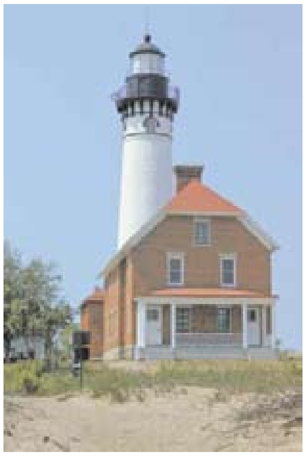
Thirteenth International Workshop on Quantum Systems in Chemistry and Physics
July 6-12, 2008

QSCP-XIII

Michigan State University, East Lansing, Michigan, USA



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13th International Workshop
on
Quantum Systems in Chemistry and Physics

Hosted by

Department of Chemistry
Michigan State University
East Lansing, Michigan 48824-1322, USA

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WORKSHOP SCHEDULE AT A GLANCE

Sunday, July 6	Monday, July 7	Tuesday, July 8	Wednesday, July 9	Thursday, July 10	Friday, July 11	Saturday, July 12
	7:00-8:30 Continental Breakfast *	7:00-8:15 Continental Breakfast *	7:00-8:30 Continental Breakfast *	7:00-8:15 Continental Breakfast *	7:00-8:15 Continental Breakfast *	7:00-8:15 Continental Breakfast *
	8:30-8:45 Opening: Vice President for Research and Graduate Studies, J. Ian Gray	8:15-10:00 Chair: K. F. Freed D. Mukherjee W. D. Allen Á. Szabados	9:00-18:00 The Henry Ford Museum Trip	8:15-10:00 Chair: J. Paldus W. A. Lester, Jr. G. K.-L. Chan D. A. Mazziotti	8:15-10:00 Chair: S. Lahmar N. Moiseyev S. Pal Y. Shigeta	8:15-10:00 Chair: C. M. Aikens H. Nakai M. Ehara J. Su
	8:45-10:30 Chair: J. Maruani W. A. Goddard III B. D. Dunietz P. Baranek					
	10:30-10:55 Break *	10:00-10:20 Break *		10:00-10:20 Break *	10:00-10:20 Break *	10:00-10:20 Break *
	10:55-12:40 Chair: W. A. Goddard III A. K. Wilson H. J. Aa. Jensen A. V. Mitin	10:20-12:40 Chair: R. I. Cukier J. Paldus S. Li M. Włoch T. D. Crawford		10:20-12:40 Chair: D. Mukherjee H. Nakatsuji P. M. W. Gill E. V. Ludeña F. E. Harris	10:20-12:40 Chair: Y. A. Wang P. K. Mukherjee A. W. Hauser G. Chałasiński C. M. Aikens	10:20-12:40 Chair: G. Delgado-Barrio P. R. Surján J. E. Peralta B. I. Dunlap J. C. Angulo
	12:40-14:00 Lunch	12:40-14:00 Lunch		12:40-14:00 Lunch	12:40-14:00 Lunch	12:40-12:45 Closing Remarks
14:00-21:00 Registration	14:00-15:45 Chair: C. J. Cramer S. Hammes-Schiffer S. S. Iyengar J. M. Lluch	14:00-15:45 Chair: D. A. Mazziotti L. Gagliardi F. R. Manby T. F. Miller III		14:00-15:45 Chair: K. C. Hunt J. P. Perdew A. Savin V. N. Staroverov	14:00-15:45 Chair: J. P. Perdew G. Delgado-Barrio S. Lahmar S. Carniato	12:45-14:00 Lunch
	15:45-16:10 Break **	15:45-16:10 Break **		15:45-16:10 Break **	15:45-16:10 Break **	
17:00-19:30 Welcome Reception and Dinner	16:10-18:30 Chair : W. A. Lester, Jr. A. J. C. Varandas A. Dubois V. Averbukh T. González-Lezana	16:10-18:30 Chair : E. J. Brändas C. J. Cramer T. Van Voorhis K. F. Freed G. A. Cisneros		16:10-18:30 Chair: H. Nakatsuji A. J. Cohen T. A. Wesołowski Y. A. Wang A. R. Ruzsinszky	16:10-18:30 Chair: G. K.-L. Chan S. Hirata P. Seidler H.-D. Meyer J. Lundell	
19:30-21:00 Chair : P. Piecuch J. Maruani J. F. Harrison	19:00-21:00 Dinner	19:00-21:00 Dinner	18:30-20:00 BBQ Dinner	19:00-21:00 Banquet Reception and Dinner	19:00-21:00 Dinner	
	21:00-22:30 Poster Session I	21:00-22:00 Concert: D. Mezzadri, S. Ruggiero-Mezzadri, and J. Kabodian will perform	20:00-21:10 Chair : L. Gagliardi E. J. Brändas J.-P. Julien	21:00-22:00 CMOA Prize Ceremony	21:00-22:30 Poster Session II	

* Part of the Morning Continuous Break Service. ** Part of the Afternoon Continuous Break Service.

Each lecture consists of 30 minutes of the lecture time and 5 minutes for a discussion.

Welcome!

Welcome to the Thirteenth International Workshop on Quantum Systems in Chemistry and Physics (QSCP-XIII) and to Michigan State University!

Held every year, QSCP meetings continue the tradition of showcasing the advances in areas such as Concepts and New Methods in Quantum Chemistry, Molecular Structure and Spectroscopy, Atoms and Molecules in Strong Electric and Magnetic Fields, Condensed Matter, Complexes and Clusters, Surfaces and Interfaces, Nano-Materials and Electronics, Reactive Collisions and Chemical Reactions, Computational Chemistry, Physics and Biology, and Biological Modeling. The emphasis of the QSCP Workshops is on broadly defined many-body methods, i.e., the development of innovative theory and its computational realization, along with their application to a broad range of scientific problems of relevance to chemistry, physics, biochemistry, and related fields. The previous QSCP meetings were organized in San Miniato/Pisa, Italy (1996), Oxford, United Kingdom (1997), Granada, Spain (1998), Marly-le-Roi/Paris, France (1999), Uppsala, Sweden (2000), Sofia, Bulgaria (2001), Bratislava, Slovakia (2002), Spetses Island/Athens, Greece (2003), Les Houches, France (2004), Carthage, Tunisia (2005), St. Petersburg, Russia (2006), and Windsor/London, United Kingdom (2007). We hope that you will find the present QSCP Workshop, which is the first to be held in North America, as inspiring, fruitful, and enjoyable as the previous meetings in the QSCP series.

We look forward to the days ahead. The remarkable progress in the study of quantum systems in chemistry, physics, and biology is exemplified by the excellent talks and poster presentations that are ahead of us. The superb level of all presentations guarantees the success of QSCP-XIII. We hope that you will all benefit from your time spent here at Michigan State University and that you will have the opportunity to meet old friends and make new ones.

We are extremely grateful for the very generous financial support provided to us by our sponsors (listed on the next page). Without their kind assistance, the QSCP-XIII Workshop would not be possible. We have been delighted to receive such an overwhelming and warm support from several prominent offices, units, and organizations at Michigan State University and from prominent private corporations.

We would like to thank all of you for participating in the Thirteenth International Workshop on Quantum Systems in Chemistry and Physics. Have a wonderful stay in Lansing!

Piotr Piecuch

Piotr Piecuch

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Schedule of Events

Thirteenth International Workshop on
Quantum Systems in Chemistry and Physics
July 6-12, 2008

QSCP-XIII

Michigan State University, East Lansing, Michigan, USA

Schedule of Events

Sunday, July 06, 2008

14:00-21:00	Registration, Henry Center Lobby
17:00-19:30	Welcome Reception and Dinner, Henry Center Atrium
19:30-21:00	Session Su-T1, A169 Henry Center Session Chair: **Piotr Piecuch**

19:30-20:15	**Jean Maruani**
20:15-21:00	**James F. Harrison**

Monday, July 07, 2008

07:00-08:30 Continental Breakfast, Henry Center Atrium

08:30-08:45 Opening Remarks, A169 Henry Center
J. Ian Gray
Vice President for Research and Graduate Studies,
Michigan State University

08:45-10:30 Session Mo-T1, A169 Henry Center
Session Chair: **Jean Maruani**

08:45-09:20 **William A. Goddard III**
09:20-09:55 **Barry D. Dunietz**
09:55-10:30 **Philippe Baranek**

10:30-10:55 Break, Henry Center Atrium

10:55-12:40 Session Mo-T2, A169 Henry Center
Session Chair: **William A. Goddard III**

10:55-11:30 **Angela K. Wilson**
11:30-12:05 **Hans Jørgen Aa. Jensen**
12:05-12:40 **Alexander V. Mitin**

12:40-14:00 Lunch, Henry Center Atrium

14:00-15:45 Session Mo-T3, A169 Henry Center
Session Chair: **Christopher J. Cramer**

14:00-14:35 **Sharon Hammes-Schiffer**
14:35-15:10 **Srinivasan S. Iyengar**
15:10-15:45 **José M. Lluch**

15:45-16:10 Break, Henry Center Atrium

16:10-18:30 Session Mo-T4, A169 Henry Center
Session Chair: **William A. Lester, Jr.**

16:10-16:45 **António J. C. Varandas**
16:45-17:20 **Alain Dubois**
17:20-17:55 **Vitali Averbukh**
17:55-18:30 **Tomás González-Lezana**

19:00-21:00 Dinner, Henry Center Atrium

21:00-22:30 Poster Session I, B106-B107 Henry Center

Tuesday, July 08, 2008

07:00-08:15	Continental Breakfast, Henry Center Atrium
08:15-10:00	Session Tu-T1, A169 Henry Center Session Chair: **Karl F. Freed**
	08:15-08:50 **Debashis Mukherjee** 08:50-09:25 **Wesley D. Allen** 09:25-10:00 **Ágnes Szabados**
10:00-10:20	Break, Henry Center Atrium
10:20-12:40	Session Tu-T2, A169 Henry Center Session Chair: **Robert I. Cukier**
	10:20-10:55 **Josef Paldus** 10:55-11:30 **Shuhua Li** 11:30-12:05 **Marta Włoch** 12:05-12:40 **T. Daniel Crawford**
12:40-14:00	Lunch, Henry Center Atrium
14:00-15:45	Session Tu-T3, A169 Henry Center Session Chair: **David A. Mazziotti**
	14:00-14:35 **Laura Gagliardi** 14:35-15:10 **Frederick R. Manby** 15:10-15:45 **Thomas F. Miller III**
15:45-16:10	Break, Henry Center Atrium
16:10-18:30	Session Tu-T4, A169 Henry Center Session Chair: **Erkki J. Brändas**
	16:10-16:45 **Christopher J. Cramer** 16:45-17:20 **Troy Van Voorhis** 17:20-17:55 **Karl F. Freed** 17:55-18:30 **G. Andrés Cisneros**
19:00-21:00	Dinner, Henry Center Atrium
21:00-22:00	Concert: Danilo Mezzadri, Susan Ruggiero-Mezzadri, and Judy Kabodian, Henry Center Atrium

Wednesday, July 09, 2008

07:00-08:30 Continental Breakfast, Henry Center Atrium

09:00-18:00 The Henry Ford Museum Trip

18:30-20:00 BBQ Dinner, Henry Center Atrium

20:00-21:10 Session We-T1, A169 Henry Center
Session Chair: **Laura Gagliardi**

20:00-20:35 **Erkki J. Brändas**
20:35-21:10 **Jean-Pierre Julien**

Thursday, July 10, 2008

07:00-08:15	Continental Breakfast, Henry Center Atrium
08:15-10:00	Session Th-T1, A169 Henry Center Session Chair: **Josef Paldus**
	08:15-08:50 **William A. Lester, Jr.** 08:50-09:25 **Garnet K.-L. Chan** 09:25-10:00 **David A. Mazziotti**
10:00-10:20	Break, Henry Center Atrium
10:20-12:40	Session Th-T2, A169 Henry Center Session Chair: **Debashis Mukherjee**
	10:20-10:55 **Hiroshi Nakatsuji** 10:55-11:30 **Peter M. W. Gill** 11:30-12:05 **Eduardo V. Ludeña** 12:05-12:40 **Frank E. Harris**
12:40-14:00	Lunch, Henry Center Atrium
14:00-15:45	Session Th-T3, A169 Henry Center Session Chair: **Katharine C. Hunt**
	14:00-14:35 **John P. Perdew** 14:35-15:10 **Andreas Savin** 15:10-15:45 **Viktor N. Staroverov**
15:45-16:10	Break, Henry Center Atrium
16:10-18:30	Session Th-T4, A169 Henry Center Session Chair: **Hiroshi Nakatsuji**
	16:10-16:45 **Aron J. Cohen** 16:45-17:20 **Tomasz A. Wesołowski** 17:20-17:55 **Y. Alexander Wang** 17:55-18:30 **Adrienn R. Ruzsinszky**
19:00-21:00	Banquet Reception and Dinner, University Club Dining Room
21:00-22:00	CMOA Prize Ceremony, University Club Dining Room

Friday, July 11, 2008

07:00-08:15	Continental Breakfast, Henry Center Atrium
08:15-10:00	Session Fr-T1, A169 Henry Center Session Chair: **Souad Lahmar**
	08:15-08:50 **Nimrod Moiseyev**
	08:50-09:25 **Sourav Pal**
	09:25-10:00 **Yasuteru Shigeta**
10:00-10:20	Break, Henry Center Atrium
10:20-12:40	Session Fr-T2, A169 Henry Center Session Chair: **Y. Alexander Wang**
	10:20-10:55 **Prasanta K. Mukherjee**
	10:55-11:30 **Andreas W. Hauser**
	11:30-12:05 **Grzegorz Chałasiński**
	12:05-12:40 **Christine M. Aikens**
12:40-14:00	Lunch, Henry Center Atrium
14:00-15:45	Session Fr-T3, A169 Henry Center Session Chair: **John P. Perdew**
	14:00-14:35 **Gerardo Delgado-Barrio**
	14:35-15:10 **Souad Lahmar**
	15:10-15:45 **Stéphane Carniato**
15:45-16:10	Break, Henry Center Atrium
16:10-18:30	Session Fr-T4, A169 Henry Center Session Chair: **Garnet K.-L. Chan**
	16:10-16:45 **So Hirata**
	16:45-17:20 **Peter Seidler**
	17:20-17:55 **Hans-Dieter Meyer**
	17:55-18:30 **Jan Lundell**
19:00-21:00	Dinner, Henry Center Atrium
21:00-22:30	Poster Session II, B106-B107 Henry Center

Saturday, July 12, 2008

07:00-08:15 Continental Breakfast, Henry Center Atrium

08:15-10:00 Session Sa-T1, A169 Henry Center
Session Chair: **Christine M. Aikens**

- 08:15-08:50 **Hiromi Nakai**
- 08:50-09:25 **Masahiro Ehara**
- 09:25-10:00 **Julius Su**

10:00-10:20 Break, Henry Center Atrium

10:20-12:40 Session Sa-T2, A169 Henry Center
Session Chair: **Gerardo Delgado-Barrio**

- 10:20-10:55 **Péter R. Surján**
- 10:55-11:30 **Juan E. Peralta**
- 11:30-12:05 **Brett I. Dunlap**
- 12:05-12:40 **Juan C. Angulo**

12:40-12:45 Closing Remarks, A169 Henry Center
Piotr Piecuch
Department of Chemistry, Michigan State University

12:45-14:00 Lunch, Henry Center Atrium

Schedule and Abstracts of the Talks

Session Su-T1

Sunday, July 06, 2008 19:30-21:00

A169 Henry Center
Session Chair: **Piotr Piecuch**
Department of Chemistry, Michigan State University

Su-T1-1 19:30-20:15 A Short History of QSCP Meetings

Jean Maruani

Laboratoire de Chimie Physique, CNRS and UPMC, 11 Rue Pierre et Marie Curie, 75005 Paris, France

Su-T1-2 20:15-21:00 Methylene: A Personal Perspective

James F. Harrison

Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824, USA

Su-T1-1

A Short History of QSCP Meetings

Jean Maruani

Laboratoire de Chimie Physique, CNRS and UPMC,
11 Rue Pierre et Marie Curie, 75005 Paris, France - maruani@ccr.jussieu.fr

The roots and development of QSCP meetings are recalled. From a congress organized in 1986 in Paris to do honor to Pr Daudel, through Franco-Bulgarian cooper-ation with Rossen Pavlov, Yavor Delchev and Peter Raychev, then European contracts in the frame of *PECO* and *COST* projects, involving a network of French, Spanish, British, Italian, Swedish, and Bulgarian scientists, to the organization of the first QSCP workshop by Roy McWeeny in 1996 in Pisa to do honor to Stefan Christov. Since then there was a meeting every year, whose proceedings have all been published:

1 – QSCP-I: San Miniato / Pisa (Italy), April 1996; main local organizer: Roy McWeeny; proceedings published in 'Topics in Molecular Organization & Engineering' (Kluwer).

2 – QSCP-II: Jesus College, Oxford (England), May 1997; main local organizer: Stephen Wilson; proceedings published in 'Advances in Quantum Chemistry' (Plenum).

3 – QSCP-III: Alixares Hotel, Granada (Spain), April 1998; main local organizer: Alfon-so Hernandez-Laguna; proceedings published in 'PTCP' (Kluwer).

4 – QSCP-IV: Marly-le-Roi / Paris (France), April 1999; main local organizer: Jean Maruani; proceedings published in 'PTCP' (Kluwer).

5 – QSCP-V: Uppsala (Sweden), May 2000; main local organizer: Erkki Brändas; proceedings published in 'Advances in Quantum Chemistry' (Plenum). This is where, at the end of the century (and millennium), the Prize of CMOA was created and announced.

6 – QSCP-VI: Boyana Palace, Sofia (Bulgaria), April 2001; main local organizer: Alia Tadjer; proceedings published in 'IJQC' (Wiley). This is where, at the beginning of a new centu-ry (and millennium), the Prize of CMOA was awarded for the first time.

7 – QSCP-VII: Bratislava (Slovakia), September 2002; main local organizer: Ivan Hubac; proceedings published in 'IJQC' (Wiley). This year, the Prize of CMOA was awarded both at the QSCP-VII workshop and the ICTCP-IV congress (Marly-le-Roi, July 2002)

8 – QSCP-VIII: Spetses Island / Athens (Greece), September 2003; main local organizer: Aristides Mavridis; proceedings published in 'IJQC' (Wiley).

9 – QSCP-IX: Les Houches / Grenoble (France), April 2004; main local organizer: Jean-Pierre Julien; proceedings published in 'PTCP' (Springer).

10 – QSCP-X: The Tunisian Academy, Carthage (Tunisia), September 2005; main local organizer: Souad Lahmar; proceedings published in 'PTCP' (Springer).

11 – QSCP-XI: Pushkin / St Petersburg (Russia), August 2006; main local organizer: Oleg Vasyutinskii; proceedings published in 'IJQC' (Wiley).

12 – QSCP-XII: Royal Holloway College / Windsor (UK), September 2007; main local organizer: Stephen Wilson; proceedings being published in 'PTCP' (Springer).

13 – QSCP-XIII: MSU / Lansing, MI (USA), July 2008; main local organizer: Piotr Piecuch; proceedings to be published in 'PTCP' (Springer).

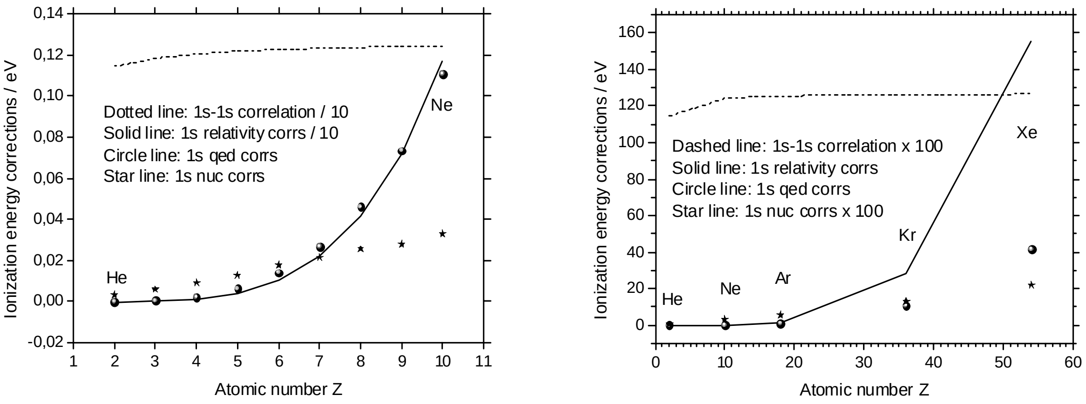
14 – QSCP-XIV: It is the tradition of QSCP meetings not to disclose the venue of the next meeting before the banquet dinner, after the ceremony of award of the Prize of CMOA. But believe it, it will be an exciting place again!

This historical overview will be presented as an illustrated journey in picturesque cities of Western and Eastern Europe, sprinkled with anecdotes, surprising shortcuts and philosophical insights. A number of memorable photographs will be shown.

Electron Correlation and Nuclear Motion Corrections to the Ground-State Energy of Helium Isoelectronic Ions, from Li to Kr

R. L. Pavlov,[a,b] J. Maruani,[b] I. M. Mihailov,[c] Ch. J. Velchev,[a] and
M. Dimitrova-Ivanovich [a]
[a]*Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences,*
72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria
[b]*Laboratoire de Chimie Physique, CNRS and UPMC, 11 Rue Pierre et Marie Curie,*
75005 Paris, France
[c]*Institute of Solid State Physics, Bulgarian Academy of Sciences,*
72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria

Nonrelativistic energies for the ground state of Helium isoelectronic ions for Z = 3-54 are computed. Calculations are performed using explicitly correlated wavefunctions of a generalized Hylleraas type. The variational procedure used allows solving the two-electron Schrödinger equation with a practically unlimited number of parameters for trial wavefunctions expanded in products of positive powers of the Hylleraas coordinates. A nonconventional optimization procedure, involving nonlinear programming, is applied. The contribution of the various terms is assessed, including nuclear finite mass and 'polarization' corrections. Our results are compared to other theoretical results. Combined with noncorrelated relativistic energies, they yield a good agreement with available experimental data.



Relative magnitudes of various corrections to the ionization energies of He isoelectronic ions.

IP / *au*	$^{6}C^{4+}$	$^{7}N^{5+}$	$^{8}O^{6+}$	$^{9}F^{7+}$	$^{10}Ne^{8+}$	$^{11}Na^{9+}$	$^{12}Mg^{10+}$	$^{13}Al^{11+}$	$^{14}Si^{12+}$
Meas.	14.4087	20.2878	27.1688	35.0530	43.9522	54.0919	64.7401	76.7590	******
Comp.	14.4088	20.2877	27.1692	35.0545	43.9443	53.8404	64.7439	76.6568	89.5805

A few results measured, and computed using our procedure.

Su-T1-2

Methylene: A Personal Perspective

James F Harrison,
Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824, USA

The methylene molecule has played a prominent role in the development of computational quantum chemistry. The success that theorists had in unraveling its electronic and geometric structure was instrumental in the acceptance and incorporation of ab-initio computational theory into the fabric of chemistry. I will review the experimental and theoretical work that lead to our understanding of this remarkable molecule.

Session Mo-T1

Monday, July 07, 2008 08:45-10:30

A169 Henry Center
Session Chair: **Jean Maruani**
Laboratoire de Chimie Physique, CNRS and UPMC

Mo-T1-1 08:45-09:20 First Principles Based Predictions of Properties and Processes for Complex Chemical Systems

William A. Goddard III

Charles and Mary Ferkel Professor of Chemistry, Materials Science, and Applied Physics; Director, Materials and Process Simulation Center (MSC) California Institute of Technology Pasadena CA 91125, USA

Mo-T1-2 09:20-09:55 Exploring Conductance Switching Properties of Molecular Scale Devices - A Computational Approach

Trilisa Perrine, Alexander Prociuk, Barry D. Dunietz

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA

Mo-T1-3 09:55-10:30 A Quantum Mechanical Study of the Ferroelectric, Dielectric and Catalytic Properties of the ABO_3 and BO_2 Oxides (A= Ca, Ba and K; B = Zr, Ti, Ce and Nb)

Philippe Baranek

EDF R&D – Département MMC, Site des Renardières Avenue des Renardières – Ecuelles, 77818 Moret sur Loing Cedex, France

Mo-T1-1

QSCP-XIII in Lansing, Michigan July 7-11, 2008.

First principles based predictions of properties and processes for complex chemical systems

William A. Goddard III
Charles and Mary Ferkel Professor of
Chemistry, Materials Science, and Applied Physics
Director, Materials and Process Simulation Center (MSC)
California Institute of Technology
Pasadena CA 91125

Despite enormous advances in computer capacity, many important problems in chemical systems require new theoretical approaches to connect between first principles fundamentals and the properties of real materials

We will consider two examples.

1. Highly excited electronic systems involved in problems ranging from warm dense matter to plasma etching of materials

2. The anomalous transport and physical phenomena involved in high temperature cuprate superconductors

Exploring conductance switching properties of molecular scale devices - a computational approach.

Trilisa Perrine, Alexander Prociuk and Barry D. Dunietz

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

A computational approach is used and developed to study electron transport through molecular and nano scale devices. New models and methods to describe transient electron conductance through molecular systems under the influence of time dependent perturbations are used to study quantum interference effects affecting the time-dependent conductance.[1] We also analyze several high-profile experimental studies achieving molecular scale conductance.[2,3] The experiments demonstrate large conductance changes of single peptides upon ligation of proper metal ion[4] or fabricated molecular sockets based on surface confined terpyridine ligands.[5] Our calculations suggest structure-functions relations which have not been considered before.

References

[1] A. Prociuk and B. D. Dunietz. Time-dependent current through electronic channel models using a mixed time-frequency solution of the equations of motion. *Phys. Rev. B*, Submitted, 2008.

[2] T. Perrine and B. .D Dunietz. Carbonyl mediated conductance through metal bound peptides; a computational study. *Nanotechnolgy*, 18:424003, 2007.

[3] T. Perrine and B. D. Dunietz. Conductance of a coblat(ii) terpyridine complex based molecular transistor: A computational analysis. *J. Phys. Chem. A*, 112:2043, 2008.

[4] X. Xiao, B. Xu, and N. Tao. Changes in the conductance of single peptide molecules upon metal-ion binding. *Angew. Chem. Int. Ed.*, 45:6148–6152, 2004.

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A quantum mechanical study of the ferroelectric, dielectric and catalytic properties of the *AB*O_3 and *B*O_2 oxides (*A*= Ca, Ba and K; *B* = Zr, Ti, Ce and Nb)

Philippe Baranek
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Many of the transition metals or lanthanides oxides have a wide range of applications (fuel cell, catalysts, high-capacitors, …) due to their peculiar properties (high-dielectric constants, ferroelectricity, …). The knowledge of the bulk and surface properties is essential if targeted devices with high performance have to be designed. In this context, the first-principles calculations can be useful to understand the structural and electronic properties of these materials. This presentation illustrates this topic with the study of the pressure driven phase transitions of $KNbO_3$, the study of the protons diffusion in $BaZrO_3$ and $BaCeO_3$, the high-dielectric response of $BaTiO_3$ and $CaTiO_3$ and the study of sulphur tolerance of ceria. For each examples, the calculation have been performed at the Hartree-Fock, Density Functionnal Theory and hybrid levels. All the studied phenomena are analysed in terms of evolution of the atomic structure, spontaneous polarization, electronic population and phonons. It will be shown that a good agreement between calculated, and, other theoretical and experimental various properties can be obtained with hybrid approximations.

Session Mo-T2

Monday, July 07, 2008 10:55-12:40

A169 Henry Center
Session Chair: **Christopher J. Cramer**
Department of Chemistry, University of Minnesota

Mo-T2-1 10:55-11:30

Quantitative Modeling via the correlation consistent Composite Approach (ccCA)

Angela K. Wilson

Department of Chemistry and Center for Advanced Scientific Computing and Modeling (CASCaM) University of North Texas, USA

Mo-T2-2 11:30-12:05

Combining the Best Features of Density Functional Theory and Wave Function Theory

Hans Jørgen Aa. Jensen, Emmanuel Fromager

Department of Physics and Chemistry, University of Southern Denmark, DK-5230 Odense M, Denmark

Mo-T2-3 12:05-12:40

The Origin of Linear Scaling Phenomenon in Fock Matrix Calculation

Alexander V. Mitin

Center for Environmental Kinetics Analysis, The Pennsylvania State University, 2217 EES Building, University Park, PA 16802, USA

Mo-T2-1

Quantitative Modeling via the correlation consistent Composite Approach (ccCA)

Angela K. Wilson
Department of Chemistry and
Center for Advanced Scientific Computing and Modeling (CASCaM)
University of North Texas

Modern computational chemistry has become a viable approach to address a wide range of chemistry that is difficult or cost-prohibitive to evaluate by other means – from the description of short-lived excited states, to the understanding of complex interactions. *Ab initio* computational chemistry approaches have now reached the level where they are an invaluable aid in quantitative predictions of kinetic and thermodynamics properties. For the majority of small molecules (~2-10 main-group atoms), the accuracy obtainable by a*b initio* computational chemistry rivals, and sometimes even surpasses experiment. Computational cost, however, quickly becomes problematic for quantitative predictions, as molecule size increases, and, as the level of sophistication of methodology required increases. Composite methods have emerged as a way to reduce computational cost requirements, while still achieving quantitative accuracy in energetic predictions. Unfortunately, overall, many composite methods are still plagued with problems such as computational cost, required modifications for different portions of the periodic table (e.g., s-block elements), inability to address transition metal species, and/or significant parameterization. We have developed a composite method, the correlation consistent Composite Approach, which can be used throughout the periodic table without modification, does not require parameterization, and does address the thermochemistry of metal complexes.

