrogen passivated [001]-Si nanowires with interstitial Na atoms*

C6 Miguel Cruz-Irisson — *Electronic and magnetic properties of germanium carbide monolayer decorated with transition adatoms*

C7 Miguel Cruz-Irisson — *Theoretical Study of the electronic and vibrational properties of InAs nanowires*

C8 Miguel Cruz-Irisson — *Adsorption of carbon monoxide on Cu, Ag and Au-decorated germanene: a DFT study*

C9 Étienne Cuierrier — *The exchange-correlation factor model in density functional theory*

C10 Peyman Fahimi — *Electrical feedback hypothesis of regulation of the mitochondrial inner membrane electrical potential*

C11 Héctor I. Francisco — *Analysis of indicators relevant for the description of kinetic and exchange energy functionals*

C12 Hang Hu — *Quantum chemical simulations of thermal-mechanical coupling in high pressure and temperature materials synthesis*

C13 Alexander Ibrahim — *Equation of state and first principles prediction of the vibrational matrix shift of solid parahydrogen*

C14 Dmitri Iouchtchenko — *Constrained path integral Langevin equation integrators*

C15 Nazli Jodaeeasl — *Dynamics simulation of noble gases adsorption on homogeneous and heterogeneous carbon nanotube bundles*

C16 Adam Marr — *Calculation of hydrogen dimer spin isomer pairs binding energies*

C17 Brandon Meza-González — *Computational study of metal interactions in a modified polypropylene membrane*

C18 Lázaro A. M. Castanedo — *Genoprotection by complexation: the case of Phyllanthus orbicularis K extract*

C19 Adeniyi J. Olajide — *Solvent effects on the electronic properties of (2Z)-N'-((Z)-picolinamido) picolinamidine*

C20 Neil Raymond — Thermodynamic properties of nonadiabatic systems using Gaussian mixture distributions

C21 Andrea Ruiz — *Estudio computacional de fragmentos de ADN en diferentes conformaciones*

C22 Eduardo Valdespino — *Substituent Effect on the Photoinduced Geometrical Change of Copper Complexes*

C23 Spencer B. Yim — *Thermodynamic properties of* $H_2O@C_{60}$ *via exact diagonalization*

C24 Pierre-Olivier W.F. Roy — *Correlation factor models for second-order many-body perturbation theories*

F1 Bartolomeo Civalleri — *On optimizing gaussian basis sets for crystalline solids*

F2 Bartolomeo Civalleri — *CRYSPLOT: a new tool to visualize physical and chemical properties of crystalline solids*

F3 Alfonso Hernández-Laguna — *Compressional behavior of the aragonite-structure carbonates to 6 GPa.Atomic compressibilities.*

F4 Alfonso Hernández-Laguna — *Gas-phase thermolysis reaction of substituted cyclic diperoxides*

F5 J. Juan Peña — *The Morse potential from a radial potential.*

F6 J. Juan Peña — *Position dependent mass Schrödinger equation for q-deformed exponential-type potential.*

F7 Beibei Zhu — *Determination of bending modulus of multicomponent lipid membranes by molecular dynamics simulation of membrane buckling*

Foreword

English

QUITEL or CHITEL is the conference of theoretical and computational chemists whose native or adopted language of expression is one of the Romance (or Romanic) group of languages that primarily derived from Latin, such as Catalan, Italian, French, Portuguese, Romanian and Spanish. The conference name itself reflects that fact with acronyms corresponding to “Químicos Teóricos de Expresión Latina” (Spanish) and “Químicos Teóricos de Expressaõ Latina” (Portuguese), or “Chimici Teorici di Espressione Latina” (Italian) and “Chimistes Théoriciens d’Expression Latine” (French) [1].

The conference started in 1969 (Modena, Italy, under the impetus of Pullman and Del Rey) and is traditionally held on a rotation basis among countries whose language is or includes one of the Romance languages. In 2015, Canada, as a bilingual country with English and French as its official languages, was selected to organize QUITEL/CHITEL 2019. This is the first time in the conference history that it is held in Canada. The conference will be organized in Montreal from 25 to 30 August 2019. Montreal is the second largest city of Canada, a vibrant city in the French-Canadian Province of Québec, with a truly unique character and a fusion of cultures and history that draws from its European and native past, or as the moto states, it is an experience of America but in French.

QUILTEL/CHITEL Montreal 2019 will feature multiple symposia steered by some the World’s best scientists in theoretical and computational chemistry and associated disciplines of science and engineering who will present their latest cutting-edge research. Students and postdoctoral fellows will be well represented in all aspects of the programme along with established scientists. QUITEL/CHITEL is about inclusion: Everyone is welcome to present in any language of their preference. While conference attendees are free to deliver their presentation in any language they choose, they are encouraged to present their talks and posters in one of the Romance languages (with, preferably and if possible, accompanying slides in the same language) to keep with the spirit of the conference.

Holding a conference in Latin-derived languages is not only intellectually and culturally stimulating, ensuring great fun and diversity, but it also promotes the cooperation between its participants and underscores the particular strength of theoretical chemistry in Romance-language speaking regions of the World. We welcome you with open arms in Canada: Bienvenue au Canada!

References:

[1] P. Ugliengo, R. Dovesi, B. Civalleri, R. Orlando; “Topical collection of papers collected on the occasion of the XLI congress of the theoretical chemists of Latin expression (CHITEL 2015 - Torino - Italy)”, Theor. Chem. Acc. 136 (2). (DOI 10.1007/s00214-016-2023-5)

Français

La Conférence de chimie théorique et numérique QUITEL ou CHITEL rassemble des participants qui parlent une langue romane issue du latin, comme le catalan, l'italien, le français, le portugais, le roumain et l'espagnol.

Les acronymes formés par le nom de la conférence reflètent ce fait : « Químicos teóricos de expresión latina » (espagnol) et « Químicos Teóricos de Expressaõ Latina » (portugais), ou « Chimici Teorici di Espressione Latina » (italien) et « Chimistes théoriciens d'expression latine » (français) [1].

La toute première conférence, une initiative de Pullman et Del Rey, a eu lieu en 1969, à Modène en Italie. Depuis, elle est organisée à tour de rôle par des pays de langues romanes.

En 2015, le Canada, un pays bilingue dont les langues officielles sont l'anglais et le français, a été choisi comme hôte de QUITEL/CHITEL 2019 pour la toute première fois. La conférence aura lieu du 25 au 30 août 2019 à Montréal, une ville dynamique située dans la province francophone du Québec. Dotée d'un caractère tout à fait unique, la deuxième plus grande ville du Canada propose un amalgame de cultures et d'histoire européenne et autochtone.

QUITEL/CHITEL Montréal 2019 proposera de multiples symposiums dirigés par des scientifiques figurant parmi les chefs de file en chimie théorique et numérique, ou provenant de disciplines connexes des sciences et du génie, qui présenteront leurs plus récents travaux de recherche de pointe.

En plus des scientifiques établis, une large place sera laissée aux étudiants et stagiaires postdoctoraux dans tous les aspects du programme. QUITEL/CHITEL prône l'inclusion : les participants sont invités à donner leur présentation dans la langue de leur choix. Cependant, ils sont encouragés à présenter leurs exposés et affiches dans l'une des langues romanes (accompagnés de diapositives dans la même langue, si possible) fidèle à l'esprit de la conférence.

En plus d'être stimulante sur le plan intellectuel et culturel, cette conférence en langues latines multiples se promet de procurer un cadre agréable et diversifié propice au partage des connaissances et aux échanges. Elle encourage ainsi la coopération entre ses participants et souligne la force particulière de la chimie théorique et numérique dans les régions du monde de langue romane. Nous vous réservons un accueil chaleureux au Canada : Bienvenue à Montréal!

Références :

[1] P. Ugliengo, R. Dovesi, B. Civalleri, R. Orlando; « Topical collection of papers collected on the occasion of the XLI congress of the theoretical chemists of Latin expression (CHITEL 2015 - Torino - Italy) ", Theor. Chem. Acc. 136 (2). (DOI 10.1007/s00214-016-2023-5)

Español

La conferencia de química teórica y computacional, QUITEL o CHITEL, reúne a participantes que hablan una lengua romance derivada del latín, como catalán, italiano, francés, portugués, rumano o español.

El acrónimo formado por el nombre de la conferencia refleja este hecho: "Químicos Teóricos de Expresión Latina" (español) y " Químicos Teóricos de Expressaõ Latina" (portugués), o " Chimici Teorici di Espressione Latina" (italiano) y " Chimistes Théoriciens d'Expression Latine" (francés) [1].

La primera conferencia, una iniciativa de Pullman y Del Rey, tuvo lugar en 1969, en Módena, Italia. Desde entonces está organizada, a su vez, en países que hablan lenguas romances.

En 2015, Canadá, un país bilingüe cuyos idiomas oficiales son el inglés y el francés, fue elegido por primera vez, como anfitrión del QUITEL / CHITEL de 2019. La conferencia se llevará a cabo del 25 al 30 de agosto de 2019 en Montreal, una ciudad dinámica, ubicada en la provincia francófona de Quebec. Con un carácter único, la segunda ciudad más grande de Canadá ofrece una amalgama de culturas e historia europea y aborigen.

QUITEL / CHITEL Montreal 2019 contará con varios simposios dirigidos por científicos destacados en la química teórica y computacional, o disciplinas relacionadas con la ciencia y la ingeniería, quienes presentarán sus últimas investigaciones.

Además de los científicos establecidos, los estudiantes y postdoctorantes participarán en todo el programa. QUITEL / CHITEL aboga por la inclusión: los participantes están invitados a dar sus presentaciones en el idioma de su elección. Sin embargo, es recomendable presentar sus charlas y carteles en una de las lenguas romances (con diapositivas en el mismo idioma, si es posible) para permanecer en el espíritu de la conferencia.

Además de ser estimulante, intelectual y culturalmente, tener una conferencia de química teórica y computacional en idiomas latinos promueve un clima de entendimiento y de diversidad y, también, fomenta la cooperación entre sus participantes, enfatizando un alto nivel de la química teórica en las regiones del mundo donde se hablan idiomas latinos. Le ofrecemos una cálida bienvenida a Canadá, y como se dice en francés ¡ Bienvenue à Montréal !

Referencias:
[1] P. Ugliengo, R. Dovesi, B. Civalleri, R. Orlando; « Topical collection of papers collected on the occasion of the XLI congress of the theoretical chemists of Latin expression (CHITEL 2015 - Torino - Italy) ", Theor. Chem. Acc. 136 (2). (DOI 10.1007/s00214-016-2023-5)

Italiano

Il QUITEL o CHITEL è la conferenza dei chimici teorici e computazionali la cui lingua di espressione originaria, o quella adottata, appartiene a uno dei gruppi di lingue romaniche (o neolatine) derivate principalmente dal latino, come il catalano, l'italiano, il francese, il portoghese, il rumeno e lo spagnolo. Il nome stesso della conferenza riflette questo fatto essendo gli acronimi per "Químicos Teóricos de Expresión Latina" (spagnolo) e "Químicos Teóricos de Expressaõ Latina" (portoghese), o "Chimici Teorici di Espressione Latina" (italiano) e "Chimistes Théoriciens d' Expression Latine "(francese) [1].

La prima conferenza risale al 1969 (Modena, Italia, organizzata da Pullman e Del Re) ed è tradizionalmente organizzata a rotazione tra paesi la cui lingua è, o include, una delle lingue romanze. Nel 2015, il Canada, quale paese bilingue con l'inglese e il francese come lingue ufficiali, è stato eletto per organizzare il QUITEL / CHITEL 2019. Questa è la prima volta, nella storia della conferenza, in cui essa sarà ospitata in Canada. La conferenza sarà organizzata a Montreal dal 25 al 30 agosto 2019. Montreal è una città vivace nella provincia franco-canadese di Québec, con un carattere davvero unico e una fusione di culture e storia che attinge dal suo francese, dall' inglese e dagli idiomi nativi, o come afferma il motto, è un'esperienza dell'America ma in francese.

Il QUILTEL / CHITEL Montreal 2019 è organizzato in una serie di simposi con la presenza di alcuni dei migliori scienziati del mondo nel campo della chimica teorica e computazionale e discipline ad esse connesse, che discuteranno le loro ricerche di frontiera. Gli studenti e i postdoc troveranno piena rappresentanza in tutti gli aspetti del programma, insieme agli scienziati più affermati. Il QUITEL / CHITEL è una conferenza in cui l'inclusione è fondamentale: tutti sono invitati a esprimersi in qualsiasi lingua di loro preferenza. Mentre i relatori sono liberi di presentare le loro ricerche in qualsiasi lingua desiderino, sono pure incoraggiati a svolgere le presentazioni e i posters in una delle lingue romanze (anche preferibilmente, se possibile, con le relative diapositive in quella lingua) per mantenere lo spirito inter-linguistico della conferenza.

Organizzare e vivere una conferenza in lingue di derivazione latina non è solo un grande divertimento stimolando intellettualmente e culturalmente, ma promuove anche la cooperazione tra i suoi partecipanti e sottolinea la forza speciale della chimica teorica nelle regioni del mondo di lingua romanza. Vi diamo il benvenuto a braccia aperte in Canada: Bienvenue au Canada!

Riferimenti:

[1] P. Ugliengo, R. Dovesi, B. Civalleri, R. Orlando; "Topical collection of papers collected on the occasion of the XLI congress of the theoretical chemists of Latin expression (CHITEL 2015 - Torino - Italy)", Theor. Chem. Acc. 136 (2). (DOI 10.1007/s00214-016-2023-5)

Português

QUITEL ou CHITEL é a conferência internacional de químicos teóricos e computacionais cuja linguagem de expressão nativa, ou adotada, é um dos grupos de línguas românicas que derivam, principalmente, do latim como catalão, italiano, francês, português, romeno, espanho, etc. O nome da conferência é o acrônimo de "Químicos Teóricos de Expresión Latina" (espanhol) e "Químicos Teóricos da Expressão Latina", ou "Chimici Teorici di Espressione Latina" (Italiano) e "Chimistes Théoriciens dExpression Latine" (francês) [1].

A conferência teve inicio no ano de 1969 (Modena, Itália, por Pullman e Del Rey) e é tradicionalmente realizada em alternância entre os países cuja língua é (ou inclui) uma das línguas românicas. No ano de 2015, o Canadá, um país bilíngue que têm o inglês e francês como suas línguas oficiais, foi eleito para organizar QUITEL/CHITEL 2019. Esta é a primeira vez na história em que a conferência será realizada no Canadá, na cidade de Montreal no período de 25 a 30 de agosto de 2019. Montreal é um lugar vibrante da província franco-canadense de Quebec, uma cidade com um caráter verdadeiramente único e com uma fusão de culturas e história extraídas de seu passado francês, inglês e nativo, sendo uma experiência na América em francês.

O QUILTEL/CHITEL Montreal 2019 será organizado em vários simpósios, com participação de alguns dos mais renomados cientistas do mundo para apresentar suas mais recentes pesquisas em química teórica e computacional ou em áreas correlatas. Estudantes e pós-doutorados são bem vindos em todos os aspectos do programa bem como os cientistas estabelecidos. O QUITEL/CHITEL tem o espirito da inclusão: Todos são bem vindos para fazer suas apresentações no idioma de sua preferência. Os participantes podem apresentar os trabalhos em qualquer idioma e são incentivados a apresentar suas palestras e pôsteres em uma das línguas românicas (de preferência também, e se possível, acompanhando os slides no mesmo idioma) mantendo o espírito da conferência.

Fazer uma conferência em línguas derivadas do latim não é apenas intelectualmente e culturalmente estimulante, mas também promove a cooperação entre seus participantes e ressalta essa força particular da química teórica nas regiões de língua românica do mundo.

Esperamos você de braços abertos no Canadá: Bienvenue au Canada!

Referência:

[1] P. Ugliengo, R. Dovesi, B. Civalleri, R. Orlando; "Topical collection of papers collected on the occasion of the XLI congress of the theoretical chemists of Latin expression (CHITEL 2015 - Torino - Italy)", Theor. Chem. Acc. 136 (2). (DOI 10.1007/s00214-016-2023-5)

Organization

Organizers

Cherif Matta

Mount Saint-Vincent University

Halifax (NS), Canada

Gilles Peslherbe

Concordia University

Montréal (QC), Canada

Pierre-Nicolas Roy

University of Waterloo

Waterloo (ON), Canada

Coordinator

Denise Koch

Concordia University

Montréal (QC), Canada

Volunteers - Concordia University

- Philippe Archambault
- Ritu Arora
- Hang Hu
- Nazli Jodaeeasl
- Adeniyi Olajide

PROGRAM CHITEL/QUITEL 2019

	Sunday August 25	Monday August 26	Tuesday August 27	Wednesday August 28	Thursday August 29	Friday August 30
8:00		REGISTRATION (MB-3.270)				
8:20						
8:40		Opening Remarks (MB-3.270)	REGISTRATION (MB-3.270)	REGISTRATION (MB-2.270)	REGISTRATION (MB-3.270)	REGISTRATION (MB-3.270)
		Light-Matter Interactions & Ultrafast Science (MB-3.270)	*Density Functional Theory II* (MB-3.270)	*Biochemistry & Biophysics II* (MB-2.270)	*Electron Densities & Bonding II* (MB-2.270)	*Reaction Dynamics* (MB-3.270)
		Chair: Nadine Halberstadt	*Chair:* Paul Johnson	*Chair:* Joaquin Barroso	*Chair:* Piero Ugliengo	*Chair:* Esmail Alikhani
9:00		**André Bandrauk**	**Paul Ayers**	**Joelle Pelletier**	**Carlo Gatti**	**Pascal Larregaray**
9:20						**Marius Lewerenz**
9:40		**Ilaria Ciofini**	**Matthias Ernzerhof**	**Ann English**	**Esmail Alikhani**	**Patrick Ayotte**
10:00		**Dennis Salahub**	**Paul Geerlings**	**Stéphanie Baud**	Frédérick Guégan	**Nadine Halberstadt**
10:20		COFFEE BREAK (MB Atrium)	COFFEE BREAK (MB Atrium)	COFFEE BREAK (MB Atrium)	COFFEE BREAK (MB Atrium)	COFFEE BREAK (MB Atrium)
		Pullman's Symposium on Quantum Biochemistry (MB-3.270)	*Biochemistry & Biophysics I* (MB-3.270)	*Electron Densities & Bonding I* (MB-2.270)	*Theory & Applications V* (MB-3.270)	*Organic & Organometallic Chemistry and Catalysis I* (MB-3.270)
		Chair: Fernando Cortés Guzmán	*Chair:* Joelle Pelletier	*Chair:* Paul Geerlings	*Chair:* Nelaine Mora Diez	*Chair:* E. Laura Coitiño
10:40		**Victor Batista**	**E. Laura Coitiño**	**Jesús Hernández-Trujillo**	Michael Martínez	**Ana Martinez**
11:00				**Fernando Cortés-Guzmán**	Kalil Bernardino	
11:20		**Nelaine Mora Diez**	**Daniel Vercauteren**	**Michael Hilke**	**Gabriel Souza**	Philippe Archambault
11:40		**Riccardo Spezia**	**Céline Toubin**	**Alain Rochefort**	**Cecile Malardier-Jugroot**	Liliana Mammino
12:00		**Marc Baaden**	Maria Rossano-Tapia	Pablo Carpio-Martinez	Kevin Lefrançois-Gagnon	Walid Lamine
12:20		LUNCH (MB 9)	LUNCH & POSTER SESSION (MB Atrium)	LUNCH (MB 9)	LUNCH (MB Atrium)	LUNCH (MB Atrium)
		Theory & Applications I (MB-3.270)		*Theory & Applications III* (MB-2.270)	*Theory & Applications VI* (MB-3.270)	*Solid State, Extended Systems & Materials* (MB-3.270)
		Chair: Dennis Salahub		*Chair:* Jesús Hernandez-Trujillo	*Chair:* René Fournier	*Chair:* Sergei Manzhos
13:40		**Robert Mawhinney**		**Lou Massa**	**Alejandro Toro-Labbé**	**Piero Ugliengo**
14:00		Franz Martinez				
14:20		**Patrizia Calaminici**		**Alfonso Hernández-Laguna**	**Joaquin Barroso**	**Bartolomeo Civalleri**
14:40		**Andreas Köster**		**Benoît Champagne**	**Alberto Vela**	**Irina Paci**
15:00		COFFEE BREAK (MB Atrium)		COFFEE BREAK (MB Atrium)	COFFEE BREAK (MB Atrium)	COFFEE BREAK (MB Atrium)
		Density Functional Theory I (MB-3.270)	*Theory & Applications II* (MB-3.270)	*Theory & Applications IV* (MB-2.270)	*Theory & Applications VII* (MB-3.270)	*Organic & Organometallic Chemistry and Catalysis II* (MB-3.270)
		Chair: Robert Mawhinney	*Chair:* Jean-Michel Gillet	*Chair:* Daniel Vercauteren	*Chair:* Armand Soldera	*Chair:* Céline Toubin
15:20		**Paul Johnson**	**António Varandas**	**Jean-Michel Gillet**	**René Fournier**	Julien Pilmé
15:40		Tárcius Ramos	**Gustavo Arteca**		Jacques Desmarais	**Claude Legault**
16:00		**Paula Homem-de-Mello**	**Sergei Manzhos**	**Armand Soldera**	**Roberto Rivelino**	Ricardo Matute
16:20		Eliel Carvajal	Lazaro A. Monteserin Castanedo	**François Légaré**	Miguel San Miguel	Closing Remarks & Departure
16:40						
17:00	REGISTRATION (MB-9th floor Conference Center - Lobby)				BUSINESS MEETING	
17:20						
17:40						
18:00	OPENING MIXER (MB-9EFG)			BANQUET Dinner-cruise (7-11PM) Boarding starting at 6PM Cruise departure at 7PM		

To π or not to π? The topography of non-covalent interactions

M. Esmaïl Alikhani

Laboratoire MONARIS, Sorbonne Université / CNRS, Paris, France

esmail.alikhani@upmc.fr

Aromatic cyclic molecules containing a hetero-atom have usually two attractive sites for hydrogen or halogen bond donors: n-pair and delocalized π electron. A well description between two type interactions (σ- or π- bonding) is a challenge for the quantum chemical methods. The main purpose of this presentation is to answer the following three questions:

1. Are the electronic correlation taken into account in the ab initio techniques reliable electronic structure? To what extent is a DFT method ((DFT-D, RSH-DFT, LC-DFT, Double Hybrid-DFT) adequate to handle these interactions?
2. Among the different physicochemical concepts (MEP, QTAIM, ELF, SAPT-DFT, and NBO) what are the most effective models to explain the nature of these two types of interactions? Can these models be considered as predictive theoretical tools?
3. Are the theoretical results in agreement with the experimental findings?

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Structure électronique des thionitrates et effets de la protonation sur leur réactivité

Philippe Archambault, Vinod Parmar, Ann English et Gilles Peslherbe

Centre de Recherche en Modélisation moléculaire et Département de Chimie et Biochimie,
Université Concordia, Montréal, Québec, Canada

p.archambault@concordia.ca; gilles.peslherbe@concordia.ca

Les thionitrates ($RSNO_2$) sont des composés importants qui ont été proposés comme intermédiaires lors de la décomposition de nitrates organiques [1,2], dont certains représentent un fort potentiel thérapeutique en tant que précurseurs du monoxyde d'azote (NO), un puissant vasodilatateur [3]. Ceux-ci méritent donc une étude approfondie de leur structure électronique et réactivité. Il semblerait que les thionitrates soient stables en milieu acide, mais la stabilité même de ces composés reste à éclaircir au vu d'études expérimentales incomplètes et aux résultats ambigus. La protonation (ou déprotonation) est une étape fondamentale de nombreuses réactions chimiques et biochimiques, et la stabilité et réactivité d'intermédiaires peuvent être fortement influencées par un micro-environnement acide ou basique (par exemple dans le site actif d'une protéine contenant des résidus protonés ou déprotonés). Il est donc nécessaire d'étudier non seulement les $RSNO_2$, mais également les effets de la protonation sur leur structure électronique pour bien caractériser leur réactivité et stabilité. Dans cette contribution, nous présentons donc les résultats de calculs de chimie quantique de haut niveau pour CH_3SNO_2 (comme modèle de thionitrate) et ses isomères protonés.

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Electronic structure analysis of solvent effects on nucleobase pairing

Philippe Archambault, Gilles Peslherbe and Heidi Muchall

Centre for Research in Molecular Modeling and Department of Chemistry and Biochemistry,
Concordia University, Montreal, Quebec, Canada

p.archambault@concordia.ca; gilles.peslherbe@concordia.ca

Non-covalent interactions such as hydrogen bonding and π-stacking are a driving force for folding and stabilizing nucleic acid structures. These interactions between bases govern structural properties and have been considered essential to nucleic acid research [1]. The conformational flexibility of nucleic acids arises largely due to interactions with the aqueous surrounding. Water plays an important role not only in their stability but also their functionality [2]. For instance, solvent effects significantly influence complex biochemical processes such as DNA replication and biomolecular recognition by modulating hydrogen bonding interactions within base pairs [3,4]. The role of hydration in Watson-Crick and non-Watson-Crick base pairing motifs is investigated by density-functional theory with water represented by either explicit molecules or dielectric field. Effects on the hydrogen-bonding interactions in the base pairs are characterized from the calculated electron densities with the Quantum Theory of Atoms in Molecules [5] whilechanges in orbital interactions are quantified using Natural Bond Orbital [6] analyses. Understanding the nature of solvent-mediated non-covalent interactions in nucleobas pairing is crucial to shed light ontp their structure-function and guide therapeutic targeting of DNA and RNA.

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Structure of the death complex between glyceraldehyde-3-phosphate dehydrogenase and seven-in-absentia homolog 1 (GAPDH-Siah1)

Ritu Arora, Vinod Parmar, Ann M. English and Gilles H. Peslherbe

Centre for Research in Molecular Modeling, PROTEO and Department of Chemistry,
Concordia University, Montreal, Quebec, Canada

ritu.arora@mail.concordia.ca; gilles.peslherbe@concordia.ca; ann.english@concordia.ca.

Tetrameric GAPDH is an important glycolytic enzyme with a diverse range of functions. Monomeric and dimeric forms of GAPDH also have been identified in cells and are implicated in many of its physiological and pathophysiological functions. Previous investigations revealed the putative role of GAPDH in apoptosis, linked to its complexation with Siah1, an E3 ubiquitin ligase. S-nitrosylation of GAPDH triggers binding to Siah1, whose nuclear localization signal facilitates GAPDH translocation, eventually leading to apoptotic cell death. Despite this death complex being of vital biological significance, very little is known about its structure. Computational modeling of the association of tetrameric GAPDH with four Siah1 dimers has been reported. However, S-nitrosylation leads to instability in the protein structure of GAPDH that alters the equilibrium between its tetrameric and monomeric forms. Our electrostatic surface analyses reveal that the GAPDH monomer, but not the tetramer, has a large complementary electrostatic surface area for Siah1 binding. Also, molecular docking analyses based on interaction-refined shape complementarity principles confirm strong complexation between monomeric GAPDH and Siah1. In particular, the most favorable docking poses of the complex disclose that the S-loop of the GAPDH monomer becomes less disordered upon interaction with Siah1, thereby promoting complexation. Therefore, we propose that stabilization of the S-loop is the main driving force that elicits Siah1 to compete for the GAPDH monomer against its tetramer. Molecular dynamics simulations of the best docking complexes are ongoing to test this hypothesis.

Shape transitions in geometrically-confined grafted polymers

Gustavo A. Arteca

Département de Chimie et Biochimie, Laurentian University, Sudbury, Ontario, Canada

Gustavo@laurentian.ca

Configurational transitions in polymers vary strongly depending on molecular composition (*e.g.*, homo- vs heteropolymers, random vs block-polymers) and also their topology (*e.g.*, linear, branched, or knotted). In addition, these transformations can be affected by environment factors, including temperature, solvation, the presence of solutes, as well as “geometrical confinement.”

The notion of geometrical confinement covers a wide range of phenomena, including forcing polymers into narrow cavities, compressing or adsorbing them, and bringing them close to AFM-tips or other polymer chains. All these factors induce configurational (or entropic) constraints; how these constraints translate into shape transitions depends on the nature of the confinement.

In this communication, we deal with the simplest case, namely, a “island” of grafted linear chains. Using Monte-Carlo simulations on homopolymers with excluded-volume interaction, we show that this model can give rise to something akin to the so-called escape transitions observed in self-attractive polymers. These “dodging” transitions yield "non-uniform" configurations, that is, those where the chain exhibits both compact and non-compact regions.

Using the interrelation between molecular size and chain-entanglement, we estimate the configurational phase where escape transitions are possible even in uncompressed repulsive polymers. Using a range interactions, confining geometries, and grafting densities, we show that there are critical chain lengths and critical geometrical arrangements for the occurrence of these shape transitions. We discuss briefly how these effects might be recognized experimentally, as well as some possible applications.

ACKNOWLEDGMENT

Jessica Harrison; Michael Richer. NSERC, Canada.

Flexible wavefunction ansatze for N-electron systems

Paul W. Ayers, Taewon D. Kim, Ramon Alain Miranda-Quintana,
Michael Richer, Gabriella Sanchez-Diaz and Lian Pharoah

Department of Chemistry & Chemical Biology McMaster University, Hamilton, Ontario, Canada

ayers@mcmaster.ca

A flexible ansatz for N-electron wavefunctions that subsumes the wavefunctions used in traditional configuration interaction approaches, coupled cluster methods, geminal-product wavefunctions, electron-group-function approaches, matrix-product states, and tensor-network states is presented. In this approach, desirable properties of wavefunctions (e.g., quasiparticle interpretations; size-consistency) are expressed as properties of a function that determines the coefficients of Slater determinants as (generally nonlinear) functions of the input parameters. Some of these key properties will be presented, allowing us to generate entirely new wavefunction forms that have desirable formal properties and yet, in some cases, are fully applicable to strongly correlated systems. A perturbative form of this approach will also be presented; the perturbative expression is especially useful for generating initial guesses for the wavefunction optimization.

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Separation of ortho-H_2O using magnetic focusing in a molecular beam

Patrick Ayotte[1], *Pierre-Alexandre Turgeon*[1], *Jonathan Vermette*[1],
Isabelle Braud[1], *Xavier Michaut*[2] *and Gil Alandrowicz*[3]

[1]Département de chimie, Université de Sherbrooke, Sherbrooke, Quebec, Canada

[2]LERMA, Observatoire de Paris, PSL Research University, CNRS, Paris, France

[3]Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel

patrick.ayotte@usherbrooke.ca

The properties and behaviour of the nuclear spin isomers (NSI) of the water molecule are of great interest in astrophysics since the ortho:para ratio (OPR) is assumed to provide insight into the formation mechanism and history of comets as well as other celestial bodies. Technological advances are also foreseen for ortho-H_2O enriched samples in magnetic resonance applications. Motivated by these perspectives, methodological bottlenecks need to be overcome: 1-the development of efficient separation protocols, and 2-the improvement in storage strategies for water sample enriched in either of its NSI through a better understanding of their inter-conversion mechanism. We will show how magnetic focusing in a supersonic molecular beam provides a convenient method for preparing water vapour strongly enriched (i.e., >50:1) in the ortho-H_2O NSI. We will also show that rare gas matrices can be an efficient condensed phase storage medium for enriched samples whose lifetime remains however, limited by the slow interconversion kinetics of NSI causing sample enrichments to decay over several hours. Closer examination of the NSI inter-conversion kinetics of isolated water molecules, trapped in rare gas matrices, revealed that it increases significantly in $H_2{}^{17}O$ and $H_2{}^{18}O$ compared to normal water, and that it increases rapidly above T~10K. The temperature and isotope effects provide valuable insight into the role of confinement on the intramolecular couplings (i.e., spin-rotation and spin-spin) responsible for the inter-conversion between the ortho and para NSI of the water molecule. Finally, perspectives for the application of ortho-H_2O to study chemical dynamics at ice surfaces will be discussed.

Virtual molecular reality and interactive modeling.

Marc Baaden[1,2]

[1]CNRS, Université de Paris, Laboratoire de Biochimie Théorique, Paris, France

[2]Institut de Biologie Physico-Chimique-Fondation Edmond de Rothschild,
PSL Research University, Paris, France

baaden@smplinux.de

For several years now, my team pursues the goal to study complex molecular assemblies through interactive visualization, manipulation and analysis approaches to aid hypothesis generation and exploration of complex datasets. The UnityMol framework [1] forms a central tool for these investigations and is based on the Unity3D game engine. A first line of research tries to help with the 3D context, for instance through content-guided navigation, exploded views and semantic links between molecular objects and their analysis data [2].

Concerning the molecular representations, we extended the UnityMol repertoire to include specific visualizations for sugar molecules [3] and have now also included coarse-grained systems by default. These are particularly apt for interactive simulations, even in the classroom or via crowdsourcing. A particular focus lies on the integration of dedicated hardware such as large, high-resolution display walls, or more recently head-mounted virtual reality headsets or augmented reality setups. Among the success stories for these developments I will report on the deployment of the virtual reality version of UnityMol at several industrial partner sites, in particular within UCB Biopharma.

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Circularly polarized Xrays via high-order harmonics

André D. Bandrauk and Kai-Jun Yuan

Laboratoire Chimie Computationnelle et Photonique Moléculaire,
Faculté des Sciences Université de Sherbrooke, Québec, Canada

andre.bandrauk@usherbrooke.ca

Attosecond(1 asec=10**-18s) pulses at photon energies corresponding to the fundamental edge of matter, the soft XRay region about 200 eV permit the probing, imaging of electron dynamics from atoms, to molecules and solid state. A soft XRay pulse duration of 43 asec has now been achieved using intense femtosecond (1fs=10**-15s) linearly polarized driving pulses [1].The main source of linear polarization asec pulses is high order harmonic generation, HHG, a highly nonlinear nonperturbative response of bound electrons to ultrashort(fs) intense(I>10**14 W/cm**2) mid-IR laser pulses. HHG is now understood as due to laser induced electron recollision of an ionized electron with its parent cation [2]. Recollision is suppressed in circular polarization whereas as shown as early as 1995 combinations of bichromatic counter-rotating circularly polarized intense ionizing pulses with frequencies w1/w2=n1/n2 for n integer induce recollision and copious harmonics [3-4] of circular polarization [5]. Circular bichromatic HHG has shown to be **universal** with a first maximum intensity up to photon energies Ip+2Up and a maximum energy cut-off at Ip+3.17Up where Ip=ionization potential, ponderomotive energy Up depends at intensity I as (in atomic units) I/4w**2, w=(w1+w2)/2 [6]. High level simulations performed with molecular TDSEs (Time Dependent Schroedinger Equations) show that circularly polarized HHG, from which one can generate asec circular pulses is most efficient when the net symmetry of intense high frequency bichromatic pulses is compatible with molecular symmetry [7]. This allows for the generation of circular quantum electronic currents ,new sources of asec magnetic field pulses [6]. The new ability to generate circularly polarized XRay asec pulses based on circular HHG in a table top set-up [8] is currently helping to develop a new X-Ray light science such as circular polarized Laser Induced Electron Diffraction, LIED, for the imaging of attosecond electron dynamics in molecules [9].

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Studies of natural and artificial photosynthesis

Victor S. Batista

Yale University, Department of Chemistry, New Haven, CT, USA

victor.batista@yale.edu

Mechanistic investigations of the water-splitting reaction of the oxygen-evolving complex (OEC) of photosystem II (PSII) are fundamentally informed by structural studies of oxomanganese complexes. Many physical techniques have provided important insights into the OEC structure and function, including X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy as well as mass spectrometry (MS), electron paramagnetic resonance (EPR) spectroscopy, and Fourier transform infrared spectroscopy applied in conjunction with mutagenesis studies. However, experimental studies have yet to yield consensus as to the nature of the reaction mechanism responsible for oxygen evolution. Computational modeling studies, including density functional (DFT) theory combined with quantum mechanics/molecular mechanics (QM/MM) hybrid methods for explicitly including the influence of the surrounding protein, have proposed chemically satisfactory models of the fully ligated OEC within PSII that are maximally consistent with experimental results. The computational models are useful for rationalizing spectroscopic and crystallographic results and for building a complete structure-based mechanism of water-splitting as described by the intermediate oxidation states of oxomanganese complexes. This talk summarizes our recent advances in studies of the OEC of PSII and semiconductor materials functionalized biomimetic catalysts for artificial photosynthesis.

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Singlet fission as a viable exciton transference mechanism through photosynthetic pigments.

Joaquín Barroso–Flores[1]*, David Casanova*[2]*, Jacinto Sandoval–Lira*[1]*,*
María Eugenia Sandoval–Salinas[2] *and Gustavo Mondragón–Solórzano*[1]

[1]Instituto de Química, Universidad Nacional Autónoma de México. Circuito Exterior s/n
Ciudad Universitaria, Coyoacán, Mexico City, Mexico

[2]Kimika Fakultatea, Euskal Herriko Unibertsitatea & Donostia International Physics Center,
Paseo Manuel de Lardizabal, Donostia-San Sebastián, Euskadi, Spain

jbarroso@unam.mx

Photosynthesis is the basic biochemical process, which sustains life on Earth; research of all its physical and chemical steps has potential impact in development of sustainable energy sources as well as the understanding of the origins of life. Among the various steps involved, the various excitonic transference mechanisms between pigments remain the least understood. Singlet Fission (SF) is a photochemical process in which a molecule in an excited state decays to a pair of coupled triplet states, one of which may be centered in a neighboring molecule propagating in this way the excitation absorbed by the first molecule. To this day, this process has been observed in polyacene crystals and other artificial materials but its presence in photosynthesis could help resolve some of the features associated with the high efficiency of the energy transference. Restricted Active Space with Double Spin Flip (RAS-2SF) calculations show that the SF process between specific orientations of various kinds of bacteriochlorophyll (BChl–*a*, –*b,* and –*d*) pigments is at least in principle possible as shown by the calculation of the coupling between adiabatic states which were quantified by the norm of the transition density matrix, $\|\gamma\|$, which range from 0.4 to 0.65 units. Naturally occurring photosystem II arrangements can in principle exhibit SF between their respective pigments; the iconic Fenna-Matthews-Olson photosystem is assessed herein as well as the carotenoid–assisted systems 5YQ7 and 6ET5.

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Structural bioinformatics: a tool to improve ECM understanding and description

Stéphanie Baud[1,2], *Camille Besançon*[1], *Hua Wong*[1], *Manuel Dauchez*[1,2],
Jessica Prévoteau- Jonquet[1] *and Nicolas Belloy*[1,2]

[1] Unité de recherche MEDyC (Matrice Extracellulaire et Dynamique Cellulaire) UMR CNRS 7369,
Université de Reims Champagne Ardenne, Reims, France

[2] Plateau de Modélisation Moléculaire Multiéchelle (P3M),
Université de Reims Champagne- Ardenne, Reims, France.

stephanie.baud@univ-reims.fr; nicolas.belloy@univ-reims.fr; manuel.dauchez@univ-reims.fr

The extracellular matrix (ECM) is a three-dimensional network of macromolecules that is the architectural support for cells and allows tissue cohesion. This dynamic structure regulates many biological functions such as adhesion, migration, proliferation, differentiation and cell survival. Molecular modelling makes it possible to understand and decipher, at the atomic or coarse-grained levels, the behavior of biological systems. In particular, it becomes an essential and powerful tool used to study the structure and structure/function/dynamics of biomolecules. In the particular context of the structural and dynamic studies of the ECM, the usual molecular modelling methods allow scientists to obtain interesting and insightful results, but often limited in terms of complexity or size of the investigated systems.

In order to improve the modelling of ECM related systems, we are developing approaches based on the Unity3D platform. The first application is related to the representation and analysis of N-glycosylations during MD simulations. We aim at visualizing the impact of the sugar motions on the protein surface through the use of UnityMol. A dedicated methodology called the Umbrella Visualization allows to display the main positions adopted by the glycosylations chains on the protein surface and thus to discuss the protein/glycan interactions. The second application is related to the modelling of the ECM at the mesoscopic level. Our rigid body dynamics, developed with Unity3D and Physics engines, is combined with VR hardware in order to visualize/interact and model large biological molecules with preliminary results showing it is possible to characterize the self-assembling nature of the basement membranes' structure.

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Dimer free energy surfaces as a probe for ionic liquids structure

Kalil Bernardino[1], *Goloviznina Kateryna*[2],
Agilio H. A. Pádua[2] *and Mauro C. C. Ribeiro*[1]

[1]Laboratório de Espectroscopia Molecular, Instituto de Química,
Universidade de São Paulo, São Paulo, SP, Brazil.

[2]Laboratoire de Chimie, École Normale Supérieure de Lyon & CNRS, 69364 Lyon, France

kalil.bernardino@gmail.com; mccribei@iq.usp.br

Ionic liquids (ILs) are unique substances that combines low melting points with zero vapor pressure. The vast number of possible combinations of cations and anions can produces ILs with wide range of physical properties that can be fine tuned if the correlation with the chemical structure is known. Computers simulations can provide this connection, but standard quantum chemical methods are too cost to simulate systems with size and timescale needed for ILs relaxation and classical forcefields are commonly employed for the molecular simulations of ILs instead. In order to fill the gap between high level quantum chemical methods and the liquid description by force fields, a free-energy method based in dimers calculations is proposed. A grid is defined for the translation of the anion around the cation and, at each point of this grid, rigid- body rotations and precessions are performed with the anion creating an ensemble of structures for which a free energy is computed. Similar surfaces can also be computed in the liquid phase by the average density of the anion at each point around the cation obtained in a molecular dynamics trajectory and similar trends are observed for dimer and liquid computed free energy surfaces, demonstrating the correlation between the two approaches. High level DFT calculations can be performed only for the dimer approach and the comparison with the results obtained from force fields demonstrate the quality of the structure predictions of the latter at condensed phase. Comparison between the results from polarizable and non-polarizable versions of CL&P force fields with DFT results displays important structure differences that cannot be easily realized by standard analyses like radial distribution functions.

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Invited Monday 14:20

IR and Raman spectra of nanosystems from auxiliary DFT

Patrizia Calaminici, Andreas M. Köster and Rogelio I. Delgado-Venegas

Departamento de Química, CINVESTAV,Avenida Instituto Politécnico Nacional 2508,
A.P. 14-740, México D.F., México

pcalamin@cinvestav.mx

In this talk, the working equations for the calculation of mixed second- and third-order auxiliary density functional theory (ADFT) energy derivatives are presented. Their implementation in the deMon2k code are discussed and validated. Results of applications of IR and Raman spectra of different nanosystems will be presented. It will be shown that these type of calculations are feasible within very reasonable times using modest computational resources by taking advantages of efficient parallelization schemes and low memory algorithms.

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Mixed quantum-classical simulations of nonequilibrium heat transport in a model molecular junction

Pablo Carpio-Martínez and *Gabriel Hanna*

Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2R3, Canada

carpioma@ualberta.ca; gabriel.hanna@ualberta.ca

The study of nonequilibrium heat transport in molecular junctions has gathered much attention in recent years due to its crucial role in the design of electronic nano-devices. Understanding the details of this process can aid in the fabrication of thermal rectifiers, thermal logic gates, thermal transistors, among others. Approximate quantum dynamical methods have been successfully used to calculate heat currents and to gain insight into the factors affecting the heat transport in a prototypical model molecular junction. This model, known as the nonequilibrium spin-boson (NESB) model, consists of a two-level system in contact with two harmonic oscillator baths at different temperatures. In this work, we assess the ability of a recently developed mixed quantum-classical dynamics method, known as Deterministic Evolution of Coordinates with Initial Decoupled Equations (DECIDE), for calculating the steady-state heat current in the NESB model in a variety of parameter regimes. Our results are compared and contrasted with those obtained using the numerically exact multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) approach, and using approximate methods, including mean field theory, Red-Field theory, and adiabatic mixed quantum-classical dynamics. Despite some quantitative differences, the DECIDE method performs relatively well, is capable of capturing the expected trends in the steady-state heat current, and, overall, performs the best out of the approximate methods. These results hold promise for DECIDE simulations of nonequilibrium heat transport in more realistic systems.

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Laplacian of the Hamiltonian kinetic energy density as an indicator of molecular interactions

Pablo Carpio-Martínez[1], *José Enrique Barquera-Lozada*[1,2], *Angel Martín Pendás*[3]
and Fernando Cortés-Guzmán[2]

[1]Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2R3, Canada

[2]Instituto de Química, Unversidad Nacional Autónoma de México, México DF 04510, Mexico

[3]Departamento de Química Física y Analítica, Facultad de Química,
Universidad de Oviedo, E- 33006-Oviedo, Spain

carpioma@ualberta.ca; fercor@unam.mx

The role of the kinetic energy in the formation of a chemical bond is still a center of controversy. One school states that a lowering of the kinetic energy associated with electron delocalization is the key stabilization mechanism of covalent bonding. The opposite school holds that a chemical bond is formed by a decrease in the potential energy due to a concentration of electron density within the binding region. In this work, we present a topographic analysis of the Hamiltonian Kinetic Energy Density (KED) and its laplacian with the objective of gaining more insight into the role of the kinetic energy within chemical interactions. Our study is centered in atoms, diatomic and organic molecules and weakly interacting dimers. We show that the laplacian of the Hamiltonian KED exhibits a shell structure in atoms and that their outermost shell merge when a molecule is formed. A covalent bond is characterized by a concentration of kinetic energy as well as potential energy and electron densities along the internuclear axis. In the case of the weakly interacting systems, the external shell of the molecules merge into each other resulting in an intermolecular surface comparable to that obtained by the Non-covalent interaction (NCI) analysis.

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Crystal structure and mechanical properties of Sr_2FeNbO_6 under high pressure

Eliel Carvajal[1], José L. Rosas[2], José M. Cervantes[1], Jesús A. León-Flores[2], Martín Romero[3] and Raúl Escamilla[2]*

[1] Escuela Superior de Ingeniería Mecánica y Eléctrica-Culhuacán, Instituto Politécnico Nacional.
Av. Santa Ana 1000, Ciudad de México, 04440, México

[2] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México. A.P. 70-360, Ciudad de México, 04510, México

[3] Facultad de Ciencias, Universidad Nacional Autónoma de México. Apartado Postal 70-399, Ciudad de México, 04510

*eliel.carvajal@gmail.com

The Sr_2FeNbO_6 (SFNO) compound is an antiferromagnetic (AFM) and semiconductor material with a gap of ~2 eV, it is ideal for working as a photocatalyst for the hydrogen generation or as cathode in fuel cells; however, the synthesis' cost slowed down the research on this material. Recently, we reported a less expensive way to obtain SFNO, by the molten salts method. Due to the great potential shown by this material for applications, it is pertinent to continue studying it; then, in this work, the crystal structure and mechanical properties of SFNO, under high pressure, were studied through the density functional theory, in the LDA+U using the CA-PZ exchange-correlation functional. The AFM and semiconductor behaviors were reproduced getting a gap of 2.O6 eV. Geometry optimization calculations were performed without restrictions under pressure; then, elastic constants (EC) and mechanical properties were calculated in the GGA, with the PBE functional. All calculations lead to a tetragonal structure while the lattice parameter values decreased due to the rising pressure. The EC agree with the stability criteria and values also increase as a function of the pressure value. Consequently, the shear (G) and bulk (B) modulus ratio G/B decreases from 0.68 to 0.42 when pressure changes from 0 and 50 GPa, respectively; that indicates SFNO goes from being a brittle material to a ductile one, for pressure values greater than 20GPa. Conversely, the Poisson ratio increases from ~0.22 for 0 GPa to 0.32 for 50 GPa and this indicates a mixture of ionic and covalent bonds as would be expected for the SFNO.