Combining the Best Features of Density Functional Theory and Wave Function Theory

Hans Jørgen Aagaard Jensen and Emmanuel Fromager
Department of Physics and Chemistry, University of Southern Denmark,
DK-5230 Odense M, Denmark

Density-functional theory (DFT) is widely used nowadays in quantum chemistry, in particular because it is computationally relatively cheap and thus can be used for large scale calculations. However, even if current standard approximate functionals in many cases provide a satisfactory description of the short-range dynamic correlation (Coulomb hole), the static correlation effects (degeneracy or near degeneracy) and the London dispersion interaction effects are in general not treated adequately. On the other hand, the static correlation effects can be described in wave-function theory (WFT), for example, with a multiconfigurational self-consistent field (MCSCF) model, but then an important part of the dynamic correlation has to be neglected. It can be recovered with perturbation-theory based methods, for example CASPT2 or NEVPT2, but their computational complexity prevents large scale calculations.

It is therefore of high interest to develop a hybrid WFT/DFT model which combines the best of both approaches. Different formulations have been proposed to merge WFT and DFT. One approach consists in calculating the dynamic correlation from the density of a MCSCF wave function. The correlation functional must then be adapted to the active space to avoid double counting of the dynamic correlation, which is technically not trivial. This complication can be overcome by splitting the two-electron interaction into long-range and short-range parts as proposed by Savin[1]. In this approach the long-range interaction is treated within WFT and the short-range interaction treated within DFT. As we have to use approximate wave functions and approximate short-range functionals the following question arises: *Can we define an optimal long-/short-range separation and is it universal?*

These questions we addressed in a paper published last year[2], and in this presentation I shall try to convince you that for typical chemistry applications the answers are in practice yes and yes. A major point for “real life applications” is that the range-separated WFT/DFT hybrid model can be expected to fix many of the problem cases in standard DFT models as B3-LYP, PBE, CAM-B3LYP etc, while behaving as the standard models wrt CPU time and accuracy for all the problems where (some of) the standard models are satisfactory.

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Mo-T2-3

The Origin of Linear Scaling Phenomenon in Fock Matrix Calculation

Alexander V. Mitin
Center for Environmental Kinetics Analysis, The Pennsylvania State University,
2217 EES Building, University Park, PA 16802, USA

An application of fast multipole method[1] and quantum chemical tree code[2] in Fock matrix construction significantly extend a possibility of large-scale *ab initio* calculations. This was reached because the Fock matrix can be constructed by these methods for time that scales significantly below than quadratic with respect to a problem size. In many cases it is close to the linear one.

The explanations of linear scaling phenomenon also were presented in works[1,2]. However, they cannot be considered as convincing ones because both of them are based on estimation that a number of two-electron Coulomb integrals scales at least quadratically with respect to a problem size[3]. But an estimation is not a proof. For this reason it cannot be excluded that a linear scaling phenomenon of Fock matrix construction observed in these methods is a consequence that a number of two-electron integrals linear scales with respect to a problem size.

To check this assumption the scaling property of a number of two-electron integrals has been investigated recently[4]. It was analytically shown that asymptotic values of all multi-center two-electron integrals are equal to zero. Hence, at large distances between centers the only one-center two-electron integrals are nonzero. A number of such integrals linearly scales with a problem size. Therefore, a total number of nonzero two-electron integrals scales asymptotically linearly with respect to a problem size. Asymptotic curves of a number of nonzero two-electron integrals have been constructed by counting the nonzero integrals in large-scale calculations with different basis sets. The largest calculations with 6-31G basis included about 27000 contacted and 64000 primitive Gaussian functions. The calculations show that at 10^{-4} 10^{-5} cutoff precision a number of two-electron integrals scales almost linearly while for higher precisions the scaling is below quadratic although is not yet linear one.

It has been noted also that all known linear scaling Fock matrix calculations in fact have been performed with delta density algorithm. In this connection an influence of this algorithm on Fock matrix scaling property has been investigated in the present study on an example of Fock matrix calculation from stored two-electron integrals. The calculations have been performed for a set of test molecules with different basis sets in large range of a number of basis functions. It has been demonstrated that the use of this algorithm indeed leads to linear scaling Fock matrix construction even at those cutoff precisions of two-electron integrals at which a number of two-electron integrals is still a not linear scaling function.

Examples of large scale *ab initio* calculations with inclusion of all two-electron integrals and a number of contracted basis functions of about 10000 and more will be presented.

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Session Mo-T3

Monday, July 07, 2008 14:00-15:45

A169 Henry Center
Session Chair: **William A. Goddard III**
Division of Chemistry and Chemical Engineering,
California Institute of Technology

Mo-T3-1 14:00-14:35

Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations

Sharon Hammes-Schiffer

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802, USA

Mo-T3-2 14:35-15:10

Quantum Wavepacket Ab Initio Molecular Dynamics: Applications to Hydrogen Tunneling in Biological Enzymes and Vibrational Properties in Hydrogen-Bonded Clusters

Srinivasan S. Iyengar

Department of Chemistry, Indiana University, 800 E. Kirkwood Ave, Bloomington, IN 47405, USA

Mo-T3-3 15:10-15:45

Quantum Dynamics Simulation of the Operation of the Proton Wire in Green Fluorescent Protein

José M. Lluch, Oriol Vendrell, Ricard Gelabert, Miquel Moreno

Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra Barcelona, Spain

Nuclear–Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations

Sharon Hammes-Schiffer
Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802, USA

Recent advances in the development of the nuclear-electronic orbital (NEO) approach will be presented. In the NEO approach, both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions, and the variational method is utilized to minimize the energy with respect to all molecular orbitals as well as the centers of the nuclear basis functions. This approach is particularly useful for the description of hydrogen transfer and hydrogen bonding. For these applications, the hydrogen nuclei, as well as all electrons, are treated quantum mechanically to include nuclear quantum effects such as zero point energy and hydrogen tunneling. The multiconfigurational self-consistent-field (NEO-MCSCF), nonorthogonal configuration interaction (NEO-NOCI), second-order perturbation theory (NEO-MP2), and density functional theory (NEO-DFT) methods have been developed to include correlation effects. Electron-proton dynamical correlation is highly significant because of the attractive electrostatic interaction between the electron and the proton. An explicitly correlated Hartree-Fock (NEO-XCHF) scheme has been formulated to include explicit electron-proton correlation directly into the nuclear-electronic orbital self-consistent-field framework with Gaussian-type geminal functions. In contrast to previous approaches, which produce nuclear wavefunctions that are too localized and severely overestimate hydrogen vibrational frequencies, the NEO-XCHF method provides accurate nuclear wavefunctions and hydrogen vibrational frequencies. This method is computationally practical for many-electron systems because only electron-proton correlation is treated explicitly. Moreover, the NEO-XCHF method facilitates the development of electron-proton functionals in the framework of density functional theory. The strengths and challenges of these approaches will be discussed, and applications to hydrogen transfer and hydrogen bonding systems will be presented.

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Quantum wavepacket ab initio molecular dynamics: Applications to hydrogen tunneling in biological enzymes and vibrational properties in hydrogen-bonded clusters

Srinivasan S. Iyengar
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Bloomington, IN-47405

Abstract:

This talk is arranged in three parts: The first part of the talk deals with the discussion of a computational methodology developed within our group. The approach combines quantum wavepacket dynamics with ab initio molecular dynamics and is potentially useful in studying problems where nuclear quantum effects can play an important role. Computational bottlenecks and associated solutions are also discussed. The second and third portions of the talk deal with applications of this approach that result in interesting insights in (a) hydrogen tunneling in biological enzymes, and (b) solvation structure, dynamics, and simulation of vibrational spectroscopy in hydrogen-bonded molecular clusters.

References:

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6. X. Li, D. T. Moore and S. S. Iyengar, "Insights from first principles molecular dynamics studies towards infra-red multiple-photon and single-photon action spectroscopy: Case study of the proton-bound di-methyl ether dimer". *J. Chem. Phys.* **128**, 184308 (2008).

Quantum Dynamics Simulation of the Operation of the Proton Wire in Green Fluorescent Protein

José M. Lluch, Oriol Vendrell, Ricard Gelabert and Miquel Moreno
Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Spain.

A complete nuclear quantum dynamics simulation (by the MCTDH method) of the proton-shuttle operating in the Green Fluorescent Protein (GFP) has been carried out on a high quality, high dimensionality potential energy surface describing the photoactive $\pi\pi^*$ excited state, and including both motion of the three protons and of the donor and acceptor atoms of the hydrogen bonds. The results of the simulations show that proton transfer along the wire is essentially concerted, synchronous and very fast, with a substantial amount of the fluorescent species forming within several tens of femtoseconds. In this regard, a careful analysis of the population of the fluorescent species indicates that at least two dynamical regimes are present for its formation. Within the first hundreds of femtoseconds the dynamics is very fast and impulsive. Later on, a slower pace of formation appears representing the leaking of products of partial operation of the wire to the final, most stable state.

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Session Mo-T4

Monday, July 07, 2008 16:10-18:30

A169 Henry Center
Session Chair: **William A. Lester, Jr.**
Department of Chemistry, University of California, Berkeley

Mo-T4-1 16:10-16:45

Accurate Molecular Potentials by Conventional Ab Initio Methods

António J. C. Varandas

Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

Mo-T4-2 16:45-17:20

Non Perturbative Descriptions of Ion-Molecule Collisions at Intermediate and High Energies

A. Dubois,[*] N. Sisourat,[*] J. Caillat,[*] P. D. Fainstein,[‡] I. Sundvor,[†*] L. Saelen,[†*] J. P. Hansen[†]

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Mo-T4-3 17:20-17:55

Quantum Chemical Approach to Interatomic Decay Rates in Clusters

V. Averbukh,[a] K. Gokhberg,[b] P. Kolorenc,[c] L. S. Cederbaum[b]

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Mo-T4-4 17:55-18:30

Quantum Mechanical Studies on Insertion Atom-Diatom Reactions

Tomás González-Lezana

Instituto de Física Fundamental, CSIC, Serrano 123 28006 Madrid, Spain

Accurate Molecular Potentials by Conventional Ab Initio Methods

A.J.C. Varandas
Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

We report recent progress on predicting accurate potential energy surfaces at a high level of ab initio theory by performing calculations with small basis sets and then scaling and/or extrapolating the energy to the target basis set. The method does not use parameters alien to the electronic structure methods and can be almost as cost-effective as Kohn-Sham density functional theory when using raw MP2 energies. Applications range from diatomic to medium-size systems, some of which will be illustrated at the conference. Given the unavoidable inaccuracies and point wise nature of the calculated *ab initio* potential energy surfaces, we then focus on their modeling using DMBE theory. The global DMBE form so obtained can then be upgraded to spectroscopic accuracy either iteratively via accurate ro-vibrational calculations or by energy switching/morphing it with a local spectroscopic form. Examples will include global potentials for the H_2O and H_2S molecules. Ongoing CBS extrapolations of tensorial properties (polarizabilities) will also be reported.

NON PERTURBATIVE DESCRIPTIONS OF ION-MOLECULE COLLISIONS AT INTERMEDIATE AND HIGH ENERGIES

A. Dubois*, N. Sisourat*, J. Caillat*, P. D. Fainstein‡, I. Sundvor† *, L. Saelen† * and J. P. Hansen†

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Scattering experiments between charged particles and molecules have recently displayed novel many-body phenomena involving coherent interplay between electrons and nuclei. For example, electronic emission spectra have recently displayed interference phenomena resulting in oscillatory relative double differential cross sections [1, 2]. This is the signature of the multi-center character of the molecule.

For intermediate collision energies these effects may be smeared out since the the electron dynamics is completely entangled in an attosecond transient multi-center structure (three centers for atomic ion-diatomic molecule collisions). However new kind of dynamical features may be observed and are extremely sensitive to the detailed electronic structure of the molecular target, the projectile and the geometry of the collision complex [3].

In the conference we shall present a study of such effects in simple ion-molecule collision systems in the intermediate and high impact energy range. The theoretical description of the electronic and rovibrational processes is complex in this regime, due to the large number of open channels, involving electron transfer and ionization, and the important momentum change of the electrons transfered from one to the other nucleus. We shall present two original semiclassical approaches to solve such problems, based on the numerical solution of the time-dependent Schrödinger equation, (i) a basis expansion approach and (ii) a full numerical grid-method.

The basis state method is most suitable for studies of geometrical effects for electron transfer as the final channels are here correctly described. The grid method is perfect for processes where charge transfer plays a minor role, ie. ionization dominates. In both cases we display strong orientation effects with unique signatures of two- and three-center dynamics in the time evolution (cf. Fig. 1) as well as for measurable quantities.

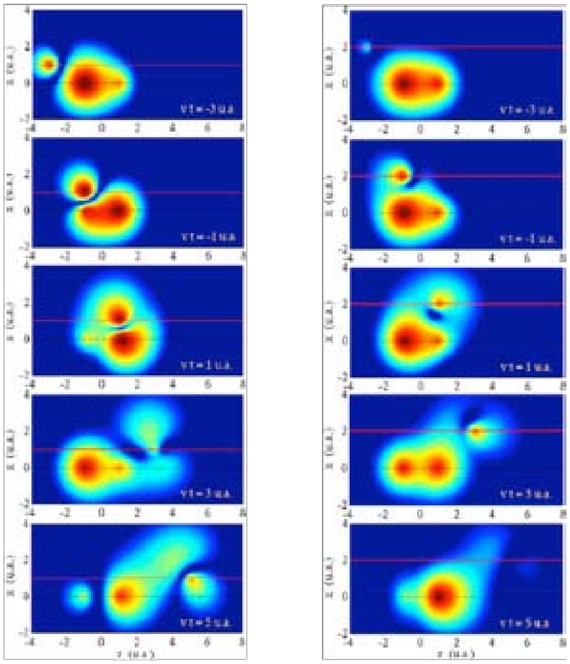

Fig. 1. Snapshots of the probability density during the collision between He^{2+} and H_2^+ for two different impact velocities: v = 0.3 a.u. (left), v=1.0 a.u. (rigth). The impact parameter is 1 a.u.

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Quantum Chemical Approach to Interatomic Decay Rates in Clusters

V. Averbukh[a], K. Gokhberg[b], P. Kolorenc[c], and L. S. Cederbaum[b]

[a]*Max Planck Institute for the Physics of Complex Systems, D-01187 Dresden, Germany*
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Since their theoretical prediction a decade ago[1], interatomic (intermolecular) Coulombic decay (ICD) and related processes have been in the focus of intensive theoretical[2] and experimental[3] research. The spectacular progress in this direction has been stimulated both by the fundamental importance of the discovered electronic decay phenomena and by the exciting possibility of their practical application, for example in spectroscopy[4].

Interatomic decay phenomena take place in inner-shell-ionized clusters due to electronic correlation between two or more cluster constituents. These processes lead to the decay of inner-shell vacancies by electron emission and in many cases also to disintegration of the multiply ionized cluster. The primary objective of the theory is, thus, to predict the kinetic energy spectra of the emitted electrons and of the resulting cluster fragments. These spectra are determined by an interplay between the electronic decay process and the nuclear dynamics[5]. Key to the reliable prediction of the observable quantities is, thus, the knowledge of the time scale of the interatomic decay. In this talk, I will review the recent developments in the *ab initio* quantum chemical methods for the calculation of interatomic decay rates in excited[6], singly ionized[7] and doubly ionized[8] systems as well as some of their applications to various types of inner-shell-ionized clusters, e.g. rare gas systems and endohedral fullerenes.

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Quantum Mechanical Studies on Insertion Atom-Diatom Reactions

Tomás González-Lezana
Instituto de Física Fundamental, CSIC, Serrano 123 28006 Madrid, Spain

Atom-diatom reactive scattering collisions can mainly proceed via two possible dynamical mechanisms. On one hand, the reaction can be the result of a sudden direct collision in which the rupture of the diatomic bond in the reactants and the formation of the products occur in a extremely short of time (*abstraction mechanism*). On the other hand, the process can take place by the formation of an intermediate complex with a finite lifetime of some rotational periods (*insertion mechanism*). For this kind of reactions the potential energy surfaces usually display a deep potential well which supports a large number of bound and quasibound states. The study of the *insertion* processes by means of exact quantum mechanical methods is in general limited by computational difficulties. In these situations, the application of statistical techniques turns to be extremely helpful. In particular, we will review the results of some recent investigations on several atom-diatom processes carried out by means of a statistical quantum method [1,2].

The reactions considered in this talk include cases in which the *insertion* mechanism seems to be the dominating pathway (as collisions between H_2 and an C, N, S or O atom [1-5]), ion-diatom reactions (as those involved in the H_3^+ system and isotopic variants [6-8]) and processes with an existing competition between the *insertion* and *abstraction* dynamics (for example $O(^1D)$+HCl, H+O_2 [2,9,10] and Si+O_2 [11]). The comparison of the statistical predictions with both exact results and experimental measurements reveal the validity of this approach to investigate the dynamics of some of these atom-diatom reactions.

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Session Tu-T1

Tuesday, July 08, 2008 08:15-10:00

A169 Henry Center
Session Chair: **Karl F. Freed**
James Franck Institute, University of Chicago

Tu-T1-1 08:15-08:50

Development and Applications of Nonperturbative Approximants to a State-Specific Multireference Coupled Cluster Theory: Discussion of Two Distinct Variants

Sanghamitra Das,[a,b] Dipayan Datta,[b] Rahul Maitra,[b] Debashis Mukherjee[a,b]

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Tu-T1-2 08:50-09:25

Methodological Advances in State-Specific Multireference Coupled Cluster Theory

Wesley D. Allen, Francesco A. Evangelista, Andrew C. Simmonett

Center for Computational Chemistry and Department of Chemistry, University of Georgia, Athens, Georgia 30602 USA

Tu-T1-3 09:25-10:00

Avoiding Intruders in Multiconfiguration PT

Ágnes Szabados, Péter Surján

Laboratory of Theoretical Chemistry, Loránd Eötvös University, Budapest, Hungary

Development and Applications of Nonperturbative Approximants to a State-Specific Multireference Coupled Cluster Theory: Discussion of Two Distinct Variants

Sanghamitra Das[a, b], Dipayan Datta[b], Rahul Maitra[b] and Debashis Mukherjee[a, b]
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In this talk, two useful nonperturbative approximants to the recently formulated state-specific multi-reference coupled cluster theory (SS-MRCC) will be developed and pilot numerical applications presented. The parent formalism is rigorously size-extensive and with the use of a complete active space leads to a size-consistent theory as well when localized orbitals are used. The method naturally obviates the notorious intruder problem when the target state energy is well-separated from the virtual functions. The wave operator in this formalism is of the Jeziorski-Monkhorst type, and, for a state-specific theory, this leads to redundancy of the cluster amplitudes. Imposing the twin requirements of size-extensivity of energy and the avoidance of intruders, the redundancy problem is resolved successfully. In the working equations, the cluster amplitudes for the operators acting on the different model functions are coupled. The two non-perturbative approximants suggested in this talk are designed to reduce the complexity of the working equations via well-defined nonperturbative approximations in two different ways. In the first variant, to be called the uncoupled state-specific MRCC (UC-SS-MRCC), we use an analogue of the anonymous parentage approximation in the coupling term, which leads to considerable simplification of the working equations, yet with very little deterioration of the quality of the computed energy. In the second variant, to be called internally contracted inactive excitations in SS-MRCC (ICI-SS-MRCC), the cluster amplitudes for all the inactive double excitations are regarded as independent of the model functions. Since the all-inactive double excitation amplitudes are the most numerous, this variant leads to a dramatic reduction in the total number of cluster amplitudes. Our pilot numerical applications on a host of molecules indicate that the ICI-SS-MRCC performs remarkably well, closely paralleling the performance of the rigorous SS-MRCC. While the UC-SS-MRCC uses equations closely resembling those in the parent theory, the variant ICI-SS-MRCC uses a manifestly contracted set of equations for the all-inactive double excitations.

Tu-T1-2

Methodological Advances in State-Specific Multireference Coupled Cluster Theory

Wesley D. Allen, Francesco A. Evangelista, and Andrew C. Simmonett

Center for Computational Chemistry and Department of Chemistry,
University of Georgia, Athens, Georgia 30602 USA

State-specific and rigorously size-extensive Mukherjee multireference coupled cluster theory (Mk-MRCC) has been developed into a powerful method for chemical research in several recent studies.[1-3] The first production-level program (PSIMRCC) for Mk-MRCCSD has been coded into the freely available PSI3 package.[4] This breakthrough was aided by the derivation of closed-form expressions for the terms coupling different references in the amplitude equations.[2] Moreover, a hierarchy of Mk-MRCCSDT-n (n = 1a, 1b, 2, 3) methods for the iterative inclusion of connected triple excitations has been formulated and implemented for the first time.[3] The effectiveness of our Mk-MRCC methods is established by extensive computations on benchmark problems, including F_2, C_2, O_2, O_3, NH, NF, CH_2, SiH_2, and H_2CO. For F_2, at the complete basis set (CBS) limit, Mk-MRCCSD applied with a (2,2) active space and localized orbitals gives (r_e, D_e, ω_e) = (1.4134 Å, 38.5 kcal mol^{-1}, 915 cm^{-1}), in exceptional agreement with the spectroscopic values of (1.4119 Å, 38.3 kcal mol^{-1}, 917 cm^{-1}). Similarly, for CH_2 and O_2, CBS Mk-MRCCSD predicts singlet-triplet splittings [ΔE(S-T)] within 0.2 kcal mol^{-1} of experiment.

In chemical applications of Mk-MRCCSD theory, outstanding results have been obtained for the optimum geometric structures, vibrational frequencies, and adiabatic excitation energies of *ortho*-, *meta*-, and *para*-benzyne. Our CBS Mk-MRCCSD extrapolations yield ΔE(S-T) = 38.9, 20.8, and 4.7 kcal mol^{-1}, respectively, for these three diradicals, as compared to the corresponding experimental values of 37.5, 21.0, and 3.8 kcal mol^{-1}. For antiaromatic systems, Mk-MRCCSD/cc-pVTZ theory provides the first reliable automerization barriers of cyclobutadiene (D_{4h}–D_{2h}, 9.2 kcal mol^{-1}), perfluorocyclobutadiene (D_{4h}–D_{2h}, 14.5 kcal mol^{-1}), and cyclooctatetraene (D_{8h}–D_{4h}, 7.0 kcal mol^{-1}). In the C_8H_8 case, the Mk-MRCCSD/cc-pVTZ singlet-triplet splitting is 12.8 kcal mol^{-1}, within 0.7 kcal mol^{-1} of experiment. Finally, we report Mk-MRCC predictions of UV/Vis spectra of novel carbenes that have led to the first isolation and identification of these species in matrix isolation experiments. Notably, application of a four-reference Mk-MRCCSD/aug-cc-pVTZ wave function reveals that the S_1 open-shell singlet state of the elusive hydroxymethylene species has a twisted (C_1) geometric structure with a torsion angle of 108.4° and excitation energy T_0 = 56.8 kcal mol^{-1}, corresponding precisely to the onset of electronic absorptions observed near 510 nm.

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[1] F. A. Evangelista, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **125**, 154113: 1-16 (2006).

[2] F. A. Evangelista, W. D. Allen, and H. F. Schaefer, *J. Chem. Phys.* **127**, 024102: 1-17 (2007).

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[4] T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Janssen, E. T. Seidl, J. P. Kenny, and W. D. Allen, *J. Comput. Chem.* **28**, 1610-1616 (2007).

Avoiding Intruders in Multiconfiguration PT

Ágnes Szabados and Péter Surján
Laboratory of Theoretical Chemistry, Loránd Eötvös University, Budapest, Hungary

We investigate the problem of intruders in the framework of multiconfiguration perturbation theory (PT)[1,2]. In the spirit of the minimal dressing – proposed in single-reference PT by Lepetit and Malrieu[3] – we study the possibility of replacing the amplitudes of doubly excited configurations by the diagonalization of a dressed $2x2$ matrix. This approach has the potential to remedy the ill effect of quasi-degeneracy while preserving size-consistency of the formalism. We investigate extension of the theory to the multireference case, discuss connections with related multireference approaches and provide pilot test calculations.

[1] Z. Rolik, Á. Szabados and P.R. Surján, *J. Chem. Phys.* **119**, 1922 (2003).

[2] Á. Szabados, Z. Rolik, G. Tóth and P.R. Surján, *J. Chem. Phys.* **122**, 114104 (2005).

[3] M.-B. Lepetit and J.-P. Malrieu, *Chem. Phys. Lett.* **208**, 503 (1993).

Session Tu-T2

Tuesday, July 08, 2008 10:20-12:40

A169 Henry Center
Session Chair: **Robert I. Cukier**
Department of Chemistry, Michigan State University

Tu-T2-1 10:20-10:55 Externally and Internally Corrected CCSD Approaches

Josef Paldus,[a,b] **Xiangzhu Li**[a]

[a] Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario Canada, N2L 3G1; [b] Department of Chemistry and (GWC)^2-Waterloo Campus, University of Waterloo, Waterloo, Ontario Canada, N2L 3G1

Tu-T2-2 10:55-11:30 Block-Correlated Coupled Cluster Theory for Bond Breaking Potential Energy Surfaces

Shuhua Li

School of Chemistry and Chemical Engineering, Key Laboratory of Mesoscopic Chemistry of Ministry of Education, Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing, 210093, P. R. China

Tu-T2-3 11:30-12:05 Recent Developments and Applications of the Renormalized Coupled-Cluster Methods

Marta Włoch,[a,b] **Piotr Piecuch**,[b,c] **Jeffrey R. Gour**[b]

[a]Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931, USA; [b]Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA; [c]Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824, USA

Tu-T2-4 12:05-12:40 Locally Correlated Coupled Cluster Theory and Molecular Chirality

T. Daniel Crawford

Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, USA

Externally and Internally Corrected CCSD Approaches

Josef Paldus [a,b] and Xiangzhu Li [a]
[a] *Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario Canada, N2L 3G1*
[b] *Department of Chemistry and (GWC)^2-Waterloo Campus, University of Waterloo, Waterloo, Ontario Canada, N2L 3G1*

The single-reference (SR) coupled-cluster (CC) methods proved to be very valuable in computations of molecular electronic structure. This is especially the case of the CCSD(T) method, which is sometimes referred to as the "gold standard" of quantum chemistry. Yet, all these approaches are unable to properly describe static and/or non-dynamic correlation effects arising, respectively, due to degeneracy and/or quasidegeneracy of reference configuration(s). The latter is invariably present when describing molecular systems far away from their equilibrium geometry, as is the case when breaking genuine chemical bonds or, generally, when handling open-shell systems. All such situations are characterized by a rapidly increasing role played by higher-than-pair clusters. Even in nondegenerate cases an account of three-body clusters is important when accurate results are desired.

At the SR level, we may overcome these shortcomings, at least partially, by relying on various *internally* or *externally* corrected CC approaches. The latter ones rely on some suitable external source of the most important three- and four-body clusters that are neglected in the standard CCSD method. They are typified by the reduced multi-reference (RMR) approaches[1] that employ a modest-size MR CISD wave function as an external source. The former ones rely solely on the CC equations, as does the above mentioned CCSD(T) method that, unfortunately, also fails in the presence of quasidegeneracy. This led to the development of its renormalized versions, culminating in fully-size extensive CR-CC(2,*n*) approaches[2]. Very recently, we have introduced partially linearized (pl) MR methods[3] that also enjoy full size-extensivity.

After outlining basic tenets of these approaches, we will present a number of examples that illustrate their relative merits and shortcomings. In particular, we shall address the problem of a triple-bond breaking in the nitrogen molecule[4], a symmetry breaking in ABA-type radicals[5], and the singlet-triplet splitting in diradicals[6]. Time permitting we will mention other applications (transition metal compounds and reaction barrier heights) or an extension of the idea of external corrections to genuine MR CC methods of the state-universal type.

[1] X. Li and J. Paldus, *J. Chem. Phys.* **107**, 6257 (1979); *Mol. Phys.* **98**, 1185 (2000) and *loc. cit.*
[2] M. Włoch, J.R. Gour, and P. Piecuch, *J. Phys. Chem. A* **111**, 11359 (2007) and *loc. cit.*
[3] X. Li and J. Paldus, *J. Chem. Phys.* **128**, 144118 (2008); **128**, 144119 (2008).
[4] X. Li and J. Paldus, *J. Chem. Phys.* **113**, 9966 (2000); (submitted).
[5] X. Li and J. Paldus, *J. Chem. Phys.* **126**, 224304 (2007); *Int. J. Quntum Chem.* (in press).
[6] X. Li and J. Paldus, *Chem. Phys. Lett.* **431**, 179 (2006); X. Li, J.R. Gour, J. Paldus, and P. Piecuch, (submitted); X. Li and J. Paldus, (unpublished results).