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Si/LaTiO$_3$ heterojunction: a theoretical study

J. M. Cervantes[1], J. L. Rosas[2], E. Alva1, R. Oviedo-Roa[3],
E. Carvajal[1] and M. Cruz-Irisson[1]

[1] Instituto Politécnico Nacional, ESIME-Culhuacán, Av. Santa Ana 1000, 04440, Ciudad de México, México

[2] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, A.P. 70-360, 04510, Ciudad de México, México

[3] Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, 07730, Ciudad de México, México

eliel.carvajal@gmail.com

LaTiO$_3$ perovskite is a Mott-Hubbard insulator; however, its electronic and magnetic properties can be modulated by substitutional defects, quantum confinement or heterojunction with some semiconductor material such as Si. For this work, those effects were studied using the Density Functional Theory (DFT). The model used was made up cutting a slab from the LaTiO$_3$ bulk phase, in such a way that the system is two dimensionally (2D) confined, free surfaces are parallel to the (01) crystallographic planes and has TiO$_2$ termination. Then, to form a Si monolayer on the LaTiO$_3$ slab, Si atoms were placed at high symmetry absorption sites as follows: top sites for Ti and O atoms, and hollow sites located at the center of the ring formed by O and Ti atoms. Another analyzed model was built by replacing La with Li atoms in the LaTiO$_3$ bulk phase; then the resulting structure is a perovskite formed by a sequence of atomic planes LaO/TiO$_2$/LiO/TiO$_2$. As well as the Li-free case, this is a 2D confined perovskite system; also, Si atoms were placed at the aforementioned absorption sites. Results shown that the electronic and magnetic properties of each system notoriously depend on the confinement and the substitutional Li defects. For all cases, Si atoms interact strongly with O and Ti atoms; this fact was evidenced by means of the electronic density difference analysis and there are suggestions of covalent and ionic Ti-Si and O-Si bonds, respectively.

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Thermochromism in crystals and co-crystals – a quantum chemistry investigation

Benoît Champagne[1], *Andrea Carletta*[1], *Tom Leyssens*[2], *Jean Quertinmont*[1],
Johan Wouters[1] *and Freddy Zutterman*[1]

[1]Namur Institute of Structured Matter, University of Namur, 61 Rue de Bruxelles, B-5000 Namur, Belgium

[2]Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain,
1 Place Louis Pasteur, B-1348 Louvain-La-Neuve, Belgium

benoit.champagne@unamur.be

Ph0otochromic and thermochromic compounds are widely studied because of their potential applications in sensing devices. Still, most of these studies rely on characterizations performed in solutions whereas there is a need for understanding and optimizing their properties in the solid state. Salicylideneanilines (or anils), which are characterized by a tautomer equilibrium, between an enol and a keto form of different colors, present remarkable thermochromic and photochromic properties. The enol form is usually the most stable but appropriate choice of substituents and conditions (solvent, crystal, host compound) can modify the thermodynamics and kinetics of the transformation. One strategy to optimize the switching behavior and the related optical properties consists in forming co-crystals. In this presentation we discuss the quantum chemistry components of a multidisciplinary approach, which also includes synthesis of the chromophores, crystal formation, and physico-chemical characterizations. In particular, our latest achievements towards describing the structure-property relationships of co-crystals of anils with co-formers (featuring H- and X-bonding interactions) will be discussed. This encompasses i) the prediction of the crystal structures and of the key geometrical parameters, ii) the evaluation of the relative energy of the different keto and enol forms, iii) the simulation of the NMR signatures, to help in determining the enol-keto equilibrium constant in the solid state, and iv) the prediction of the UV/visible absorption spectra. In all cases, the focus is set on analyzing the effects of the interactions in the solid state between the chromophore and the co-former. Different methods are employed, from embedding techniques to periodic boundary conditions approaches.

Density based methods and descriptors for the modelling of molecular devices

Ilaria Ciofini

Institute of Chemistry for Health and Life Sciences (i-CLeHS),CNRS Chimie Paristech, Paris FRANCE

ilaria.ciofini@chimie-paristech.fr

Theoretical tools enabling the description and the prediction of excited states' properties and reactivity are increasingly appealing for the rational design of new compounds and for the understanding and the optimization of the existing ones. Ideally, these methods should both correctly reproduce the potential energy surfaces (PES) of the excited states, within and far from the Franck Condon region, and deliver a coherent picture of all photochemical processes occurring. Due to intrinsic complexity of the electronic excited states, this task is very hard for any quantum method especially when dealing with chemically relevant systems in realistic conditions.To this end, in the last years, we introduced some strategies for the description of excited states, coupling Time-Dependent density functional theory (TD-DFT) with descriptors based on electron density. This type of indexes was primarily aiming at the diagnostic and description of excited states with a charge-transfer character, but recently extended to provide a qualitative identification of decay channels (both radiative or non-radiative). In this talk we will give an overview of these approaches – also coupled with embedding techniques for the description of the environment – and of their application to molecule-based devices.

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Extending and assessing composite electronic structure methods to the solid state

B. Civalleri[1], L. Donà[1] and J. Gerit Brandenburg[2]

[1]Dipartimento di Chimica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy

[2]Interdisciplinary Center for Scientific Computing, University of Heidelberg,
Im Neuenheimer Feld 205A, 69120 Heidelberg, Germany

bartolomeo.civalleri@unito.it

A hierarchy of simplified Hartree-Fock (HF) and density functional theory (DFT) methods have been recently proposed for the fast electronic structure computation of large systems [1]. The covered methods are a minimal basis set Hartree–Fock (HF-3c), a small basis set hybrid functional (PBEh- 3c), and its screened exchange variant (HSE-3c), all augmented with semi- classical correction potentials [1]. Here, we extend their applicability to inorganic covalent and ionic solids, layered materials as well as porous materials. The new methods have been dubbed HFsol-3c, PBEsol0-3c and HSEsol-3c, respectively, to indicate their parent functional as well as the correction potentials. They have been implemented in the CRYSTAL code [2] to enable routine application for molecular as well as solid materials. We validate the new methods on diverse sets of solid state benchmarks that cover more than 90 solids ranging from covalent, ionic, semi-ionic, layered, and molecular crystals. While we focus on structural and energetic properties, we also test band gaps, vibrational frequencies, elastic constants, and dielectric and piezoelectric tensors. Finally, we apply revised composite methods to study porous materials such as metal-organic frameworks. Overall, results not only show that the revised methods perform equally well as the original ones but also that the range of applicability is significantly extended and improved. Hybrid composite methods appear to be most promising and show accuracy competitive to converged basis set dispersion corrected DFT with substantial increase in computational efficiency.

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On optimizing gaussian basis sets for crystalline solids

Bartolomeo Civalleri, Loredana E. Daga and Lorenzo Maschio

Dipartimento di Chimica, Università di Torino and NIS (Nanostructured Interfaces and Surfaces) Centre,
Via P. Giuria 5, 10125 Torino, Italy.

bartolomeo.civalleri@unito.it

It is customary in molecular quantum chemistry to adopt a basis set expressed in terms of atom-centered functions, usually Gaussian-type orbitals. Many libraries are then available in which the basis sets are classified according to either their size (triple-ζ, quadruple-ζ,...) or the method/property they are optimal for (correlation-consistent, linear-response,...) but not according to the chemistry of the system to be studied. In fact, the vast majority of molecules is quite homogeneous in terms of electron charge density (i.e. atomic distances) and types of bond involved (mo0stly covalent or weakly bonded). This is not the same for solids, in which the same chemical element can show metallic, ionic, covalent or dispersively bound character in different crystalline forms or compounds. This situation calls for a different approach to the choice of basis sets, namely a system–specific optimization of the basis set that requires a practical algorithm that could be used on a routine basis.

In this work we develop an optimization method for Gaussian basis sets based on an algorithm – similar to the direct inversion of the iterative subspace [1,2] – that we name BDIIS. The total energy of the crystalline solid is minimized together with the condition number of the overlap matrix as proposed for condensed phases in ref. [3]. The method has been implemented in the CRYSTAL17 code [4]. Here, the details of the method are presented and its performance in optimizing valence orbitals is shown. As demonstrative systems we consider simple prototypical solids such as diamond/graphene, NaCl and LiH, and we show how basis set optimization has certain advantages also towards the use of large (quadruple-ζ) basis sets in solids.

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CRYSPLOT: a new tool to visualize physical and chemical properties of crystalline solids

Bartolomeo Civalleri[1], *Giorgia Beata*[1,2] *and Gianpaolo Perego*[2]

[1]Dipartimento di Chimica, Università di Torino and NIS (Nanostructured Interfaces and Surfaces) Centre,
Via P. Giuria 5, 10125 Torino, Italy.

[2]Aethia Srl, 10010, Colleretto Giacosa, Italy

bartolomeo.civalleri@unito.it

Visualization tools are becoming more and more important to analyze, help in understanding and present scientific data. Here we present a new visualization tool dubbed as CRYSPLOT [1].

CRYSPLOT is an online web-oriented tool (http://crysplot.crystalsolutions.eu) to visualize computed properties of periodic systems. It is targeted for plotting properties of crystalline solids (e.g. band structure and density of states (DOSs); electron charge density maps, profiles and differences; electrostatic potential maps; simulated infrared, Raman and reflectance spectra;…) as computed with the CRYSTAL code [3]. Along with plotting, CRYSPLOT also permits the modification and customization of plots to meet the standards required for scientific graphics.

CRYSPLOT has been designed with advanced and freely available graphical Javascript libraries, namely: Plotly [3]. The programming language used for CRYSPLOT is Javascript. Our code parses the input files, checks if the uploaded files are correct and, if they are, it reads the data and organizes them into objects ready to be plotted with plotly.js library. It is modular and flexible so that it is very simple to add other input data formats.

Overall, CRYSPLOT is a modern and flexible online tool that makes CRYSTAL more users friendly. It is totally free, easy to use and accessible to users from all over the world through its web page [1]. The new graphical tool is presented along with selected applications.

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Testing the redox switch for oligomerization hypothesis in human peroxiredoxin 6: structure, dynamics and reactivity over different oligomeric and redox states

E. Laura Coitiño

Laboratorio de Química Teórica y Computacional (LQTC), Instituto de Química Biológica,
Facultad de Ciencias y Centro de Investigaciones Biomédicas (CeInBio), Universidad de la
República, Montevideo, 11400, UdelaR
laurac@fcien.edu.uy

Human peroxiredoxin 6 (*hPrdx6*) is a moonlighting protein with different physiological functions attributed to a single structure of 25 kDa found as B-type antiparallel homodimers both in crystals and in solution. The protein acts as a thiol-dependent glutathione peroxidase (*1-Cys peroxiredoxin*) contributing to eliminate H_2O_2 from cell respiration and to reduce short-chain and phospholipid hydroperoxides into non deleterious species. In the base of this protective role against oxidative stress, a single conserved cysteine in the active site (C47, C_P) catalyzes the process, oxidizing itself to a sulfenic acid intermediate (C_PSOH) that is further involved in intramolecular disulfide bonding (C_PS-S) to an external thiol (glutathione, GSH, presumably mediated by *glutathione π-transferase*, *π-GST*, implying homodimer destabilization) and restored to the native state by physiological reductants. *hPrdx6* is also involved in regulation of phospholipid turnover acting as an *acidic calcium-independent intracellular phospholipase A2* (*aiPLA2*) through a second independent active site through a still not well-known mechanism. Very recently a *lysophosphatidylcholine acyl transferase* (*LPCAT*) activity has also been characterized and implied as a critical component in the remodeling pathway of phospholipids, contributing to lung surfactant synthesis and repair of damaged cell membranes.

Using a combination of *state-of-the-art* simulation and computational modeling strategies including conventional/accelerated MD and constant pH simulations and QM/MM modeling of *hPrdx6* under quasi-physiological conditions in both reduced and oxidized states and monomer/homodimer forms we have addressed several of the open questions in the research agenda of the structure-function relationships for this protein. Inspecting the molecular mechanism beneath the peroxidase activity, our models support the idea that oxidation to C_PSOH triggers homodimer destabilization in solution, preparing the protein for heterodimerization with *π-GST* at the resolution step of the catalytic cycle. Protein architecture at C_P environment and reactivity is examined and compared with human 2-cys atypical peroxiredoxin (*hPRdx5*, also addressed in our group) and a detailed mechanism of the C_PSOH reduction by ascorbate provided. The impact on the structure and dynamics of the homodimer by T177 phosphorylation that notably accelerates the *aiPLA2* activity is also examined, characterizing a molten globe conformation and binding of a DCCP phospholipid.

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Spin and energetic contributions to the valence shell

Fernando Cortés-Guzmán, David I. Ramírez-Palma and
Lillian G. Ramírez-Palma

Universidad Nacional Autónoma de México, Instituto de Química, Ciudad Universitaria
Ciudad de México, 04510 México

fercor@unam.mx

In this paper, we recovered the spirit of Linnett's and Gillespie's works, which states that the molecular geometry results from the distribution of α and β spin set of electrons. Here, we showed a systematic topological analysis of the spin, α, and β electron density of several first-row transition metal complexes, to understand their role in the formation of the metal-ligand interactions. Our tool was the atomic graph, a topological object that summarizes the valence shell polarization of an atom, where the charge depletions orientation determines the position of the ligands. The features of the atomic graph are the result of catastrophe processes between the spin components of the atomic graphs. In this way, the charge depletion observed in the valence shell of a metal center is originated, after a catastrophe process, when the size of the depletion of one spin shell exceeds that of the concentration of the other spin shell. When the metal-ligand distances were analyzed, we found that a certain distance (DST) a polarization change of the valence shell occurs along with the transfer of spin density from the ligand to the metal, reaching a maximum at the equilibrium distance. DST determines the communication of the spin information between two chemical species. Finally, a connection between the shape of the spin atomic graphs and the spin intra-atomic energy (IQA) were found, by a nonlinear relationship that reproduces the classification of atomic graphs.

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Electronic properties of hydrogen passivated [001]-Si nanowires with interstitial Na atoms

L.G. Arellano[1], *F. Salazar*[1], *A. Miranda*[1], *A. Trejo-Baños*[1],
M. Cruz-Irisson[1] *and L. A. Pérez*[2]

[1]Instituto Politécnico Nacional, ESIME-Culhuacán, Ciudad de México, México

[2]Instituto de Física, Universidad Nacional Autónoma de México, Ciudad de México, México

lucia.arellano.gin2017@gmail.com

Although materials for Li batteries have been extensively studied, alternatives such as Na batteries have acquired a renewed interest due to the abundance of Na compared to Li, however the investigation of new materials for Na batteries anodes is still scarce. In this work, a density functional study of the electronic properties of hydrogen passivated silicon nanowires (H-SiNWs) with interstitial sodium (Na) atoms is presented. The nanowires were modeled with a diameter close to 1.7 nm, grown along the [001] crystallographic direction, and concentrations between 1 and 12 interstitial Na atoms per unit cell. The initial positions of the Na atoms within the nanowire structure correspond to the T_d ones. The results reveal that the former semiconducting nanowires become metallic for all the Na concentrations. The formation energy increases as a function of the concentration of Na atoms, revealing a loss of energetic stability due to the atomic radii of the Na atoms strongly modifying the Si-Si bonds. The effect of removing the Na atoms of the metallic sodiated H-SiNWs, was studied showing that for concentrations from 1 to 10 Na atoms, the resulting structure corresponds to the initial semiconductor H-SiNW, while for the concentration of 12 Na atoms, the resulting semiconductor H-SiNW presents a different atomic arrange with a smaller band gap in comparison to the obtained for all the other concentrations, which indicate that a semiconductor-metal-semiconductor transition can be obtained by the insertion/extraction of Na atoms in the H-SiNWs. These results open the possibility to consider the H-SiNWs as potential candidates to anodic materials in sodium rechargeable batteries.

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Electronic and magnetic properties of germanium carbide monolayer decorated with transition adatoms

Akari N. Sosa[1], *Héctor Muñoz*[1], *Álvaro Miranda*[1], *Margarita C. Crisóstomo*[2], *Luis A. Pérez*[3] and *Miguel Cruz-Irisson*[1]

[1]Instituto Politécnico Nacional, ESIME Culhuacán, Av. Santa Ana 1000, CP 04440, Ciudad de México

[2]Instituto Politécnico Nacional, CECYT 8 Narciso Bassols, Av. de las Granjas 628,
C.P. 02519, Ciudad de México, México

[3]Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364,
01000 Ciudad de México, México.

asosacamposeco@gmail.com; amirandad.ipn@gmail.com

The germanium carbide monolayer (GeC-ML), analogous to graphene, has attracted the attention of the scientific community due to its interesting structural, optical and electronic properties. We studied in this work the adsorption of some transition metals atoms of the 3*d* series (Ti, V, Cr, Mn, Fe, Co and Cu) in a GeC-ML modeled through the technique of supercell with a dimension 5×5, in the framework of the Theory of Functional Density. The transition metals were adsorbed at the top (T), bottom (D), bridge (B) and hollow (H) sites of GeC-ML. The adsorption energies are similar to those obtained in graphene because the interaction between the metal atoms and the monolayer is smaller than the cohesion energy of the metal atoms in bulk. The atom of Mn is adsorbed preferentially on the Ge atom (site T), the atoms of Co and V are adsorbed preferentially on the C atom (site D), Cu and Fe are adsorbed on the bond between C and Ge (site B), while Cr and Ti are adsorbed at the intermediate site between the 3 atoms of C and the 3 of Ge (site H). The results indicate that the adsorption of metallic atoms could have applications in sensors, hydrogen storage and ion batteries of Li, Na and K.

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Theoretical Study of the electronic and vibrational properties of InAs nanowires

Miguel Cruz-Irisson, Fernando Salazar, Eladio López and Alejandro Trejo

Instituto Politécnico Nacional, ESIME Culhuacan, Av. Santa Ana 1000 C.P. 04440, Ciudad de México, México

fsalazar.posadas@gmail.com

InAs nanowires are attractive for applications in optoelectronics, however its theoretical characterization is still scarce, specially for their vibrational properties. In this work the electronic and vibrational properties of InAS nanowires were studied using the density functional and density functional perturbation theories and the superecell scheme. The nanowires were modeled by removing atoms outside as circumference in the [001] direction of an otherwise perfect InAS crystal. Results show that the electronic band gap and the phonon frequency intervals depend upon the ratio of In and As at the nanowire surface. With the In rich surface having a larger electronic band gap than the As counterpart, and different modes in frequency intervals owning to the different mass of In and As that changes the frequency of the In-H and As-H bending and stretching modes, also the shift of the optical modes towards lower frequencies and the broadening of the band gap according to the quantum confinement scheme was observed. These results could be useful for engineering of the optoelectronic properties of InAs nanowires for different applications in electronics.

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Adsorption of carbon monoxide on Cu, Ag and Au-decorated germanene: a DFT study

Akari N. Sosa[1], *José E. Santana*[1], *Álvaro Miranda*[1], *Fernando Salazar*[1],
Luis A. Pérez[2] *and Miguel Cruz-Irisson*[1]

[1]Instituto Politécnico Nacional, ESIME-Culhuacán, Av. Santa Ana 1000, C. P. 04440,
Ciudad de México, México

[2]Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, 01000
Ciudad de México, México

asosacamposeco@gmail.com; amirandad.ipn@gmail.com

Two-dimensional (2D) nanostructures in the honeycomb lattice are currently materials of interest due to their unique electronic properties. Their large surface-to-volume ratio makes them ideal for chemical detectors. In this work, the structural and electronic properties of the adsorption of CO molecule on Cu, Ag and Au-decorated on germanene has been investigated by performing density-functional-theory calculations. The results indicate that Cu, Ag and Au atoms are strongly binds to germanene, and we found that the CO molecule bind weakly to pristine germanene. The interaction between CO with the Cu, Ag and Au-decorated germanene has a chemisorption nature, as evidenced by the large adsorption energy and the short distance between the adsorbed molecule and transition metal atoms, resulting in enhanced chemical activity and sensitivity toward CO molecule compared to pristine germanene. The charge transfer, adsorption energy and the electronic properties induced by the molecule adsorption are discussed. It is found that for all the cases a charge transfer between the TM-decorated germanene and the adsorbed CO molecule has been observed. For CO, the adsorption induces the redistribution of the states in the valence and conduction bands. These can lead to the change of the transport properties of the decorated germanene, by which the adsorbed CO can be detected. A detailed knowledge of the geometry and electronic properties of these systems are required for the design and further optimization for future applications of germanene based gas sensing, catalysis and microelectronics.

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The exchange-correlation factor model in density functional theory

Étienne Cuierrier, Yongxi Zhou and Matthias Ernzerhof

Département de Chimie, Université de Montréal, Montréal, Québec, Canada

etienne.cuierrier@UMontreal.ca; matthias.ernzerhof@UMontreal.ca

Density Functional Theory (DFT) is the most widely used approach for electronic structure calculations. In the Kohn-Sham scheme, only the exchange-correlation energy E_{xc} needs to be approximated; to this end, we model the spherically averaged exchange-correlation hole $\rho_{xc}(\boldsymbol{r}, u)$, which represents the reduction of the electronic density at a distance u from a reference electron at a position $\boldsymbol{r}$. Previously in our group, an exchange factor $f_x(\boldsymbol{r}, u)$ was developed to approximate the exchange hole $\rho_x(\boldsymbol{r}, u) = f_x(\boldsymbol{r}, u)\rho(\boldsymbol{r}, u)$. In this expression, $\rho(\boldsymbol{r}, u)$ is the angle average of the electron density over all possible orientations of $\boldsymbol{u}$: $\rho(\boldsymbol{r}, u) = \int \frac{d\Omega_{\boldsymbol{u}}}{4\pi}\rho(\boldsymbol{r} + \boldsymbol{u})$. This method is a variation of the *Weighted Density Approximation* and it has the potential of being one-electron, self-interaction error (SIE) free. Furthermore, our group developed a correlation factor ansatz in which the exchange hole yielding the exact exchange-energy per particle is multiplied by the correlation factor $\rho_{xc}(\boldsymbol{r}, u) = f_c(\boldsymbol{r}, u)\rho_x(\boldsymbol{r}, u)$. Our previous models of f_c were not SIE free, however. To rectify this problem, we are developing an exchange-correlation factor to approximate the hole $\rho_{xc}(\boldsymbol{r}, u) = f_{xc}(\boldsymbol{r}, u)\rho(\boldsymbol{r}, u)$. The exchange-correlation factor is constructed non-empirically by satisfying physical and mathematical constraints. Preliminary results for atomization energies obtained with simple models of $f_{xc}(\boldsymbol{r}, u)$ are encouraging.

ACKNOWLEDGMENT

The financial support provided by *The Natural Sciences and Engineering Research Council of Canada* (NSERC) is gratefully acknowledged. Computations were made on the supercomputer Mammouth from Université de Sherbrooke managed by Calcul Québec and Compute Canada.

Self-consistent treatment of spin-orbit coupling in periodic systems from a two-component approach: implementation in the CRYSTAL code and lessons learned along the way

Jacques K. Desmarais[1,2,3], *Jean-Pierre Flament*[4] *and Alessandro Erba*[3]

[1]Department of Geological Sciences, University of Saskatchewan, SK S7N 5E2, Saskatoon, Canada

[2]Department of Physics and Engineering Physics, University of Saskatchewan, SK S7N 5E2, Saskatoon, Canada

[3]Dipartimento di Chimica, Università di Torino, Via Giuria 5, 10125, Torino, Italy

[4]Université de Lille, CNRS, UMR 8523 – PhLAM – Physique des Lasers Atomes et Molécules,
59000, Lille, France

jkd788@mail.usask.ca; alessandro.erba@unito.it

We present an implementation into the CRYSTAL code for self-consistently treating spin-orbit coupling (SOC) with Hartree-Fock and Density Functional Theory (DFT) calculations on systems periodic in 0D, 1D, 2D and 3D, from a Kramers' unrestricted two-component approach. To our knowledge, this is the first implementation for self-consistently treating SOC in periodic systems with Kramers unrestricted exact nonlocal Fock exchange (KUFE). The treatment of SOC including KUFE turns out to be crucial, as we have recently shown that the inclusion of a small fraction of KUFE in the Hamiltonian plays a fundamental role in allowing for a proper treatment of SOC with DFT. We also discuss the development of our "signed-canonical" non- collinear formulation of the DFT. A proper formulation of non-collinear DFT is also necessary for treating SOC, because the total energy obtained from the calculation otherwise varies according to the spatial orientation of the system using the usual collinear procedure (i.e. the collinear formulation is said to not be rotationally invariant). A rotationally invariant non-collinear procedure has already been established for the local-density approximation, and results in a very robust and numerically stable formulation. This is instead not the case for the generalized-gradient approximation (GGA). We show that all existing formulations are not rotationally invariant for GGAs, both from a formal and numerical point of view. What is more, all non-collinear formulations suffer from serious numerical instabilities in regions of space with small magnetization, and the existing ones do not reduce, either formally or numerically, to the collinear limit (i.e. a different energy is obtained with the existing non-collinear formulations versus the collinear formulation when the magnetization is everywhere parallel). We show that all these problems can be resolved using our proposed "signed-canonical" non-collinear formulation of the DFT, combined with a screening algorithm to deal with spatial regions of small magnetization.