Block-correlated coupled cluster theory for bond breaking potential energy surfaces

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In this talk, I will present the general formulism of block correlated coupled cluster (BCCC) theory with a complete active-space self-consistent-field (CASSCF) reference function.[1-2] This theory provides an alternative multireference coupled cluster framework to describe ground-state electronic structures of those molecules with significant multireference characters. In this approach, a multireference block is defined to incorporate the nondynamic correlation, and all other blocks involve just a single spin orbital. The cluster operators are truncated up to the four-block correlation level, leading to the BCCC4 scheme. The resulting CAS-BCCC4 method computationally scales as the traditional single-reference CCSD, which is expected to be applicable for medium-sized molecules. We have applied the present approach to investigate the potential energy surfaces for single, double, and triple bond breaking in a series of diatomic molecules (such as F_2, H_2O, N_2), and electronic structures of some typical diradicals and triradicals.[3-4] A comparison of our results with those from full configuration interaction calculations and experimental values (when available) shows that the present approach can provide quantitative descriptions for ground-state potential energy surfaces involving the bond breaking processes.

1. S. Li, *J. Chem. Phys.* **120**, 5017 (2004).
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3. J. Shen, T. Fang, W. Hua, S. Li, *J. Phys. Chem. A* 112, 4703, 2008.
4. T. Fang, J. Shen, S. Li, *J. Chem. Phys.* Accepted, 2008.

Recent Developments and Applications of the Renormalized Coupled-Cluster Methods

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[a]*Department of Chemistry, Michigan Technological University, Houghton, Michigan 49931, USA*
[b]*Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA*
[c]*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824, USA*

The size extensive completely renormalized coupled-cluster method, termed CR-CC(2,3),[1] which has recently been extended to open-shell systems, will be presented. The most important formal and computational details of the CR-CC(2,3) approach and the key elements of the underlying biorthogonal formulation of the method of moments of coupled-cluster equations, on which the CR-CC(2,3) approach is based, will be discussed. It will be shown that while the CR-CC(2,3) and related renormalized coupled-cluster methods preserve the philosophy of the conventional and widely used CCSD(T) approach, in which a non-iterative correction due to triply excited clusters is added to the CCSD (coupled-cluster singles and doubles) energy, including the relatively low computer costs and ease of use that characterize CCSD(T), they eliminate the failures of CCSD(T) and other traditional single-reference approaches in the bond-breaking/biradical regions of potential energy surfaces. The calculations of potential energy curves involving bond breaking, activation energy for the isomerization of cyclopropane involving trimethylene biradical as a transition state, and singlet-triplet energy gaps for the challenging biradical/magnetic HHeH and $(HFH)^-$ systems will be used to demonstrate the effectiveness of the CR-CC(2,3) scheme. The closed and open-shell CR-CC(2,3) options available in the GAMESS package[2] will be introduced as practical solutions for chemists interested in studies of reaction pathways involving single bond breaking, radicals, and biradicals. Thanks to their "black-box" nature, the CR-CC(2,3) calculations can be performed by non-experts who would like to understand chemical problems involving larger non-dynamical correlation effects without resorting to multi-reference calculations which might be prohibitively expensive and require a great deal of expertise and experience.

[1] P. Piecuch and M. Włoch, *J. Chem. Phys.* **123**, 224105 (2005); P. Piecuch, M. Włoch, J.R. Gour, and A. Kinal, *Chem. Phys. Lett.* **418**, 467 (2006); M. Włoch, J.R. Gour, and P. Piecuch, *J. Phys. Chem. A* **111**, 11359 (2007).
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Tu-T2-4

Locally Correlated Coupled Cluster Theory and Molecular Chirality

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The most significant obstacle to the application of advanced quantum chemical methods such as coupled cluster theory to large molecules is the “polynomial scaling wall” — the high-degree polynomial scaling of methods such as coupled-cluster theory with the size of the system. Although methods that diminish this wall by exploiting the localizability of electron correlation have yielded impressive results for energetics and potential surfaces, their efficacy for numerous other properties remains unclear. This paper will discuss recent progress in our group[1] toward the development of locally correlated coupled cluster models for chiroptical response, *viz.* optical rotation and circular dichroism spectra of large chiral molecules.[2]

[1] T.D. Crawford, M.C. Tam, and M.L. Abrams, *J. Phys. Chem. A* **111**, 12057-12068 (2007).
[2] N.J. Russ and T.D. Crawford, *Phys. Chem. Chem. Phys.*, in press.

Session Tu-T3

Tuesday, July 08, 2008 14:00-15:45

A169 Henry Center
Session Chair: **David A. Mazziotti**
Department of Chemistry, The University of Chicago

Tu-T3-1	14:00-14:35	The Study of Highly Charged Ions in Solution: A Combined Quantum Mechanical and Molecular Dynamics Simulation Approach **Laura Gagliardi** *Department of Physical Chemistry, University of Geneva 30, Quai Ernest Ansermet CH-1211 Geneva Switzerland*
Tu-T3-2	14:35-15:10	Gas-Phase Quantum Chemistry Methods for Condensed-Phase Problems **Frederick R. Manby** *School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK*
Tu-T3-3	15:10-15:45	Model for Simulating Coupled Electronic and Nuclear Dynamics in Liquids **Thomas F. Miller III** *Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125, USA*

Tu-T3-1

The Study of Highly Charged Ions in Solution: A Combined Quantum Mechanical and Molecular Dynamics Simulation Approach

Laura Gagliardi
Department of Physical Chemistry
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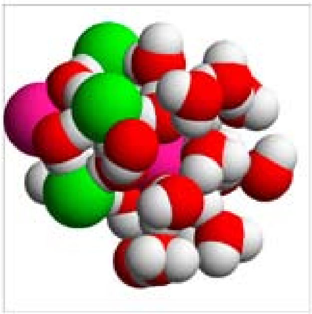
CH-1211 Geneva Switzerland

We will present the results of our latest study of lanthanide and actinide ions in solution using a combined quantum chemical and molecular dynamics simulation approach. Solutions containing Ln (III) cations (Ln=La, Gd and Er) and Cl(-) have been studied in order to understand the coordination of Ln(III) as a function of the concentration of Cl(-).[1] The intermolecular potentials have been generated fully *ab initio* using the NEMO approach[2,3] to intermolecular forces. Some general strategies to model systems containing highly-charged heavy element will be discussed.

[1] D. Hagberg, C. Beuchat and L. Gagliardi The coordination of Ln(III) ions in water, in preparation 2008.

[2] O. Engkvist, P.-O. Åstrand, and G. Karlström. Accurate intermolecular potentials obtained from molecular wave funcions: Bridging the gap between quantum chemistry and molecular simulations. *Chem. Rev.*, **100**, 4087-4108, 2000.

[3] D. Hagberg, E. Bednarz, N.M. Edelstein and L. Gagliardi A quantum chemical and molecular dynamics study of the coordination of Cm(III) in water *J. Am. Chem. Soc.*, **129**, 14136 -14137 2007.



Gas-phase quantum chemistry methods for condensed-phase problems

Frederick R Manby
School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

We have been working on methods for extending the domain of applicability of gas-phase methods, such as MP2 and coupled-cluster theory, into the realm of condensed-phase problems. After a brief summary of our progress with enzymes and solids, I will give an overview of the status of our work on accurate simulation of liquids. The method is based on various approaches to computing energies through many-body expansions, allowing for a huge range of different methods that approach the accuracy of standard methods for very large (and potentially infinite) systems.

Model for Simulating Coupled Electronic and Nuclear Dynamics in Liquids

Thomas F. Miller, III
Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, CA 91125, USA

We describe our recent efforts to simulate the coupled dynamics of electrons and nuclei in the condensed phase. The ring polymer molecular dynamics (RPMD) model is used to simulate the diffusion of an excess electron in supercritical helium over a range of fluid densities. The accuracy of the RPMD model is tested against numerically exact path integral statistics through the use of analytical continuation techniques. At fluid densities approaching those of typical liquids, the RPMD model provides an accurate description for the fast, highly quantum mechanical dynamics of the excess electron. In this regime where the dynamics of the electron is strongly coupled to the dynamics of the atoms in the fluid, trajectories that can reveal diffusive motion of the electron must be long in comparison to $\beta\hbar$.

Session Tu-T4

Tuesday, July 08, 2008 16:10-18:30

A169 Henry Center
Session Chair: **Erkki J. Brändas**
Department of Quantum Chemistry, Uppsala University

Tu-T4-1 16:10-16:45 Electronic Structure Challenges Associated with Dioxygen Activation at Mono- and Binuclear Copper Enzyme Site Models

Christopher J. Cramer

Department of Chemistry and Research Computing Center, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN, USA

Tu-T4-2 16:45-17:20 Exploring Electron Transfer and Bond Breaking with Constrained DFT

Troy Van Voorhis

Department of Chemistry, Massachusetts Institute of Technology,
77 Massachusetts Ave., Cambridge, MA 02139, USA

Tu-T4-3 17:20-17:55 Self-Consistent Determination of Protein Secondary and Tertiary Structure from Sequence Alone

Joe DeBartolo,[a,b,d] Andrés Colubri,[b,d] Abhishek Jha,[a,b,c,d] James E. Fitzgerald,[b,d] Karl F. Freed,[b,c] Tobin R. Sosnick[a,b]

[a]Department of Biochemistry and Molecular Biology; [b]Institute for Biophysical Dynamics; [c]Department of Chemistry; [d]The James Franck Institute, The University of Chicago, Chicago, IL 60637, USA

Tu-T4-4 17:55-18:30 The Gaussian Electrostatic Model: Towards a Molecular Density Based Force Field

G. Andrés Cisneros,[a] Jean-Philip Piquemal,[b] Thomas A. Darden[a]

[a]NIEHS, 111 T.W. Alexander Dr., Box 12233 MD F0–08 RTP, NC 27709, USA;
[b]Laboratoire de Chimie Théorique, Université Pierre et Marie Curie (Paris VI), UMR 7616 du CNRS, Case Courrier 137, 4, place Jussieu,
75252 Paris cedex 05, France

Tu-T4-1

Electronic Structure Challenges Associated with Dioxygen Activation at Mono- and Binuclear Copper Enzyme Site Models

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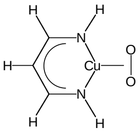

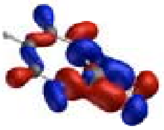

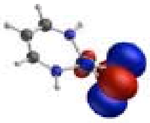

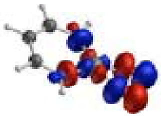

The activation of molecular oxygen at monocopper centers plays an important role in biology, in particular with regard to the biosynthesis of neurohormones by the Cu-containing enzymes dopamine beta-monooxygenase (DβM) and peptidylglycine alpha-hydroxylating monooxygenase (PHM). Similarly, activation at binuclear sites occurs in such enzymes as oxytyrosinase and catechol oxidase. The modeling of 1:1 and 2:1 supported Cu/O_2 adducts poses enormous challenges to density functional and wave function many-body theories because of widely varying nondynamical and dynamical electron correlation effects associated with different geometries, spin states, and ligand characteristics.

As Cu cycles in oxidation state from I (closed-shell d^{10}), to II (open-shell d^9), to III (closed-shell d^8), and the O_2 fragment cycles from molecular oxygen (triplet neutral), to superoxide (doublet anion), to peroxide (closed-shell dianion), a rich variety of spin-spin coupling interactions can be accessed. Treating varying degrees of multideterminantal character in a balanced fashion is key to quantitative and, in some cases, even qualitative accuracy. A summary of salient points will be presented together with some details of the new restricted-active-space RASPT2 model, which extends the range of multireference second-order perturbation theory to larger active spaces than those that can be addressed with the complete-active-space CASPT2 alternative. Time permitting, applications to mechanistic studies and catalyst design will be described.

Key references include:

(1) Gherman, B. F.; Cramer, C. J. *Inorg. Chem.* **2004**, *43*, 7281.
(2) Cramer, C. J.; Włoch, M.; Piecuch, P.; Puzzarini, C.; Gagliardi, L. *J. Phys. Chem. A* **2006**, *110*, 1991.
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(4) Cramer, C. J.; Tolman, W. B. *Acc. Chem. Res.* **2007**, *40*, 601.
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Exploring Electron Transfer and Bond Breaking with Constrained DFT

Troy Van Voorhis
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Electron transfer reactions are the centerpiece of artificial photosynthetic complexes, organic LEDs and essentially all of redox chemistry. This talk will highlight ongoing work being carried out in our group aimed at developing methods that can accurately simulate the reaction dynamics in these types of systems. Specifically, this talk will focus on the *electronic structure* problem inherent in describing electron transfer: How can we treat charge transfer states on the same footing with the electronic ground state? How do we make connections between a phenomenological picture like Marcus theory and a more rigorous approach like DFT? How do we describe bond formation (in particular proton transfer) that is often intimately connected with the process of electron transfer? Time permitting, we will mention some applications of these methods to organic light emission, photoinduced dynamics and/or redox catalysis.

Tu-T4-3

Self-consistent Determination of Protein Secondary and Tertiary Structure from Sequence Alone

Joe DeBartolo[a,b,d], Andrés Colubri[b,d], Abhishek Jha[a,b,c,d], James E. Fitzgerald[b,d], Karl F. Freed[b,c], and Tobin R. Sosnick[a,b]

1Department of Biochemistry and Molecular Biology, 2Institute for Biophysical Dynamics, 3Department of Chemistry, [4]The James Franck Institute, The University of Chicago, Chicago, IL 60637.

Since the demonstration that the amino acid sequence of a protein encodes its structure, the prediction of structure from sequence remains an outstanding problem that impacts numerous scientific disciplines, including the therapeutic design of medicines and the numerous genome projects. The exponential growth in the number of deciphered genomes has provided the protein sequences for millions of new proteins whose properties are completely unknown. The lengthy experimental procedures (X-ray and NMR) for determining individual protein structures necessitate the development of fast throughput computational methods for protein structure prediction. The most common methods for predicting protein structure extensively use the similarity of the target sequence to all or portions of sequences of proteins with known structures. This sequence similarity, called homology, is often combined with machine learning methods for determining the structure. By iteratively fixing the secondary structure assignments of individual residues during Monte Carlo simulated annealing simulations of folding, a coarse grained model *without homology information* or explicit side chains outperforms current homology-based secondary structure prediction methods. The computationally rapid algorithm also generates tertiary structures with backbone conformations of comparable accuracy to existing all-atom methods for many small proteins, particularly for sequences with low homology. Hence, given appropriate search strategies and scoring functions, reduced representations can accurately predict secondary structure as well as provide three-dimensional structures, thereby increasing the size of proteins approachable by *ab initio* methods and the accuracy of template-based methods, especially for sequences with low homology.

The Gaussian electrostatic model: Towards a molecular density based force field

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The simulation of biological systems at present relies mainly on the use of classical empirical force fields (FFs). Most of these FFs separate the interactions in bonded and non bonded contributions. In general, the non bonded terms are represented by a collection of point charges for the Coulomb interaction and a 6-12 Van der Waals term to represent the exchange and dispersion contributions. However, it is well know that the use of these isotropic pairwise potentials results in a loss of accuracy. We have recently shown that unperturbed frozen densities can be used to calculate intermolecular Coulomb interactions analytically [1]. This formalism has been the foundation for the development of a novel FF, the Gaussian electrostatic model (GEM) [2]. GEM reproduces each component of the constrained space orbital variation (CSOV) decomposition method [3] by using fitted molecular densities to calculate the intermolecular interaction components. This model relies on the use of Hermite Gaussian functions as the expanding basis for the fragment molecular density. Furthermore, two reciprocal space based methods have been extended to improve computational speed [4].

We will present Coulomb and exchange–repulsion results for a series of dimers to show accuracy and transferability of the fitted densities. All intermolecular interaction energies are in agreement with respect to CSOV, with an average error of 0.1 and 0.15 kcal/mol for Coulomb and exchange respectively. Timing results for Coulomb energy–force calculations for $(H_2O)_n$ n= 64, 128, 256, 512 and 1024 under periodic boundary conditions are employed to test the reciprocal space based methods. The use of these methods enables the calculation of the largest system (over 650000 primitives) in 6.947 seconds on a single 3.5 GHz Xeon CPU. Finally, the results of an initial QM/MM implementation involving GEM will be presented and compared to conventional QM/MM methods [5]. These results show that point charges significantly under-polarize the QM subsystem at hydrogen bonding distances, while GEM provides the correct polarization response for the water dimer.

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Session We-T1

Wednesday, July 09, 2008   20:00-21:10

A169 Henry Center
Session Chair: **Laura Gagliardi**
Department of Physical Chemistry, University of Geneva

We-T1-1 20:00-20:35   A Quantum Mechanical Description of the Laws of Relativity

<u>Erkki J. Brändas</u>

Department of Quantum Chemistry, Uppsala University, Uppsala, Sweden

We-T1-2 20:35-21:10   EROS: Extended Recursion in Operators Space as a New Impurity Solver for Dynamical Mean Field Theory

<u>Jean-Pierre Julien</u>,[a,b] Robert C. Albers[a]

[a] LANL, Theoretical Division T-11, Los Alamos NM 87545, USA; [b] Universite J. Fourier and CNRS Institut Neel, BP166, 38042 Grenoble, France

A Quantum Mechanical Description of the Laws of Relativity

Erkki J. Brändas
Department of Quantum Chemistry, Uppsala University, Uppsala, Sweden

We have examined the old purported dilemma of quantum mechanics versus the theory of relativity[1,2]. By proposing a first principles, relativistically invariant theory, via an analytic extension of quantum mechanics into the complex plane we offer a model that (i) include features such as time- and length-scale contractions[3] and (ii) suggest incorporation of gravitational interactions[2], (iii) the Einstein general relativistic law of light deflection[2] and (iv) the compatibility with the Schwarzschild metric in a spherically symmetric static vacuum[1]. The present viewpoint asks for a new perspective on the age-old problem of quantum mechanics versus the theory of relativity as the relation with the Klein-Gordon-Dirac relativistic theory confirms some dynamical features of both the special and the general relativity theory.

[1] E. Brändas, *Are Einstein's Laws of Relativity a Quantum Effect?* in Frontiers in Quantum Systems in Chemistry and Physics, eds. by J. Maruani et. al, Kluwer Academic Publishers, **Vol. 18,** (in press) 2008.
[2] E. Brändas, *Quantum Mechanics and the Special- and General Theory of Relativity*, Adv. Quant. Chem. **54**, (2008) 115-132.
[3] E. Brändas, *Some Theoretical Problems in Chemistry and Physics*. Int. J. Quant. Chem. **106**, (2006) 2836-2839.

EROS: Extended Recursion in Operators Space as a New Impurity Solver for Dynamical Mean Field Theory

Jean-Pierre Julien [a,b], and Robert C. Albers [a]
[a] *LANL, Theoretical Division T-11, Los Alamos NM 87545, USA*
[b] *Universite J. Fourier and CNRS Institut Neel, BP166, 38042 Grenoble, France*

We suggest a new impurity solver for the DMFT based on a recursion process in an operators space, the so-called Liouville space. It is applicable at zero temperature limit. The Green function and the self-energy are developed as continued fractions where the coefficients are energy-independent and determined step by step. This approach, in its first levels, enables to recover known approximations (Hubbard I, Hubbard III) and is extendable further systematically to any level of accuracy, retrieving for example, the features of Fermi liquid behaviour with the 3 peaks characteristics.

Session Th-T1

Thursday, July 10, 2008 08:15-10:00

A169 Henry Center
Session Chair: **Josef Paldus**
Department of Applied Mathematics, University of Waterloo

Th-T1-1 08:15-08:50 Some Recent Developments in Quantum Monte Carlo

William A. Lester, Jr.

Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry
University of California at Berkeley, Berkeley, CA 94720-1460, USA and
Chemical Sciences Division, Lawrence Berkeley National Laboratory,
Berkeley, CA 94720, USA

Th-T1-2 08:50-09:25 Ab-Initio Density Matrix Renormalization Group and Tensor Network Wavefunctions

Garnet K.-L. Chan

Department of Chemistry and Chemical Biology Cornell University,
Ithaca NY, 14853-1301, USA

Th-T1-3 09:25-10:00 Two-Electron Reduced-Density-Matrix Methods

David A. Mazziotti

Department of Chemistry and The James Franck Institute The University of
Chicago, Chicago, IL 60637, USA

Some Recent Developments in Quantum Monte Carlo

William A. Lester, Jr.
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University of California at Berkeley, Berkeley, CA 94720-1460, USA
and
Chemical Sciences Division, Lawrence Berkeley National Laboratory
Berkeley, CA 94720, USA

The quantum Monte Carlo method has become recognized for its capability of describing the electronic structure of atomic, molecular and condensed matter systems to high accuracy. This talk will focus on new developments connected with trial function construction and extension of the approach to a QM/MM (quantum mechanics/molecular mechanics) formulation for the inclusion of solvent. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by the CREST Program of the U. S. National Science Foundation. The calculations were carried out at the U. S. National Energy Research Supercomputer Center (NERSC).

Ab-initio Density Matrix Renormalization Group and Tensor Network wavefunctions

Garnet Kin-Lic Chan
Department of Chemistry and Chemical Biology
Cornell University, Ithaca NY14853-1301

In recent years, the Density Matrix Renormalization Group has opened up the ab-initio simulation of complex multireference quantum chemical problems involving very large numbers of active electrons. I will give examples from our recent work that demonstrate the power of the method in studies on light-harvesting pigments, conjugated polymers, and prototype metal-insulator transitions.

From a quantum chemical perspective, the density matrix renormalization group is based on a new class of wavefunctions with an intriguing structure. These wavefunctions form part of a much wider set of so-called "tensor networks" which appear to correctly describe the qualitative correlations in many strongly interacting problems. I will discuss these and other developments at the end of my talk.

Two-electron Reduced-Density-Matrix Methods

David A. Mazziotti
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The University of Chicago, Chicago, IL 60637 USA

The ground-state energy of an atom or molecule as well as all of its one- and two-electron properties can be computed from the ground-state two-electron reduced density matrix (2-RDM).[1] While the significance of the 2-RDM was recognized in the mid-1950s, a direct calculation of the 2-RDM without the wave function was impeded for many years by the need to constrain the 2-RDM to derive from an *N*-electron wave function. These constraints became known as *N*-representability conditions. Two general approaches to the direct calculation of the 2-RDM for many-electron atoms and molecules have recently emerged: (i) the variational calculation of the 2-RDM subject to *N*-representability constraints known as positivity conditions,[2] and (ii) the non-variational calculation of the 2-RDM from solving the anti-Hermitian contracted Schrödinger equation.[3] These two approaches will be discussed with special emphasis on the most recent advances in the variational 2-RDM method.[4]

[1] *Two-electron Reduced-Density-Matrix Mechanics with Application to Many electron Atoms and Molecules*, edited by D. A. Mazziotti, Advances in Chemical Physics Vol. 134 (John Wiley and Sons, New York, 2007).

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[4] A. E. DePrince and D. A. Mazziotti, Phys. Rev. A. **76**, 049903 (2007); A. E. DePrince and D. A. Mazziotti, J. Chem. Phys. (in press); G. Gidofalvi and D. A. Mazziotti, *J. Chem. Phys.* **127**, 244105 (2007); G. Gidofalvi and D. A. Mazziotti (in preparation).

Session Th-T2

Thursday, July 10, 2008   10:20-12:40

A169 Henry Center
Session Chair: **Debashis Mukherjee**
Raman Center of Atomic, Molecular and Optical Sciences, Indian Association for the Cultivation of Science

Th-T2-1 10:20-10:55   Some Recent Progress in the General Method of Solving the Schrödinger Equation and in the SAC/SAC-CI Methodology

Hiroshi Nakatsuji

Quantum Chemistry Research Institute, Kyodai Katsura Venture Plaza 106, Goryo Oohara 1-36, Nishikyo-ku, Kyoto 615-8245, Japan

Th-T2-2 10:55-11:30   Resolutions of the Coulomb Operator and a Generalized Poisson Equation

Sergey A. Varganov, Andrew T. B. Gilbert, Peter M. W. Gill

Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

Th-T2-3 11:30-12:05   Some Recent Advances in the Exact Non-Born-Oppenheimer Treatment of Hookean Three-and Four-Particle Systems

Xabier Lopez,[1] J. M. Ugalde,[1] L. Echevarria,[2] Eduardo V. Ludeña[3]

[1]Donostia International Physics Center (DIPC) and Kimika Fakultatea, Euskal Herriko Unibertsitatea, Posta Kutxa 1072, 20080 Donostia, Euskadi, Spain;
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[3]Centro de Química, Instituto Venezolano de Investigaciones Científicas, IVIC, Apartado 21827, Caracas 1020-A, Venezuela

Th-T2-4 12:05-12:40   Fully Correlated Wavefunctions for Small Atoms

Frank E. Harris

Department of Physics, University of Utah, Salt Lake City, UT, USA, and Quantum Theory Project, University of Florida, PO Box 118435, Gainesville, FL, USA

Some Recent Progress in the General Method of Solving the Schrödinger Equation and in the SAC/SAC-CI Methodology

Hiroshi Nakatsuji
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In St. Petersburg and in London, I have explained the progress in the general method of solving the Schrödinger equation (SE) of atoms and molecules and in the SAC/SAC-CI methodology. Here again, I report our recent progress in these subjects. The free ICI method for solving the SE is very stable and rapidly converging and so have been applied to various subjects [1-12]. For example, in the non-relativistic limit, the excitation energies of helium atom were calculated very accurately and reproduced the experimental values up to five digits, showing the accurate predictive power of the SE. To develop such predictive quantum theory, we have introduced the local SE method that does not necessitate the analytical integrations over the complement functions. Some recent progress will be explained.

The SAC/SAC-CI method is a useful established electron-correlation theory for studying ground, excited, ionized and electron attached states of molecules: from singlet to septet ground and excited states and applicable to large and even giant molecular systems [13]. Some recent applications of the SAC-CI method involve the photo-biological processes in human vision retinal proteins [14-17], the origin of circular dichroism in DNA etc [18]. We have also studied the mechanism of the photo-induced phase transition [19].

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[18] T. Miyahara, H. Sugiyama, H. Nakatsuji, to be submitted
[19] T. Miyahara, H. Nakatsuji, to be submitted.

Resolutions of the Coulomb Operator and a Generalized Poisson Equation

Sergey A. Varganov, Andrew T.B. Gilbert and Peter M.W. Gill
Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

The Resolution of the Identity (RI) is widely used in many-body algorithms. It expresses the completeness of a set of functions $f_i(\mathbf{r})$ that satisfy the orthonormality condition

$$\left\langle f_i \middle| f_j \right\rangle = \delta_{ij}$$

and, if we adopt the summation convention, it can be expressed concisely as

$$\left| f_i \right\rangle \left\langle f_i \right| \equiv \mathbf{I}$$

where $\mathbf{I}$ is the identity operator. In the first part of my lecture, I will discuss functions that satisfy the Coulomb-orthonormality condition

$$\left\langle f_i \middle| r_{12}^{-1} \middle| f_j \right\rangle = \delta_{ij}$$

and which yield the Resolution of the Coulomb Operator[1]

$$\left| \phi_i \right\rangle \left\langle \phi_i \right| \equiv r_{12}^{-1}$$

Such resolutions are potentially useful in a range of post-Hartree-Fock methods.

The Poisson Equation

$$\nabla^2 V = -4\pi\rho$$

relates a charge density $\rho(\mathbf{r})$ to its Coulomb potential $V(\mathbf{r})$. In the second part of my lecture, I will discuss the Generalized Poisson Equation[2]

$$V_\mathrm{S} = 4\pi\sigma(i\nabla)\rho$$

that relates $\rho(\mathbf{r})$ to its *short-range* Coulomb potential $V_\mathrm{S}(\mathbf{r})$. This generalization should be useful within the new generation of quantum chemistry methods that treat the short- and long-range parts of the Coulomb operator separately.

[1] S.A. Varganov, A.T.B. Gilbert, E. Deplazes, P.M.W. Gill, *J. Chem. Phys.* **128**, 201104 (2008)
[2] S.A. Varganov, A.T.B. Gilbert, P.M.W. Gill, *J. Chem. Phys.* **128**, (2008) in press

Th-T2-3

SOME RECENT ADVANCES IN THE EXACT NON-BORN-OPPENHEIMER TREATMENT OF HOOKEAN THREE- AND FOUR-PARTICLE SYSTEMS

Xabier Lopez[1], *J.M. Ugalde*[1], *L. Echevarria*[2], *and Eduardo V. Ludeña*[3]

[1]Donostia International Physics Center (DIPC) and Kimika Fakultatea, Euskal Herriko Unibertsitatea, Posta Kutxa 1072, 20080 Donostia, Euskadi, Spain
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ABSTRACT

The Hookean model systems under consideration are formed by three and four charged particles with arbitrary masses where the interaction between particles with the same charge is Coulombic and that between particles with different charges is harmonic.