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Insights from MD simulations on NO diffusion in hemoglobin

Ann M. English, Maria S. Shadrina and Gilles H. Peslherbe

Department of Chemistry and Biochemistry, Centre for Research in Molecular Modeling and PROTEO, Concordia University, 7141 Sherbrooke Street West, Montreal, Quebec H4B 1R6

ann.english@concordia.ca; gilles.peslherbe@concordia.ca

O_2 delivery by the adult hemoglobin tetramer (HbA) is the classical paradigm of cooperativity in protein ligand binding. The **R**-to-**T** quaternary transition in HbA is vital for this cooperativity. We have performed MD simulations, which reveal transient gas tunnels in HbA not observed in crystal structures. Although the tunnel topology does not vary with quaternary state, the O_2 population in the cavities and the preferred O_2 escape portals vary significantly. Notably, most O_2 molecules escape from the β-subunit into HbA's central cavity in the **T** but not **R** state. Nitric oxide (NO) is a key vasodilator in the vasculature and an O_2-dependent mechanism protects NO from conversion to vasoinactive NO_3^- by the oxyhemes of HbA. NO addition to the –SH group of Cysβ93 in HbA's β-subunit is implicated since the –SNOH adduct can subsequently release NO. Thus, we hypothesized that NO transfer from the β-deoxyheme to Cysβ93 occurs *intramolecularly* within the β-subunit to prevent free NO scavenging by the oxyhemes of neighboring HbA molecules. Indeed, as we reported for O_2, molecules of NO placed in the β-distal heme site of **T**-state deoxyHbA rapidly diffuse into its interior and enter the central cavity. In **R**-state oxyHbA, the central cavity contracts, bringing Cysβ93 and NO closer and promoting –SNOH formation. Our simulations clearly suggest that HbA's **R**-to-**T** conformational changes are designed to ensure fast *intramolecular* NO diffusion from the β-heme to Cysβ93 in synergy with cooperative O_2 heme binding in order to match O_2 delivery with tissue metabolic demand.

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Invited Tuesday 9:40

Analyzing and approximating the exchange-correlation hole through the factorization approach

Matthias Ernzerhof

Department of Chemistry, University of Montreal

matthias.ernzerhof@umontreal.ca

To represent the exchange-correlation hole $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$ of density functional theory, we select the correlation factor ansatz $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u}) = f_C(\mathbf{r},\mathbf{r}+\mathbf{u})\ \rho_X(\mathbf{r},\mathbf{r}+\mathbf{u})$. The correlation factor $f_C(\mathbf{r},\mathbf{r}+\mathbf{u})$ turns the exchange hole $\rho_X(\mathbf{r},\mathbf{r}+\mathbf{u})$ into the exchange-correlation (XC) hole. The X-hole, in turn, can be factorized according to $\rho_X(\mathbf{r},\mathbf{r}+\mathbf{u}) = f_X(\mathbf{r},\mathbf{r}+\mathbf{u})\ \rho(\mathbf{r}+\mathbf{u})$. We show how existing approximations to the exchange-correlation energy $E_{XC}[\rho]$ can be used to construct XC holes -or equivalently- $f_C(\mathbf{r},\mathbf{r}+\mathbf{u})$ and $f_X(\mathbf{r},\mathbf{r}+\mathbf{u})$. Furthermore, there are various theories available that relate $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$, $f_C(\mathbf{r},\mathbf{r}+\mathbf{u})$, and $f_X(\mathbf{r},\mathbf{r}+\mathbf{u})$ to wave function theory; examples are the adiabatic connection, density scaling, and density functional perturbation theory. Employing these theories and factorization models for the XC holes of conventional approximations to $E_{XC}[\rho]$, we combine wave function theory and density functional theory and obtain improved versions of $E_{XC}[\rho]$. We discuss applications of these new functionals to various properties such as atomization energies, reaction barrier heights, and ionization potentials.

Electrical feedback hypothesis of regulation of the mitochondrial inner membrane electrical potential

Peyman Fahimi[1,2], *Lazaro A. M. Castanedo*[1,3],
Thanh-Tung Nguyen-Dang[2] *and Chérif F. Matta*[1-4]

[1]Department of Chemistry and Physics, Mount Saint Vincent University,
Halifax, Nova Scotia, Canada B3M 2J6

[2]Département de chimie, Université Laval, Québec, Québec, Canada G1K 7P4

[3]Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3

[4]DepartmentofChemistry, DalhousieUniversity,Halifax,NovaScotia,Canada B3H 4J3

peyman.fahimi.1@ulaval.ca; cherif.matta@msvu.ca

An electrical feedback hypothesis of regulation of the mitochondrion is proposed. It is suggested that in order to maintain the integrity and stability of the life-sustaining electrochemical gradient, *i.e.* homeostasis, a feedback control is in operation. When the electric field of inner mitochondrial membrane is stronger than its optimal value, the pressure on the membrane due to the electrical gradient increases the viscosity of the two-dimensional liquid crystalline membrane, which, as a consequence, decreases the lateral rate of diffusion of all species inside the membrane (including ubiquinone/ubiquinol (Q/QH)). Since the diffusion of Q/QH is the rate- limiting step of the electron transport chain (ETC) occurring in the inner mitochondrial membrane, the reduced mobility of these species slows-down the ETC itself. Since the rate of the ETC determines the rate of pumping of protons from the matrix to the intermembrane space, and as a result, the build-up of the proton gradient is reduced in response to an increase proton gradient-dependent increase in the electric field. In other words, the pressure-induced slowing down of diffusion "puts the breaks", so to speak, on the ETC to restore it optimal value. In contrast, when the electric field reaches dangerously low levels, ATP synthase stops allowing proton through it to promote the accumulation of protons in the intermembrane gap while the weaker electric field produces lower pressure on the membrane that result in a lower viscosity and a faster flux in the components of the ETC effectively accelerating the pumping of more protons per unit time to restore the field to its optimum value.

Continued….

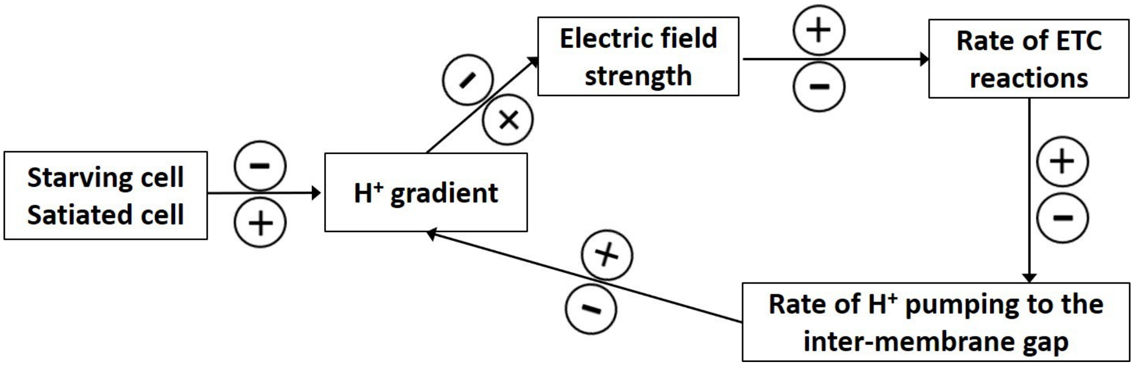

Fig. 1: The cybernetic hypothesis: A starving cell has a lower proton gradient which gives rise to a weaker electric field. The rate limiting step of the electron transport chain (ETC) and the steps leading to it, which is inhibited by stronger external fields, is accelerated, and as a result, the flux through the ETC reactions speeds-up to oppose the effect of starvation and maintain cellular life.

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Melting-like transitions in silver clusters with 8 to 20 atoms

René Fournier, Maryam Moshi, and Ramon A. Miranda-Quintana

York University, Department of Chemistry

renef@yorku.ca

Melting-like transitions in nanoparticles and clusters are of fundamental interest, and are important for nanotechnology, but are still poorly understood. We report Monte Carlo simulations on silver clusters of 8, 12, 16 and 20 atoms at temperatures ranging from below, to above, the melting-like transition. We obtained density functional theory (DFT) energies with the TPSS functional for thousands of cluster geometries generated by random distortions of low-energy isomers. These data were fitted to an accuracy (generalization error) of 5 to 10 meV/atom by ridge regression with a 10-fold cross-validation protocol using geometric features that are invariant to translations, rotations, and atom permutations. Parallel tempering simulations at several temperatures were carried out using the fitted potential. Heat capacity-temperature curves smoothed by local linear regression (LOESS) give estimates for the cluster melting points: 575 K (8-atom), 485 K (12- atom) and 715 K (20-atom). For comparison, the melting point of bulk silver is 1235 K. We examine potential energy distribution curves and descriptors of geometry such as the pair distribution function to obtain other estimates of melting temperature and to find evidence for a solid-liquid equilibrium over a range of temperature centered about the melting point.

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Analysis of indicators relevant for the description of kinetic and exchange energy functionals

Héctor I. Francisco[1], Javier Carmona-Espíndola[2] and José L. Gázquez[1]

[1]Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química,
Av. San Rafael Atlixco 186, Cd. de México, 09340, México.

[2]Conacyt-Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química,
Av. San Rafael Atlixco 186, Cd. de México, 09340, México.

hifr@xanum.uam.mx; jcarmona@yahoo.com.mx

One of the most important challenges within density functional theory is to improve the quality and accuracy of exchange energy functionals, as well as to generate new kinetic energy functionals that explicitly depend on the electron density and perform well in the calculation of chemical properties. Improving these functionals involves the incorporation of indicators that characterize the different regions of an atom or a molecule. The usual indicators are the reduced density gradient s, the reduced density Laplacian q, iso-orbital-indicators as $\alpha = (\tau_{KS} - \tau_W)/\tau_{TF}$, $z = \tau_W / \tau_{KS}$, $t^{-1} = \tau_{KS}/\tau_{TF}$, $\beta = \alpha/(\alpha + (5/3)s^2 + 1)$ and some interaction indices such as the electron localization function $ELF = 1/(1+\alpha^2)$ and the strong covalent interaction $SCI = 1/\alpha$, where τ_{KS}, τ_W and τ_{TF} are the kinetic energies densities of Kohn-Sham, Weizsacker and Thomas-Fermi, respectively. In this work we perform a study that allows one to find the physically important regions of each one of them, which have the greatest contribution to the energy. An additional outcome that results from the study of these quantities, lies in the fact that they themselves can be used to describe different type of interactions between molecules.

ACKNOWLEDGMENT

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Novel paths for the study of spin polarized systems and phase change materials

Carlo Gatti[1,2], *Giovanni Macetti*[3], *Jean-Yves Raty*[4] *and Matthias Wuttig*[5]

[1]CNR-ISTM, Istituto di Scienze e Tecnologie Molecolari, via Golgi 19, 20133 Milano, Italy

[2]Istituto Lombardo Accademia di Scienze e Lettere, via Brera 28, 20121 Milano, Italy

[3]Dipartimento di Chimica dell'Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy

[4]CESAM and Physics of Solids Interfaces and Nanostructures, B5 Université de Liège,
B4000 Sart-Tilman, Belgium

[5]Institute of Physics IA, RWTH Aachen University, 52074, Aachen, Germany

c.gatti@istm.cnr.it

In a recent paper on *Current Developments and Future of Quantum Crystallography* (QCr), options are discussed on "how QCr can evolve to become a complete and independent domain of natural sciences". While pursuing this goal is a worthy endeavour, efforts to export QCr knowledge in domains where it is poorly known but potentially useful are also relevant. Attempts in either direction are highlighted in this talk. Concerning the first, the concept of Source Function (SF) is extended to electron spin density (SDs) distributions and used as a way to analyze the magnetic patterns in metal complexes molecular crystals. Extraction of chemical information from the SD is not a trivial task and further precious insight is provided by *partial* Source Function SD reconstructions using subsets of atoms. The SF SD also serves as a useful tool for discussing the SD accuracy and for disclosing the origin of the SD discrepancies when approaches of increasing quality are used. The study of the relationships between chemical bonding and technologically relevant properties in chalcogenide phase-change materials (PCMs) represents, instead, a successful example of exporting QCr know-how in new domains. PCMs are widely used for data storage and photonics, as they can be easily transformed between their amorphous and crystalline states (CS), which have significantly different optical properties and a pronounced difference in resistivity. This contrast of properties has been summarized in five specific fingerprints for PCMs CS and in terms of *metavalent* bonding (MVB), a distinct mode of bonding, occurring only in the crystalline phase. A 2D map of bonding in solids was thus established by using electron sharing indices and charge transfer descriptors. Peculiar combinations of their values lead to steep variations in a third dimension related to the material's response properties. Though the necessity of introducing a new type of bonding may be questioned, the susceptibility to steep property changes emerges as a relevant feature of bonding, too often overlooked in usual QCr bond descriptions.

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New avenues in conceptual density functional theory

Paul Geerlings[1], Tom Bettens[1], Robert Balawender[2] and Frank De Proft[1]

[1]General Chemistry(ALGC), Vrije Universiteit Brussel, Pleinlaan 2, Brussels, Belgium

[2]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka44, Warsaw, Poland

pgeerlin@vub.be

Within the context of Conceptual Density Functional Theory (CDFT) and as a sequel to our work on the Linear Response Function recent work is presented on the use of Alchemical Derivatives to explore Chemical Space. Particular attention is paid to the alchemical transmutation of a neutral atom in its neighbouring atom, involving both a change in the nuclear charge and the number of electrons. A proof of concept study indicates that starting from some energetical properties of a given, reference, atom, the energetics of its neighbour can be predicted. Applications to the evaluation of first and second atomic electron affinities are given. A new avenue in CDFT is presented by extending the number of variables in the fundamental functional $E=E\ [N,v]$ (where N is the number of electrons and v the external potential) by inclusion of external mechanical forces F in it, leading to a functional $E = E[N,v,F]$. The traditional conceptual DFT quantities such as a electronegativity, hardness then are also pulling force for diatomics is brought into relation with the redox behaviour of biomolecules under external forces depend on the external force, bridging Conceptual DFT with Mechanochemistry. Trends in the mechanochemical response indices are discussed for a series of diatomic molecules.

Possible quantum crystallography solutions for N-representable one-electron reduced density matrices reconstruction

J.-M. Gillet[1]*, S. Gueddida*[1]*, B. de Bruyne*[1]*, Z. Yan*[1]*, I. Kibelin*[2]*, M. Souhassou*[3]*,*
N. Claiser[3]*, C. Lecomte*[3] *and P. Cortona1, B. Gillon*[2]

[1]Structures, Properties and Modelling of Solid slab. UMR8580 , CentraleSupelec, Paris- Saclay University,
3 rue Joliot-Curie, 91191 Gif-sur-Yvette, France

[2]Leon Brillouin lab., UMR12, CEA-CNR, Bât 503 CEA Saclay, 91191 Gif sur Yvette Cedex, France

[3]CRM2, UMR 7036, Faculté des Sciences et Technologies, Université de Lorraine, BP 70239,
Boulevard des Aiguillettes, 54506 Vandoeuvre-lès-Nacy cedex, France

jean-michel.gillet@centralesupelec.fr

One of the goals of Quantum Crystallography is to study to what extent experimental tools of crystallography such as X-ray, electron, neutron diffraction, in their polarized and non-polarized versions can be used to gain better access to fundamental quantum properties such as the N-electron wavefunction. Being directly related to the electron probability density in positionspace, all these structure factors are believed to be the most essential part of our experimental knowledge of the wavefunction. Moreover, the Hohenberg and Kohn theorem has sometimes reinforced the idea that electron-position probability density should be the ultimate asset in the quest for the wavefunction. But as the theorem gives general proof of principle that either quantity is enough to recover the other, it does not indicate that it would hold for the non-pure states no that real-life experimental data would be sufficient. Therefore, complementary information needs to be found for consolidating any attempt in wavefunction reconstruction. As a first step from the electron density towards the N-electron wavefunction, the one-electron reduced density matrix (1-RDM) is a good indicator of our ability to exploit scattering data, with little prior knowledge or model. In recent years, our collaboration has developed methods to extend the range of scattering experiments to gain access to better 1-RDMs which fulfill N-representability conditions. Two such possible approaches will be described in the cases of spin-resolved and charge-only 1-RDM for model systems. The purpose is to assess the quality of a 1-RDM reconstruction using coherent-elastic and incoherent-inelastic pseudo-experimental data and critically compare the result to the original, periodic ab-initio derived, 1-RDM standard reference.

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Exploring chemical reactivity through excitability and polarizability

Frédéric Guégan[1,2], *Henry Chermette*[1] *and Christophe Morell*[1]

[1]Institut des Sciences Analytiques de Lyon, UMR CNRS-Université de Lyon 5280, 69622 Villeurbanne Cedex, FRANCE

[2] Present address: Institut de Chimie des Milieux et Matériaux de Poitiers, UMR CNRS-Université de Poitiers 7285, 86000 Poitiers, France

frederic.guegan@univ-poitiers.fr; christophe.morell@isa-lyon.fr

Rationalising molecular reactivity and selectivity is a central goal in chemistry. Many theoretical frameworks were proposed over time, and many of them rely on the computation of some reactivity descriptors derived from first-principles. These descriptors often share a similar conceptual basis, relating reactivity and selectivity of a system to the ability of its electron cloud to distort during a chemical event. Excitability, on the other hand, describes the propensity of a system to reach its excited states. It is also expected to be linked to a propensity of the electron cloud to distort, this time under a perturbation induced by an irradiation with light.

Both reactivity and excitability appear formally connected. Interestingly, this connection was first proposed by Walsh (in the 1940's) and more recently by Pearson (in the late 1980's), but very few developments have explicitly followed this idea, though several reactivity descriptors are in line with this proposition (for instance frontier molecular orbitals or the state-specific development of the dual descriptor).

Here, we propose a new set of reactivity descriptors, derived within a Rayleigh-Schrödinger perturbation theory framework, thus explicitly involving the excited states of the system under study. From the first order response of the electron density to an electrostatic perturbation, qualitative insight on reactivity/selectivity is retrieved, while more quantitative information is obtained from the first and (especially) second order energy responses.

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Real time dynamics and He-induced electronic transitions in doped helium nanodroplets at 0.4 K

Nadine Halberstadt[1], *François Coppens*[1], *Louis Merle*[1],
Patricia Vindel Zandbergen[1], *Manuel Barranco*[1,2,3] *and Marti Pi*[2,3]

[1]Laboratoire des Collisions, Agrégats, Réactivité, IRSAMC, UMR 5589, CNRS et Université Toulouse 3 – Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse Cedex 09, France

[2]Departament FQA, Facultat de Fisica, Universitat de Barcelona, Barcelona, Spain

[3]Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona, Barcelona, Spain

nadine.halberstadt@irsamc.ups-tlse.fr

We report theoretical investigations on the real time dynamics of photo-excited alkali atoms on the surface of superfluid He nanodroplets. He nanodroplets are intriguing, quantum fluid objects of finite size. Helium density functional theory (He-DFT) approach and its time-dependent version (He-TDDFT) are the best compromise between accuracy and feasibility to study the stability and real time dynamics of doped helium droplets with a size comparable to experiments.[1] Comparing with highly detailed recent experiments such as those combining pump-probe spectroscopy with velocity map imaging allows to show the importance of energy transfers between the excited atom and this unusual quantum solvent[2,3]. Approximated (Zero-Point Averaged Dynamics) dynamics[4,5] shows the existence of helium-induced electronic transitions.

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Invited Wednesday 14:20

The compressibility of micas: muscovite-phlogopite series minerals

Alfonso Hernández Laguna[1], *N. Hernández-Haro*[2], *J. Ortega-Castro*[2],
C. Pérez del Valle[3], *D. Muñoz-Santiburcio*[4], *I. Vidal-Daza*[5], *A. Sánchez-Navas*[1,5],
E. Escamilla-Roa1[6] *and C. I. Sainz-Diaz*[1]

[1]Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), 18100 Armilla, Granada, Spain

[2]Departament de Química, Universitat de les Illes Balears, Palma de Mallorca, Spain

[3]Département de Chimie Moléculaire, Université Grenoble Alpes, France

[4]CIC nanoGUNE, 20018 San Sebastian, Spain

[5]Universidad de Granada, 18071 Granada, Spain

[6]Department of Computer Science, Electrical and Space Engineering, Luleå University of Technology, 97187 Luleå, Sweden.

Alfonso.hernandez@iact.ugr-csic.es

Micas are one of the most common series minerals of the layered hydrous silicates, which occur in diverse crustal rocks (igneous, metamorphic, and sedimentary rocks), and they have been also found in Earth's upper mantle and in subduction slabs. For these reasons they undergo increasing pressure (P) processes. So, their compressibilities are important to know.

Muscovite (Ms) and phlogopite (Phl) are the ideal end members (EM) of the Ms-Phl series minerals, which can ideally be represented by following formula: $KAl_x\square x/2Mg_{3-3x/2}$ $(Si_3Al)O_{10}(OH)_2$, where □ represents the octahedral vacancy, x = 0 represents for Phl EM, and x= 2 represents for Ms EM. Five compositions are considered: Phl, X(Ms)=0.25, 0.50, 0.75, and Ms (X(Ms)=½x).

The Ms-Phl series has been studied with Quantum ESPRESSO 5.4, GGA, B86PBE-XDM, PW and PAW up to a P of 9 GPa; Equations of States were fitted to a Birch-Murnagham equation. Atomic compressibilities are studied by the QTAIM theory.

The calculated crystalline structures and bulk moduli agree with the known experimental structures. The Ms-Phl excess free energy at different P are studied as a function of composition, founding a gap of solubility which is narrowed at increasing P. Atomic compressibilities are also calculated all along the series. Atomic compressibilities are studied in the different sheets of the crystal structure and as a function of the composition.

Compressional behavior of the aragonite-structure carbonates to 6 GPa.Atomic compressibilities

Alfonso Hernández-Laguna[1]*, Isaac Vidal-Daza*[2]*,*
Antonio Sánchez-Navas[2] *and Claro I. Sainz- Díaz*[1]

[1] Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Av. de las Palmeras, 4,
18100 Armilla, Granada, Spain

[2] Universidad de Granada, 18071 Granada, Spain.

alfonso.hernandez@iact.ugr-csic.es

Carbonates are an important group of minerals, which are present in the Earth's crust forming mainly part of sedimentary and metamorphic rocks. Aragonite ($CaCO_3$), strontianite ($SrCO_3$), cerussite ($PbCO_3$) and witherite ($BaCO_3$) are naturally isostructural orthorhombic group. They are studied at increasing pressure to 6 GPa with DFT at PW level, B86bPBE correlation exchange functional, XDM for dispersion forces and PAW pseudopotentials. Compressibility of the system has been structurally calculated at different levels: bulk, axes, interatomic distances, and atomic compressibilities. Results are compared with the known experimental data in literature and agree with the majority of them. A softening at 3 GPa is found for the *b* axis of the witherite, which agrees with some of the experimental results. The main compression direction is along the *c* axis, and the geometric features included in this direction are C···C distances and C volumes. The bulk modulus is linear function of these structural moduli. The weak bonding properties along C···C look like to be determinant for the compressional properties of this series of minerals. The distances of the C to the bases of the octahedron show different compressional behavior, and the difference between both distances increases with the pressure and cations. The increasing volume of cations in the series lows down K_0 and K_0' (derivative of K_0 with respect to pressure). The volume of the C atoms is a linear function of the C compressibility.