We obtain exact non-Born-Oppenheimer solutions for the Hookean model of dipositronium (a four-particle system formed by two electrons and two protons) and for the family of systems formed by two positive and two negative particles all with the same mass M. In particular, for all these systems, we discuss the effect of symmetry on the wavefunction (spatial, spin, and charge and parity exchange) as well as the relationship between mass and the type of correlation function (between particles with the same charge) appearing in the exact solution.

Based on these exact non-Born-Oppenheimer solutions, we also examine the problem of the definition of molecular structure, which in the Born-Oppenheimer treatments is given in terms of the topological characteristics of the one-particle density. We show for these systems that there is not a unique definition of the one-particle density on account of the arbitrary choice of the origin of coordinates. Under different choices we explore the emergence of molecular structure.

Finally, we consider these Hookeans model systems in the presence of external magnetic fields as feasible models for single and double quantum dots. In this context we examine the effect of the dot radius and the external magnetic field on the correlation between particles with the same charge and in particular we analyze the phenomenon of particle localization leading to the arisal of Wigner-type molecules.

Fully Correlated Wavefunctions for Small Atoms

Frank E. Harris
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Quantum Theory Project, University of Florida, PO Box 118435, Gainesville, FL, USA

Accurate wavefunctions are extremely valuable for gaining understanding of quantum systems; independent-particle descriptions are inherently inadequate for this purpose due to their inability to take proper account of electron correlation. We consider here the use of *fully correlated* wavefunctions, i.e. formulations in which all the interparticle distances occur explicitly. The most widely-used approach of this kind has been that originated for the He atom by Hylleraas, who appended powers of the inter-electron distance to an orbital description of the electron-nuclear distribution. An alternative, which we consider here, is to include all the interparticle distances in an exponential form; such a wavefunction can be termed *fully exponentially correlated*.

Once all the interparticle distances of a few-body system have been introduced into the wavefunction in an equivalent fashion, there is no longer a simplification achievable by assuming any of the particles to have infinite mass (so-called *adiabatic* systems), and a fully exponentially correlated wavefunction is seen to be suitable for *nonadiabatic* systems, and in particular for exotic quasiatoms such as Ps^- (the $e^+e^-e^-$ system), Ps_2 ($e^+e^-e^+e^-$), or mesonic systems, e.g. $\mu^+ e^-e^-$.

For three-body systems, fully exponentially correlated wavefunctions are fairly easy to work with, in part because the number of *shape coordinates* is equal to the number of interparticle distances, which therefore form a symmetric set of shape coordinates. Moreover, the shape coordinates separate naturally from those describing overall translation and rotation, and the volume element in the shape space takes a simple form. However, for four-body systems, the situation is far more complex. The volume element in shape space is exceedingly complicated, and energy matrix elements do not reduce to simple integrals.

The basic integrals for four-body fully exponentially correlated wavefunctions were evaluated by Fromm and Hill in 1986. However, mathematical complexities in the evaluations introduced computational difficulties and unexplained behavior that we now discuss and elucidate. This understanding permits us to obtain compact, but rather accurate wavefunctions for the Li ground state.

An alternative to the use of exponential functions is to employ fully correlated Gaussians. We also present formulas that systematize this application of Gaussian functions and show how the formulas can be represented graphically.

Supported by U.S. National Science Foundation Grants PHY-0601758 and DMR-0325553.

Session Th-T3

Thursday, July 10, 2008 14:00-15:45

A169 Henry Center
Session Chair: **Katharine C. Hunt**
Department of Chemistry, Michigan State University

Th-T3-1 14:00-14:35

Restoring the Gradient Expansion for Exchange in a Generalized Gradient Approximation for Solids, Surfaces, and Organic Molecules

John P. Perdew,[a] A. Ruzsinszky,[a] G. I. Csonka,[b] L. A. Constantin,[a] X. Zhou,[a] O. A. Vydrov,[c] G. E. Scuseria,[c] K. Burke,[d] S. Grimme[e]

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Th-T3-2 14:35-15:10

Size-Consistency and Degeneracy in Density Functional Approximations

Paola Gori-Giorgi, Andreas Savin

Laboratoire de Chimie Théorique, CNRS and Université Pierre et Marie Curie (Paris VI), France

Th-T3-3 15:10-15:45

Exact and Approximate Optimized Effective Potentials

Viktor N. Staroverov

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Restoring the Gradient Expansion for Exchange in a Generalized Gradient Approximation for Solids, Surfaces, and Organic Molecules

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Standard generalized gradient approximations (GGA's) like PBE or B88 are biased by construction toward an accurate description of atoms, which requires a gradient coefficient for exchange that is about twice the one derived for slowly-varying electron densities. Restoration of the gradient expansion for exchange, while worsening atomic total energies and atomization energies, greatly improves the description of condensed phases including bulk solids, planar surfaces of solids, and certain large organic molecules. In particular: (1) The lattice constants of solids, which are about 1% too short in the local spin density (LSD) approximation and 1% too long in the PBE GGA, are about right in the new "PBEsol" GGA [1]. (2) Jellium surface exchange and exchange-correlation energies, that are too low in standard GGA's, are about right in PBEsol [2]. (3) Isodesmic stabilization energies of n-alkanes, isomerization energies of hydrocarbons, and geometries of sterically overcrowded aromatic systems, for which standard GGA's often fail, are often improved by the PBEsol GGA. Solids share with many organic molecules a rather dense packing of singly- (or metallically) bonded atoms.

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Th-T3-2

Size-consistency and Degeneracy in Density Functional Approximations

Paola Gori-Giorgi and Andreas Savin

Laboratoire de Chimie Théorique, CNRS and Université Pierre et Marie Curie (Paris VI)

The electronic structure calculations based upon energy density functionals are highly successful and widely used both in solid state physics and quantum chemistry. Moreover, the Hohenberg-Kohn theorems and the Kohn-Sham method provide them with a firm basis. However, several basic issues are not solved, and hamper the progress to achieve high accuracy. In spite of the claim sometimes found in literature, that density functional approximations are size-consistent, this is not the case. We base our analysis on the non-intensive character of the (spin) electronic density in the presence of degeneracy. Some of the issues concerning fractional electron numbers are addressed from the same point of view, analyzing the behavior of the exact functionals for the He and Hooke's atom series as well as the hydrogen molecule when the number of electrons varies between one and two.

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Exact and Approximate Optimized Effective Potentials

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The Kohn–Sham potential associated with the exact-exchange functional is difficult to obtain to high accuracy by solving the optimized effective potential (OEP) equation, so it is often modeled approximately. We emphasize that a poor approximation to the exact OEP may yield a deceptively accurate energy via the conventional exact-exchange energy functional, and that a more stringent quality test should include comparison of this energy with the value obtained by the Levy–Perdew virial relation. Recently we reported[1] significant discrepancies between conventional and virial energies for various model exact-exchange potentials including the Slater, Becke–Johnson,[2] and common energy denominator-type approximations. This talk will focus on solutions of the OEP equation obtained as expansions in finite auxiliary basis sets by the Yang–Wu method.[3] We show that virial energy discrepancies of these potentials vanish if the Kohn–Sham and auxiliary basis sets are perfectly balanced but remain surprisingly small for defective and spurious OEPs obtained with unbalanced bases (in fact, two orders of magnitude smaller than for seemingly reasonable model exact-exchange potentials). We also show how the Levy–Perdew virial relation can be used to obtain a perfectly smooth OEP for any given finite orbital basis.

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Session Th-T4

Thursday, July 10, 2008 16:10-18:30

A169 Henry Center
Session Chair: **Hiroshi Nakatsuji**
Quantum Chemistry Reasearch Institute, QCRI

Th-T4-1 16:10-16:45

Insight into Density Functional Theory

Aron J. Cohen, Paula Mori-Sanchez, Weitao Yang

Department of Chemistry, Duke University, Durham, NC 27708, USA

Th-T4-2 16:45-17:20

Embedding a Quantum Chemical System in Orbital-Free Environment: Exact Theory and Approximants for Practical Applications.

Tomasz A. Wesołowski

Department of Physical Chemistry, University of Geneva, 30 quai Ernest-Ansermet, 1211 Geneva, Switzerland

Th-T4-3 17:20-17:55

Orbital-Corrected Orbital-Free Density Functional Theory

Y. Alexander Wang

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Z1

Th-T4-4 17:55-18:30

Understanding and Correcting the Self-Interaction Error in the Electrical Response of Hydrogen Chains

Adrienn Ruzsinszky,[a] John P. Perdew,[a] Gábor I. Csonka,[b] Gustavo E. Scuseria,[c] Oleg A. Vydrov[d]

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Insight into Density Functional Theory

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Density functional theory of electronic structure is widely and successfully applied in simulations throughout engineering and sciences. However, there are spectacular failures for many predicted properties, which can be traced to the delocalization error and static correlation error of commonly used approximations. These errors can be characterized and understood through the perspective of fractional charges and fractional spins introduced recently. Reducing these errors will open new frontiers for applications of density functional theory.

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Th-T4-2

Embedding a quantum chemical system in orbital-free environment: exact theory and approximants for practical applications.

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Our work concerns electronic structure of molecules or other polyatomic systems which are embedded in a condensed matter environment. To this end, we apply orbital-free embedding strategy, in which a reference system of non-interacting electrons is used to obtain a selected component of the total electron density [1]. Embedded orbitals obtained from one-electron equations (Eqs. 20-21 in Ref. [1]) can be used to derive a range of properties including electronic excitation energies [2, 3].

In the first part, examples using one-electron equations for embedded orbitals implemented to derive various properties of embedded molecules will be reviewed. They include: *i*) electronic excitation energies in molecular clusters used as models of hydrogen-transfer chains in biological systems and *ii*) electronic excitations for dye molecules inside zeolite-L framework used in the construction of artificial antennae systems.

In the second part, we address formal issues related to the applied formalism: *i*) construction of such approximants to the orbital-free effective embedding potential which take into account exact properties of this quantity [4] and *ii*) two formal theorems concerning generalization of the orbital-free embedding strategy in which the orbital-free effective embedding potential is used in combination with other than non-interacting electrons reference systems for the embedded molecule such as: embedded wavefunction representing interacting electrons [5] or embedded one-matrix [6].

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Orbital-Corrected Orbital-Free Density Functional Theory

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Density functional theory (DFT) has been firmly established as one of the most widely used first-principles quantum mechanical methods in many fields. Each of the two ways of solving the DFT problem, *i.e.*, the traditional orbital-based Kohn-Sham (KS) and the orbital-free (OF) [1] schemes, has its own strengths and weaknesses. We have developed a new implementation of DFT, namely orbital-corrected OF-DFT (OO-DFT) [2], which coalesces the advantages and avoids the drawbacks of OF-DFT and KS-DFT and allows systems within different chemical bonding environment to be studied at a much lower cost than the traditional self-consistent KS-DFT method. For the cubic-diamond Si and the face-centered-cubic Ag systems, OO-DFT accomplishes the accuracy comparable to fully self-consistent KS-DFT with at most two non-self-consistent iterations [2] via accurately evaluating the total electronic energy before reaching the full self-consistency [2-5]. Furthermore, OO-DFT can achieve linear scaling by employing currently available linear-scaling KS-DFT algorithms and may provide a powerful tool to treat large systems of thousands of atoms within different chemical bonding environment much more efficiently than other currently available linear-scaling DFT methods. Our work also provides a new impetus to further improve OF-DFT method currently available in the literature.

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Understanding and Correcting the Self-Interaction Error in the Electrical Response of Hydrogen Chains

Adrienn Ruzsinszky[a], John P. Perdew[a], Gábor I. Csonka[b], Gustavo E. Scuseria[c], and Oleg A. Vydrov[d]

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Semi-local density functionals like the local spin density and generalized gradient approximations are known to overestimate [1, 2, 3, 4] the polarizabilities and especially the hyperpolarizabilities of long-chain molecules, the latter by as much as a factor of ten or more. These quantities are much better predicted by exact-exchange methods (Hartree-Fock or Optimized Effective Potential). When a static electric field is applied to a chain of atoms, charge transfer occurs along the backbone of the chain. This induced polarization is a non-local effect, and the local and semi-local approximations are not able to capture the non-locality in the potential, so they fail to provide the counteracting response field which reduces the polarizabilities. The source of this failure of the semi-local approaches for the electrical response is rooted in the self-interaction error inherent to the semi-local approximations. We show here that the semi-local functionals, after full [5] or scaled-down [6] Perdew-Zunger self-interaction correction, are about as good as the exact-exchange methods for these quantities.

The response coefficients of the hydrogen chains, unlike those of bulk solids, show a strong nonlinear dependence upon length or *n*. We propose a simple charge-transfer model [7] which explains this effect. This transfer is driven by the external electric field, and opposed by the chemical hardness of each H_2 unit. Unlike the situation in a bulk solid, this charge transfer is not suppressed (or even much affected) by electrostatic interactions among the transferred charges for $n \leq 7$. Self-interaction-free approaches increase the chemical hardness of an H_2 unit in comparison with semi-local density functionals, and so reduce the charge transfer. The physical picture behind the model is validated and its limitations are revealed by a population analysis of the charge density from selfconsistent electronic structure calculations.

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Session Fr-T1

Friday, July 11, 2008 08:15-10:00

A169 Henry Center
Session Chair: **Souad Lahmar**
Department of Physics, IPEST

Fr-T1-1 08:15-08:50 Photo Induced Conical Intersections in Molecular Optical Lattices: The Phenomenon and its Consequences

Nimrod Moiseyev

Schulich Faculty of Chemistry and Minerva Center of Nonlinear Physics in Complex Systems, Technion – Israel Institute of Technology, Haifa 32000, Israel

Fr-T1-2 08:50-09:25 Multi-Reference Coupled-Cluster Approach for Spectra and Properties

Sourav Pal

Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

Fr-T1-3 09:25-10:00 Quantum Mechanics in Terms of Cumulant: Quantum Cluster

Yasuteru Shigeta

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Fr-T1-1

Photo Induced Conical Intersections in Molecular Optical Lattices: The Phenomenon and its Consequences

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Conical intersections appear in the potential energy surfaces (PES) of molecules which consist of *more* than two atoms. For principal reasons, no conical intersections exist in the case of free diatomic molecules. We will show that diatomic molecules which interact with the standing laser waves produce periodic arrays of laser induced conical intersections, such that the rovibrational and the translational molecular motions are strongly coupled to each other. Similarly as for the usual conical intersections in field free polyatomic molecules, also the laser induced conical intersection introduces infinitely strong local non-adiabatic couplings between the involved nuclear degrees of freedom. An effect of the laser induced conical intersections on trapping of cold diatomic molecules by light will be discussed.

Based on N. Moiseyev, M. Sindelka and L.S. Cederbaum, submitted for publication.

Multi-Reference Coupled-Cluster Approach for Spectra and Properties

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Development and application of Fock space multi-reference coupled-cluster (FSMRCC) method for high performance electronic structure, spectra and properties will be highlighted. We will present our recent formulation of analytic response of FSMRCC, which has facilitated the efficient computation of analytic energy derivatives using FSMRCC method. In particular, our applications to molecular electric properties will be highlighted. Recent computation of electronic excitation energies of model quantum dots using FSMRCC method as well as resonance and width of electron-molecule resonance will also be presented.

QUANTUM MECHANICS IN TERMS OF CUMULANT: QUANTUM CLUSTER

Yasuteru Shigeta

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Recent experimental advances offer new information across many different time scales of interest, ranging from submillisecond slow macroscopic structural transitions to subpicosecond electronic rearrangements, and femtosecond nonadiabatic dynamics. In order to describe these phenomena, one should adopt quantum mechanics, which cost too much. In contrast to quantum dynamics, classical dynamics methods are routinely used to study complex chemical problems that can involve many thousands of particles, such as protein folding and docking. In proteins, the Amino I modes are of such high frequency that the quantum effects cannot be neglected, even if the experiments are performed at room temperature. Thus, quantum effects, such as zero point energy, tunneling, and resonance, are essential, and cannot be avoided.

Rencently, we have developed a quantal cumulant dynamics (QCD) in order to treat large quantum systems with low costs [1-5]. The key ideas are that a coordinate shift operator acting on a potential operator is introduced and that a cumulant expansion technique is applied to evaluate the expectation value of the shift operator. In the presentation, we derive the coupled equations of motion of coordinates, momenta, cumulants that consist of symmetric-ordered products of the coordinate and the momentum fluctuation operators. We apply the methodology to describe quantum nature of structural transitions of Morse clusters. We have evaluated a Lindemann index of small quantum clusters and observed quantum isotope effects on their melting behavior. The quantum effects shallow the potential and elongate the equilibrium distance of the Morse potential. These features result in increase of transition temperatures of freezing and melting toward those of classical ones.

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Session Fr-T2

Friday, July 11, 2008 10:20-12:40

A169 Henry Center
Session Chair: **Y. Alexander Wang**
Department of Chemistry, University of British Columbia

Fr-T2-1 10:20-10:55

Spectroscopy of Alkali Atoms Under Liquid Helium Confinements

Prasanta K. Mukherjee

Spectroscopy Department, Indian Association for the Cultivation of Science
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Fr-T2-2 10:55-11:30

Alkali Trimers on He Nanodroplets: Ab Initio Calculations, Shell Models and Laser Spectroscopy

Johann Nagl, Gerald Auböck, Andreas W. Hauser,
Olivier Allard, Carlo Callegari, Wolfgang E. Ernst

Institute of Experimental Physics, Graz University of Technology, Graz, Austria

Fr-T2-3 11:30-12:05

Transition Metal Clusters: The Next Frontier of Ab Initio Approach

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Fr-T2-4 12:05-12:40

TDDFT Studies of Optical Properties of Silver and Gold Nanoparticles

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Spectroscopy of Alkali Atoms under Liquid Helium Confinements

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Laser induced fluorescence studies on the alkali and many other atoms embedded in liquid helium yield substantial data for the spectral line shifts, line profiles and other spectroscopic properties. Pilot calculations have been performed using different ab-initio methods for interpreting the principal resonance line shifts and line profiles for alkali atoms in which the effect of the confinement due to surrounding liquid helium is appreciable. The effect of such confinement is to produce a cavity like structure of nano dimension around the central defect atom. Liquid helium environment has been simulated by using Monte Carlo technique. Time dependent density functional calculations (TDDFT) on such simulated structure have been performed to find the line shift and line profile of Na D line. Symmetry adopted cluster configuration interaction (SAC-CI) method has also been applied for estimating the line shift for the same transition in Na atom. In addition, relativistic density functional theory (RDFT) within local density approximation (LDA) has been applied to estimate the shift of the principal resonance lines of Na, Rb and Cs atoms embedded in suitably assigned He clusters. The estimated results are found to be in good agreement with existing data obtained from laser spectroscopic experiments and other theoretical methods.

Alkali Trimers on He Nanodroplets: Ab initio calculations, Shell Models and Laser Spectroscopy

Johann Nagl, Gerald Auböck, Andreas W. Hauser, Olivier Allard,
Carlo Callegari and Wolfgang E. Ernst
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A supersonic beam of helium nanodroplets ($He_N = 10^4$) is doped with alkali atoms, which are unique dopants as they remain on the droplet surface. Capture of multiple alkali atoms per cluster leads to molecular formation. The droplets can dissipate released binding energy very efficiently by evaporating He atoms and provide a cold environment (T=0.4 K). Whereas the formation of strongly bound low-spin molecules tends to destroy the droplet, the weakly bound high-spin van der Waals molecules (triplet dimers, quartet trimers) survive the formation process. Experimentally we have identified, in the wavelength range 10500-17500 cm^{-1}, a variety of electronic spectra of the homo- and hetereonuclear trimers K_3, Rb_3, K_2Rb, KRb_2 in their quartet states.

To help the assignment we calculate the quartet manifolds of the first few electronic excitations for all these (bare) trimers with ab initio methods and provide their PES as functions of the normal modes Q_s (breathing mode) and Q_x (symmetric bending mode). We find several regular patterns in the level structure, and rationalize them in terms of harmonic-oscillator states of the three valence electrons in a quantum-dot-like confining potential.[1]

For the homonuclear trimers K_3 and Rb_3 we further compute the doublet manifolds of the first electronic excitations. A simplified description of these systems as single-electron excitations in a standard electron-droplet model provides a qualitative explanation for the electronic state structure of the low-spin alkali trimers.[2]

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Transition Metal Clusters: the Next Frontier of Ab Initio Approach

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Transition metal (TM) clusters are of great importance as models and precursors of variety of metallic aggregates: from small clusters, to larger nanostructures, and the bulk. Because of their complex electronic structure, related to intra- and inter-shell electron-correlation and relativistic effects, the clusters elude approximate approaches that neglect any of these factors, and present unprecedented challenge for quantum chemistry. We will discuss these issues starting from the perspective of TM-helium interactions that expose the intricate anisotropy of TM atoms in weak interactions, and helps to evaluate the usefulness of different ab initio methods. The metal-helium interactions are presently also of practical interest as helium is the buffer gas employed to cool candidates for Bose-Einstein condensates (BEC). Next, we will have a look into the realm of TM dimers with the emphasis on the spin-parallel forms that, again, are of importance in the quest for BEC, but also relevant in the context of spin-polarized metallic state. Finally, we will have a glance at atomic metal trimers and anomalous many-body interactions that render them unique, and particularly difficult objects to examine.

TDDFT Studies of Optical Properties of Silver and Gold Nanoparticles

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Noble metal nanoparticles are characterized by sharp peaks in their extinction spectra called surface plasmon resonances. Experimentally and theoretically, clusters such as Ag_{20} have also been shown to exhibit sharp peaks in their absorption spectra. Time-dependent density functional theory has been employed to calculate the absorption spectrum for neutral and charged tetrahedral Ag_n (n = 10, 20, 35, 56, 84, 120) clusters. Orbital and shell fillings are important considerations in order to obtain sharp absorption spectra. For silver tetrahedra, the peak location is found to extrapolate linearly with 1/L, where L is the length of a side of the tetrahedron, and with $1/N^3$, where N is the number of electrons in the cluster. This extrapolation agrees well with results from discrete dipole approximation calculations. Silver nanorods also exhibit similar size dependence. The wavelength of their absorption maxima extrapolates linearly with aspect ratio (e.g. length). The nanorod orbitals and length dependence agree with a simple particle-in-a-box model. Self-assembled arrays of silver tetrahedra and nanorods can potentially possess well-defined excitation energies. The TDDFT predicted red/blue shifts, oscillator strengths, and longitudinal/transverse characterizations in these arrays agree qualitatively with those for larger particles.

Small (< 2 nm) gold nanoparticles display multiple peaks in their optical absorption spectra rather than the strong plasmon resonance peak of larger nanoparticles. This characteristic is likely due in part to the structure of these systems. Recent crystal structure determination of the Au_{102} and Au_{25} nanoparticles is currently enabling in-depth research into the properties and reactivity of these systems. In this presentation, the level of theory required to accurately compute the core structure and optical absorption spectrum of the Au_{25} nanoparticle will be discussed. Precise core geometries are required in order to obtain good predictions for the splitting between the first two spectral peaks. The model potential used to compute the excitation spectrum is critical. Solvent effects play a relatively minor role.

Session Fr-T3

Friday, July 11, 2008 14:00-15:45

A169 Henry Center
Session Chair: **John P. Perdew**
Department of Physics, Tulane University

Fr-T3-1 14:00-14:35 ^{4}He$_{N}$-ICl(X) Clusters: Size Evolution Arrangements and its Incidence on Photo-Predissociation Rates

G. Delgado-Barrio, M. P. de Lara-Castells, R. Prosmiti, D. López-Durin, P. Villarreal

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Fr-T3-2 14:35-15:10 Ab Initio Investigation of Di- and Tri-Atomic Molecular Systems: Electronic Structure, Reactivity and Spectroscopy

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Département de Physique, Faculté des Sciences de Tunis – Tunisie

Fr-T3-3 15:10-15:45 Resonant Inelastic X-Ray Scattering in K-shell Cl Core-Excited Chlorinated Molecules: A Theoretical Overview

Stéphane Carniato

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^4He_N-ICl(*X*) Clusters: Size Evolution Arrangements and its Incidence on Photo-predissociation Rates

G. Delgado-Barrio, M. P. de Lara-Castells, R. Prosmiti, D. López-Durán, and P. Villarreal
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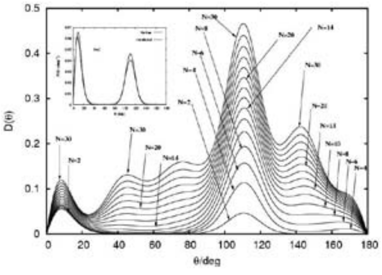
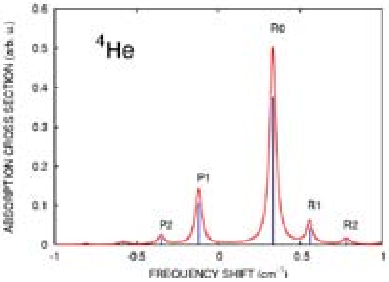
Accurate CCSD(T) *ab initio* calculations on He-ICl(*X*) and further on He_2-ICl(*X*) [1] show that the surface can be described as the sum of N triatomic potentials plus the He-He interactions. This allows to study, by a Hartree approach [2], the cluster size evolution of different properties. The high degree of anisotropy is reflected in the helium angular distributions around ICl, depicted in figure on the left, for sizes N≤30. Since the method provides with wave-functions, we have simulated the infra-red spectra involving the vibrational excitation v=0-->1 of the dopant by dressing the stick lines with N-dependent Lorentzian functions. The stereo effect is evidenced through a model of Vibrational Predissociation in which the above mentioned distributions are used to average angular dependent VP widths for the trimer [3]. After extrapolation, the simulated IR absorption spectrum, shown in the figure on the right, exhibits only P and R branches with lack of Q branches, in agreement with the experiments on OCS molecules in ^{4}He nano-droplets [4].





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Ab Initio Investigation of Di- and Tri-atomic Molecular Systems: Electronic Structure, Reactivity and Spectroscopy

S. Lahmar
S. Ben Yaghlene, B. Edhay, H. Ghalila, F. khadri and A. Zaidi

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This work deals with theoretical studies of di- and tri-atomic molecular systems.
Our calculations consist in an accurate investigation of the adiabatic potential energy functions (PEFs) of these systems in the electronic states correlating to the lowest dissociation limits, using a high level *ab initio* methods (CASCF, MRCI, CCSD(T)) with large basis sets.
The study of these functions (minimas, saddle points, potential barriers, relative position of the electronic states, location of intersections, conical intersections...) and additional calculations taking into account angular momentum couplings (like spin orbit couplings...) allow us to predict the stability, and the reactivity of the considered systems.
For the lowest stable systems, the nuclear motion problem is then solved by perturbational and variational approaches and sets of spectroscopic data (spectroscopic constants, ro-vibrational levels, lifetimes, …) are calculated.

Resonant Inelastic X-Ray Scattering in K-shell Cl Core-Excited chlorinated molecules: a theoretical overview

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The knowledge of Potential-Energy-Surfaces (PES) in chemical-physics is crucial to understand chemical reaction paths, photo-dissociation or molecular dynamics phenomena. The determination of PES is in general difficult to be achieved directly from standard spectroscopic measurements, requiring sophisticated ab-initio (Post-HF, QMC,..) calculations. However, in some specific cases (dissociative core-excited states of chlorine molecules), the PES can be extracted from experiments giving unique opportunity to compare theory/experiments.

A key point for exploration of core-excited PES from experimental x-ray measurements is high spectral resolution, which is limited both by physical and instrumental factors. Continuous technical advances have improved the spectral resolution of x-ray spectrometers [1, 2], leaving only two physical limitations as major factors, namely, lifetime and vibrational broadening. However, the lifetime broadening is very large ($\lesssim$ 1 eV) for chlorine inner shells with binding energies in the tender-hard x-ray region.

X-ray Raman scattering (RXRS) has an great advantage over standard x-ray absorption technique since it provides lifetime-broadening removed resolution [3, 4]. Furthermore, vibrational broadening in Resonant x-ray Raman scattering (RXRS) is quenched when PES involved in the process are parallel: (1) away from resonance if both ground and final states potential surfaces are parallel; (2) on resonance if the core-excited and final states are parallel.
Based on theoretical approach using the concept of effective duration time of the x-ray scattering process, we will describe how RXRS measurements in tender X-region [5] opens a new way of studying ultrafast nuclear dynamics of core-excited polyatomic molecules. More specifically, we will show that RXRS can provide a tool to map PES of HCl core-excited states [6]. We will also demonstrate that angular polarized RIXS analysis of the K_α X-ray Raman scattering spectra [7] acts as a probe of molecular environment of small chlorine molecules (HCl and CF_3Cl) through the direct measurement of the $2p_{x,y,z}$ populations in spin-orbit component.