Gas-phase thermolysis reaction of substituted cyclic diperoxides

Alfonso Hernández-Laguna[1]*, Nelly L. Jorge*[2]*, Daniel Roca-Sanjuán*[3]*,*
André Grand[4] *and Claro I. Sainz- Díaz*[1]

[1]Instituto Andaluz de Ciencias de la Tierra, CSIC-UGR, Av. Las Palmeras 4, 18100 Armilla, Granada, Spain

[2]Área de Química Física Facultad de Ciencias Exactas y Naturales y Agrimensura, UNNE,
Avda. Libertad 5460, 3400 Corrientes, Argentina

[3]Instituto de Ciencia Molecular, Universitat de València, Apartado 22085, ES-46071 Paterna, Spain

[4]Université Grenoble Alpes, CEA, CNRS, INAC-SyMMES, 38000 Grenoble France.

alfonso.hernandez@iact.ugr-csic.es

The organic peroxides are interesting compounds with a broad range of properties from antimalarial and antimicrobial activities to explosive character. Mechanism of reaction of the gas-phase thermolysis reaction of tetroxane [1,2,4,5 formaldehyde diperoxide (FDP/tetroxane)], methyl-derivatives, and other substituted derivatives were studied by DFT calculations, considering in some cases position isomers. Kinetic experiments were performed for FDP and di-butanal-tetroxane (DBT) by gas chromatography in the injection chamber of the gas reactor device. Different temperatures have been applied, and as a result activation energies (Ea) and kinetic constants were found. The critical points of the singlet (**S**) and triplet (**T**) potential energy surfaces (PES) were calculated. Three mechanisms are considered: i) **S**-concerted; ii) **S**-stepwise; and iii) **T**-stepwise. Experimental Ea's are in agreement with Ea's calculated with BHandHLYP/6-311+G** of FDP and DBT. The concerted mechanism has a very high Ea. The first intermediate of the reaction through **S**-stepwise-PES is an open diradical structure, **o**, yielding, after some steps, two molecules of aldehyde/ketones and O_2 at **S** state as products. The **S-o** and **T-o** are similar in structure and energies, so a crossing from the **S**- to **T**-PES is produced at the **o** intermediate as a consequence of a spin-orbit coupling. Therefore, reaction follows after the crossing by the **T**-PES, yielding O_2 at the **T** state. The reaction energy (Er) at the **T**-PES is more in agreement with the Er of the exothermic experimental peroxide products. Ea, Er, and O···O distances are studied as a function of the number of methyl groups and the position- isomerization.

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The role of H…H bonding in the biphenyl crystal

Jesús Hernández-Trujillo[1], *Bruno Landeros-Rivera*[2], *Vojtech Jancik*[3],
Diego Martínez-Otero[3] *and Rafael Moreno-Esparza*[1]

[1]Facultad de Química, Universidad Nacional Autónoma de México

[2]Universidad Autónoma Metropolitana Iztapalapa

[3]Instituto de Química, Universidad Nacional Autónoma de México

jesusht@unam.mx

This contribution presents a combined experimental/theoretical study of the biphenyl crystal in order to assess the presence of intramolecular H...H bonding. This type of interactions was proposed before in a theoretical study of isolated molecules where biphenyl played a central role; despite the controversy surrounding its existence, increasing experimental and theoretical evidence suggests the importance of H...H bonding in chemistry. An X-ray diffraction study of the biphenyl crystal was conducted at 100 K followed by a multipolar refinement using the Hansen-Coppens formalism to obtain the experimental electron density. The corresponding molecular graph showed the presence of intramolecular H...H bond paths, thus confirming the existence of such interactions in the solid. This stage was followed by a quantum chemical study in which a geometry optimization of the crystal was carried out (with the cell parameters fixed to the experimental values) at the B3LYP-D*/POB-TZVP level of calculation. Good agreement between the experimental and theoretical crystal geometries was obtained and the existence of two small imaginary vibrational frequencies suggests the possibility of the experimental planar biphenyl moiety to be an average of two slightly non-planar arrangements. The topological analysis of the theoretical electron density corroborated the presence of relatively strong stabilizing non-covalent intramolecular H...H bonding in this prototypical crystal. In addition, several types of intermolecular contacts were identified, and an energy decomposition analysis confirmed the dominance of the dispersion contribution to intermolecular pairwise interactions.

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Using machine learning to determine molecular properties from electron densities

M. Hilke, D. Bernardi, A. Cheng, D. Ittah, D. Lopez,
M. Saathoff and A. Vuong

Department of Physics, CPM and INTRIQ, McGill University, Montreal, QC-H3A 2T8, Canada

hilke@physics.mcgill.ca

Machine learning has emerged as a powerful tool to classify images through training of a deep convolution neural network. An input image is then associated to an image category. Machine learning (ML) can also be extended to quantum properties such as orbitals and electron densities, which is sometimes referred to quantum ML. In this work we study the case of an input, which stems from a quantum problem. We evaluate the local density of states of molecular systems, such as graphene flakes and macroscopic systems such as a two-dimensional electron gas. As outcome we want to identify the underlying structure, like edge structure and underlying disorder potential. For instance, we considered the case of a two-dimensional electron gas in a magnetic field subjected to a random potential characterized by amplitude, impurity shape, depletion depth and roughness. We used an iterative Green's function method to evaluate the local density of states and conductance and train the neural network to recognize various properties of the system with different disorder configurations. Using multiple neural regression layers at the output allows us to predict the potential characteristics as well as the magnetic field, energy and localization properties, simply from the local density of states with over 95% confidence. Finally, the trained neural network is applied to experimental data, obtained by scanning gate microscopy on disordered graphene at low temperatures, to determine the properties of the effective underlying disorder potential.

Design of dyes based on density functional theory and molecular dynamics descriptors

*Paula Homem-de-Mello, Esther M. C. de Lima, Felipe C. T. Antonio,
Fernanda Bettanin, Jhonathan R. Souza, Mateus Zanotto, Michele Ap. Salvador,
Cleiton D. Maciel, Yuri A. Aoto and Mauricio D. Coutinho-Neto*

ABCSim, Center for Natural Sciences and Humanities (CCNH),
Federal University of ABC (UFABC), Santo André, Brazil.

paula.mello@ufabc.edu.br

Electronic excitations are the basis of the use of dyes in different systems: from dye- sensitized solar cells (DSSC) to applications in the treatment of diseases, such as photodynamic therapy (PDT). Proposing dyes with higher efficiency for these applications is a joint venture between theorists and experimentalists. For both applications, basically the dye absorbs light radiation and transforms that energy into electrical current, in the case of DSSCs, or in free radicals, in the case of PDT. Thus, understanding the states involved in electronic excitation is the first step in planning for new molecules, followed by evaluating the medium effects on electron transfer processes. We have been studied different classes of dyes, organic and metallic complexes, with experimental results about either singlet oxygen yield or energy conversion efficiency. We have employed mainly time (in)dependent density functional theory to obtain different structural and electronic properties for both ground and excited state. Molecular dynamics simulations have also been performed, especially for the study of aggregation and interaction with the solvent and then performed sequential QMMM simulations. Then, we are proposing substitutions on the molecular structures to verify the effects on geometry and on electronic properties of the ground and excited states, as well as on the self-aggregation and interaction with the solvent and the molecular oxygen. From these simulations, the descriptors have been obtained to design new and more active molecules.

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Quantum chemical simulations of thermal-mechanical coupling in high pressure and temperature materials synthesis

Hang Hu and Gilles H. Peslherbe

Department of Chemistry and Biochemistry, Concordia University,
7141 Sherbrooke Street West Montréal, Québec, Canada,

hang.hhu@gmail.com; gilles.peslherbe@concordia.ca

The diamond anvil cell (DAC) now allows experimental studies of phase transitions in materials under much higher pressure (700GPa) and temperature (5000ºC) then previously feasible. In a typical DAC experiment, the initial substrate undergoes mechanical compression followed by thermal heating. Individually, increasing pressure and temperature often have opposite effects on materials, as the former contracts and the latter tend to expand the crystal lattice. The exact nature of the thermal-mechanical coupling inside the DAC necessary for the chemical transformation to take place is still poorly understood and difficult to decipher experimentally. We propose a simulation technique mimicking pressure jumping experiments which allows to unveil pressure- selected reactive coordinates and reaction trajectories in unprecedented structural detail, yielding reaction energy, stress and shear profiles necessary to examine thermal- mechanical coupling effects. In addition to reaction profiles, pressure *vs* temperature phase transition diagrams can also be generated. The simulation methodology is applied to cubic carbon nitride (c-C_3N_4) and cubic boron nitride (c-BN), both superhard materials with available experimental data for high pressure and temperature phases. The simulated pressure *vs* temperature curve agrees well with experimental results. The reaction profiles exhibit multiple bond breaking and forming steps during phase transition; *shear flow* is shown to be associated with bond breaking and forming processes at the onset of mechanical work coupling with thermal heat, while the stress profile is not significantly perturbed In the process. This novel simulation methodology seems promising for guiding future high pressure and temperature materials synthesis.

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Equation of state and first principles prediction of the vibrational matrix shift of solid parahydrogen

Alexander Ibrahim[1]*, Lecheng Wang*[1]*, Tom Halverson*[2]*,*
Robert J. Le Roy[1] *and Pierre-Nicholas Roy*[1]

[1]Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo,
Ontario N2L 3G1, Canada

[2]Department of Chemistry and Biochemistry, Texas Tech University, P.O. Box 41061,
Lubbock, Texas 79409-1061, United States

a68ibrahim@uwaterloo.ca; pnroy@uwaterloo.ca

The properties and applications of solid parahydrogen (*para*-H_2) have become a subject of considerable interest over the past several decades. As a quantum crystal, solid *para*-H_2 exhibits many exotic quantum behaviours at low temperatures, and its large lattice constant and weak intermolecular interactions make it an excellent host for matrix isolation spectroscopy. In this project we use a path-integral Monte Carlo (PIMC) simulation alongside a new, highly accurate *para*-H_2 dimer potential energy curve to generate the equation of state (EOS) of solid *para*-H_2. Systematic errors associated with the use of finite simulation parameters in PIMC simulations are eliminated by extrapolation. In agreement with experiments, the HCP crystal structure of solid *para*-H_2 was found to be more stable than the FCC crystal structure. We use the EOS generated in this work to calculate the pressure as a function of density, which is then compared with previous simulation results and experiments. The vibrational matrix shift of solid *para*-H_2 at its equilibrium density is calculated and found to agree very well with experiment.

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Constrained path integral Langevin equation integrators

Dmitri Iouchtchenko, Kevin Bishop and Pierre-Nicholas Roy

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

diouchtc@uwaterloo.ca; pnroy@uwaterloo.ca

Several techniques exist to extract free energy differences from classical molecular dynamics simulations, but there are far fewer that are directly applicable to simulations which include quantum effects, such as those based on the path integral Langevin equation (PILE) integrator. Rather than starting from a restraint method, such as umbrella sampling, we propose a modification to the PILE that introduces an exactly-solvable constraint. By constraining the reaction coordinate at only a single path integral bead, we may use force-based estimators to compute the derivative of the free energy. Integration of this quantity allows for the systematic calculation of quantum free energy differences.

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Dynamics simulation of noble gases adsorption on homogeneous and heterogeneous carbon nanotube bundles

Nazli Jodaeeasl and Roya Majidi

Department of Physics, Shahid Rajaee Teacher Training University, Lavizan, Tehran, Iran

Nazli.asl.ir@gmail.com

We have used molecular dynamics simulation to investigate the application of single-walled carbon nanotube (SWCNTs) bundles as noble gas storage materials. Adsorption of He, Ne, Ar, Kr and Xe have been studied. We have performed simulations using one model of bundles consisting of nanotubes having all the same diameter (homogeneous) and two different configurations of bundles of carbon nanotubes of different diameters (heterogeneous). The adsorption coverages were calculated. The results indicate that adsorption takes place both in the internal pore volume and at the external surface of the open-ended carbon nanotubes. It is also found that small gases such as He and Ne can adsorb in interstitial channels (ICs) between three adjacent tubes of bundles, but Ar, Kr, and Xe gases adsorb only in the (ICs) of one of the models of heterogeneous SWCNTs bundles. These results demonstrate that the configuration of the bundle has a considerable effect on the adsorption capacity and (SWCNTs) bundles have desirable characteristics as an adsorbent.

Fonctions d'onde modèles pour la corrélation forte d'électrons

Paul A. Johnson, Frédéric Berthiaume, Laurie Carrier, Samuel Cloutier,
Charles-Émile Fecteau et Marianne Gratton

Département de chimie, Université Laval, 1045 av. de la Médecine, bureau 1220 Québec (Québec), G1V 0A6

paul.johnson@chm.ulaval.ca

Les systèmes faiblement corrélés sont bien décrits en termes d'électrons individuels. La contribution dominante est donnée par le déterminant de Slater des orbitales occupées, auquel des petites corrections sont apportées par d'autres déterminants de Slater dont les orbitales occupées ont été remplacées par des orbitales virtuelles. Cette interprétation permet donc une courte expansion de la fonction d'onde. Pour les systèmes fortement corrélés, ce n'est pas le cas. De nombreux déterminants de Slater contribuent sensiblement à la fonction d'onde physique, ce qui rend l'interprétation des électrons individuels incorrecte. Pour mieux comprendre ces types de systèmes nous travaillons avec des modèles exactement solubles qui décriront le comportement des électrons au premier ordre. Nous affirmons que si le modèle est approprié, l'expansion de la fonction d'onde sera courte. L'objectif est donc de développer des méthodes précises et peu couteuses pour les électrons fortement corrélés.

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Hybrid functionals in ADFT: accuracy and performance assessment

Andreas M. Köster

Departamento de Química, Centro de Investigación y de Estudios Avanzados, Av. Inst. Politécnico Nacional
2508, Col. San Pedro Zacatenco, CDMX, C.P. 07360, México

akoster@cinvestav.mx

The implementation of hybrid functionals in the framework of auxiliary density functional theory (ADFT) employing the variational fitting of the Fock potential is described. The accuracy and performance of the resulting four-center electron repulsion integral free approach is discussed with respect to conventional theoretical implementations and experiments. Illustrative benchmark calculations and applications are presented.

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Exploring the reactivity of cellulose under non-thermal atmospheric plasma conditions

Walid Lamine, Frédéric Guégan amd Gilles Frapper

IC2MP UMR 7285, Université de Poitiers - CNRS, 4, rue Michel Brunet TSA 51106–86073,
Cedex 9 Poitiers, France

walid.lamine@univ-poitiers.fr; frederic.guegan@univ-poitiers.fr; gilles.frapper@univ-poitiers.fr

Recently, much attention has been paid to designing new approaches to cellulose conversion into platform chemicals and biofuels. However, depolymerization of this abundant biopolymer (45% of the annual biomass production) to produce processable polysaccharides is heavily hindered by its highly crystalline structure. Besides common pretreatment methods (*i.e.* ball-milling or ionic liquid), nonthermal atmospheric plasma (NTAP) was found to be a promising technology for increasing reactivity of recalcitrant cellulose towards hydrolysis. Given the complex cocktail of excited species, and particularly radicals generated during NTAP treatment, exact mechanism governing depolymerization of cellulose is difficult to elucidate. In line with previous studies, we first considered hydroxyl radicals HO° as initiators of the mechanism. We thus studied discrete cellulose models, ranging from cellobiose to cellotetraose, and their reactivity towards hydroxyl. Here we have shown that degradation of glycosidic bonds may be obtained through a sequence of H-abstraction, fragmentation and hydrolysis reactions. However, an alternative and unexpected scenario can also be proposed. DFT calculations indeed revealed that ionization of cellulose oligomers always leads to radical cations displaying an intriguing two-center/one electron (2C-1e) bond, localized in the immediate vicinity of a glycosidic bond. In all cases, ionization potentials are found to be lower than those of O_2 and N_2, thus suggesting cellulose itself could be the actual initiator of a radical mechanism. This would in turn open new perspectives in the study of reactivity under NTAP conditions.

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Scattering dynamics of N_2 off W(100) at low collision energies: reconciling theory and experiments.

Pascal Larregaray[1,2], *Cesar Ibarguën Becerra*[1,2], *Alejandro Peña-Torres*[1,2,3], *Heriberto F. Busnengo*[4], *Joseba I. Juaristi*[3,5,6] *and Cédric Crespos*[1,2]

[1] Université Bordeaux, ISM, UMR5255, F-33400 Talence, France

[2] CNRS, ISM, UMR5255, F-33400 Talence, France

[3] Centro de Física de Materiales CFM/MPC(CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5,
20018 Donostia- San Sebastiań, Spain

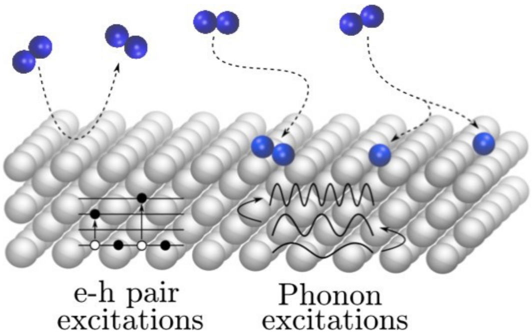
[4] Instituto de Física de Rosario (CONICET-UNR) and Facultad de Ciencias Exactas,
Ingeniería y Agrimensura, Universidad Nacional de Rosario, Avenida Pellegrini 250,
2000 Rosario, Argentina

[5] Donostia International Physics Center(DIPC), Paseo Manuel de Lardizabal 4,
20018 Donostia-San Sebastiań, Spain

[6] Departamento de Física de Materiales, Facultad de Químicas (UPV/EHU), Apartado1072,
20080 Donostia-San Sebastiań, Spain

pascal.larregaray@u-bordeaux.fr

In the last decades, the scattering dynamics of N_2 off W(001) has been the subject of theoretical investigations, which were found unable to describe low-collision-energy molecular beam experiments. This discrepancy was suggested to originate from the neglect of van der Waals interactions in the construction of the potential energy surface. By making use of a newly developed potential energy surface, accounting for such dispersion interactions, we show that quasi-classical dynamics simulations, including dissipation to surface electrons and phonons, lead to an adequate description of the low-collision-energy experiments. This work highlights the prominent influence of van der Waals forces on gas−metal scattering dynamics observables in the low-collision-energy regime.



Invited Wednesday 16:20

Probing the insulator to metal phase transition in VO_2 using high harmonic spectroscopy

François Légaré[1], *Mina R. Bionta*[1], *Elissa Haddad*[1], *Adrien Leblanc*[1],
Vincent Gruson[1,2], *Philippe Lassonde*[1], *Jérémie Chaillou*[1], *Nicolas Émond*[1],
Martin R. Otto[3], *Bradley J. Siwick*[3] *and Mohamed Chaker*[1]

[1]Centre Énergie Matériaux et Télécommunications, Institut National de la Recherche Scientifique, 1650 Boulevard Lionel-Boulet, Varennes, Québec, J3X 1S2, Canada.

[2]Department of Physics, The Ohio State University, 191 West Woodruff Avenue,
Columbus, Ohio, 43210, USA.

[3]Department of Physics and Department of Chemistry, Center for the Physics of Materials, McGill University, 801 Sherbrooke Street W, Montreal, Québec, H3A 2K6, Canada.

legare@emt.inrs.ca

When heated above ~343 K, VO_2 experiences a complete atomic rearrangement of the crystal lattice structure from a monoclinic insulator ($M1$ phase) to a metallic rutile crystalline structure (R phase). When initiating this IMT via photo-doping, in addition to the well-known $M1$ and R phase, it was discovered in 2014 through ultrafast electron diffraction (UED) measurements that a monoclinic metallic phase ($\mathcal{M}$) can be reached. The question we asked: Is high harmonic spectroscopy sensitive to the evolution of the IMT?

We track the IMT dynamics in VO_2 by measuring the yield of an intraband harmonic, requiring a conduction band with an anharmonic band structure. A mid-infrared laser pulse (drive) at 10 μm is used to drive high harmonic generation (HHG) from a 100 nm thick, epitaxial VO_2 sample. The sample is photoexcited with a 50 fs, 1.5 μm laser pulse (pump) to initiate the IMT. The fifth harmonic is recorded as a function of the time delay. Within the range of pump fluence where the observation of $\mathcal{M}$ phase has been observed with UED, we measured a drop of the harmonic signal at zero delay when electrons are promoted to the conduction band, followed by a recovery of the harmonic yield within a picosecond as measured using UED. This demonstrates the potential of high harmonic spectroscopy as a complementary technique for tracking ultrafast dynamics in solids.

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CYLview: a free molecular analysis and representation program for chemists.

Claude Y. Legault and *Raphaël Robidas*

Department of Chemistry, Université de Sherbrooke, 2500 boul. De l'Université,
Sherbrooke (Québec), J1K 2R1, Canada.

claude.legault@usherbrooke.ca

The efficient analysis and communication of scientific results is a vital portion of the work of any chemist. This aspect is even more important for computational chemists, due to the amount and complexity of the results obtained. Tools to maximize the efficiency of this process are thus critical. The present major challenge with the preparation of publication quality representations of structures is the need to use multiple programs to achieve the desired result. In this regard, CYLview was specifically created to accelerate the evaluation and analysis of computed structures, as well as to generate in the same program high quality representations, containing all the information (e.g. bond distances, angles, atom numbering) needed for professional publications and presentations. The steady increase in computing resources has led to the study of ever larger structures that are inherently more difficult to depict; static two dimensional images of three dimensional structures over a certain size lead to a loss of spatial orientation and distracting clutter. CYLview overcomes these issues by using powerful visual cues, such as fog and focal blur. This free software has grown in popularity over the years, with now more than 2500 registered users. The current features of the program will be presented. New developments will be presented to stimulate feedback and suggestions from the researchers.

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Spectroscopie et dynamique théorique de dopants moléculaires dans des agrégats d'hélium liquide

Marius Lewerenz

Laboratoire de Modélisation et Simulation Multi Echelle, MSME, UMR 8208 CNRS,
Université Paris Est Marne la Vallée, 5 Blvd Descartes, 77545 Marne-la-Vallée Cedex, France

Marius.Lewerenz@u-pem.fr

Des nano-gouttes d'hélium sont un environnement chimique qui est à la fois liquide, dense et très froid ($T < 1$ K) qui a attiré beaucoup d'intérêt depuis environ 20 ans. Une espèce atomique ou moléculaire (un dopant D) implantée dans une telle matrice subit des perturbations spécifiques de ses propriétés spectrales. La dynamique de photodissociation d'un dopant est très fortement influencée par la possibilité d'un transfert d'énergie vers l'hélium. Un fort obstacle pour la description théorique de ce genre de système est la nature quantique de l'hélium liquide. Les techniques de modélisation doivent respecter cette nature quantique globale et se prêter à des calculs avec un nombre important d'atomes. Nous avons développé un code performant pour la méthode exacte indépendante du temps du Monte Carlo quantique à diffusion (DMC) qui permet la prévision des perturbations vibrationnelles apportées à un dopant par le bain quantique et les modifications que le dopant apporte à la structure locale de son environnement. Ces calculs demandent en amont la construction de surfaces de potentiel précises et multidimensionnelles par des techniques de structure électronique fortement corrélées. La puissance de cette combinaison de méthodes sera illustrée par des applications à des ions moléculaires implantés comme CO^+ et OH^+, pour lesquels une détection expérimentale avec un tri de taille d'agrégat est envisageable. Le décalage de la fréquence de vibration calculé pour ces diatomiques est une fonction non- monotone et non-triviale de la taille de l'agrégat d'hélium. Pour étudier des phénomènes dépendants du temps dans l'hélium nous avons développé la technique approximative ZPAD (zero point averaged dynamics). Quelques premiers résultats obtenus avec cette méthode pour la photodissociation des molécules I_2 seront présentés. Nous calculons des distributions de vitesses de photo-fragments IHe_n sortant des agrégats et la distribution de la taille n. Ces deux grandeurs sont observables par la technique VMI (velocity map imaging).