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Session Fr-T4

Friday, July 11, 2008   16:10-18:30

A169 Henry Center
Session Chair: **Garnet K.-L. Chan**
Department of Chemistry and Chemical Biology, Cornell University

Fr-T4-1 16:10-16:45   Electronic and Vibrational Many-Body Methods for Molecules and Macromolecules

So Hirata

Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, FL 32611-8435, USA

Fr-T4-2 16:45-17:20   Vibrational Coupled Cluster Theory

Peter Seidler, Ove Christiansen

The Lundbeck Foundation Center for Theoretical Chemistry and Center for Oxygen Microscopy and Imaging, Department of Chemistry, University of Århus, Denmark

Fr-T4-3 17:20-17:55   Dynamics and Infrared Spectroscopy of the Zundel Cation

Hans-Dieter Meyer, Oriol Vendrell

Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

Fr-T4-4 17:55-18:30   Computer Experiments on Noble Gas Hydrides

Jan Lundell

Department of Chemistry, University of Jyväskylä, P.O.Box 35 (Survontie 9), FI-40014 University of Jyväskylä, Finland

Electronic and Vibrational Many-Body Methods for Molecules and Macromolecules

So Hirata
Quantum Theory Project
Departments of Chemistry and Physics
University of Florida, Gainesville, FL 32611-8435

(1) Hierarchical electronic and vibrational methods such as those based on coupled-cluster and perturbation theories are not yet applicable to macromolecules of any chemical compositions. However, when particular classes of macromolecules such as periodic insulators and molecular crystals are considered, one can apply these methods by exploiting known characteristics of their wave functions. We introduce two such schemes: one allowing the anharmonic phonon frequencies of polymers to be computed by electronic and vibrational perturbation theories and the other predicting the structures and phonons of molecular crystals.

(2) The bifluoride ion (FHF^-) can be viewed as a vibrational analogue of the classic electronic Schrödinger problem for H_2^+. We present the vibrational self-consistent field and configuration interaction predictions of the anharmonic vibrational frequencies, vibrationally averaged values of bond lengths and NMR indirect spin-spin coupling constants, and zero-point binding energy, all of which agree excellently with the observed. We also examine the accuracy of the Born–Oppenheimer (BO) separation and diagonal BO corrections (DBOC) between light (hydrogen) and heavy (fluorine) nuclei motions by solving the vibrational Schrödinger equation on a cylindrical grid. It is shown that BO works remarkably well (and DBOC better) even when the mass ratio is only 10.

Vibrational Coupled Cluster Theory

Peter Seidler and Ove Christiansen
The Lundbeck Foundation Center for Theoretical Chemistry and
Center for Oxygen Microscopy and Imaging,
Department of Chemistry, University of Århus, Denmark

Within the Born-Oppenheimer approximation, the motion of the nuclei is determined by a potential energy surface (PES) set up by the electrons. Vibrational energy levels and vibrational contributions to molecular properties can be obtained by solving the Schrödinger equation for the nuclei moving in this PES.

Vibrational coupled cluster[1,2] (VCC) theory is introduced as an alternative to the well-known vibrational configuration interaction (VCI) method. To obtain excitation energies, response theory has furthermore been applied[3]. At an abstract level, the VCC method resembles the familiar coupled cluster method of electronic structure theory. In the details however, the working equations are very different due to the distinguishability of the vibrational degrees of freedom.

An algorithm capable of handling arbitrary excitation spaces for both VCC and VCI has been constructed. So far, VCC has proven to be significantly more accurate than VCI for identical excitation spaces. However, the exponential parameterization in VCC theory is considerably more complicated to handle computationally than the linear VCI parameterization. Therefore, current research is directed at developing efficient algorithms to make VCC competitive with VCI in terms of CPU time. Presently, an efficient algorithm for the case of two-mode Hamiltonians and two-mode excitation spaces has been constructed that scales with the number of modes to the third power for both VCI an VCC. This algorithm has been used to calculate ground state and excitation energies for model systems with up to 264 coupled modes[4].

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[3] P. Seidler and O. Christiansen, *J. Chem. Phys.*, **126**, 204101 (2007)
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Dynamics and Infrared Spectroscopy of the Zundel Cation

Hans-Dieter Meyer and Oriol Vendrell
Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg,
Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

Accurate infrared (IR) spectroscopy of protonated water clusters prepared in the gas phase has become possible in recent years [1,2], opening the door to a deeper understanding of the properties of aqueous systems and the hydrated proton, which are of main interest in central areas of chemistry and biology.

In this presentation we discuss a full (15D) quantum simulation of the infrared absorption spectrum and dynamics of the protonated water dimer ($H_5O_2^+$) — also known as Zundel cation — by the multiconfiguration time-dependent Hartree (MCTDH) [3] method. The main features of the IR spectrum are explained and assigned. In particular a complicated doublet structure at about 1000 cm^{-1}, which was not understood, is explained as a Fermi-resonance structure involving the proton transfer motion and wagging motion (water pyramidalization). Also the couplings of various fundamental motions which shape the spectrum between 800 and 2000 cm^{-1} are explained and their spectral lines are assigned [4,5].

A picture of the cation arises in which the central proton motion determines the dynamics of various other modes, mostly water bending and water pyramidalization, and controls the switch between H_3O^+- and H_2O-like structures.

From a methods perspective, we show that a full quantum-dynamical description of such a complex molecular system can still be achieved, providing explicative and predictive power and a very good agreement with available experimental data. To account for the interatomic potential and the interaction with the radiation we make use of the potential energy surface and dipole-moment surfaces recently developed by Bowman and collaborators, which constitute the most accurate *ab initio* surfaces available to date for this system [6].

[1] N.I. Hammer, E.G. Diken, J.R. Roscioli, M.A. Johnson, E.M. Myshakin, K.D. Jordan, A.B. McCoy, J.M. Bowman, S. Carter, *J. Chem. Phys.* **122**, 244301 (2005).
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[5] O.V., F. Gatti, H.-D. Meyer, *J. Chem. Phys.*, **127**, 184303, (2007)
[6] X. Huang, B.J. Braams, J.M. Bowman, *J. Chem. Phys.* **122**, 044308 (2005).

Computer Experiments on Noble Gas Hydrides

Jan Lundell
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The electronic structure of noble gas atoms in their ground state is extremely stable, causing the unique chemical inertness of these elements. However, over the years many noble-gas-containing molecules have been prepared. One recent development sparking a renaissance in the chemistry of noble gases has been the preparation and spectroscopic characterisation of noble gas hydrides of the form HNgY (where Y is an electronegative fragment).[1-3]

In general, the HNgY molecules are easily detected by IR spectroscopy due to their extremely intense Ng–H stretching absorptions, and the position of the stretching band is very characteristic for each Y. In addition to the Ng–H absorption bands, other vibrational transitions like combinations, overtones, and fundamental bands characteristic of the Y residue in the HNgY molecules have been observed. The rich spectral data available from the experiments indicate that the HNgY molecules are rather anharmonic in nature.

Computational predictions of the vibrational spectra of HNgY have always played an important role in the experimental search and identification of these compounds. Moreover, anharmonic vibrational calculations of HNgY molecules are equally important both because of their usefulness for experimental identification of these molecules, and because of their relevance to dynamic processes in these systems.

In this presentation, the current status of research on noble gas hydrides is summoned. Furthermore, results of computer experiments are presented, which indicate that the currently experimentally verified family of neutral noble gas hydrides could be much larger and much more diverse than found up-to-now.

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[2] L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell and M. Räsänen, *Nature* **406**, 874 (2000).

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Session Sa-T1

Saturday, July 12, 2008   08:15-10:00

A169 Henry Center
Session Chair: **Christine M. Aikens**
Department of Chemistry, Kansas State University

Sa-T1-1 08:15-08:50   Excited States for Degenerate Systems

Hiromi Nakai

Department of Chemistry and Biochemistry, Faculty of Advanced Science and Engineering, Waseda University 3-4-1 Okubo,
Shinjuku-ku, Tokyo 169-8555, Japan

Sa-T1-2 08:50-09:25   Photochemistry of Biological Chemosensor, Organic Light-Emitting Diodes, and Inner-shell Electronic Processes

Masahiro Ehara

Research Center for Computational Science, Institute for Molecular Science, 38
Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan

Sa-T1-3 09:25-10:00   Simulation of Large-Scale Excited Electron Dynamics

Julius Su, William A. Goddard III

California Institute of Technology, 1200 E. California Blvd,
Pasadena, CA 91125, USA

Sa-T1-1

Excited States for Degenerate Systems

Hiromi Nakai
Department of Chemistry and Biochemistry,
Faculty of Advanced Science and Engineering, Waseda University
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Excitations in high-symmetry systems lead to several different excited states which possess the same excitation nature between degenerate orbitals. For example, excitations between degenerate HOMOs and LUMOs in $(B_{12}H_{12})^{2-}$, which are both fourfold in I_h point group, i.e., g_u and g_g symmetries, respectively, give five singlet excited states such as A_u, T_{1u}, T_{2u}, G_u, and H_u. This is mathematically derived by the reduction of the direct product:

$$G_u \otimes G_g = A_u + T_{1u} + T_{2u} + G_u + H_u$$

Accurate methodologies such as SAC-CI and TDDFT have been applied to obtain the excited states in various molecules with degenerate π-bonding orbitals: {$D_{\infty h}$: N_2, P_2, As_2, C_2H_2; $C_{\infty v}$: CO, CS, CSe, SiO, GeO; I_h: C_{60}, $(B_{12}H_{12})^{2-}$; O_h: MoF_6, $Mo(CO)_6$; T_d: CrO_4^{2-}, MoO_4^{2-}, MnO_4^-, TcO_4^-, RuO_4, OsO_4}. We have discovered the following general rules for the energy orderings and splittings in these excited states having the same excitation nature:

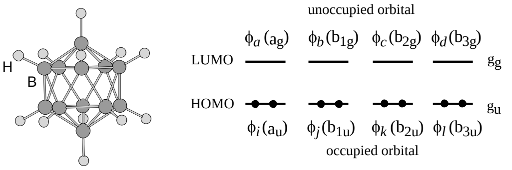

Fig. 1. Structure and molecular orbitals of $B_{12}H_{12}^{2-}$.

(i) The highest transition is dipole-allowed.
(ii) The energy splitting between the highest state and the others is largest.

A frozen-orbital analysis (FZOA), which corresponds to the CIS within the minimal active space, could rationalize the energy orderings and splittings. The excitation energies in FZOA are decomposed into three terms: $\Delta E = A + B + C$. The explicit formula in case of the HOMO-LUMO transitions in $(B_{12}H_{12})^{2-}$ are given in Table I. The schematic picture of the excitation-energy splittings are illustrated in Fig. 2.

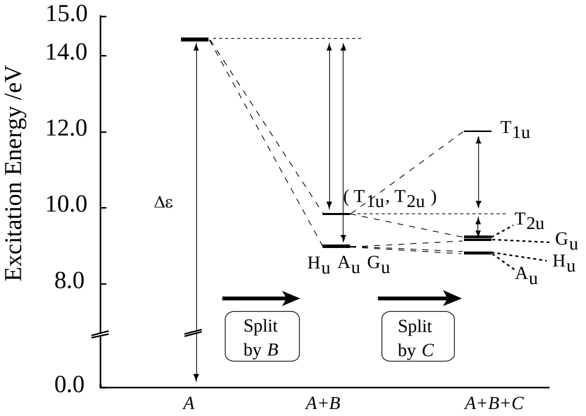

Fig. 2. Schematic picture of energy splitting in $B_{12}H_{12}^{2-}$.

Table I. FZOA energy components of HOMO → LUMO excitation energies for $(B_{12}H_{12})^{2-}$

State	A	B	C
A_u	$\varepsilon_a-\varepsilon_i$	$1/4(-J_{ia}+2K_{ia})+3/4(-J_{jb}+2K_{jb})$	$3/2\{-(ij\vert ab)+2(ia\vert bj)\}+3/2\{-(jk\vert cb)+2(jc\vert bk)\}$
T_{1u}	$\varepsilon_a-\varepsilon_i$	$1/2(-J_{ib}+2K_{ib})+1/2(-J_{kd}+2K_{kd})$	$1/2\{-(ij\vert ab)+2(ib\vert aj)\}+1/2\{-(jk\vert cb)+2(jb\vert ck)\}+\{-(ik\vert db)+2(ib\vert dk)\}+\{-(jk\vert da)+2(ja\vert dk)\}$
T_{2u}	$\varepsilon_a-\varepsilon_i$	$1/2(-J_{ib}+2K_{ib})+1/2(-J_{kd}+2K_{kd})$	$1/2\{-(ij\vert ab)+2(ib\vert aj)\}+1/2\{-(jk\vert cb)+2(jb\vert ck)\}-\{-(ik\vert db)+2(ib\vert dk)\}-\{-(jk\vert da)+2(ja\vert dk)\}$
G_u	$\varepsilon_a-\varepsilon_i$	$3/4(-J_{ia}+2K_{ia})+1/4(-J_{jb}+2K_{jb})$	$-3/2\{-(ij\vert ab)+2(ia\vert bj)\}+1/2\{-(jk\vert cb)+2(jc\vert bk)\}$
H_u	$\varepsilon_a-\varepsilon_i$	$(-J_{jb}+2K_{jb})$	$\{-(jk\vert cb)+2(jc\vert bk)\}$

[1] H. Nakai, H. Morita, H. Nakatsuji, *J. Phys. Chem.*, **100** (39), 15753 (1996).
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[3] H. Nakai, H. Morita, P. Tomasello, and H. Nakatsuji, *J. Phys. Chem. A*, **102** (11), 2033 (1998).
[4] T. Baba, Y. Imamura, M. Okamoto, H. Nakai, *Chem. Lett.*, **37** (3), 322 (2008).

Photochemistry of Biological Chemosensor, Organic Light-Emitting Diodes, and Inner-shell Electronic Processes

Masahiro Ehara
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We have investigated wide varieties of “excited-state chemistry” and established “theoretical fine spectroscopy” with the SAC-CI method.[1] In this talk, we present our recent challenges to photochemistry of biological chemosensor, organic light-emitting diodes, and inner-shell electronic processes.

Fluorescent artificial chemosensor has been intensively developed, since it enables the directly and real-time measurements of the enzyme activities. Recently, a novel molecular fluorescent probe which can selectively recognize the phosphoprotein has been developed.[2] This fluorescent artificial chemosensor shows drastic fluorescence change in the presence of Zn^{2+} ion in solution. We have studied the photochemistry of this fluorescent probe and the photoinduced electron transfer mechanism.

Organic light emitting diode (OLED) is one of the promising candidates for the next generation electro-optical devices such as panel display. It is important to predict the photo-physical properties of OLED theoretically for the molecular design. We studied the absorption spectra, emission spectra, and excited-state geometry of some OLED molecules like polyphenylenevinylene, fluorene-thiophene, and Ir complexes.[3]

Developments of high-resolution x-ray photoelectron spectroscopy and accurate theoretical methods have allowed precise knowledge and assignments of the inner-shell electronic processes. Recently, we have investigated the various kinds of core-electronic processes like core-electron binding energy, inner-shell satellite spectra with vibrational progression, and valence-Rydberg coupling and its thermal effect.[4] We present here the summary of our recent works on core-electronic processes.

[1] H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978); ibid. **67**, 329, 334 (1979); H. Nakatsuji, *in Computational Chemistry, Review of Current Trends*, (World Scientific, Singapore, 1997); M. Ehara, J. Hasegawa, H. Nakatsuji, *SAC-CI Method Applied to Molecular Spectroscopy, in Theory and Applications of Computational Chemistry: The First 40 Years, A Volume of Technical and Historical Perspectives*. (Elsevier, 2005).

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Simulation of large-scale excited electron dynamics

Julius Su and William A. Goddard III

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To study electron dynamics in large-scale highly excited systems, we have developed eFF, a molecular dynamics model which includes electrons. In eFF, electrons are represented by Gaussian wave packets whose size and position vary with time, and the nuclei are represented by point charges. The particles interact via an effective potential which is so simple that forces acting between thousands of nuclei and electrons can be computed in less than a second on a modern processor. Using eFF, we explore the thermodynamics of warm dense hydrogen [1], and find excellent agreement with path integral methods and diamond anvil and shock compression experiments over a temperature range of 0 to 100,000 K and densities up to 1 g/cm^3. We also simulate the Auger process (Figure 1) in a diamond nanoparticle ($C_{196}H_{112}$), and discover direct and indirect pathways for the desorption of atomic fragments from the surface, in agreement with recent experiments.

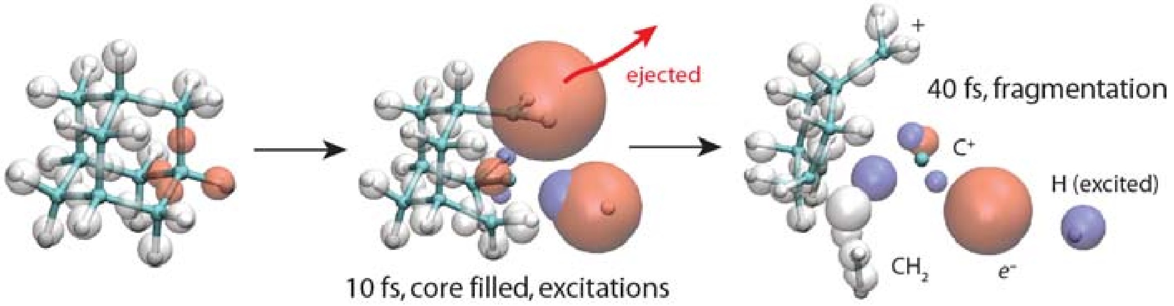

Figure 1. Auger process in adamantane. After a core electron is ionized from a tertiary carbon at time zero, a valence electron fills the core, another valence electron is ejected, and the molecule fragments over tens of femtoseconds.

[1] J. T. Su and W. A. Goddard III, *Phys. Rev. Lett.* **2007**, 99, 185003.

Session Sa-T2

Saturday, July 12, 2008   10:20-12:40

A169 Henry Center
Session Chair: **Gerardo Delgado-Barrio**
Departamento de Física Atómica, Molecular y de Agregados, IMAFF (CSIC)

Sa-T2-1 10:20-10:55

Bloch-Equation-Based Exact Effective π-Electron Hamiltonians for Curved Systems

Péter R. Surján,[1] Péter Szakács,[1] Debashis Mukherjee,[1] Sanghamitra Das[1]

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Sa-T2-2 10:55-11:30

Magnetic Exchange Couplings from Noncollinear Spin Density Functional Theory

Juan E. Peralta

Department of Physics, Central Michigan University, Mt. Pleasant, Michigan 48859, USA

Sa-T2-3 11:30-12:05

V-Representable and Fractional-Occupation-Number Perturbation Theory

Brett I. Dunlap, Igor V. Schweigert

Code 6189, US Naval Research Laboratory, Washington DC 20375, USA

Sa-T2-4 12:05-12:40

Information Planes and Complexity Measures for Atomic Systems, Ionization Processes and Isoelectronic Series

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Bloch-equation-based exact effective π-electron Hamiltonians for curved systems

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Debashis Mukherjee and Sanghamitra Das
Indian Association for the Cultivation of Science, Kolkata 700032, India

The Feshbach effective Hamiltonian in Löwdin's partitioning technique is energy dependent, thus it is not suitable to set up a model for several energy levels. Turning to the energy-independent matrix partitioning scheme, we show how it emerges from the non-perturbative form of the nonlinear Bloch equation for the wave operator. For non-planar but partly conjugated chemical systems such as fullerenes or nanotubes this theory can be used to derive effective π-electron models from ab initio or all-valence Hamiltonians, ensuring the exactness of selected energies levels at around the Fermi level. The techique is used to explain the observed metallic band structure of nanotubes with small diameter, e.g., the (5,0) tube, which was expected to be an insulator by naive arguments. The analysis shows that the increased curvature of the conjugated surface enhances second neighbor hopping interactions which are directly responsible for the unexpected electronic structure of these systems.

Magnetic Exchange Couplings from Noncollinear Spin Density Functional Theory

Juan E. Peralta

Department of Physics, Central Michigan University, Mt. Pleasant, Michigan 48859

I will briefly describe how we generalize the treatment of the electronic magnetization in density functional calculations to the case where the magnetization vector can vary in any direction in space and suggest how this can be employed to extract magnetic parameters, in particular magnetic exchange couplings, from the calculations. The advantage of this approach is twofold: It provides a physically motivated picture of the transition from a low-spin to a high-spin state, and it opens the possibility of using perturbation theory for the evaluation of magnetic exchange couplings. The later simplifies the way magnetic exchange couplings are predicted using first-principles, avoiding the non-trivial search for different spin-states that needs to be carried out with present methods. I will show proof-of-concept calculations in small systems such as the H-He-H-He-H chain and Cr_2, where the results can be intuitively rationalized.

V-Representable and Fractional-Occupation-Number Perturbation Theory

Brett I. Dunlap and Igor V. Schweigert
Code 6189, US Naval Research Laboratory, Washington DC 20375

The Kohn-Sham potential determines the self-consistent-field molecular orbitals, and the changes in that potential determine the perturbed orbitals in density-functional theory. In analytic density-functional theory (ADFT) that potential is expanded in an analytic basis set that is roughly as large as the orbital basis set—order N. The fitted Kohn-Sham potential is called the Sambe and Felton (SF) potential. This changes the focus of perturbation theory from the set of order-N^2 particle-hole excitations to the order-N change in the SF potential, which is developed through third order, based on earlier studies of variational fitting in perturbation theory.[1] The role of degeneracy, specifically of electronic configurations of the methoxy radical, in the decomposition and ultimately the hypervelocity chemistry of pentaerythritol tetranitrate (PETN) is illustrated. The role of the corresponding fractional occupation numbers in perturbation theory is given by the commutator of the Fock and density matrices. There are no distinctions between occupied, virtual, or Fermi-level electrons in the theory; thus there are no phases in the theory. The quality of the SF basis and the accuracy of derivatives are not related.

The Office of Naval Research, directly and through the Naval Research Laboratory, supported this work. IVS thanks the National Research Council and Naval Research Laboratory for a Postdoctoral Associateship.

[1] B. I. Dunlap, Phys. Rev. A **76**, 062512 (2007).

Information Planes and Complexity Measures for Atomic Systems, Ionization Processes and Isoelectronic Series

J.C. Angulo[a,c] and J. Antolín[b,c]

[a]*Departamento de Física Atómica, Molecular y Nuclear, Universidad de Granada, 18071-Granada, Spain*
[b]*Departamento de Física Aplicada, EUITIZ, Universidad de Zaragoza, 50018-Zaragoza, Spain*
[c]*Instituto 'Carlos I' de Física Teórica y Computacional, Universidad de Granada, 18071-Granada, Spain*

Measuring the complexity of a general system is an important area of contemporary research which has roots in Information and Bayesian theories. Up to the present date, different definitions of the complexity have been proposed. Some of the most relevant ones are composed of two factors, associated to the concepts of localization and delocalization, which define the so-called informational planes. This this case, for instance, of the López-Ruiz, Mancini and Calbet complexity[1], built up in terms of Shannon entropy and disequilibrium. More recently, Fisher information has been shown to play a relevant role for quantifying complexity, as also occurs with variance, by defining the Fisher-Shannon[2] and Cramer-Rao[3] information planes and the associated complexity measures. It is natural to wonder about the advantages of considering each of the aforementioned complexities, attending to the kind of systems or processes we are dealing with. In the present work, a deep study of those complexity measures and their constituents is carried out for a great variety of many-electron systems, by means of their one-particle distributions in both conjugated spaces (namely, position and momentum) as well as for the product or phase space. It is clearly stated how complexities not only detect uncertainty but also structure and organization, as shown by the strong dependence of the informational quantities on relevant structural characteristics of the systems (e.g. shell structure)[2,3] and the variations they suffer when adding or removing electrons (i.e. ionization processes), as well as for systems belonging to a given isoelectronic series (i.e. when modifying the nuclear charge keeping the number of electrons)[4]. For carrying out the numerical analysis, wavefunctions obtained within a Hartree-Fock framework have been employed[5,6], for studying 370 different many-electron systems, namely 103 neutral atoms and 96 singly charged ions, as well as 189 atomic systems corresponding to 9 isoelectronic series.

[1] R. López-Ruiz, H.L. Mancini and X. Calbet, *Phys. Lett. A* **209**, 321 (1995).
[2] J.C. Angulo, J. Antolín and K.D. Sen, *Phys. Lett. A* **372**, 670 (2008).
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[4] K.D. Sen, J. Antolín and J.C. Angulo, *Phys. Rev. A* **76**, 032502 (2007).
[5] T. Koga, K. Kanayama, S. Watanabe and A.J. Thakkar, *Int. J. Quantum Chem*. **71**, 491 (1999).
[6] T. Koga, K. Kanayama, S. Watanabe, T. Imai T and A.J. Thakkar, *Theor. Chem. Acc.***104**, 411 (2000).

Schedule and Abstracts of the Poster Sessions

Thirteenth International Workshop on
Quantum Systems in Chemistry and Physics
July 6-12, 2008

QSCP-XIII

Poster
Session I

Michigan State University, East Lansing, Michigan, USA

Session Mo-P1

Monday, July 07, 2008 21:00-22:30
B106-B107 Henry Center

Mo-P1-1 Geometry of Space: Crucible for Matter Formation

Michael J. Basso

US Army Communication –Electronics Command, Research, Development, and Engineering Center, Fort Monmouth, New Jersey 07703, USA

Mo-P1-2 Sampling for Convolution with Prolates

Tatiana Levitina,[a] Erkki J. Brändas[b]

[a]Institut Computational Mathematics, TU Braunschweig, Braunschweig, Germany;
[b]Department of Quantum Chemistry, Uppsala University, Uppsala, Sweden

Mo-P1-3 Toward the Construction of a Flexible Water Model Capable of Polarization and Charge Transfer

Jiahao Chen, Todd J. Martínez

Department of Chemistry, Frederick Seitz Materials Research Laboratory and the Beckman Institute, University of Illinois at Urbana-Champaign, 600 S Mathews Ave, Urbana, IL 61801, USA

Mo-P1-4 Met-Enkephalin Conformation Space Exploration Studied by Molecular Dynamics Distance and Hamiltonian Replica Exchange Methods

Li Su, Robert I. Cukier

Department of Chemistry and the Quantitative Biology Modeling Initiative,
Michigan State University, East Lansing, MI 48824, USA

Mo-P1-5 Electrostatic Continuum Models: Influence of Nonlinear Electrostatics on Transfer Energies Between Liquid Phases

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Mo-P1-6 QED Approach to Atoms, Ions and Nuclei in a Super Strong Laser Field. Nuclear Quantum Optics

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Mo-P1-7 QED Many-Body Perturbation Theory In Calculating Parity Violating Effects, Nuclear Quadrupole Moments and Hfs for Heavy Isotopes

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Mo-P1-8 Constrained Optimized Potential Method for Excited States: Application to the HeH Potential Curves

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Mo-P1-9 Active-Space Equation-of-Motion Coupled-Cluster Methods for Ground and Excited States of Radicals and Other Open-Shell Species

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Mo-P1-10 Incomplete Bessel Functions in Periodic-System Electronic Structure Computations

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Mo-P1-11 Study of the Neutral Formamide Hydrolisis Reaction in Aqueous Solution Using Free Energy Curves Obtained from Ab Initio Potentials and Molecular Dynamics Simulation

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Mo-P1-12 A New Look at the Transition State: Wigner's Dynamical Perspective Revisited

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Mo-P1-13 Study of Hydrogen Adsorption on Ti Dopped BC_3 Nanotubes Using DFT Methods

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Mo-P1-14 Kinetic Monte Carlo Simulation of the Yttria Stabilized Zirconia (YSZ) Fuel Cell

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Mo-P1-15 Local Correlation Calculations Using Cluster-In-Molecule Standard and Renormalized Coupled-Cluster Methods

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Mo-P1-16 Applications of a Semi-Explicit Density Functional Method for N-Electron Systems

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Mo-P1-17 The Laplacian of $\rho(r)$ as a Novel Criterion to Discern Between Pericyclic and Pseudopericylic Processes

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Mo-P1-18 Density Functional Study of Hydrogen Adsorption on the (1 1 1) Palladium Surface using Generalized Gradient Approximation (GGA) Designed for Solids(PBEsol)

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Geometry of Space: Crucible for Matter Formation

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A unique concept offers a new perspective on the formation of the basic building blocks of matter as a geometrical consequence of space. It presents an alternative to conventional thinking and provides a bridge to a new physics that incorporates basic forms of space, both real and virtual. The importance of the concept is its simplicity, and that it produces values of known particle masses and measured natural constants in dimensionless numbers. However, these results require the acceptance that these quantities are the consequence of the interaction between real and virtual space in the form of common geometrical figures. For example, the concept of a regression model based on H. Yukawa's quantized mass energy of the Strong Force (137 Me) presumes it is held together internally by another smaller mass energy field, which itself is held together by yet a smaller mass energy field, producing a converging series of fields which approaches a limit value designated as a 'Gluon.' It is proposed that there are two geometric models which describe the Up and Down Quarks; one with a cubic center (Down Quark), the other, with two pyramids joined at their vertex (Up Quark), each holding eight Gluons. From three quarks (2 Up and 1 Down), a Proton is formed. As a second example, it is proposed that the interaction between two intersecting Standard Spheres, each having a Standard volume of (Vo), as compared to the volume outside the common value (Vx)) is the building block for the formation of particles. A simple, dimensionless relationship derived from this intersection can describe both volumes as $Vx / Vo = 1/8(12D - D^3)$, where D is a dimensionless factor, of the standard radius (Ro), for the distance between the centers of the intersecting spheres. Applying this concept, a geometrical configuration forms a dimensionless mass ratio value of (1836.1) = Mp/Me and the dimensionless value of the Gravitational constant (G). A third example is a geometrical configuration of four touching Standard Spheres and a hyperboloid which provides the calculated value for the Electroweak Mixing Angle β[1,2] when one applies a Gudermannian function $\text{gd } v = \Phi = \arctan(\sinh v)$. The last example presented demonstrates a geometrical connection between the Muon and the Proton. Specifically shown is the calculation of the mass ratio (Mu/Me) of the Muon as a dimensionless ratio utilizing the curvature at a specific point on expression $Vx / Vo = 1/8(12D - D^3)$. The specific point (D), when compared with the value for (π), can be given in two components where $D = \pi(1 + 0.00191987)$. The value (0.0191987) is unique to the Proton indicating a connection between the two particles. This new concept proposes that simple geometries of space can provide an alternative explanation for matter formation and established constants within nature, as measured in the laboratory.

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Sampling for Convolution with Prolates

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During the last years the interest in Finite Fourier Transform (FFT) eigenfunctions, often referred to as ’prolates’, has increased significantly among scientists both in the field of quantum chemistry as well as in the signal processing community. These prolates are band-limited and highly concentrated at a finite time-interval. Both features are acquired by the convolution of a band-limited function with a prolate. This will permit the interpolation of such a convolution using the Walter and Shen sampling formula[1] essentially simplifying the computations[2]. The Fourier transform of the convolution may not necessarily be continuous and the concentration interval is twice as large as that of the prolate[3]. Rigorous error estimates are given as dependent on the truncation limit and the accuracy achieved is tested by numerical examples.

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Toward the construction of a flexible water model capable of polarization and charge transfer

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Of the available methods for treating polarization in classical molecular dynamics simulations, only fluctuating-charge models[1] such as EEM[2], QEq[3], fluc-q[4] and CHARMM C22[5] can potentially describe both charge transfer and polarization. However, these current models predict unphysical non-integer charge separation at dissociation. Also, they predict dipole polarizabilities that are not correctly size-extensive. Our QTPIE model[6] is a modification of QEq that describes correct charge transfer at dissociation limits for overall neutral systems. Here, we use coplanar, linear water chains to show that unlike other fluctuating-charge models, QTPIE predicts the correct direction of charge transfer. Also, we investigate the origin of the super-linear scaling of the dipole polarizabilities, and show how QTPIE can reproduce the correct scaling properties of the dipole polarizabilities and dipole moments without *a priori* constraints on charge transfer. Unlike other previously proposed solutions to this problem, we are able to retain a useful treatment of intermolecular charge transfer. We also show that calculations in the TINKER molecular mechanics package using QTPIE are about five times as expensive as conventional fixed-charge calculations. Finally, we report on our progress toward the development of a flexible water model that uses QTPIE to capture both polarization and charge transfer effects.

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Met-enkephalin conformation space exploration studied by molecular dynamics distance and Hamiltonian replica exchange methods

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The conformational states of the zwitterionic form of the pentapeptide Met-enkephalin were explored with the use of explicit solvent molecular dynamics (MD). The N and C termini are ionized, as appropriate to polar solvent conditions and, consequently, there is a competition between open forms driven by polar solvation of the ammonium and carboxylate groups and closed forms driven by their salt-bridge formation. Normal MD started from an open state does not sample closed conformations. Sampling was enhanced with a distance Replica Exchange Method (DREM)[1] and with a Hamiltonian Replica Exchange Method (HREM)[2]. The DREM introduces replicas of the original MD system that differ in terms that restrain the system to different distances along a chosen reaction coordinate. The HREM introduces replicas that differ in the strength of the interactions in the potential energy function (MD force field). These replicas are run independently and, periodically, attempts at exchange of their configurations are made with the acceptance of exchange determined by a Metropolis-Hastings Monte Carlo rule. The potential of mean force (PMF) along an end-to-end distance reaction coordinate was obtained with the DREM. The PMF shows a stable salt-bridge state and the presence of a large region of open states, as hypothesized for conformationally promiscuous small opiate peptides. The HREM systems differ by scaling the peptide-peptide and peptide-solvent electrostatic and Lennard-Jones potentials, with the goal of improving the sampling efficiency with a limited number of systems. A small number of systems were found to be sufficient to sample closed and open states. A Principal Component Analysis[3] (PCA) shows that the HREM-generated fluctuations are dominated by the first two principal modes. The first corresponds to the end-to-end reaction coordinate found in the DREM, and the first mode PMF is similar to the DREM PMF. The second mode describes the presence of two conformations that both correspond to the salt-bridge state distance. The conformers differ in the values of neighboring psi and phi dihedral angles since such psi/phi compensation can still produce the same end-to-end distance. The two dimensional PMF constructed from the first two PCA modes captures most of the significant backbone conformational space of Met-enkephalin.

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Electrostatic Continuum Models: Influence of Nonlinear Electrostatics on Transfer Energies between Liquid Phases

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Abstract

Continuum electrostatic models are widely used for reducing the computational labor required to apply methods of molecular mechanics, molecular dynamics, and quantum mechanics to condensed media and thereby to extend computations to much larger systems. The most common Born model describes the response of the continuous media in terms of a static dielectric constant for each medium. However, when applied to a liquid environment, comparison of the Born model predictions with experiment, e.g., for free energies of transferring charges between hydrophilic and hydrophobic phases and pK_a shifts on transfer between phases, agreement with experiment requires the use of physically quite unrealistic dielectric constants for proteins, lipids, etc., and/or equally unrealistic atomic radii. This leads to questions concerning the physical origins for this failure of the Born model. We partially resolve this question by applying the Langevin-Debye (LD) model which models the medium by a continuous distribution of particles with both point polarizability and point dipoles. The LD model contains an added dependence of the electrostatic response on the solvent's optical dielectric constant and the gas and liquid phase dipole moments, features absent in the popular Born model. The LD model reduces to the Born model in the linear limit of weak fields but, more generally, includes added contributions describing the self-consistent, nonlinear, many-body response of the proximal dipoles in the solvent, leading to the phenomenon of dielectric saturation. The LD model is applied to simple representation of three biologically relevant systems: (1) globular proteins, (2) lipid bilayers, and (3) membrane proteins. The linear Born treatment greatly overestimates both the electrostatic (solvation) self-energy and the transfer free energy from water to hydrophobic environments (such as a protein interior). Using experimental dielectric constants, the energy cost of charge burial in globular or membrane proteins of the Born model is reduced by almost 50% with the nonlinear theory as is the pK_a shift, and the computed shifts yield good agreement with experimental trends. Selected calculations for the electrostatic interaction between a pair of ions shed light on the underlying fundamental assumptions of the widely used generalized Born models.

QED Approach to Atoms, Ions and Nuclei in a Super Strong Laser Field. Nuclear Quantum Optics

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A consistent QED approach [1,2] is applied to studying the interaction of the atoms and ions of plasma with an super intense electromagnetic (laser) field. Method bases on description of atom in a field by the k- photon emission and absorption lines. The lines are described by the QED moments of different orders, which can be calculated with the use of the Gell-Mann and Low S-matrix adiabatic formalism (T=0). In relativistic version the Gell-Mann and Low formulae expresses an imaginary part of the energy shift Im E{a} through the QED scattering matrix, including interaction of atom with electromagnetic field and field of the photon vacuum. We present QED S-matrix energy formalism (T not equal 0) for calculation of the spectral lines shape in dense plasma. For any atomic level we calculate Im E{a}(w) as function of the laser pulse central frequency w (resonant curve). We calculate the moments for resonance, connected with concrete atomic a-p transition (a,p-discrete levels; k photons is absorbed). To calculate the moments we need to get the expansion of E{a} into the perturbation theory series. Numerical modelling carried out for H, Cs, Ar, Yb, Tm atoms and H-, Li- and Ne-like ions. QED approach to description of radiation atomic lines for atoms and ions in plasma is generalized on a case of the confined atomic systems. Modelling nuclear ensembles in a super strong laser field provides opening the field of nuclear quantum optics and is carried out in our work too. The direct interaction of super intense laser fields in the optical frequency domain with nuclei is studied and the AC Stark effect for nuclei is described within the operator perturbation theory and the relativistic mean-field (RMF) model for the ground-state calculation of the nucleus [3,4]. We find that AC-Stark shifts of the same order as in typical quantum optical systems relative to the respective transition frequencies are feasible with state-of-the-art or near-future laser field intensities.

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Mo-P1-7

QED Many-Body Perturbation Theory In Calculating Parity Violating Effects, Nuclear Quadrupole Moments and Hfs for Heavy Isotopes

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Relativistic calculation of the spectra, hyperfine structure (hfs) parameters for heavy atoms and multicharged ions with account of relativistic, correlation, nuclear, QED effects is carried out. Method is based on the gauge-invariant QED perturbation theory and generalized dynamical nuclear model [1,2]. The charge distribution in a nucleus is modelled within the Gauss and Fermi models. The inter-electron interaction corrections contribution arising due to the energy dependence of the effective inter-electron potentials on energies is accounted for. The accounted magnetic dipole and octupole interactions correspond to the first and the third terms of the partial-wave expansion for the first matrix element while the electric quadrupole interaction corresponds to the second term of the partial-wave expansion for the second matrix element. The data for the energies and constants of the hyperfine structure for valent states $6s_{1/2}$, $7s_{1/2}$, $6p_{1/2,3/2}$, $7p_{1/2,3/2}$, $5d_{3/2}$ of cesium ^{133}Cs and states $[5p^6]$ $6s_{1/2}, 6p_{1/2}$, $6p_{3/2}$,, $6d_{3/2}$ of *Cs* –like ion of Ba are presented. Nuclear electric quadrupole moments *Q,* the hfs constants for states of $6s6p\ ^3P_1$ in atom of ^{201}Hg and $7s7p\ ^1P_1, ^3P_1, ^3P_2$ in atom of ^{223}Ra are defined. The contribution due to inter electron correlations to the hyperfine structure constants is about 120-1200 MHz for different states, contribution due to the finite size of a nucleus and radiative contribution is till 2 dozens MHz (for constant *A*). For element of ^{223}Ra our value is Q=1,22barn. The role of the nuclear effects contribution (core-polarization ones, which are induced by valent protons of a nucleus), temporal distribution of magnetization in a nucleus (effect of Bohr-Weisskopf) and non-accounted high order QED corrections is analyzed. We present the calculation results for energy levels, hyperfine structure intervals, E1-,M1-transitions amplitudes in heavy atoms of Cs, Pb too. As example let us give here the calculation result for parity non-conserving 6s-7p dipole amplitude in Cs. Our calculation gives value: $D=\langle 6s|Dz|7s\rangle= -0.918\cdot 10^{-11}$ i|e|a(-Qw/N). For comparison let us present other knwon results (c.f.[2]): $D=-0.91\cdot 10^{-11}$ i|e|a(-Qw/N) by Dzuba etal; $D=-0.935\cdot 10^{-11}$ i|e|a(-Qw/N) by Bouchiat etal (Paris); $D=-0.935\cdot 10^{-11}$ i|e|a(-Qw/N) by Johnson etal (Indiana). Comparison of calculated D value with measurement of Noeker etal gives the following data of weak nuclear chare in Cs and Wainberg angle: (-Qw/N)=0,918±0,020 (exp.)±0,010 (theor.) and $\sin^2\vartheta_W=0,231\pm 0,007$ (exp.)±0,004 (theor.) that is in a good agreement with average world value $\sin^2\vartheta_W=0,230\pm 0,005$.

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Constrained optimized potential method for excited states: Application to the HeH potential curves

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The optimized effective potential (OEP) method has been recognized, at present, as a useful technique for obtaining multiplicative potentials of the density functional theory (DFT). It is known that the exchange-only OEP potential in a combination with a correlation potential based on many-body perturbation theory using the Kohn-Sham (KS) determinant as a reference yields good accuracy in calculations of the *ground state* properties. There is far less reported experience for the OEP studies of electronically excited states, especially having the same spin and spatial symmetry as the ground state. Calculations for *atoms* have shown that the ensemble KS theory, with exact ensemble-exchange potential, can be as accurate as the ground state calculations [1]. However, for *molecules* the OEP experience is less satisfactory.
Recently, a constrained OEP approach for excited states has been proposed [2-4]. It is based of DFT for individual excited states that implement a simple method for construction of KS determinants describing the excited states of interest. In addition the excited state KS determinant is orthogonal to the determinants of state of lower energy. In this work we further develop and apply this approach to practical calculations of excited potential curves of the HeH molecule. We demonstrate that the developed earlier OEP methodology for the ground state can be applied to DFT excited state problem with the same computational efforts. In particular, the second-order orbital-dependent correlation energy correction for excited states can be derived from the Moller-Plesset *like* perturbation theory based on the KS orbitals optimized for a given excited state.
All calculations were carried out with basis sets *optimized* directly both for the state under consideration and every geometry. This allows us to minimize the error associated with truncation of basis sets and, thus, to observe more clearly the errors of the method itself. Comparisons of computed potential curves with those obtained by the configuration interaction method with extended basis sets are discussed.

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Active-Space Equation-of-Motion Coupled-Cluster Methods for Ground and Excited States of Radicals and Other Open-Shell Species

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The electron-attached (EA) and ionized (IP) equation-of-motion coupled-cluster (EOMCC) methods, which utilize the idea of applying a linear electron-attaching or ionizing operator to the correlated, ground-state, CC wave function of an *N*-electron closed-shell system in order to generate the ground and excited states of an (N±1)-electron system, and their symmetry-adapted-cluster configuration interaction (SAC-CI) counterparts, provide an ideal framework for performing orthogonally spin-adapted calculations for radical species. The problem with these approaches is that their basic, low-order approximations are often insufficient for accurately describing excited states and potential energy surfaces along bond-breaking coordinates of radicals, and so higher order excitations must be accounted for.[1-4] Unfortunately, the inclusion of higher order excitations in the EA- and IP-EOMCC and SAC-CI schemes makes the resulting calculations prohibitively expensive, restricting the use of these approaches to relatively small systems and basis sets. To deal with this difficulty, we have recently developed the active-space variants of the EA- and IP-EOMCC[1-3] and SAC-CI[4] methods, in which one considers only small subsets of all higher-than-double, higher than 2-particle-1-hole (2*p*-1*h*), and higher than 2-hole-1-particle (2*h*-1*p*) excitations in the cluster, electron-attaching, and ionizing operators, respectively, which are selected through the use of a suitably defined set of active orbitals. In this presentation, we will discuss the fundamental theoretical aspects of the active-space EA- and IP-EOMCC and SAC-CI methodologies. We will then focus on the efficient computer implementation of the active-space EA- and IP-EOMCC methods including up to 3*p*-2*h* and 3*h*-2*p* excitations, referred to as EA- and IP-EOMCCSDt,[1-3] and active-space SAC-CI methods including up to 4*p*-3*h* and 4*h*-3*p* excitations.[4] In order to illustrate the performance of the resulting approaches, we will present the results of calculations for the adiabatic and vertical excitation energies and potential energy surfaces of the low-lying states of several radicals, including CH, OH, SH, C_2N, CNC, N_3, and NCO.[1-5] These calculations reveal that active-space methods with up to 3*p*-2*h* and 3*h*-2*p* terms provide accurate results for excited states within the Franck-Condon region while active-space methods with up to 4*p*-3*h* and 4*h*-3*p* terms are needed to accurately describe potential energy surfaces of radicals along bond breaking coordinates. Furthermore, the calculations show that the active-space schemes are capable of producing results that are virtually identical to those produced by their expensive parent EA- and IP-EOMCC and SAC-CI schemes with 3*p*-2*h*/3*h*-2*p* and 4*p*-3*h*/4*h*-3*p* excitations at a fraction of the computational cost.

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Incomplete Bessel Functions in Periodic-System Electronic Structure Computations

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When Ewald-type convergence-acceleration processes are applied to electronic-structure computations for periodic systems using a Gaussian-type-orbital basis, the partitioning of the resultant integrals between direct and reciprocal (Fourier) space causes the occurrence of functions that can be identified as "incomplete" versions of the Macdonald function ordinarily assigned the symbol K_n. These incomplete Bessel functions, therefore designated $K_n(x,y)$, are needed for the argument range $x>0$, $y\geq0$. These functions also occur in hydrology problems, where they are known as *leaky aquifer functions*, and in addition they have been discussed under the name *generalized incomplete gamma functions*, notably by Temme and colleagues. Moreover, they have the reputation of being difficult to evaluate.

The $K_n(x,y)$ satisfy a variety of functional relations, and we and others have developed a number of expansions for the K_n useful in various ranges of x and y. When used for systems of one-dimensional periodicity, the needed range of the index n is from zero to four times the maximum value of l, the orbital angular momentum. Thus, for general use, one might expect to need n to values reaching, in worst cases, as high as n=12. The accuracy needed in electronic structure computations is normally absolute (rather than relative), and we have tentatively determined that an absolute accuracy of $\delta=10^{-10}$ would be acceptable in most problems. The functions $K_n(x,y)$ decay exponentially in x, and with the chosen δ value all K_n with $x>20$ can be approximated as zero. However, for small x a wider range of y becomes relevant.

Some of the evaluation methods require values of the exponential integral $E_1(z)$, and some involve values of the Macdonald functions $K_0(z)$ and $K_1(z)$. Since electronic structure computations typically involve extremely large number of integral evaluations, we deemed it necessary to develop highly efficient evaluation procedures for E_1, K_0, and K_1. Since these auxiliary functions are used in the context of recursive procedures that are not entirely stable, we determined that they were needed to an absolute accuracy of 10^{-15}. We obtained expansions for these functions that are not much more extensive than those presented, e.g., in the *Handbook of Mathematical Functions*, but are many orders of magnitude more accurate. Based on all these considerations, we have identified a collection of procedures that give $K_n(x,y)$ to the target accuracy over its entire range.

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Study of the Neutral Formamide Hydrolisis Reaction in Aqueous Solution Using Free Energy Curves Obtained from Ab Initio Potentials and Molecular Dynamics Simulation

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In the present work a theoretical study of the neutral formamide hydrolysis: $HCONH_2 + H_2O \rightarrow HCOOH + NH_3$ in aqueous solution by means of molecular dynamics simulation, with solute-solvent interaction potentials derived from *ab initio* quantum calculations, is carried out. We opted to construct these potentials by fitting the solute-solvent interaction energies (calculated at the MP2 level including the counterpoise correction of the basis) to functions of the Lennard-Jones type which include not only the van der Waals interactions but also the electrostatic interactions. The molecular parameters of these interaction potentials were obtained by fitting parts of the potential to different components of the interaction energy, as the exchange energy (EX), the electrostatic (ES), the polarization (PL), and the dispersion (DIS), all taken from performing a decomposition following the scheme proposed by Morokuma et al.[1].

We used the solvent as reaction coordinated and the free energy curves for the calculation of the properties related with the reaction mechanisms. To construct free energy curves, we use as reaction coordinate the difference in the solute-solvent interaction energy of a given set of solvent molecules in the presence of the reactant, transition state, and product structures[2]. The difference ΔE_s fluctuates during the MD simulation, and its values are collected as a histogram of the number of times N_s that a particular value Δe of the macroscopic variable ΔE_S appears in the simulation. The probability $P_s(\Delta e)$ of finding the system in a given configuration allows us to compute the free energy $G_S(\Delta e)$.

In sum, the free-energy curves of the species involved in the reaction provide a good description of the thermodynamics of the hydrolysis of organic molecules in an aqueous medium. These curves give an acceptable response to the reaction and activation energies of the reactive process when compared with other theoretical[3] and experimental[4] studies, considering that: (a) the parameters of the interaction potential U_{SW} come from using ab initio energies related to that interaction and not from using geometric-mean combining rules or parameter tables for model molecules; (b) the basis set used to describe the interacting systems is sufficiently extensive (including polarization and diffuse functions) to reproduce adequately the transition states; and (c) the methodological approach taken allows the participation of one or more solvent molecules in the reaction mechanism.

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A New Look at the Transition State: Wigner's Dynamical Perspective Revisited

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The notion of a transition state is one of the grand unifying concepts in chemistry. Many theories of chemical reactions explicitly assume that once reactants pass through the transition state then they cannot return. This no-recrossing rule serves to define the transition state and is central to transition state theory. Despite its ubiquity in chemistry it is only recently that the existence of the transition state in more than two degrees-of-freedom has been proven. No general theory has existed for actually finding the transition state. Here, combining methods of celestial mechanics with recent advances in dynamical systems theory, we provide a theory that is rigorously valid for an arbitrary number of degrees-of-freedom. Equally important, advances in computational power make the method applicable in practice for large systems. Knowledge of the transition state, a phase space object, allows us to differentiate, with exquisite precision, between reactive and nonreactive molecular configurations wherever they lie in phase space.

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Mo-P1-13

Study of Hydrogen Adsorption on Ti Dopped BC_3 Nanotubes using DFT methods

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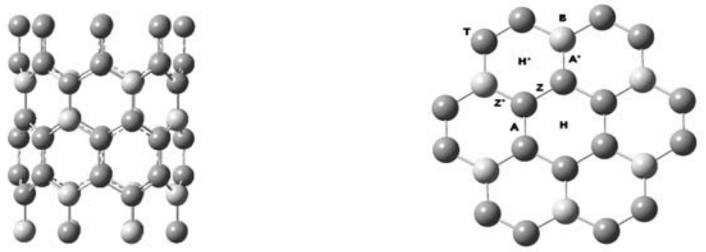
One of the problems in the practical implementation of hydrogen as a fuel is the lack of an efficient media for hydrogen storage in ambient conditions. A single Ti atom adsorbed on nanotube surface has shown to bind up to four H_2 molecules. By completely coating the nanotube surface, a storage capacity reaches to 8 wt. % [1]. However, a serious problem that largely reduces the storage capacity is the clustering of metal atoms on nanotube surface [2].

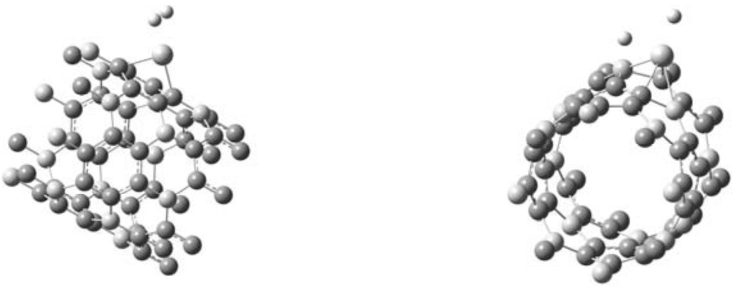


(a) **(b)**

Fig. 1 A (4,0) BC_3 nanotube (a) and its different binding sites (b).

In this work, we have studied hydrogen adsorption on a titanium-dopped (4,0) BC_3 nanotube (Fig. 1). It is believed that B atoms enhance the metal binding and inhibit clustering [3]. Geometry optimizations show that only the H and H′ sites are favorable for Ti adsorption. Other arrangements are relaxed to these structures. The spin-unpolarized binding energies for H and H′ sites are 5.25 and 4.86 eV, respectively. These energies are larger than 2.2 eV, which is obtained for carbon nanotubes, because the electron deficient B atoms have higher affinity for Ti atom.

A series of single energy calculations were performed as a hydrogen molecule approaches the Ti atom, and when the forces acting on H_2 were large enough, the system were fully relaxed using DFT calculations. The hydrogen molecule were approached the Ti in both parallel and perpendicular directions (relative to nanotube axis). The optimized geometries are shown in Fig. 2. For H site, the hydrogen molecule in both orientations shows molecular adsorption. The H–H bond length is increased from 0.74 to 0.81 Å. However, for H′ site, the hydrogen molecule is dissociated upon adsorption. The Ti–H distances are 1.74 and 2.01 Å and the H–H distance increases to 2.67 Å.



(a) **(b)**

Fig. 2 Optimized structures for H_2 molecule adsorbed on a Ti atom in H (a) and H′ (b) sites.

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Kinetic Monte Carlo simulation of the Yttria Stabilized Zirconia (YSZ) fuel cell

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A Kinetic Monte Carlo (KMC) model is developed to simulate non-symmetrically the cathode side of a Yttria Stabilized Zirconia (YSZ) fuel cell, in order to translate experimental, and ultimately theoretical rates into an atomistic model of the fuel cell[1]. The KMC model consists of a set of several electrochemical reaction rates, adopted from experiments and first-principles calculations. The KMC simulations are used to model these simultaneously occurring events, to determine potential limitations in cathode/YSZ performance. The focus of this work is ionic current density *(J)*, studied as a function of various physical parameters: oxygen partial pressure (P_{O2}), external applied bias voltage (V_{ext}), temperature *(T)*, dopant concentration (*mol %* Y_2O_3), relative permittivity (ε) of YSZ, and geometrical features of the YSZ electrolyte. This simple model can be used as a baseline to translate elementary chemical reaction rates into atomistic simulations of working solid oxide fuel cell cathodes, pertinent to the complete set of experimental operating conditions.

This work is supported by the Office of Naval Research, both directly and through the Naval Research Laboratory.

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Local Correlation Calculations Using Cluster-In-Molecule Standard and Renormalized Coupled-Cluster Methods

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A linear scaling local correlation approach, termed 'cluster-in-molecule' and abbreviated as CIM (Ref. 1) is extended to the coupled-cluster (CC) theory with singles and doubles (CCSD) and CC methods with singles, doubles, and non-iterative triples, including CCSD(T) and the completely renormalized CR-CC(2,3) approach.[2] As in the original CIM work that dealt with the second-order many-body perturbation theory and CC doubles (CCD) approach, the main idea of the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods is the realization of the fact that the total correlation energy of a large system can be obtained as a sum of contributions from the occupied orthonormal localized molecular orbitals and their respective occupied and unoccupied orbital domains. Unlike the earlier implementations of the CIM-CCD approach,[1] which utilized pilot CCD codes with the explicit nested loop structure, the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods developed in this work are characterized by the high computational efficiency in both the CIM and CC parts, enabling the calculations for much larger systems than previously possible. This is achieved by combining the natural linear scaling of the CIM ansatz with the fully vectorized CC codes that rely on the use of diagram factorization and recursively generated intermediates. By comparing the results of the canonical and CIM-CC calculations for normal alkanes and water clusters, it is demonstrated that the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) approaches recover the corresponding canonical CC correlation energies to within 0.1-0.4 % or so, while offering the linear scaling of the computer costs with the system size and savings in the computer effort by orders of magnitude. By examining the dissociation of dodecane into $C_{11}H_{23}$ and CH_3 and several lowest-energy structures of the $(H_2O)_n$ clusters with n=10-20, it is shown that the CIM-CC methods accurately reproduce the relative energetics of the corresponding canonical CC calculations.

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Applications of a semi-explicit density functional method for N-electron systems

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A simple semi-explicit density functional for the energy of a N-electron system is obtained with the following assumptions: (i) from a distance *R* from any nuclei the single-particle wavefunctions are approximated by local plane waves, as in the standard Thomas-Fermi-Dirac model, and (ii) in the vicinity of any nucleus, the density is constructed by means of a sum of single-particle wavefunctions obtained from the analytical resolution of the Schrödinger equation with a Taylor expansion of the effective potential. Then, the density is matched at the border between the two regions.

The results for the energy and other density-dependent properties, such as radial expectation values are close to Hartree-Fock values (within a few percent) for all atoms and ions, averaging over shell effects. This procedure provides simple estimations of average properties of the electron cloud that can be used as a zero-th order approximation in other more accurate calculations. Moreover, analytical forms for the density can be used for minimizing the energy functional, which provides an adequate strategy for the approach of more complex systems.

Application of this method to different problems such as low-energy electron scattering (including atomic polarization) or excited states of alkaline atoms will be discussed.

The Laplacian of ρ (r) as a Novel Criterion to Discern between Pericyclic and Pseudopericylic Processes

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In this contribution we present preliminary results concerning a set of [4+2] cycloadditions reactions that contain both pure pericyclic or pseudopericyclic processes and others that can be seen as intermediate or dubious cases[1]. A novel criterion based on the analysis of critical points of the Laplacian of the Charge density, $\nabla^2\rho(\boldsymbol{r})$, in the framework of the Quantum Theory of Atoms in Molecules developed by Bader[2], will be proposed[3]. A detailed analysis of the topology of $\nabla^2\rho(\boldsymbol{r})$ along the reaction coordinate will provide clear mechanistic differences between pericyclic and pseudopericyclic processes and will allow one to discern the intermediate cases. As we will show there is no need to invoke disconnections in the orbital array at the TS´s in order to a proper classification of processes studied since the QTAIM makes use of the electronic density instead of the molecular orbitals. Calculations were done at B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels of theory.

We have concluded that "pure" pseudopericyclic reactions require two pseudopericyclic contacts between the terminal atoms of fragments of the lump-hole type, i.e. two (3,-3)LonePair→(3, +1) interactions[4] (or alternatively (3,-1) →(3, +1) interactions)[4] that readily link the two fragments from the reactant minimum (usually a vdW complex)[2]. Along the reaction path the fragments rearrange to attain an optimum alignment of the lump with the hole. Since hardly geometric change happens the energy barriers are predicted to be low.