Transferability of substituent properties from atoms in molecules

Kevin M. Lefrancois-Gagnon and Robert C. Mawhinney

Lakehead University, 955 Oliver Road, Thunder Bay, ON, P7B 5E1

kgagnon@lakeheadu.ca; rmawhinn@lakeheadu.ca

Chemists think of substituents as discrete entities that exist in different molecular environments. The Quantum Theory of Atoms in Molecules provides a theoretical foundation for this intuition by defining atoms as quantum mechanical open systems with additive properties. This leads to a clear definition of substituents as groups of these atoms whose properties are the sum of the properties of atoms in the group. To recover the traditional concept of a substituent, these properties should be transferable between different systems. If so, these properties would be applicable in correlation analysis studies in place of traditional empirical constants, such as Hammett's or Taft's. Using Gaussian16 and AIMAll software, the properties of 116 substituents were evaluated in different molecular environments. Using B3LYP/def2-TZVPPD model chemistry, we investigate whether properties vary in a series of substrates, including aromatic, AH_3 (A=C, Si, Ge), and different carbon-based hybridisations ($CHCH_2$, CCH, $CHCCH_2$). Changes in properties were quantified by linear regression methods, and by direct assessment of magnitudes of change. In some systems, geometric effects lead to non-transferability, as in the case of an amino substituent, which is planar in some substrates, but trigonal pyramidal in others. Ultimately, this work aims to develop a model of reactivity that employs predictable intrinsic substituent properties.

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Nanomaterials at the interface: link between computation and experiment

Cecile Malardier-Jugroot[1]*, Matt McTaggart*[1]*, Xia Li*[1]*, M. Szewczuk*[3]*, M. Sambi*[3]*,*
B. Qorri[3] *and M. Jugroot*[2]

[1]Department of Chemistry and Chemical Engineering, Royal Military College of Canada

[2]Department of Mechanical and Aerospace Engineering, Royal Military College of Canada

[3]Department of Biomedical & Molecular Sciences, Queen's University

cecile.malardier-jugroot@rmc.ca

The need for efficient, coupling between theoretical prediction and experimental synthesis and characterization has been shown to be paramount for the development of efficient photoelectrodes with specific and unique properties for solar energy utilization. This synergy between experiments and theory is essential to predict efficiently novel materials and understand their properties for improved photosystem. This observation is not specific to light absorbing materials but is very general to nanomaterials were the properties are different from bulk properties and requires the combination of simulation and experiment for an efficient optimization and development of novel materials.

The presentation will highlight the benefits of this coupling for applications in:

1. the development of support-less nanoreactors with active metal catalyst, which can benefit from both the catalytic center and the confinement effect in aqueous environments [1-3]
2. the design and synthesis of targeted drug delivery carriers for cancer treatment to improve the efficacy of the chemotherapeutic drugs as well as to reduce the side effects linked to the treatment [4-6]

To this end, several structural methods are used to characterize the average interactions within the system: *ab initio* and molecular mechanics theoretical predictions will be compared to experimental methods to encompass the length scale necessary for the study of nanomaterials. The dynamics of the system is characterized independently using classical molecular dynamics and is complemented by experiments on time scales ranging from ps to ns.

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Intramolecular hydrogen bonds and mutual orientations of the monomers in the stabilization of trimeric acylphloroglucinols

Liliana Mammino

School of Mathematical and Natural Sciences, University of Venda, South Africa

sasdestria@yahoo.com

Acylphloroglucinols (ACPLs) are a class of compounds structurally derived from 1,3,5-trihydroxybenzene and characterized by the presence of at least one CRO group, where R is more often an alkyl chain. Many ACPLs show biological activities such as antibacterial, antiviral, anticancer, antimalarial, antioxidant and antidepressant. Computational studies of monomeric ACPLs (M-ACPLs) highlighted the dominant stabilizing role of the intramolecular hydrogen bond (IHB) between the sp^2 O of CRO and a neighboring phenol OH (first IHB) and the considerable stabilizing influence of additional IHBs when donors or acceptors are present in substituents. ACPLs in which two or more monomers are joined by methylene bridges often show enhanced biological activity with respect to M-ACPLs. A study of dimeric ACPLs highlighted the stabilizing role of the intermonomer IHBs (IMHBs). The current work focuses on trimeric ACPLs (T-ACPLs), providing adequate representativeness of the most common structural features (the nature of R and of substituents in *meta* to CRO, the replacements of one or more phenol OHs by $COCH_3$ groups or by keto O, etc.). Calculations were performed at the HF/6- 31G(d,p) and DFT/B3LYP/6-31+G(d,p) levels, as in the previous studies on ACPLs, to enable meaningful comparisons. The results confirm the stabilizing roles of IHBs within each monomer and of the IMHBs. Two molecular shapes may result from the mutual orientations of the three monomers, an open-type shape and a half-bowl shape; their influence on the conformers' relative energies and molecular properties is analyzed. The results for T-ACPLs are compared with those of D-ACPLs and of M-ACPLs.

Advances in rectangular collocation for solution of the Schrödinger equation

Sergei Manzhos[1] *and Tucker Carrington*[2]

[1]Centre Énergie Matériaux Télécommunications, Institut National de la Recherche Scientifique Université du Québec, 1650 boulevard Lionel-Boulet, Varennes QC J3X1S2, Canada.

[2]Chemistry Department Queen's University Kingston, Ontario K7L 3N6 Canada.

sergei.manzhos@emt.inrs.ca (S.M.)

I will present key advantages and recent advances in the rectangular collocation approach. The method allows solving the Schrödinger equation, electronic or nuclear, without converging integrals. It is therefore possible to obtain good solutions from a small number of samples of the potential which could also be located in a limited volume of space. The rectangular nature of the matrix equation facilitates basis optimization and, when applying the KEO numerically, it is easy to use any basis functions. Singularities of the potential are dealt with trivially. As a result, the method can handle problems which pose difficulties with the variational approach, such as vibrational spectra at interfaces (where potential energy surfaces are usually unavailable and ab initio calculations are costly) and use of Slater type functions (which are advantageous in full potential calculations but do not result in analytic integrals). I will also present recent results of machine learning optimization of the collocation point set as well as highlight some disadvantages of the method.

Calculation of hydrogen dimer spin isomer pairs binding energies

Adam Marr, Thomas Halverson, Austin Tripp and Pierre-Nicholas Roy

Department of Chemistry, University of Waterloo, 200 University Avenue West,
Waterloo,Ontario, N2L 3G1, Canada

armarr@uwaterloo.ca; pnroy@uwaterloo.ca

The weakly-bound van der Waals dimer $(H_2)_2$ has long been a source of fascination and study; the existence of quadrupoles in individual hydrogen monomers and collisions between molecules produces a complex set of absorption lines in the dimer spectrum. While pure para hydrogen (pH_2) pairs have been explored extensively in the literature, there has been less consideration surrounding dimers involving one or more ortho hydrogen (oH_2) molecules. In particular, we extend the *ab initio* 6D potential energy surface developed by R. J. Hinde for pH_2-pH_2 to pH_2-oH_2 and oH_2-oH_2 combinations. As part of this method for the full diagonalization of the dimer system, we derive the matrix elements for the angular component of the potential energy analytically, using Wigner 3j-Symbols. The use of this form allows for a better understanding of the symmetries inherent in each of the dimer systems. For an alternative means of comparison, we assess and modify the approximate 1D Adiabatic Hindered Rotor previously developed for pH_2-pH_2 and other dimer pairs. The success of each approach can be readily evaluated by calculation of binding energies for given quantum states. In turn, these values are compared to known experimental dimer Raman and Infrared (IR) lines. This work will be used to develop more complex systems involving chains and/or clusters of various hydrogen spin isomer combinations.

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Agonists and antagonists of dopamine: a theoretical study

Ana Martínez[1], *Ilich A. Ibarra*[2] *and Rubicelia Vargas*[3]

[1]Departamento de Materiales de Baja Dimensionalidad, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior SN, Ciudad Universitaria CP 04510, CDMX, México.

[2]Laboratorio de Fisicoquímica y Reactividad de Superficies (LaFReS), Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior SN, Ciudad Universitaria CP 04510, CDMX, México.

[3]Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Vicentina, Iztapalapa, AP Postal 55-534 CP 09340, CDMX, México.

martina@unam.mx

Schizophrenia and Parkinson's disease can be controlled with dopamine antagonists and agonists. In order to improve the understanding of the reaction mechanism of these drugs, in this investigation we present a quantum chemical study of 20 antagonists and 10 agonists. Electron donor acceptor capacity and global hardness are analyzed using Density Functional Theory (DFT) calculations. Following this theoretical approach, we provide new insights into the intrinsic response of these chemical species. In summary, antagonists generally prove to be better electron acceptors and worse electron donors than dopamine, whereas agonists present an electron donor-acceptor capacity similar to that of dopamine. The chemical hardness is a descriptor that captures the resistance of a chemical compound to change its number of electrons. Within this model, harder molecules are less polarizable and more stable systems. Our results show that the global hardness is similar for dopamine and agonists whilst antagonists present smaller values. Following the Hard and Soft Acid and Bases (HSBA) principle, it is possible to conclude that dopamine and agonists are hard bases while antagonists are soft acids, and this can be related to their activity. From the electronic point of view, we have evolved a new perspective for the classification of agonist and antagonist, which may help to analyze future results of chemical interactions triggered by these drugs.

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CO_2 Conversion on Perovskite-Based Solid Oxides.

Franz Martinez and *Sathish Ponnurangam*

Schulich School of Engineering, Department of Chemical and Petroleum Engineering.
University of Calgary. Calgary, AB, Canada.

franzmichel.martinez@ucalgary.ca, sathish.ponnurangam@ucalgary.ca.

Perovskite-based solid oxides can be used to convert CO_2 to syngas via electrolysis at high temperature. Besides being a viable way of generating fuels, this process is of great interest due to its potential to help reduce CO_2 emissions. However, full atomistic understanding of the conversion mechanism on perovskite-based solid oxides is far from complete. In this work, we use DFT calculations to investigate the energetics of the conversion from CO_2 to CO on perovskites and to generate a dataset of optimized geometries, equations of state, surface energies, andslab—CO2/CO interactions. Then, we use the dataset to parametrize the reactive force field ReaxFF to explore the dynamics of the conversion at different temperatures and compositions of the perovskite surface. Of interest, our results show the modes in which CO_2 is adsorbed at high temperature; activation of the C=O bond; the main intermediates involved in the conversion; and their role to produce CO. These results serve as a base to explain the elementary steps involved in the mechanism of CO_2 conversion on perovskites at high temperature. Altogether, this information will allow us to understand the most favorable conditions for the reaction to occur and aid in improving the design of perovskite-based solid oxide electrocatalysts.

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Testing one-parameter hybrid exchange functionals in confined atoms

Michael Adán Martínez Sánchez[1], *F. Adrián Duarte Alcaraz*[2], *Marcos Rivera Almazo*[1], *R. Arturo Rosas Burgos*[3], *Rubicelia Vargas*[1] *and Jorge Garza*[1]

[1]Departamento de Química, División de Ciencias Básicas e Ingeniería. Universidad Autónoma Metropolitana-Iztapalapa. San Rafael Atlixco 186, Col. Vicentina. Iztapalapa. C.P. 09340. Ciudad de México, México.

[2]Departamento de Investigación en Física. División de Ciencias Exáctas y Naturales, Universidad de Sonora. Blvd. Luis Encinas y Rosales S/N, Col. Centro. Hermosillo. C.P. 83000. Sonora México.

[3]Departamento de Física. División de Ciencias Exáctas y Naturales . Universidad de Sonora. Bl

michael@xanum.ua; jgo@xanum.uam.mx

In this work the performance of one-parameter hybrid exchange functionals designed with a fraction of the exact exchange (EE) and a fraction of the PBE exchange functional is analyzed for atoms immersed in the center of a spherical cavity with penetrable and impenetrable walls, taking as reference the exchange delivered by the Hartree-Fock method (HF). We found that these hybrid functionals qualitatively give a good description for atoms confined by impenetrable walls; however, when an atom is confined by penetrable walls the situation changes since they predict results appreciably different to the reference for small confinement radii. Besides, we show that generalized- gradient functionals are unable to give a good description of confined atoms when the electron density is squeezed by finite potentials over small regions and how one-parameter hybrid exchange functionals alleviate some of the encountered problems. Although the model of the confined atom is extremely simple, it can reproduce some features predicted by sophisticated methods of electronic structure designed for crystal systems, therefore, this model can be useful to test exchange functionals defined within the Kohn-Sham density-functional-the

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Density matrix expression of Quantum Crystallography (QCr)

Lou Massa

Hunter College, CUNY

lmassa@hunter.cuny.edu

Typical contemporary X-ray crystallography delivers the geometries and the electron densities of molecules or periodic systems in the crystalline phase. Energies, electron momentum densities, information relating to the pair density such as electron delocalization measures – all crucial to chemistry – are simply missed. Quantum crystallography (QCr) expressed in a density matrix formalism is an emerging line of research aimed at filling this gap and is solving the crystallographic problem under the constraints of quantum mechanics. In this way, not only geometries and electron densities become experimentally accessible, but also the entire panoply of quantum mechanical properties that are in the output of any quantum chemical software package. However, for QCr to go beyond the case of smaller systems, due to the exponential bottleneck that plagues quantum mechanical calculations, fragmentation techniques may be employed. When combined with a fragmentation technique, termed the "kernel energy method (KEM)", QCr's reach to larger molecules is extended considerably to almost "any size", including systems of up to many tens of thousands of atoms. KEM has made this doable with any chemical model and is capable of providing the entire quantum mechanics of large molecular systems. The smallness of the crystallographic R-factor adjudicates the accuracy of the quantum mechanics extracted from the crystallography.

Insights into the competition between E1cb and E1cb/E2 borderline mechanisms of the 1,2-elimination of β-phenylmercaptoethyl phenolate

Ricardo A. Matute[1,2], *Daniela E. Ortega*[1], *Rodrigo Ormazábal-Toledo*[1] *and Renato Contreras*[3]

[1]Centro Integrativo de Biologíá y Química Aplicada (CIBQA), Universidad Bernardo O'Higgins, Santiago 8370854, Chile

[2]Departamento de Química, Universidad de Chile, Facultad de Ciencias, Casilla 653, Santiago, Chile

[3]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

rmatute@caltech.edu

The mechanistic dichotomy of elimination reactions concerning E1cb/E2 mechanisms has been studied for the 1,2-elimination of β-phenylmercaptoethyl phenolate. The nucleofugality of the leaving group was assessed with a descriptor based on the electrophilicity, which presents linear correlation with the substituent constant. The Hammett plot with both descriptors suggests that the mechanism takes place with formation of a carbanion intermediate, thus supporting an E1cb and not the E2 mechanism previously attributed to the title reaction. The partition energy scheme using distortion/interaction-activation strain analyses allowed to characterize not only the nature of the transition states but also the associated electronic activity occurring along the intrinsic reaction coordinate. According to NBO analysis and specific correlations, the solvent molecules are involved in the stabilization of the carbanion intermediate. These results are rationalized using parabolic models for the potential energy wells as in the case of the formalism of the Marcus theory for electron transfer reactions. Finally, the E1cb/E2 borderline mechanisms are discussed in terms of bonding stepwise and dynamically concerted processes.

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Towards universal substituent constants: model chemistry sensitivity of descriptors from the quantum theory of atoms in molecules

Robert C. Mawhinney and Kevin Lefrancois-Gagnon

Department of Chemistry, Lakehead University, Thunder Bay, ON Canada P7B 5E1

robert.mawhinney@lakeheadu.ca

The Quantum Theory of Atoms in Molecules (QTAIM) provides a theoretical foundation to determine the properties of functional groups through additive atomic contributions. Many studies have used QTAIM in their analyses with a variety of electronic structure methods, but it is unknown if the properties measured using one model chemistry can be compared to those measured by a second. Here, we evaluate the sensitivity of QTAIM functional group and bond critical point properties to the choice of model chemistry, examining six density functionals combined with seven basis sets. High-level B2PLYPD3-BJ/aug-cc-pV5Z reference values are provided for 116 functional groups and the property sensitivity with respect to these values are evaluated on the basis of (1) absolute deviations and (2) linear relationships. Functional group properties (charges, dipoles, quadrupoles, and volumes) were found to be mostly insensitive to the choice of model chemistry, but structural and topological inconsistencies cause larger deviations when the 6-31G(d) basis set is used. Bond critical point properties exhibited more variation with model chemistry, but those incorporating hybrid functionals and triple-zeta basis sets provide values suitable for use in regression studies.

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Computational study of metal interactions in a modified polypropylene membrane

Brandon Meza-González[1], *Rosa María Gómez-Espinosa*[2] *and*
Fernando Cortés-Guzmán[1]

[1]Universidad Nacional Autónoma de México, Instituto de Química, Ciudad Universitaria,

Ciudad de México, 04510 México

[2]Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM,
Carretera Toluca-Atlacomulco Km. 14.5, Toluca, México

brand.meza@gmail.com; fercor@unam.mx

Water pollution by heavy metals is a worldwide problem. It has been observed that sodium acrylate is a compound capable of coordinating metals and that supported on membranes improves their use in the treatment of wastewater. In this work a polypropylene membrane has been modeled computationally in order to obtain a relationship between the experimental data obtained by our research group and the electronic structure properties. To find stationary points on the potential energy surface of a model of polyacrylate and its complexes with Pb^{2+}, Cu^{2+} and Cd^{2+}, a Born-Oppenheimer molecular dynamics (BOMD) was carried out. PBE-D3/DZVP-MOLOPT-SR-GTH theoretical level was employed using periodic conditions in CP2K 4.1 code. We studied the coordination sphere of one and two divalent cations within an oligomer of 6, 12 and 36 acrylate units. The analysis of the trajectories allows us to identify local minima, which were then fully optimized at the M06-2X/LANLDZ theoretical level with the Gaussian 09 software. For thethree cations, the most stable geometry shows that oligomer interacts with the metal centers by means of one to four η^1-carboxylate groups. All systems were in the lowest possible spin state, which are the more stable configuration. The free energy changes of the coordination process show a similar trend to the experimental removal efficiency observed for a membrane with 29.4% grafting degree, indicating that the coordination site model describes the interactions between metals and polymer matrix with low grafting degree in an adequate way.

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Contributed Tuesday 16:20

Could thermodynamics have driven the selection of present day nucleosides/nucleotides in early evolutionary times?

Lázaro. A. Monteserín Castanedo[1,2] *and Chérif F. Matta*[1,2]

[1]Dept. of Chemistry & Physics, Mount Saint Vincent University, Halifax, NS, B3M 2J6, Canada

[2] Dept. of Chemistry, Saint Mary's University, Halifax, NS, B3H 3C3, Canada.

Lazaro.Monteserin.Castanedo@smu.ca; cherif.matta@msvu.ca

The question of on what basis early prebiotic conditions favored the selection and assembly of particular building blocks of nucleic acids is addressed. All known natural nucleic acids, whether DNA or RNA, are polymers of nuclotides in the β-configuration at the C1' carbon of the furanose sugar and never in the α-configuration, but why? Has thermodynamics, for example, driven the evolutionary selection and chemical synthesis of one of the two possible isomers?. This question is addressed at the PM7 semiempirical level of theory to estimate the relative stabilities of thousands of randomly-generated rotational conformers of both the α- and β-configurations in vacuum, and in water. Thermodynamic properties were then calculated from standard statistical mechanics. For each configuration, the most stable conformations obtained at the semiempirical level were then re-optimized using density functional theory (DFT) (B3LYP/6-31G(d,p)). Preliminary results suggest that β-ribonucleosides appear to be marginally more stable thermodynamically than their α-counterparts under all studied solvation conditions. It is possible that this slight thermodynamic advantage drove evolution to select the observed present-day β-nucleic acids. (See Figs 1, 2).

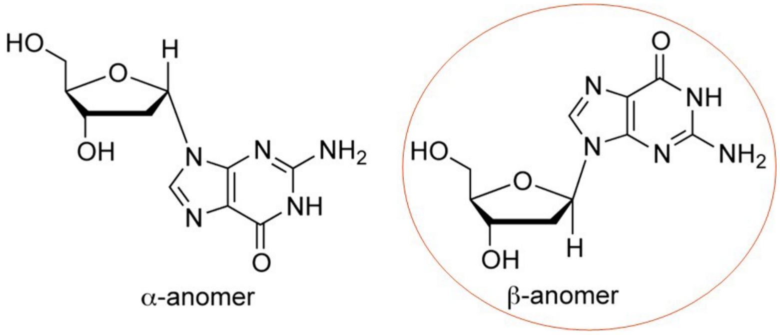

Fig. 1 (*Left*) An α-DNA nucleoside (adenosine, dA), which is never observed in present day nucleic acids. (*Right*) The β-isomer of dA which exists in present day nucleic acids.

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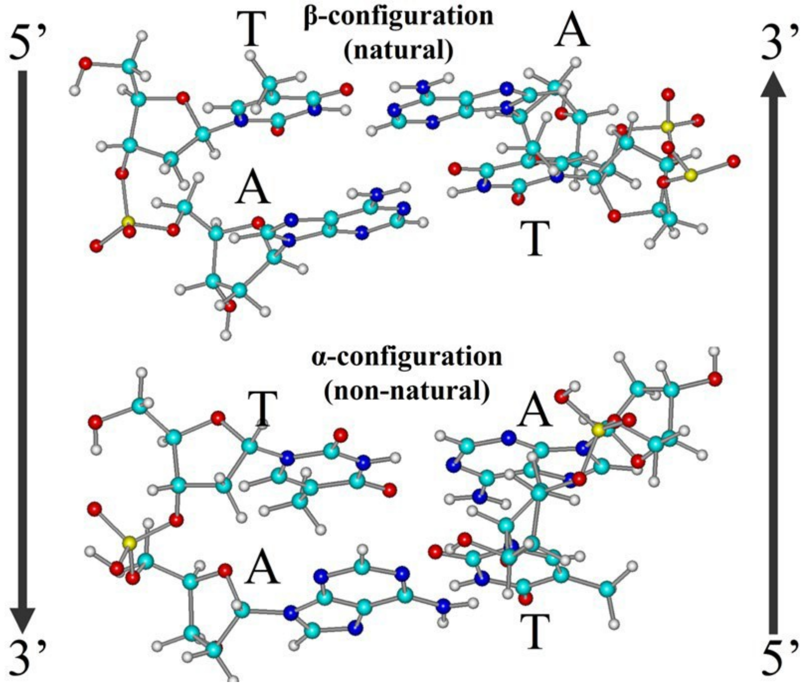

Fig. 2 (*Top*) Natural β-configuration of present day DNA double-helical structure in Watson-Crick pairing mode. (*Bottom*) A molecular model that demonstrates the possibility of having perfectly good. Watson-Crick base pairing in the “wrong/non-natural” α-DNA.

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Genoprotection by complexation: the case of *Phyllanthus orbicularis* K extract

Lázaro A. M. Castanedo[1,2], *Angel Sánchez Lamar*[3], *Cercis Morera Boado*[4], *Ania de la Nuez Veulens*[5] *and Chérif F. Matta*[1,2,6,7]

[1]Department of Chemistry and Physics, Mount Saint Vincent University, Halifax,
Nova Scotia, Canada B3M 2J6.

[2]Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3

[3]Faculty of Biology, University of Havana, Cuba, 25th street, No. 455 Vedado,
Plaza de la Revolución, Havana, Cuba, 8321321

[4]Faculty of Chemistry, University of Havana, Cuba, Zapata e/G y Carlitos Aguirre. Vedado,
Plaza de la Revolución, Havana, Cuba

[5]Department of Computational Medicine, Institute of Nephrology "Abelardo Bush López",
26th Street and Rancho Boyeros Avenue, Plaza de la Revolución, Havana, Cuba

[6]Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

[7]Helmy Institutes for Medical Sciences, Zewail City of Science and Technology, Ahmed Zewail Road,
October Gardens, 6th of October City, Giza, Egypt.