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[4] (3,-3), (3,-1), (3,+1), … stand for the (rank,signature) notation for different critical points of the $\nabla^2\rho(\boldsymbol{r})$ scalar field in the QTAIM theory.

Density Functional Study of Hydrogen Adsorption on the (1 1 1) Palladium Surface using Generalized Gradient Approximation (GGA) Designed for Solids(PBEsol)

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PBEsol[1], a revised version of Perdew-Burke-Ernzerhof (PBE) Generalized Gradient Approximation (GGA), restored the first-principles gradient expansion for the exchange energy over a wide range of density gradients to eliminate the bias toward atomic energies in PBE. PBEsol has been reported to improve equilibrium properties for many densely-packed solids and their surface.
A comparative study of hydrogen atom adsorption on (1 1 1) palladium surface has been performed with different exchange-correlation functionals (LDA, PBE and PBEsol). For this preliminary study, the Pd atoms were frozen at their bulk positions. PBEsol yields values between Local Density Approximation (LDA) and PBE as expected. Compared to the experimental data, PBEsol improves the adsorption height, however, worsens the adsorption energy over PBE.

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Thirteenth International Workshop on
Quantum Systems in Chemistry and Physics
July 6-12, 2008

QSCP-XIII

Poster Session II

Michigan State University, East Lansing, Michigan, USA

Session Fr-P2

Friday, July 11, 2008 21:00-22:30

B106-B107 Henry Center

Fr-P2-1 Spectroscopy of Hadronic Atoms and Superheavy Ions: Spectra, Energy Shifts and Widths, Hyperfine Structure for Different Nuclear Models

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Fr-P2-2 Bridging Quantum Chemistry and Nuclear Structure Theory: Coupled-Cluster Calculations for Closed-and Open-Shell Nuclei

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Fr-P2-3 Spreading Measures of Information-Extremizer Distributions: Applications to Atoms

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Fr-P2-4 Extrapolating Potential Energy Surfaces by Scaling Electron Correlation: Isomerization of Bicyclobutane to Butadiene

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Fr-P2-5 Relativistic Multi-Body Calculation of the Beta Decay Probabilities In Optimized Model of the Dirac-Fock Atom and Chemical Environment Effect

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Fr-P2-6 QED Many-Body Approach to Calculating Electron Collision Strengths for Multicharged Ions In A Plasma: Debae Approximation

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Fr-P2-7 Nonlocal Dielectric Functions on the Nanoscale: Screening of Induction and Dispersion

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Fr-P2-8 The Gas-Phase Ozonolysis of ß-Caryophyllene (O_3 + ß-$C_{15}H_{24}$): A Theoretical Study

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Fr-P2-9 Multiply Charged Helium Isoelectronic Ions with Z = 2 to 118. I. Ground State Energies, Mass Correction and Mass Polarization Effects

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Fr-P2-10 Interactions in Open-Shell Systems by the Pauli Blockade Method

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Fr-P2-11 Electronic Structure and Dynamics of O-NO_2 Bond Fragmentation

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Fr-P2-12 Water Cage Effects in the Optical Absorption Step of Aqueous Remediation of Trinitrotoluene Using Iron-porphyrin Photo-catalysts

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Fr-P2-13 Water Cage Effects on Electron Transfer Orbitals (ETOs) in the Aqueous Remediation of Trinitrotoluene Using Iron-porphyrin Catalysts

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Fr-P2-14 Short Hydrogen Bonds in the Solid State: How Intermolecular Interactions and Crystal Field Affect the H-Bond Geometry and Dynamics

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Fr-P2-15 Quantum Dynamics with Trajectories: Optimal Spawning and Conservation of Energy

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Fr-P2-16 Simulating Reactive Scattering Dynamics at Gas-Liquid Interfaces with Hybrid QM/MM-Direct Dynamics: A Theoretical Study of the F(^{2}P) + Squalane Reaction

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Fr-P2-17 Fully Optimized Auxiliary Basis Sets for MP2-F12 Methods

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Fr-P2-18 Projected Entangled Pair States as a Multi-Dimensional Ansatz for Effective Recovery of Non-Dynamic Correlation from Huge Active Spaces

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Spectroscopy of Hadronic Atoms and Superheavy Ions: Spectra, Energy Shifts and Widths, Hyperfine Structure for Different Nuclear Models

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A great interest to this topic has been stimulated by inaugurating the heavy-ion synchrotron storage cooler ring combination SIS/ESR at GSI. With this facility, which allows to produce store and cool fully stripped heavy ions beams up to U^{92+}, new ways are opened in the field of atomic and nuclear physics from this side. Paper is devoted to calculation of the spectra, radiative corrections, hyperfine structure parameters for exotic hadronic (pion, kaon, hyperon) atoms and heavy ions. One of the main purposes is establishment a quantitative link between quality of the nucleus structure modeling and accuracy of calculating energy and spectral properties of systems. An approach [2] to relativistic calculation of the spectra for superheavy ions with an account of relativistic, correlation, nuclear, radiative effects within the gauge-invariant QED perturbation theory is used. Zeroth approximation is generated by the effective ab initio model functional, constructed on the basis of the comprehensive gauge invariance procedure [2]. The wave functions zeroth basis is found from the Klein-Gordon (pion atom) or Dirac (kaon, hyperon) equation. The potential includes the Dirac-Fock potential, the electric and polarization potentials of a nucleus. For low orbits there are the important effects due to the strong hadron-nuclear interaction (pion atom). The energy shift is connected with a length of the hadron-nuclear scattering (scattering amplitude for zeroth energy). For superheavy ions the correlation corrections of high orders are accounted for within the Green function method. The magnetic inter-electron interaction is accounted for in the lowest order, the Lamb shift polarization part- in the Uehling-Serber approximation and the self-energy part – within the Green functions method. We carried out calculation:1).energy levels, hfs parameters for superheavy H and Li-like ions for different models of the charge distribution in a nucleus and super heavy atoms Z=114-118; 3). Shifts and widths of transitions (2p-1s,3d-2p, 4f-3d) in the pionic, kaonic atoms (^{18}O, ^{24}Mg etc.) and also K^{-}-^{4}He.

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Bridging Quantum Chemistry and Nuclear Structure Theory: Coupled-Cluster Calculations for Closed- and Open-Shell Nuclei

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The coupled-cluster theory, which is based on the exponential ansatz for the wave function, provides an ideal formalism for performing highly accurate calculations for many-body quantum systems at a relatively low computational cost. Though it was originally introduced within the context of nuclear physics, most of the development and use of the coupled-cluster theory have been performed within the area of quantum chemistry, where it has become one of the preeminent *ab initio* approaches for studying molecular structure and reactivity. Thanks in part to the great success of the coupled-cluster approaches in chemistry, the coupled-cluster theory has had a recent resurgence in the area of nuclear physics, paving the way for studies of medium and heavy mass nuclei for which many other methods, such as the shell model approach, are simply not practical due to their high computational costs.

In this presentation, we will discuss our work in applying quantum chemistry inspired coupled-cluster approaches to the study of nuclear structure. We will focus on the results of our coupled-cluster calculations for the ground and low-lying excited states of several closed- and open-shell nuclei, including ^{15}O, ^{15}N, ^{16}O, ^{17}O, ^{17}F, ^{55}Ni, ^{56}Ni, and ^{57}Ni, using several different types of modern as well as effective nucleon-nucleon interactions. These results reveal that the coupled-cluster approaches are capable of successfully describing the ground and excited states of a variety of nuclei, producing highly accurate energies of the same quality as much more computationally demanding methods, including various levels of shell model. Along with the results for binding and excitation energies, we will show the results of accurate coupled-cluster calculations for properties other than energy, including matter density, charge radius, and charge form factor. The relatively low costs of coupled-cluster calculations, which are characterized by the low-order polynomial scaling with the system size, enable us to probe large model spaces with up to 7 or even 8 major oscillator shells (336 and 480 single-particle states, respectively), for which non-truncated shell-model calculations for nuclei with A=15-17 active particles are presently not possible. We will argue that the use of coupled-cluster methods and computer algorithms proposed by quantum chemists to calculate properties of nuclei is an important step toward the development of accurate and affordable many-body theories that cross the boundaries between various physical sciences.

Spreading measures of information-extremizer distributions: applications to atoms

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A complete information-theoretic knowledge of any distribution describing a physical system or process requires not only quantifying different information measures (e.g. Shannon and Tsallis entropies, Fisher information, variance) but also determining their optimal values when only a partial knowledge on the distribution is available (i.e. to solve the so-called *information-extremization problem*). The main aim of the present work is focussed on studying the content of structural information of the one-particle densities in both position and momentum spaces for neutral atoms with nuclear charge Z=1-103 throughout the periodic table. In doing so, the aforementioned spreading measures for different extremizer distributions (namely, the solutions of maximum Shannon[1] and Tsallis[2] entropy and minimum Fisher information[3] problems), variationally obtained when constrained by the knowledge of radial expectation values, are numerically analyzed within a Hartree-Fock framework, emphasizing their dependence on the nuclear charge Z as well as on the order of the considered constraints. Such a study widely generalizes similar previous ones[4], in which the numerical analysis takes as reference system the D-dimensional ground-state Hydrogen atom. Here, some of the results obtained (according to the extremized measure, constraints order and nuclear charge) are shown to be strongly correlated with the shell-filling process, being also discussed the different role played by each conjugated space, as well as the phase one, in the description of periodicity patterns displayed by each measure.

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Extrapolating Potential Energy Surfaces by Scaling Electron Correlation: Isomerization of Bicyclobutane to Butadiene

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The recently proposed potential energy surface (PES) extrapolation scheme, which predicts smooth molecular PESs corresponding to larger basis sets from the relatively inexpensive calculations using smaller basis sets by scaling electron correlation energies,[1] is applied to the PESs associated with the conrotatory and disrotatory isomerization pathways of bicyclo[1.1.0]butane to buta-1,3-diene. The relevant electronic structure calculations are performed using the completely renormalized coupled-cluster method with singly and doubly excited clusters, and a non-iterative treatment of connected triply excited clusters, termed CR-CC(2,3), which is known to provide a highly accurate description of chemical reaction profiles involving biradical transition states and intermediates. A comparison with the explicit CR-CC(2,3) calculations using the large correlation-consistent basis set of cc-pVQZ quality shows that the cc-pVQZ PESs obtained by the extrapolation from the smaller basis set calculations employing the cc-pVDZ and cc-pVTZ basis sets are practically identical, to within fractions of a millihartree, to the true cc-pVQZ PESs. It is also demonstrated that one can use a similar extrapolation procedure to accurately predict the complete basis set (CBS) limits of the calculated PESs from the results of smaller basis set calculations at a fraction of the effort required by the conventional point-wise CBS extrapolations.

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Relativistic Multi-Body Calculation of the Beta Decay Probabilities In Optimized Model of the Dirac-Fock Atom and Chemical Environment Effect

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New theoretical schemes for an account for the atomic chemical environment effect on the β decay characteristics are proposed. As method of calculation of the relativistic atomic fields and electron wave functions, the gauge invariant Dirac-Fock (GIDF) type and Dirac-Kohn-Sham (GIDKS) approaches are used [1,2]. The numerical results for atomic chemical environment effect on the β decay are presented for the following β transitions: ^{33}P-^{33}S, ^{35}S-^{35}Cl, ^{63}Ni-^{63}Cu, ^{241}Pu-^{241}Am. Comparison of the Fermi function values is carried out for different approximations of the exchange effect account, calculation with using wave functions on the boundary of the charged spherical nucleus and with using squires of the amplitudes of expansion of these functions near zero. As example, some data of our calculation are presented in the table 1.

Table 1. The atomic chemical environment effect on the β decay probability

Decay of neutral atom			Decay of ionized atom			Present Calculation Scheme
At.	E_{bn}, eV	f(E_{bn} ,Z)	Ion	$E_{гр}$, eV	f (E_{bn} ,Z)	
$S^{(0)}$	167420 167450	1,36849(-2) 1,36935(-2)	$S^{(2+)}$	167390 167420	1,36798(-2) 1,36884(-2)	GIDF
$S^{(0)}$	167420 167450	1,37982(-2) 1,38069(-2)	$S^{(2+)}$	167390 167420	1,37927(-2) 1,38014(-2)	GIDKS

The value 167450eV is accepted for the boundary energy under of decay of the $S^{(0)}$. Analogously the value 167420eV was used for decay of the $S^{(+2)}$ in the first variant of calculation. The pair of the energy values: 167420eV and 167390eV has been chosen in the second variant of calculation correspondingly. The experimental value for E_{bn} is as follows: 167400±100eV. Two versions of calculation give practically the same values for changing half decay period under changing the ionic feature: $\Delta f/f=0,037$ % (GIDF scheme) and $\Delta f/f=0,039\%$ (GIDKS scheme).

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QED Many-Body Approach to Calculating Electron Collision Strengths For Multicharged Ions In A Plasma: Debae Approximation

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We present the uniform energy approach, formally based on the QED perturbation theory (PT) [1,2] for the calculation of electron collision strengths and rate coefficients in a multicharged ions (in a collisionally pumped plasma). An account for the plasma medium influence us carried out within a Debae shielding approach. The aim is to study, in a uniform manner, elementary processes responsible for emission-line formation in a plasma. The electron collision excitation cross-sections and rate coefficients for some plasma Ne-like multicharged ions are calculated within QED energy approach [1]. The energy shift due to the collision is arisen at first in the second PT order in the form of integral on the scattered electron energy ε_{sc}:

$$\mathrm{Im}\Delta E = \pi G(\varepsilon_{iv}, \varepsilon_{ie}, \varepsilon_{in}, \varepsilon_{sc})$$

where G is the squared combination of the two-particle matrix elements:

$$V(1,2;4,3) = \sqrt{(2j_1+1)(2j_2+1)(2j_3+1)(2j_4+1)}(-1)^{j_1+j_2+j_3+j_4+m_1+m_2} \times$$

$$\times \sum_{\lambda,\mu}(-1)^{\mu}\begin{bmatrix} j_1 \ldots\ldots j_3 \ldots\lambda \\ m_1 .- m_3 \ldots\mu \end{bmatrix}\begin{bmatrix} j_2 \ldots\ldots j_4 \ldots\lambda \\ m_2 .- m_4 ..\mu \end{bmatrix}(Q_{\lambda}^{Qul} + Q_{\lambda}^{Br})$$

The values $Q_{\lambda}^{\mathrm{Qul}}, Q_{\lambda}^{\mathrm{Br}}$ are corresponding to the the Coulomb part $exp(i|\omega|r_{12})/r_{12}$ i and Breiht part $exp(i|\omega|r_{12})\, \alpha_1\alpha_2/r_{12}$. of the inter particle interaction. The cross-section is σ=-2 ImΔE. To test the results of calculations we compare the obtained data for some Ne-like ions with other authors' calculations and available experimental data. The inclusion of Na-like states, accounting for diffusion-like processes, can increase the population inversion for the "lasing candidates" by at least a factor of two for a wide range of plasma conditions. Besides, we are calculating the functions, which describe the population distribution within each Rydberg series dependent on the Rydberg electron energy. These functions bear diagnostic information.

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Nonlocal Dielectric Functions on the Nanoscale: Screening of Induction and Dispersion

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For a pair of nonoverlapping molecules, we derive the induction and dispersion energies within a nonlocal dielectric model for the screening of intramolecular charge interactions. The theory holds within the Born-Oppenheimer approximation. Each molecule acts as a dielectric medium for the other, with the nonlocal dielectric function $\varepsilon_v(r,r';\omega)$ introduced by Jenkins and Hunt,[1] in analysis of intermolecular interaction energies at first order. The function $\varepsilon_v(r,r';\omega)$ is determined by the charge-density susceptibility $\chi(r,r';\omega)$,[2,3] within linear response: $\varepsilon_v(r,r';\omega)$ yields the effective potential $\varphi_{eff}(r,\omega)$ at point r, when an external potential $\varphi_{ex}(r',\omega)$ acts at the point r'. Screening of the Coulomb interactions between the averaged charge density within each molecule determines the induction energy, while the dispersion energy depends on the screening of interactions between spontaneous quantum mechanical fluctuations in the charge density. Induction and dispersion energies both reflect the *intermolecular* screening of the Coulomb interactions within each of the molecules, but the forces on the nuclei derive from *intramolecular* screening. Although induction and dispersion energies are determined (to leading order) within linear response, nonlinear response must be included via a quadratic screening function $\varepsilon_q(r,r',r'';\omega,\omega')$, in order to derive the forces on the nuclei treated as test charges within the interacting molecules.

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The gas-phase ozonolysis of β-caryophyllene (O_3 + β-$C_{15}H_{24}$): a theoretical study

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The O_3-initiated oxidation of β-caryophyllene, a sesquiterpene with a potentially important role in the formation of atmospheric secondary organic aerosol (SOA) in forested areas,[1-5] was theoretically characterized for the first time using quantum chemical calculations followed by statistical kinetic analysis. The most relevant portion of the lowest-lying singlet potential energy surface was constructed using B3LYP and MPW1B95 methods in combination with 6-311G(d,p), 6-31+G(d,p) and 6-311++G(3df,3pd) basis sets. Whereas O_3-addition onto the exocyclic double bond is negligibly slow, ozone adds fast, without barrier onto the endocyclic >C=C< bond, forming highly energized primary ozonides (POZ), in both the trans- and cis-configurations. These POZs are located at *ca.* –64 kcal/mol relative to the initial reactants and rapidly inter-convert via a barrier E_b of only 8 kcal/mol. About 35% of the nascent, chemically activated POZs undergo prompt ring-opening, overcoming barriers of 18 to 21 kcal/mol, leading to two highly activated Criegee Intermediates (CI-1* and CI-2*, in a *ca.* 50:50 ratio), each in syn- and anti-configurations. The syn ↔ anti conversions face high barriers of *ca.* 33 kcal/mol, and therefore are negligibly slow. The other 65% POZs are stabilized by collisions with air molecules; they also decompose – though much more slowly – into the same CIs, but with too little internal energy for prompt subsequent reactions. On the other hand, the 35% highly activated CIs*, with initial internal energies up to 90 kcal/mol, partly react promptly (i) via 1,4 H-shifts (E_b of 17 to 28 cal/mol) to form hydroperoxides that rapidly decompose to yield $^{\bullet}OH$ radicals; and (ii) by ring-closure (E_b of 21 to 24 kcal/mol) via dioxiranes to yield mainly organic esters or acids, whereas a smaller fraction of the hot CIs* undergo collisional stabilization. It should be mentioned that ca. 45% of the vibrationally excited, nascent dioxiranes are stabilized, and then they also rearrange thermally within 2 m to generate the same esters/acids. Our RRKM/ME calculations, based on the B3LYP potential energy surface and B3LYP rovibrational parameters, predict the following over-all first-generation product yields at room temperature and atmospheric pressure, in good agreement with the experimental data from the Mainz group[5] given in parentheses: 75 ± 10% stabilized CIs (exptl. ca. 80%), 9 ± 5% $^{\bullet}OH$ radicals (exptl. ca. 6-10%), and 16 ± 10% acids/esters (exptl. ca. 10%). The overall thermal rate coefficient over the T = 220-450 K range was computed using variational TST, and can be expressed as: $k(T) = 8.3 \times 10^{-24} \times T^{3.05} \times \exp(1028/T)$ cm^3 $molecule^{-1}$ s^{-1}, showing a slightly temperature dependence. Our results confirm the view that by their unusually fast reactions with O_3, $k(298\ K) \approx 1 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, producing very-low-volatility oxygenates, sesquiterpenes in general and β-caryophyllene in particular are important SOA precursors in forested areas.

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Multiply Charged Helium Isoelectronic Ions with Z = 2 to 118. I. Ground State Energies, Mass Correction and Mass Polarization Effects

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Multiply charged Helium isoelectronic ions are responsible for the properties and characteristics of high-temperature astrophysical and laboratory plasmas, as well as for processes occurring within these plasmas.

In previous work we have computed the ground state electron energies, mass correction and mass polarization effects of He isoelectronic ions with $Z = 2 - 54$. Results were obtained by solving the two-electron Schroedinger equation, using as trial wave functions explicitly correlated wave functions ($ECWF$) of a generalized Hylleraas type, in an expansion series with positive powers of the Hylleraas coordinates. The analytical and numerical procedure used for determining the coefficients lead to solving a 4^{th} order algebraic system of non-lineal integro-differential equations. The method allowed to obtain numerical results of up to 6^{th} decimal accuracy, comparing with the most precise results for He isoelectronic ions with $Z = 2 - 10$.

The present work reports ground state electron energies, mass correction and mass polarization effects for the main nuclides of He isoelectronic ions with nuclear charge $Z = 2 - 118$. The same type of $ECWF$ is utilized. The variational procedure used for determining the coefficients is discrete, leading to an eigenvalue problem. The method developed yields numerical results that practically coincide with those presented in for ions with $Z > 10$. The dependence of energies versus Z is investigated, as well as the relative and absolute contributions of mass correction and mass polarization effects to the ground state electron energies.

This approach can be regarded as a basis for investigating relativistic corrections and QED effects at a next stage. The accuracy of the results obtained allows direct usage in precise theoretical approaches for plasma diagnostics.

Interactions in Open-Shell Systems by the Pauli Blockade Method

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Abstract

The extension of the self-consistent field Pauli blockade method[1,2] to the open-shell systems is presented. The performance of the model is tested on some small canonical systems and on a few large ones. Also, the three-body variant of the method is applied to study three-body effects in trimers such as Be_3, Li_3, Na_3, Na_2Be. The inclusion of correlation effects to the intermolecular interaction energies is accounted for by the use of DFT description of interacting monomers. The results are compared with those obtained from different *ab initio* methods, e.g. SAPT.

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Electronic Structure and Dynamics of O-NO_2 Bond Fragmentation

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Decomposition of a high-energy molecule is accompanied by extensive changes in its electronic configuration and thus presents a formidable challenge for *ab initio* Born-Oppenheimer molecular dynamics simulations. For example, to reproduce the O-NO_2 bond fragmentation in nitric esters, the electronic structure method employed to drive molecular dynamics must seamlessly describe the transition from the initial closed-shell configuration to a singlet diradical intermediate. We investigate the behavior of variational single-determinant methods in the region on the potential energy surface where the singlet diradical state becomes energetically favorable and discuss challenges for the corresponding molecular dynamics simulations.

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Water Cage Effects in the Optical Absorption Step of Aqueous Remediation of Trinitrotoluene using Iron-porphyrin Photo-catalysts

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This article focuses on molecular level photo-absorption involved in aqueous remediation of trinitrotoluene (TNT) using iron-porphyrin as a photo-catalyst. We will be concerned with the structure and minimum extent of the water molecule cage adsorbed to the iron-porphyrin that is needed to adequately describe the optical absorption step. Inclusion of the cage effects is needed to understand room temperature solvation effects on optical absorption and ultimately catalytic energy/charge transfer with docked remediants. We find that the water cage effects for singlet, triplet, and quadruplet spin states leads to near energy degeneracy relative to bond breaking-making of the water shell. Cages of up to 60 water molecules were considered. The minimum water cage contains ten water molecules. At that point, the optical absorption for the theoretical calculations is converging with the quintuplit and triplet states having about the same ground state enthalpy, within a Kcal/mol.

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Water Cage Effects on Electron Transfer Orbitals (ETOs) in the Aqueous Remediation of Trinitrotoluene using Iron-porphyrin Catalysts

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Photo-electron transfer from iron porphyrin (FePor) to a docked remediant molecule, trinitrotoluene (TNT), through their mutual water cage is demonstrated and is shown to be important for subsequent chemical reactions initiating remediation. There are new states found in the optical absorption due to the water cages. This leads to the introduction and definition of electron transfer orbitals (ETOs). There is developed a procedure for determining ETOs both theoretically and experimentally. One finds two types of ETO states within the visible excitation range for the FePor-water complex. The most dramatic being a state with density spanning the water molecule axially ligated to the iron and other occurs through the pyrrole rings of the catalyst. It is further shown that both FePor catalyst and TNT are electron traps in water so that photo-electrons generated from optical excitation are either trapped at the TNT or recombine at the catalyst. This allows the catalytic center to function in concert with its water cage as a redox center acting on adsorbed molecules during the time interval before electron-hole recombination. The electron transfer initiates the remediation of TNT in a pathway that first yields trinitrobenzaldehyde or trinotrobenzol then to trinitrobenzoic acid.

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Short Hydrogen Bonds in the Solid State: How Intermolecular Interactions and Crystal Field Affect the H-Bond Geometry and Dynamics

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The role of short hydrogen bond in molecular biology motivates an extensive research of systems containing short H-bonds, both at experimental and computational level. Since most of experimentally determined geometry parameters of short H-bonds are derived from crystallographic diffraction measurements, there exists a clear need to devote considerable part of computational studies to the crystalline phase. The formalism for the implementation of periodic boundary conditions into *ab initio* and DFT quantum-mechanical (QM) methodology has been known for years and periodic QM studies of crystalline systems are recently gaining momentum due to the enhanced capability of computers.

Among the factors that govern the characteristics of short H-bonds, the location of proton within the H-bond and the proton dynamics are probably the most important ones. We will present our recent DFT studies of structure and dynamics of a variety of crystalline systems containing short inter- and intramolecular H-bonds of the O-H…O type, including enolized β-diketones, picolinic acid *N*-oxide and complexes of pyridine *N*-oxide and carboxylic acids. All periodic calculations have been carried out by the Crystal06 and CPMD 3.9 program packages. We will demonstrate that the periodic intermolecular interactions have a notable effect on the H-bond geometry, vibrational frequencies and other properties.[1] On the example of picolinic acid N-oxide and its 4-chloro substituted derivative we will show that the influence of crystal field on H-bond geometry can readily prevail over the electronic effects of substituents. An attempt will be made to devise correlation between the packing of molecules within the crystal and the H-bond geometry. We will address to the H-bond dynamics in the crystal and its impact on the symmetry features determined by neutron crystallography. On the example of tetraacetylethane we will show that despite the fact that the isolated system is chemically symmetrical, the explicit C-H…O intermolecular interactions in the crystal induce asymmetry, most probably by hindering the rotation of methyl groups which is known to be significantly coupled to the proton potential. Detailed understanding of these aspects represents an important step forward in the H-bond research and will trigger additional experimental and computational work in the near future.

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Quantum Dynamics with Trajectories: Optimal Spawning and Conservation of Energy

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Importance of conical intersections has long been recognized. It has played important roles in photochemistry, e.g., photodissociations, photoisomerizations, ion fragmentations, energy transfers, and visual pigment rhodopsin. Femtosecond spectroscopy has advanced recently which enables the experimental study of ultrafast photochemical reactions. On the other hand, *ab initio* accurate quantum mechanical numerical simulations with ability to describe quantum effects and nonadiabatic transitions are needed but still remain as a challenging problem.

AIMS (*ab initio* multiple spawning) method developed by Martinez group is an effective algorithm to simulate quantum dynamics with trajectories. Spawning and basis set expansion enables AIMS to describe the nonadiabatic transitions happening near the conical intersections of multiple potential energy surfaces. Trajectories in AIMS propagate according the classical equations of motion, and the amplitude of each trajectory is accurately and effectively calculated by solving the exact Schrodinger equation. AIMS method has been employed to study various systems with quantum effects and nonadiabatic effects.

We have recently improved AIMS method by inventing a rigorous algorithm for spawning. An optimal spawning algorithm beyond the simple momentum-jump is needed to guarantee the an ideal criteria of nonadiabatic transitions, i.e., matrix coupling element $\left\langle \chi_i \middle| H^{IJ} \middle| \chi_j \right\rangle$ between the two basis functions on the different electronic states should be maximized subject to the constraint of total energy conservation. In addition, difference between the classical and quantum mechanical expressions of total energy can be subtle and critical when one has to consider quantum effects in the proton transfer processes. This difference is not just the zero point energy itself. More rigorous treatment is needed and has been considered in the optimal spawning and propagation of trajectories in AIMS method.

Simulating Reactive Scattering Dynamics at Gas-liquid Interfaces with Hybrid QM/MM-Direct Dynamics: A Theoretical Study of the $F(^2P)$ + Squalane Reaction.

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The structure and dynamics of chemical interfaces at phase boundaries (*e.g.* gas-liquid interface) continues to be of significant importance to chemistry and only recently has the complexity of these surface interactions been realized. Probing the reactivity of a liquid surface [squalane ($C_{30}H_{62}$)] with scattering [$F(^2P)$] provides a good interfacial system to study theoretically, as Nesbitt *et al*. have recently resolved the quantum-state reaction dynamics via direct absorption detection of the rovibrational states of HF with high resolution infrared spectroscopy.[1] Previously, our group has developed a simulation model that merges classical molecular dynamics of the entire system with a quantum mechanical treatment of the atoms in a reaction region(s) at each time step. This computational model provides a type of "on-the-fly" direct dynamics applicable to larger scale chemical processes that include the making/breaking of chemical bonds, which is not characterized in standard force field models. In the current study we compute reaction statistics from over 1000 trajectories, where the incident fluorine atom has an initial translational energy of 1 eV. The reactive pathways that were observed were limited entirely to H abstraction, which was not the case in the previous studies by Kim and Schatz[2] that utilized this same simulation model for 5 eV incident $O(^3P)$ + squalane. In addition, inelastic scattering of F was also observed, but to a lesser extent. Reaction and collision statistics have been analyzed for trends in angle of incidence, the carbon/hydrogen reaction site for the absorption/desorption process. Overall the HF desorbs from the surface quite rotationally and vibrationally hot in comparison to the squalane surface temperature.

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Fully Optimized Auxiliary Basis Sets for MP2-F12 Methods

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Electron correlation treatments utilizing a one-electron orbital expansion are capable of providing very high accuracy. However, due to the poor description of the correlation cusp in such approximate wave functions, they suffer from painfully slow convergence of the energy with respect to the size of the orbital basis set, a problem exacerbated by the steep computational scaling of such methods. This can be remedied by the explicit inclusion of interelectronic coordinates in the wave function, but such an approach then requires the difficult calculation of numerous three- and four-electron integrals. By employing the resolution of the identity (RI), these integrals can be approximated as products of two-electron integrals through the use of an auxiliary basis set.[1] Up until now, few attempts have been made to optimize such basis sets. We present our fully optimized auxiliary basis sets for the first- and second-row atoms, matched to the recently-developed cc-pV*n*Z-F12 basis sets[2] and intended for use with the explicitly correlated MP2- and CCSD-F12 methods (which differ from R12 methods in their use of an exponential correlation factor). In spite of being much more compact than existing basis sets frequently used to approximate the many-electron integrals, the errors arising from their use are very small, even at the double-ζ level. Furthermore, since they are carefully matched to the orbital basis sets, linear dependence issues are avoided when the CABS procedure[3] is invoked in explicitly correlated calculations, facilitating their use in generating smooth potential energy surfaces.

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Projected Entangled Pair States as a multi–dimensional ansatz for effective recovery of non-dynamic correlation from huge active spaces

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Modern quantum chemistry methods became very efficient in addressing dynamic correlation. However, the success of quantum chemical approaches is still limited if one considers the treatment of non–dynamic correlation. Thus, many inorganic systems revealing many closely degenerate states are still not within quantitative reach for current methods. Density Matrix Renormalization Group (DMRG) was proved to be very successful for the treatment of the multireference effects in one–dimensional systems, the multi–dimensional systems with a large active spaces are still too demanding for DMRG and other traditional quantum chemistry method.

Here, we present a generalization of the DMRG ansatz to a multi–dimensional case that is able to effectively recover the non–dynamic correlation for two–dimensional lattices. Such a generalization is known in physics as Projected Entangled Pair States (PEPS) and was proved to work successfully for two–dimensional model systems. We present the theory of PEPS listing possible advantages and problems arising form such a treatment. Additionally, we list preliminary examples from our version of the PEPS code. We investigate the usefulness of PEPS to multidimensional chemical systems that can be effectively projected onto a two–dimensional lattice. To the most known examples of such systems, which require huge active space, are molecular magnets.

Finally, we note that PEPS describes non–dynamic correlation well, but dynamic correlation is not recovered successfully for calculations with small number of parameters. We discuss the possible remedies that allow us to account for the dynamic correlation.

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Thirteenth International Workshop on
Quantum Systems in Chemistry and Physics
July 6-12, 2008

QSCP-XIII

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Michigan State University, East Lansing, Michigan, USA

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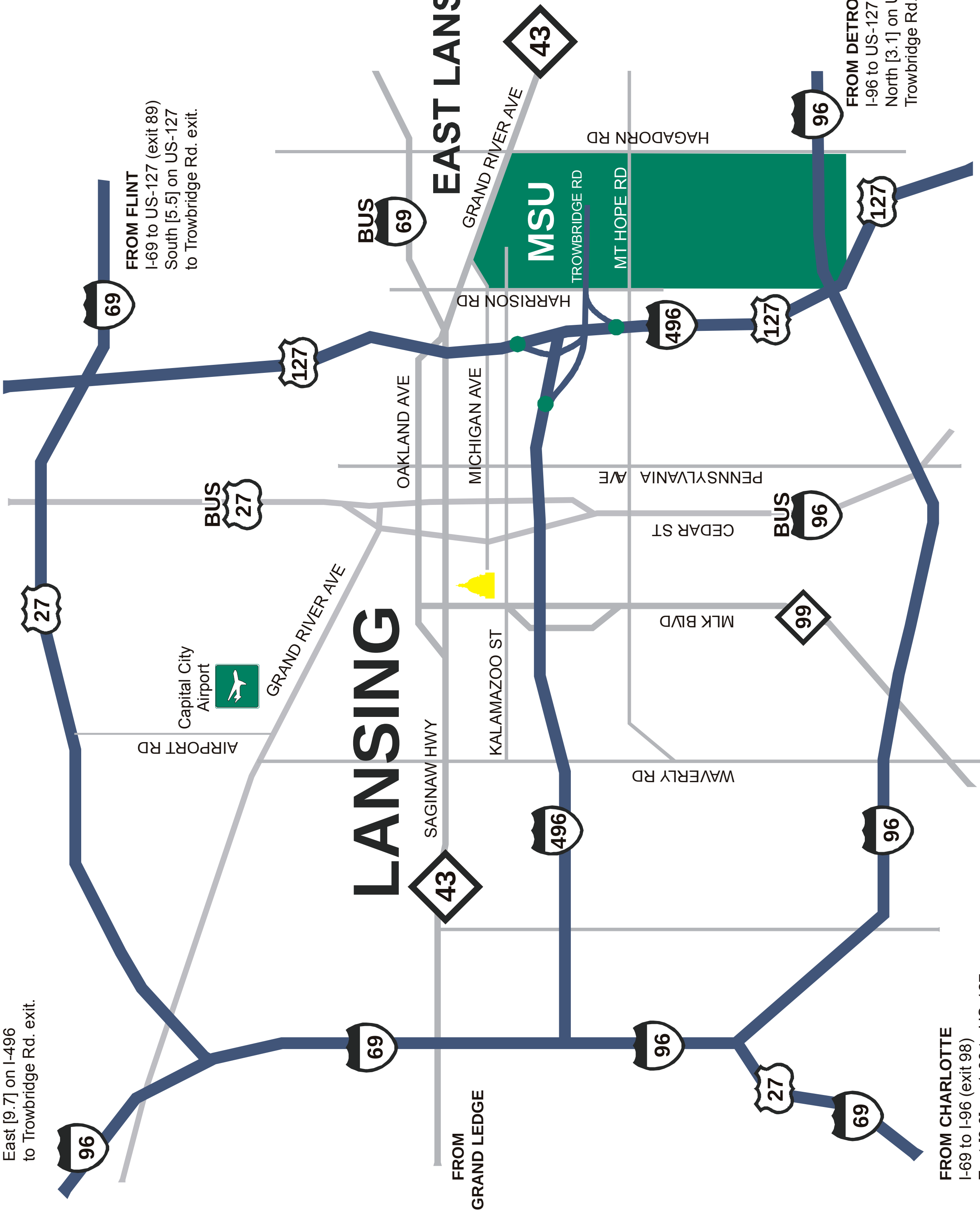
Maps

Lansing Area



FROM ST. JOHNS
South [8.5] on US-127 to Trowbridge Rd. exit.
East [.5] on Trowbridge to Harrison Rd.

FROM FLINT
I-69 to US-127 (exit 89)
South [5.5] on US-127
to Trowbridge Rd. exit.

FROM DETROIT
I-96 to US-127 (exit 106)
North [3.1] on US-127 to
Trowbridge Rd. exit.

FROM MASON AND JACKSON
US-127 to Trowbridge Rd. exit.

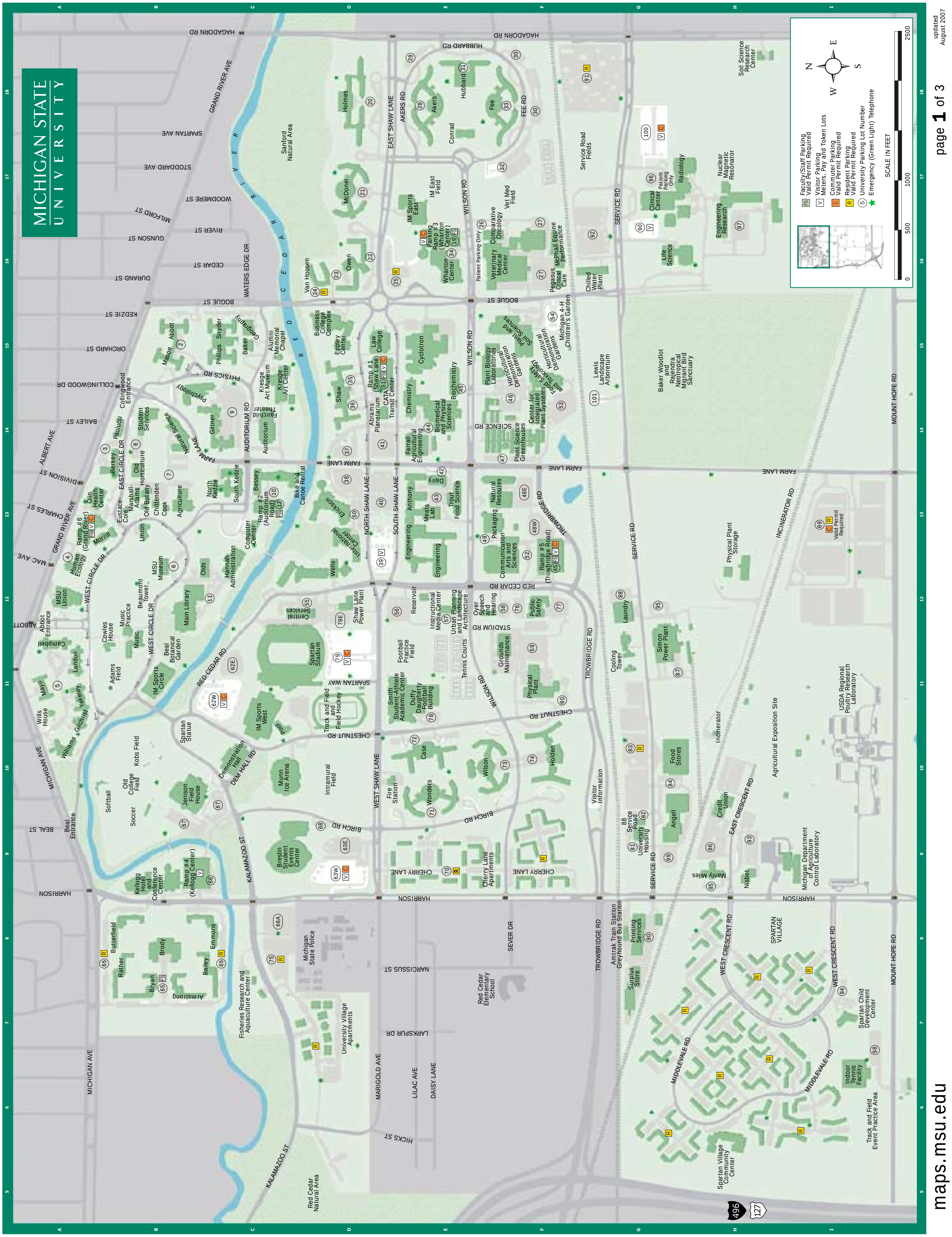
FROM EATON RAPIDS
M-99 to I-96
East [5.2] on 1-96 to US-127
North [3.4] on US-127
to Trowbridge Rd. exit.

FROM CHARLOTTE
I-69 to I-96 (exit 98)
East [9.0] on 1-96 to US-127
North [3.4] on US-127 to
Trowbridge Rd. exit.

FROM GRAND LEDGE

FROM GRAND RAPIDS
I-96 to I-496 (exit 95)
East [9.7] on I-496
to Trowbridge Rd. exit.

MSU Campus


MICHIGAN STATE UNIVERSITY
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updated August 2007
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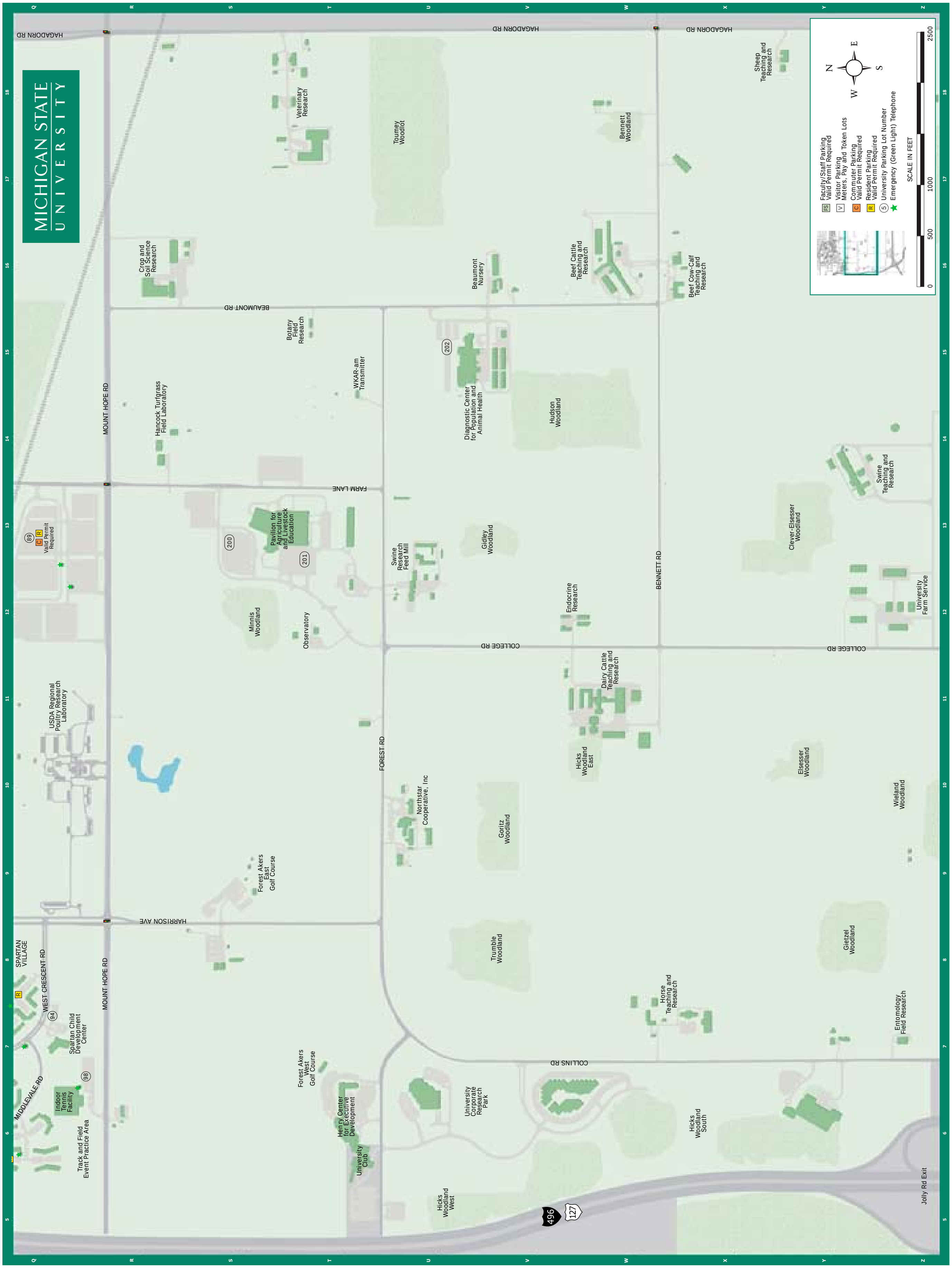
Faculty/Staff Parking Valid Permit Required
Visitor Parking Meters, Pay and Token Lots
Commuter Parking Valid Permit Required
Resident Parking Valid Permit Required
University Parking Lot Number
Emergency (Green Light) Telephone
SCALE IN FEET
0
500
1000
2500
N
S
E
W
HAGADORN RD
GRAND RIVER AVE
MICHIGAN AVE
HARRISON
BOGUE ST
FARM LANE
RED CEDAR RD
SHAW LANE
WILSON RD
SERVICE RD
MOUNT HOPE RD
TROWBRIDGE RD
KALAMAZOO ST
RED CEDAR RIVER
Spartan Stadium
Main Library
MSU Union
Breslin Student Events Center
Munn Ice Arena
Veterinary Medical Center
Sanford Natural Area
Baker Woodlot and Rajendra Neotropical Migrant Bird Sanctuary
Agricultural Exposition Site
Spartan Village
Red Cedar Natural Area
Kellogg Hotel and Conference Center
Wharton Center
Beaumont Tower
Michigan State Police
University Village Apartments
Cherry Lane Apartments
Amtrak Train Station Greyhound Bus Station
496
127



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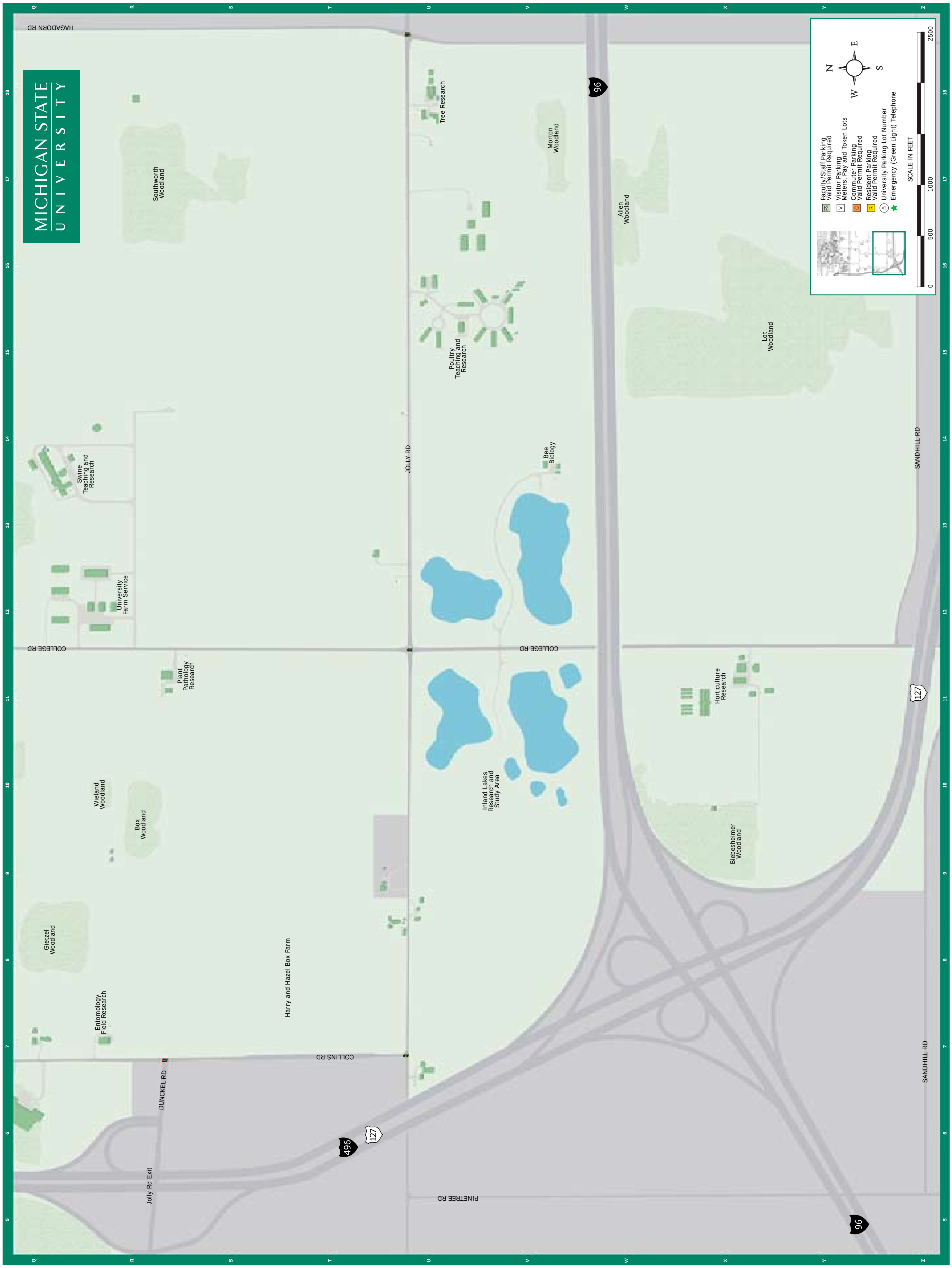

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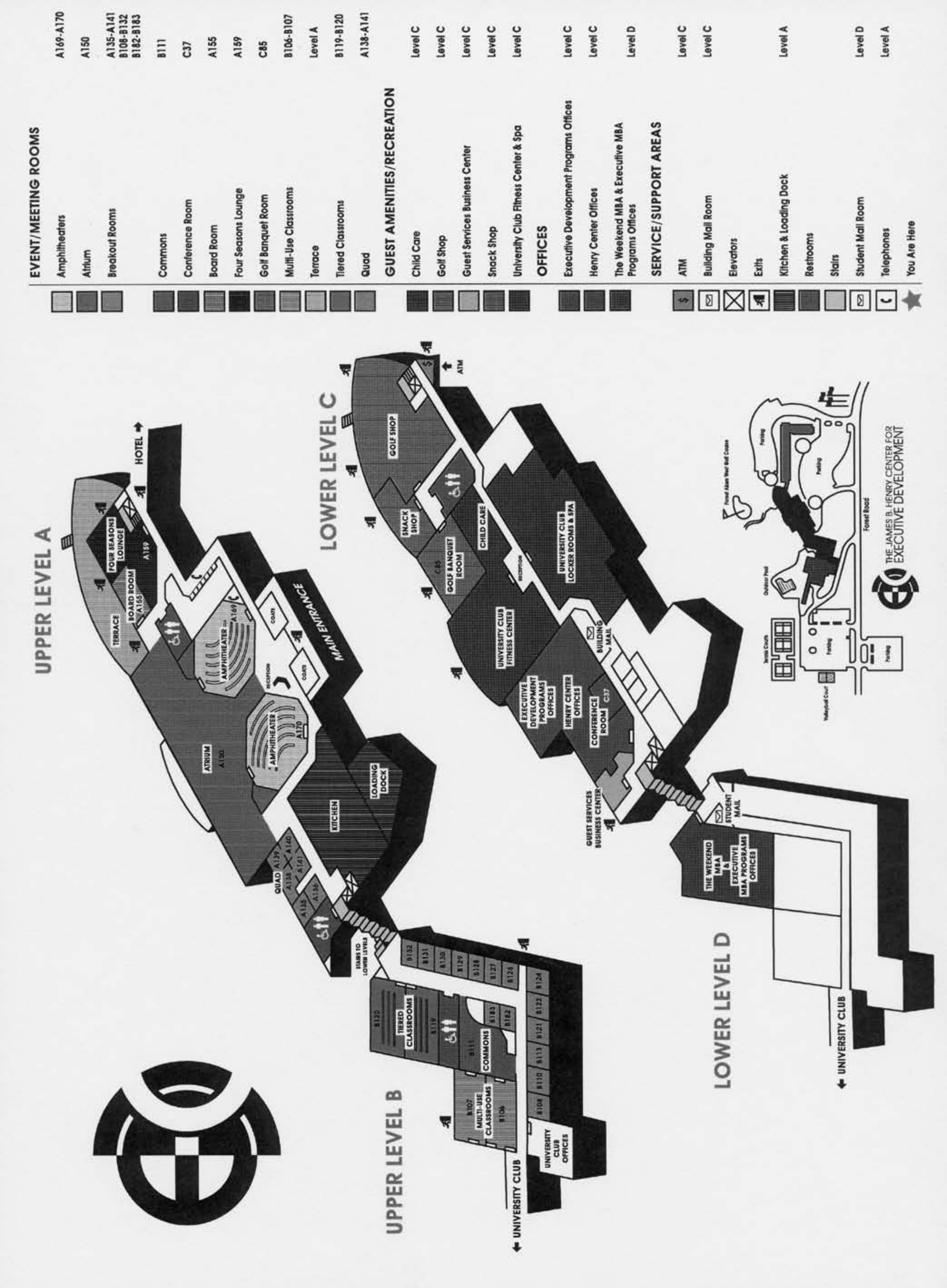
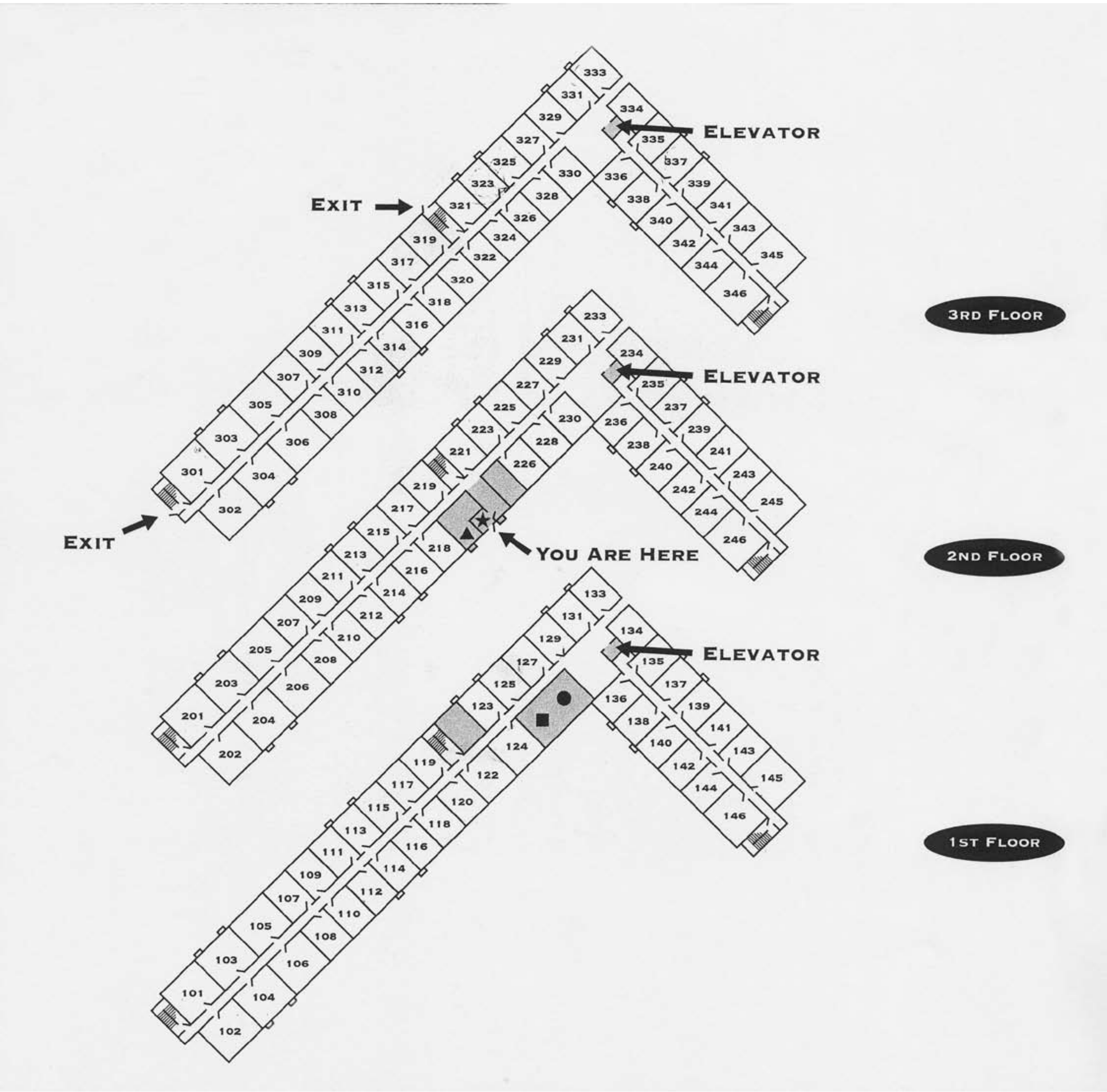
Henry Center



Candlewood Suites



Notes

Event Locations

Event	Room
Lectures	Henry Center A169
Poster Sessions	Henry Center B106 and B107
Continental Breakfast	Henry Center Atrium
Breaks	Henry Center Atrium
Lunches	Henry Center Atrium
Welcome Reception and Dinner on July 6	Henry Center Atrium
Dinner on July 7	Henry Center Atrium
Dinner on July 8	Henry Center Atrium
Concert on July 8	Henry Center Atrium
BBQ Dinner on July 9	Henry Center Atrium
Banquet Reception and Dinner on July 10	University Club Dining Room
CMOA Prize Ceremony	University Club Dining Room
Dinner on July 11	Henry Center Atrium
Registration and Help Desk	Henry Center Lobby

In addition to the above events, the Four Seasons Lounge in the Henry center will be open from 8:00 pm to midnight from July 6 to July 11.

MICHIGAN STATE
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Department of
Chemistry