Lazaro.Monteserin.Castanedo@smu.ca; cherif.matta@msvu.ca

The aqueous extract of the herb *Phyllanthus orbicularis* Kunth inhibits the mutagenicity of certain aromatic amines (*m*phenylendiamine (*m*-PDA), 4-aminobiphenyl (4-ABP), and 2-amino-1-methyl-6- phenylimidazo[4,5-*b*]pyridine (PhIP)). Meanwhile, the phenolic compound 2–6 di-*sec*butylphenol (DSBP) was isolated from this plant's extract. Computational evidence is presented to support the possibility of a direct complexation between DSBP and each one of these three amines. This complexation is proposed as a possible mode of genoprotective action of the active ingredient(s) present in this extract. Semiempirical dispersion-corrected PM6-D and dispersion-corrected density functional theory (DFT) calculations, corrected for basis set superposition error (BSSE), and followed by statistical thermodynamics analysis demonstrate that the phenol-amines complexes are stable (in the following order of decreasing stability: PhIP > *m*-PDA > 4-ABP. This complexation between the phenol (protector) and each one of the environmentally hazardous amines may interfere with their metabolic bioactivation preventing their conversion into ultimate mutagens. Results from multiple quantum chemical methods, including statistical mechanical analysis, are consistent which lends stronger support to the mechanism than would occur from any one method alone [1] (See figs 1 and 2).

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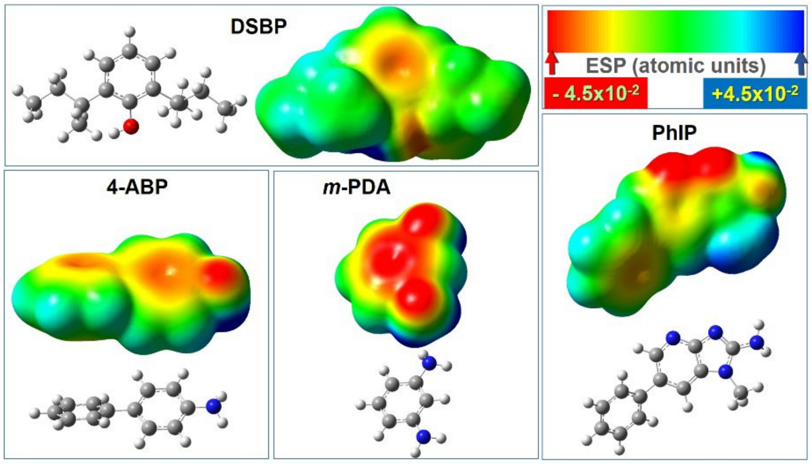

Fig. 1 Representations of the molecular electrostatic potential (ESP), in atomic units (a.u.), color-coded as indicated by the scale at the upper right corner, mapped on the electron isodensity envelope $\rho = 0.01$ a.u.

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Studying Primary and Secondary Antioxidant Activity

Nelaine Mora-Diez

Thompson Rivers University, Department of Chemistry, Kamloops, British Columbia, Canada

nmora@tru.ca

Free radicals (FR) are very reactive species that can damage proteins and other biomolecules forming carbon-centred protein radicals, among others, which may subsequently become other species. Antioxidants counteract the effect of FR and depending on their mechanisms of action they can be classified as either primary or secondary antioxidants with varying definitions. The protein model N-formyl-leucinamide, whose lateral aliphatic chain can be damaged in four carbon sites, is used to study the primary antioxidant activity of dihydrolipoic acid (DHLA), glutathione and Trolox. The thermodynamics and the kinetics of the hydrogen atom and single electron transfer repair reactions are studied in polar and non-polar environments. Chelators are a group of secondary antioxidants that can bind and thus inactivate or reduce the activity of pro-oxidant metals. Complexes between antioxidants and Cu(II) or Fe(III) can sometimes slow down the initial step of the Haber-Weiss reaction and reduce the potential damage caused by •OH radical formation in the second step (the Fenton reaction). The second part of this presentation examines the secondary antioxidant activity of lipoic acid and DHLA by exploring the various complexes these species could form with Cu(II) or Fe(III) in aqueous solution at physiological pH.

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Solvent effects on the electronic properties of (2*Z*)-*N*'-((*Z*)-picolinamido) picolinamidine

Adeniyi J. Olajide and *Nelson O. Obi-Egbedi*

University of Ibadan, Nigeria.

adeniyi.olajide@mail.concordia.ca; nobiegbedi@yahoo.com

Azines have received much attention due to their wide range of applications especially in drug development and their relevance in the telecommunication sector due to their Non-Linear Optical (NLO) properties.

Solvent environment affects the energy and intensity of absorption band of a molecule. The UV-visible electronic spectra of (2*Z*)-*N*'-((*Z*)-picolinamido) picolinamidine (PAZ) have been studied spectrophotometrically in different solvents of varying dielectric constants. Solvent effects on electronic properties such as dipole moments, electronegativity, electron affinity, frontier molecular orbital energies (E_{HOMO} and E_{LUMO}) and energy gap (ΔE) of PAZ were also studied using TD-DFT theory with B3LYP/6-311G(2df,2pd) basis set in gas phase, polar and non-polar solvents. Three bands were observed in the spectra of the solvent except for methanol, ethanol and 2,2,4-trimethylpentane having four bands. The bands were designated I, II, III, IV in the order of increasing energy. There is a gradual increase in the calculated electronic properties of the molecule as the dielectric constant of the media increases. The band I, which is of the least energy is attributed to $nnnn \rightarrow \pi\pi\pi\pi^*$ transition which is due to the presence of a heteroatom in the ring system of PAZ. On the basis of the extinction coefficients, the bands I, II and III can be designated as L_b, L_a, and B_b transitions respectively.

Optical and dielectric properties of nanocomposite materials

Irina Paci, David Hally, Archita Adluri and Chris Rowan

Department of Chemistry, University of Victoria, Victoria, BC, V8W 2Y2

ipaci@uvic.ca

Nanocomposite materials combine the versatility of a traditional (polymer, oxide, ceramic) matrix material with the field-response properties of metallic nanoparticles. New materials with distinct and sometimes highly tunable properties are thus obtained. The incorporation of only a small volume fraction of nanosized particles in a host medium is often enough to significantly alter physical, chemical, and mechanical properties. Ag and Au nanoparticles are an effective way to enhance the complex permittivity of high-k oxides and polymers; however, the scale of many modern devices pushes inclusion dimensions below the metal–insulator transition at ~ 2 nm. We describe the implementation of a methodology within the modern theory of polarization, by which the dielectric response in these molecular-scale nanocomposites can be obtained from first-principles calculations. Our methodology also allows partitioning of the response into inclusion and matrix contributions. The method was applied by our group to a series of nanocomposite materials, starting with Ag/MgO composites. We find that the major contributions to the enhanced response in the nanocomposite, over the initial dielectric oxide, come from both the Ag–O interaction at the inclusion–matrix interface, and the molecular structure of the composite.

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Interfacing between experimental and computational enzyme engineering

Joelle N. Pelletier

Département de chimie et Département de biochimie, Université de Montréal

joelle.pelletier@umontreal.ca

Despite key advances in enzyme engineering, our capacity to predict the effects of mutations on function remains nebulous. A central consideration in our incapacity to predict sequence-function relationships is the fact that proteins are dynamic, yet we rarely treat them as such. The complexity of protein dynamics, and therefore of observing and interpreting dynamics in the context of enzyme function, is daunting. We report computational developments to facilitate advances in this area. We first examine different motional timescales and how we can observe these experimentally. Computational methods are poised to make reliable predictions at many of the timescale relevant to function, at a fraction of the cost. We then query enzyme structures for ligand binding while performing dynamic simulations. We examine the cytochrome P450 BM3 system, to predict the trajectory of entry of gases and ligands into the active-site cavity. We apply the Implicit Ligand Sampling and Adaptive Biasing Force methods to successfully predict, in one single simulation, all residues known to be important for fatty acid substrate binding, thus confirming predictive accuracy. Traditional experimental methodologies had required several years and hundreds of enzyme variants to come to the same conclusion. We rank the potential mutational hot-spots and experimentally demonstrate reduced activity upon mutation, as expected. Residual activity resulted from second-shell binding residues which we also predicted and validated experimentally. The simulations allow accurate docking of diverse substrates, as opposed to standardly used docking methods that are based on a single crystal structure, and transfer well to other cytochrome P450s. We look ahead to the potential for large experimental datasets to train smarter design algorithms for enzyme engineering.

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The Morse potential from a radial potential.

J. Juan Peña[1], Jesús Morales[1], J. Avendaño[2] and Jesús García-Ravelo[2]

[1]Universidad Autónoma Metropolitana Azc., CBI - Área de Física Atómica Molecular Aplicada,
Av. San Pablo 180, 02200, CDMX, México.

[2]Instituto Politécnico Nacional, Escuela Superior de Física y Matemáticas Ed. 9, U.P.A.L.M.
Zacatenco, 07738, CDMX, México.

jjpg@azc.uam.mx; g.ravelo@hotmail.com

Despite the two-parameter Morse potential is one-dimensional, its connection with others radial exponential-type potentials, characterized by three parameters, lies in the fact that, analytically, both become the same when its equilibrium distance (bound length) is great enough. In this work, a multi-parameter radial exponential-type potential with hypergeometric solutions, useful in the description of diatomic molecules, is studied under the limiting case in which one of its parameters, namely, the equilibrium bound length r_e tends to infinite. It is shown that under this limit, the potential under study tends to the Morse potential. To do so, the exponential-type potential must be written in such a way that its characteristic parameters such as its depth V_0, the equilibrium bound length r_e and the range of the potential k^{-1}, appear explicitly in the potential function in order to identify them with those of the Morse potential and then apply the aforementioned limit. The above is strengthened with the fact that vibrational and rotational spectroscopic calculations for diatomic molecules are practically indistinguishable when we use the Morse potential and when we use other radial exponential-type potentials. Regarding the energy spectrum and the number of bound states of the radial exponential-type potential, when this limit is applied, they tend to the corresponding ones of the Morse potential. Nevertheless, under this regime, the corresponding wave-functions do not tend one with each other, this is due to the different boundary conditions that each potential imposes on its wave functions.

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Position dependent mass Schrödinger equation for *q*-deformed exponential-type potential.

J. Juan Peña, Gerardo Ovando and Jesús Morales

Universidad Autónoma Metropolitana Azc., CBI - Área de Física Atómica Molecular Aplicada,
Av. San Pablo 180, 02200, CDMX, México.

jjpg@azc.uam.mx; gaoz@azc.uam.mx

In quantum chemical calculations there has been of particular relevance the position-dependent-mass (PDM) quantum Hamiltonian, which is used, for example, for describing the motion of electrons in graded crystals or in the treatment of nuclear many-body problems. On the other hand, exponential-type potentials are used as models in the theoretical treatment of vibrational properties of diatomic molecules. At this regard, q-deformed exponential-type potentials have been proposed with the aim to improve the evaluation of the corresponding theoretical spectra. Also, although some efforts have been dedicated to solve the PDM Schrödinger equation (PDMSE) for some specific potentials and PDM distributions, only few has been realized with q-deformed potentials. So, in this work, by using the solutions of the Schrödinger equation for a class of multiparameter exponential-type potentials and $m(x)=1/(1-q\exp(-\lambda x))$ distribution, we propose a method to solve the corresponding q-deformed PDM Hamiltonian. As a useful application of the proposal, it is shown that the solutions of several q-deformed potentials are generated by the simple selection of the parameters involved. Furthermore, the method can be straightforwardly extended to consider alternative forms of mass distributions which can be used, advantageously, in quantum theoretical calculations.

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Quantum chemical topology analysis of heavy elements

J. Pilmé[1]*, J. Graton*[2]*, G. Montavon*[3] *and N. Galland*[2]

[1]Sorbonne Université, LCT, CNRS, Paris, France

[2]Université de Nantes, CEISAM, CNRS, 2 rue de la Houssinière, Nantes, France

[3]IMT Atlantique/Université de Nantes, SUBATECH, CNRS, Nantes, France

pilme@lct.jussieu.fr

It is acknowledged that the relativistic quantum treatments are required when a molecule involves a heavy-element. Although it has been shown that the influence of the spin-orbit coupling (SOC) on the molecular structure or on bonding may be strong, the investigation of this relativistic effect on the electronic structure is rather difficult. In this contribution, we present a strategy to analyze quasirelativistic wave functions and bonding schemes. We have extended the topological analysis of the electron density (QTAIM) and the Electron Localization Function (ELF) well established in the nonrelativistic field for long time ago, to quasirelativistic quantum calculations. The quantum chemical topology approach provides a straightforward way to highlight the SOC effects on the classical chemical paradigms. In addition, this approach allows studying complex molecular systems as opposed to small and/or symmetric model systems. Illustrations of the SOC effects on the bond representation will be given for selected compounds of astatine (At, $Z = 85$), the heaviest halogen element, and notably the ability of astatine to form intermolecular interactions by halogen bonding. Astatine is of high potential interest as radiotherapeutic agent for the nuclear medicine applications, but its chemical behavior is largely unknown which currently hinders the development of radiotherapeutic agents.

Theoretical description of the first and second hyperpolarizabilities responses of ion pairs in solution

Tárcius N. Ramos[1,2], *Sylvio Canuto*[1] *and Benoît Champagne*[2]

[1]Instituto de Física, Universidade de São Paulo, Rua do Matão 1371, 05508-090, São Paulo, SP, Brasil.

[2]Theoretical Chemistry Lab, Unit of Theoretical and Structural Physical Chemistry,
Namur Institute of Structured Matter, University of Namur, rue de Bruxelles, 61, B-5000 Namur, Belgium

tarcius@if.usp.br; benoit.champagne@unamur.be

The Electric Field-Induced Second Harmonic Generation (EFISHG) response has been largely used to describe the first (β) and the second (γ) hyperpolarizabilities in solution. Although the EFISHG technique cannot be applied to charged compounds (due to the external static electric field) it can be used to describe ion pairs as neutral complexes. In this work, we theoretically simulated several organic ion pairs in solution to estimate the EFISHG and the Hyper Rayleigh Scattering (HRS) responses. A multiscale computational approach was required to create representative geometrical configurations of the complexes using classical force fields; to compute the electronic structure of each configuration using quantum mechanics methods and to perform statistical analyses describing the behaviour of the nonlinear optical properties. The general β response was dominated by the component along the molecular axis and showed a larger increase in compounds with stronger charge donor group. In opposition to the HRS, the EFISHG response was modulated by the dipole moment, which were dependent of the relative ion position. The γ contributions ranged from 5%-15% in the total EFISHG response. The multiscale approach provided semi quantitative results compared with the experiment although additional efforts are still required to improve such comparison mainly to take in account the dissociation.

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Thermodynamic properties of nonadiabatic systems using Gaussian mixture distributions

Neil Raymond, Dmitri Iouchtchenko, Pierre-Nicholas Roy and Marcel Nooijen

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

neil.raymond@uwaterloo.ca; pnroy@uwaterloo.ca; nooijen@uwaterloo.ca

Our focus is on obtaining time-independent properties at thermal equilibrium of electronically nonadiabatic systems. Nonadiabatic systems are of importance in numerous fields such as photochemistry, biology, quantum information processing, and electro-chemistry. Properties of interest include: the partition function Z, internal energy U, heat capacity Cv, and Gibbs energy G.

Only nonadiabatic systems that can be described by a vibronic Hamiltonian, obtained through electronic structure calculations, are investigated. In our most recent work we introduced our path integral Monte Carlo (PIMC) method using Gaussian mixture distributions (GMD) for investigating these precalculated vibronic Hamiltonians. Hamiltonians are evaluated in a product basis of nuclear and electronic degrees of freedom, without employing any mapping schemes such as the Meyer–Miller–Stock–Thoss (MMST) representation.

The partitioning of the full vibronic Hamiltonian into a harmonic oscillator operator and a coupling operator is a key step in our methodology. Using this form of the Hamiltonian, the partition function of the full system can then be expressed as the product of two factors: the normalization factor of a distribution (that is evaluated analytically) and a Monte Carlo estimator (of the coupling contribution to the partition function).

The advantage of this formulation is computational efficiency. We stochastically evaluate the Monte Carlo estimator using a Gaussian mixture model (GMM). A powerful property ofGMMs is the ability to form smooth approximations to arbitrarily-shaped densities. Our partitioning of the Hamiltonian is therefore motivated by the computational benefits provided by GMMs.

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Electronic properties of low-dimensional materials

Roberto Rivelino[1], *Renato B. dos Santos*[1], *Fernando de B. Mota*[1],
Caio M. C. de Castilho[2,1] *and Gueorgui K. Gueorguiev*[3]

[1]Instituto de Física, Universidade Federal da Bahia, 40210-340 Salvador, Bahia, Brazil

[2]Centro Interdisciplinar em Energia e Ambiente (CIEnAm), Universidade Federal da Bahia, 40170-115 Salvador, Bahia, Brazil

[3]Department of Physics, Chemistry and Biology (IFM), Linköping University, 581 83 Linköping, Sweden

rivelino@ufba.br

Recent progress in the synthesis of several types of two-dimensional (2D) or nearly 2D materials has paved the way for new electronic applications at the nanoscale. For example, studies of 2D silicon-based materials has been boosted because of the discovery of stable monolayers of silicene. While this pure hexagonal silicon phase behaves as a gapless semiconductor, hindering its direct application in electronic devices, silicene-like SiX and XSi_3 binary sheets (X = B, C, N, Al, and P) exhibit versatile electronic properties. These 2D hetero-sheets can be metals, semimetals or semiconductors, depending on the chemical nature of the dopant. In the case of X = B, the corresponding SiB sheets become metallic, giving rise to high conductivity materials with both high structural and thermal stability, which exhibit negative differential resistance depending on the stoichiometry. Other stable class of 2D system refers to the buckled honeycomb XBi and XBi_3 bismides (X = B, Al, Ga, In, and Tl) sheets. We have investigated structural, electronic and dynamic properties of these low-dimensional systems by employing density functional theory to propose technological applications for them. In particular, the 2D binary XBi compounds give rise to sizable-gap Z_2 topological insulators. We investigate the robustness and the electronic behavior of most of these 2D materials by applying strain or chemical modifications, such as partial or total hydrogenation/halogenation. Our results indicate that SiB and the group-III elements XBi preserve their electronic behavior under such changes.

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Tracking weak interactions and ghost atoms in adsorbed layers

Alain Rochefort

Engineering Physics Department, Polytechnique Montréal, Montréal, Canada

alain.rochefort@polymtl.ca

In adsorbed molecular systems where the molecule-surface interactions are weak, the resulting molecular assemblies usually show a well-defined range order that is driven by the intermolecular interactions and the molecule-substrate structure matching. The presence of metal adatoms on surfaces induces additional structural constrains and creates anchoring sites on which molecules become strongly bonded. In most cases, the presence of such metal adatoms within an ordered molecular network cannot be clearly revealed by imaging techniques such as STM microscopy. With the help of DFT and STM simulations, we have investigated the formation of different organized adlayers in the absence and presence of metal adatoms. Although DFT calculations allow to accurately explore the configurational space of molecular adsorption, STM contrasts can also be used to reveal signatures of weak interactions. In this presentation, I will show a few examples where such STM signatures are used to discriminate between adsorption sites where subtle molecule-surface interactions can be probed with STM. In addition, a new developed STM simulation package called DyFlex-STM to investigate large scale molecular systems will be introduced.

Multiphoton absorption studies of fluorescent proteins and fluorescent protein chromophores

Maria Rossano-Tapia and *Alex Brown*

Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Canada

rossanot@ualberta.ca; alex.brown@ualberta.ca

Fluorescent proteins (FPs) have been used extensively as probes in living systems, e.g., for tagging organelles in cells, monitoring the brain, or as part of Ca^{2+} indicators. Among the properties of FPs that make them useful in vivo probes, the multi-photon absorption processes they can undergo stand out. The absorptive and fluorescent properties of FPs depend on many factors, including, the structure of the protein and the chromophore, and, how the chromophore interacts with the amino acids and water molecules surrounding it as it is embedded in the protein barrel. To further understand the photophysical processes of the FPs, computational tools can be employed as a complement to experimental measurements. Although the excited state properties of the chromophore can be examined using quantum mechanical (QM) approaches, the complete FP cannot be handled solely using QM methods. To solve this problem, combined quantum mechanical/molecular mechanical (QM/MM) methods have been used to study FPs. Here we present recent results examining the two-photon absorption (TPA) cross-sections of FPs containing non-canonical amino acids using the QM/MM scheme of the polarized embedding model. Additionally, as an attempt of finding a method that could compute TPA cross-sections with a better ratio of accuracy/cost than the up-to-now explored methods, e.g., TD-DFT and CC2, we present TPA results obtained for the same non-canonical chromophores as they are isolated from the protein using time-dependent density functional theory tight-binding (TD-DFTB2) and the few-states model.

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Correlation factor models for second-order many-body perturbation theories

Pierre-Olivier W.F. Roy, Yongxi Zhou and Matthias Ernzerhof

Département de Chimie, Université de Montréal, C.P. 6128 Succursale A, Montréal, Québec H3C 3J7, Canada

pierre-olivier.roy.2@umontreal.ca ; matthias.ernzerhof@umontreal.ca

Hybrid density functionals, which combine wave function-based methods with density functional theory (DFT), usually rely on empiricism to achieve high accuracy. On the other hand, in the correlation factor approach recently developed in our group, the exchange-correlation (XC) hole is modeled. This allows to use the many known physical constraints on the XC hole to reduce the degree of empiricism needed for the development of hybrid functionals. Our objective is to develop a novel formulation that allies perturbation theory with DFT. As a first step, we propose correlation factor models for the XC hole in the second-order perturbation theory approximation. We then apply corrections to the obtained XC hole using constraints known from DFT. The potential of the method is showed for the description of a variety of chemical systems, including single-bonded, multiple-bonded, and Van der Waals molecules.

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Estudio computacional de fragmentos de ADN en diferentes conformaciones

Andrea Ruiz, Verónica Domínguez, Edgar Vidal,
Alexandra Deriabina, Eduardo González and Valeri Poltev

Facultad de Ciencias Físico Matemáticas [Puebla] (FCFM Benemérita Universidad Autónoma de Puebla).
Av. San Claudio y 18 sur, edif. 11A, Ciudad Universitaria, Col. San Manuel, Puebla,
Pue. C.P. 72570 01 (222) 229 5500 Ext. 7550- México

andremilluiz@gmail.com; poltev@fcfm.buap.mx

La estructura de los dúplex de ADN se presenta en una amplia variedad de conformaciones. Anteriormente, utilizando el método DFT, mostramos que las regularidades conformacionales de los dúplex con dos cadenas correspondientes a las familias BI y A, están predeterminadas en los mínimos de energía de los desoxidinucleósidos monofosfato (dDMP) [1]. Sin embargo, existen en el banco de datos numerosas estructuras con pares de Watson y Crick que presentan cambios conformacionales en sus cadenas azúcar-fosfato (SPB). En este trabajo se estudiaron tres diferentes clases de fragmentos de ADN [2], clasificadas como 116 y 117 que son similares a la conformación BI con ángulos de torsión en la cadena SPB diferentes, mientras que la clase 110 es una conformación intermedia entre BII y A. Realizamos las optimizaciones de los dDMP, neutralizando los grupos fosfato con Na+, empleando cálculos de Mecánica Molecular con tres campos de fuerzas AMBER y cálculos de Mecánica Cuántica con el método DFT con diferentes funcionales. Los resultados obtenidos para los SPB en conformación BI y 117 muestran queestos corresponden a mínimos de energía, mientras que los SPB en conformación 110 y 116 no corresponden. Las cadenas BI de los fragmentos dúplex experimentales cumplen con las reglas de traslape entre las bases, sin embargo, después de la optimización se disminuye el traslape entre las bases de la cadena 110 y aumenta el traslape entre las bases de la cadena BI.

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[2] P.Cech et al., *BMC Bioinformatics*, **2013**, *14***,** 205

RECONOCIMIENTO

Apoyo de VIEP-BUAP

Dynamique électronique dans des environnements polarisables

Dennis R. Salahub[1]*, Xiaojing Wu*[2]*, Jean-Marie Teuler*[2]*, Fabien Cailliez*[2]*,*
Carine Clavaguéra[2]*, Aurelio Alvarez-Ibarra*[2] *and Aurélien de la Lande*[2]

[1]Department of Chemistry, Centre for Molecular Simulation, Institute for Quantum Science and Technology,
Quantum Alberta, University of Calgary, 2500 UniversityDrive NW, Calgary, AB, Canada T2N 1N4

[2]Laboratoire de Chimie Physique, CNRS – Université Paris-Saclay, 15 avenue Jean Perrin,
91405 Orsay, CEDEX, France.

dsalahub@ucalgary.ca; aurelien.de-la-lande@u-psud.fr

Nous proposons une méthodologie pour simuler la dynamique électronique à l'échelle attoseconde de systèmes moléculaires de grande taille. Notre approche est basée sur une combinaison de la méthode « Real-Time Time-Dependent Density Functional Theory » (RT-TDDFT) avec la mécanique moléculaire polarisable (MMPol), dans le cadre du modèle chargeponctuelles-dipôles de l'induction électrostatique. Nous avons implémenté cette méthodologie dans le logiciel deMon2k, logiciel qui dépend étroitement des densités électroniques exprimées dans une base de fonctions auxiliaires. Dans le cadre de simulations RT-TDDFT/MMPol, les densités fittées permettent une dramatique réduction du coût des calculs sur trois fronts i) le potentiel de Kohn-Sham, ii) le champ électrique créé par le nuage (fluctuant) électronique, ce qui entre en compte dans l'interaction QM/MM, et iii) l'analyse de la densité fluctuante on-the-fly. Nous présentons les spectres d'absorption d'un colorant en phase gazeuse, obtenus dans l'eau non-polarisable et dans l'eau polarisable. De plus, notre méthode a été utilisé pour analyser la réponse dépendante des distances dans l'environnement d'un peptide perturbé par un champ électrique. Nous avons montré que l'induction sur les sites MM permet à l'énergie d'excès d'être dissipée de la région QM vers l'environnement. A cet égard la première couche de solvatation joue un rôle essentiel. Finalement, les effets de retard ont été examinés pour deux situations, i) le peptide dans un environnement polarisable susmentionné et ii) la radiation de molécules par des projectiles chargés à des vitesses relativistes. Une mise à jour sera présentée.

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A Chemical Perspective of the Glass Transition thanks to MD

Armand Soldera, François Godey and Alexandre Fleur

Department of Chemistry, Laboratory of Physical Chemistry of Matter, Université de Sherbrooke,
Sherbrooke (Québec), J1K 2R1, CANADA

Armand.Soldera@USherbrooke.ca

To describe physical properties, simulated systems must be correlated to reality in the most effective way. Experimentally, materials are usually in thermodynamics equilibrium. However, mechanical equilibrium is not reached easily. A specific procedure is thus carried out: the volume of the simulated cell is varied until a minimum in energy is attained. We show how reaching this state is important to calculate mechanical properties and to get reproducible glass transition temperature (T_g). Based on the ensuing accurate results, we argue that atomistic simulation acts as an overcranking used by high-speed cameras to reveal slow-motion, paving the way to interesting opportunities in the description of the glass transition from an atomistic viewpoint. More specifically, the transition from the amorphous state to the glass phase may be detailed in terms of the degrees of freedom freeze. By studying conformational transitions in carbon-chain polymers of polyethylene, we thus clearly establish a relation between local dynamics and the classical dihedral potential energy diagram of a carbon-carbon bond. This methodology is applied to a carbon-chain polymer with a side-group, polystyrene. A direct link is proved between activation energy and T_g. This work thus provides the cornerstone for linking molecular structure to macroscopic polymer properties, and in particular, T_g.

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The computational resources were provided by Calcul Québec and Compute Canada, through the financial support of the Canadian Foundation Innovation (CFI). This work was supported by the Université de Sherbrooke, the Fonds Québécois de la Recherche sur la Nature et les Technologies (FRQNT), and the Natural Sciences and Engineering Research Council of Canada (NSERC).

Computational Modelling of Metallic Nanoestructures Growth from Electron-Beam/Laser-Radiation on Metal Oxides

Miguel A. San-Miguel

Institute of Chemistry, State University of Campinas, Brazil

smiguel@unicamp.br

The structural study of α-Ag$_2$WO$_4$ at atomistic level using electron microscopy pointed out the discovery of a novel phenomenon that was not reported in the literature before. Hence, the electron beam irradiated on this material from electron microscopes, and more recently using femtosecond laser, causes the formation of metallic silver nanostructures. This phenomenon has also been reported for other systems such as Ag$_2$MoO$_4$, Ag$_2$CrO$_4$, Ag$_3$PO$_4$, and AgVO$_3$.

There is major interest on the understanding of the electron-semiconductor interactions leading to the formation of metallic Ag from a fundamental level. We have examined, from computational methods based on the density functional theory and *ab initio* molecular dynamics simulations, the structural and thermodynamical aspects of the atom diffusion stages and Ag filaments growth from α-Ag2WO4 and Ag3PO4 crystals upon electron irradiation. Our calculations supply an atomistic approach to the local geometry, and the electronic structure of the surfaces exposed to the electron beam irradiation and gain insight into the initial stages of the metallic Ag growth process on these materials.

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Invited Thursday 11:20

Electron scattering cross sections for $C_2H_6O_2$ isomers

Gabriel L. C. de Souza

Departamento de Química, Universidade Federal de Mato Grosso, 78060-900, Cuiabá, MT, Brazil

gabriellcs@pq.cnpq.br

In this work, a theoretical investigation on the electron interactions with the C2H6O2 isomers ethylene glycol (ETG) and dimethyl peroxide (DMP) is presented. Differential cross sections (DCS), integral cross sections (ICS), and momentum transfer cross sections (MTCS) for elastic scattering as well as total cross sections (TCS) and total absorption cross sections were determined in the 1-500 eV range. To describe the electron-target interaction and solve the scattering equations, a molecular complex optical potential (MCOP) approach combined with the Padé approximant technique was employed in the same manner reported previously [1]. DCS computed for ETG have shown the *f*-wave pattern while the respective quantities for DMP presented the *d*-wave. Regarding ICS results, the resonance found at around 10 eV in previous investigations for electron scattering with ethanol and dimethyl ether was also detected for both molecules studied in this work. Interestingly, DMP exhibited an additional resonance feature at around 5 eV, which was assigned through the accomplishment of the ICS and MTCS computations for electron-H2O2 collisions. This resonance at 5 eV (that can also be observed in the MTCS and TCS results for DMP) was assigned to the O-O bond, having □* character and being related to the *Bu* scattering symmetry. This work represents the first study regarding electron collisions with these isomers to date. We encourage experimental and theoretical investigations to be performed about electron interactions with ETG and DMP (and also H2O2) in order to validate (and to add information to) the findings presented in this work.

[1] V. A. S. da Mata, R. A. Mendes, and G. L. C. de Souza, *Phys. Rev. A* **2018,** *98*, 042707

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Chemical dynamics simulations to elucidate unimolecular fragmentation of complex molecular ions in the gas phase

Riccardo Spezia

Laboratoire de Chimie Théorique, Sorbonne Université, UMR 7616 CNRS, Paris.

riccardo.spezia@sorbonne-universite.fr

In last years, we have developed an approach to understand and predict collision induced dissociation (CID) of ions in mass spectrometry. This is based on quasi-classical trajectories where the reactive ion can be activated in different ways. Chemical dynamics was found to be useful from both a fundamental and applicative point of view. In fact, it was possible to elucidate non-statistical phenomena which can play an important role in determining fragmentation products, like shattering fragmentation, non-IRC dynamics, bifurcations or roaming. Furthermore, these simulations are useful to help experimentalists in understanding the CID spectra with important applications as, for example, in metabolomics. The combined use of chemical dynamics and semi-empirical Hamiltonians allowed to study relatively large systems, like peptides, sugars or nucleotides. Finally, we will discuss how it will be possible to consider some nuclear quantum effects to improve the estimation of reaction barriers.

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Remarks on the Mechanism of Chemical Reactions: A Focus on Activation Processes

Alejandro Toro-Labbé

Laboratorio de Química Teórica Computacional (QTC), Facultad de Química y de Farmacia.
Pontificia Universidad Católica de Chile. Santiago, Chile.

atola@uc.cl

In this talk, we are going to review and discuss the mechanisms and the energy involved in the activation processes of different chemical reactions. Activation processes have been studied in many different contexts, mainly with the aim of getting insights into the physical nature of the chemical events that triggers these processes. The reaction force analysis (RFA) has proven to be very useful to help describe chemical events taking place within different regions along the reaction coordinate, these chemical events have been characterized as being of structural and/or electronic nature and they drive a chemical reaction in a cooperative way. On the other hand, the reaction electronic flux (REF) is a natural tool to identify and characterize the electronic activity taking place during a chemical reaction, this activity is rationalized in terms of bond strengthening/formation and/or bond weakening/breaking processes and has been linked to the change of specific local electronic populations. The merge between RFA and REF provides the context to analyze activation processes from the perspective of ***(a)*** the energy decomposition scheme that emerges from the RFA; and ***(b)*** from the Marcus potential function within the context of the RFA. Activation energies will be characterized in terms of reaction works defined within the different regions along the reaction coordinate, thus producing interesting insights on energy barriers and rate constants.

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Toward a molecular level understanding of heterogeneous processes relevant for the atmosphere or the interstellar medium

Céline Toubin

Laboratoire de Physique des Lasers, Atomes et Molécules Universite de Lille, UMR CNRS 8523,
59655 Villeneuve d´Ascq - France

Celine.toubin@univ-lille.fr

On the one hand, atmospheric aerosol and ice particles are strongly implicated in atmospheric chemistry, in climate and human health. They pose some of the biggest remaining uncertainties in assessments of the human impact on changes to environment. On the other hand, chemical processes in interstellar media touch upon important questions of resources and the origin of life. In both research areas, significant progress has been achieved in the past decades, showing the importance of the atomistic approach to fully understand the catalytic processes in these particular environments. One of the major challenges for modeling these aspects at the molecular level is being able to describe precisely both the heterogeneous reaction mechanism if any and the explicit influence of the environment. A second difficulty is to establish a direct comparison with experimental data in particular due to timescales and size discrepancies.

This talk will show through examples, relevant to both the interstellar and atmospheric chemistry, different applications based on molecular simulations, classical Molecular Dynamics for the sampling and electronic structure to account for quantum effects. Comparisons with experiments will be also addressed in the context of physicochemical processes at atmospheric interfaces.

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From astrochemistry to prebiotic chemistry through the eyes of computer molecular modeling

Piero Ugliengo

University of Torino, Department of Chemistry, Via P. Giuria 7, 10125 Torino - ITALY

piero.ugliengo@unito.it

Life, as we know today, is mainly characterized by proteins, nucleic acids and membranes. The basic building blocks, *i.e.* amino acids, nucleic bases and lipids are handled by the complex metabolism of the actual cells to make all the needed polymers essential to life. The first question is to understand how and where these building blocks where synthesized before the existence of living organisms. Deep interstellar space, where one is not expecting to find molecules more complex than H_2 shows, instead, more than 200 complex molecules detected by radio astronomy. Comets and meteorites are rich of organic molecules, from amino acids to simple lipids which can be brought to the primordial Earth by early bombardment. Also, intense geochemical and volcanic activities coupled with the primordial atmosphere of the early Earth or through submarine hydrothermal processes, may have provided many of the needed chemical building blocks. A question remains, however: how these building blocks can merge together to end up with the primordial nucleic acids and proteins or polysaccharides? All these reactions are condensation reactions, in which a water molecule is eliminated during the polymerization and are thermodynamically disfavored in liquid water. There is evidence that mineral surfaces help for the condensation reaction to occur. Many of the above topics are addressed experimentally. However, atomistic details are usually missing, and accurate quantum mechanical calculations are of help to elucidate the reaction mechanisms and energetics. This talk shows selected examples from astro- to prebiotic chemistry of the role of computer modeling.

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Substituent Effect on the Photoinduced Geometrical Change of Copper Complexes

Eduardo Valdespino, Luis Gutiérrez-Arzaluz, Fernando Cortés-Guzmán

Instituto de Química, Universidad Nacional Autónoma de México, Ciudad de México, 04510, México

q.evaldespino@gmail.com; luis.gtz.arzlz@gmail.com; fercor@unam.mx

The photophysical and photochemical properties of copper (I) complexes (CIC) with bis-diimine ligands have drawn attetion due to their photoinduced geometric change and the accompanying metal-ligand charge transfer (MLCT). Due to these qualities, CIC have found purpose as redox mediators, hole-transport materials in solar cells, and molecular switches. CIC have a D_{2d} geometry at the ground state, with its ligands perpendicular to each other. These complexes undergo a conformational change from a tetrahedral to a square-planar geometry when the metal center is oxidized. In contrast, when a CIC experiences a vertical photoexcitation to the S_1 state, a partial and reversible MLCT is observed, and the resulting flattening of the geometry is incomplete. Here, we examine the effect of substitution in the photoexcitation and conformational change of copper (I) complexes with phenanthroline. To this end, we studied the flattening motion of mono- and di-substituted complexes by scanning the dihedral angle between the two phenanthroline ligands from 10° to 170° in four electronic states: S_0, S_1, T_1, and T_2. The exploration of the potential energy surfaces was done within the DFT and TD-DFT formalisms, at the τHCTH-hyb/LanL2DZ level, as implemented in the Gaussian 09 program. All complexes present minima at ~89° in the ground state, whereas in the excited states they exhibit maxima at the same angle. The vertical transition energies from S_0 to S_1 range from 1.5 to 2.0 eV, close to the experimental value (2.13 eV) reported for the unsubstituted ligand. We found that increasing electron-donating power of the substituents magnifies the geometrical distortion in these complexes.

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Optimal low-cost basis sets & global potentials

António J. C. Varandas[1,2]

[1]School of Physics and Physical Engineering, Qufu Normal University, 273165 Qufu, China

[2]Coimbra Chemistry Centre and Chemistry Department, University of Coimbra, 3004-535 Coimbra, Portugal

varandas@uc.pt

After a brief remark on the Born-Oppenheimer approximation, we address two topics. The first is extrapolation of electronic structure calculations to the limit of a complete one-electron basis set (CBS). Starting with a survey of recent work, our recent proposal of so-called optimal basis sets is addressed. Optimal DZ and TZ basis sets of both non-augmented and augmented correlation consistent type are then suggested for directly CBS extrapolating the correlation energy, whose calculation is a major bottleneck in quantum chemistry. They are shown to perform accurately, with correlation energies obtained from (*oVdZ*, *oVtZ*) and (*oAVdZ*, *oAVtZ*) extrapolations typically outperforming by threefold to fivefold the ones obtained with traditional ansatzes of similar quality. Their performance for other molecular properties is also illustrated.

The second topic is on elemental carbon clusters. Starting with C2, C3, and C4, recent ab initio-based global potential energy surfaces for such species are first surveyed based on the double many-body expansion (DMBE) and combined-hyperbolic-inverse-power-representation (CHIPR) methods. Because global fits are of overwhelming difficulty for large cluster sizes, the predictive capability of DMBE theory when truncated at the first few-body terms is also examined. A brief survey of ongoing work on other potential energy surfaces and prospective remarks conclude the talk.

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Robust prediction of spin-crossover in transition metal complexes

Alberto Vela and Luis Soriano

Departamento de Química, Centro de Investigación y de Estudios Avanzados (Cinvestav-Zacatenco)
Av. Instituto Politécnico Nacional 2508, 07360 Ciudad de México,

avela@cinvestav.mx

Spin-crossover (SCO) in transition metal complexes is of great importance in the development of magnetic materials whose properties are used in flat screens, memory and electrical devices, to mention a few. This phenomenon has been widely studied with Density Functional Theory (DFT) using a large variety of exchange-correlation (XC) functionals with disappointing outcomes, pointing towards the incapability of current Density Functional Approximations (DFAs) in reliably predicting the energy differences between the high- and low-spin configurations in transition metal complexes. HF-DFT, using DFT optimized geometries, also offers an excellent alternative to describe SCO in manganocenes with ligands in the cyclopentadienyl rings going from hydrogen to tert-butyl, providing results in excellent agreement with available CCSD calculations. Multiconfigurational-SCF calculations indicate that these systems have an important static correlation contribution. We conclude that gas-phase energy differences between the high and low spin configurations cannot predict SCO. In the case of neutral complexes, like manganocenes, we have found that a robust approach to predict the existence of SCO is the periodic calculation, using the geometry of the complexes in the solid state. For charged complexes, like those containing iron, the inclusion of the counterions distorts enough the crystal field of the transition metal, leading to high-low spin energy differences in agreement with the observation of SCO.

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Investigation of cyclic ligands inhibiting CD2-CD58 interactions using molecular dynamics and molecular docking approaches

Daniel P. Vercauteren[1], *Adèle Laurent*[2], *Laurence Leherte*[1], *Denis Jacquemin*[2,3]

[1]Unité de Chimie Physique Théorique et Structurale, Department of Chemistry,
Namur MEdicine & Drug InnovationCenter (NAMEDIC), Namur Institute of Structured Matter (NISM),
University of Namur, Rue de Bruxelles 61, B-5000 Namur (Belgium),

[2]University of Nantes, CEISAM UMR CNRS 6230 UFR sciences et techniques,
2 Rue de la Houssinière BP 92208, F-44322, Nantes Cedex 03 (France)

3 Institut Universitaire de France, 103 Bd St Michael, F- 75005 Paris Cedex 5 (France)

Daniel.vercauteren@unamur.be

The CD2-CD58 protein-protein interaction is known to favor the recognition of antigen presenting cells by T cells. Molecular Dynamics (MD) and molecular docking calculations are carried out to study the structural, energetics, and dynamical properties of three known cyclic CD58 ligands, named P6, P7 and RTD-c. Each ligand, connected via turn inducers, mimics the C and F β-strands of protein CD2. The MD analyses focus on the location of the ligands on the surface of CD58 and on the direct and water-mediated hydrogen bonds they form with that receptor. Ligand P6, with a sequence close to the experimental β-strands of CD2, presents characteristics that explain its higher experimental affinity, e.g., the lower mobility andflexibility at the CD58 surface, and the larger number and occurrence frequency of ligand-CD58 Hbonds. For the two other ligands, the structural modifications lead to changes in the binding pattern with CD58 and its dynamics. In parallel, a large set of molecular docking calculations, carried out with various search spaces and docking algorithms, are compared to provide a consensus view of the preferred ligand binding modes. The analysis of the ligand side chain locations yields results that are consistent with the CD2-CD58 crystal structure and suggest various binding modes of the experimentally identified hot spot of the ligands, i.e., Tyr86. P6 is shown to form a number of contacts that are also present in the experimental CD2-CD58 structure.

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Thermodynamic properties of $H_2O@C_{60}$ via exact diagonalization

Spencer B. Yim and *Pierre-Nicholas Roy*

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

sbyim@uwaterloo.ca; pnroy@uwaterloo.ca

The behaviour of molecules confined within various nanoscale geometries have been found to exhibit interesting quantum properties. These properties include effects such as spatial anisotropy induced rotational level splitting, “quantum rattling” which refers to the translational movement of the molecule, trans-rotational coupling, and ortho-para conversion. These systems are highly complex with important long-range effects, so it is hard to try to describe the thermodynamics and predict the behaviour of these materials or clusters of molecules. We may begin by investigating the properties of a single such system, that may serve as a base to further our knowledge of the many-body problem. In this work, several thermodynamic properties of a single $H_2O@C_{60}$ molecule are calculated from energy levels and basis functions resulting from Exact Diagonalization (ED). The energy levels were converged against those obtained in the literature from a previous calculation. Thermodynamic properties such as internal energy, heat capacity, ortho-para ratio, dielectric susceptibility as well as several imaginary time autocorrelation functions are presented. We predict that the heat capacity of the system exhibits a clear Shottky anomaly at low temperature.

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Determination of bending modulus of multicomponent lipid membranes by molecular dynamics simulation of membrane buckling

Beibei Zhu[1] *and Anchang Shi*[2]

[1]Department of Basic Education, Zhejiang University of Water Resources and Electric Power, Hangzhou, China;
Department of Physics and Astronomy, McMaster University, Hamilton, Canada

[2]Department of Physics and Astronomy, McMaster University, Hamilton, Canada

babe@zju.edu.cn; shi@mcmaster.ca

The bending modulus, K_c, is one of the most important material properties of lipid membranes. It plays a vital role in various biological processes. Therefore an accurate evaluation of K_c is an important research topic both in experiment, theory and simulations. In the current work, we extracted K_c of lipid bilayer membranes from coarse-grained molecular dynamics simulations with the MARTINI force field using the membrane buckling technique developed by Deserno and coworkers [J. Chem. Phys. 138, 214110 (2013)]. First we validated this method by calculating K_c for single-component lipid bilayers self-assembled from DPPC, DOPC or DLPC at 323 K. The calculated value of K_c is consistent with the reported value in the literature. Then we calculated K_c for three kinds of binary lipid mixtures and the ternary lipid mixture, DPPC/DOPC, DPPC/DLPC, DOPC/DLPC and DPPC/DOPC/DLPC at 323 K. The calculated results indicate that the stiffness of the multicomponent lipid membranes depends on the concentration of the various lipids and varies between that of the hardest and softest lipid bilayers

List of Presenting Authors

Mohammad Esmaïl Alikhani
Philippe Archambault
Ritu Arora
Gustavo Arteca
Paul Ayers
Patrick Ayotte
Marc Baaden
André Bandrauk
Joaquin Barroso
Victor Batista
Stéphanie Baud
Kalil Bernardino
Patrizia Calaminici
Pablo Carpio Martínez
Eliel Carvajal
Benoît Champagne
Ilaria Ciofini
Bartolomeo Civalleri
Laura Coitiño
Fernando Cortés-Guzmán
Miguel Cruz Irisson
Étienne Cuierrier
Jacques Desmarais
Ann English
Matthias Ernzerhof
Peyman Fahimi
René Fournier
Héctor Francisco
Carlo Edoardo Gatti
Paul Geerlings
Jean-Michel Gillet
Frédéric Guégan
Nadine Halberstadt
Alfonso Hernández-Laguna
Jesús Hernández-Trujillo
Michael Hilke
Paula Homem-de-Mello
Hang Hu
Alexander Ibrahim
Dmitri Iouchtchenko
Nazli Jodaeeasl
Paul Johnson
Andreas Köster
Walid Lamine
Pascal Larregaray
Kevin Lefrançois-Gagnon
François Légaré
Claude Legault
Marius Lewerenz
Cécile Malardier-Jugroot
Liliana Mammino
Sergei Manzhos
Adam Marr
Ana Martínez
Michael Martínez
Franz Michel Martinez Rios
Lou Massa
Ricardo Matute
Robert Mawhinney
Brandon Meza-González
Lázaro Andres Monteserín Castanedo
Nelaine Mora-Diez
Adeniyi Olajide
Irina Paci
Joelle Pelletier
José Juan Peña
Julien Pilmé
Tárcius Ramos
Neil Raymond
Roberto Rivelino
Alain Rochefort
Maria del Sagrario Rossano Tapia
Pierre-Olivier Roy
Andrea Ruiz Millán
Dennis Salahub
Miguel San-Miguel
Armand Soldera
Gabriel Souza
Riccardo Spezia
Alejandro Toro-Labbé
Céline Toubin
Piero Ugliengo
Eduardo Valdespino
António Varandas
Alberto Vela
Daniel Vercauteren
Spencer Yim
Beibei Zhu

Banquet Venue & Directions

The banquet is held on the AML Cavalier Maxim boat departing from the Old Port of Montreal at 7PM on Wedenesday, August 28.

Boarding starts at 6PM. You will receive your boarding pass upon arrival at the boat. **Please wear your name badge for identification at the entrance of the boat.**

Directions by public transportation and by car can be found in the following document:

Directions to the Old
Port of Montreal

Once at the Old Port, the following document displays the location of the boat:

Directions to the boat